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# Nanoparticle loading effect on the performance of the paraffin thermal energy storage material for building applications

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## Abstract

In this paper, the melting properties such as the thermal energy storage capacity and phase-change temperatures of paraffin are investigated. The paraffin is also modified as nano-PCM by dispersing small fractions (0.2% and 0.5% mass fractions) of highly conductive nanoparticles. The material used in this study has a melting temperature of 22 °C, making it suitable for domestic building applications. Additionally, the thermal conductivity and heating rate of the paraffin and paraffin with multiwall carbon nanotubes (MWCNTs) are studied experimentally. The results show that the paraffin with 0.2% and 0.5% mass fractions of MWCNTs could increase the thermal conductivity by 35% and 49% with respect to pure paraffin. The maximum thermal conductivity of 0.203 $W\ m^{-1}\ K^{-1}$ is observed for the paraffin with 0.5% mass fraction of MWCNTs. Additionally, the heat of fusion slightly reduced by increasing the mass fraction of MWCNTs. The result implies that the materials used in this study could be used for building applications.

**Keywords** Nano-PCM · Thermal energy storage · Heating · Cooling

## Abbreviations

| | |
|---|---|
| CNT | Carbon nanotube |
| MWCNT | Multi-wall carbon nanotube |
| TEM | Transmission electron microscopy |
| GA | Gum arabic |
| DSC | Differential scanning calorimetry |
| mass | Mass |
| V | Volt |
| A | Ampere |
| $a$ | Accuracy of equipments |
| $S$ | Repetition |

## Subscripts

| | |
|---|---|
| tot | Total |
| eqp | Equipment |
| rep | Repetition |

## Introduction

As the energy demand increases, sustainable forms of energy production and energy saving are becoming of vital priority. Increased energy usage from nonrenewable sources presents many environmental and human health concerns [1]. Renewable energies such as solar, wind, biogas and geothermal are considered remarkable alternatives for fossil fuels because of their sustainability. An excessive way to use the thermal energy of the sun is employing thermal energy storage (TES) due to the intermittent nature of solar energy [2]. The stored energy can be transformed to the desired form by the subsequent operations. The latent heat thermal energy storage system (LHTES) is a great method for energy storage due to its high storage density and temperature stability compared to the sensible heat storage [3]. These LHTES employ phase-change materials (PCMs). The PCMs are able to store and deliver a significant amount of energy during their melting and solidification processes. The LHTES is suitable for many solar applications such as solar domestic hot water systems [4], thermal management and heat recovery from various systems like photovoltaic and electrical systems [5, 6], free cooling and heating [7, 8] and thermal inertia and thermal protection [9].

The PCMs fall in three groups of organic, inorganic and eutectics [10]. Paraffin as an organic material is one of the

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most used PCMs due to its preferable properties like consistent melting properties, large latent heat, chemical stability, low cost, noncorrosiveness, small volume change during melting/solidification and nontoxicity [5, 11]. However, paraffin has a low thermal conductivity which slows the melting and solidification process and limits its applications.

Many studies investigated methods to increase the thermal conductivity of paraffin. One of the proved techniques to achieve enhanced thermal properties is the dispersion of high thermal conductivity nanomaterials [12] in the PCMs (nano-PCMs) [13, 14]. Sharma et al. [3] investigated the thermal properties and heat storage of palmitic acid–$TiO_2$ composite as a nano-PCM. They dispersed nano-$TiO_2$ particles into the base fluid in mass fractions of 0.5, 1, 3 and 5% and studied their thermo-physical properties. They showed that the melting temperature does not change significantly; however, there was a little variation in the latent heat of fusion. The thermal conductivity enhancement of 12.7, 20.6, 46.6 and 80% was observed for the nanoparticle mass fractions of 0.5, 1, 3 and 5%, respectively. Nourani et al. [15] performed an analysis of the thermal behavior of paraffin–nano-$Al_2O_3$ using sodium stearoyl lactylate as a dispersant. They prepared nano-PCM with mass fractions of 2.5, 5, 7.5 and 10% and conducted differential scanning calorimetry (DSC) tests. Their results showed that the thermal conductivity enhancement ratios for the sample containing 10% mass fraction of $Al_2O_3$ nanoparticles are 31% and 13% in the solid and liquid phases, respectively. They concluded that the proposed PCM can be used for various TEM applications. Wu et al. [11] studied the preparation and melting/solidification characteristics of Cu, Al and C/Cu nanoparticles dispersed in paraffin. They revealed that Cu had a better heat transfer rate compared to other studied nanoparticles. They also investigated the effects of various dispersants to achieve the highest stability of nano-PCM. The results showed that the latent heat of Cu/paraffin is reduced compared to pure paraffin; however, the melting/solidification temperature remains approximately constant. On the other hand, they revealed that by using 1 mass% Cu/paraffin, the heating and cooling times can be reduced by 30.3 and 28.2, respectively.

In this study, the effect of novel materials used generally in free cooling and heating applications is investigated. Free cooling is a viable and sustainable solution in order to reduce energy consumption in buildings. This consists of storing cold in summer nights using PCMs and delivering the cold to reduce the cooling loads. However, free heating is exploiting solar heat in winter nights [9, 16]. Osterman et al. [8] performed a parametric analysis on free cooling and heating of rooms. They used a TES system containing paraffin in 30 plates with a melting temperature of 22 °C and applied the initial and boundary conditions expected in reality. They showed the annual energy saving of 670 kWh in case of cooling/heating the ambient air and 300 kWh in case of indoor air. Dolado et al. [17] studied melting/solidification in real-scale PCM/air heat exchanger using a finite difference method. They studied heat transfer between air and a slab macro-encapsulated PCM. They found that shorter melting/solidification times can be achieved by increasing air mass flow rate, increasing the rugosity of the slab surface, reducing PCM slabs thickness and reducing the air gap between PCM slabs. Butala and Stritih [18] studied free cooling of buildings using PCMs experimentally. They employed paraffin with a melt temperature of 22 °C as a PCM. They studied various air temperatures and velocities and different heat fluxes. The results from their work show that for free cooling the PCM should be selected such that the melting temperature enables complete melting and solidification processes. Therefore, PCM selection depends on the local climate. Zeinelabdein et al. [19] reviewed studies on LHTES systems for free cooling applications.

The study of materials used in building applications is vital. The use of nanomaterials could result in higher thermal properties due to their high thermal conductivity. It is evident from the literature that the study of PCM with small fractions of multiwall carbon nanotubes (MWCNTs) is rare.

Here, the PCM with a melting temperature of 22 °C is mixed with various mass fractions of MWCNTs that can be used in free cooling applications. The properties of PCM and the nano-PCM are studied. Moreover, the cyclic analysis of heating and cooling were experimentally investigated.

## Experimental

### Materials preparation

Paraffin from Rubitherm GmbH is used as a PCM to prepare the nano-PCM. The properties of this paraffin given by the manufacturer are summarized in Table 1. The

**Table 1** Thermo-physical properties of paraffin provided by the manufacturer

| Thermal properties | |
|---|---|
| Melting range | 20–23/°C |
| Heat storage capacity | 190/kJ $kg^{-1}$ |
| Specific heat capacity | 2/kJ $kg^{-1}$ $K^{-1}$ |
| Density in solid state at 20/°C | 0.76/kg $L^{-1}$ |
| Density in liquid state at 50/°C | 0.7/kg $L^{-1}$ |
| Heat conductivity (both phases) | 0.2/W $m^{-1}$ $K^{-1}$ |
| Volume expansion | 12.5/% |
| Flash point | > 150/°C |

MWCNTs with an outer diameter of < 8 (nm), length of 30 (nm) and purity of 95% (from US Research Nanomaterials Inc.) are used in the study. The transmission electron microscopy (TEM) image of MWCNTs is shown in Fig. 1. Firstly, the MWCNTs are added to the PCM with proper concentration. In order to prevent agglomeration, the prepared suspension is put in an ultrasonic bath and stirred vigorously and simultaneously. This process is performed about half an hour using an ultrasonic bath (Elma, Elmasonic, S60H, Germany) with a frequency of 37 kHz, a power of 400 watts, under 100 percent amplitude and a temperature of 40 °C [20]. Each suspension of nanoparticle and the pure PCM needs a surfactant to become stable. Thus, gum arabic (GA) is added to the suspension as a surfactant. While the suspension is put in the ultrasonic bath and is stirred vigorously, the various nanoparticle mass fractions (i.e., 0.2 and 0.5 mass%) are added to PCM slowly. This process is last nearly 1.5 h. Finally, the nano-PCM is well prepared.

## Thermal properties measurement

The thermal conductivity of the samples is measured using the KD2 Pro thermal properties analyzer instrument. The thermal conductivity is measured in both phases to evaluate the effect of a small amount of highly conductive MWCNTs in the paraffin. The differential scanning calorimetry (DSC) technique is used to measure the thermal energy storage properties of paraffin and paraffin with 0.2 and 0.5% mass fractions of MWCNTs (nano-PCM). The Netzsch DSC 200 F3 Maia® instrument is used to perform the DSC analysis between the temperature range of 0 and 100 °C and at a heating rate of 10 °C $\text{min}^{-1}$.

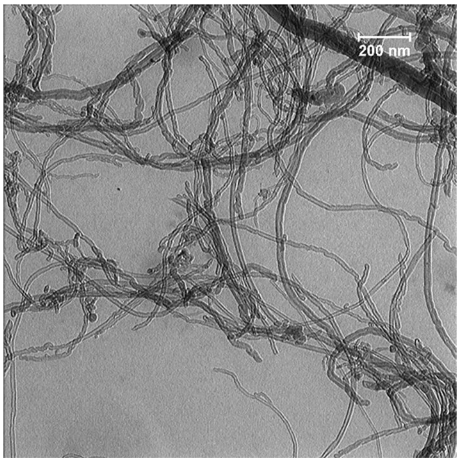


**Fig. 1** Transmission electron microscopy (TEM) image of MWCNTs

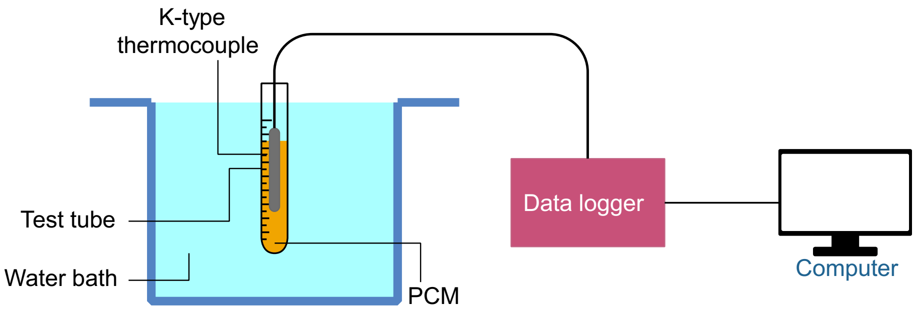
## Experimental

The addition of highly conductive MWCNTs could alter the heating and cooling of the PCM due to the change in thermo-physical properties. The experimental setup shown in Fig. 2 is used to study the heating and cooling periods of the PCM. A k-type thermocouple is fixed in the middle of a test tube containing PCM or nano-PCM. The test tube is placed in water baths. The water baths are baths with an arbitrary constant temperature. These baths have a controlling temperature system. In hot bath, the temperature is fixed at 17 C, and the cold bath has a temperature of 28 C. The bath temperature is shown by its indicator (TC4Y). The controlling system contains a TC4Y indicator, a SSR (solid state relay), a 500 W heater and a PT100 thermocouple. For example, in hot bath, if the temperature is less than the desired temperature (28 °C), the TC4Y indicator sends a signal to the SSR to control the electric current such that the temperature remains constant at 28 °C. A data logger (Testo 177-T4, UK) is used to record the temperature every 1 min.

## Uncertainty analysis

The accuracy of the experimental results can be evaluated by the uncertainty analysis. All experiments are repeated at least three times to ensure the repeatability of data. The k-type thermometers used in tests are calibrated using a standard thermocouple with an accuracy of ± 0.5 °C. The total uncertainty of parameter $\upsilon$ can be expressed as [21]:

**Fig. 2** A schematic of the experimental setup



$$\delta v_{\text{tot}} = \sqrt{\left(\delta v_{\text{eqp}}\right)^2 + \left(\delta v_{\text{rep}}\right)^2} \tag{1}$$

where $\delta v_{\text{eqp}}$ is the equipment uncertainty and $\delta v_{\text{rep}}$ is the repetition of uncertainty.

The equipment and repetition uncertainties are given as follows:

$$\delta v_{\text{eqp}} = \frac{a}{\sqrt{3}} \tag{2}$$

$$\delta v_{\text{rep}} = \frac{S}{\sqrt{n}} \tag{3}$$

where $a$ is accuracy of measurement equipment and $S$ is repetition.

The total uncertainty of various parameters in this study is reported in Table 2.

## Results and discussion

### Thermal energy storage capacity and phase-change temperatures

The measurement of the latent heat is very important in the applications of PCMs for thermal energy storage. The DSC test is performed to evaluate the effect of adding a small amount of MWCNTs on the melting enthalpy and melting temperature of the PCM. The latent heat of fusion is the area under the peaks of the DSC curve. The melting temperature range of the samples is measured by the onset and peak temperatures of the DSC curve. The melting onset temperature is obtained by drawing a tangent line at the point of maximum slope of the face section of the DSC curve.

The DSC curves of paraffin and nano-PCMs of 0.2 and 0.5 mass% are shown in Fig. 3. The first peak occurs due to the solid–solid phase transition and is not completely revealed in the figure due to the minimum temperature in the DSC test. However, the second peak represents the solid–liquid phase transition. It can be seen from Fig. 3 that the DSC curves of PCM and nano-PCMs have a similar shape. The area under the peak and therefore the heat of fusion are reduced by increasing the mass fractions of MWCNTs. This effect is also observed by Ho and Gao [22]. Furthermore, the melting onset temperature slightly decreases by using the MWCNTs which shows that adding highly conductive MWCNTs has a small effect of the temperature range. The melting range and the total latent heat of fusion of samples are summarized in Table 3.

The melt onset temperature reduces slightly with increasing the MWCNTs mass concentrations. Table 3 shows that the onset temperature reduces by 0.3 and 0.8 for the nano-PCM with 0.2% and 0.5% mass concentrations. That’s because adding these nanoparticles leads to increase in overall thermal conductivity of the nano-PCM (in comparison with PCM) and so sooner melting occurs. This shows that the addition of small mass fractions of nanoparticles moderately affects the melt temperature. Previous studies on nano-PCM also obtained similar results [15, 22]. As expected, the table reveals that the latent heat of fusion increases with increasing the MWCNTs mass

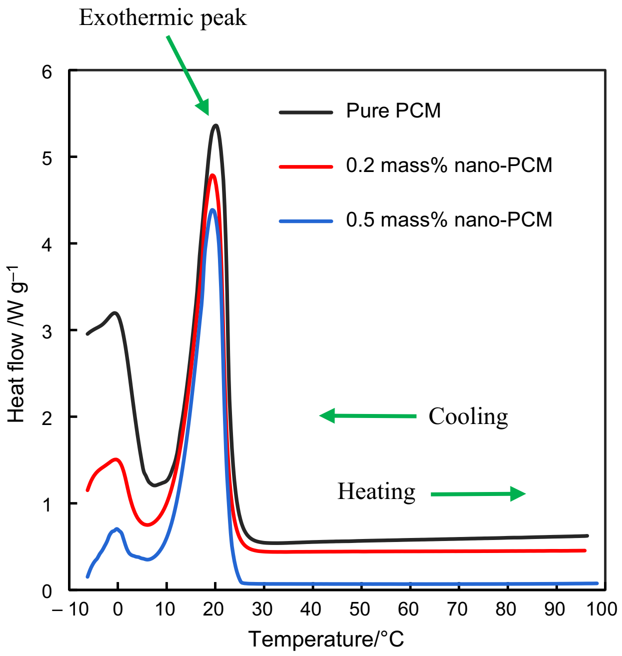


**Fig. 3** DSC curves of the PCM and nano-PCMs

**Table 2** Uncertainty of parameters in the experiments

| Equipment and model | Measurement section | Accuracy | Total uncertainty |
|---|---|---|---|
| Hg thermometer | Ambient temperature | ± 0.5/°C | ± 0.27/°C |
| k-type thermocouple | Temperature (chipset and heat sink) | ± 0.5/°C | ± 0.38/°C |
| Digital multimeter (VC9805, China) | Voltage | ± (0.5% + 1)/V | 0.05/V |
| Digital multimeter (VC9805, China) | Ampere | ± (0.8% + 1)/A | 0.02/A |

**Table 3** Melting range and latent heat of fusion of samples

| Samples | Melting range/°C | Latent heat of fusion/kJ kg$^{-1}$ |
|---|---|---|
| Pure paraffin | 17.8–24.7 | 210 |
| Paraffin with 0.2 mass% MWCNT | 17.3–24.5 | 184.3 |
| Paraffin with 0.5 mass% MWCNT | 17.2–24.1 | 180.1 |

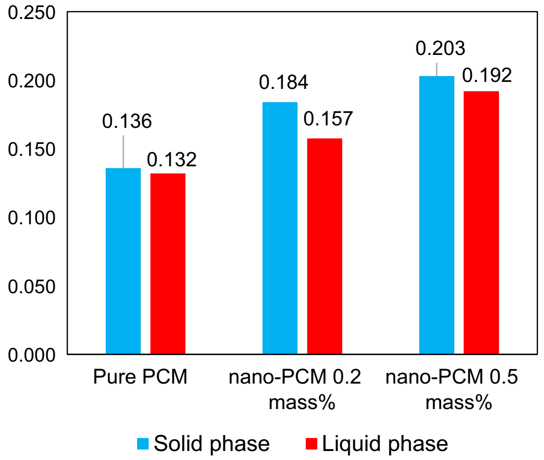


**Fig. 4** Thermal conductivity of various materials

concentrations. The heat of fusion reduces by 12.2% and 14.2% for the paraffin with 0.2 and 0.5 mass% MWCNTs.

## Thermal conductivity analysis

The measured values of the thermal conductivity for both phases of solid and liquid are presented in Fig. 4. The conductivity tests are performed at temperatures of 17 and 26 °C for solid and liquid phases, respectively. The use of MWCNTs has a significant influence on the thermal conductivity of the PCM as expected. It can be seen in Fig. 4 that the thermal conductivity increases as the mass concentration of MWCNTs increases. Moreover, the thermal conductivity of the solid phase is slightly larger than the liquid phase in all samples.

The results of thermal conductivity and thermal conductivity enhancement are summarized in Table 4. Paraffin with 0.5 mass% shows the highest thermal conductivities of 0.203 and 0.192 in solid and liquid phases, respectively. The enhancement in thermal conductivity is 49.26% in solid phase and 45.45% in the liquid phase for paraffin with 0.5 mass%. However, for paraffin with 0.2 mass%, the thermal conductivity increases by 35.29% and 18.94% in solid and liquid phases, respectively.

## Heating and cooling periods

Since the heating and cooling rates have a significant impact on the performance of a thermal storage system, the time–temperature response of various materials used in this study is obtained. The temperature range of 17–25 °C is used as a range usually encountered in the free cooling of building applications. Figure 5a, b shows the heating and cooling periods of PCM and nano-PCM with 0.2% and 0.25% mass fractions. These heating curves are obtained from the experimental setup to study the thermal performance of the materials. It can be seen in Fig. 5a that the time required to reach 25 °C from 17 °C is 53, 43.3 and 41 min for PCM and nano-PCM with 0.2% and 0.5% mass fractions, respectively. Hence, the MWCNTs nanoparticles increased the heating rates significantly. Also, the time to reach the steady-state temperature of about 28 °C is increased by 2.7 and 6.7 min for nano-PCMs with 0.2% and 0.5% mass fractions. The melting period is 39, 31.7 and 30.7 for the PCM and nano-PCM with 0.2% and 0.5% mass fractions of MWCNTs.

Figure 5b indicates that the rate of heat transfer is also increased in the cooling period. The solidification time, respectively, takes 41.5, 41 and 40.7 min for PCM and nano-PCM with 0.2% and 0.5% mass fractions of MWCNTs. The observed enhancement of the heat transfer rate is due to the increase in the thermal conductivity in both phases of nano-PCMs.

**Table 4** Thermal conductivity (W/m K) of paraffin and paraffin/MWCNT and the enhancement percentage

| Samples | Solid phase | Improvement in the solid phase/% | Liquid phase | Improvement in the liquid phase/% |
|---|---|---|---|---|
| Pure paraffin | 0.136 | – | 0.132 | – |
| Paraffin with 0.2 mass% MWCNT | 0.184 | 35.29 | 0.157 | 18.94 |
| Paraffin with 0.5 mass% MWCNT | 0.203 | 49.26 | 0.192 | 45.45 |

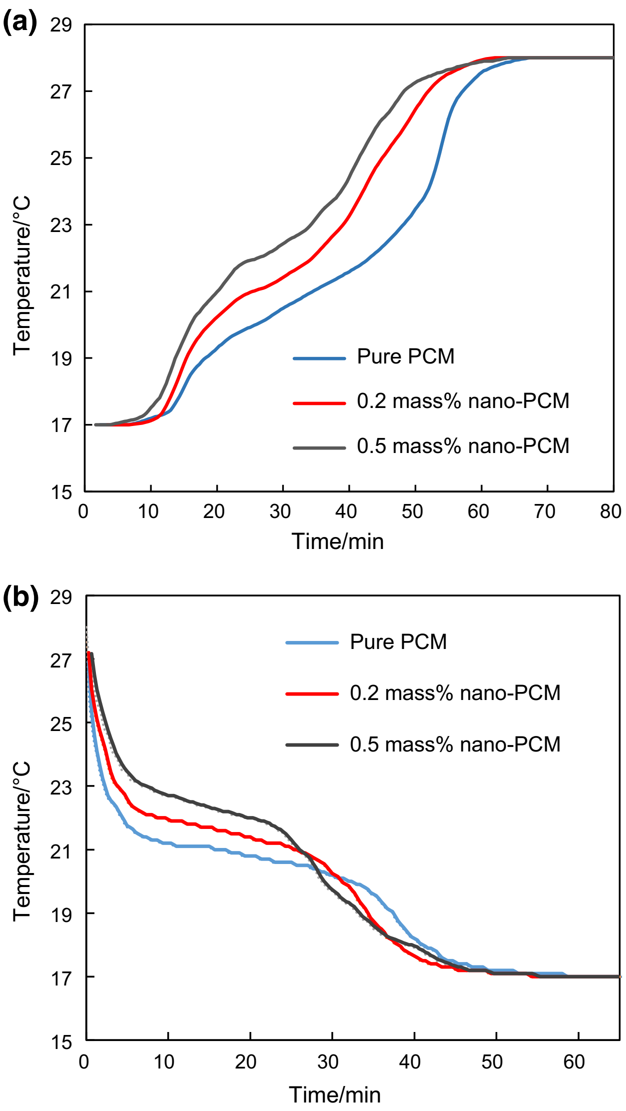


**Fig. 5** Temperature–time response of PCM and nano-PCM with 0.2 and 0.5 mass% of MWCNT obtained from the experimental setup: **a** heating period and **b** cooling period

## Conclusions

This study presents the experimental investigation of paraffin as a PCM and paraffin/MWCNT as a nano-PCM. These materials are used as thermal storage in building applications. The thermal properties such as melting temperature, latent heat of fusion and thermal conductivity are studied. The findings are summarized as follows:

The heat of fusion is decreased by adding small fractions of MWCNTs. The heat of fusion is 210 kJ kg$^{-1}$, 184.3 kJ kg$^{-1}$ and 180.1 kJ kg$^{-1}$ for the paraffin, paraffin 0.2% mass fraction and 0.5% mass fraction of MWCNTs.

The thermal conductivity of paraffin increases by adding highly conductive MWCNTs. The increase is more significant in the solid phase compared to the liquid phase. The paraffin with 0.2% and 0.5% mass fractions of MWCNTs increases the thermal conductivity by 35% and 49% compared to pure paraffin, respectively.

The heating rate of materials is studied using an experimental setup in the temperature range of 17–25 °C, and the time–temperature response of the system is obtained. The time required for PCM and nano-PCM with 0.2% and 0.5% mass fractions to reach 25 from 17 °C is 159, 130 and 123, respectively. The results show that the proposed materials can be used in building applications.

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