THERMAL APPLICATIONS OF HYBRID PHASE CHANGE MATERIALS: A Critical Review

by

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Review paper
https://doi.org/10.2298/TSCI190302112T

Phase change materials (PCM) with their high latent heat capacity have a great ability to store energy during their phase change process. The PCM are renowned for their applications in solar and thermal energy storage systems for the purpose of heating and cooling. However, one of the major drawbacks of PCM is their low thermal conductivity due to which their charging and discharging time reduces along with the reduction in energy storage capacity. This reduction in the energy storage capacity of PCM can be improved by producing organic-inorganic hybrid form-stable PCM, with the combination of two or more PCM together to increase their energy storage capacity. Nanoparticles that possess high thermal conductivity are also doped with these hybrid PCM (HPCM)to improve the effectiveness of thermal conductivity. This paper presents a short review on the applications of HPCM in energy storage and building application. Apart from this a short section of applications of composite PCM (CPCM) is also reviewed with discussions made at the end of each section. Results from the past literature depicted that the application of these HPCM and CPCM enhanced the energy storage capacity and thermal conductivity of the base PCM and selection of a proper hybrid material plays an essential role in their stability. It is presumed that this study will provide a sagacity, to the readers, to investigate their thermophysical properties and other essential applications.

Key words: *PCM, HPCM, latent heat, CPCM, thermal energy storage, solar energy storage, buildings*

Introduction

With the reduction in the fossil fuels and increase in the energy demand, it has become necessary to store thermal energy to meet the energy demands and to create a balance between energy demand and supply [1, 2]. As the fossil fuels are depleting gradually there is a need to shift towards renewable energy resources to fulfill the energy [3, 4] As the energy output of renewable energy resources is very uncertain therefore, we need to create the thermal energy storage (TES) system to save the energy for later use. The designed TES should have high storage capacity and it should be economical and efficient [5].

The TES is one of the eco-friendliest technologies which is being utilized to handle heating/cooling issues in limited temperature range [6]. However, one of the basic tasks in TES to use those materials that have high latent heat capacity, thermal conductivity and should have

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high reliability [3, 7-9]. The PCM can store thermal energy as latent heat [10] of vaporization (liquid to vapor conversion) or latent heat of fusion (solid to liquid conversion), however, nowadays heat of fusion is mainly used [11-13]. Over the last two decades the use of PCM in TES systems has got a special interest as they have the ability to store and release energy during their phase change process [14-17]. The PCM with high heat of fusion, solidifies and melts at certain temperatures thus, it can stow and deliver huge amount of energy [18]. However, the charging-discharging time of PCM is shortened due to their less thermal conductivity [19].

Researchers have worked to improve the thermal conductivity of PCM by creating organic-inorganic HPCM. These hybrid form-stable PCM can be prepared through doping of particles, possessing high thermal conductivity, which is an efficient method [20-22]. Form-stable HPCM are very effective as they can store thermal energy during their phase transition [23-29] and they can be used widely as they are unproblematic to develop and can be utilized directly without any encapsulation [19, 30-33]. These HPCM can be used in different applications like energy storage systems, solar applications, thermal comfort in the building.

The HPCM used by different researchers is shown in fig. 1. Other means to enhance the thermal conductivity of PCM involve the use of heat pipes, extended surfaces, micro- and macro-encapsulation and addition of nanoparticles having high thermal conductivity. These nanoparticles, when added to the base PCM, enhance its thermal characteristics. The present study gives the review of hybrid PCM and their applications in different fields. A short study comprising of applications of CPCM is also discussed at the end. This study mainly focuses on the thermal applications of HPCM and to elaborate the thermal conductivity effect as the heat transfer rate is majorly dependent on it. Discussions have been done at the end to account the thermal conductivity intensification by the application of HPCM, CPCM and suggestions for the future studies are presented.

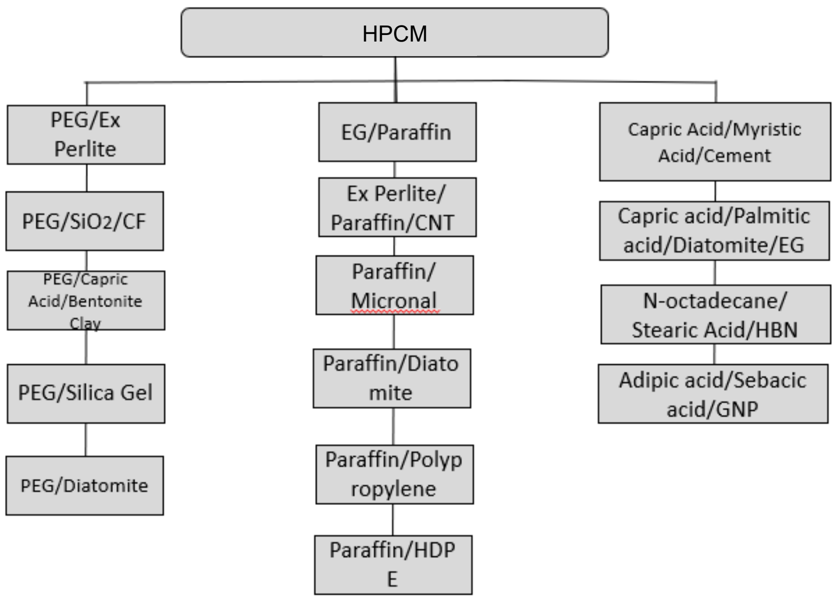


Figure 1. The HPCM prepared by researchers for different applications

Thermal energy storage

Karaipekli *et al.* [34] studied the thermal characteristics of expended perlite/paraffin composite by introducing carbon nanotubes (CNT) in it. The CNT with mass fractions, 0.3%, 0.5% and 1%, increased the thermal conductivity of pure PCM composite. Additionally, CNT having 1% mass fraction increased the thermal conductivity up to 113.3%. Zhang *et al.* [35] prepared HPCM by adding tetrabromobisphenol-A (TBBP-A), with 5%, 10%, 15%, 20%, and 25% concentration and decabrominated-dipheny ethane (DBDPE), having 5%, 10%, 15%, and 20% concentration, into polyethylene glycol (PEG)/toluene PCM mixture and studied its thermal characteristics. The results showed that the prepared HPCM possessed high phase change enthalpy *i.e.* 86.69 J/g with 21.3 limiting oxygen index. Results depicted that the prepared PCM composite had good fire resistance property and high TES capacity. A highly conductive shape stable HPCM was prepared by Wang *et al.* [36] by blend mixing of PEG, silica gel and β-aluminum nitride (5-30 wt.%). It was concluded that the thermal conductivity of base HPCM was enhanced from 0.387 W/mK to 0.7661 W/mK *i.e.* 97.9% by the addition of and β-aluminum nitride.

Seki *et al.* [37] blended sebacic acid and adipic acid together with different compositions. Graphene nanoparticles with mass fraction 0.1 wt.%, 0.3 wt.%, and 0.5 wt.% were added to the prepared mixture. Results depicted that the addition of graphene nanoparticles enhanced the thermal conductivity to 0.117, 0.122, and 0.131 W/mK (from 0.110 W/mK) *i.e.* 6.3%, 10.9%, and 12.7%, respectively. Xu and Li [38] added 0.26 wt.% of MWCNT to the mixture of paraffin/diatomite CPCM and discovered that the thermal conductivity of the CPCM was enhanced by 42.45% along with the heat storing and releasing capacity of paraffin. Ye *et al.* [39] prepared a mixture of Na_2CO_3/MgO PCM composite (with 60:40 weight ratio) and added MWCNT ranging from 0.1 wt.% to 0.5 wt.%. They checked the thermal conductivity of the HPCM at different set point temperatures *i.e.* 40 °C, 75 °C, and 120 °C. It was derived from the results that with the addition of 0.5 wt.% of MWCNT the thermal conductivity of the CPCM was increased from 0.750W/mK, 0.825W/mK, and 0.881W/mK to 1.127 W/mK, 1.295 W/mK, and 1.489 W/mK at the defined test temperatures.

Tang *et al.* [40] developed a mixture of fatty acid eutectics and diatomite by mixing 12:88 proportion of palmitic acid (PA) and capric acid (CA) with diatomite. They mixed 10, 20 and 40g of PA-CA mixture with 20 g of diatomite and expended graphite (EG) was added with the weight concentration of 3 wt.% and 5 wt.%. It was found that the 5 wt.% of EG enhanced the PCM thermal conductivity up to 25.2% and 53.7% during melting and solidification. Karaman *et al.* [41] added 10 wt.% of EG to a mixture of PEG/diatomite having 45:45 mass ratio and found that the CPCM thermal conductivity was increased by 103%. Sari [42] added 3 wt.% of expended and exfoliated graphite to the mixture of paraffin/high density PE and check the thermal conductivity enhancement at two different temperature ranges *i. e.* 42-44 °C and 56-58 °C. There was the thermal conductivity enhancement of 14% and 24% at these temperatures.

Su *et al.* [43] added 10 wt.% hexagonal boron nitride (HBN) to the mixture of n-octadecane and stearic acid to prepare HPCM composite. The results revealed that by adding HBN the thermal conductivity of CPCM was emhanced by 8% in solid state and 16.7% in melting state. Hong *et al.* [44] prepared form-stable PCM by mixing superwetting polypropylene (PP) aerogel with 1060 wt.% of paraffin. The thermal conductivity of the HPCM was enhanced up to 0.534 W/mK which was twice of pure paraffin (0.207 W/mK).

Zhang *et al.* [45] prepared a mixture of expended perlite and PEG through the process of vacuum impregnation as shown in fig. 2. They added 33.63 wt.% of CF in order to increase the thermal conductivity of HPCM to enhance the TES capacity. Results revealed that thermal conductivity of HPCM reached up to 0.479 W/mK which was 2.97 times of PEP. They concluded that the prepared composite showed efficient thermal stability and reliability and there-

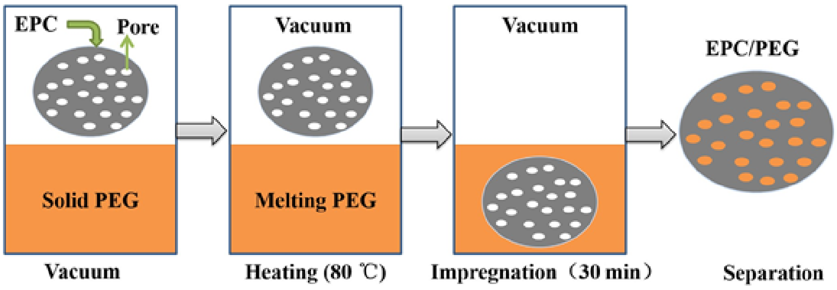


Figure 2. Schematic diagram of vacuum impregnation process to prepare HPCM [45]

fore it can be used as filler material for energy-efficient buildings. The summary of HPCM used for TES system is shown in tab. 1.

Discussion

As far as the aim to increase the thermophysical properties of PCM is associated, researchers have worked to increase the latent heat storage capacity of PCM by creating organic-inorganic shape stable HPCM through doping of particles which possess high thermal conductivity to enhance the thermal conductivity as well. The enhancement in the thermal conductivity is efficient for storing/release capacity of HPCM. For TES system, researchers [34-45] studied the thermal characteristics of the prepared HPCM and then concluded that the prepared HPCM is either efficient enough to store TES or not. However, from the literature studied it has been revealed that almost all the HPCM have increased the thermal conductivity of base PCM and hence the TES capacity. Figure 3 shows the improvement in thermal conductivity with respect to weight concentration of HPCM obtained by researchers.

The concentration of particle in CPCM and the choice of combination to prepare a PCM composite holds a vital role in the thermal conductivity enhancement of HPCM. The particle concentration has the direct relation with the thermal conductivity enhancement, the thermal conductivity will increase by increasing the particle concentration [46-48]. Addition of GNP in adipic acid and sebacic acid [37] at 0.1, 0.3, and 0.5 wt.% enhanced the thermal conductivity up to 6.3%, 10.9%, and 12.7%, respectively. Ex Perlite/Paraffin/CNT [34] at 1 wt.%

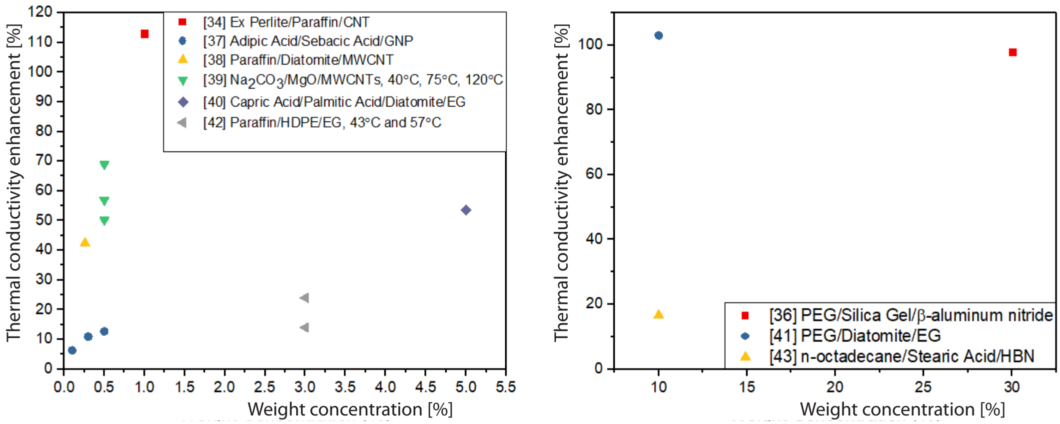


Figure 3. Improvement in the thermal conductivity with respect to weight concentration obtained by different researchers for TES system

Table 1. Summary of HPCM used in TES system

References	Base PCM	Composite material	Concentration [wt.%]	Results (thermal conductivity enhancement)
[34]	Ex Perlite/ Paraffin	CNT/PCM	0.3 0.5 1	CNT having 1% mass fraction increased the thermal conductivity up to 113.3%
[35]	PEG	TBBP-A/ DBDPE	TBBP-A / DBDPE 0 / 20 5 / 15 10 / 10 15 / 5 20 / 0	The prepared HPCM possessed high phase change enthalpy *i.e.* 86.69 J/g showing high TES capacity
[36]	PEG/Silica Gel	β-aluminum nitride/PCM	30	The thermal conductivity of base HPCM was enhanced from 0.387 W/mK to 0.7661 W/mK *i.e.* 97.9% by the addition of and β-aluminum nitride
[37]	Adipic acid/ Sebacic acid	GNP/PCM	0.1 0.3 0.5	The addition of graphene nanoparticles increased the thermal conductivity of the HPCM up to 6.3%, 10.9% and 12.7%, respectively
[38]	Paraffin/ Diatomite	MWCNT/PCM	0.26	The thermal conductivity of the HPCM was improved by 42.45% along with the heat storing and releasing capacity of paraffin
[39]	Na_2CO_3/MgO	MWCNT/PCM	0.1 wt.% to 0.5 wt.%	Adding MWCNT with 0.5wt.% concentration, the thermal conductivity of the HPCM was increased up to 50.2%, 56.9%, and 69% at 40 °C, 75 °C, and 120 °C.
[40]	CA/PA/ Diatomite	EG/PCM	3 5	5 wt.% of EG increased the thermal conductivity of HPCM up to 25.2% in solid state and 53.7% in liquid state
[41]	PEG/Diatomite	EG/PCM	10	The thermal conductivity of the CPCM was increased by 103%
[42]	Paraffin/HDPE	EG/PCM	3	The thermal conductivity of composite PCM was increased up to 14% and 24% at 43 °C and 57 °C
[43]	n-octadecane/ Stearic acid	HBN	10	By adding HBN to HPCM the thermal conductivity was improved by 8% in solid state and 16.7% in liquid state
[44]	Paraffin/PP	-	-	The thermal conductivity of HPCM was enhanced up to 0.534 W/mK which was twice of pure paraffin (0.207 W/mK)
[45]	Ex Perlite/PEG	CF	33.62	The thermal conductivity of HPCM reached up to 0.479W/mK which was 2.97 times of PEP

concentration achieved the maximum thermal conductivity enhancement of about 113%. Temperature also affects the thermal conductivity of base PCM, greater the temperature greater will be thermal conductivity. The Na_2CO_3/MgO/MWCNT [39] at 0.5 wt.% of MWCNT showed the thermal conductivity enhancement up to 50.2%, 56.9%, and 69% at 40 °C, 75 °C, and 120 °C. The N-octadecane/stearic acid/HBN [43] at 10 wt.% concentration showed the minimum thermal conductivity enhancement *i.e.* only 16.7% as compared to other HPCM that showed greater thermal conductivity enhancement even at low weight percentages *i.e.* below 10 wt.%.

Thermal comfort in modern buildings

The increasing energy demand and the comparing costs are the two major challenges of the building sector in whole worldwide. It is a known fact that the industrial and building sector consume tierce of the entire world energy so the method of TES has become popular in this era [49]. Thus, to maintain the thermal comfort and reduce the indoor temperature fluctuations HPCM, which are prepared in shape-stabilized form, are used for LHTES system [19, 50-55]. These type of form stable PCM composite are used in the manufacturing of concrete blocks, hollow bricks and wallboard plasters which have the potential to store latent heat thermal energy [53-57]. Different types of PCM like paraffins, poly ethylene glycols, fatty acids are most commonly used for the purpose of heating/cooling in buildings due to their high latent heat storage capacity during their phase change process [58-60] and moreover, these PCM are non-toxic and have small supercooling [61-63] A major disadvantage of PCM is their low thermal conductivity, however, this can be improved by incorporating high thermal conductivity materials [36, 64] into them.

The PCM can be incorporated with the materials which are porous, and light weighted in order to create economical and environment friendly materials [65, 66] for TES in building sector for the thermal comfort. The PCM can be integrated with the porous building clays like perlite [67-69], diatomite [41, 70-73], vermiculite [19, 54], kaolin [74, 75] and bentonite [76]. In this aspect Lachheb *et al.* [77] studied the thermal behavior of hybrid micronal/plaster to minimize the energy demand in buildings. The composite prepared, was consisted of a plaster matrix having micro-encapsulated paraffin with 10% mass fraction. The experimentation was carried out by transient guarded hot plate technique which was dependent on heat flux and temperature measurements. Schematic view of experimental set-up is manifested in fig. 4. The results depicted that the wallboard thickness affected the thermal ease of the building and it can be enhanced by increasing the thickness of the wall. They concluded that the incorporation of micro-encapsulated PCM caused the enhancement in energy storage capacity of plaster.

Sari [78] prepared bentonite-based form stable composite PCM, by impregnating 40 wt.% CA, 43 wt.% PEG, 32 wt.% dodecanol, and 18 wt.% heptadecane into bentonite clay, for the purpose of TES in buildings. Figures 5 and 6 show the photograph and SEM images of the prepared composites. The results revealed that the prepared HPCM had 38 J/g to 74 J/g latent heat capacity and it can be used in buildings for heating/cooling purpose. Sari *et al.* [79] prepared cement-PCM based composites for the establishment of low temperature LHTES targets in the buildings. The PCM mixture used, was consisted of CA and myristic acid which was soaked as a concentration of 28 wt.% in the cement through the process of vacuum embedding. The LHTES capacities of the prepared composite was determined and it was observed that the cement-based HPCM melts and solidifies at 21.13 °C and 17.90 °C having the latent heat capacity of 41.78 J/g and 39.56 J/g. Moreover, it was also revealed that the composite possessed high thermal resistance and chemical stability. A temperature difference of 0.78 °C was observed between the indoor temperatures of the cube during the heating period. All these properties make cement dependent CPCM a potential candidate for low temperature HVAC intentions in the buildings.

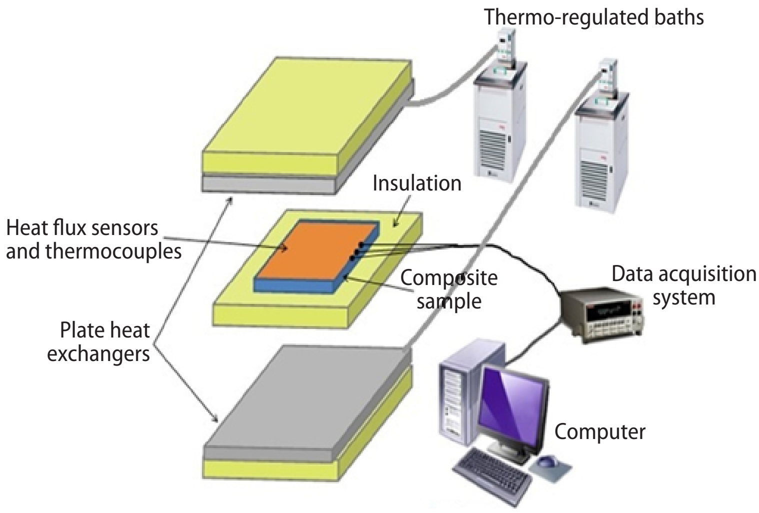


Figure 4. Schematic diagram of transient guarded hot plates method [77]

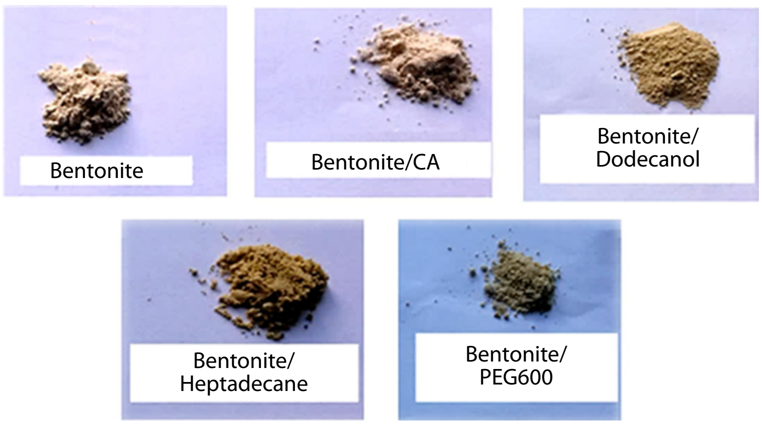


Figure 5. Images of different HPCM prepared by [78]

Shafie-khah *et al.* [80] worked to improve the efficiency of energy storage systems by incorporating more than one type of PCM into polyester mortar to reduce customer's cost in different demand response programs. Based on the simulation results it was revealed that there could be 48% reduction in customer's electricity cost by utilizing the proposed model. Kheradmand *et al.* [81-83] proposed a methodology for the incorporation of HPCM in plastic mortar for the improvement of energy efficiency in buildings. They used four different types of PCM which include RT10, MC28, MC24, and BSF26 and observed the thermal behavior of prototype containing mortar with and without PCM

The results showed that the protype with HPCM mortar had a strong ability to reduce thermal amplitude on its interior in both winter and summer seasons as compared to the condition of reference mortar prototype. Based on the experimentation it was also revealed that mortar with hybrid PCM had a good capacity to lessen the daily environmental thermal amplitudes within the test cells as compared to mortar with single PCM. The summary of HPCM used for thermal comfort in buildings is given in tab. 2.

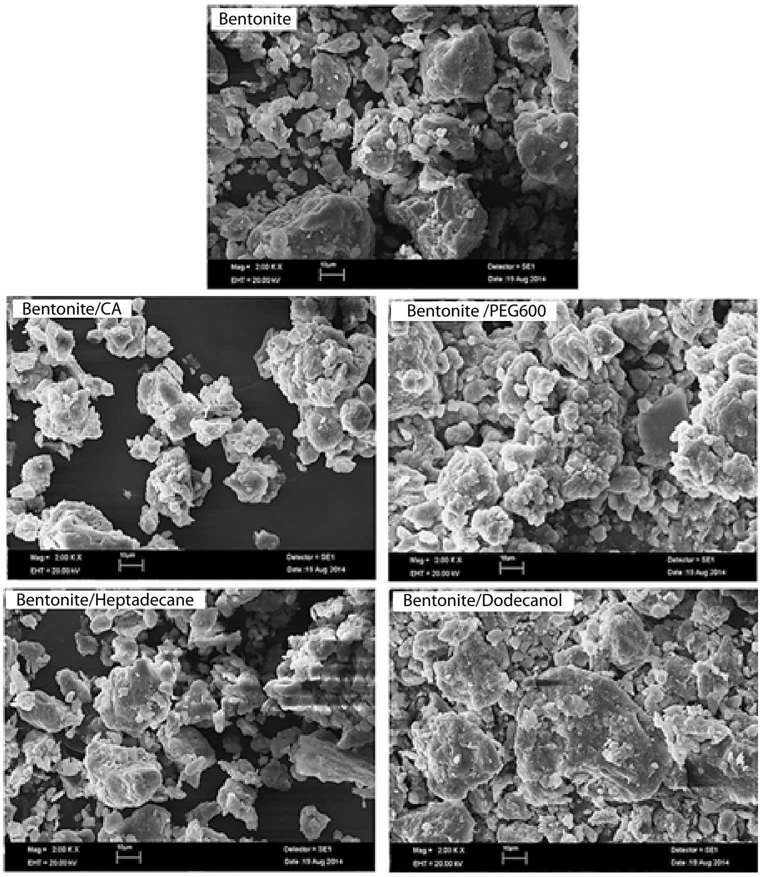


Figure 6. The SEM images of HPCM prepared by Sari [78]

Discussion

Building sector consumes one third of the total energy, hence, there is a need to store thermal energy for later use. A lot of work has been done to use such kind of materials that are capable to store large amount of energy to meet the increasing energy demand in this sector. Researchers [77-79] have studied the thermal properties of synthesized form-stable HPCM for the building applications. They mainly focused to increase the latent heat storage capacity to store the thermal energy for later use. Paraffin/Micronal/Plaster [77] composite showed the highest percentage of heat energy storage capacity *i. e.* 125%. The latent heat capacity of this PCM composite increased from 11.2 J/g to 25.2 J/g. The CA/Myristic acid/Cement [79] composite was used for low temperature HVAC application and its energy storage capacity was found to be increased up to 41.78 J/g and 39.56 J/g for solid and liquid state, respectively.

Another purpose to use HPCM in this sector was to reduce the energy consumption and load demand. Amongst all the literature studied, only Shafie-khah *et al.* [80] and Kheradmand *et al.* [81-83] worked to enhance the efficiency of energy storage systems to minimize the energy demand during peak load hours ultimately reducing the energy cost. Both the researchers achieved the energy demand reduction of 20% during day time when the energy demand is usually high. The HPCM model proposed by Shafie-khah *et al.* [80] also reduced the electricity

Table 2. Summary of HPCM used for thermal comfort in buildings

Reference	PCM	Composite material	PCM concentration [wt.%]	Thermal conductivity enhancement	Results
[77]	Paraffin	Micronal/ plaster	10%	–	The thermal storage capacity of plaster was greatly enhanced by incorporating microencapsulated PCM in it. latent heat capacity increased from 11.2 J/g to 25.2 J/g
[78]	CA/ Polyethylene glycol	Bentonite clay/PCM	40% 43% 32% 18%	65% 63% 39% 47%	The prepared composite had 38 J/g to 74 J/g latent heat capacity, and it can be used in buildings for heating/cooling purpose
[79]	CA/ Myristic acid	Cement/ PCM	28%	-	Cement dependent CPCM is a potential candidate for low temperature HVAC application, in the buildings, having 39.56 J/g and 41.78 J/g latent heat capacity. (percentage increase of 72.7)
[80]	PCM with melting temperatures 5 °C, 21 °C and 23 °C.	Polyester mortar/ PCM	18.34%	-	Electricity cost of a customer could be lessened by 48% by using HPCM /Polyester mortar in buildings; also, 20% reduction in peak load was found
[81-83]	RT10 MC28 MC24 BSF26	Plastic mortar/ PCM	20%	-	The proposed prototype reduced 20% of the load demand and had a strong ability to reduce thermal amplitude on its interior in both winter and summer seasons

cost by 48%. The HPCM prepared by Kheradmand *et al.* [81-83] had the capability to control thermal amplitude fluctuations on its interior in both winter and summer seasons. Figure 7 shows increment in LHTES capacity and reduction in energy demand, as a function of weight concentration, achieved by researchers for building application.

The results of application of HPCM in buildings show that these hybrid form-stable PCM have positive effects on the thermal management of buildings including, heating, cooling, air conditioning and ventilation. This application also decreased the energy consumption, temperature fluctuations, and it caused a reduction in electricity cost.

Composite PCM

Other methods to increase the thermal conductivity and thermal storage capacity of PCM involve the use of heat pipes [84, 85], extended surfaces, micro- and macro-encapsulation and addition of nanoparticles having high thermal conductivity [86, 87]. These nanoparticles when added to the base PCM, enhance its thermal characteristics. Numerous research work is carried in the field of composite nanoparticle enhanced PCM, however, only a few of experimental works for thermal applications of CPCM are reported in this chapter.

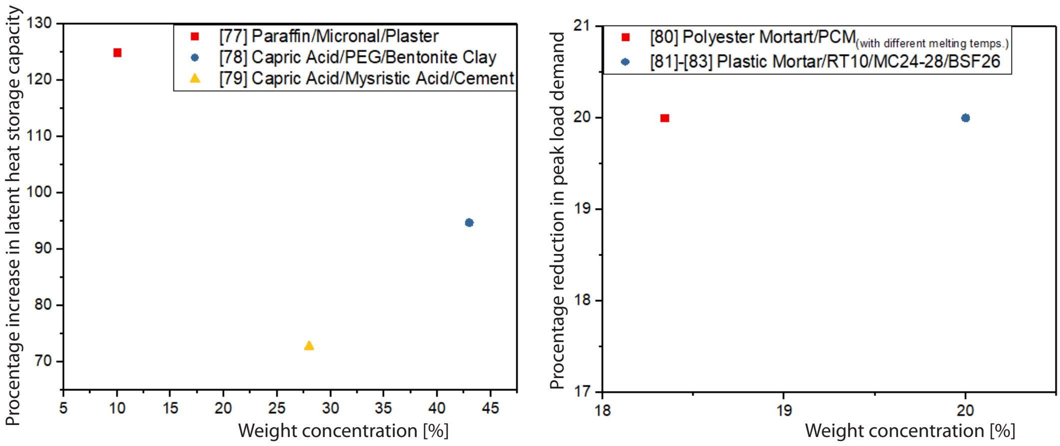
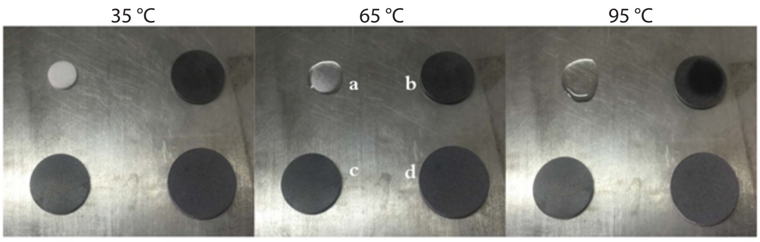


Figure 7. Shows increment in LHTES capacity and reduction in energy demand, as a function of weight concentration, achieved by researchers for building application

Thermal energy storage

Harish *et al.* [88] conducted an experimental investigation to study the consequences of single walled carbon nanohorns (SWCNH), MWCNT, and GNP on the thermal conductivity of lauric acid, which was used as a base PCM. The results revealed the maximum thermal conductivity enhancement of 223%, 171%, and 27% for 1 vol% of GNP, MWCNT, and SWCNH. It was concluded from the results that GNP showed remarkable thermal conductivity improvement because of their high aspect ratio and low thermal resistance. Cui *et al.* [89] used carbon nanofibers (CNF) and CNT to enhance the thermal conductivity of soy wax and paraffin wax. The CNF and CNT were mixed with soy wax and paraffin wax with mass ratios ranging from 1% to 10%. Results depicted that the addition of CNT and CNF to soy wax enhanced its thermal conductivity up to 0.403 W/mK and 0.469 W/mK and 0.450 W/mK for CNF/Paraffin composite. As CNF showed better thermal performance therefore, it can be considered as a potential candidate for TES systems as it enhances the thermal conductivity of PCM without lowering its latent heat capacity.

Yang *et al.* [90] added graphene oxid (GO) and boron nitride (BN) to elevate the thermal conductivity of PEG. They developed PEG/GO/BN composite by adding GO and BN having 4 wt.% and 30 wt.%, respectively. The CPCM had 900% increment in the thermal conductivity as compared to pure PEG. Tang *et al.* [91] synthesized PEG/SiO_2-Al_2O_3 composite PCM by sol-gel technique and studied its thermal characteristics. The Al_2O_3 having 0 wt.%, 3.3 wt.%, 9.3 wt.%, and 12.6 wt.% was added to PEG/SiO_2 composite. The results depicted that the phase change enthalpy of HPCM reach 124 J/g and thermal conductivity was improved by 12.8% for 3.3 wt.% of Al_2O_3 as compared to PEC/SiO_2. Another researcher Liu *et al.* [92] enhanced the thermal conductivity of PEG/SiO_2 composite by introducing carbon fiber (CF) having 1 wt.% to 5 wt.% concentration in it. Figure 8 shows the digital pictures of the CPCM at different temperature. The CF/PEG/SiO_2 was prepared by sol-gel method and its thermal properties was studied. 3 wt.% of CF gave the best results and the coefficient of thermal conductivity reached up to 0.45 W/mK. Moreover, the synthesized PCM composites depicted best capability to convert light energy into thermal energy and exhibited a great ability for the utilization of solar energy.



a – PEG6000; b – CF(2%)/PEG/SiO_2;
c – CF(3%)/PEG/SiO_2; d – CF(4%)/PEG/SiO_2;

Figure 8. Digital pictures of the CPCM at different temperature [92]

Solar energy storage

The only sustainable and carbon free energy which is enough to replace fossil fuel is the solar energy. Solar energy is being used wisely due to the immense increase in the fuel prices and shortage of commonly used energy resources [93-96]. However, the output of this energy is not constant and to make the output definite there is a need to create such materials that can convert light energy into heat energy that can be stored for later use. The advancement of solar energy transformation materials is a basic requirement to create an economical energy foundation in the present years. The present studies have aimed to capture and convert the sunlight into heat energy for solar energy storage. For that purpose, Tang *et al.* [97] prepared CNT/PEG/SiO_2 composite PCM and checked out its energy storage capacity and light to heat conversion capability. The MWCNT possess a broad span of UV-vis light absorptivity [98-104] and efficient capability to convert light into heat energy [105-107] so, they were used to be immersed into the HPCM to get the unique CNT/PEG/SiO_2 composites which were capable to convert light energy into heat energy. This CPCM was prepared by sol-gel method and the PCM used, has the capability to store heat energy during its phase change period as it possesses a high energy storage density [108, 109]. Figure 9 shows the schematic of conversion process of light-to-heat energy and its storage. The MWCNT, having 0.5 wt.%, 1 wt.%, 2 wt.%, and 3 wt.% concentration, were added to the PCM mixture. The heating time was observed to be reduced by 16.2%, 29.1%, 41.2%, and 58.1% and the thermal conductivity reached up to 0.389 W/mK to 0.463 W/mK for MWCNT/PEG/SiO_2 composites in comparison with pure PEG and PEG/SiO_2 which were 0.290 W/mK and 0.359W/mK.

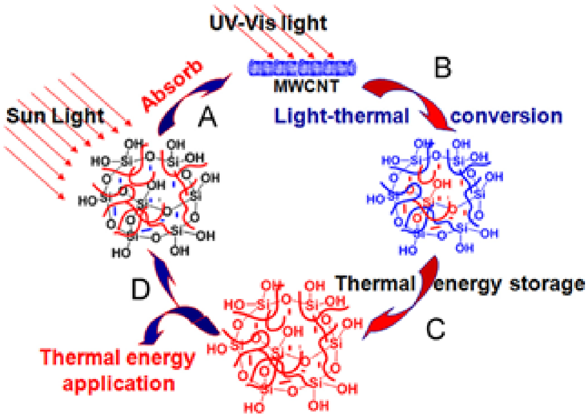


Figure 9. Schematic of conversion process of light-to-heat energy and its storage [97]

Amongst all these PCM composite combinations PEG/SiO_2 with 2 wt.% MWCNT showed the maximum thermal conductivity enhancement by 53.1% and 26.7% as compared with pure PEG and PEG/SiO_2. Results also showed that the efficiency of MWCNT PEG/SiO_2, to convert light-to-heat energy, was 0.918 moreover, this composite possessed high thermal conductivity due to which its charging time along with the discharging time was shortened [110]. It was deduced from the results, that the synthesized CPCM had high efficiency of light-to-heat conversion along with the ability to store energy and higher thermal conductivity therefore it can be used in solar energy utilization applications.

Yang *et al.* [111] prepared hybrid graphene aerogels (HGA) which were consisted of GO and graphene nanoplatelets (GNP). The prepared HGA was then added into PEG by vacuum impregnation process, hoping to improve the thermal conductivity, shape stabilization and energy storage characteristics of this CPCM. Figure 10 shows the schematic of TES and release by CPCM. Results showed the thermal conductivity enhancement of 1.43 W/mK from 0.31 W/mK of pure PEG by 0.45 wt.% GO and 1.8 wt.% GNP along with the conversion from light-to-heat energy was achieved by this CPCM.

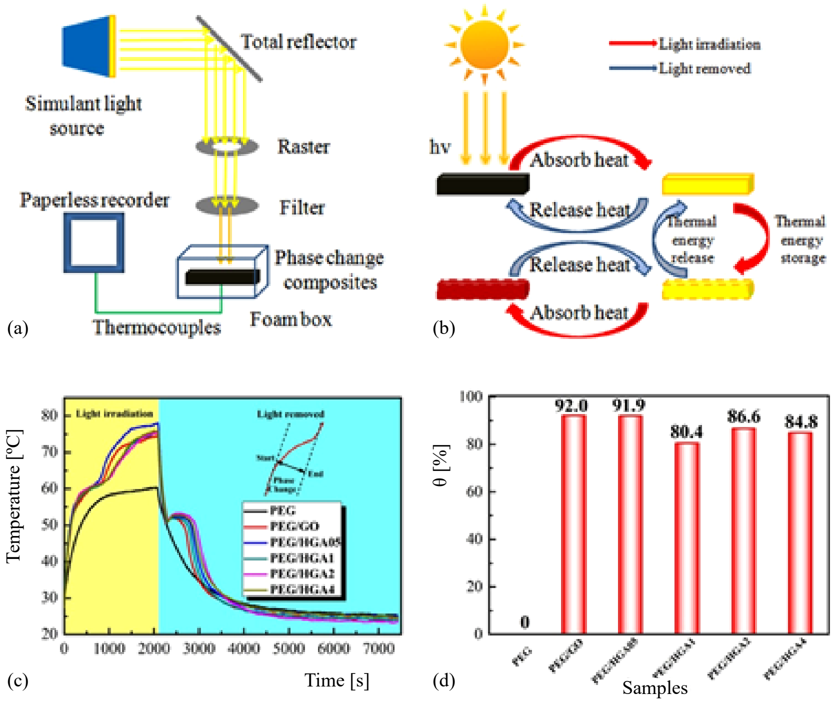


Figure 10. Schematic diagram of phenomena of TES and release; (a) experimental set-up of conversion from light-to-heat energy and its storage, (b) schematic diagram of experimental set-up shown in (a), (c) temperature evolution curves of pure PEG and PEG/HGA CPCM, (d) the efficiency (θ) of light-to-heat of the CPCM [111]

Tang *et al.* [112, 113] increased the thermal conductivity of PEG/SiO_2 by Cu doping and Ti_4O_7 doping. The Cu having 0.51 wt.%, 2.1 wt.%, and 3.9 wt.% and Ti_4O_7 having 1 wt.%, 2 wt.%, and 3 wt.% concentration was added to PEG/SiO_2 composite. In case of Cu doping the thermal conductivity achieved was 0.414 W/mk at 2.1 wt.% showing the enhancement of 38.1% as compared to pure PEG. Whereas, in the case of Ti_4O_7 the thermal conductivity was also increased. Results also showed that both Cu and Ti_4O_7 based PEG composite exhibited high shape and thermal stability. The Ti_4O_7/PEG/SiO_2 composite absorbed light energy and converted it into heat energy which was stored by the PCM. Table 3 shows the summary of applications of CPCM composites by different researchers.

Table 3. Summary of applications of CPCM composite by different researchers

References	Base PCM	Composite material	Concentration [wt.%]	Application	Thermal conductivity enhancement
[88]	Lauric Acid	GNP/PCM MWCNT/PCM SWCNH/PCM	1vol%	TES	Results showed the maximum thermal conductivity enhancement of 223%, 171%, and 27% for GNP, MWCNT and SWCNHs composites
[89]	Soy wax, Paraffin wax	CNF, CNT	1 wt.% to 10 wt.%	TES	The addition of CNT and CNF to soy wax enhanced its thermal conductivity up to 0.403 W/mK and 0.469 W/mK and 0.450 W/mK for CNF/ Paraffin composite
[90]	PEG	GO/BN/PEG	4 wt.% and 30 wt.%	TES	Thermal conductivity was enhanced by 900% as compared to pure PEG
[91]	PEG/SiO_2	Al_2O_3 /PCM	3.3 9.3 12.6	TES	The phase change enthalpy of HPCM reach 124 J/g and thermal conductivity was enhanced by 12.8% for 3.3 wt.% of Al_2O_3 as compared to PEC/SiO_2
[92]	PEG/SiO_2	CF/PCM	1 wt.% to 5 wt.%	TES	3 wt.% of CF gave the best results and the thermal conductivity coefficient reached 0.45 W/mK
[97]	PEG/SiO_2	MWCNT/PCM	0.5 1 2 3	Solar energy storage	The thermal conductivity reached up to 0.463 W/mK from 0.389 W/mK for MWCNT/ PEG/SiO_2 composites and light to heat energy conversion efficiency reached up to 92.9%
[111]	PEG	GO/GNP	GO / GNP 0.47 / 0 0.46 / 0.46 0.46 / 0.92 0.44 / 1.78 0.38 / 3.88	Solar energy storage	The thermal conductivity enhancement of 1.43 W/mK from 0.31 W/mK of pure PEG by 0.45 wt.% GO and 1.8 wt.% GNP was observed along with the light-heat energy efficiency of 90%.
[112]	PEG/SiO_2	Cu/PCM	0.51 2.1 3.9	Solar energy storage	At 2.1 wt.% Cu the thermal conductivity enhancement of 38.1% was observed as compared to pure PEG
[113]	PEG/SiO_2	Ti_4O_7 /PCM	1 2 3	Solar energy storage	$Ti_4O_7/PEG/SiO_2$ composite showed the enhancement in the thermal conductivity and also it absorbed the light energy and converted it into heat energy by 45%

Discussion

For energy storage, the researchers [97, 111-113] synthesized nanoparticle based CPCM which had high thermal conductivity, high energy storage density, high thermal reliability. Also, these CPCM, when used for solar energy applications, converted light energy into heat energy which can be stored for later use. Figure 11 shows percentage of thermal conduc-

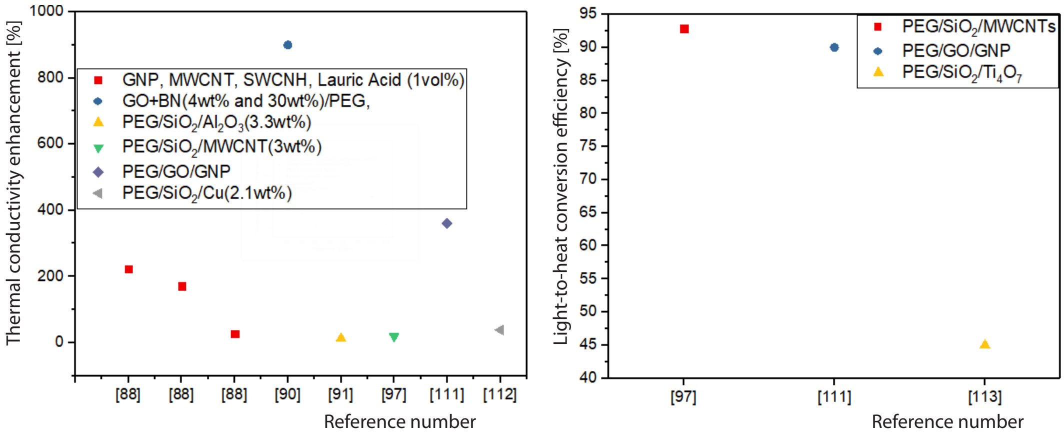


Figure 11. Percentage of thermal conductivity enhancement achieved by CPCM and light-to-heat conversion efficiency of CPCM, used for solar energy storage, achieved by researchers

tivity enhancement achieved by CPCM for TES and the efficiency of light to heat conversion of CPCM used for solar energy storage. The PEG/SiO_2/MWCNT [97] achieved the highest efficiency *i. e.* 92.9%. The PEG/GO/GNP [111] composite achieved about 90% of the efficiency and PEG/SiO2/Ti_4O_7 [113] achieved the efficiency about 45%.

On the basis of these results it can be concluded that the prepared PCM composites possessed high efficiency to convert and store light into heat energy and higher thermal conductivity therefore they can be used in thermal energy utilization applications, and they could be used widely in energy conversion and storage applications.

Conclusions

The PCM, with their TES capacity, have got great attentiveness in many engineering applications, however, the drawback lies in their low thermal conductivity. In order to enhance this thermal property researchers concentrated to generate form-stable PCM composites by combining two or more PCM along with the doping of particles, having high thermal conductivities, to make a new class of PCM commonly known as HPCM. From the literature, it is concluded that most common HPCM are PEG and paraffin based because of their large latent heat capacity, their consistent melting behavior and non-corrosiveness. This review has focused on the thermal applications of HPCM which encompass application in TES system, solar energy storage and building. Following points could be deduced as folloows.

- Selection of proper PCM and particle to create HPCM is very important as it holds a key role in the shape stability of colloidal mixture, and enhancement in the thermo physical properties of the base PCM.
- Numerous researchers [34-45, 91] synthesized HPCM for TES system and studied their thermal characteristics. They surmised that the prepared composites have improved the thermal conductivity of base PCM and hence the TES capacity.
- Thermal conductivity enhancement is directly proportional to the increase in temperature. However, there is a limit to this enhancement, if the temperature exceeds further the thermal conductivity will decrease.
- Researchers [77-79] have studied the latent heat TES capacity of synthesized HPCM for the building applications. They concluded that these hybrid form-stable composite PCM have

positive effects on the thermal management of buildings including, heating, cooling, air conditioning and ventilation.

- For the building sector, the prepared HPCM composites were also capable of reducing the energy consumption and load demand. Shafie-khah *et al.* [80] and Kheradmand *et al.* [81-83] prepared the composites and achieved 20% reduction in the energy demand. The HPCM model proposed by Shafie-khah *et al.* [80] also reduced the electricity cost by 48%.
- The CPCM [88-92, 97, 111-113] prepared, by the addition of nanoparticles to the base PCM, enhanced the thermal conductivity of the PCM
- Researchers [97, 111-113] synthesized PEG based CPCM for the purpose of converting light energy into heat energy and also studied their energy storage capacities. It was depicted from the results that the prepared PEG based CPCM possessed high efficiency to convert and store light into heat energy (max. 92.2%) and higher thermal conductivity therefore they can be used in solar energy utilization applications.

Further work is needed to explore the applications of HPCM in other fields. The problems related to the use of HPCM provide the great opportunity for researchers to create other energy storage materials in combination with PCM so that they can be utilized with much better execution.

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Paper submitted: March 2, 2019
Paper revised: March 28, 2019
Paper accepted: March 30, 2019