



## Review

## Recent developments in phase change materials for energy storage applications: A review



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## ABSTRACT

In order to overcome the increasing demand–supply energy gap due to the rapid urbanization, labor productivity, consumerism and depletion of fossil fuel resources, there is a need for the development of technologies with renewable energy sources. Phase change materials are one of the most appropriate materials for effective utilization of thermal energy from the renewable energy resources. As evident from the literature, development of phase change materials is one of the most active research fields for thermal energy storage with higher efficiency. This review focuses on the application of various phase change materials based on their thermophysical properties. In particular, the melting point, thermal energy storage density and thermal conductivity of the organic, inorganic and eutectic phase change materials are the major selection criteria for various thermal energy storage applications with a wider operating temperature range. The strategy adopted in improving the thermal energy storage characteristics of the phase change materials through encapsulation as well as nanomaterials additives, are discussed in detail. Specifically, the future research trends in the encapsulation and nanomaterials are also highlighted.

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## 1. Introduction

Energy is the key requisite to bring about technological advancement and economic development for the progression of societies all around the world [1]. The unrelenting depletion of non-renewable resources and the escalating scenario of global warming have compelled the trend to be shifted towards the use of sustainable energy resources [2,3]. Consequently, it is imperative to explore renewable and sustainable resources to meet both electrical and thermal energy conversion and storage requirements. The de-carbonization of the energy sector can be made possible by integrating renewable energy resources with various thermal energy storage systems which possess round-trip efficiency of >96% [4,5]. Currently, over 18% of the global energy consumption is derived from the renewables [6]. Renewable energy sources are undeniably favored over the exploitation of non-renewable resources due to their long-term availability, accessibility and environmental benignity [7]. However, the intermittency of the renewable energy sources, particularly the solar and wind energies, is the major constraint as far as round the clock supply of the energy from them is concerned, and special arrangements have to be made for their adaptability [8]. Integrated/hybrid energy systems comprising different technologies coupled together in order to shave the peak power demand (load leveling) are being deployed in a complementary manner [9,10]. Most of the hybrid systems utilize an auxiliary heater as the secondary energy source based on carbon-based fuels to overcome the intermittency of renewable energy sources [11]. However, the dependency on secondary energy sources/carbon-based fuels can be minimized by the application of thermal energy storage (TES) towards efficient and cleaner energy systems, thus enhancing the reliability of thermal energy from renewable sources and ultimately curbing global warming [12,13]. In addition to that, if the energy production exceeds the energy demand, TES systems can be used to store the surplus energy and bridge the demand–supply gap by delivering during the peak power demand [14,15].

The scientists and energy technologists are putting their efforts to get a steadier, more efficient, stable and round the clock energy supply from the renewables, but dealing with the energy demand requires countless efforts [16]. There has been much emphasis in taking corrective measures to overcome the global warming and

integrating the renewables into the energy systems, along with the pathway of the energy storage are the active fields of current research [17]. Certain measures are already underway demonstrating the potential of sustainable green energy systems [18]. A thorough literature survey on the phase change materials for TES using Web of Science led to more than 4300 research publications on the fundamental science/chemistry of the materials, components, systems, applications, developments and so on, during the past 25 years. As shown in Fig. 1a, the TES materials research has become very active in the past 10 years or so. In addition, the TES materials are also gaining commercial interest with several organizations protecting the technology and system design through patents (see Fig. 1b), showing technological advancements in the recent past.

The materials used for latent heat thermal energy storage (LHTES) are called Phase Change Materials (PCMs) [19]. PCMs are a group of materials that have an intrinsic capability of absorbing and releasing heat during phase transition cycles, which results in the charging and discharging [20]. PCMs could be either organic, inorganic or eutectic mixtures as shown in Fig. 2; a variety of PCMs are extensively discussed in later sections. The exothermic and endothermic phase transition of the PCMs can be utilized effectively by incorporating them in TES systems and thermal loads could be met by controlling the operating parameters of systems.

Nevertheless, there are several issues such as low thermal conductivity, poor thermal stability, high flammability, supercooling, corrosiveness, and volume and pressure variations during phase transformation and leakage of molten PCMs into the surrounding of the TES system, limiting the commercial viability of PCMs [21–23]. Researchers are focusing extensively on improving the thermophysical properties of the PCMs towards commercialization. As shown in Fig. 2, various heating/cooling strategies and performance enhancement techniques are practiced to efficiently utilize the wide range of PCMs in TES system, depending upon the process constraints. A variety of methods to overcome these concerns include the addition of different additives to improve thermal conductivity and eliminate supercooling [24,25]. Various encapsulation techniques and additives considered to prevent PCM leakage into the system will be discussed later in this article [26–28]. As seen from Table 1, it is evident that there are more commercialization activities in the USA with about 12 companies compared to other countries. In addition, China, UK, and Germany are also very

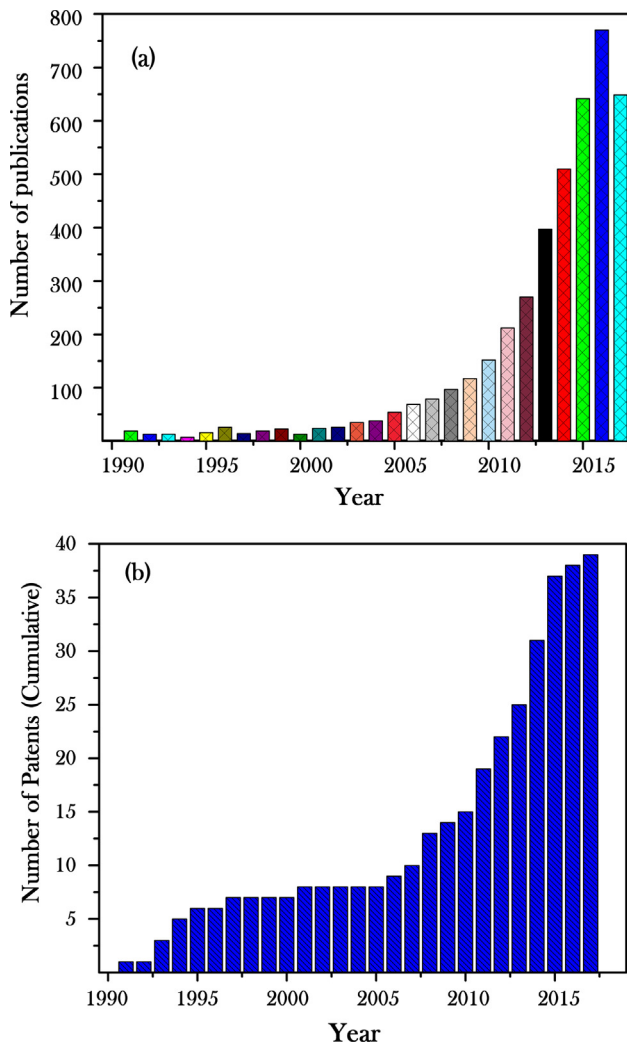


Fig. 1. Bibliometric analysis of (a) journal publications and (b) the patents, related to PCMs for thermal energy storage applications.

active in developing and commercializing PCMs for various TES applications. Since the characteristics of the PCMs vary based on the composition, operating range, durability, and other factors, the pricing is still controlled by the particular manufacturers.

With the maturity of such methodologies along with cost reduction (\$ 16 to 3 per kg) of the PCMs, a revolution in the energy storage sector is anticipated [29]. The capital cost for the TES is relatively lower (\$ 70–200 per kWh) against electrochemical storage devices such as batteries (\$ 200–300 per kWh) [30,31]. Using combined sensible/latent heat TES systems, the material costs could be lowered to as low as \$ 15 per kWh<sub>th</sub> and an exergy efficiency of around 95% can be obtained [32]. It is a common perception that shifting towards a low-carbon economy would inevitably raise the demand for energy storage to a significant extent in the near future. In brief, although the area of PCMs has nurtured in the past decade, still various aspects require further improvement through research and development for optimization of PCM technology and advance this technology to be in the forefront of energy storage. In the current review, various characteristics of the PCMs for different energy storage applications are discussed based on the recent literature on classification, selection principles, applications, future trends and advancements in the field of PCM technology for TES. In addition, details of the PCMs manufacturers, databases and software/modeling tools and patents related to PCM technology are also summarized in the Tables 1, 2 and 7.

## 2. Thermal energy storage

Various options of TES for integrating into the energy systems comprising of renewable energy resources such as solar, wind, geothermal, hydro or even with non-renewable resources as in the case of waste heat recovery exist [33]. As discussed below, the thermal energy can be stored by chemical as well as physical methods as shown in Fig. 3.

### 2.1. Physical methods of thermal energy storage

In physical TES, the heat transfer mechanisms lead to the storage of the heat energy and the capability to retain that heat depends upon the thermophysical properties of the particular material. Latent heat storage (LHS) and sensible heat storage (SHS) are classified under physical storage. In case of the SHS, thermal energy is stored as an internal energy induced by the gain in the temperature of the particular material by transfer of the heat through conduction, convection or radiation, while LHS involves the accumulation of heat at the molecular level in a material leading to phase transformation [28,34,35].

The amount of heat stored in SHS depends upon the mass, heat capacity of storage material and the temperature gradient between the initial and final states. The SHS can either be done in a solid or liquid storage media as shown in Fig. 3. In the case of solid storage media, metals and non-metals are widely used. Non-metals such as concrete, rock, gravel, brick, marble, granite, sandstone and so on are candidate materials but their low specific heat capacity and thermal conductivity are the major obstacles in the reliability of this type of storage [36–39]. Metals such as copper, aluminum, cast iron and pure iron along with other alloys are suitable for high-temperature SHS, but the higher cost of the TES system comprising of these metals is a major obstacle in commercialization [40]. Metals and graphite have high thermal diffusivities and are thus suitable for applications involving fast charging and discharging, while rock, gravel, and stone have low thermal diffusivity and are better suited for applications involving slow charging and discharging cycles. Liquid storage media for SHS include molten salts, water, thermal oils such as Caloria HT43 and other commercially available products but the low energy storage density and thermal conductivity restricts the broad spectrum application of this type of TES [40]. The high specific heat capacity of water makes it one of the promising candidates for SHS for temperatures below 100 °C [41,42], whereas molten salts have comparatively desirable thermophysical properties and are being adopted for various high-temperature TES applications [43]. Special measures are to be taken for storage assembly to prevent the corrosion, which increases the overall cost of the storage system as well [44–46].

The amount of heat stored in LHS depends upon the mass and latent heat of fusion of the PCMs. The energy storage equation for the PCMs comprises both the sensible and latent heat equations as the temperature rise of the material leads to the phase transformation. The working mechanism of PCMs involves absorption of the considerable amount of heat at reaching the phase change temperature, which is necessary for phase transition and the heat absorbed during this process is either called latent heat of vaporization or latent heat of fusion depending upon the phase of the material under consideration [19,47]. A comprehensive classification of PCMs is provided in the later section.

### 2.2. Chemical methods of thermal energy storage

In chemical TES, energy is stored and released due to the reversible reaction. Chemical methods of TES are classified as sorption storage [48–51] and thermochemical energy storage [52,53]. The

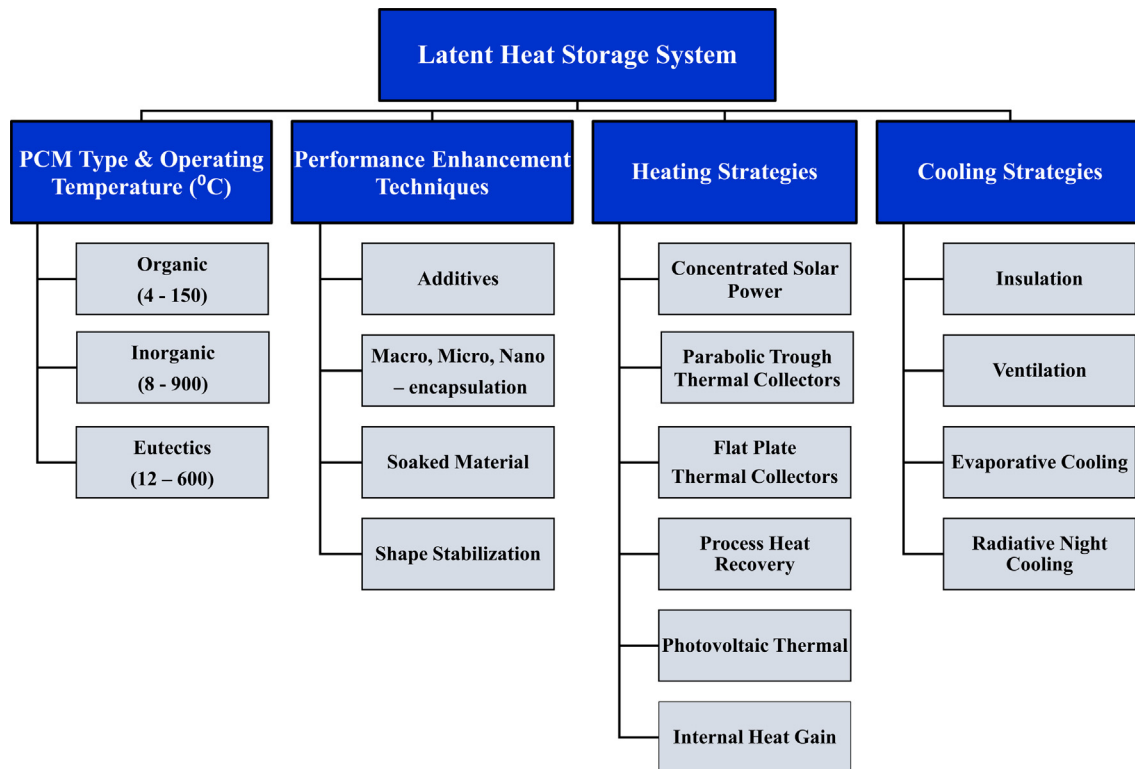


Fig. 2. Various strategies for latent heat storage systems.

thermochemical energy storage comprises solid-gas or liquid-gas or gas phase systems. Energy is stored in thermochemical heat storage as a result of dissociation reaction which is then recovered in a chemically reversible reaction and its thermal cycle consists of charging, storing and discharging [54]. The amount of heat stored in thermochemical energy storage involving solid-gas phase depends upon the pressure of the gas, whereas the heat transfer coefficient as observed by Kuwata et al. is far greater in liquid-solid systems compared to gas-solid systems [55]. They have also reported the short-term cyclic stability in the case of the solid-liquid reaction of strontium chloride and ammonia for thermochemical heat storage. Andre et al. discussed potential candidates for thermochemical energy storage based on solid-gas reversible reactions and reported various metal carbonates, oxides, and hydroxides as promising thermochemical energy storage materials depending upon their operating temperature and reaction enthalpy [53].

### 2.3. Comparison of sensible, latent and chemical thermal energy storage

An overview of operating temperature range, storage density, commercial status/viability and durability of the TES consisting of sensible, latent or chemical means of energy storage is given in Fig. 4. Typically, the storage density of LHS medium is higher than that of the SHS medium due to high enthalpy change during phase transition but the thermochemical energy storage has the highest storage density comparatively with other two modes. Currently, various thermochemical energy storage materials are in the development phase and no such system is commercially available. The commercial viability of the LHS is limited by material characteristics and thus is in the developmental phase as opposed to SHS, which is commercialized largely. It is evident from Fig. 4 that the durability of the SHS materials is approximately 20 years in comparison with LHS materials, which are one-fourth of their lifetime

and thermochemical energy storage, which is about one-tenth of the lifetime of SHS materials [56]. Among these different types of TES, LHS has the most flexible operating temperature range followed by considerably lower operating temperature ranges for sensible and thermochemical energy storage [33]. The advantage of using latent heat over sensible heat storage technology is that it has  $\sim 10$  times higher TES density, a capacity of 50–150 kWh/t and round-trip efficiency of  $\sim 75$ –96% [5,57,58].

### 3. Classification of phase change materials

PCMs for LHTES can be classified depending upon the phase change mechanism as described in Fig. 3 and phase transition temperature, as discussed below:

#### 3.1. Phase change mechanism

LHTES systems are classified into sub-categories depending upon the liquid-gas, solid-gas, solid-solid, and solid-liquid phase transformation and vice versa (see Fig. 3) [59]. TES systems comprising of liquid-gas or solid-gas phase transformation are impractical due to the large volume requirements, volumetric changes associated with the phase transition and high pressure of the system, such as the water-steam system, which is not commercially viable for large-scale TES. In the case of solid-solid PCMs, the heat associated with transformation from one crystalline form of the material to another and vice versa is responsible for TES. The heat of phase transition in solid-solid PCMs is relatively less as compared to that of solid-liquid PCMs [60]. Solid-solid PCMs such as polyalcohol [60–62], polyurethanes [63–65], crosslinked polyethylene and other polymers for TES [59] have been studied thoroughly [66,67].

Majority of the PCMs considered for TES are solid-liquid phase transition materials and are sorted on the basis of the nature of



**Table 1**

List of commercial organizations associated with PCMs.

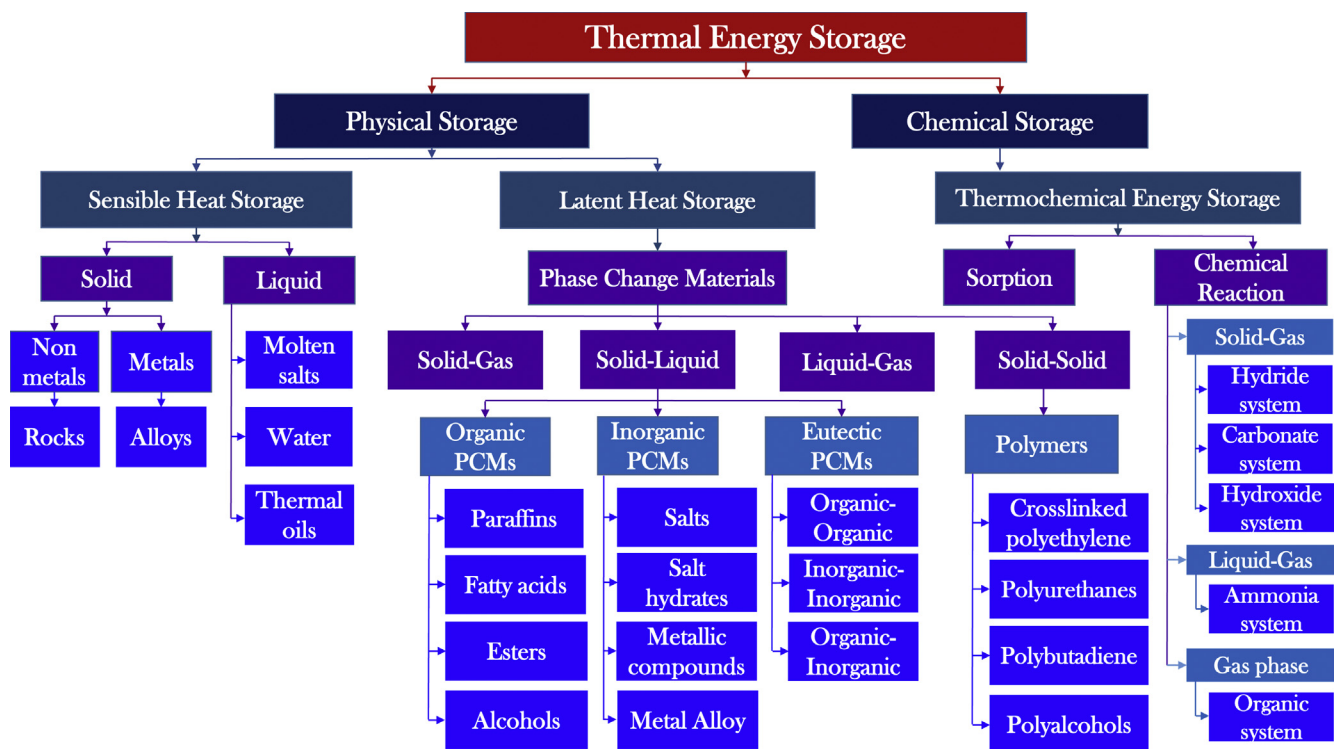
No.	Company name	Products	Country	Website
1	Entropy Solutions LLC.	PureTemp PCMs, BlockVesl, TubeVesl, MatVesl	USA	<a href="http://www.puretemp.com/">http://www.puretemp.com/</a>
2	Outlast Technologies LLC.	Thermocules™, Thermo-regulating textiles. It is a Certified Space Technology™	USA	<a href="http://www.outlast.com/en/">http://www.outlast.com/en/</a>
		Outlast® Latent Heat Systems (LHS), Thermal management systems of batteries, LHS battery matrix & matrix sheets, LHS Lithium-Ion battery sleeves, LHS W052214 & W071814,		<a href="https://www.outlastlhs.com/">https://www.outlastlhs.com/</a>
3	Honeywell International Inc.	Thermal interface materials (TIM), Core PCM offerings: PTM7000, PTM6000, PTM5000 Series, PCM45F Series, LTM Series, High compressibility PCM: TCM Series, High voltage dielectric PCM: PTM "D" Series	USA	<a href="https://www.honeywell.com/">https://www.honeywell.com/</a>
4	Microtek Laboratories, Inc.	Pure PCMs, MicroPCMs, Nextek™, Micronal®	USA	<a href="https://www.microteklabs.com/">https://www.microteklabs.com/</a>
5	RGEES LLC.	SavENRG™ PCMs, PCM pouches, Freezer bags	USA	<a href="http://www.rgees.com/">http://www.rgees.com/</a>
6	PCM Thermal Solutions	PCM heat exchangers, PCM battery jackets/wraps, PCM based Medical and biological equipment, PCM Research and Development consultation services	USA	<a href="http://www.pcm-solutions.com/">http://www.pcm-solutions.com/</a>
7	Phase Change Energy Solutions	BioPCM™, ENRG Blanket™, ENRG Panel™, PhaseStor™	USA	<a href="https://phasechange.com/">https://phasechange.com/</a>
8	DuPont™	Energain®	USA	<a href="http://www2.dupont.com/Czech_Republic_Country_Site/cs_CZ/Products_and_Services/Products/energain.html">http://www2.dupont.com/Czech_Republic_Country_Site/cs_CZ/Products_and_Services/Products/energain.html</a>
9	Advanced Cooling Technologies, Inc.	PCM heat sinks, Thermal management services	USA	<a href="https://www.1-act.com/">https://www.1-act.com/</a>
10	Encapsys, LLC	EnFinit® microencapsulated PCM	USA	<a href="http://www.encapsys.com/">http://www.encapsys.com/</a>
11	Insolcorp, Inc.	Infinite R™, Phase change building material	USA	<a href="http://www.insolcorp.com/">http://www.insolcorp.com/</a>
12	Cold Chain Technologies, Inc.	Koolit® Advanced Refrigerant PCMs, KoolTemp® GTS Enshield, PCM pallet covers	USA	<a href="http://www.coldchaintech.com/">http://www.coldchaintech.com/</a>
13	Andores New Energy CO., Ltd	ANDOR Cold Chain PCM-18 HDPE / PET 300, Plastic Ice Brick, Encapsulated PCMs, Plastic Gel Ice Packs	China	<a href="http://m.andores.com/">http://m.andores.com/</a>
14	Shanghai Lizoo Commodity Co.,Ltd	PCM dry powder, PCM panels, packs and balls, Cooling vest, PCM cooling mattress, PCM slurries for fabrics infusion, Temperature regulation textiles	China	<a href="http://www.lizoo.cn/">http://www.lizoo.cn/</a>
15	Hangzhou Phase Change Technology Co., Ltd	Microencapsulated PCM, MicroPCM Intelligent Attenuation Textiles, PCM balls/pouches,	China	<a href="http://www.phasechange.com.cn/">http://www.phasechange.com.cn/</a>
16	International Haotian Technology Co.,Ltd	Medical cool bags, Pharmaceutical shipping cool boxes.	China	<a href="http://www.medicalpolarbox.com/">http://www.medicalpolarbox.com/</a>
17	Croda International plc	CrodaTherm™ PCMs	UK	<a href="https://www.crodatherm.com/">https://www.crodatherm.com/</a>
18	Phase Change Materials Products Ltd.	Subzero eutectic PCMs, Positive Temperature Salt Hydrate & organic PCMs, High temperature salt PCMs, Solid/solid PCMs, Encapsulated PCMs	UK	<a href="http://www.pcmproducts.net/">http://www.pcmproducts.net/</a>
19	Armstrong® World Industries Ltd.	CoolZone PCM Ceilings	UK	<a href="https://www.armstrongceilings.com/">https://www.armstrongceilings.com/</a>
20	Sunamp Ltd	Sunamp Heat Batteries	UK	<a href="https://www.sunamp.com/">https://www.sunamp.com/</a>
21	Rubitherm® Technologies GmbH	RT & SP series PCMs, Cooling batteries, CSM (compact storage modules), Warming elements, Heat pads	Germany	<a href="https://www.rubitherm.eu/">https://www.rubitherm.eu/</a>
22	SGL Group- The Carbon Company	SIGRATHERM GC graphite PCM powder, SIGRATHERM LC boards infiltrated with PCM	Germany	<a href="http://www.sglgroup.com/">http://www.sglgroup.com/</a>
23	va-Q-tec AG	PCMs for heat and cold storage.	Germany	<a href="https://www.va-q-tec.com/en/">https://www.va-q-tec.com/en/</a>
24	Axiotherm GmbH	Axiotherm HeatSel, Axiotherm Heatplates, PCM	Germany	<a href="https://www.axiotherm.de/en/">https://www.axiotherm.de/en/</a>
25	Pluss Advanced Technologies Pvt. Ltd.	save® PCMs: FSM (Form stable mixtures microwaveable), FS (Form stable mixtures),OM (Organic materials), PLUS® Encapsulation.	India	<a href="http://www.pluss.co.in/">http://www.pluss.co.in/</a>
26	TEAPPCM	T-series Latest™ PCMs, S-series salts, Telecom shelters PCM, PCM filled panels, balls & jackets, PCMs for electronic component cooling.	India	<a href="http://www.teappcm.com/">http://www.teappcm.com/</a>
27	PCM Energy P. Ltd	Hot & Cold packs, PCM and heat treatment salts up to 1100 °C	India	<a href="http://pcmenergy.com/">http://pcmenergy.com/</a>
28	Chemtex Speciality Ltd.	PCM Gel, PCM Salts, Eutectic Salts	India	<a href="http://www.chemtex-speciality.com/">http://www.chemtex-speciality.com/</a>
29	KAPLAN ENERGY	Solid/liquid Standard PCM, Solid/Solid special PCM	France	<a href="http://www.kaplan-energy.com/">http://www.kaplan-energy.com/</a>
30	Cristopia	STL Technology, PCM nodules: AN.15, AN.12, AN.10, AN.3, AN.00, Design, installation, commissioning of thermal energy storage systems	France	<a href="http://www.cristopia.fr/">http://www.cristopia.fr/</a>
31	Alexium International	Alexicool	Australia	<a href="http://alexiuminternational.com/">http://alexiuminternational.com/</a>
32	PCP	Phase Change Materials: PC-21, PC-16, PC-11, PC-7, PC0, PC14, PC17, PC25, PC29	Australia	<a href="https://pcpaustralia.com.au/">https://pcpaustralia.com.au/</a>
33	GLASSX Inc.	GLASSX® crystal, GLASSX® store	Switzerland	<a href="http://glassx.ch/">http://glassx.ch/</a>
34	Climator Sweden AB	ClimSel PCMs	Sweden	<a href="http://climator.com/">http://climator.com/</a>
35	Salca	Thermusol® HD26, Thermusol® HD32, Thermusol® HD60, Coolvest, Laptop cooler, Thermopack, K-block	Netherlands	<a href="http://www.salcabv.nl/">http://www.salcabv.nl/</a>
36	Crystal Air PCM	Crystal T-Pak cassettes, Crystal sphere	Ireland	<a href="http://www.crystalairpcm.ie/">http://www.crystalairpcm.ie/</a>
37	ARANER	Thermal storage systems, Design and consultancy	Spain	<a href="http://www.araner.com/">http://www.araner.com/</a>
38	Cryopak	CryoCube™ ProBag™, TimeSaver™ CRT Series	Canada	<a href="https://www.cryopak.ca/">https://www.cryopak.ca/</a>

the materials such as organic, inorganic and the eutectics as shown in Fig. 3. Initially, the solid-liquid PCMs behave like SHS materials; their temperature starts rising as they absorb heat. Unlike conventional SHS materials, when PCMs reach their phase transition tem-

perature they continue absorbing heat without a significant rise in temperature until all the material is transformed to the liquid phase. When the temperature around a melted PCM falls, it solidifies and the stored latent heat tends to release. Organic PCMs used

**Table 2**  
Currently available material selection databases and software/modeling tools.

No.	Name	Database/software tool	Access	Content	Ref.
1	MatWeb	Online database	Free	Comprehensive property datasheets of over 125,000 materials along with their suppliers, can be exported to other advanced modeling software such as ANSYS and COMSOL.	[134]
2	MATERIA	Online database	Free	Technical details of over 2600 innovative materials with their manufacturers.	[135]
3	MPDB	Material property database	Paid/ Demo	Mechanical and thermophysical properties of around 2700 materials along with their temperature dependency. Database file can be exported to modeling/simulation software.	[130]
4	ThermoLit	NIST online database	Free	Literature report builder for measured thermodynamic properties of numerous materials available in NIST SOURCE Data Archive.	[131]
5	IDEMAT	Material selection online database and software	Free	Life cycle analysis, sustainability aspects, environmental impacts and application of over 1000 materials.	[136]
6	CES Selector	Material selection software	Paid/ Demo	Tool for comparing thermophysical, mechanical, optical properties of materials along with their environmental impact and cost analysis.	[129]
7	GRANTA MI	Material database management software	Paid/ Demo	Management of material database and provides support for integrating it in various modeling/simulation software.	[132]
8	Thermo-Calc	Thermodynamic properties calculation software	Paid/ Demo	Phase diagrams and thermodynamic properties of eutectic materials can be computed by utilizing the built-in database of alloys, salt hydrates and other important materials.	[133]
9	PCMexpress	Simulation tool	Free	Demonstrates the effect of PCMs in thermal management of the building with the economic analysis. Facilitates technologists and architects in selecting PCMs.	[137]
10	Worksheet database	Computational Tool	Free	Prediction of composition and thermophysical properties of 100 eutectic organic phase change materials with the flexibility to expand the database with user defined properties.	[138]



**Fig. 3.** Classification of thermal energy storage materials.

for TES are paraffin waxes, alkanes, esters, fatty acids, alcohols and various compounds including ketones, amides, sugars, dienes, oleochemical carbonates and so on, while the inorganic PCMs are sub-divided into salts, salt-hydrates, and metals. Among various metallic salts such as carbonates, chlorides, sulfates, fluorides, and nitrates, magnesium chloride hexahydrate and sodium sulfate decahydrate are the most appropriate PCMs. Aluminum alloys used as PCMs possess high thermal reliability for TES applications [68]. The specially engineered materials having desired thermophysical properties are designed with a mixture of the components (mole fraction) at the eutectic point as derived from their phase diagram and are known as Eutectic PCMs (EPCMs) [69]. EPCMs may consist of a eutectic mixture of multiple materials either organic components [69], inorganic components or a mixture of both as well thus

classified as organic eutectics [70–74], inorganic eutectics [75,76] and organic-inorganic eutectics, respectively [77–79]. Binary, ternary, quaternary and quinary EPCMs are well studied and reported in the literature [69]. Inorganic EPCMs includes salt eutectics and metal eutectics [68,80].

### 3.2. Phase transition temperature

PCMs are categorized on the basis of their phase transition temperature as low-, intermediate-, and high-temperature PCMs. Hoshi et al. [81] categorized PCMs with melting points below 220 °C as low-temperature materials, those with melting points between 220 and 420 °C as medium-temperature materials, and the one having melting points above 420 °C as high-temperature

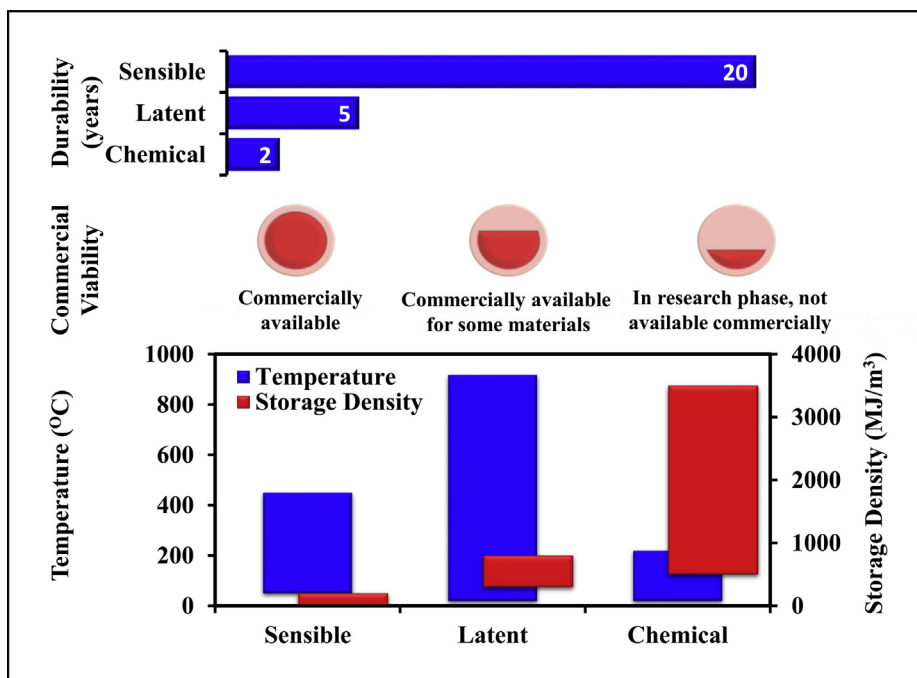


Fig. 4. Storage capabilities, commercial viabilities and durability aspects of PCMs for thermal energy storage.

materials. Fig. 5a–c show the melting points of selected organic compounds [3,77,80,82]. The organic PCMs involving paraffin, fatty acids, polyalcohols, polymeric materials such as PEG (Polyethylene glycol) and sugar alcohols such as D-threitol, erythritol, D-mannitol, and pentaerythritol are usually considered for low-

temperature applications since their operating temperatures fall within the range of 100–200 °C [83]. Most of the organic compounds have melting points below 80 °C. High-density polyethylene (HDPE) has the highest melting point of 150 °C in all the selected organic materials. Organic EPCMs fall under the category

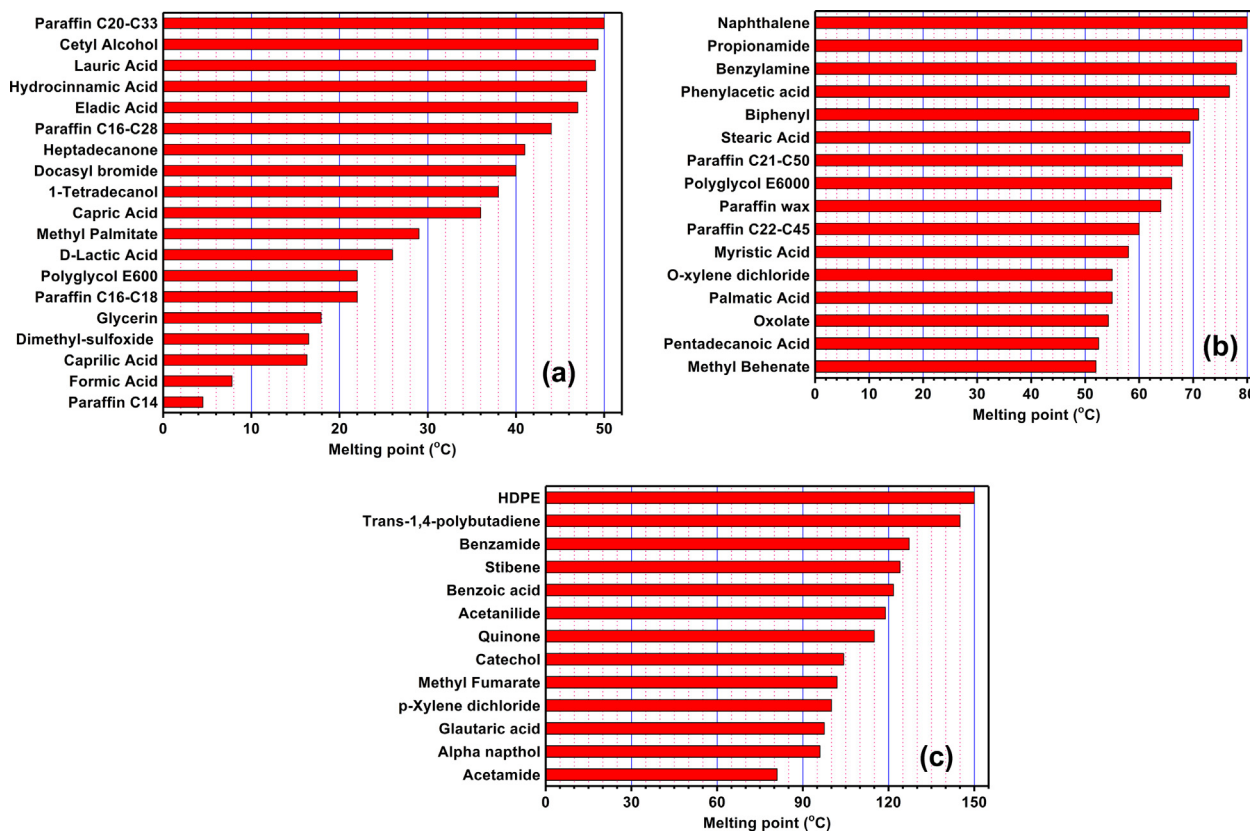


Fig. 5. Melting points of selected organic PCMs (a) below 50 °C, (b) between 50 and 80 °C and (c) over 80 °C for thermal energy storage.

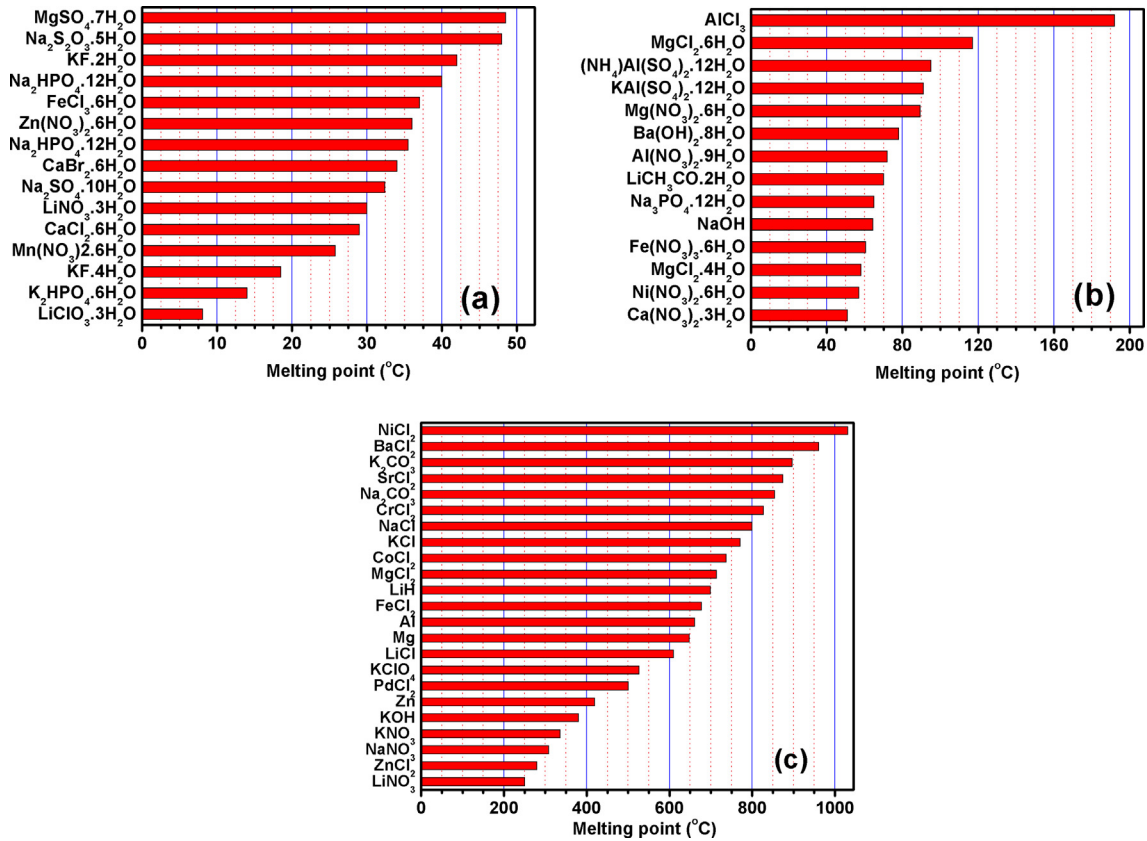


Fig. 6. Melting points of selected inorganic PCMs (a) below 50 °C, (b) between 50 and 220 °C, (c) over 220 °C for thermal energy storage.

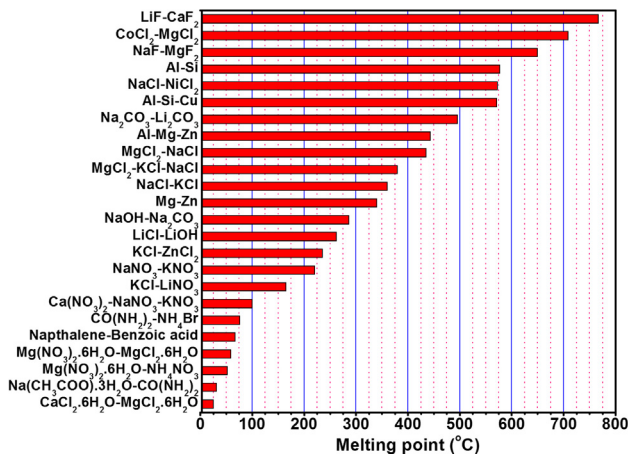


Fig. 7. Melting points of selected eutectic PCMs for thermal energy storage.

of low-temperature PCMs as well. Fig. 6a–c indicate the melting points of selected inorganic materials [35,77,80–82,84–86]. Most salt hydrates have melting points below 220 °C. However, inorganic salts have much higher melting points than hydrates up to 1000 °C. These inorganic salts such as metal carbonates, chlorides, sulfates, fluorides, and nitrates have been widely used as PCMs for high-temperature TES applications requiring operating temperature over 500 °C [85]. Fig. 7 presents the melting points from room temperature up to around 770 °C for selected eutectic mixtures [3,35,80,84–87]. As seen clearly, metal alloys and inorganic eutectics show exceptionally high melting points, which are ideal for concentrating solar power (CSP) applications. Eutectic aluminum

alloys are of great significance for high-temperature TES systems, Fig. 7 [88].

Organic PCMs are mainly employed for low and intermediate-temperature applications, whereas most of the inorganic PCMs are used for high-temperature applications [18,68,89,90]. The EPCMs can be used for low, intermediate as well as high-temperature applications depending upon the nature of their constituents [91,92]. Fatty acids such as stearic acid, palmitic acid, lauric acid, capric acid and myristic acid based quinary EPCMs possess melting temperature even below room temperature and are low-temperature PCMs [92]. Most inorganic-inorganic EPCMs fall under intermediate-temperature PCMs, while organic-inorganic EPCMs are low-temperature PCM with melting point <220 °C. Various applications of PCMs including cold storage, thermal control of buildings, solar thermal domestic water heating and space heating purposes are discussed extensively in Section 6 (Applications and commercial viability).

#### 4. Selection criteria

Various properties such as physical, thermal, chemical, and kinetic characteristics of the materials and also the cost, ease of availability, product safety, adaptability, and reliability are considered as key selection parameters of PCMs for any particular TES application. A general selection criteria of PCMs is illustrated in Fig. 8. There is a big pull from the middle and top of the triangle where the thermophysical properties of the PCM, is seen as game changers and the operating requirements of the system for demand-side management are met by considering the most appropriate options. Reliability of the shortlisted candidates is probed and the ones with exceptionally higher cyclic stability are always



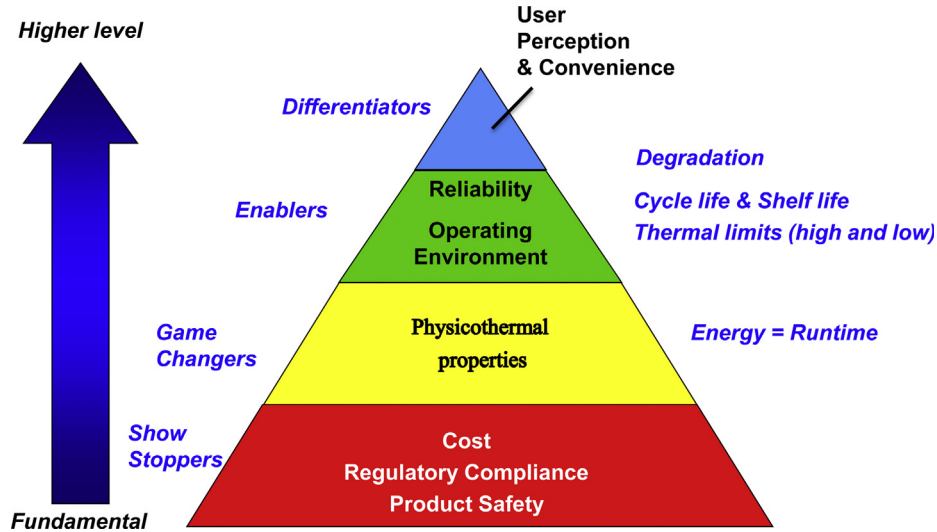


Fig. 8. General selection characteristics of PCMs for thermal energy storage applications.

considered as the most appropriate and this enables to identify the promising PCMs. End user perception and convenience is considered as a topmost priority for the successful applicability of the technology and capturing the market by competing with conventional technologies. Some significant barriers are near the bottom where the associated cost for the less expensive solution meeting all the constraints and product safety such as health hazard and toxicity are the key factors to be considered for environmental sustainability and to meet regulatory compliance. Along with the technical aspects of PCMs based TES, its environmental and social impacts are also considered as part of the evaluation criteria.

PCMs are mainly characterized by their thermal, physical, kinetic and chemical properties, apart from availability and cost aspects [82]. These properties substantiate the suitability and applicability of a PCM to be used for TES in particular applications [93]. In order to evaluate the suitability of a particular PCM for a specific application and temperature range, it is crucial to determine its thermophysical properties. There are several characterization equipment and techniques for determining chemical and thermal stabilities for selecting the PCM for specific applications. Properties such as melting/freezing temperatures, latent heat of fusion, and specific heat capacity are measured by using Differential Scanning Calorimetry (DSC) technique [94]. Thermal conductivity can be determined by various techniques such as T-history method [95–97]. In addition to this, thermal stability, thermal reliability and heat capacity for a particular PCM are determined by using Thermogravimetric Analysis (TGA), while Fourier Transform Infrared spectroscopy (FTIR) is used to investigate its chemical structure and stability [98–100]. Standards such as ASTM E1269-11 [101], ASTM C1784-14 [102] must be followed and calibration of the equipment for thermal analysis should be done in compliance with GEFTA [103] to avoid discrepancies in the outcomes. Cyclic stability is essential for the adaptation of particular PCM and is determined by performing DSC or through the T-history method for multiple melt/freeze cycles of the PCMs in order to analyze the extent of deviation of thermophysical properties.

Among the thermal properties, phase transition temperature of PCM falling within the operating temperature range is one of the key requirements while selecting it for a particular TES application. Other desirable thermal properties for ensuring optimum performance of the PCMs include desirable latent heat, higher thermal conductivity, energy density and heat capacity [3,35,82]. The

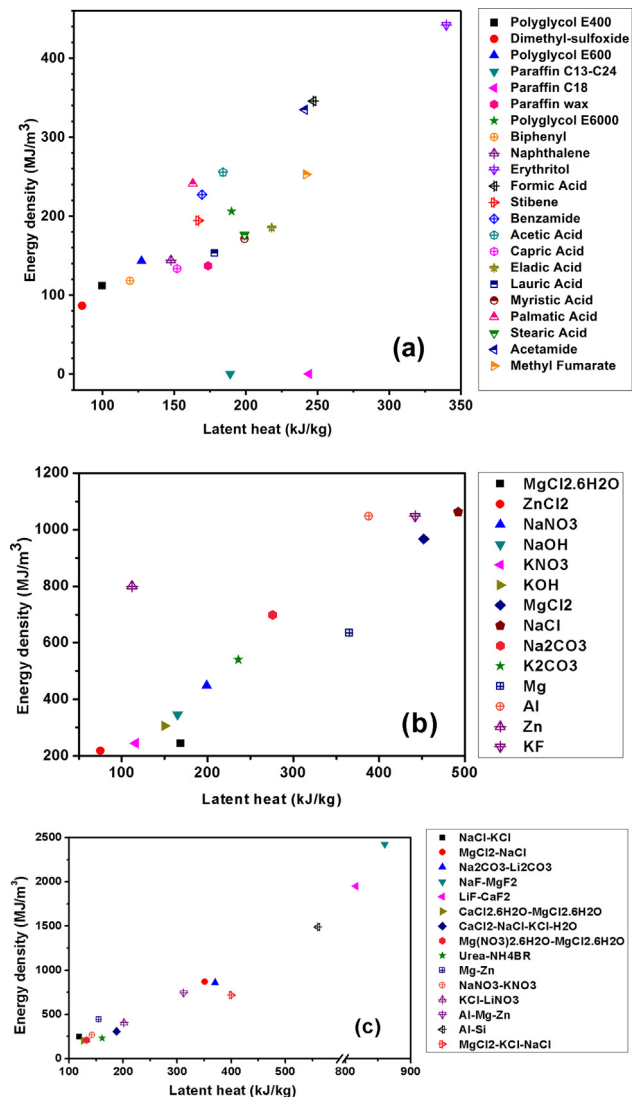


Fig. 9. Latent heat and energy density of selected (a) organic, (b) inorganic and (c) eutectic mixture PCMs.

values of latent heat and heat capacity are linked with the amount of energy a specified PCM is capable of storing or releasing [104]. A higher latent heat and heat capacity signify the energy storing/releasing capability of a PCM, while a high thermal conductivity ensures the faster rate of TES and release in a PCM [17,105,106]. The requisite physical properties for ideal PCMs include negligible volumetric changes during phase transformations, the low vapor pressure in the operating temperature range, favorability of phase equilibrium, congruent melting of constituent component(s), and desired density [82]. Apart from that, the kinetic properties required for effective utilization of PCMs for TES include the elimination of supercooling, greater nucleation rate and an adequate crystallization rate, while the suitable chemical properties include high chemical stability, reversible freezing/melting cycle, non-corrosive, non-toxic, non-explosive and non-flammable nature of PCMs [59,107–109].

The selection procedure of the most appropriate PCM for a particular application is highly complex and time consuming due to the large number of PCMs available and/or being developed currently in the field of TES. With very limited available data on the thermophysical properties for most of the materials in the literature, the selection procedure becomes highly challenging. The comparison is made after obtaining the characteristics of the investigated PCMs and there are numerous drawbacks of this method as well as there is a limited access to the data on the cost and the environmental effects of the PCMs [110].

Organic, inorganic and eutectic materials are commonly used for LHTES applications and are extensively studied. PCMs with high thermal energy storage density are commercially available, a wide range of paraffin and fatty acid based PCMs covering the operating temperature range from  $-40$  to  $151$  °C are manufactured by Rubitherm® [111] and Entropy Solutions LLC [112], respectively. Fig. 9a shows the latent heat and energy density of selected organic PCMs [80]. Both high latent heat and high energy density are preferred while selecting a PCM. Most of the selected organic materials have latent heat higher than  $100 \text{ kJ}\cdot\text{kg}^{-1}$  and energy density

higher than  $100 \text{ MJ}\cdot\text{m}^{-3}$ . Paraffin C13–C24, Paraffin C16–C28, Paraffin C18, Paraffin C20–C33, Paraffin C21–C50, and Paraffin C22–C45 have quite small energy density between  $0.14$  and  $0.19 \text{ MJ}\cdot\text{m}^{-3}$ . Formic acid, acetamide, and erythritol have relatively higher latent heat ( $> 250 \text{ kJ}\cdot\text{kg}^{-1}$ ) and energy density ( $> 300 \text{ MJ}\cdot\text{m}^{-3}$ ) compared to the other organic materials. Their melting points are  $7.8$ ,  $81$  and  $118$  °C, respectively. Fig. 9b indicates the latent heat and energy density of selected inorganic materials [35,80,81,84–86]. Generally, inorganic materials have a higher energy density than that of organic materials. All the inorganic PCMs have energy density higher than  $200 \text{ MJ}\cdot\text{m}^{-3}$ . KF,  $\text{MgCl}_2$ , and NaCl have the highest latent heat ( $> 400 \text{ kJ}\cdot\text{kg}^{-1}$ ) and energy density ( $> 900 \text{ MJ}\cdot\text{m}^{-3}$ ) among all the inorganic materials and the corresponding melting points are  $857$ ,  $714$  and  $800$  °C, respectively. Fig. 9c shows the latent heat and energy density of selected eutectic mixtures. Al–Si, LiF– $\text{CaF}_2$ , and NaF– $\text{MgF}_2$  have the highest latent heat and energy density values [3,35,80,84–87]. The latent heat values are  $560$ ,  $816$  and  $860 \text{ kJ}\cdot\text{kg}^{-1}$ , respectively. The energy density values are  $1490$ ,  $1950$ , and  $2425 \text{ MJ}\cdot\text{m}^{-3}$  and the corresponding melting points are  $577$ ,  $767$ , and  $650$  °C, respectively.

Fig. 10a shows the thermal conductivities of selected organic materials [3,77,80]. The selected organic materials have thermal conductivities in the range of  $0.13$  to  $0.33 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ . Fig. 10b indicates thermal conductivities of selected inorganic PCMs [80,81,84–86]. Inorganic materials generally have higher thermal conductivities than organic materials. Most inorganic PCMs have thermal conductivities between  $0.5$  and  $0.9 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ .  $\text{Na}_2\text{CO}_3$  has a thermal conductivity of  $2 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ , whereas NaCl has a thermal conductivity of  $5 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ . Fig. 10c presents thermal conductivities of eutectic mixtures [3,35,80,84–87]. Inorganic salt eutectics have thermal conductivities in the range of  $0.4$ – $2.1 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ , while metal eutectics have much higher thermal conductivities ( $> 70 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ ); for example, Al–Si eutectic shows the highest thermal conductivity of  $180 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ .

The paraffin and alkanes also hold the benefit of lower cost, high thermal and chemical stabilities with no toxicity and minor

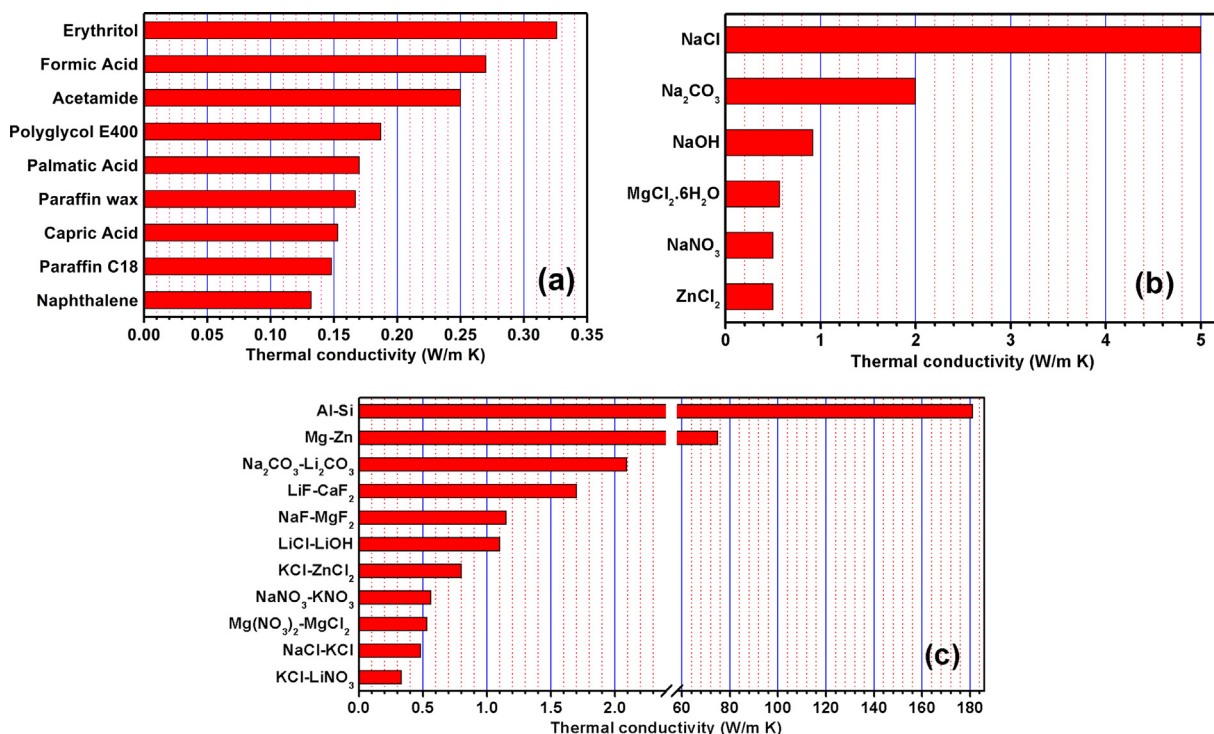


Fig. 10. Thermal conductivities of selected (a) organic, (b) inorganic and (c) eutectic mixture PCMs.

supercooling. However, the problem with organic PCMs is their lower thermal conductivity for the different organic PCMs, resulting in lower heat transfer rates for energy storage thus deviating from the desired charging and discharging cycle time. However, recent developments have struggled to address these issues by using either stable metal matrix or by incorporation of micro or nano-metallic or metal oxide particles in attempts to enhance the thermal conductivity of organic PCMs.

Table 3 compares the advantages and disadvantages of organic PCMs [98,113–116]. Salt hydrates possess high latent heat but may show congruent melting, incongruent melting or semi-congruent melting behavior, while those undergoing incongruent melting are not considered for TES applications [59]. Primary advantages include the high volumetric latent heat storage capacity, ease of availability and sharp melting point along with high thermal conductivity and high heat of fusion, which makes them suitable for CSP applications. Table 3 lists the advantages and disadvantages of inorganic PCMs [98,113,114,116–118]. Disadvantages include high volumetric changes during phase transformation, supercooling in solid-liquid transitions and inorganic PCMs become ineffective after repeated cycling. Molten-salt based PCMs are usually of low cost and have high heat-storage density. There are a couple of disadvantages as well in utilizing molten-salt PCMs. One of the major disadvantages is that they have high volume expansion ratio during phase transition, which requires certain measures while designing the TES system. Another disadvantage is the high rate of corrosion on container/piping alloys in contact with the molten-salts [90].

Table 3 also highlights the advantages and disadvantages of EPCMs [98,113,114,117,119]. The main advantages of EPCMs are their sharp melting point and their volumetric storage density, which is slightly greater than that of organic compounds. The availability of the limited data regarding the thermophysical properties is the major disadvantage while developing such type of TES materials. Some of the major issues faced by EPCMs are their lower thermal conductivity values, effects of sub-cooling, high corrosion,

lower thermal stability, phase segregation, which affects their performance and thermal energy storage capability [35,120–122]. It is proposed that metals and alloys possessing higher heat capacity values, higher thermal conductivities, and thermal durability could be more favorable candidates for high-temperature thermal energy storage applications compared to inorganic PCMs [18,123]. Moreover, it is reported that the issues of the PCMs can be successfully avoided by using various methods and techniques that are listed and described in detail in Section 7 (Future trends) [124–128].

## 5. Databases and software tools

As given in Table 2, there are several user-friendly software tools available in order to select PCMs for any particular application [129–138]. The developers of the software tools have eased the complicated selection procedure of the PCMs for the scientists and design engineers; one among them is CES (Cambridge Engineering Selector) [129] developed at the Cambridge University by Prof. Ashby [139]. Khare et al. [18] used the CES software tool for the identification of metals and alloys as a potential candidate for high-temperature TES applications and reported that Al-Si (88–12 wt%) and Al-Mg-Zn (60–34 - 6 wt%) alloys are most suitable in the temperature range of 400–750 °C. They also evaluated the environmental impacts of these alloys using the EcoAudit tool available in the CES pack. Fernandez et al. [140] used the CES selector software tool to give an overview of the most suitable materials for long-term SHS and short-term SHS within the operating temperature range of 150–200 °C. Ramalheite et al. [141] investigated and organized all the information related to digital tools for material selection, and the author reported that MatWeb [134] provides a broad spectrum of the online database for 115,000 materials. MATERIA [135] gives free online access to 2600 innovative materials and IDEMAT [136] is a digital tool to analyze the environmental impact of the materials. These tools are helpful in selecting PCMs for particular applications. Huizhen [92] employed Schrader equation for designing binary, ternary, quaternary and quinary

**Table 3**  
Advantages and disadvantages of PCMs.

Type	Advantages	Disadvantages
Organic	Freeze without much super-cooling or sub-cooling Ability to be incorporated directly Low vapor pressure in phase change process Good thermal performance Ability to melt congruently Self-nucleating properties Compatibility with conventional material of construction Availability in large temperature range No segregation Chemically stable High heat of fusion Safe and non-reactive Recyclable	Low thermal conductivity in their solid state. Some are insoluble in water Burn easily Low phase change enthalpy Low density Require large surface area High heat transfer rates are required during the freezing cycle. Volumetric latent heat storage capacity is low Flammable. This can be easily alleviated by a proper container More expensive High volumetric expansion Low heat capacity
Inorganic	High thermal conductivity Large heat storage capacity Lower volumetric expansion High heat of fusion per unit volume Less costly Non-flammable Sharp phase-change Greater phase change enthalpy Recyclable	High degree of supercooling Lack of thermal stability Phase segregation Incongruent melting and dehydration during thermal cycling Some have high weight Corrosive Prone to degradation Chemical instability Compatibility issues with some building materials Requires container and support
Eutectics	Sharp melting temperature High volumetric thermal storage density No phase segregation and congruent phase change	Lack of currently available test data of thermo-physical properties Low total latent heat capacity Some of eutectics suffer from super-cooling effect Strong Odor Costly

solid-liquid EPCM with five different fatty acids (capric acid, lauric acid, myristic acid, palmitic acid, and stearic acid) to obtain desired thermophysical properties. The mathematical models validated by DSC are useful in order to predict the thermophysical properties of various EPCMs.

## 6. Applications and commercial viability

PCMs have a variety of applications for passive and active heating/cooling as a component or integrated part of cascaded TES systems [83,142,143]. PCMs are employed on the basis of system requirements as discussed in the selection criteria [80]. Numerous applications of PCMs, which are currently in the research and development stage, include smart thermal grid, compact TES systems, and CSP plants.

The concept of incorporating PCMs into a smart thermal grid system is primarily instigated by applications with large thermal inertia integrating the inconsistent supply of renewable resources requiring the heat to be stored and supplied upon as per demand [144]. In addition to that, the idea of compact TES systems is basically attributed to the capability of PCMs to store a high amount of heat per cubic meter in comparison to any other conventional technologies thus promoting compactness of the system [145]. Integration of PCMs into CSP applications is also based on the same concept with an emphasis on performance, cost, and reliability. The use of EPCMs in CSP technology can reduce the required volume of the storage tank to a great extent, which can lead to reduced cost of materials and construction for the system [85].

PCMs can be employed in building energy storage systems [146], waste heat recovery systems [122,147,148], thermo-regulating fibers, smart textile materials [149,150], thermal management of the batteries [109,151], temperature management of the microelectronics [152], photovoltaic thermal (PV/T) applications [153], space and terrestrial thermal energy storage applications [154] and in the temperature management of greenhouses [155].

### 6.1. Energy storage in concentrating solar power systems

PCMs are very commonly used in CSP systems for TES. SHS and LHS are the two major heat storage techniques used in CSP systems. The reversibility of the phase-changing process is an advantage of PCMs for long-term usage. Because of the high heat storage capacity and repeatability, LHS using PCMs is very commonly used

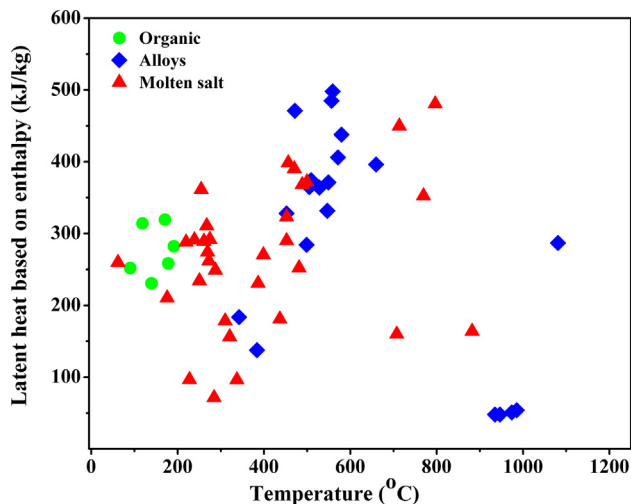


Fig. 11. Relationship between melting temperature and latent heat of high temperature PCMs.

to store thermal energy in CSP systems [156]. Fig. 11 shows the latent heat enthalpy for different types of PCMs at different temperatures [156]. Various PCMs have been investigated for applications of TES in CSP systems, mainly organic compounds (sugar alcohols < 200 °C), molten salts (>300 °C) and metallic alloys (>500 °C). Molten-salt based PCMs are usually low cost and have high heat-storage density, although the major disadvantage is the corrosion of containers, pipes, and valves [156].

Vapor pressure, thermal and structural properties of several molten-salt and metallic alloy based PCMs have been studied at the National Renewable Energy Laboratory (Golden, CO, USA). Typically, thermal properties of  $\text{MgCl}_2\text{-KCl-NaCl}$  (59.98–20.42–19.60 wt%) ternary molten-salt compound was studied by using DSC/TGA from 120 to 450 °C during three heating and cooling cycles. The average melting point was found to be 380 °C and the average heat of fusion was  $198.55 \text{ kJ}\cdot\text{kg}^{-1}$  [123]. Laing et al. studied the design of high-temperature LHTES systems for CSP applications and reported that graphite or aluminum fins in the design of the TES system proved to be the most cost-effective. These researchers at DLR-German Aerospace Center also introduced this sandwich concept comprising of fins in the LHTES notably for CSP applications and reported that no degradation was observed after 172 cycles in the sodium nitrate ( $\text{NaNO}_3$ ) based PCMs having the melting point of 306 °C [157]. Xu et al. reviewed PCMs for TES application in CSP and concluded that by employing PCMs for TES in CSP despite using SHS, reduction in the size of storage tanks can be achieved, ultimately leading to significant shrinkage in the construction and materials cost of CSP technology. The author reported lithium carbonate to be the most expensive PCM followed by aluminum fluoride and potassium hydroxide, while magnesium fluoride and sodium chloride as the cheapest [85].

Galione et al. [158] used a multi-layered solid PCM (MLSPCM) concept for designing a TES prototype for CSP applications. In this study, the tested MLSPCM prototype showed greater energy storage capability and efficiency as compared to single-solid thermocline tanks of the same volume. Aldoss and Rahman [159] compared the single-PCM and multi-PCM based TES design, multi-PCM TES system showed better performance compared to single-PCM based TES system. Performance of multi-PCM TES system enhances with the increase in the number of stages and the authors recommend three stages to be appropriate. Elfeky et al. [160] performed a numerical investigation by developing a transient Concentric-Dispersion model to compare the single-PCM and multi-stage PCM based high-temperature TES for CSP. Phase change process within the three-stage PCMs unit and single PCM unit are analyzed for different thermophysical properties. The three-stage PCM unit showed faster charging, and a higher heat transfer rate and overall working efficiency than the single-PCM unit for charging-discharging under similar working conditions. Abdulla and Reddy [161] provided a comparison between single and multi-layered packed bed TES system for CSP plants. Discharging time for the single and multi-layered packed bed TES system is 4.19 and 5.32 h, respectively. Extra discharge of 1 h is observed upon introducing PCM with a width of 10% at top and bottom of the multi-layered system. Tank size of the multi-layered configuration is much smaller than the single configuration for a common energy output, which decreases the associated cost. Multi-layered configuration is most appropriate for the CSP plant and a detailed economic analysis needs to be done for analyzing the prospects of integrating multi-layered TES configuration in CSP plants.

Singh et al. [58] analyzed the LHTES system based on graphite foam-sodium chloride as a PCM for CSP applications, and reported the round-trip efficiency of the graphite foam-NaCl PCM in TES system is greater than 96%. Performance enhancement and increment in the heat transfer and thermal conductivity are observed as a result of added graphite foam in NaCl, while the number of pipes



carrying heat transfer fluid (HTF) in the LHTES system reduced by a factor of twelve as compared to non-graphite foam system thus graphite foam-NaCl PCM is a promising TES material for CSP plants operating on the  $s\text{-CO}_2$  cycle. Zhao et al. [162] performed heat transfer analysis on  $\text{MgCl}_2$  based LHTES system for CSP applications using COMSOL software. They studied the effect of adding graphite foam in  $\text{MgCl}_2$  and reported a significant increase in the thermal conductivity and performance efficiency of the LHTES system comprising of graphite foam- $\text{MgCl}_2$  PCM. Also, the number of HTF pipes in LHTES tank was reduced by a factor of eight as compared to a non-graphite foam system.

An economic evaluation of LHTES system for large-scale CSP systems was conducted by Christopher et al. [163]. In this study, the size and cost of the LHTES system are compared with a two-tank sensible heat storage system. It has been found that the LHTES systems are economically competitive in comparison to sensible heat storage and have the potential to reduce the capital cost by at least 15%.

### 6.2. Passive thermal management in batteries

Demand for rechargeable batteries, most importantly for lithium-ion batteries (LIBs), grows rapidly due to their high energy densities for use in portable electronics, battery powered tools, and electric vehicles. The main barriers in using these batteries for large fleets of vehicles on public roads are the safety, costs related to cycle and calendar life, and performance. These challenges are coupled with thermal effects in batteries. For a better battery pack, the rate of heat dissipation must be fast enough so that the battery pack never reaches the thermal runaway temperatures [164]. However, larger power demands and increasing energy density of lithium-ion battery packs result in higher operating temperatures. Most of the commercial LIB chemistries tend to degrade or age at or above  $60^\circ\text{C}$ , which leads to rapid loss of capacity over subsequent charge/discharge cycles as well as reduced overall power output. In order to address these concerns, numerous studies into both active and passive thermal management systems for batteries have been undertaken for many applications that use LIBs. Thermal management systems rely on the transfer of heat away from the cell surface, thereby inhibiting core temperature rise and limiting material degradation. PCMs are very commonly used to effectively mitigate large temperature escalation during discharging as well as charging, thereby relieving performance degradation over the life of the battery and increasing the safety of the battery system [165].

Passive thermal management using PCMs for LIBs in all-electric vehicles (EV) and hybrid electric vehicles (HEV) have been studied by Said et al. [166] at the Illinois Institute of Technology. In this study, a graphite matrix filled with commercial PCM was used and the results indicated that the capacity of a Li-ion battery module with PCM can be safely utilized even under extreme temperature and operating conditions. In a recent study conducted in 2017 by Wang et al. [167], a passive thermal management system for three different types of LIBs was investigated using copper foam saturated with PCMs. This coupling of copper foam with PCM resulted in better thermal management properties than that of PCM alone. Javani et al. [168] studied the thermal management of a lithium-ion cell using PCMs, which absorbs the heat dissipated by the Li-ion cell during operation thus maintaining the temperature of the battery. PCM layer thicknesses of 3, 6, 9, and 12 mm were deployed on the Li-ion cell and the effect was investigated. Samimi et al. [169] investigated a carbon fiber-PCM composite for thermal management of Li-ion cells. The enhanced thermal conductivities of these specialized materials resulted in efficient temperature management of the Li-ion battery pack. Passive thermal management of batteries for stationary applications is currently possible, while for portable batteries the safety, size, and

associated weight of devices are most important constraints and needs further research.

### 6.3. Thermal storage in buildings

TES using PCMs for space heating and cooling of buildings is becoming popular due to the cost of fossil fuels and environmental concerns. In extremely cold or hot areas, electrical energy consumption varies greatly during the day and the night partly due to the varying demand for domestic heating or cooling. PCMs in passive or active storage systems are able to minimize these variations and are studied extensively. Zeinelabdein et al. [170] provided a review and identified the performance affecting parameters of the PCMs for thermal management in buildings and concluded the night cooling strategy using PCMs to be the most effective. Tatsidjodoung et al. [40] comprehensively reviewed the materials having a potential for TES in building applications. Kenisarin and Mahkamov [118] analyzed the research and developments for passive thermal control in the buildings using PCMs and provided thermal characteristics of the available commercial PCM based products for building applications. Zhenjun et al. [171] studied nano-enhanced PCMs for temperature management in buildings, a PCM ceiling ventilation system coupled with the solar PVT was investigated and with the application of nano-enhanced PCMs, 25% more heat was discharged in the building. Yin et al. [172] proposed a solar roofing system of PV modules integrated with a TES assembly based on PCM, and reported that the circulation of HTF through the assembly at the bottom of the PV modules will harvest the heat and transfer it to PCMs (as shown in Fig. 12), thus improving the utilization efficiency of the PV modules. The stored heat can be utilized for the thermal management of the building envelope. Amin et al. [173] analyzed the thermal properties of beeswax/graphene as a PCM and reported a 22.5% increment in the latent heat value of 0.3 wt% graphene/beeswax PCM. The author concluded the nanoplatelets graphene-based PCM to have a potential application in the thermal management of buildings thus reducing the energy demand in buildings. Sharifi et al. [174] evaluated PCM-impregnated gypsum boards for reducing the energy demand in buildings and determined that the PCM having a melting point closer to the comfort zone of the building envelope helps to prolong the envelope temperature within the comfort zone and reduces the temperature rise in the building, ultimately reducing the cost and energy requirement for temperature management of the building. These PCM-incorporated gypsum boards can also be used for thermal management of existing buildings. Ramakrishnan et al. [175] investigated the thermal performance of the PCMs incorporated in buildings by performing numerical simulations. With integrating Bio-PCM™ mat (melting points:  $27^\circ\text{C}$  and  $29^\circ\text{C}$ ) on the walls and ceilings of a non-air-conditioned building, temperature reduction of 32 and 65%, respectively in the discomfort period during the heat wave period was observed. However, special design considerations, particularly for ventilation of a building, are necessary in order to efficiently utilize the PCMs. Organic PCMs such as fatty acid gives a pungent odor after certain melt/freeze cycles. Also, special safety measures should be considered while incorporating PCMs in buildings as organic materials may catch fire under favorable conditions.

### 6.4. Solar water heating

Solar water heaters are becoming popular nowadays and are alternatives to gas or electric hot water systems. One single solar water heater can reduce  $\sim 50$  tons of  $\text{CO}_2$  emissions to the atmosphere in a 20-year period. However, efficient TES systems are important for storing solar thermal energy for water heating purposes. Solar-thermal energy can be stored in the form of latent heat

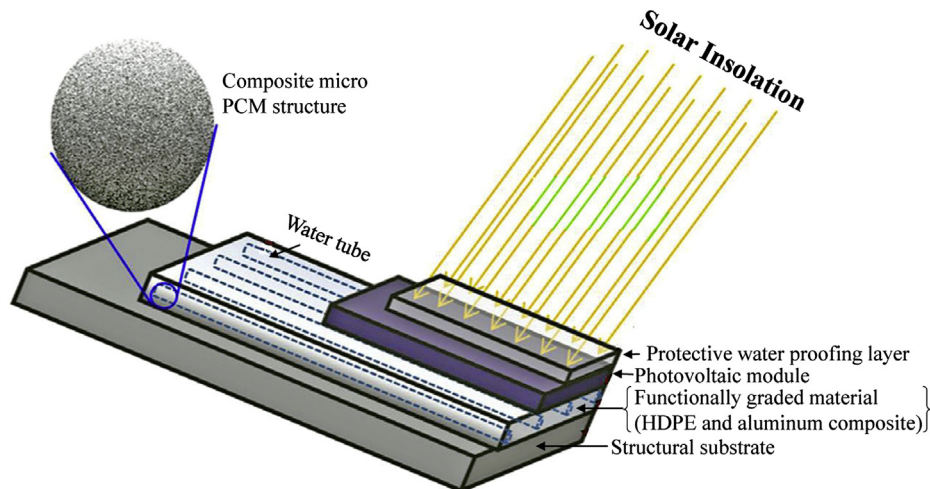


Fig. 12. Solar roofing assembly using PCMs for thermal energy storage.

by using a suitable PCM. Integration of solar thermal heating systems with solid-liquid PCMs based TES technology would enhance the efficiency of existing solar-thermal water heating systems. The amount of heat that a water tank installed with PCM can absorb is much higher than that of a normal water tank filled with only water. Fewer fluctuations in the temperature of the stored water are another key advantage of the latent heat storage systems based on PCMs [176–179].

Paraffin wax (MP: 54 °C) is a very commonly used latent heat storage PCM for solar water heating. Hasan et al. studied some fatty acids as potential candidates for PCM latent heat storage for domestic water heating and recommended that myristic acid, palmitic acid, and stearic acid, with melting temperatures between 50 and 70 °C are the most promising PCMs for solar water heating [180]. Tayeb et al. [181] developed a hot water heating system using  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  as the PCM and compared it with the simulation model that gives the optimum flow rate of the inlet water supply required to maintain the constant temperature of the water at the outlet. Font et al. [182] conducted a preliminary study for the design of a device for a domestic water heater using a solid-solid PCM. Numerical simulation has been made using a unidirectional model and verified with the experimental results. More than three decades ago, Bhargava et al. [183] theoretically studied a solar water heater integrated with PCM and concluded that the efficiency of the system and the outlet water temperature during the evening hours increases with a higher thermal conductivity of the solid-liquid phases of the materials. Vikram et al. [184] investigated a solar water heater based on paraffin PCM in India. The system consisted of two simultaneously functioning heat-absorbing units, one of them a solar water heater and the other a heat storage unit consisting of PCM.

### 6.5. Cold storage

Apart from hot thermal energy storage, PCMs also offer a promising solution to cold storage as well. Cold thermal energy storage (CTES) using PCMs is a well-studied field and commercial products with operating temperature ranging from -37 to 4 °C are manufactured by Rubitherm® Technologies GmbH [111], Entropy Solutions LLC. [112], and many other manufacturers as shown in Table 1. More research needs to be done for the performance improvement of CTES as its exergy efficiency ranges below 20% [185]. Xiaolin et al. [186] summarized the characteristics, modification techniques and the practical utilization of clathrate hydrates as cold storage materials. Xiaolin et al. [186] specifically

discussed refrigerant clathrate hydrates, hydrocarbon clathrate hydrates and introduced eutectic clathrate hydrates. Shi et al. [187] studied the cold storage performance of a 40 wt% tetra-n-butyl ammonium bromide (TBAB) clathrate hydrate slurry and reported two storage approaches for the systems comprising TBAB clathrate hydrate slurry as the cold storage medium. Sun et al. [188] summarized the formation and dissociation of  $\text{CO}_2$  hydrate and its potential application as cold storage media. The authors reported the dissociation enthalpy of  $\text{CO}_2$  hydrate as  $500 \text{ kJ} \cdot \text{kg}^{-1}$  which is even higher than ice, R11 and R141b. Thus  $\text{CO}_2$  hydrate is a promising option for cold storage applications and its other applications include rapid chilling of the meat by direct contact method but still, much research is needed on low-pressure  $\text{CO}_2$  hydrate systems to integrate them in commercial systems such as air conditioning applications. Xiaolin et al. [189] studied battery storage and phase change cold storage for photovoltaic cooling systems at three different locations,  $\text{CO}_2$  clathrate hydrate is reported as the most promising cold energy storage media comparatively with ice and capric acid-lauric acid eutectic mixture for PV cooling systems.

### 6.6. Photovoltaic-Thermal

A passive thermal management of a PV cell using PCMs is helpful in improving the overall efficiency of the system. PV/PCM is a novel technology incorporating a PV module and PCM coupled in a single module for thermal management of the silicon-based PV cells, ultimately improving the reliability of the system [190,191]. Hasan et al. [192] investigated the application of PCMs for temperature management in the PV modules and reported a 1.3% improvement in the electrical conversion efficiency and 41% of the heat was recovered from the surface of the module. The recovered heat was utilized for water heating applications as reported by the author. An investigation on limiting the rise in surface temperature of a PV module was performed by Huang et al. [193], where two PCMs for the thermal management of a photovoltaic module were investigated. A commercially available PCM Rubitherm® RT25 significantly maintained the surface temperature of the PV module and in return improved the electrical conversion efficiency of the system. The author also reported that a granular PCM GT40 can also be used in order to control the surface temperature of the PV module but it is not as efficient as RT25. Kibria et al. [194] investigated the thermal performance of a PV module using three different PCMs integrated into a TES system and reported a 5% improvement in the thermal performance of the PV device.

The author declared the PCMs to be effective in limiting the temperature rise of the PV module during insolation hours. Browne et al. [195] characterized a novel PV/T/PCM system comprising of a PV module, thermal storage PCMs assembly, and a heat exchanger and found a 5.5 °C increment in the temperature of the water as compared to the PV/T system without PCM. Kant et al. [196] performed a computational fluid dynamic analysis of a PV module integrated with PCM considering the angle of inclination, wind speed and convective heat transfer between the PV module and PCM, and reported a 6 °C temperature drop at the PV module surface as a result of the PCM layered at the back of the PV module, ultimately increasing the performance of the PV module by 5%. Hasan et al. [197] monitored the cooling effect provided by paraffin-based PCM coupled at the back of the PV module and the PV/PCM system increased the annual electrical energy of PV modules by 5.9%. Islam et al. [198] reported that a PV/T/PCM system provided ~ 33% (< 50%) more TES potential as compared to a conventional PV/T/water system (PV/T/W). In addition, the availability period of thermal energy is found to be extended up to 75–100%. The power output is enhanced by 9% with 6 °C more reduction in PV module temperature compared to PV/T/W systems and summarized that microencapsulated PCMs can offer more operational reliability in case of PV/T systems. PV/PCM systems are in development phase. Technological challenges such as the weight of the PV/PCM system, system cost, and limited PCMs for this application are the major challenges in the commercialization of this technology.

#### 6.7. Storage integrated thermophotovoltaics

In thermophotovoltaics (TPV) technology, thermal radiation is directly converted to electrical power by photovoltaic cells. The operating temperature range is >1000 °C, TPV has advantages over CSP as it does not involve any mechanically moving part and thus low maintenance cost [199]. The solar energy that can be harvested during insolation period can be stored in TES systems comprising of PCMs and used efficiently at night for power generation applications by coupling TES system with TPV. A heat-to-electricity efficiency greater than 50% is reported in the literature, which makes the system more versatile [200–202]. Veeraragavan et al. [199] conducted a night-time performance analysis of a PCM-based TES integrated with a solar TPV system and found average night power density up to 30.8 W·m<sup>-2</sup> with a storage duration of 7.3 h. Silicon as a PCM having 1800 kJ·kg<sup>-1</sup> latent heat is an attractive option for this application, but larger storage tanks have the disadvantage of low power output. The need for heat transfer enhancement in the design of the PCM storage tank is highly recommended for efficient systems.

#### 6.8. Thermal regulating textiles

Thermal-regulating fibers are comprised of PCMs having melting point in the range of 28–35 °C. When the ambient or body temperature rises the PCMs incorporated in the textile fiber tend to absorb the heat and undergo phase transformation ultimately storing the latent heat. As soon as the ambient or body temperature starts falling, the heat stored in the PCM incorporated fiber is released thus keeping the covered body in comfort zone. Iqbal et al. [203] reported the development of thermo-regulating fiber incorporated with microencapsulated PCMs, and the latent heat of this PCM-incorporated polypropylene fiber was found to be 9.2 kJ·kg<sup>-1</sup>. This type of fiber has applications as smart textiles in curtains, high altitude clothing, and furniture and in automobile interiors. Zhao et al. [204] prepared microencapsulated PCM with n-octadecane as a core, natural silk fibroin as a shell and reported

a latent heat of 88 kJ·kg<sup>-1</sup> which indicates this novel material is a promising choice for thermo-regulating textiles.

#### 6.9. Space/district heating systems and smart thermal grid

PCMs are employed in TES integrated with district heating systems for utilization of solar energy during low or no solar insolation. The solar energy is harvested using solar thermal collectors which transfer the heat by means of a HTF to the TES systems comprising of solid-liquid PCMs. Lund et al. [144] introduced the concept of 4th Generation District Heating (4GDH) and gave an insight to the smart thermal grids with application to district heating. The district heat management is done from a centralized facility that comprises a piping network and TES system connecting the town and cities. The integration of all the available heat sources including solar energy, surplus heat recovery, heat pumps and geothermal heat to the centralized storage facility helps to meet the fluctuation and intermittency of the renewable energy resources. Li et al. [205] reviewed the prospects for the integration of the renewables, TES and smart thermal grid specifically for district heating applications and proposed thermal management for the district heating systems comprising of advanced TES system with integration to the smart thermal grid. Colella et al. [144] performed CFD study on the discharging of a LHTES system consisting of technical grade paraffin wax as a PCM for district heating applications and discussed various configurations of LHTES based on PCMs with the need for enhancing the thermophysical properties of the PCMs in order to meet the fluctuations and heat fluxes in small-scale space heating applications. The standby losses of the PCMs based LHTES is one of the major concern, while integration of the TES with renewables and the concept of the smart thermal grid are a step towards the green energy.

#### 6.10. Microelectronics

PCMs based on chalcogenide glasses are very commonly used in non-volatile memory devices. Non-volatile memory refers to memory devices that can retain stored information even when electric power is not applied, usually utilized as secondary storage devices in computers, cell phones, digital music players, and digital cameras. These glasses change phase from a crystalline state to an amorphous state and vice versa [206]. Typical chalcogenide glasses are very commonly used in non-volatile memory devices, for example, Ge-Se-Te, Ge-As-Se, As-S, As-Se and so on [207]. These non-oxide glasses prepared with chalcogen elements with special phase change properties are usually more expensive than the commonly available oxide glasses. Although the main application of these phase-changing glasses is in non-volatile memory devices, there are several other applications of these phase-change glasses in electronics and optoelectronics as well.

Thermal management of electronic circuits has become more critical with a drastic reduction in the size of the circuits due to technological advancements. The micro-sized circuit can be cooled with implementing cooling systems based on PCMs for the more efficient functioning of the electronic devices. Krishna et al. [208] studied the thermal performance of nano-enhanced PCM for cooling of the electronics, and authors prepared nano-enhanced tricosane by adding Al<sub>2</sub>O<sub>3</sub> in tricosane and observed >25% temperature fall in the heat pipe along with 30% of energy provided to the heating load being stored in the nano-enhanced PCM. Colla et al. [209] investigated nano-enhanced PCMs prepared by adding 0.5 and 1 wt% aluminum oxide in paraffin waxes (Rubitherm®) RT45 and RT55 respectively for passive cooling of electronic devices. The authors performed numerical analysis using ANSYS Fluent on solid-liquid phase transformation of the nanomaterials additives composite PCMs for thermal management of



electronic devices. The major hindrance in order to adopt PCMs for this application is the leakage of the PCMs in the surrounding media which is a safety concern. Therefore much research needs to be done on the shape stabilization, and leakage prevention of the PCMs. These aspects are discussed in Section 7 (Future trends).

### 6.11. Other applications

Fig. 13 displays other applications of PCMs such as for storing, processing and packaging food. Devahastin et al. investigated paraffin wax as a PCM for a TES-integrated solar dryer in the processing sweet potatoes [210]. Lu et al. conducted an experimental study on the food display cabinets of supermarkets having novel designs integrated with PCMs for uniform cooling of the food [211]. Johnston et al. reported nano-structured calcium silicate PCM as a candidate material in order to provide thermal buffering for packaging the food [212].

Temperature management and energy storage are the most important requirements for extraterrestrial missions. Yimer et al. [213] developed an analytical model to study lithium hydride PCM for TES systems in space applications. Lafdi et al. conducted a numerical study to investigate the thermal performance of graphite-foam-incorporated PCM for TES in terrestrial applications [154] and reported >5 times increment in the average output power of the TES system as compared to the system without graphite foam. Wu et al. [214] studied shape-stabilized PCMs for thermal management of the spacecraft in extreme thermal conditions. The authors reported that shape-stabilized PCMs are helpful in order to overcome the faults of spacecraft thermal control by absorbing the heat when external heat flux of the spacecraft varies drastically.

In the potential application for thermal management of automotive engines, numerous PCMs are reported in the literature for exhaust gas heat recovery, controlling emissions of internal combustion engines and passive temperature management of electric vehicles [215]. Gumus et al. [216] developed a TES device based on  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  as a PCM for pre-heating an internal combustion engine and observed a 17.4 °C increase in the engine temperature in less than 10 min. A thermal efficiency of 57.5% along with a decrease in combustion emission as compared to the cold start from the engine due to the pre-heating of the catalytic converter has also been reported. Kauranen et al. [217] reported that a diesel-fueled heater for the temperature optimization of a diesel

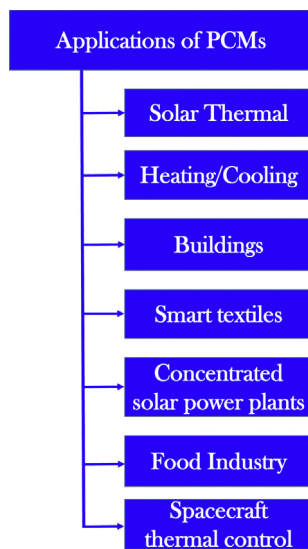


Fig. 13. Various applications of PCMs.

engine can be replaced with a latent heat accumulator based on PCM. An exhaust heat recovery system combined with a PCM-based latent heat accumulator was evaluated on a laboratory dynamometer. Javani et al. [218] developed a nanoparticle and PCM mixture based LHTES systems for passive thermal management of electric vehicles. The authors considered a shell-and-tube configuration for the TES system and reported that with the addition of the carbon nanotubes in PCM the thermal characteristics of the storage medium were improved, thus reducing the number of the copper tubes in the TES device.

With advancement in medical science, various PCMs are reported for biomedical usages such as microencapsulated PCMs for the thermal protection of tissue surrounding tumors during cryosurgery, and transport and storage of medicines [59].

## 7. Future trends

The majority of developments and studies about PCMs have undoubtedly been directed to low-temperature applications such as district heating/cooling and drying processes. High-temperature applications such as TES in the solar thermal power or industrial process heat sectors are less developed. For this reason, most of the current research and development is focused on CSP thermal storage and other high-temperature storage systems. However, a detailed investigation is necessary into other applications for high-temperature TES that can enhance the thermal properties and suppress the supercooling characteristics of PCMs.

PCMs have a high latent heat during the phase transformation, but low conductivity can affect charging/discharging energy rates. Consequently, it is necessary to have high thermal conductivity to obtain fast thermal charging and discharging during the phase transformations. On the other hand, there are some PCMs that solidify below their normal freezing point. In other words, once the PCM reaches its freezing temperature it remains liquid and on approaching the temperature well below the melting point, the solidification process is initiated. This condition is known as supercooling and can limit the use of the PCM depending on the application concerned. In consequence, a decrease in the temperature below the phase change temperature that triggers crystallization is sought in order to release the latent heat, which is only released after crystallization. This condition is not desirable in energy storage applications [115,219].

In this section, recent developments and research trends on PCM properties such as thermal conductivity enhancement, supercooling suppression through nanoencapsulation and nanomaterials additives, are discussed. Fig. 14 shows a summary of these approaches.

### 7.1. Encapsulation of PCMs

Encapsulation is the process by which a particle is enclosed by a coating material or embedded in a matrix (either homogeneous or heterogeneous) in order to form a capsule. The capsules may have a regular shape (e.g. spherical, tubular, and oval) or can be made in an irregular shape. Sometimes, an additional air pocket is provided inside the core part to accommodate the volume changes during the phase transformation. The shell should be strong enough to sustain the stresses that are generated due to volumetric changes during the phase change process of the PCM. The core may be solid or dispersed into a carrier fluid, in which case the material is called a microencapsulated phase change material slurry (MPCS) [220–224]. This process is one of the methods used to address some problems related to PCMs, including low conductivity, thermal instability and supercooling, which lead to a decrease in the rate of heat release and the thermal efficiency of the system. In the



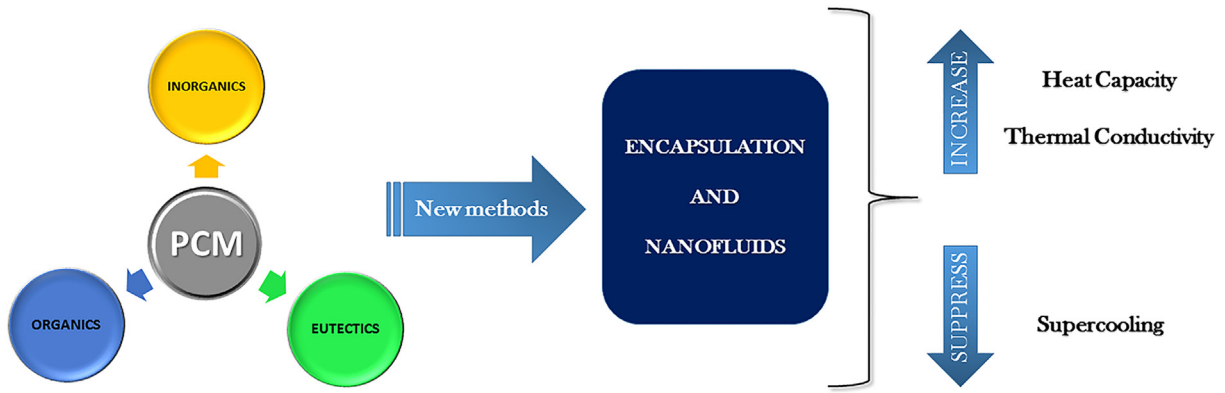


Fig. 14. Schematic summary of future trends in PCMs.

same way, it is possible to avoid contact of PCMs with the environment and to control the volume change previously referred to. Encapsulation of PCMs serves as a way to increase the surface area, protecting the PCM from environmental factors, increasing the compatibility of the PCM, and reducing corrosion [225–231].

7.1.1. Methods of encapsulation

There are many methods to encapsulate and obtain different kinds of capsules. Fig. 15 shows the different methods of encapsulating PCMs that have been studied. It is necessary to clarify that all the methods described are used to encapsulate organic PCMs,

except the combined mechanic and the electroplating method, and those highlighted in the Figure are used to encapsulate inorganic PCMs [228,231–237]. Both organic and inorganic PCMs can be classified into four categories according to the encapsulation method, physico-mechanical, chemical, physical, and physico-chemical [226,228].

7.1.1.1. Physico-mechanical methods. In physico-mechanical methods, the capsule wall is mechanically applied or condensed around the capsule core, and moderate-sized capsules, i.e. microcapsules, are obtained. Capsules obtained through chemical methods are

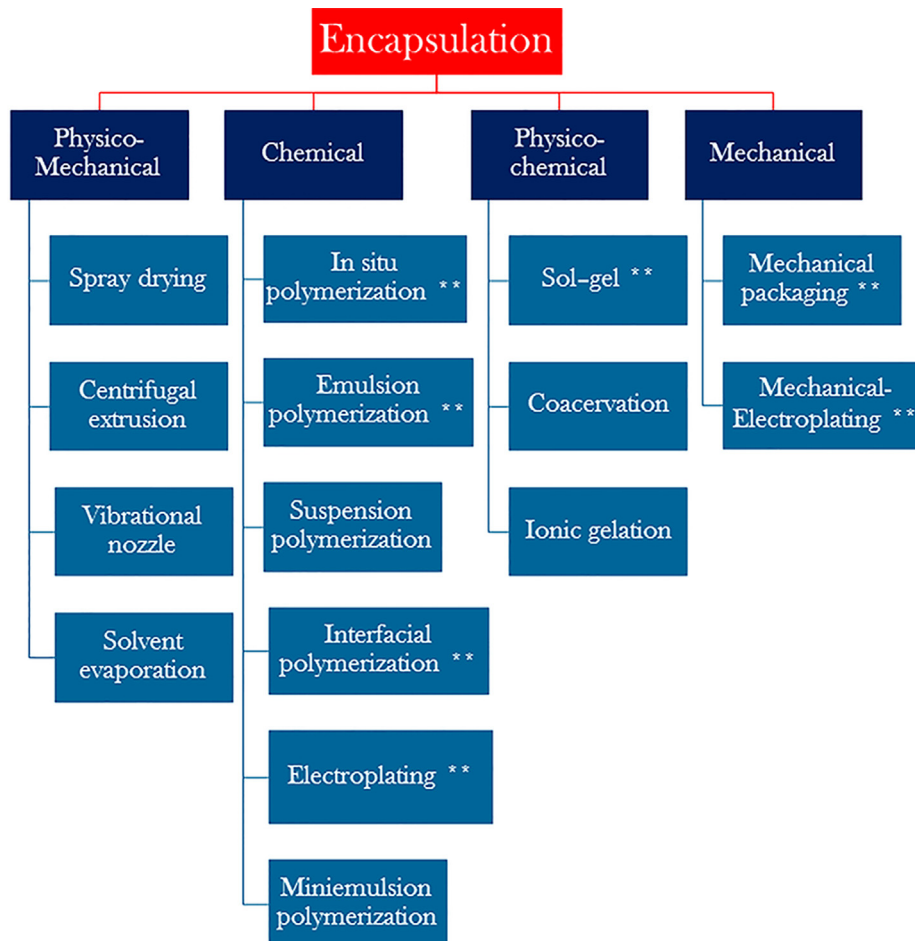


Fig. 15. Encapsulation methods of various PCMs and \*\* are for the inorganic PCMs.

smaller and have more heat capacity. Physico-mechanical methods include spray drying, centrifugal extrusion, vibrational nozzle, and solvent evaporation.

**7.1.1.2. Chemical methods.** Chemical methods are in situ polymerization, emulsion polymerization, suspension polymerization, interfacial polymerization, and electroplating. The last of these has been the least used, as reported by Zhang et al. [238]. In their work, they proposed copper capsules coated with refractory metal coatings, which supported 1000 thermal cycles of loading-discharge from 1050 to 1150 °C without any leakage.

**7.1.1.3. Physico-chemical method.** The physico-chemical method, gelation or coacervation leads to a solid and stable particle. There are three methods within this category, sol-gel, coacervation, and ionic gelation processes.

**7.1.1.4. Mechanical methods.** Meanwhile, mechanical packaging and mechanical-electroplating are among the mechanical methods.

### 7.1.2. Classification of encapsulation

Encapsulation can be classified into three types depending on the final diameter of the capsule:

- nanoencapsulation (<1 μm)
- microencapsulation (1 μm to 1 mm)
- macroencapsulation (1 mm to >1 cm)

Salunkhe and Shembekar [228] reported that the main parameters of the encapsulation process are the thickness of the coating material, the size of the encapsulation, the thickness of the shell and the geometry of the encapsulation [228,239].

**7.1.2.1. Nanoencapsulation.** Nanoencapsulation is one of the most recently developed techniques to encapsulate the PCMs for preventing PCMs leakage, thermophysical properties improvement, heat transfer enhancement, and increment in the reliability (charging-discharging cycle life). Fuensanta et al. [240] investigated the nanoencapsulation of a paraffin RT80 in a styrene-butyl acrylate copolymer shell and demonstrated excellent thermal stability with a slight decrease in melting point. Fang et al. [241] reported nanoencapsulated polystyrene/n-tetradecane composite PCM as latent functionally thermal fluid, which presents a better coefficient of heat conductivity and specific heat capacity than pure water, and remained complete after 40 freezing cycles. The melting and freezing temperatures of the NanoEncapsulated PCMs (NEPCMs) were determined as 4.04 and –3.43 °C, and the latent heats were determined as 98.71 and 91.27 kJ·kg<sup>-1</sup>. Tahan Latibari et al. [242] reported the elaboration of the nanocapsules with PA (palmitic acid) as core and SiO<sub>2</sub> as shell materials, with an encapsulation efficiency of 88% at pH 12. The capsules showed high stability after 2500 melting/solidifying cycles. Finally, they demonstrated a thermal conductivity enhancement presented by nanocapsules compared with the raw PA.

**7.1.2.2. Microencapsulation.** Micro-encapsulated PCMs have attracted considerable interest in the recent past. Micro-encapsulation provides opportunities to fabricate advanced PCMs with a greater heat transfer area, reduced reactivity with the outside environment and controlled volume changes during the phase transition [243]. Microcapsules are particles (diameters 1–1000 μm) that contain core PCM material surrounded by a coating or shell. Commonly used shell materials for the protection of PCMs are urea-formaldehyde resin, melamine-formaldehyde resin, and

polyurethanes. However, the use of microencapsulated PCMs in various TES applications is limited due to their high cost.

**7.1.2.3. Macroencapsulation.** According to both the techniques, when macroencapsulation is compared to microencapsulation, the latter provides faster charging and discharging rates due to an enhanced surface area. In the study carried out by Calvet et al. the macroencapsulation of a blend of polyolefins manufactured by hot molding using two kinds of graphite conductive additive (graphite flakes (GF) and expanded natural graphite (ENG)) is shown [244].

### 7.1.3. Working principle of encapsulated PCMs

Fig. 16a–b shows the working principle of the encapsulated PCM. The core part is the PCM and the shell part is the material used to encapsulate, Fig. 16a. After heating, the PCM is melted inside the capsule while the shell remains solid, Fig. 16b. The temperature of the PCM remains constant throughout the melting process/phase transition, and it stores an amount of heat depending upon its thermophysical properties during this phase change process. Upon cooling below the melting point the PCM returns to its initial solid state by releasing the absorbed heat, Fig. 16a.

As reported by Salunkhe et al. [228] during the melting and solidification process, some decisive parameters are the Nusselt number (Nu), Rayleigh number (Ra), Stefan number (Ste) and Grashof number (Gr). For instance, taking into account that the Ste is the ratio of sensible heat to the latent heat of the PCM, Eq. (1), depending on this number, it is possible to obtain higher melting rate when the number is lower or to improve the solidification rate by increasing the Ste.

$$Ste = \frac{C_p(T_f - T_0)}{\Delta H} \quad (1)$$

Similarly, the same authors assure that due to moving interface boundary, the prediction of the flow and heat transfer characteristics during melting and solidification of PCM is a very complicated task, studied by Josef Stefan for the first time [245].

Kalaiselvam et al. [246] investigated the solidification and melting of the phase change materials encapsulated inside the cylindrical enclosures. Two models for solidification and three models for melting was used to find the interface locations at various time steps. They found that for solidification, the analytical model with conduction and heat generation present good results. At the same time, they determined the parameters decisive for solidification, like Stefan number (Ste) and heat generation parameter (β).

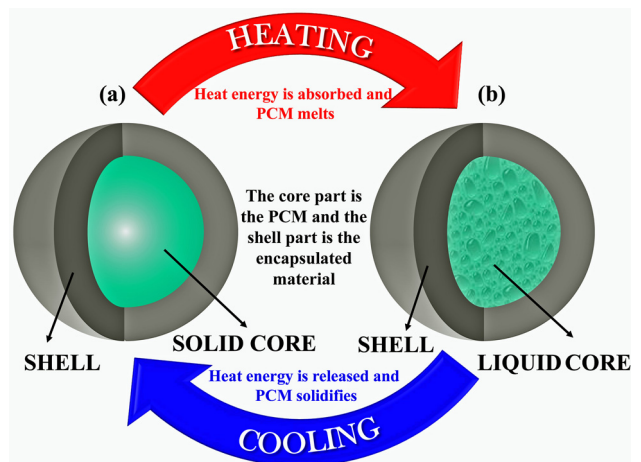


Fig. 16. Working principle of the encapsulated PCMs.

Related to melting, this process is evaluated by conduction and later characterized by natural convection, and the decisive parameter was the thermal conductivity.

Dhaidan et al. [247] reported in a review about the melting and convention of PCMs in different shaped containers, with an emphasis on the geometrical parameters such as the aspect ratio, diameter or radius in spherical, and eccentricity in annular cavities. The authors reported the heat transfer is initially dominated by conduction, as time passes the volume of the molten liquid layer increases and a fusion is dominated by convection. Tan et al. [248] realized an experimental and computational investigation of the PCM inside the spherical capsule and determined that the conductive heat transfer dominates during the early period, after that the melting of the top region of the sphere is much faster than the bottom region. Similar behavior was reported by Bechiri et al. [249], this investigation shows the effects of volumetric heat generation during melting and solidification of nano-enhanced PCM encapsulated in a horizontal cylindrical container, validating that the solid-liquid interface moves from the exterior wall and up to the center of the cylinder.

#### 7.1.4. Performance enhancement of PCMs

Despite the good thermal properties provided by encapsulated PCMs, such as high specific thermal capacity, thermal conductivity, and latent heat of fusion, these materials continue to be affected by the problem of supercooling. To suppress supercooling, encapsulation techniques and nucleation agents have been investigated. Al-Shannaq et al. investigated the microencapsulation of the commercial PCM Rubitherm® RT21 (PCMMC) with Rubitherm® RT58 and 1-octadecanol as nucleating agents [107]. When 5% of RT58 was used, a shifting of the crystallization temperature from 10.9 to 19.8 °C was obtained without negative impacts on the thermal behavior and no significant change in the surface morphology. With 1-octadecanol, despite a reduction in PCMMC supercooling, poor thermal properties, higher mass loss and changes in the particle morphology were noticed. Meanwhile, Park et al. investigated nanocapsules of paraffin with polyurea as a shell, embedding magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles. As a result, the thermal conductivity of the nanocapsules increased and the supercooling degree of paraffin decreased [250].

Cingarapu et al. [251] investigated the addition of encapsulated Zn particles to alkali chloride eutectic salt. In this case, thermal conductivity was improved by 45% with 10 wt% addition of the

nanoparticles and stability of up to 200 melt/freeze cycles is reported. Tahan Latibar et al. [252] studied PCM nanocapsules with PA (palmitic acid) as core and SiO<sub>2</sub> as shell materials. The chemical stability and thermal reliability are proven through a thermal cycling test of 2500 melting/freezing cycles. Additionally, the thermal conductivity of the nano-PCMs was improved compared to that of pure PA, and the latent heat of melting and freezing cycle changed from 180.9 to 177.3 kJ·kg<sup>-1</sup> and from 181.2 to 178.6 kJ·kg<sup>-1</sup>, respectively.

Calvet et al. [244] prepared macrocapsules comprising of blended polyolefins with GF and ENG and characterization showed that the thermal power of the spherical macrocapsules (nodules) is increased by 46% using 20% by weight of GF and by 138% using 15% by weight of consolidated expanded natural graphite (CENG) and most macrocapsules were still complete after 40 freezing-thaw cycles.

Sukhorukov et al. demonstrated that nanocapsules are structurally more stable than microcapsules, besides their small size, large specific surface area, and high heat transfer rate [253]. Among the methods used for encapsulation, the interfacial polymerization method, emulsion polymerization, miniemulsion polymerization, in situ polymerization method, and solgel-method have been used for nanoencapsulation. Due to the small size and high specific surface area of nanocapsules, the possible applications of this kind of encapsulation could be in the fields of intelligent buildings, thermal regulating fabric and thermal control of electronic devices [253–255]. Table 4 consolidates the research carried out over the past 10 years on the core and shell materials on PCMs encapsulation and the thermal properties obtained. This includes the information taken directly from each reference. The melting point reported for the encapsulated PCMs was between 21.48 and 53.85 °C, the main encapsulation method used was emulsion polymerization, and the maximum suppression in the degree of supercooling observed was 26 °C [107,256–264].

After extensive research on microencapsulation, and considering that the particle size strongly influences the stability of the capsule, as well as the viscosity increases and possible fracture of the microcapsule in the process fluid flow may occur, continued research on nanoencapsulation methods, PCMs suitable for this type of encapsulation and applications of nanoencapsulated materials are necessary. Thus, the performance of PCMs in their specific heat capacity and thermal conductivity could be further enhanced. The future research trends can be summarized into the following aspects:

**Table 4**

Major approaches on Encapsulation of the PCM in the recent past.

Year	Core material	Shell material	Latent heat (J/g)	Melting point (°C)	Capsule mean size (µm)	Thermal conductivity (W/m K)	Encapsulation method	Reduction of supercooling (°C)	Ref.
2005	N-octadecane, N-nonadecane, and N-eicosane	Urea-melamine-formaldehyde	165	36.4	0.3–6.4	–	In situ polymerization	26	[258]
2013	N-octadecane and Paraffin	Methacrylic acid and N-butyl methacrylate	130.3	53.9	6–74	–	Suspension-like polymerization	–	[259]
2013	Disodium Hydrogen Phosphate Heptahydrate	Modified Polymethylmethacrylate	150	51	0.4–68 6.8	–	Suspension copolymerization-solvent	15	[260]
2014	N-octadecane	N-octadecyl Methacrylate –Methacrylic acid	974–93	26.5–29	1.6–1.68	–	Suspension-like polymerization	3–4	[261]
2014	N-nonadecane	Poly(methyl methacrylate)	139.2	31.2	0.1–35	0.18	Emulsion polymerization	–	[262]
2014	N heptadecane	Polystyrene	136.9	21.5	5.4–6.3	0.13	Emulsion polymerization	0.11	[263]
2014	Paraffin Octadecane	Melamine-Formaldehyde resin	213	–	5–15	–	Emulsion polymerization	13.6	[264]
2015	Rubitherm® RT21	Methyl methacrylate and pentaerythritol tetraacrylate	58 59.5	–	–	–	Suspension polymerization	10	[107]

- Investigation into the enhancement of structural stability is necessary on thermal cycling.
- Suppression of supercooling through optimized microencapsulation and nanoencapsulation methods.
- Development of high energy materials such as encapsulated molten salts and hydrated salts.
- Selection and effective encapsulation process of the most suitable shell materials with the focus on a cost reduction.
- Refinement of nanoencapsulation methods for enhancing efficiency, uniform particle size distribution, and stability towards various applications (solar thermal energy storage, electronic thermal control devices, and thermal management systems of the batteries).

## 7.2. Nanomaterials additives

Nanoparticles, nanosheets, nanofibers, nanotubes, nanowires, nanorods or droplets have also been evaluated for the improvement of the specific heat and the thermal conductivity of PCMs. The preparation of the nanofluids can be done by two different methods, one-step or two-step method. In the one-step method, the production of nanoparticles and their dispersion in the fluid are simultaneous, while the two-step method begins with the preparation of the nanoparticles with different processes, after which the dispersion of the nanoparticles in the fluids is done through forms of agitation such as magnetic agitation, ultrasonic agitation, high-shear mixing, homogenizing, or ball milling. The second method is the most commonly used due to its scalability and profitability. Most of the studies on nanofluids are based on the abnormal results of the increase in conductivity after the addition of the nanoparticles [219].

He et al. [263] investigated the addition of  $\text{TiO}_2$  nanoparticles in the aqueous solution of saturated  $\text{BaCl}_2$ , finding that thermal conductivity increases nearly linearly with the volume fraction of the nanoparticles. An increment of 16% in thermal conductivity was observed at room temperature and a 12% increment at  $-5^\circ\text{C}$ . One of the most used materials for the improvement of PCM properties is carbon, especially in the form of nanotubes. Harish et al. [264] reported an abnormal increasing trend in the thermal conductivity of the alkanes upon seeding with carbon nanotubes. Thermal conductivity measurements were carried out using the transient hot-wire technique, although there is controversy regarding the use of this technique in liquids with nanosuspensions since the nanoparticles present “Brownian motion”. With 0.25% of carbon, the thermal conductivity in the solid phase increased by 250%, while 10% increment was achieved in the liquid phase. Liu et al. reported 15% increment in the thermal conductivity for PCM of  $\text{BaCl}_2$  aqueous solution with 1.13 wt% of  $\text{TiO}_2$ , with a decrement in the storage time of the ice storage from 541 to 421 min and the total melting time from 269 to 160 min due to the high thermal conductivity of the nanoparticle additives in PCMs [265].

Some authors explained the anomalous enhancement of thermal conductivity after the addition of the nanoparticles in the PCMs [219,266–269]. There are four possible mechanisms to explain this, as shown in Fig. 17. Firstly, the Brownian motion of the particles enabling direct solid-solid transport of heat from one particle to another. Brownian motion of the particles is too slow to carry significant amounts of heat through the nanofluid. However, this can help the formation of agglomerates, which can greatly improve the thermal conductivity. Secondly, the molecular level stratification of the liquid at the liquid-particle interface. However, some experiments and simulations have shown that the typical thickness is only of the order of some atomic distances, around 1 nm. Given its size, it cannot be possible that this is the reason for the increase in thermal conductivity. Thirdly, in the nat-

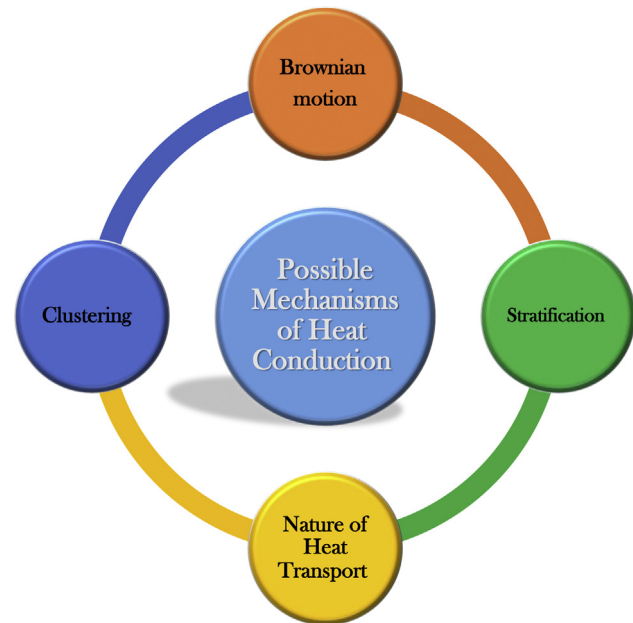


Fig. 17. Mechanisms of heat conduction in Nanofluids.

ure of transportation of the particles, the heat transport is done by the phonon, i.e. the lattice vibrations. The fourth mechanism refers to the formation of clusters. The heat moves faster in the clusters, therefore with a higher effective volume, there is higher thermal conductivity.

Mo et al. and Liu et al. investigated other nanoparticles used to suppress the supercooling [270,271]. The first showed different water-based nanofluids with  $\text{TiO}_2$  nanoparticles. Two different containers, a glass test tube, and a polypropylene plastic test tube were studied. It was found that for the same concentration of nanoparticles the supercooling degree of the nanofluid in the glass container was higher than that in the plastic container. However, it is possible to conclude that the nanoparticles and the container simultaneously influenced the supercooling degree of the nanofluid. Liu et al. investigated the graphene oxide nanosheets as an additive to water PCM and demonstrated that the temperature of the supercooling is reduced by 69% for the deionized water.

Other properties such as heat capacity have been studied. Shin and Banerjee et al. investigated the addition of 1% mass silica nanoparticles in alkali metal chloride salt eutectics [272]. The specific heat capacity of the nanoparticle-based PCM was enhanced by 14% compared with the salt eutectic without doping. Shin and Banerjee et al. also reported a 25% increment in the specific heat capacity of lithium carbonate and potassium carbonate eutectic (62:38 by molar ratio) doped with 1 wt% of alumina. Similarly, melting time has been investigated [266,272]. Wu et al. numerically investigated the fusion process of the paraffin doped with copper nanoparticles [273]. After the addition of 1 wt% copper particles in the paraffin, the melting time reduced by 13%, showing that the addition of the nanoparticles is an effective way to improve the heat transfer in LHTES systems. Table 5 summarizes the research carried out over the past 10 years on different additives in PCMs and the thermal properties obtained. It is evident from the Table that alumina is the most commonly used additive, but the thermal conductivity has been improved by 250% using carbon nanotubes, while thermal conductivity increased by 52.1% with the combination of silica and alumina as additives. On the other hand, both the latent heat and degree of supercooling were reduced with the use of nanoparticle additives [263–266,272,274–276].



**Table 5**

Major approaches on nanofluids PCM in the recent past.

Year	Base fluid	Additive		Thermal conductivity enhancement (%)	Heat capacity enhancement (%)	Latent heat decrement (%)	Reduction of supercooling (°C)	Ref.
		Additive (size, nm)	Weight (%)					
2009	Water	Al <sub>2</sub> O <sub>3</sub> (20)	0.2	10.5	–	–	2.3	[276]
2009	BaCl <sub>2</sub> -Water	TiO <sub>2</sub> (20)	1.13	15.7	–	–	–	[267]
2011	Alkali metal chloride	SiO <sub>2</sub> (20–30)	1	–	14.5	–	–	[268]
2012	BaCl <sub>2</sub> -Water	TiO <sub>2</sub> (20)	0.5	16.7	10–80	9.6	0.57	[265]
2013	Alkane	CNTs (0.7–2)	0.25	250	–	–	–	[266]
2014	Li <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> (10)	1	–	32	–	–	[274]
2016	NaNO <sub>3</sub> -KNO <sub>3</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (2)	1	–	52.1	–	–	[277]
2016	Na(CH <sub>3</sub> COO)·3H <sub>2</sub> O	Nano-Cu (10–30)	0.5	25.1	–	3.3	0.5	[278]

Despite of the advances in the study of nanofluids, especially on nanoparticle additives in PCMs, it is possible to find some fields that are yet to be studied. The future research trends can be summarized into the following aspects:

- Optimization of particle size distribution, operating temperature range, and shape stability of the additive materials.
- Evaluation of the long-term stability based on the compatibility of the nanoparticle additives with the base fluid through particle size/aggregation, corrosion rate etc., in pilot scales.
- Development of earth-abundant nanoparticle additives for economic viability and environmental sustainability.
- In-depth analysis of physical principle and mechanism behind the improvement of the thermal properties of the PCMs through modeling and experimental verification/validation.
- Design, development, and evaluation of composites of different types of nanoparticles (also encapsulation with nanoparticles) to gain synergy in improving thermo-physical properties of the PCMs towards TES.
- Exploring other applications to exploit the improved characteristics of the PCMs with nanoparticles.

### 7.3. Other thermal performance enhancement techniques

The low thermal conductivity of PCMs especially organic PCMs leads to poor heat transfer between the PCM and the HTF, therefore leading to a low thermal efficiency of the system. However, the methods for thermal conductivity improvement are not restricted to encapsulation of the material and the use of conductive materials as additives. Ibrahim et al. [277] and Wei et al. [110] reported the embedding of porous materials in PCM as a promising method to reasonably enhance the thermal conductivity of the PCM with the excellent conductivity of the added materials. Materials are embedded in the form of metal foams of aluminum, copper, and nickel, other materials include polyethylene and the most commonly used expanded graphite (EG). The thermal conductivity was increased with this kind of materials, such as for a composite between shape-stabilized PCM (SSPCM) with EG the thermal conductivity was roughly 8200% higher than that of the paraffin. And for inorganic molten salt such as sodium nitrate (NaNO<sub>3</sub>) an increment of two, four and seven times in thermal conductivity was observed comparatively with pure sodium nitrate upon adding 5, 10 and 20 wt% EG respectively [114,278,279]. Nevertheless, some metal particles are incompatible with certain classes of

PCMs, and for that reason, the dispersion of low-density materials such as carbon fibers, whose thermal conductivity is similar to metals such as aluminum and copper, have been studied as another method to increase the thermal conductivity of PCM [277].

Increase in thermal conductivity and heat transfer enhancement improves the overall performance of the TES system comprising of PCMs. The latter is possible by the application of several methods, including the use of extended surfaces such as fins or heat pipes, along with the use of multiple PCMs with different melting points in the form of cascaded arrangement. Ibrahim et al. reported the most researched materials for the manufacturing of fins, such as graphite sheets, aluminum, stainless steel, carbon steel, and copper. Aluminum is the most promising metal given that it has a low cost and appropriate properties such as high thermal conductivity and low density [277]. The same authors specified that broadly there are two types of heat pipe: wickless or gravity assisted heat pipe and wick assisted or screen mesh heat pipe both operating with a variety of working fluid. Similarly, Wei et al. [110] reported the use of multiple PCMs in order to improve the heat transfer and to achieve a constant temperature difference between the HTF and the PCM during the loading and unloading of the cycles increasing the thermal performance of the system.

On the other hand, there is also a possibility of increasing the heat transfer by combining two or more techniques, such as by combining normal fins with heat pipes but also combining porous materials with both the fins and heat pipes, which are least used so that further investigation is necessary [277]. In addition, the combination of the thermophysical properties enhancement techniques can lead to the development of more reliable TES systems.

## 8. Comparison of PCMs and overview of technologies

Table 6 summarizes the details of the characteristics studied in several recent publications (2015–2018) and the major inferences deduced on the PCMs [9,28,280–327]. The Table is self-explanatory and detailed information can be accessed from the cited references.

Table 7 brings together various recent patents on PCMs and TES systems. The list of patents in Table 7 is not comprehensive but shows the technology developments towards thermal energy storage applications. However, the patents listed in the Table provides an idea that the technology is being matured for commercialization. Developments concerning the storage medium and the entire storage system are thus addressed [328]. Various parameters and performance indicators such as durability, charging-discharging

**Table 6**  
Comparison of PCM properties and the major outcomes from recent literature.

Ref.	Year	Characteristics/parameters studied	Inferences or major outcomes made
[280]	2018	Design, development and experimental evaluation of thermal resonator and special phase change composite material with ultra-high thermal effusivity for harvesting ambient thermal energy	Thermal resonator is fabricated with specially designed materials comprising of impregnated copper and nickel foam with graphene and octadecane as PCM. Energy is harvested as a result of the temperature fluctuations from diurnal frequencies during day (heating) and night (cooling) time. 350 mV and 1.3 mW is yielded around 25 °C with 10 °C amplitude and a power density of 20 $\mu\text{W}\cdot\text{cm}^{-2}$ and 2 $\mu\text{W}\cdot\text{cm}^{-3}$
[281]	2018	Evaluation of thermophysical properties, impact of PCM viscosity, bulk density, heat flux amplitude and pore density. Experimental and comparative study of aluminum and graphite foams as performance enhancement additives in PCM for the design of thermal battery	PureTemp 37 and paraffin wax PCMs are employed. Superior thermal performance of graphite foam based PCM system is observed because of its high thermal conductivity, small pore size and low density. Under high heat flux, high pore density foam with high viscosity PCM showed promising characteristics
[282]	2018	Evaluation of preparation techniques and characterization of 40 wt% $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ and 60 wt% $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ mixture with expanded graphite (EG) flakes and EG matrix, respectively	Vacuum impregnation technique yielded the product with optimal properties in 1 h. Percentage encapsulation increases with the preparation time and EG proportion. EG suppresses the supercooling by 65% in this inorganic mixture and acts as nucleating agent
[283]	2018	Fabrication and thermal characterization with differential scanning calorimetry and thermography of vanadium oxide ( $\text{VO}_2$ ) dispersed glass as potential solid-solid PCM	The phase transition temperature and transition enthalpy of glass system ( $30\text{BaO}-10\text{TeO}_2-60\text{V}_2\text{O}_5\cdot 120\text{VO}_2$ ) with $\text{VO}_2$ powder are observed as 68 °C, 14.3 $\text{J}\cdot\text{g}^{-1}$ , respectively. Fabricated glass matrix possessed temperature retention properties and its thermal conductivity is 0.8 $\text{W}\cdot(\text{m}\cdot\text{K})^{-1}$ at 77 °C
[284]	2018	Experimental evaluation of thermal performance and melting behavior of paraffin and paraffin/copper foam composite phase change material (CPCM). Development of mathematical model using one-temperature volume averaging method and validation with experimental results	Melting temperature and latent heat of paraffin is identified as 48.4 °C and 148.8 $\text{J}\cdot\text{g}^{-1}$ , respectively. Thermal conductivity of paraffin and copper foam is 0.3 and 380 $\text{W}\cdot(\text{m}\cdot\text{K})^{-1}$ , respectively. Copper foam enhances thermal performance by reducing thermal resistances in pristine paraffin and melting time of CPCM reduces by 20.5%. Numerical outcomes agrees with experimental results
[285]	2018	Crystallization behavior of stearic acid (SA), octadecane (OCC) and octadecanol (OCO) PCM confined in mesoporous silica (MS) and thermal characterization of composites with various PCM proportions.	Thermal conductivity of the composite PCMs is doubled and melting enthalpy decreases due to MS. In OCO/MS composite, phase transition and crystallization is affected by pore confinement and newly formed H-bond between PCM molecules and MS. Thermal behavior and crystallinity in SA/MS and OCC/MS composite is confined by $\text{SiO}_2$
[286]	2018	Preparation and characterization of PEG/mesoporous ZSM-5 based composite PCM	Composite PCM is prepared by vacuum impregnation. Melting point and latent heat is 56.3 °C and 76.4 $\text{J}\cdot\text{g}^{-1}$ , respectively. 200% increment in the thermal conductivity is observed comparatively with pure PEG
[287]	2018	Numerical and experimental investigation of paraffin PCM based thermal management system for cylindrical battery in metal and acrylic housing, respectively	Melting rate of PCM is slower in acrylic housing and solid PCM adheres to it. Melting front of PCM is isolated from battery and the inner wall in case of metal housing. Battery overheating is observed in case of acrylic housing, therefore metal housing emerges as a promising choice
[288]	2018	Generalized energy storage efficiency (ESE) diagrams against dimensionless parameters is developed by adapting enthalpy based 1-D transient model for latent heat TES system in CSP application	TES tank size can be determined using ESE diagrams considering the desired storage efficiency and charging-discharging time period while TES tank size in term of heat transfer fluid cutoff temperature is obtained using generalized volume strategy. Dimensionless charge and discharge time, tank height and $H_{\text{CRM}}$ are decision variables used.
[289]	2018	Preparation, characterization and thermal cyclic testing of eutectic $\text{Ca}(\text{NO}_3)_2\text{-NaNO}_3$ and expanded graphite (EG) based shape stabilized phase change material (SSPCM)	Binary eutectic $\text{Ca}(\text{NO}_3)_2\text{-NaNO}_3$ with molar ratio 3:7 is prepared. Three SSPCMs are developed by adding 5, 6 and 7 wt% EG in binary eutectic, respectively. Melting point and latent heat of SSPCM with 7 wt% EG is 216.8 °C and 89.8 $\text{J}\cdot\text{g}^{-1}$ , respectively and thermal conductivity increases by 7.3 times compared to pure binary eutectic. After 500 melt-freeze cycles, small change in thermophysical properties is observed.
[290]	2018	Cyclic thermal characterization to analyse the thermophysical properties and corrosion characteristics of organic PCM glutaric acid (GA) on aluminum, copper and stainless steel (SS) containers	Melting point and latent heat of GA is identified as 94.9 °C and 184.8 $\text{J}\cdot\text{g}^{-1}$ , respectively. After 2000 melt-freeze cycle melting temperature and latent heat of GA varies by 0.47 and 0.48%, respectively. Corrosion rate of SS container for GA is 0.3 $\text{mg}\cdot(\text{cm}^2\cdot\text{year})^{-1}$ and is least amongst the studied metals
[291]	2018	Preparation, cyclic thermal characterization, stability and corrosion analysis of Capric Acid/Cetyl Alcohol based binary eutectic PCM. ASTM G1-03 is adopted for corrosion testing on aluminum, copper and stainless steel 316 (SS316)	Eutectic comprising of 70/30 wt% capric acid/cetyl alcohol with melting temperature and latent heat 22.89 °C and 144.92 $\text{J}\cdot\text{g}^{-1}$ is identified as suitable eutectic PCM for low temperature TES applications at price of INR 98/kg. Minimal deviation in thermophysical properties is observed after 1000 melt freeze cycles. Corrosion rate of SS316 is 0.6 $\text{mg}\cdot(\text{cm}^2\cdot\text{year})^{-1}$ after 12 weeks.
[292]	2018	Cooling power figure of merit is applied to analyze composite PCM heatsinks and insulants. Design guidelines for compact high power and energy density heatsink and insulant materials	Performance of PCM composites can be quantified on the basis of energy storage and power densities, based on Stefan problem. Fractional loading of high thermal conductivity ( $k$ ) additive should be kept low ( $\sim <10\%$ ) relative to PCM and regular in orientation to achieve upper bounds of characteristics. Discontinuous high- $k$ particles in PCM results in interfacial thermal resistance. Appropriate length scales are vital for achieving the desired characteristics
[293]	2018	Preparation and characterization of Nano-PCM comprising of organic PCM and CuO spherical nanoadditives. Evaluation of the variation in thermal conductivity and viscosity with temperature and CuO concentration	Nano-PCM is prepared by two-step technique, CuO nanoparticles are modified by sodium oleate followed by ultrasonic stirring in octadecane. Thermal conductivity and viscosity of Nano-PCM increases by 9 and 60%, respectively compared with pristine octadecane. For NanoPCM (10% w/v CuO concentrations) viscosity decreases by 35% with increase in temperature
[294]	2018	Development and testing of $\text{MgCl}_2$ /graphite foam based lab-scale latent heat TES prototype. Charging and discharging of the PCM and its melt front movement is analyzed for cyclic operation. Comparison of the results from COMSOL Multiphysics software simulations are with experimental value	Graphite foam significantly enhances the heat transfer characteristic of $\text{MgCl}_2$ PCM. Three prototypes are tested and their temperature profiles during charging-discharging modes for multiple cycles deviated within 3% of average value. Prototypes with different porosities of graphite foam showed similar thermal performance. Simulation results deviates $< 4\%$ with experimental.

Table 6 (continued)

Ref.	Year	Characteristics/parameters studied	Inferences or major outcomes made
[295]	2018	Preparation of graphene coated nickel (GcN) foam saturated paraffin as a PCM and experimental investigation for thermal management of Li-ion battery using enhanced PCM, and comparison with Nickel foam/PCM	Thermal conductivity of the enhanced PCM increases by 23 time, latent heat and specific heat decrease by 30 and 34%, respectively. Under 1.7 A discharge current, battery surface temperature is 17% low using GcN/PCM comparatively with nickel foam.
[296]	2018	Preparation, thermal characterization, stability and chemical compatibility testing of Stearic Acid (SA)/Carbonized sunflower straw (CSS) PCM	Vacuum impregnation technique is adopted to prepare SA/CSS PCM. Melting point and latent heat is identified as 66.4 °C and 186.1 J.g <sup>-1</sup> , respectively. 106% increment in the thermal conductivity of SA/CSS is observed comparatively with SA. Degradation temperature is 216.4 °C, well above its melting point.
[297]	2018	Preparation and thermal characterization of 31.5 mol% MgCl <sub>2</sub> -68.5 mol% KCl/expanded graphite (EG)/graphite paper (GP) composite PCM. Effect of adding graphite paper on thermal characteristics	Thermal conductivity of MgCl <sub>2</sub> -KCl/EG block increases with the increment in packing density of EG and above 280 kg.m <sup>-3</sup> its latent heat starts decreasing. Thermal conductivity of the composite block increases by 2.03 times after adding GP. After 1000 melt-freeze cycles composite possesses thermal stability.
[298]	2018	Preparation and characterization of composite PCM comprising of paraffin wax, and graphene, multi-walled carbon nanotubes (MWCNTs) as thermal performance enhancement nanoparticles	Composite PCMs comprising of paraffin/graphene, paraffin/MWCNTs and paraffin/graphene/MWCNTs combinations are prepared by melt blending followed by ultrasonication. PCM with 1 wt% graphene and MWCNTs, respectively charging time decreases by 35 and 18.3%. Thermal conductivity of composite with 3/7 mass ratios of graphene/MWCNTs increases by 124%.
[299]	2018	Preparation, characterization and thermal cyclic testing of composite PCM comprising of Erythritol (Ery) and modified MWCNTs	MWCNTs are modified by acid oxidation, mechanochemical process and ball milling, respectively and dispersed in Ery. Thermal conductivity of composite PCM containing 1 wt% MWCNTs increases from 0.196 to 0.978 W.(m.K) <sup>-1</sup> , latent heat is > 300 J.g <sup>-1</sup> for all combinations. Ery/acid-oxidized MWCNTs composite exhibits stable thermophysical properties after 10 melt-freeze cycles.
[300]	2018	Preparation, chemical and thermal characterization, and thermal cyclic testing of novel silver coated nanoencapsulated phase change materials (NanoPCMs)	n-Octadecane PCM is nanoencapsulated and surface activated using dopamine followed by treatment in Tollens's reagent. FT-IR, XPS, XRD, SEM, and TEM demonstrated fabrication of silver layer which resulted in increment of thermal conductivity of NanoPCM from 0.246 to 1.346 W.(m.K) <sup>-1</sup> while melting point and latent heat is identified as 27.7 °C and 32.74 J.g <sup>-1</sup> , respectively and remained same after 100 melt-free cycles.
[301]	2018	Preparation and characterization of carbon fiber (CF)/polyethylene glycol (PEG)/silica (SiO <sub>2</sub> ) composite PCM	CF/PEG/SiO <sub>2</sub> composite PCM is prepared by sol-gel and in-situ doping method. Melting point, latent heat and thermal conductivity of CF(3 wt%)/PEG/SiO <sub>2</sub> is identified as 57.5 °C, 142.6 J.g <sup>-1</sup> and 0.45 W.(m.K) <sup>-1</sup> , respectively. CF enhances the light-thermal conversion due to its high absorbability.
[302]	2018	Thermal cyclic testing and characterization of D-mannitol. Design and testing of D-mannitol based TES cell	Melting point and latent heat of D-mannitol is identified as 167 °C and 297 J.g <sup>-1</sup> , respectively. After 200 melt-freeze cycles the latent heat reduces to 240 J.g <sup>-1</sup> . Subcooling is identified by DSC. 3.8 kg D-mannitol is employed to build a TES cell with 0.44 kWh storage capacity, charging-discharging cycle showed the supercooling phenomena and further studies on D-mannitol are recommended.
[303]	2018	Preparation, characterization and thermal cyclic testing of n-dodecanol/graphene oxide (GO)/melamine resin based composite microcapsuled PCM (MEPCM) and evaluating the influence of oxidation degree of GO on thermal performance of MEPCM	Series of GO with different oxidation degree is prepared using Hummers method by varying oxidation time. MEPCM is synthesized and latent heat is identified as 170 J.g <sup>-1</sup> which remains consistent after 100 melt-freeze cycles. 72% increment in the thermal conductivity of MPCM comprising of GO with maximum degree of oxidation is observed.
[304]	2018	Preparation and characterization of shape stabilized PCM comprising of carbon nanotubes (CNTs) and lauric acid (LA)	LA is confined in CNTs through vacuum based infiltration purification method. Thermal conductivity of CNTs/LA PCM increases by four times but latent heat and melting temperature reduces comparatively with pure LA.
[305]	2017	Development, characterization and testing of PCM system with optically controllable heat release mechanism for long term TES. Design criteria of photo switching dopants for PCM	Tridecanoic acid PCM is doped with azo-benzene. Introduction of photo-switching dopants in PCM created an activation energy barrier for solidification process, and resulted in optically controllable PCM system. 200 J.g <sup>-1</sup> thermal energy can be store for 10 h. Experiment demonstrated UV activation and triggering of PCM crystallization.
[306]	2017	Development, characterization and thermal cycling of performance enhanced Li <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub> mixture for TES	Three mixtures comprising of EG, MWCNTs and graphene nanosheets (GNSs), respectively in (32.1%)Li <sub>2</sub> CO <sub>3</sub> -(33.4%)Na <sub>2</sub> CO <sub>3</sub> -(34.5%)K <sub>2</sub> CO <sub>3</sub> composite with melting points 404.7, 405.9 and 405.4 °C, respectively are prepared. EG resulted in 59.1% increment in thermal conductivity of composite. Stable thermophysical properties are observed after 30 melt-freeze cycle.
[307]	2017	Synthesis and characterization of a biodegradable solid-solid phase change material (SSPCM) for TES	Polyethylene glycol based SSPCM is synthesized through solvent free-polyaddition. Melting point and transition enthalpy is identified as 41 °C and 128 J.g <sup>-1</sup> , respectively. SSPCM is stable up to 302 °C. After 100 thermal cycles SSPCM possessed stable thermophysical properties.
[308]	2017	Preparation and characterization of erythritol PCM/Short carbon fibres (SCFs) for TES	Two types of SCFs are loaded as 1, 2, 4, 7 and 10 wt%, respectively in erythritol. FTIR demonstrated the physical mixing of SCF and PCM. 407% increment in thermal conductivity for PCM with 10 wt% SCFs is observed, with a promising latent heat of 340.4 J.g <sup>-1</sup> .
[309]	2017	Development, characterization and thermal cyclic testing of shape stabilized phase change material (ss-PCM) comprising of stearic acid (SA) and modified expanded vermiculite with carbon (EVC)	Starch is carbonized in-situ in layers of expanded vermiculite (EV) to obtain EVC. ss-PCM is prepared through direct vacuum impregnation, 63.12 wt% SA is retained in ECV without leakage. Melting temperature, latent heat, thermal conductivity of SA/EV and SA/EVC are 67.7 °C, 148.4 J.g <sup>-1</sup> , 0.34 W.(m.K) <sup>-1</sup> and 67.12 °C, 134.3 J.g <sup>-1</sup> , 0.52 W.(m.K) <sup>-1</sup> respectively.
[310]	2017	Performance evaluation of lab scale latent heat TES prototype, and effect of flowrate and inlet temperature of heat transfer fluid (HTF) on charging-discharging and melt fraction	TES prototype of 10 MJ storage capacity, comprises of PCM mixture KNO <sub>3</sub> -NaNO <sub>3</sub> -NaNO <sub>2</sub> with 53:7:40 mass ratios, respectively. Charging/discharging time is 124/131 min. Small discharging time is observed at, low inlet temperature and high flow rate of HTF, respectively
[311]	2017	Preparation and characterization of Nano-enhanced phase change material (NePCM) comprising of functionalized graphene nanoplatelets (fGNP) and polyethylene glycol (PEG 400) PCM	Three NePCMs are prepared by adding 0.1, 0.25 and 0.50 wt% fGNP in PEG-400, respectively. A 23% increment in thermal conductivity is observed for 0.50 wt% fGNP/PEG 400, with melting temperature and latent heat of 276.3 K and 97.2 J.g <sup>-1</sup> , respectively.

(continued on next page)

Table 6 (continued)

Ref.	Year	Characteristics/parameters studied	Inferences or major outcomes made
[312]	2017	Design, development and testing of passive cooling system comprising of nano-enhanced PCM (n-PCM) and micro fins with different configurations for Building-Integrated Concentrated Photovoltaics (BICPV)	n-PCM is prepared by adding 0.5 wt% CuO in Rubitherm RT42. Melting temperature and latent heat of n-PCM are 44.2 °C and 146.9 J.g <sup>-1</sup> , respectively. Micro-fins/n-PCM configuration reduces the surface temperature of BICPV by 12.5 °C. Fin effectiveness of 1.32 is achieved for micro-fins/PCM configuration. n-CuO in n-PCM agglomerated after melt-freeze cycles.
[313]	2017	Evaluation of corrosive properties of Micronal <sup>®</sup> , SP22 PCM, capric acid (CA), two binary eutectics PCM; CA, lauric acid(LA), and CA, palmitic acid(PA). Metals and plastics tested are copper, brass, aluminum, stainless steel, mild steel and Perspex.	Micronal <sup>®</sup> , SSP22, CA and binary eutectics CA/LA;45/55 wt%, CA/PA;75/25 wt% having melting temperature 20.9, 16.9, 27.5 and, 18.9, 17.7 °C, respectively are maintained at 45 °C in test tube. Metals and plastics are immersed for 722 days, weight of immersed bodies is measured after 7 days. Stainless steel is most resistant to corrosion, and aluminum is least among metals. Perspex shows minimal corrosion but has low thermal conductivity.
[314]	2017	Preparation and characterization of form stable PCM comprising of capric–myristic–stearic acid (CMS) eutectic mixture and flexible cellulose acetate (CA) nano-fibrous felts (nano-felts)	CMS is prepared by melting blending of 76.97, 18.55, 4 wt% capric acid, myristic acid and stearic acid, respectively. CMS is absorbed in electrospun CA nano-fibrous felts to obtain a form stable PCM system with melting point and latent heat of 21.9 °C and 101.8 J.g <sup>-1</sup> , respectively which corresponds to its theoretical value.
[315]	2017	Fabrication, characterization and cyclic reliability of Graphene/TiO <sub>2</sub> /Paraffin composite encapsulated PCM	n-Eicosane is encapsulated with crystalline TiO <sub>2</sub> with graphene nanosheet through polycondensation. Latent heat of the composite is 160 J.g <sup>-1</sup> , addition of 5 wt% graphene nanosheets increases the thermal conductivity from 0.64 to 0.98 W.(m.K) <sup>-1</sup> and enhances the solar photocatalytic activity.
[316]	2017	Development, characterization and leakage testing of shape stabilized PCM system comprising of meso-structured onion-like silica (MOS) and stearic acid (SA)	MOS is added in, SA dissolved in absolute alcohol followed by stirring and drying. SEM and TEM demonstrated the presence of nanosized onion structures. Melting point and latent heat is identified as 72.7 °C and 108 J.g <sup>-1</sup> , respectively. No leakage is observed for 70 wt% SA in MOS after 50 melt-freeze cycles.
[317]	2017	Preparation, characterization and thermal cyclic testing of form-stable composite phase change material (CPCM) comprising of PEG, waste sawdust and EG. Effect of 1, 3, 5 wt% EG on thermophysical properties of the CPCM	CPCM is obtained by mixing waste sawdust, PEG and EG in wt. ratios 4:16:1. Melting point and latent heat of CPCM with 5 wt% EG is identified as 58.6 °C and 145.3 J.g <sup>-1</sup> , respectively. 5 wt% EG increases the thermal conductivity by 23.8%. After 200 melt-freeze cycles, thermophysical properties remained identical. Supercooling extent decreases by 19.2%, compared to pure PEG.
[318]	2017	Preparation and thermal characterization of form-stable phase change composite (fs-PCC) comprising of PEG, diatomite (Dt) and single-walled carbon nanotubes (SWCNs)	Dt and SWCNs mixture is added in liquid PEG followed by ultra-sonication and filtration. Melting point and latent heat of fs-PCC is identified as 59.6 °C and 109.8 J.g <sup>-1</sup> , respectively. Addition of porous diatomite and well-dispersed SWCNTs increases the thermal conductivity of PEG by 260%. No leakage is observed in fs-PCC containing 60 wt% PEG, after 200 melt-freeze cycles
[319]	2017	Development and characterization of composite PCM comprising of aqueous sodium acetate trihydrate (SAT) and ethylene glycol. Fabrication and thermal evaluation of heat pack using T-History method	Six different combinations of SAT and ethylene glycol are prepared by physical mixing. Melting point and latent heat of SAT-3 wt% ethylene glycol composite is identified as 53.5 °C and 249.3 J.g <sup>-1</sup> , respectively. Heat retention time of heat pack enhanced by 10% compared with heat pack containing pure SAT.
[320]	2017	Preparation, characterization and thermal cycling of paraffin/porous Al <sub>2</sub> O <sub>3</sub> -graphite foams (PAGFs) PCM system	Paraffin/PAGFs PCM is prepared by vacuum impregnation method. Melting point, latent heat and thermal conductivity is measured as 49.1 °C, 113.9 J.g <sup>-1</sup> , and 0.76 W.(m.K) <sup>-1</sup> , respectively and remains stable after 200 melt-freeze cycles
[9]	2017	Preparation and thermal characterization of fatty acid eutectics and triallyl isocyanurate composite PCMs.	Composite PCMs possess reliable thermal characteristics and cyclic stability (after 100 melt-freeze cycles performed) with phase transition temperature 26–40 °C and latent heat of ~ 110 J.g <sup>-1</sup> .
[321]	2016	Preparation, characterization and thermal cycling of PCM composite comprising of PEG and diatomite	Pore size enlargement of diatomite is accomplished with 5 wt% NaOH. Diatomite supported PEG composite PCM is prepared by vacuum impregnation method and PEG load reached 70 wt%. Melting point and latent heat is measured as 58.8 °C and 127 J.g <sup>-1</sup> , respectively. After 200 melt/freeze cycles the composite possessed stable thermophysical properties.
[322]	2016	Preparation and characterization of PCM composite comprising of Rubitherm 65 (RT65), carbon foams (CF) and multi-walled carbon nanotubes (MWCNTs). Development and testing of three thermal modules (TM) for thermal management of electronic devices	Composite PCM is prepared by melt blending. CF acts as base structure. TM module comprising of CF with RT65/1 wt% MWCNTs showed promising results. CF with high thermal conductivity in TM decreases the average temperature more significantly in pulsed power spike mode.
[323]	2016	Preparation and characterization of PCM composite comprising of capric acid (CA), myristic acid (MA), palmitic acid (PA) and, exfoliated amorphous graphite (xG-A) and exfoliated flake graphite (xG-F)	Eutectic CA-MA-PA with mass ratios 64.8:22.6:12.6 is prepared through melt blending. Optimum mass ratio of PCM composite CA–MA–PA/xG is 95:5 Melting point, latent heat and thermal conductivity is measured as 17.5 °C, 143.7 J.g <sup>-1</sup> , and 0.17 W.(m.K) <sup>-1</sup> , respectively. xG-F increases the thermal conductivity by 114%
[324]	2016	Preparation and characterization of PCM composite comprising of lauric acid (LA), palmitic acid (PA), polyethylene terephthalate (PET) and AgNO <sub>3</sub>	Eutectic LA-PA with mass ratios 77.51/22.49 is prepared through melt blending followed by addition of PET and AgNO <sub>3</sub> , followed by electrospinning process. LA-PA/PET/AgNO <sub>3</sub> and LA-PA/PET/Ag are prepared with 0.1, 0.5 and 1 wt% AgNO <sub>3</sub> . Latent heat of electrospun LA-PA/PET/Ag-0.5 decreases by 12%
[28]	2016	Synthesis, determination of thermophysical properties and cyclic durability and mechanical strength of next generation latent heat thermal energy storage PCM system for high temperature applications	Microencapsulated PCM comprising of α-Al <sub>2</sub> O <sub>3</sub> shell and Al-25 wt% Si core (melting temperature 557 °C, latent heat 233 J.g <sup>-1</sup> ) is synthesized. High specific heat capacity and excellent thermal durability is observed after performing 3000 melt-freeze cycles
[325]	2015	Development and characterization of shape stabilized composite phase change material (ss-CPCM) comprising of PEG and radial mesoporous silica (RMS)	ss-CPCM is prepared through vacuum impregnation method. Melting point and latent heat of ss-CPCM with 80 wt% PEG is measured as 57.2 °C and 129.6 J.g <sup>-1</sup> . After 200 melt-freeze cycles no leakage is detected. The supercooling extent of PEG reduces to 19% in ss-CPCM
[326]	2015	Development and thermal characterization of organic PCM nanoparticles for in-Product Labeling system	Paraffin wax and fatty acid based polymer encapsulated PCMs are prepared by one-pot method. Nanoparticle barcodes are formed by adding nanoparticles into objects. Each melting peak is assigned one or zero depending upon the heat flux. Information is decoded by counting the melting peaks
[327]	2015	Development and characterization of light weight thermal energy storage cement based-composite (LW-TESSCs) comprising of paraffin and expanded vermiculite calcined at 800 °C (EVM-800)	Paraffin/EVM-800, 0.6:1 wt ratios is prepared by vacuum impregnation. Melting point and latent heat of composite PCM is identified as 27 °C and 77.6 J.g <sup>-1</sup> , respectively. LW-TESSCs is prepared by replacing sand with paraffin/EVM-800 composite and thermal stability is identified by TGA



**Table 7**  
List of patents – PCMs and applications.

	Title of the patent (Patent number)	Year	Related to either materials or applied aspects	Country of origin	Major claim
1.	Encapsulation of thermal energy storage media (# US 9,765,251 B2)	2017	Materials	USA	In one embodiment, a PCM is encapsulated by forming a phase change material pellet
2.	Method of encapsulating a PCM with a metal oxide (# 9,493,695 B2)	2016	Materials	USA	Macro-encapsulation of PCMs using a metal oxide such as SiO <sub>2</sub> over polyimide coated pellets
3.	Latent heat storage using renewable PCMs (# US 9,434,674 B2)	2016	Materials	USA	Method of producing a diol diester, which includes reacting a fatty acid alkyl ester, and using it as PCM
4.	Thermal energy storage system combining sensible heat solid material and PCM (# US 2016/0201995 A1)	2016	Materials and applied aspects	USA	A system for storage and recovery of thermal energy by using at least one PCM (solid-liquid) and a sensible heat solid material
5.	Nanoparticle-enhanced PCMs with improved thermal energy storage (# US 9,027,633 B2)	2015	Materials	USA	Nanoparticles dispersed with a base PCM to enhance thermal conductivity
6.	Method for manufacturing a heat exchanger containing a PCM, exchanger obtained and uses at high temperatures (# US 2015/0266144 A1)	2015	Materials and applied aspects	USA	Heat exchanger module comprising fluid circulation module with metallic alloys or salts based PCMs
7.	Energy storage and thermal management using PCMs in conjunction with heat pipes and foils, foams or other porous media (# US 2014/0284020 A1)	2014	Materials	USA	Energy storage device comprising enclosed chamber, foils or foams made of thermally conductive materials, a PCM and heat pipe
8.	Metallic composite PCMs and methods of using the same (# US 2014/0109895 A1)	2014	Materials	USA	TES module with one or more phase change alloys of variable phase transition temperature between 400 and 1200 °C and a latent heat of >200 J.g <sup>-1</sup>
9.	Carbonate PCMs (# US 8,679,365 B1)	2014	Materials	USA	PCMs that include oleochemical carbonates, which are prepared from oleochemical alcohols derived from animal fats and vegetable oils or other bio-based substances
10.	Phase change aggregates including particulate PCM (# US 2013/0298991 A1)	2013	Materials	USA	Methods for producing aggregates from particulate PCM slurry, suspension or emulsion by combining a cementitious binder and an absorbent with the PCM
11.	Thermal energy storage with a PCM in a non-metal container (# US 2013/0308279 A1)	2013	Materials and applied aspects	USA	A thermal energy storage apparatus that absorbs thermal energy from a heat generating device. Apparatus contains a PCM in a non-metal container
12.	Thermal energy storage materials (# US 8,091,613 B2)	2012	Materials	USA	Thermal energy storage materials based on metallic alloys
13.	LHTES (Latent Heat Thermal Energy Storage) device for electric vehicle, system comprising the same and method for controlling the same (# US 2012/0152511 A1)	2012	Materials and applied aspects	USA	LHTES device with a chamber containing thermal conductivity enhancement units and PCM
14.	Latent heat storage devices (# US 2007/0175609 A1)	2007	Applied aspects	USA	Device for storing latent heat for PCM with heat exchange interface
15.	Water heating unit with integral TES (# 6,463,212 B1)	2002	Materials and applied aspects	USA	Water heater with material having a thermal energy capacity of at least 25 calories.g <sup>-1</sup> and a freezing/melting temperature of about 20–100 °C
16.	Thermal energy storage and delivery system (# 6,059,016)	2000	Materials and applied aspects	USA	Thermal energy storage apparatus configured for heating and cooling for vehicles
17.	Building products incorporating PCMs and method of making same (# 5,755,216)	1998	Materials	USA	Building blocks having hollow cores filled with a PCM for TES applications
18.	Compositions for TES or thermal energy generation (TEG) (# 5,552,075)	1996	Materials	USA	New compositions comprising a silica based gel or dry powder with a water/urea PCM for TES and TEG
19.	Thermal energy storage apparatus using encapsulated PCM (# US 4,807,696)	1989	Materials and applied aspects	USA	A novel thermal energy storage material using encapsulated PCM
20.	Phase change thermal energy storage material (# US 4,702,853)	1987	Materials	USA	A PCM composition comprising a non-chloride hydrate having a phase change transition temperature in the range of 70–95 °F, and latent heat of transformation of at least about 35 calories.g <sup>-1</sup>

time, round-trip efficiency, maturity status of the technology, environmental and safety issues, cost, and technical suitability of major energy storage technologies along with TES are evaluated in Table 8 [5,329–342]. It is evident from Table 8 that the TES technology show greater potential to overcome the intermittency of the renewable sources. Even though the LHTES comprising of PCMs is currently one of the most promising options for many sectors, but it might not be suitable for the transportation sector. However, the TES systems can be coupled with electric vehicles to meet the

electricity demand for charging purposes and reduction in the carbon emissions with further technology development [342].

Every energy storage technology has a certain environmental impact; in the case of LHTES materials recycling is difficult. The environmental cost associated with the production of the chemicals always exists, such as materials used for the encapsulation of the PCMs are toxic in nature. However, PCMs based LHTES has a far less environmental impact compared with other energy storage technologies as given in Table 8. PCMs when utilized for

**Table 8**  
Comparison of various energy storage technologies.

	Thermal energy storage	Batteries	Fuel cells	Super capacitors	Superconducting magnet	Flywheels	Compressed air	Pumped hydro
Power (MW), Scale	50	<50, Medium	0.250	0.001–0.1	<10	<2	30–350, Large	100–4000, Large
Energy Density	50–150 kWh/t	50–80 kWh/m <sup>3</sup>	–	0.020 kWh/kg	0.2–2.5 kw/m <sup>3</sup>	0.1–0.2 kWh/kg	0.5–12 kWh/m <sup>3</sup>	0.35–1.12 kWh/m <sup>3</sup>
Durability (years)	20	3–12	<20	8–10	15	20	20–30	30
Storage Period	Days-Months	Hours-Days	–	–	Hours-Day	Hours	Months	Months-year
Charging Time	Very Good	Good	Fair	Excellent	Excellent	Very Good	Fair	Fair
Discharge duration	As needed	1 min-8 h	As needed	<1 min		3–120 s	60–20 h	4–12 h
Response Time	milliseconds	milliseconds	seconds	milliseconds -seconds	milliseconds	seconds	minutes	<3 min
Cost (\$)	70–200/kWh	200–300/kWh, 250–300/kWh	15/kWh, 1100–2600/kWh	82000/kWh, 120/kWh	2000–72000/kWh, 975/kWh	100–300/kWh	2–150/kWh, 400–500/kWh	10–20/kWh, 600/kWh
Maintenance Cost	Very Low-Low	Moderate-High	Low-Moderate (\$10/kWh/yr)	Moderate- High (\$5–6/kWh/yr)	Moderate-high (\$8–26/kWh/yr)	Moderate (\$7.5–8/kWh/yr)	Low-Moderate (\$2–4/kWh/yr)	High-Very High
Round Trip Efficiency (%)	75–96	75–85	40–70	95	90–95	85–90	57–70	65–85
Environmental issues	Benign, material recycling	Chemical Disposal	Operational benignity	Chemical disposal	Benign	Light	Carbon emmsions	Effects wildlife, and ground water level
Safety Issues	High temperature caution	Chemical handling, overcharging caution	Hydrogen safety caution	Acids caution	Magnetic field	Containment	None for in reservoir, pressure cautions for in vessel storage	Reservoir, Exclusion area
Applications	Passive/Active cooling and heating, Peak Shaving, CSP plants	Peak shave, UPS, portable devices, EVs	Portable applications, Co-generation, Space industry	Short term, Power source	Regulate power grid	Peak Shaving	Stabilization of conventional generation	Peak shaving
Maturity	Commercial, Very active R&D for performance enhancement	Commercial, Very active R&D	Few comercial units, Very active R&D	Some commercial products	Commercial, design concept of large scale systems	Low speed commercial, high speed prototype testing	Commercial, R&D for vessel type	Commercial
Technical suitability for storage	Renewable	YES	YES	NO	NO	YES	NO	YES
Load leveling	YES	YES	YES	NO	NO	NO	YES	YES
Renewables back-up	YES	YES	YES	NO	NO	NO	YES	NO
Emergency back-up	YES	YES	YES	NO	NO	YES	YES	NO
Transport sector	NO	YES	YES	YES	NO	NO	NO	NO
Ref.	[5,331,333–335,338–342]	[331,332,336,337,339,341,342]	[337,339,341,342]	[332,336,339,341,342]	[331,336,339,341,342]	[331,332,336,339,341,342]	[329–331,335–337,339,342]	[330–332,336,337,339,342]

cooling application reduces the usage of ozone-depleting CFCs, while PCMs are integrated into heating systems they reduce the consumption of carbon-based fuels, consequently decreasing the CO<sub>2</sub> and NO<sub>x</sub> emissions to the environment. PCMs with 20% market penetration in California State of the USA by 2005 resulted in the reduction of 260,000 tons of CO<sub>2</sub> annually and 1.6 tons of NO<sub>x</sub> per day. This saving in NO<sub>x</sub> emission is equivalent to the amount saved through 100,000 on-the-road electric vehicles [334]. Therefore, PCMs may help to curb the global warming if more efficient, and cost-effective LHTEs systems are developed by researchers.

## 9. Conclusion

This review has focused on recent developments on TES using PCMs, in which latent heat is exploited. The PCMs with higher thermal storage density lead to reduction of storage tank size/volume, in addition to a range of flexible operating temperatures. However, large-scale commercial application of latent heat PCMs is still limited and the durability is lower than that of sensible heat materials. Many of the recent publications are directed at solving problems related to improving performance stability, reducing supercooling and lowering cost towards thermal storage applications in power plants. The selection of organic, inorganic and EPCMs is based on kinetic, thermodynamic properties and availability along with their melting point, latent heat, energy density, and thermal conductivity characteristics as well as cost. Even though inorganic materials show high energy density, high thermal conductivity, and relatively higher melting temperatures, they are more corrosive and exhibit supercooling. This review also brought out various commercial applications of PCMs and the most promising is towards smart thermal grid system along with intermittent renewable energy sources. Towards enhancing the PCMs properties, specifically encapsulation and nanomaterial additives are the two most prominent approaches in increasing surface area, protecting from the environment, increasing the compatibility with storage materials and reducing corrosion. In particular, nanomaterials are being used for increasing the specific heat and thermal conductivity of the PCMs. Various properties of the PCMs are also compared from recent literature with very specific applications. The patents on PCMs reviewed towards the end throws light on the developments in the application areas for TES. It is interesting to note that the material costs can be about \$15 per kWh<sub>th</sub> with combined sensible/latent heat TES systems.

## Conflict of interest

The authors declared that there is no conflict of interest.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.ijheatmasstransfer.2018.09.126>.

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