

CARBON NANOTUBES IMPROVE PCM'S HEAT TRANSPORT CHARACTERISTICS: DURING SOLIDIFICATION

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ABSTRACT

By distributing a tiny quantity of multi-walled carbon nanotubes (MWCNT) in petroleum ether, this study attempts to create a new type of NFPCM, which will improve heat transfer qualities and analyse the NFPCM's features as it solidifies. At 30C, MWCNT is dispersed in liquid paraffin with a volume concentration of 0.15, 0.3, 0.45 and 0.6 percent without the need for dispersing agents. The rheology measurement depicts Newtonian fluid behaviour in the shear range of 1–10 Pa. DSC (differential scanning calorimetric) data demonstrate that the NFPCM's freezing/melting temperature does not vary, although there is a minor noticeable shift in the heat generation values. It is necessary to test the heat capacity of different NFPCM (nanofluid phase change materials). The increase in thermal conductivity is proportional to the rise in MWCNT volume fraction and has only a minor temperature dependency. As a result, the NFPCM with such a volume concentration of 0.6 percent has significantly improved heat transmission and reduced solidification time by 33.64%. For several years, traditional phase change materials have been plagued by serious issues in heat transfer performance.

Keywords: Carbon nanotubes, phase change materials, energy storage technology.

Introduction

Many applications have time-dependent energy requirements, but the various sources are able to provide those demands in a number of ways. Energy-efficient storage systems must be used to match the source and use points dynamically. With time-based utility rates, thermal energy storage (TES) technology have gained a great deal of interest in recent years because of their ability to shift energy use to a later time period while also lowering total energy consumption. Latent heat thermal storage (LHTS) employing phase change materials (PCM) is the most promising and favoured form of TES because of its high storage density and little temperature variance from store to retrieval [9]. Paraffins, which have a high mass storage density and melt/solidify uniformly without any subcooling, are the industry's most often employed phase change materials. There are many more forms of phase change materials. As a bonus, they are resistant to water and chemical reactions. With their low cost and simplicity of recycling, they are ideal for TES. They can withstand temperatures of up to 500 degrees Celsius with little volume change and low vapour pressure. As the liquid-solid border advances farther from the heat transfer, the

developing molten/solidified layer's heat capacity also grows. This is a serious constraint, as the thermal conductivity of these materials is quite low. Energy charging and discharging rates are reduced, resulting in a fluctuation in surface heat transfer that is undesirable for a number of different applications. Researchers became concerned about the PCMs' poor performance and set out to find a way around it. Several research has been published in recent years on how to improve the PCMs' thermal conductivity. A variety of fins, a metal matrix, high conductivity particles dispersed in PCMs, and encapsulation of the core in many layers of shell materials are among the approaches described. All of the preceding procedures can improve the thermal conductivity, but the weight and volume of the storage system will rise as a result.

Researchers have tried a novel concept of mixing nanoparticles with the base material to improve the heat transport capabilities of the base materials due to quick pioneering advances in nanotechnology. Nanoparticles of fewer than 100 nm in size are suspended in a base substance of the same name. Carbon nanotubes (CNTs) and nanopowders (Al, Cu, SiC, CuO, etc.) are examples of nanoparticles (CNT). It was only after a breakthrough in

which only 0.3 percent of copper particles 10 nm in size increased ethylene glycol's thermal conductivity by 40 percent that other impressive work was announced, which utilised various nanoparticles to create nanofluids. Carbon nanotubes are distinct from other types of carbon because of their structure and size, which make them superior in many ways. The CNT's thermal conductivity has been widely discussed in scientific literature as a possible enhancer for thermal energy storage devices, which has garnered a lot of interest from researchers [6]. Because of its lighter weight and lower density, the CNT has shown to be an excellent replacement for traditional storage media [1]. The thermophysical characteristics, such as thermal conductivity, viscous, specific heat, and numerical modelling of nanofluids for thermal characterisation, have been the subject of several investigations. Thermal storage using NFPCM is a relatively new field compared to convection heat transfer, which is more commonly used for cooling purposes [7]. NFPCM may be prepared using a novel method that incorporates carbon nanotubes into liquid paraffin without the need for surfactants. NFPCM's thermal and heat transport properties are also studied throughout the solidification process through experiments [2].

Evaluation of heat transfer improvement

NFPCM thermal conductivity and structural strength have been the subject of several studies aimed at achieving thermal stability criteria in a wide range of industrial applications. The thermal conductivity and storage capacity of BaCl₂ with scattered TiO₂ nanoparticles were studied by Liu et al. There was a 15.65% increase in thermal conductivity, increasing linearly with nanoparticle volume fraction and temperature. Adding nanoparticles to PCMs improves heat transmission and acts as a nucleating agent, minimising supercooling in the suspensions. Nanofluids PCM's better thermal characteristics and quicker nucleation have been shown to shorten the latent heat storage end-time [3] significantly. Hitenol BC-10 was used as a surfactant in a study by Wu et al. to examine the melting and freezing properties of Cu/Paraffin nanofluids. Even though the reductions in latent heat were

minor, they accounted for 11.1 and 11.7 percent of the overall decreases in evaporative heat content. Small variations in latent energy and phase change temperatures were found after 100 refrigerating cycles with the addition of Cu nanoparticles. In a paraffin emulsion, Ho et al. evaluated the effective thermophysical parameters of alumina nanoparticles (Al₂O₃), including density, dynamic viscosity, latent heat of fusion, and thermal conductivity. As a result of the relative increase in dynamic viscosity, emulsifying alumina nanoparticles in paraffin was found to be particularly problematic, especially for natural convection-dominated thermal energy storage applications. It was discovered that nanoparticles' temperature and weight fraction do not depend linearly on each other for the increase in thermal conductivity. Moghadassi and colleagues studied MEG and paraffin fluids containing CuO nanoparticles to determine the influence of thermal conductivity on different particle concentrations, particle sizes, and base fluid types [8]. CuOparaffin nanofluids are claimed to have an even higher increase in thermal conductivity because of their high thermal conductivity and large interfacial shell thickness. However, the reduced viscosity of CuOMEG nanofluids led to an increase in heat conductivity. The thermal conductivity of PCMs was increased by around 20% with the dispersion of metal/metal nano particles in all of the above studies. Doping the PCM with carbon nanotubes/carbon nanofiber offers enormous promise for LHTE. According to a few research, the subject of CNT-enhanced PCM thermal performance is still in its infancy and offers a wide range of possibilities and problems. Thermal storage space of a paraffin/expanded graphite (EG) composite with a higher thermal stability has been explored by Sari et al. The extended graphite's porous nature made impregnation of liquid paraffin in EG exceedingly simple, even when there was no leakage from the EG's pores when melting. Thermal conductivity increased by 272.2 percent, and the density of the composites PCM was measured at 721 kg/m³, which was lower than the density of pure paraffin (758 kg/m³) at the acceptable EG mass fraction of 10 weight percent. A 32% decrease in melting time was noted, as well as

the fact that it may be used immediately without the need for further storage. An experimental and theoretical investigation has been conducted by Shaikh et al. regarding a change in the kinetic energy of shell wax, doped with SWCNTs, MWCNTs, and carbon nanofibers (CNF). Due to higher intermolecular attraction, the wax/SWCNT composite had a superior thermal conductivity, which resulted in a rise in latent heat. If the CNT/wax contact potential is larger than that between wax molecules, then the heat of fusion might be raised. Compared to actual measurements of latent heat, the analytical model's numerical predictions were spot on, and thus provided a solid foundation for subsequent research into the parametric investigation of various phase transition features with nanoparticle additions. According to Wang et al., CNT/CNF may be used as a heat transfer filler in LHTS.

NFPCM Preparation

PCM and carbon nanotubes employed in this study are described here.

- (1) NFPCM's PCM is paraffin, which has a melting temperature of 18–23C and a solidification temperature of 22–19C. Rubitherm Technologies in Germany provided the PCM for this project. According to the manufacturer, the thermo-physical parameters of paraffin RT 20 may be found in Table 1.

Property	Value
Thermal conductivity	0.2 W m ⁻¹ K ⁻¹
Melting range	18–23°C
Freezing range	22–19°C
Solid density (at 15°C)	0.88 kg l ⁻¹
Liquid density (at 25°C)	0.77 kg l ⁻¹
Flash point	154°C
Kinematic viscosity (at 50°C)	25.71 mm ² s ⁻¹
Heat storage capacity (15–30°C)	134 kJ kg ⁻¹

Table 1: RT 20's thermal and physical attributes

- (2) USA-based Cheap Tubes sells multiwall carbon nanotubes. MWCNT has an average diameter of 30–50 nm, a length of 10–20 μm, and a surface area of 60 m²/g. Entanglement is

visible in the carbon nanotubes' Transmission Electron Microscope (TEM) picture depicted in Figure 1. The nanotubes are ultrasonically sonicated for 90 minutes in dry conditions in order to separate them.

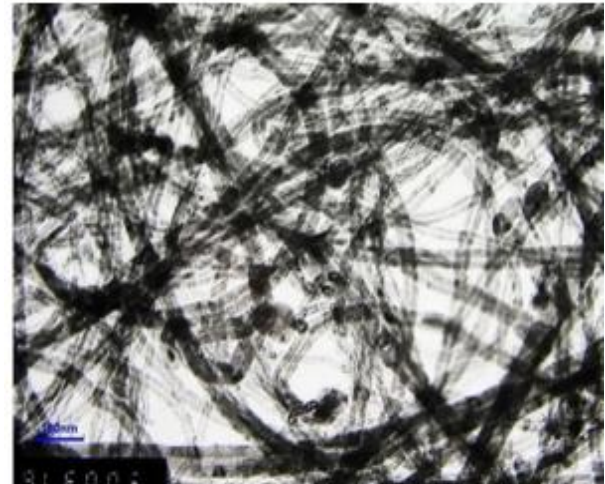


Figure 1: Transmission Electron Microscope image of MWCNT

The NFPCM is prepared via a new two-step procedure. For 60 minutes, a magnetic stirrer is used to disseminate the MWCNT in liquid paraffin. No dispersants or surfactants were utilised in the preparation of these samples, which had a volume fraction of 0.15, 0.3, 0.45, and 0.6 percent of MWCNT. For 30 minutes, the NFPCM were continuously sonicated in an ultrasonic bath at a specific temperature of 30C to guarantee that the specimens were kept above the melting of paraffin. A transmission electron microscope (H-7500) with an accelerated voltage of 5 kV is used to acquire the SEM image of the NFPCM. Dispersed CNT has a diameter ranging from 32 to 46 nm, as seen in Fig. 2.

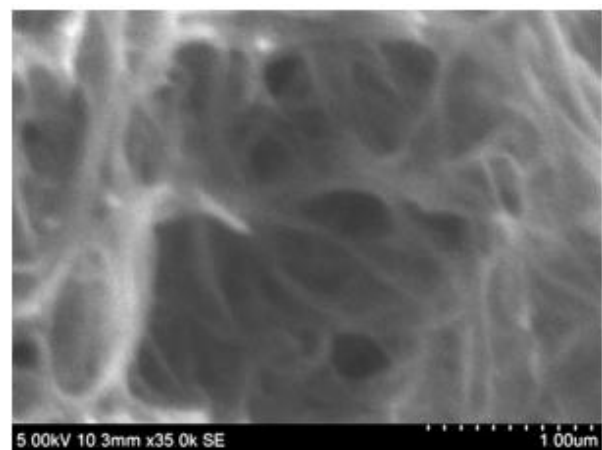


Figure 2: Scanning electron microscope image of NFPCM

Thermophysical qualities measurement

It is critical to consider how the heat conductivity of a PCM changes as a function of temperature during charging and discharging in thermal storage applications. To better understand the heat transfer properties during the phase transition process, estimating the temperature-dependent changes in thermal conductivity [5]. A KD2 Pro analyser and a cold storage circulator are used to test this. The KD2 Pro analyser uses the transient line heat source method to determine the thermal conductivity of the samples. Data display and storage are included inside the sensor probe, which is 60 millimetres long by 1.27 millimetres wide. Between 0.2 and 2 and 0.02 to 0.2 $\text{Wm}^{-1} \text{K}^{-1}$, the accuracy of this measurement range is 5 percent. During a single scan, the sensor performs 90 measurements. The water bath temperature is precisely controlled to within 0.03C utilising a refrigerated/heating circulator to keep the NFPCM at the desired temperature. NFPCM samples are preserved in a water bath while being measured. Temperature of 18, 20, 22, 25, 30 and 35C are used for the tests. Each temperature is measured many times to ensure that the findings are consistent.

An instrument called a Bolin CVO rheometer is used to test the viscosity at 30C with various CNT concentrations (0.15 to 0.45). Modelling is done using the shear stress range 0–10 Pa and the controlled shear rate model. A DSC calorimeter fitted with a cooling attachment is used in a nitrogen atmosphere to analyse the impact of the CNT inclusion in the PCM on the melting/freezing and energy storage behaviours of the NFPCM. Temperature ranges from 0°C to 30°C are used for the DSC measurements, with a scan rate of 1 and 3C/min. Testing conditions for all NFPCM samples are the same.

For solidification test, experimental setup

Heat transport experiments on the NFPCM's solidification are depicted schematically in Figure 3. Copper canisters with a diameter of 6.6 cm are placed in a tank filled with ethylene glycol and water, where they are maintained in an upright position.

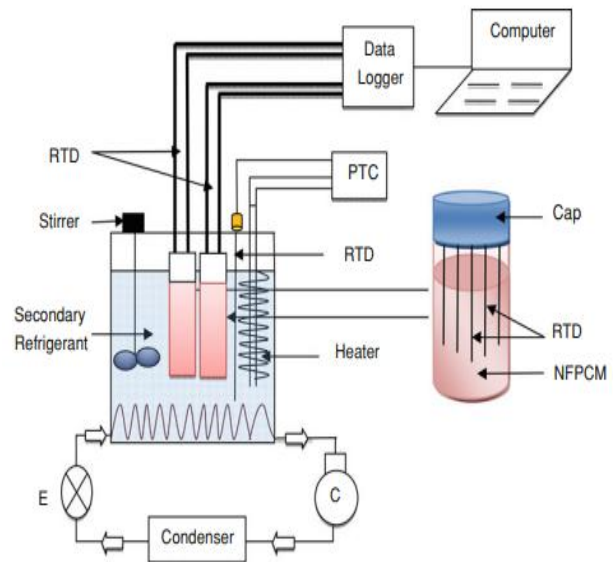


Figure3: For solidification test, experimental setup

It is possible to examine both NFPCM samples side by side in a single experiment by carefully pouring the liquid samples into the container to avoid any holes. A 2,000 W heating coil and a 5-kW chiller unit replicate the needed bath temperature for the tank. PTC controllers are used to keep the bath temperature constant, as the chiller unit operates at a constant load. An RTD sensor detects the heat of the bath, and the output of the heating coil is adjusted accordingly. From above, a mechanical stirrer powered by an electrical motor of 9 W (speed 1,280 rpm) keeps the bath in the tank at a constant temperature. Each NFPCM container has five PT-100 RTDs arranged horizontally, as illustrated in the image inset. To prevent the impacts of the top and bottom of the container, the RTDs are spaced uniformly apart by 1.1 centimetres. Agilent 34970A is used to store the measurements from the RTDs during the studies, with a precision of 0.004 percent. During the solidification process, the NFPCM's heat transmission properties are studied. The temperature of the NFPCM in the cylindrical containers is kept constant at 25C for all trials, with just a 0.5C difference in temperature between the NFPCM at the wall and the centre. The PTC keeps the heat from the surrounding bath below the PCM solidification temperature at a consistent value. For the duration of the experiment, the surrounding bath maintains a nearly constant temperature due to the presence of the stirrer. The studies are carried out in a

13C bath with each NFPCM. The temperature of the NFPCM at five separate sites is continually measured and monitored as the solidification progresses until the entire NFPCM area reaches a thermodynamic balance with the environment. To confirm the reproducibility of the measurements, a number of tests are carried out.

Temperature conductivity

The PCM's thermal conductivity is a critical property for LHTS applications since the conduction resistance it provides is the major means of heat transmission during solidification and melting. As a result, improving thermal conductivity is an important factor in thermal storage system design, as is obtaining precise temperature measurements of thermal conductivity [4].

The thermal conductivity of several NFPCMs as a function of temperature. For all NFPCMs, the solid state's thermal conductivity is significantly greater than that of its liquid counterpart. Solidification begins to increase thermal conductivity and it reaches its peak towards the end of crystallisation. The greater thermal conductivity of the NFPCMs near the phase transition temperature is a desired aspect to make it favourable for any thermal storage applications due to the PCM's intrinsic weak thermal conductivity.

Carbon nanotubes can increase thermal conductivity by varying the PCM volume fraction by a percent volume fraction of the overall PCM volume fraction for a temperature change. It is defined as $(k_{nf}-k_o/k_o)/k_o$, representing the thermal conductivity of NFPCM and pure paraffin. As can be observed from the graph, the NFPCM with 0.6 vol. percent improves thermal conductivity by 40–45 percent in both the liquid and solid stages. The inclusion of carbon nanotubes in the PCM increases the intermolecular interaction between the MWCNTs, which in turn improves the thermal conductivity of the material. These two effects work together to improve the material's thermal conductivity. Although the heat conductivity of NFPCM increases from 45 to 25 percent during the transition from solid to liquid state, it subsequently rises roughly to 45 percent when the NFPCM has completely melted and is in its liquid condition. Even

when carbon nanotubes are present, the PCM's molecular instability during the phase transitional phase diminishes the enhancing impact. When the volume percentage of MWCNT drops, a similar effect is shown for other sample of NFPCM with decreasing orders of improvement in thermal conductivity.

NFPCM's viscosity

Measurement of the viscous forces of different NFPCM at 30C with regard to shear stress. The figure indicates that viscosity decreases significantly as the shear stress increases to 1 Pa for all NFPCM. This clearly demonstrates the shear thinning characteristic. Non-Newtonian behaviour at the low shear stress range is seen at the higher (0.6 percent) volume fraction of MWCNT. Zhang et al. found similar findings with microencapsulated PCM. When the shear stress is increased from 1 to 10 Pa, the viscous of NFPCM remains almost constant, thus indicating Newtonian behaviour of NFPCM. The average Newtonian viscosity of NFPCM and pure PCM, respectively, is represented by \ln_f and l_o , in the definition of relative viscosity as (\ln_f/l_o) . Viscosity increases abnormally as the volume percentage of MWCNT increases, and this will reduce the thermal impacts of the NFPCM.

The NFPCM underwent a DSC analysis

Data on PCM's DSC melting/freezing curves at 1 and 3 c/min scan speeds. When scanning at a rate of 3 C/min, the PCM's peak starting to melt and freezing temperatures are shown to be 21.30 C and 16.63 C, respectively, with a supercooling degree of 4.67 C. In comparison, at a rate of 1 C/min, the supercooling degree drops to 2.19 C with peak melting and freezing temperatures of 20.58 C and 18.39 C, respectively. As the scanning rate lowers from 3C/min to 1C/min, the commencement of solidification is delayed. Variable NFPCM heating/cooling DSC curves. There is a correlation between the MWCNT concentration and the NFPCMs' freezing temperature. The freezing point rises from 19.46 to 20.05C at 1C/min and from 19.75 to 20.07C at 3C/min when MWCNT at 0.15 vol. percent is added. In the NFPCMs up to 0.45 vol. percent MWCNT, the same behaviour of a rise in freezing temperature is found at both

scanning rates, clearly indicating the nucleating effect of carbon nanotubes in NFPCMs. Adding 0.15 vol. percent MWCNT reduces NFPCM supercooling to a maximum of 37.44 and 35.97 percent at the scanning speeds of 1 and 3C/min, respectively. All NFPCMs with different MWCNT concentrations show a reduction in the degree of supercooling. There is an ideal concentration range of MWCNT where the degree of supercooling is minimised, while the impact is greater at lower concentrations of MWCNT.

Temperature disparity of the NFPCM through the solidification procedure

At three evenly separated radial sites in a container, the transient temperature fluctuation of the pure PCM and NFPCM (0.6 vol. percent CNT) is illustrated. PCM and NFPCM temperatures decline quicker at site 1 without any modification in the gradient at phase transition temperatures. This phenomenon has been seen as a result of the solidified PCM's insignificant conductive resistance and the container's extremely low convective resistance. Therefore, it is extremely easy to disperse the heat generated by the freezing of PCM at that area. There is, however, a dramatic shift in temperature gradient near the phase transition range in the interior places (2 and 3). This is because the solidified PCM has a larger conducting resistance and is subcooled towards the wall surface. As a result, the surface's ability to remove heat slows, resulting in a slower decline in temperature.

For PCM and NFPCM, a change in the transition temperature is also seen between positions 2 and 3. NFPCM has a smaller shift than pure PCM, but it's still noticeable. This means that the PCM's solidification temperature varies depending on where in the container it is located. Depending on where the PCM is located, the PCM's heat release rate may vary. We saw the same result in our DSC studies using different scanning rates on the same PCM. Since the heat release rate influences the temperature, it can be assumed that the crystallisation temperature for every PCM varies as a result.

Also, the 14C temperature for pure PCM at places 1, 2, and 3 takes 5,580, 8,790, and 16,380 s, whereas the NFPCM takes 5,580,

6,960, and 10,830 s to reach the same temperature for 14C. The improved thermal conductivity of the NFPCM is the reason for this decrease in solidification time. When the coolant is kept at a constant 13C, the PCM and NFPCM at the container's core experience transient temperature changes. The time-temperature curve is clearly pushed to the left as the carbon nanotube volume fraction increases. When comparing pure PCM to NFPCM (0.6 vol. percent MWCNT), a decrease in solidification time of up to 33.64 percent can be seen. Carbon nanotubes in the NFPCM may have contributed to the increased heat release rate observed.

Conclusions

PCM thermal performance may be improved by including MWCNT into the PCM, making the PCM appropriate for latent heat thermal storage. Following an examination of the improvements in the characteristics of various NFPCMs, the following conclusions may be drawn from the experimental data.

1. 30–45 percent improvement in heat conductivity over pure PCM is realised in the NFPCM's liquid and solid forms. The NFPCM's thermal conductivity grows continuously when the MWCNT concentration is increased.
2. In the low shear stress range (0–1 Pa), the NFPCMs exhibit shear thinning behaviour, whereas they exhibit Newtonian behaviour in the high shear stress range (1–10 Pa). However, when the volume percentage of MWCNT increases, the anomalous rise in viscosity of NFPCM reduces its beneficial thermal properties.
3. As the nucleating agent for the freezing process, carbon nanotubes increase the freezing temperature faster than PCM alone. The lower the concentration of MWCNT in the PCM, the greater the reduction in supercooling; hence further research is needed to determine the ideal concentration of MWCNT in the PCM for different latent heat storage uses.
4. As the solidified PCM cools, its lower conductive resistance and subsequent subcooling are suppressed by carbon nanotubes incorporated into the PCM at the interior sites.

Due to its improved thermo-physical features, such as a little change in freezing/melting temperature and no decrease in latent heat capacity, MWCNT added to pure PCM can be regarded the most prospective storage medium for LHTS. The commercialisation of carbon

nanotubes in the PCM is contingent on their cost and availability, despite being technically viable. LHTS systems will soon be technically and economically practical for a wide range of applications because of ongoing research into carbon nanotubes' large-scale production.

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