

# A review on thermophysical properties of nanoparticle dispersed phase change materials



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## ABSTRACT

A review of current experimental studies on variations in thermophysical properties of phase change material (PCM) due to dispersion of nanoparticles is presented in this article. Dispersed carbon nanotubes/fiber and different metal/metal oxide nano particles in paraffin and fatty acids might be a solution to improve latent heat thermal storage performance. Thermophysical properties such as thermal conductivity, latent heat, viscosity and super cooling of phase change materials (PCM) could be changed for different physical properties of dispersed nanoparticle such as size, shape, concentration and surface properties. Among the nano particles, comparatively carbon nanotubes and carbon nano fiber have shown better performance in enhancing the thermal properties of PCM for their unique properties. The present review will focus on the studies that describe how the surface, chemical and physical properties of nanoparticle could affect the thermal properties of PCM with the help of available explanations in the literature.

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## Nomenclature

$D$	diameter (nm)
$\Delta H$	phase change enthalpy (J/kg)
$K$	thermal conductivity (W/m K)
$L$	length ( $\mu\text{m}$ )
$L$	latent heat (J/kg)
$M$	mass of PCM (g)
$T$	temperature ( $^{\circ}\text{C}$ )

## Greek Symbols

$A$	thermal diffusivity ( $\text{m}^2/\text{s}$ )
$B$	coefficient of volumetric expansion (1/K)
$P$	density ( $\text{kg}/\text{m}^3$ )

## Subscript

$F$	fluid
$L$	liquid
$M$	melting
$S$	solid

## Abbreviations

Ag NWs	Ag nanowires
CNF	carbon nanofiber

CNT	carbon nanotubes
CTAB	cetyltrimethylammonium bromide
LHTES	latent heat thermal energy storage
MWCNT	multi walled carbon nanotubes
NePCM	nanoparticle-enhanced phase change materials
PA	Palmitic acid
PANI	Polyaniline
PCM	phase change material
PEG	polyethylene glycol
PVA	polyvinylalcohol
PW	paraffin wax
SDS	sodium dodecyl sulfate
SW	Soy Wax
SWCNTs	single walled carbon nanotubes
TD	1-Tetradecanol
TEA	Triethylamine
TEMED	Tetramethylethylenediamine
TES	Thermal Energy Storage

## 1. Introduction

The needs of energy for a wide variety of applications in different forms and stages are time dependent with the limitation of available energy sources. This indicates that the available sources of energy and applications should be complemented strongly with an efficient energy storage system. On the subject of renewable energy technologies, thermal energy storage system is an expanding field of innovation. In recent years, the Thermal Energy Storage (TES) technologies have been grabbed the attention of researchers for its exceptional behavior, storing energy for usage in a later period, which would lead to a reduction in the overall energy demand. Among the various TES methods, LHTS has been investigated in last two decades, LHTS system's using PCMs were the most favorable for their high-energy storage density with small temperature variations [1]. In spite of these great advantages, most PCM's have a limitation of their own i.e., very low thermal conductivity [2]. To reduce the thermal energy charging/discharging time of TES system and temperature difference, enhancing the thermal conductivity of PCM is one of the ways to improve the effectiveness of the PCM-based TES systems. As a result, from the previous findings, to increase the performance of TES, PCM has been the major research priority topic recently [3]. Many researches have been conducted on this topic introducing high conductive metal fins and fibers in various forms such as fins, honeycomb, wool, and brush, to enhance the thermal conductivity of PCM [4]. However, the metal fillers/fins/fibers increase the weight and cost of the storage systems. In addition, determining the proper configurations of these fixed enhancers and their interactions with conduction or convection heat transfer involved in solid-liquid phase poses challenges. On the other hand, rapid pioneer advancement in the nanotechnology field, an innovative concept of using ultrafine nano sized particles which usually possess a nominal diameter of the order of 10–50 nm, have become commercially available in various metals and metal oxides. These highly conductive nanoparticles have been used to develop advanced heat transfer fluids called nano fluids with considerably enhanced thermal conductivity compared to the base liquids [5]. Accordingly, utilization of fabricated nano particles opens a great number of opportunities for new technological innovations

in materials synthesis, discovering functionality-tested NEPCM (Nano particle enhanced phase change materials). Introducing nano particles in PCM, the thermo physical properties i.e., thermal conductivity, latent heat, viscosity, super cooling, etc. of the base PCM could be changed intensively. Recently Khodadadi et al. [6] and Ramm Dheep and Sreekumar [7] presents a review article showing the suitability of nano particles in enhancing the thermal conductivity of phase change materials for thermal energy storage.

In literature, various works have been accompanied to investigate the thermo physical properties of PCM with the dispersion of nanoparticles in which different studies focus on different properties of NePCM. In this context, an extensive literature review has been performed to demonstrate the effects on thermo physical properties of PCM due to dispersion of different nano particles. Furthermore, nonmoving high conductive fixed inserts and metal foam based insert that is not in nano scale is not included in the study.

## 2. Nano particle enhanced PCMs

Most of the research works in literature were conducted on improvement of thermal properties of PCMs such as paraffin's and fatty acids. Paraffin draws a great attraction to researchers for its desirable characteristics i.e., good heat storage density, melting or solidification compatibly with little or no sub cooling, non-reactiveness with most common chemical reagents and low cost [8]. Fatty acids shows the similar properties as paraffin [9]. However, the main drawback of these PCM's is their low thermal conductivity [10]. Dispersing high conductive nano particles could be a solution to enhance the thermal conductivity of these PCM's. Few research works presented in Table 1 are focused to investigate the thermal properties of these PCM's with different nano particles.

## 3. Effects on thermophysical properties due to nano particle dispersion in PCMs

### 3.1. Effects on thermal conductivity

The rate of energy stored and released are highly dependent on the thermal conductivity of the PCMs at both solid and liquid state.

**Table 1**  
Summary of published experimental studies related to NePCM considering the base PCM, and nano structured enhancers.

Author	PCM used		Dispersed nano materials		
	Materials	Property	Materials	Property	Size
Elgafy and Lafdi [11]	Paraffin wax	$T_m$ : ~67 °C, $m$ : 20 g, $\alpha$ : 0.0015 m <sup>2</sup> /s	CNF	$\rho < 2260$ kg/m <sup>3</sup>	$D$ : 100 nm, $l$ : 20 $\mu$ m
Zeng et al. [12]	1-Tetradecanol (C <sub>14</sub> H <sub>30</sub> O)	$L$ : ~234.2 J/g	Ag	N/A	500 nm and multi-shaped
Shaikh et al. [13]	Paraffin wax (shell wax 100)	$L$ : 156,300 J/kg	SWCNT, MWCNT, CNF	N/A	SWCNT: 1 nm  MWCNT: 10 nm CNF: 100 nm
Wang et al. [14]	Palmitic acid (PA), 98% pure	$T_m$ 62.5 °C, $k \sim 0.22$ W/m K, $L_s \sim 208$ J/g	MWCNTs	N/A	$D$ : 30 nm, $l$ : 50 $\mu$ m, Specific surface area 60 m <sup>2</sup> /g
Zeng et al. [15]	1-Tetradecanol (TD) as PCM and PCM containing Polyaniline (PANI) as supporting material	$T_m \sim 35$ °C, $\Delta H$ : 221.25 J/g, $\Delta H$ : 119.14 J/g, (TD with PANI), $k \sim 0.33$ W/m K	MWCNTs	$k \sim 3000$ W/m K	$D$ : 10–30 nm, $l$ : 5–15 $\mu$ m
Zeng et al. [16]	Palmitic acid (PA)	$T_m \sim 59.48$ °C, $T_f \sim 58.78$ °C, $\Delta H$ (melt): 200.3 J g <sup>-1</sup> , $\Delta H$ (freeze): -201.9 J g <sup>-1</sup> , $k \sim 0.318$ W/m K, surfactants CTAB, SDBS	MWCNTs	$k \sim 3000$ W/m K	$D$ : 10–30 nm, $l$ : 5–15 $\mu$ m (Long) $l$ : 1–2 $\mu$ m (Short)
Liu et al. [17]	Saturated BaCl <sub>2</sub> aqueous solution	$T_f \sim 58.78$ °C, pH: 8	TiO <sub>2</sub>	N/A	20 nm
Wu et al. [18]	Double distilled water	$P$ : 0.6008 W/m K, Sodium dodecylbenzenesulfonate (referred as SDBS) was used as surfactants	Al <sub>2</sub> O <sub>3</sub>	N/A	Spherical-shape, 20 nm
Wang et al. [19]	Paraffin wax	$k \sim 0.24$ W/m K, $T_m$ : 52–54 °C, $L_s$ : 165.3 kJ/kg	MWCNT treated by ball milling for 720 min	N/A	$D$ : 30 nm, $l$ : 50 $\mu$ m, Specific surface area 60 m <sup>2</sup> /g
Ho and Gao [20]	Paraffin (n-octadecane)	$T_m$ : 26.5 °C $T_f$ : 25.1 °C, $L$ : 243.1 kJ/kg	Al <sub>2</sub> O <sub>3</sub>	N/A	159.6 and 196.0 nm for 5 and 10 wt%
Wu et al. [21]	Paraffin	$T_m$ : 58–60 °C $L \sim 205$ kJ/kg (melting) 202 kJ/kg (freezing) purity 99.9% surfactants: gum	Cu, Al, and C/Cu nano powders	N/A	25 nm
Zeng et al. [22]	1-Tetradecanol	$k \sim 0.32$ W/m K, $L_s$ : 220 J/g	Ag nano wires	N/A	N/A
Wang et al. [23]	Paraffin wax (PW)	$T_m$ : 325 ~ 327 K, $L_s$ : 142.2 J/g	Al <sub>2</sub> O <sub>3</sub>	$\rho$ : 8954 g/cm <sup>3</sup>	20 nm
Wang et al. [24]	Palmitic acid (PA) 98%	$T_m$ : 62.5–64 °C, $k \sim 0.223$ W/m K (Solid) and 0.154 W/m K (Liquid)	MWCNT treated by acid oxidation method, mechanochemical reaction method, ball milling method, and the method of grafting following acid oxidation	N/A	$D$ : 30 nm, $l$ : 50 $\mu$ m, specific surface area 60 m <sup>2</sup> /g
Wang et al. [25]	Paraffin wax (PW) 99.99% pure	$T_m$ : 58 ~ 60 °C, $L$ : 200.9 kJ/kg at 60.2 °C	Cu nanoparticle 99.99% pure	N/A	$D$ : 25 nm, Specific surface area: 30–50 m <sup>2</sup> /g
Cui et al. [26]	Paraffin and soy wax	$T_m$ : 52–54 °C K: 0.324 W/m K (soy wax), 0.320 W/m K (Paraffin wax)	CNF, CNT	$k \sim 4000$ W/m K (CNT) and ~1950 W/m K (CNF)	CNF: $D$ : 200 nm  CNT: $D$ : 30 nm, $l$ : 50 $\mu$ m, SSA: 60 m <sup>2</sup> /g and 95% pure
Wu et al. [27]	Paraffin	$T_m$ : 58–60 °C	Cu nano particle average particle size of 25 nm, Hitenol BC-10 was used as surfactants	N/A	25 nm
Zhang et al. [28]	Organic liquid PCM n-hexadecane(C <sub>16</sub> H <sub>34</sub> )	Liquid phase, surfactants: SDS, CTAB, PVA, PEG, TEMED, TEA, glacial acetic acid, SA, Tween-80, Tiron X-100, 1-decanol	MWCNT	N/A	Outer diameter 10–20 nm, length 0.5–2 $\mu$ m
Fan and Khodadadi [29]	Cyclohexane based PCM	$\rho_L$ : 779 kg/m <sup>3</sup> , $\rho_s$ : 856 kg/m <sup>3</sup> $C_{pL}$ : 1763 J/kg K, $C_{pS}$ : 1800 J/kg K	CuO	$\rho$ : 6310 kg/m <sup>3</sup> (L)  $C_p$ : 540 J/kg K (S)	Diameter: 5–15 nm
Jesumathy et al. [30]	Paraffin wax	$T_m$ : 6.5 °C, $\kappa$ : 0.24 W/m K (at 30 °C)	CuO	N/A	Mean size 40 nm
Zhang et al. [31]	Polyethylene glycol (PEG) acting as PCM	N/A	GnPs	$T_m$ : 50.9 °C, $H_m$ : 178.3 kJ/kg, $T_f$ : 35.7 °C, $H_f$ : 160.6 kJ/kg	Diameter: 35 $\mu$ m, thickness: 80 nm
Kalaiselvam et al. [32]	60% n tetradecane PCM, 40% n hexadecane PCM	N/A	Al, Al <sub>2</sub> O <sub>3</sub>	N/A	N/A
Harikrishnan and Kalaiselvam	Oleic acid as PCM	Latent heat of fusion 140.2 kJ/kg, Specific heat: 2.043 kJ/kg K, density:	CuO	N/A	1–80 nm

(continued on next page)

Table 1 (continued)

Author	PCM used		Dispersed nano materials		
	Materials	Property	Materials	Property	Size
[33] Kumaresan et al. [34]	Paraffin	887 kg/m <sup>3</sup> $T_m$ : 18–23 °C, solidification range: 22–19 °C, $k$ : 0.2 W/m K, Heat storage capacity: 134 kJ/kg	MWCNT	N/A	$D$ : 30–50 nm, $l$ : 10–20 $\mu$ m, Specific surface area
Meng et al. [35]	Mixture of Capric acid (CA), Lauric acid (LA) and Palmitic acid (PA)	Mass ratio of LA:CA:PA = 3:5:2	MWCNT treated by nitric acid.	N/A	60 m <sup>2</sup> /g $D$ : 8–15 nm, $l$ : 50 $\mu$ m, Specific surface area
Fan and Khodadadi. [36]	Cyclohexane	$C_{pf}$ : 1762.8 J/kg K, $C_{pm}$ : 1800 J/kg K, $k_f$ : 0.127 W/m K, $k_m$ : 0.136 W/m K, $L$ : 325.57 kJ/kg, $T_f$ : 6.5 °C	CuO	N/A	60 m <sup>2</sup> /g N/A
Li et al. [37]	Stearic acid	$L$ : 200.2 kJ/kg, $k$ : 0.26 W/m K	MWCNT, Graphene, Graphite	$k \sim 3000$ W/m °C (MWCNT) and 4840–5300 W/m K (Graphene)	N/A
Yavari et al. [38]	1-Octadecanol	$L$ : 250 kJ/kg, $T_m$ : 66 °C, density 0.812 g/cm <sup>3</sup> , $k$ : 0.38 W/m K	Graphene	4840–5300 W/m K	NA
Warzoha et al. [39]	Paraffin	$T_m$ : 329.15 K., density: 880 kg/m <sup>3</sup> , $k$ : 0.2 W/m K, $L$ : 271.6 kJ/kg	Herringbone style graphite nano fibers	$k$ : 25 W/m K, $\rho$ : 2.1 g/cm <sup>3</sup> (L)	Nanofiber length: 1–20 $\mu$ m, Nanofiber diameter: 2–100 nm
Yu et al. [40]	Paraffin wax	$T_m$ : 58–60 °C	S-MWCNTs C-S-MWCNTs L-MWCNTs CNFs GNPs	N/A	Length: 0.5–2 $\mu$ m dia: 8–15 nm Length: 0.5–2 $\mu$ m dia: 8–15 nm Length: 5–15 $\mu$ m dia < 10 nm Len: 10–30 $\mu$ m $d$ : 150–200 nm Dia: 5–10 $\mu$ m Thick: 4–20 nm
Mehrli et al. [41]	Paraffin	$T_m$ : 60 °C	Graphene oxide (GO) sheet	4–100 W/m K	N/A
Karunamurthy et al. [42]	Paraffin (N-docosane)	$T_m$ : 52–55 °C	CuO	N/A	N/A
Teng and Yu [43]	Paraffin	1.94 kJ/kg K (solid) and 2.4 kJ/kg K (liquid) Density 785 kg/m <sup>3</sup> , $k$ : 0.214 W/m K $T_m$ : 55–65 °C	Alumina (Al <sub>2</sub> O <sub>3</sub> ), Titania (TiO <sub>2</sub> ), Silica (SiO <sub>2</sub> ), and Zinc oxide (ZnO)	N/A	20–30 nm
Teng and Yu [44]	Paraffin	$T_m$ : 60.46 °C	MWCNTs	N/A	$d = 20$ –30 nm
Hu et al. [45]	Sodiumacetatettrihydrate (SAT)	$T_m$ : 58 °C	Aluminum nitride (AlN)	N/A	50 nm
Parameshwaran et al. [46]	Organic ester (SNOE)	$L$ : 89.69 kJ/kg (freezing) 94.41 kJ/kg (melting) $K$ : .257 W/m K $L$ : 207.6 J/kg	Silver nanoparticles (AgNP)	N/A	15–18 nm
Ji et al. [47]	Palmitic acid (PA)		MWNTs	N/A	Diameter 20–40 nm and length 10–15 $\mu$ m
Zhong et al. [48]	Octadecanoic acid (OA)	Density: 840 kg/m <sup>3</sup> Specific heat: 2.300 J/g K	Graphene aerogel (GA)	Density: 227 kg/m <sup>3</sup> Specific heat: 1.121 J/g K	N/A
Kim and Drzal [49]	Paraffin (n docosane)	$k$ : 0.184 W/m K $T_m$ : 42–44 °C	GnP	$k$ : 2.183 W/m K N/A	Thickness < 10 nm and average diameter 15 $\mu$ m
Mei et al. [50]	Capric acid (CA)	$k$ : 0.2–0.3 W/m K $T_m$ : 29.62 °C $L$ : 139.77 J/g $k$ : 0.3650 W/m K	Halloysite nanotube (HNT) and graphite	N/A	N/A
Li [51]	Paraffin		Nano-graphite (NG)	N/A	Diameter: 35 nm purity: 99.95%
Hu et al. [52] He et al. [53]	Pentaerythritol (PE) BaCl <sub>2</sub> aqueous solution	$L$ : 209.33 J/kg $L$ : 244.5 J/g $k$ : 0.53 W/m K at –5 °C $T_m$ : –8.16 °C $T_m$ : 56–58 °C $k$ : 0.2293 W/m K $T_m$ : 64.0–71.0 °C $L$ : 203 kJ/kg $k$ : 0.33/0.17 W/m K $T_m$ : 62.40 °C	Nano-AlN TiO <sub>2</sub>	N/A N/A	50 nm 20 nm
Yang et al. [54]	Paraffin		Nano-Si <sub>3</sub> N <sub>4</sub>	$k$ : 17.6 W/m K	N/A
Choi et al. [55]	Stearic acid		MWCNTs Graphene	N/A	MWCNTs: 25 nm Graphene: 7 nm
Mehrli et al. [56]	Palmitic acid (PA)	$L$ : 206.32 kJ/kg $k$ : 0.28 W/m K	Nitrogen-doped graphene (NDG)	N/A	N/A



Table 1 (continued)

Author	PCM used		Dispersed nano materials		
	Materials	Property	Materials	Property	Size
Motahar et al. [57]	n-Octadecane	$T_m$ : 25 °C	TiO <sub>2</sub>	N/A	30 ± 5 nm
Sahan and Paksoy [58]	Paraffin	$k$ : 0.48 W/m K $T_m$ : 46–48 °C	Nanomagnetite (Fe <sub>3</sub> O <sub>4</sub> )	N/A	N/A
Mehrali et al. [59]	Palmitic acid (PA)	$T_m$ : 60–65 °C  $L$ : 205.53 kJ/kg $k$ : 0.29 W/m K (solid) 0.21 W/m K (liquid)	Graphene nanoplatelets (GNPs)	Parallel to surface: 3000 W/m K Perpendicular to surface: 6 W/m K	Thickness (nm) Less than 2 nm

At the same time, different PCMs used in various TES systems have a great variation in operation temperature. In case of high conductive nano particle dispersed PCMs, the effect of thermal conductivity is an important factor to choose the appropriate PCM for that system. The performance of nanoparticle dispersed PCM in terms of thermal conductivity depends on mass concentration, surface and physical properties of nanoparticles that is dispersed.

### 3.1.1. Dispersing Carbon nanotubes and nanofiber

Nano sized metal particle exhibits particular thermal, magnetic, and optical properties. As the size decreases, the ratio of surface to volume increases. This increases the heat transfer ability of nanoparticles [60]. Dispersing nano particles could enhance the conductivity of PCMs as well as it could also affect the phase change properties [61]. Among the different nanoparticles, CNT and CNF as shown in Fig. 1 have some exclusive physical properties that made them a good candidate in the field of PCM based LHTS. With strong resistance to chemical attack and corrosion, CNF is compatible with most PCMs. The thermal conductivity of CNF is considerably high (~4000 W/m K) [26], and its density is less than 2260 kg/m<sup>3</sup> [11]. Carbon nano tube (CNT) is another nano material that has low weight and high thermal conductivity (~1950 W/m K) [26], which has shown tremendous potential for heat transfer applications.

The concentration of CNT/CNF loading, the size, as well as the surface property, intermolecular attraction and thermal resistance of CNT/CNF could be vital in thermal conductivity enhancement of PCMs.

**3.1.1.1. Aspect ratio, loading, size and Brownian motion of CNF and CNT.** Among the investigators, Elgafy and Lafdi [11], the group of researcher, experimentally increased the thermal conductivity of Paraffin wax (PW) by dispersing CNF at room temperature in various concentrations. They found that the specific heat of PW

decreased and thermal diffusivity increased for increasing the CNFs content. In other words, the nano composite has less ability to store heat; it has high ability to conduct heat. Similar effects were also described by Cui et al. [26]. They dispersed both CNF and CNT in PW and Soy Wax (SW) respectively to compare the thermal properties of the composites. They reported that the CNF/PCMs mixture had better thermal conductivity than CNT/PCMs at room temperature. From their experiment it was ensured that, the agglomeration, bundle and entangle behavior of CNT limit its efficiency in matrix [63]. Actually, individual CNT (~30 nm) is much smaller than individual CNF (~200 nm) [26]. In comparison with CNT, CNF could be uniformly dispersed in the matrix due to its large diameter and weaker Van der Waals force between the fibers which lead CNF to show better thermal conductivity of the composite than CNT.

Uniform dispersion of CNT/CNF is a key influence to enhance the thermal conductivity of the composite. In case of CNT, the small diameter in nanometer scale with high aspect ratio (>1000) [64], the surface area of CNT is very large which makes it more difficult to disperse uniformly in matrix. For an example, in a cube of 1.0 mm<sup>3</sup> the surface area might be  $2.8 \times 10^{-5}$  m<sup>2</sup> for 0.1 vol% of CNT in a composite [65] that increases with nanoparticle loading indicated in Fig. 2.

A large surface area will provide a large interface area between the CNT and matrix. This interface size of CNT/polymer composite could be about approximately 500 nm [66]. It was reported even a few nanometer thick interfacial region could pose a tremendous problem in uniform dispersion [65]. Commercially produced CNTs held together in bundles and agglomerates that result in diminished mechanical property of the composite as compared with the theoretical predictions related to individual CNTs.

A dependency of thermal resistance ( $R_{th}$ ) on dispersing time of Multi Wall Carbon Nanotube (MWCNT) in PCM was investigated

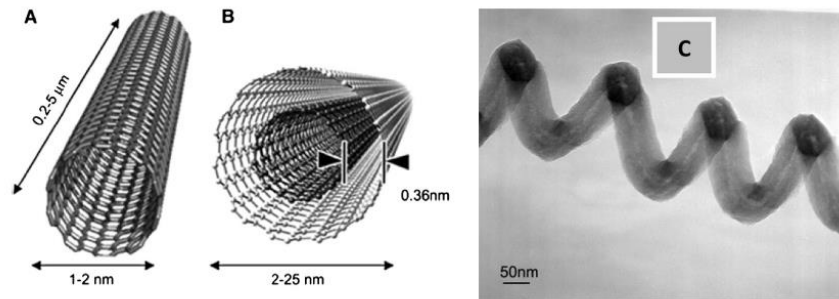


Fig. 1. (A, B): Conceptual drawing of SWCNTs and MWCNT, and (C) Carbon nano fiber [62].

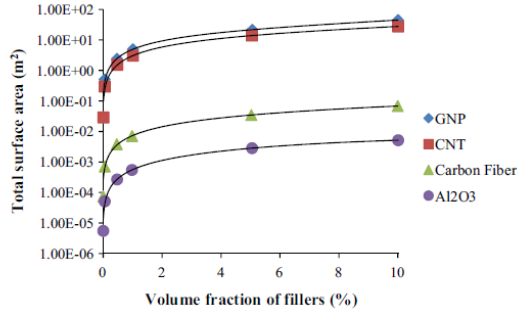


Fig. 2. Variation in surface area with different filler loading [65].

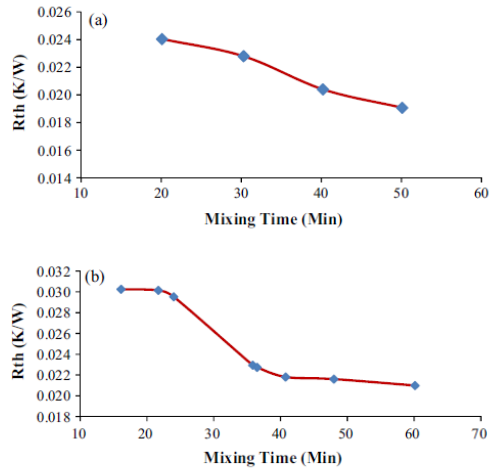


Fig. 3. (a)  $R_{th}$  Change with dispersing time for CNT-PEG1000, and (b)  $R_{th}$  Change with dispersing time for CNT-Tetradecanol [67].

by Xinhe et al. [67]. Thermal resistance is a system property and a measurement of the degree to which an object or material resists a heat flow. Significantly, they explored that the thermal resistance of PCM/CNT composite was decreased with increasing dispersion time causing the CNT to be well dispersed in PCM as shown in Fig. 3. This indicates that higher dispersing time could enhance the thermal conductivity of nano particle dispersed solutions.

As with dispersing time of nano particle in a solution, there is a great influence on CNT length in the thermal conductivity

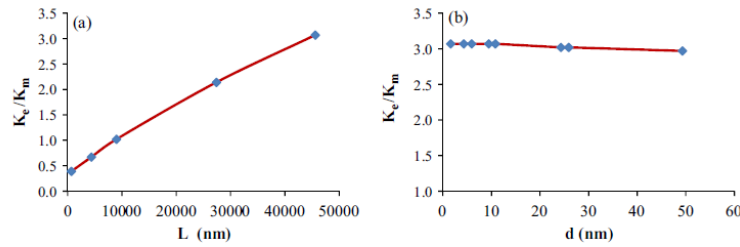


Fig. 4. Effect of the nano tube length (a) and diameter (b) on the thermal conductivity enhancement in carbon nano tube composites [68].

enhancement of composite which was predicted by Xue [68]. The model indicates that in a composite the effective thermal conductivity increases rapidly with the increasing nano tube length whereas the effective thermal conductivity changes very little even when the nano tube diameter changes by more than one order of magnitude (Fig. 4). Although this model well agreed with the experimental data of CNT/ethylene glycol suspensions, this prediction should be verified in PCMs also.

Wang et al. [19] inspected MWCNT in PW and found that for both PCM and NePCM; thermal properties change drastically near the melting point. This phenomenon is weakly depended on the temperature when the temperature is lower than solidification or higher than the melting point. They revealed that the thermal conductivities of PW and PW/MWCNT composite suddenly fell down when the PCM turned into a liquid state and suddenly increased near the melting point in solid state as shown in Fig. 5. The same was also reported by other researchers [14,24,34,69]. The reason is that when the temperature increases, there is a better accelerated molecular vibration in the matrix in case of orderly solid structure causing the thermal conductivity to increase suddenly. The sudden fall of thermal conductivity when PCM turns to a liquid state might be caused by the orderly stable microstructure in solid turning into a disorderly structure in liquid state [19]. Fascinatingly, the thermal conductivity of the PCM was enhanced with the increased mass fraction of MWCNT, which was nonlinear in behavior. This was due to (i) continual networking of the MWCNT (ii) a better stability of the CNT in PCM that lead to a higher inter-molecular attraction between them.

MWCNT was also studied in 1-Tetradecanol (TD) containing (Polyaniline) PANI, a new kind of synthesized form-stable organic PCM composite by Zeng et al. [15]. They found that the thermal conductivity of the composites improved significantly as the loadings of MWCNT increased. The formed stable PCM will not let MWCNT to precipitate even though it was heated to beyond the melting point which is the main advantage to possess a long-term stability of thermal conductivity [70]. Teng and Yu [44] also experimentally analyzed the performance of paraffin with three different concentration (1, 2, 3 wt%) MWCNT. The author described that MWCNT can reduce the melting onset temperature but increases the solidification onset temperature of pure paraffin. Mei et al. [50] prepared a novel form-stable nanocomposite phase change material (PCM) by absorbing capric acid (CA) into halloysite nanotube (HNT). The study reveals that nanocomposite PCM is cost-effective latent heat storage material due to its properties like high adsorption capacity of CA, high heat storage capacity, good thermal stability, low cost and simple preparation method. The HNTs have a high adsorption capacity of CA due to its nano tubular structure and large specific surface area and can absorb CA by the capillary and surface tension force [71–73].

An important issue that should be considered while enhancing the thermal conductivity of PCM with nano particles is that the

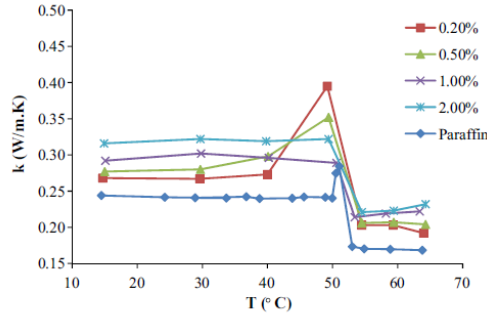


Fig. 5. Dependence of the thermal conductivity of pure PW and composites on the temperature [19].

thermal conductivity enhancement could differ from the value predicted by effective medium theory. The same was also reported by some researchers [19,24,69]. The reason of this discrepancy was explained by Huxtable et al. [74]. They showed that the thermal conductivity of the composite would be much lower than the value estimated when nanotubes form a percolating network in composite. The interface thermal conductance is the dominant that controls the thermal conductivity of the composite. They also found that the heat transportation of nano tube composite would be limited due to remarkably small interface thermal conductance, which is approximate  $12 \text{ MW m}^{-2} \text{ K}^{-1}$ , resulting in lower thermal conductivity than the value estimated from the intrinsic thermal conductivity of nanotubes. Hence, the predicted result of thermal conductivity enhancement may differ from the experimental result.

**3.1.1.2. Interfacial thermal resistance and surface modification of CNT, CNF.** CNT composites are perfect thermal interface materials due to percolation, a physical phenomenon in which highly conductive particles dispersed randomly in a matrix forms at least a single continuous chain connecting the opposite faces of the matrix. This percolation can act as a thermal passageway for the heat transfer. CNTs are long svelte having a hexagonal carbon arrangement in wall side and they are often capped at each end [75]. The seamless hexagonal ring arrangements without any dangling bonds, the CNT walls are normally non-reactive and have exceptionally small interface thermal conductivity. The mechanochemical reaction or chemical modifications to the CNTs surface is a possible approach to manage the interfacial interaction. The chemical fictionalization could significantly reduce the tube-matrix thermal boundary resistance as well as the intrinsic tube conductivity [76]. Therefore, pretreatment of CNT surface might play a significant role to enhance the thermal conductivity of the composite. In this concept, a big influence in the thermal conductivity enhancement in Palmitic acid (PA) with MWCNT was investigated by pretreatment of MWCNT surface with acid oxidation, mechanochemical reaction, ball milling, and grafting with hydroxyl groups and carboxylic groups [14,16,24].

The thermal resistance of the surface of CNTs could dominate the thermal conductivity enhancement of the composite while they are in a small fraction. In CNT composites, a very vital factor for their thermal transport property is the nano tube matrix interface thermal resistance, which is known as Kapitza resistance ( $R_K$ ) [68]. The ranges of Kapitza resistance between nano particles and different matrix could be in value between  $0.77 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$  and  $20 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$  [77]. In addition, the Kapitza resistance across a CNT and matrix was found about  $8.3 \times 10^{-8} \text{ K m}^2 \text{ W}^{-1}$

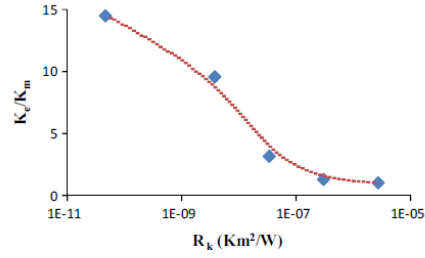


Fig. 6. Effects of the interface thermal resistance on the thermal conductivity enhancement in carbon nano tube composite [68].

[74]. Theoretical research showed that the interface thermal resistance attributed the weak atomic bonding at the particle matrix interface of nano composite [78]. Xue [68] presented a model for the effective thermal conductivity for carbon nano tube composites by incorporating the interface thermal resistance with an average polarization theory and found that the effective thermal conductivity decreased rapidly with increasing interface thermal resistance as indicated in Fig. 6. Hence, in order to increase the thermal conductivity in CNT composite, the Kapitza resistance should be minimized as much as possible. It was found that, if the carbon nano tube is chemically treated, the thermal conductivity enhancement of CNT composite can be changed [75]. Chemical bonding plays an important role to reduce the problem of the interface resistance [76].

A stronger chemical bond could be introduced to the surface of CNT by acid and alkali treatment while dispersing in Palmitic acid (PA) as PCM [24]. When it is treated, the CNT covalently attaches to PA matrix molecules with the  $\text{sp}^3$  hybridized atoms on its surface that is produced from the oxidation of  $\text{sp}^2$  hybridized atoms. In acid oxidation of CNT, a newly introduced  $-\text{COOH}$  groups appeared on its surface breaking the  $\text{C}-\text{C}$  covalent bond around the oxidized carbon atom as shown in Fig. 7. These introduces vacancies into the surface of the CNT. The vacancies led a sharp reduction in thermal conductivity of CNTs [80]. While in "mechanochemical reaction with hydroxyl groups", there are  $-\text{OH}$  groups between the tube and the matrix molecules. These  $-\text{OH}$  groups do not break the  $\text{C}-\text{C}$  covalent bond in the MWCNT intending to increase the thermal conductivity. Therefore, the hydroxyl group MWCNT treated by mechanochemical reaction has the highest thermal conductivity [24]. As a comparison, CNT treated with a mixture of concentrated nitric and sulfuric in PA [69] showed poor result than potassium hydroxide and the pristine CNTs in mechano-chemical reaction with ball milling. Refs. [14,24] indicated in Fig. 8. In the same time, the functionalization of on MWCNT with carboxylic groups has significant effects on enhancing the thermal conductivity of liquid paraffin based suspension as stated by Yu et al. [40]. Enhancement

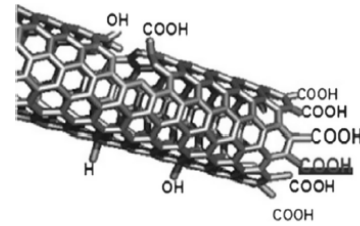


Fig. 7. Schematic representation of the attack to the MWCNT during the oxidation process [79].



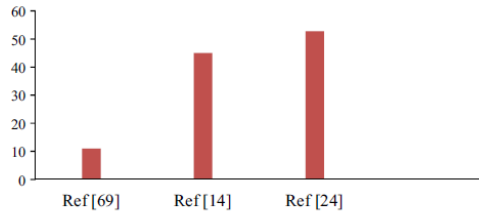


Fig. 8. Comparison of thermal conductivity enhancement by Wang et al. [14,24,69] at 55 °C with 1 wt% MWCNT in PA with different chemical mechanism.

in thermal conductivity and studies on thermo-physical properties of Palmitic acid (PA)/MWCNT composite was also experimented by Ji et al. [47]. MWCNT dispersed in PA was functionalized by oxidation (O-MWCNTs) and also by adsorption of pyrogallol (f-MWCNTs). They described that, Pyrogallol was adsorbed on to the MWCNTs due to the  $\pi$ - $\pi$  interactions between the benzene rings of pyrogallol and the graphitic surface of the nanotubes [81]. In the study, the introduced hydroxyl groups from the pyrogallol molecules have been confirmed by the FTIR spectra. The f-MWCNTs contain more oxygen than the O-MWCNTs, indicating that the pyrogallol molecules were adsorbed on the O-MWCNTs. As a result of the adsorption of pyrogallol, f-MWCNTs have a better dispersibility than O-MWCNTs in the PA solution and increased the thermal conductivity. Similarly, Mei et al. [50] prepared a novel form-stable nanocomposite phase change material (PCM) by absorbing capric acid (CA) into halloysite nanotube (HNT) and stated that, the abundant hydroxyl groups existing in inner surface of HNT can form hydrogen bond with carboxyl group of CA, which is helpful to absorb CA [82] and increase the thermal conductivity of the composite.

Elgafy and Lafdi [11] investigated the thermal behavior of pure PW with the surface treated nanoparticles at solidification process. They concluded that the CNFs surface characteristic could have a great influence on the thermal conductivity enhancement. As such, 4% pristine CNFs (treated surface) nano composite has a higher cooling rate than that of 4% untreated surface nano composite. Due to the surface treatment of CNF, the specific area and the surface energy was changed which increased the heat transfer rate as depicted in Fig. 9. In this perspective, heat transfer phenomena at nano scale might be surface dependent.

Recently Meng et al. [35] prepared Fatty acids/CNTs as composite shape-stabilized PCMs with a combination of three fatty acids [Palmitic acid (PA), Capric acid (CA) and Lauric acid (LA)]. In their study, MWCNT was used not only as a thermal conductivity enhancer but also as a supporting matrix for the inorganic PCMs. The CNT was mixed with concentrated nitric acid. Interestingly, they found the morphologies of the pristine CNTs and the treated CNTs were quite different as indicated in Fig. 10. They described that there exist some particles adherence to the surface of the pristine CNTs leading to the enlargement of the CNTs size. This indicates the multi-porous structure of pristine CNT has absorbed some impurities that lead to the phenomenon of agglomeration. Nevertheless, when CNT was treated and dispersed, its size became smaller which indicated the reduced impurity content. The oxidation of the strong concentrated nitric acid not only made the CNT shorter but also efficiently removed the impurities that were absorbed in CNTs. Furthermore, due to multi-porous structure and better ability of physical absorption in PCM, CNTs could be used as proper supporting materials for shape stabilization of PCM. The good absorption properties and porous structure of the CNT make the fatty acids tightly attached to the CNTs channel and reduce the drip of internal fatty acids that ensures the stability of fatty acids. In addition, due to higher thermal conductivity of CNT, the internal fatty acids can show higher thermal response. As a result, the

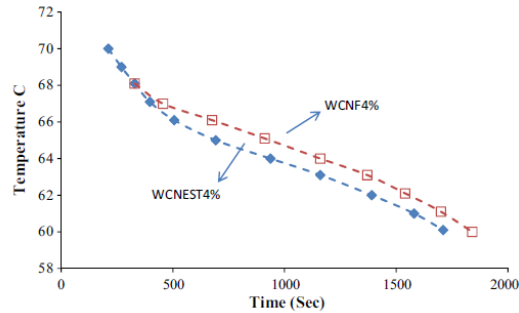


Fig. 9. Cooling rate for nano composite with surface treated and untreated CNFs [11].

thermal conductivity of the composite could be increased up to  $0.67 \text{ W m}^{-1} \text{ K}^{-1}$  [35].

### 3.1.2. Dispersing graphite and graphene

Nano composite materials made of stearic acid and different carbon additives (MWCNT, graphene and graphite) was investigated by Li et al. [37]. They observed that the Graphite based nano composite has 12 times higher thermal conductivity than that of pure stearic acid indicated Fig. 11. Their experiment showed that by adding carbon additives, the conduction heat transfer of the nano composite increased. But it also weakened the natural convection ability in liquid state. Another experiment of nano structured phase change composite (graphene/1-octadecanol) was conducted by Yavari et al. [38]. It was found that the thermal conductivity of graphene composite increased about 140% than that of pure 1-octadecanol without incurring a large reduction in phase change enthalpy. Uniform dispersion of graphene flakes facilitated the heat transfer and allowed the phonon to travel efficiently through the graphene fillers and between the flakes.

Recently Warzoha et al. [39] investigated herringbone style graphite nano fibers (HGNTF) in organic paraffin. They investigated the solid and liquid phase thermal boundary resistances (TBRs) between the nanoparticles and the surrounding PCM and/or between contacting nanoparticles. They found that, the TBR at the HGNTF-PCM interface is nearly double the TBR across the HGNTF-HGNTF interface in both solid and liquid phases. Thermal conductivity of the HGNTF/PCM nano composites increases exponentially in the PCM's solid phase as the nanoparticles begin to percolate. However, the PCM's liquid phase thermal conductivity does not increase significantly until the nanoparticles reach a critically dense state within the PCM, which is beyond the percolation threshold. Mehrali et al. [41] investigated a new form-stable composite phase change materials (PCMs) prepared by vacuum impregnation of paraffin within graphene oxide (GO) sheets. The thermal conductivity of the composite PCM was highly improved from 0.305 to 0.985 (W/m K).

Zhong et al. [48] has reported on the thermal behavior of octadecanoic acid (OA) PCM consisting of graphene aerogel (GA). Here GA acts as supporting material in which OA was impregnated with the help of capillary forces. The thermal conductivity of GA/OA was about  $2.635 \text{ W/m K}$  with a GA of 20 vol%, which was about 14 times larger than that of OA ( $0.184 \text{ W/m K}$ ). The composite PCM presents a high heat storage capacity of  $181.8 \text{ kJ/kg}$ , which was slightly decreased compared to the OA ( $186.1 \text{ kJ/kg}$ ). Similar phenomenon was described by Li [51] who prepared paraffin based composite PCM by incorporating nano graphite. The thermal physical properties of paraffin wax with 1, 2, 3, 5 and 7 wt% of



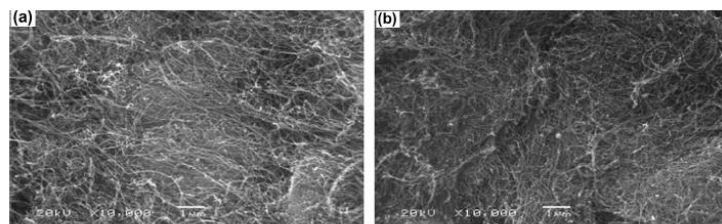


Fig. 10. SEM images of CNTs (a) untreated CNTs, and (b) treated CNTs [35].

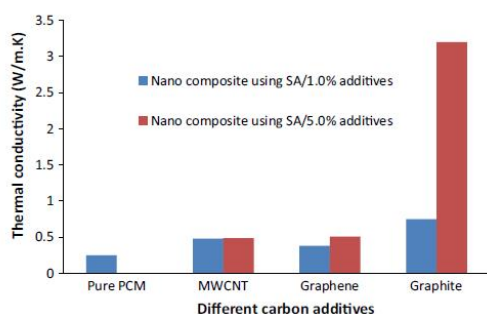


Fig. 11. Thermal conductivity of stearic acid with different carbon nano additives [37].

exfoliated graphite nanoplatelets (xGnP) was experimentally studied by Kim and Drzal [49]. The thermal conductivity of paraffin/xGnP composite increased with xGnP loading percentage. Interestingly it was also found that the latent heat of paraffin/xGnP composite PCMs did not decrease as loading xGnP contents to paraffin.

### 3.1.3. Dispersing metal nano particles

Beside CNT and CNF, different metal nano particles such as Ag, Ag Nano wires (AgNWs) and Cu were used to enhance the thermal conductivity of different PCMs. Zeng et al [22] dispersed AgNWs in 1-Tetradecanol to examine the thermal conductivity of the composite. It was reported that the thermal conductivity of Ag NWs/TD composite PCMs was even higher than CNTs/TD composite PCMs [15,16] as Ag NWs had a high aspect ratio, high interface thermal conductivity and stronger ability to mix with PCM.

An experimental comparison in cooling/heating rate with different metal nano particle in paraffin was conducted by Wu et al. [21]. The finding was, Cu/Paraffin composite had a better cooling/heating rate i.e., better thermal conductivity than Aluminum, Carbon/Copper nano particle dispersed paraffin composite in the same condition showed in Fig. 12. In case of dispersing Cu in paraffin, the value of thermal conductivity enhanced nonlinearly with the concentration of Cu nano particle [21,25,27].

Interestingly dispersing Cu nano particles in PCM, the concentration of the Cu nanoparticle was maximum 2 wt% in the literature. Actually, the higher the concentration of Cu in paraffin will cause easier agglomeration of Cu nano particles. The enhancement in thermal conductivity of the composite per wt% could be reduced due to this easy agglomeration of Cu nano particles. The performance of surface-functionalized crystalline silver nanoparticles dispersed Organic ester was investigated by Parameshwaran et al. [46] and found that the thermal conductivity of the PCM composite increased by 10–67% more compared to base PCM. In their study the size of silver nanoparticles (15–18 nm) behave extremely

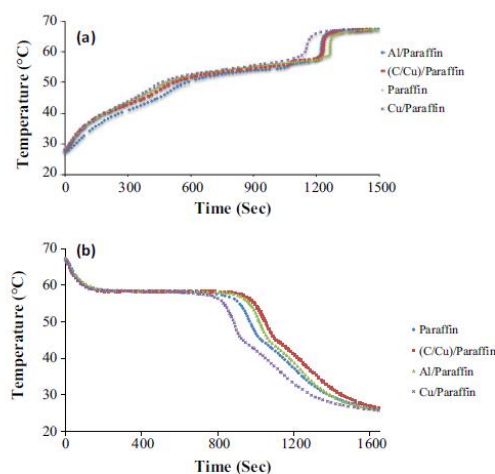


Fig. 12. (a) Heating curve of PCMs with different metal nano particles (b) Cooling curve of PCMs with different metal nano particles [21].

well in improving the thermal conductivity of the base PCM as the inter particle repulsive forces and the Brownian motion of AgNP was appreciable.

The effect of concentration or volume fraction, nano particle “size and shape” could play a significant role to enhance the thermal conductivity in composite [83]. As thermal conductivity increases with concentrations of nano particles, it may give a negative impact on other properties of PCM such as dispersion stability, latent heat, viscosity, and specific heat. Hence, it is cautioned that care should be taken when adding nano particles. In Table 2, it can be seen that in NePCM the dispersion range of nano particle varied in a range of 0.1–5 wt%. Hence, there should be more researches justifying the optimum concentration of nanoparticles that should be dispersed in PCM to enhance the thermal conductivity of the composite with minimizing the negative impacts in the other properties.

### 3.1.4. Dispersing metal oxide nano particles

Like metal nano particles, metal oxide nanoparticle such as CuO, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> were also examined as thermal conductivity enhancer of PCMs by several researchers. Ho and Gao [20] and Wang et al. [23] dispersed Al<sub>2</sub>O<sub>3</sub> (Alumina) in Paraffin (n-octadecane) and in PW respectively. As stated by Ho and Gao [20], nanoparticle-in-paraffin emulsion showed a relative increase of more than 17% of thermal conductivity in 60 °C temperature due to the enhanced Brownian motion of nano particles in the paraffin

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