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Thermal conductivity enhancement of phase change materials : A literature review

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Abstract

Recently the higher demand of fossil fuels and increasing attention of risks related to environmental issues have contributed to find other renewable sources of energy use to the different industrial and daily domestic activities. Due to this the use of phase change materials (PCMs) in thermal energy storage systems attract more and more attention in recent years due to their contribution to enhanced energy efficiency. However, their low thermal conductivity presents one of the issues that should be resolved. The necessity of increasing the thermal conductivity of PCMs is evident due to its low charging/discharging rates which is important during thermal cycling. In order to overcome the issue of low thermal conductivity. Several studies have been developing new type of PCMs by introducing high thermal conductive filler such as carbon additives or metal foams. Carbon materials are so far the best fillers to increase the effective thermal conductivity of PCM since only small volume fraction is needed and they have high thermal conductivity and low density. The thermal conductivity enhancement using carbon material is the point of focus of this work. Many studies have been done on improving the heat transfer of PCMs. In general, the studies are divided into several categories depending on the types of thermal conductivity enhancers.

1. Introduction

Due to the higher energy demand of fossil fuels and climate change awareness the use of different renewable energy sources is attracting a serious attention [1-3]. The industrial, commercial and domestic activities; the electrical energy consumption varies considerably between peak and off peak periods. Better power generation management can be achieved if some of the peak load could be transferred to the off peak load period, which can be achieved by the thermal energy storage which is widely available in nature in form of solar and geothermal energy.

As a matter of fact, thermal energy can be stored as latent energy by heating and cooling a material. Phase change materials are mostly used to store such thermal energy [4-10]. However, their low thermal conductivity is one of the main problems that should be overcome [11-16]. Higher thermal conductivity could be achieved by using some additives with the aim of increasing the energy charging/discharging rates. Additive could be classified into material based carbon or metal foams. The thermal conductivity enhancement is the point of focus of this review.

2. Thermal conductivity enhancement of phase change materials

2.1. Thermal conductivity enhancement of phase change materials using carbon material

2.1.1. Expanded graphite

Xu et al. [15] prepared $LiNO_3 - KCl - NaNO_3/EG$ composite PCM using the capillary method with 5 wt%, 10 wt%, 15 wt%, 20 wt%, and 25 wt% EG. At 25wt% mass fraction of EG, they found out that no leakage was observed. Using the SEM images, it has been proven that $LiNO_3 - KCl - NaNO_3$ composites were intensely absorbed by EG. In their experiments, the thermal conductivity and the compress density show a strong linear relationship. However, the thermal conductivity of the eutectic salt under a compress density of $1.482 g/cm^3$ was 1.608W/mK. When the compress density of the composite PCM varies from 0.9 to 2 g/cm^3; the thermal conductivity varies from 18.57 to 31.53 W/mK which was 11.5-19.6 higher than that of the pure salt. Zichen et al. [16] use also EG as a high thermal conductivity enhancer and $MgCl_2.6H_2O$ as PCM. It has low thermal conductivity, liquid leakage, high supercooling and poor thermal reliability after numerous thermal cycles. To overcome those issue, EG with different mass fraction (9 wt%, 13 wt%, 16.67 wt%, and 20 wt%) was mixed with$MgCl_2.6H_2O$. The thermal conductivity data of composite PCMs with 9 wt%, 13 wt%, 16.67 wt%, and 20 wt% of EG was respectively measured to be 0.942 W/m K, 1.053 W/m K, 1.354 W/m K and 1.658 W/m K. Also, DSC analysis showed that the addition of EG decreased the degree of supercooling by 29.4°C. Zhong et al [17] prepared three kinds of porous composite phase change materials using three types of binary salts ($LiNO_3 - KCl, LiNO_3 - NaNO_3$ and $LiNO_3 - NaCl$) as the phase change materials and expanded graphite as the high thermal conductive additive. The thermal conductivity was significantly increased. It is analyzed that, after impregnation of the salt into the EG, the thermal conductivity of $LiNO_3 - KCl$ is intensified by 5.0 times; $LiNO_3 - NaNO_3$, 6.9 times; and $LiNO_3 - NaCl$, 4.9 times. Yuping et al. [18] developed a novel shape stabilized phase change material by impregnating hydrated salts into expanded graphite. He found out that the thermal conductivity of hydrated salts/EG was high as 3.615 W/mK (uncoated) and 3.646 W/mK (coated with paraffin wax). Heking et al. [19] prepared NaCl-$CaCl_2$/EG composite phase change materials at different fraction of EG. It is found that the thermal conductivity increased linearly with the content of EG and the density of the composite. At 20 wt% of EG and 2 g/cm^3, the thermal conductivity was 4.937 W/mK higher which 701.1 % higher than binary eutectic chloride. Huang et al. [20] prepared a $LiNO_3/KCl - EG$ composite phase change material. Increasing the content of EG in the composite from 10% to 30%, the thermal conductivity has been improved from 1.85 times to 6.65 times respectively. Jumbing et al. [21], prepared $NaNO_3$-KNO_3/EG with different mass rates of EG. The results showed that the addition of EG have give a great rise to thermal conductivity coefficient which has increased to 4.884 W/mK.

2.1.2. Carbon fiber

Recently, carbon materials have become one of the best fillers for enhancing the thermal conductivity, due to the fact that they possess high thermal conductivity and low density. There have been many studies on the preparation of phase change material composites using carbon fiber [22-25]. Zhao et al. [26] used graphite fiber to prepare Carbon bonded carbon fiber (CBCF) monoliths. The CBCF were filled with paraffin wax to for the PCM composite. The in-plane thermal conductivity of the PCM composite was significantly increased up to 57 times over the pure wax, while the out-of-plane thermal conductivity was also increased by 3.7 to 5.5 times. In addition, the improvements in thermal conductivity showed almost linear relationship with the volume fraction of carbon fibers in the PCM composites.Takahiro et al. [27] prepared a phase change material composite with a percolating network of Carbon Fiber. Two types of methods have been used: The conventional melting dispersion method and a novel hot press method. Erythritol was chosen as the phase change material and carbon fiber as the high thermal conductive filler. It is found that the Phase material composite prepared by the hot press method presents a high thermal conductivity; furthermore, It is found that the Phase material composite prepared by the hot press method presents a high thermal conductivity, furthermore, a percolating filler network can be easily formed in this case as it is shown in Fig.1. Frusteri et al. [28] investigated the influence of carbon fiber on the thermal conductivity enhancement of an organic PCM44. Different lengths of carbon fiber have been randomly distributed and the thermal conductivity has been measured. It was demonstrated that a linear relationship exists between the carbon fiber content and the thermal conductivity. The best results were obtained using a micro-fiber (length=0.2mm).

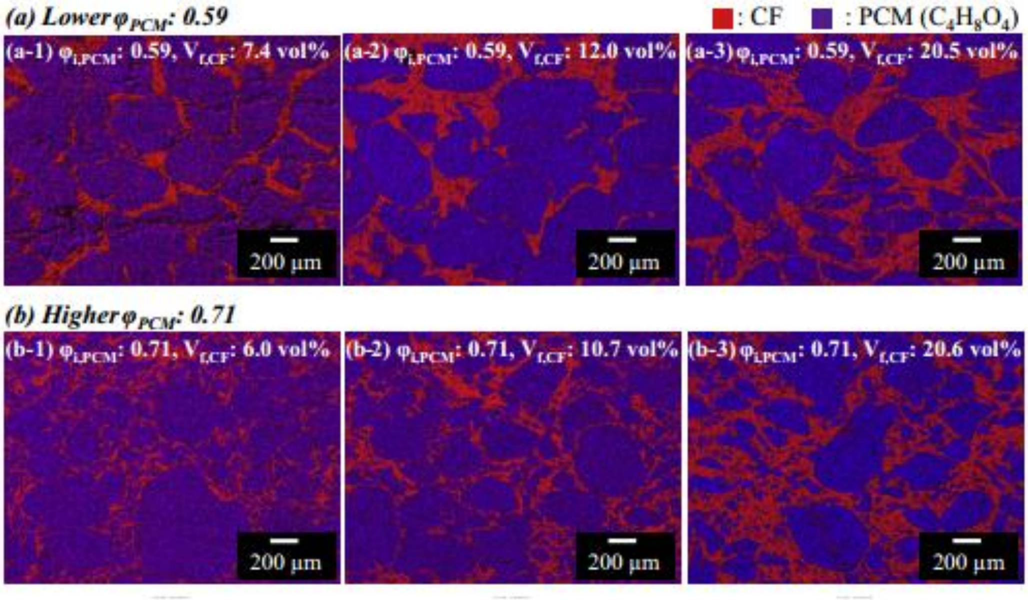


Figure 1: EDS mapping from the cross section of the PCCs: (a) a lower packing ratio of 0.59 and (b) a higher packing ratio of 0.71 [27]

2.1.3. Carbon nanotubes

Tingting et al. [29] reported the preparation of a new polyethylene glycol (PEG)/diatomite form-stable phase change composite (fs-PCC) with single-walled carbon nanotubes (SWCNs) as nano-additive. The obtained results showed that the thermal conductivity of the PCC has been increased from 0.24 W/mK in case of pure PEG to 0.87 W/mK with a small fraction off SWCNTS (2wt%). Zhang et al. [30] studied the effect of the introduction of CNTs as a additive for improving the thermal conductivity of paraffin-carbon nanotubes/expanded perlite form-stable composite phase change materials (PA-CNTs/EP FS-CPCMs). The vacuum impregnation method was used to prepare the composite with different mass fraction of CNT. The thermal conductivity of PA-CNTs/EP FSCPCMs5.27 (0.516Wm−1 K−1) was 4.82 times that of PA-CNTs/EP FS-CPCMs0. The thermal storage and release properties of PA-CNTs/EP FS-CPCMs were significantly improved as compared with those of PACNTs/EP FS-CPCMs0. Feng et al. [31] prepared a new composite where the MWCNTs was chosen as the high thermal conductivity enhancer, Na_2CO_3 was used as phase change material and MgO as a supporting material. With the increase of MWCNTS amount and temperature of use, the thermal conductivity has been significantly increased. Feng et al. [32] reported the preparation of Na_2CO_3/MgO composite phase change materials with added Multi walled carbon nanotubes (MWCNTs). Na_2CO_3 was used as phase change material and MgO as a supporting material. It is found that the thermal conductivity increased with an increase of the MWCNTS loading and an increase in the temperature of use.

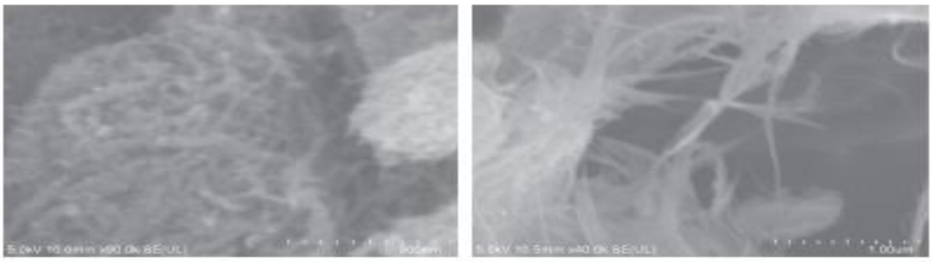
In order to improve the performance of salt phase change materials, Tao et al. [33] prepared carbonate salt/nanomaterial composite phase change material using four kinds of carbon nanometerials with different microstructure as Fig. 2 illustrates. The results show that nanomaterial with columnar structure such as single walled carbon nanotubes (SWCNT) are more efficient at enhancing the thermal conductivity of the PCM salt up to 56.98%.

2.1.4. Comparison of different types of carbon additives:

The comparison of the thermal conductivity enhancement using the different types of carbon additives are listed in Table 1. The following conclusions can be drawn:

- The thermal conductivity is significantly increased in case of high aspect ratio of carbon additive

- The addition of small amount of CNTs can contribute to the larger enhancement of thermal conductivity
- The EG and graphite powder are promising additives to enhance the thermal conductivity


(a) MWCNT (b) SWCNT

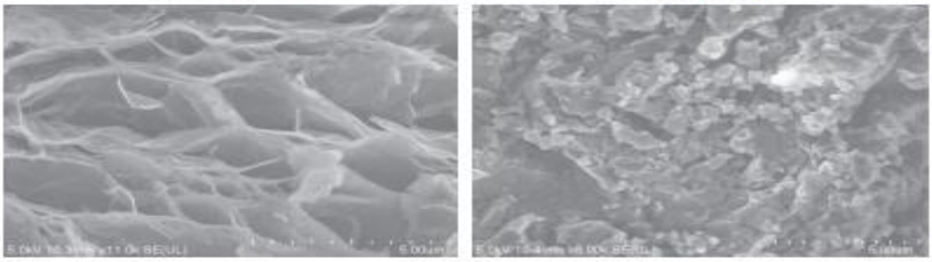

(c) Graphene (d) C_{60}

Figure 2: Carbon nanomaterial microstructure by SEM. [33]

Table 1: Comparison of the thermal conductivity enhancement with some types of carbon additives

Carbon additive	PCM	k_{PCM}(W/m.K)	Fraction	k_{PCC}(W/m.K)	Increase (%)
Expanded Graphite	Eutectic $LiNO_3$/ KCl [20]	1.749	30 wt%	11.63	665
	Ternary eutectic chloride [34]	1.174	5 wt%	2.084	178
	Form stable PCM [35]	0.43	20 wt%	4.59	1067
Carbon fiber	Erythritol [27]	0.733	25 vol%	≈30	4000
Grafted CNTs	Paraffin [36]	0.2312	4 wt%	0.7903	342
Short SWCNT	Water [37]	0.580	0.48 vol%	0.604	104
Long SWCNT	Water [37]	0.580	0.48 vol%	0.627	108
MWCNT	Water [37]	0.580	0.48 vol%	0.598	103
Graphite powder	Bakelite [38]	1.4	30 vol%	4.84	346
Graphene	Paraffin [39]	0.25	10 wt%	2.7	1080

Table 2: Comparison of the thermal conductivity enhancement with some types of metal additives

Metal	PCM	k_{PCM}(W/m.K)	Fraction	k_{PCC}(W/m.K)	Increase (%)
Copper foam[40]	Paraffin	0.354	88.89 %	16.01	4500
Nickel foam [40]	Paraffin	0.354	90.61 %	2.33	658
β-AIN powder [41]	Polyethylene glycol	0.2985	30 wt%	0.7661	257%
Al [42]	Paraffin	0.25	9 wt%	5	2000%

2.2. Thermal conductivity enhancement of phase change materials using metal foam

Recently, more interest was given to the development of high thermal conductive PCMs using metal foams. High thermal conductivity, porosity and strong mixing capability are the main properties of metal foams which make it as one of the most promising high thermal conducting additives. Table 2 lists some of the experimental results.

Xiao et al [43] prepared paraffin/metal foam composite PCM where copper and nickel were the metallic foam matrix. The results show that the thermal conductivity of the paraffin increased three times more than the pure paraffin. Thapa et al [44] used the copper foam as the high thermal conductive filler and icosane wax as the PCM for low thermal energy storage application. The thermal conductivity of the composite was 3.78 W/mK which is higher than that of the pure icosane wax.

Bauer and Wirtz [45] developed a plate like structural thermal energy storage composite consisting of a central core of aluminum foam packed with PCM. The effective thermal conductivity of the composite is significantly increased. Jiang et al. [46] prepared two kinds of shape-stabilized PCMs composites using Al foam impregnated with paraffin or stearic acid and the results show that the PCMs were well impregnated into the Al foam because with no crack appearing on the surface of the PCMs.

Li et al [47] prepared a salt hydrate/copper foam composite phase change material using Sodium acetate trihydrate (SAT) as thermal energy storage phase change material. The thermal conductivity of copper foam/SAT composite PCM is about 11 times higher than that of pure SAT. Moreover, the charging and discharging times can be reduced significantly. Additionally, the charging time is only 40% of that of the pure SAT. Huang et al [48] fabricated Myristyl alcohol (MA)/metal foam composite phase change materials (CPCMs) by vacuum melting infiltration of nickel foam and copper foam; MA acts as the PCM. Effects of pore size and thermal properties were analyzed and compared. There was reported inverse relation between pore diameters. The thermal conductivity of the MA/nickel foam and MA/copper foam was increased by 1.80 and 7.51 times respectively as compared to pure MA.

Metal salts are another form of metallic additives with high thermal conductivity and reliable stability. Fauzi et al. [49] found that adding 10% sodium laurate to Myristic acid (MA)/palmitic acid (PA) eutectic mixture leads to the increase of thermal conductivity from 0.225 to 0.235 W/m. K. Wang et al. [41] prepared a high thermal conductivity form-stable PCM by blending polyethylene glycol, silica gel and β-Aluminum nitride (β-AIN) powder. The thermal conductivity of the composite PCMs increased from 0.2985 W/m.K (pure polyethylene glycol) to 0.7661W/m.K when the amount of β-AIN was 30 wt%.

2.3. Comparison of different ways to enhance the thermal conductivity of Phase change materials

Among the methods mentioned in our review we can positively opine that using the carbon additives could be a good choice to enhance the thermal conductivity due to their low density, thermal stability and diversity. As for metal additives, they have a higher thermal conductivity enhancement, but their use is limited due to their instability during thermal cycling. However, the selection of those enhancement methods is based on the price, experimental conditions and reliability.

Conclusions and outlook

A review of experimental work to enhance the thermal conductivity of phase change materials was discussed. The actual review presents different approaches to improve the thermal conductivity, using carbon additives such as: expanded graphite, carbon fiber, graphene, etc or metal additives like copper foam, nickel foam, etc. in both categories, the thermal conductivity of phase change material composites has been enhanced. However, the selection of any additive is based on the stability of both components (PCM and additive) in the composite, the economic costs and environmental impact etc.

As a matter fact, we believe that the wettability of PCM on the additive surface is also an important parameter that should be taken by consideration before preparing PCM/additive composite. In literature, there are few studies on the wettability of high thermal conductivity enhancer (carbon additives or metals foams) by PCM. The preparation of new material with good wetting could be a novel research idea and approach.

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