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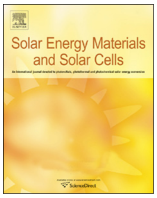

A novel CNT encapsulated phase change material with enhanced thermal conductivity and photo-thermal conversion performance

Yanfeng Chen[a,b,1], Qi Zhang[b,c,1], Xiaoyan Wen[d], Huibin Yin[a,*], Jian Liu[a,*]

[a] Key Laboratory of Distributed Energy Systems of Guangdong Province, Department of Energy and Chemical Engineering, Dongguan University of Technology, Dongguan 523808, China
[b] School of Chemistry and Chemical Engineering, South China University of Technology, China
[c] Department of Biomedical Engineering, University of Minnesota Twin Cities, USA
[d] Automotive Engineering Institute of Guangzhou Automobile Group Co., Ltd., China

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ABSTRACT

Phase change material is one of the most promising materials in thermal energy storage systems. In this work, a new phase change composite of Stearic Acid@Multi-walled carbon nanotubes (SA@MWCNTs) is prepared by a simple vacuum absorption method. The as-prepared composite is determined by scanning electronic microscope (SEM), Fourier transformation infrared spectroscope (FT-IR) and X-ray diffractometer (XRD). The results show that outside diameters of the PCM composite are about 50–60 nm and Stearic Acid is encapsulated in the MWCNTs without chemical reaction. The DSC results indicate that the melting temperature and latent heat of the composite are 59.28 °C and 91.94 J g^{-1}, respectively. The encapsulation ratio of Stearic Acid is calculated to be 47% from the results of the DSC measurements. The as-prepared SA@MWCNTs composite was dispersed into the water to form stable suspension, and the suspension shows remarkable photo-thermal conversion performance with temperature increases from 30 to 80 °C. The receiver efficiency of this new kind of heat transfer fluid maintain 85% in wide temperature range. Furthermore, the PCM composite could maintain its phase transition perfectly after 50 melting–freezing cycles, and no leakage of paraffin was observed by SEM. The high heat storage capability and excellent photo-thermal conversion performance of the composite enable it to be a potential material to store solar energy in practical applications.

1. Introduction

Sustainable energy generation is one of the most important challenges facing society today [1]. The perceived shortage of fossil fuels as well as environmental considerations will constrain the use of fossil fuels in the future. Therefore, researchers are motivated to find alternative sources of energy. In recent years, the use of solar energy has had a remarkable edge [2]. Solar energy has been explored through solar thermal utilization, photovoltaic power generation, and so on [3,4]. Solar thermal utilization is the most popular application among them. In conventional solar thermal collectors, plates or tubes coated with a layer of selectively absorbing material are used to absorb solar energy, and then energy is carried away by working fluids in the form of heat [5,6]. In this case the efficiency is limited by not only how effective the absorber captures solar energy but also how effectively the heat is transferred to the working fluid. An approach that has been proposed to enhance the efficiency of collectors while simplifying the system is to directly absorb the solar energy within the fluid volume, the so-called direct absorption solar collector. In the last century, black liquids containing millimeter to micrometer-sized particle were used as heat transfer fluid in solar collectors because of their excellent photothermal properties. However, the applications of these suspensions are limited because of severe abrasion, sedimentation, and plug problems of coarse particles. Recently, nanofluids have been applied as working fluids in direct solar collectors [1,7,8]. Nanofluid is a new class of heat transfer fluids containing stably suspended nano-sized particles, fibers, or tubes in the conventional heat transfer fluids such as water, engine oil, ethylene glycol, etc. [9–13]. Nanoparticles offer the potential of improving the radiative properties of liquids leading to an increase in the efficiency of direct absorption solar collectors. Several researchers have reported that nanofluids could effectively improve the solar energy utilization, especially carbon-based nanofluids for their excellent photothermal property. Zhu et al. reported that carbon black nanofluids of high-volume fraction had better photothermal properties and higher

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[*] Corresponding authors.
E-mail addresses: yinhb@dgut.edu.cn (H. Yin), liujian@dgut.edu.cn (J. Liu).
[1] The authors contributed equally to this work.

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thermal conductivity and also exhibited a shear thinning behavior [14]. Sani et al. found that thermal properties and sunlight absorption of nanofluids consisting in aqueous suspensions of single wall carbon nanohorns were higher than pure water, make this new kind of nanofluids very interesting for increasing the overall efficiency of the sunlight exploiting device [15–17]. Poinern et al. showed that nanoparticles of functionalized carbon nanospheres had the potential to improve the photothermal properties of the working fluid [18].

To increase the utilization efficiency of solar energy, thermal energy storage is an important technology [19]. A lot of heat transfer fluids were developed to be applied in the direct solar thermal collectors, especially the low temperature heat transfer fluids such as water, ethylene glycol, conducting thermal energy storage with sensible heat storage technique. Compared with sensible heat storage techniques, latent heat storage technology using various phase change materials (PCMs) as the working media is particularly attractive due to its advantages of high energy storage density and isothermal nature during the phase change process. PCMs generally refers to materials having large latent heats of fusion with regards to melting and solidifying at a nearly constant temperature [20]. Most recently, PCMs have been recognized as being applicable to the sector of “high technology”, such as smart drug delivery [21], information storage [22], barcoding [23], and detection [24]. With PCMs dispersed in the heat transfer fluids, the heat can be quickly transferred to the PCMs, leading to an increase of the energy storage capacity of the heat transfer fluid. However, the direct utilization of the PCMs for heat storage is subject to some restrictions because of their leakage during the solid–liquid phase transitions and low thermal conductivity. To prevent the PCMs from interacting adversely with the heat transfer fluid, the PCMs are usually encapsulated by other robust materials [25]. There have been intensive efforts in exploring potential encapsulated methods for PCMs. For instance, the impregnation of paraffin in exfoliated graphite [26] or aerogel [27], the microencapsulation of PCMs [28]. Among these, microencapsulation is one of the most straightforward technology used in the heat transfer fluid. However, the preparation technology of the nanocapsule which is better for the heat transfer fluid preventing sedimentation is relatively difficult. Moreover, the most used organic polymers shell of the nanocapsule such as urea–formaldehyde resin [29,30] and polyurethane [31] have relatively lower thermal conductivity, decreasing the heat transfer performance of microencapsulated PCMs based slurry.

Herein, a novel Stearic Acid@Multi-walled carbon nanotubes PCM composite was prepared by a simple vacuum absorption method. The as-prepared composite has an advisable encapsulated capacity of Stearic Acid, high thermal storage capability, and good thermal stability, and these new materials based heat transfer fluids are able to harvest visible light and convert it to thermal energy more effectively compared with traditional PCMs for latent heat thermal energy storage, indicating that the composite based novel kind of phase change slurry has great potential to store solar thermal energy in direct solar thermal collectors.

2. Experiment

2.1. Materials

Stearic Acid (AR) was purchased from Shanghai RichJoint Chemical Reagents Co., Ltd. (CAS number: 57-11-4). MWCNTs (diameter inside: 30–50 nm, diameter outside: 50–60 nm, length: 5–30 µm, specific surface area: $120\,m^2\ g^{-1}$) was purchased from Chengdu Organic Chemicals Co. Ltd. The surfactant OP80 and SPAN80 were purchased from Aladdin reagent (Shanghai) Co. LTD.

2.2. Preparation of Stearic Acid@MWCNTs composite and the composite based nanofluids

We adopted a purification method that consists of refluxing in a mixture of concentrated sulfuric acid and nitric acid (mass ratio = 3:1, 200 mL) and resuspending the nanotubes (30 g) in water followed by filtration with a cross-flow filtration system [32]. Finally, passing the resultant purified MWCNTs suspension though a polytetrafluoroethylene filter produced the purified MWCNTs.

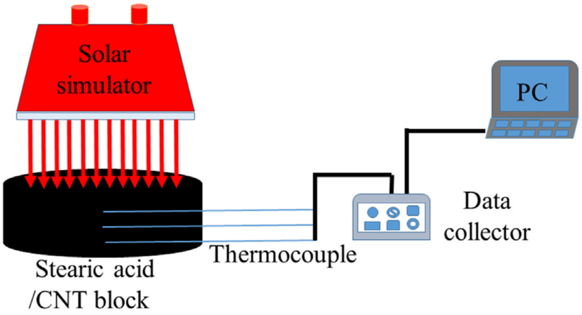

Fig. 1. Solar-driven transition diagram of the Stearic Acid@MWCNTs composite.

The Stearic Acid@MWCNTs composite PCM was prepared by using vacuum impregnation system, as shown in Fig. 1. MWCNTs was put in a conical flask heated in 90 °C, then the melted Stearic Acid was poured into it under vacuum. After 5 min, the untreated Stearic Acid@MWCNTs was obtained. Then petroleum ether was used to wash the Stearic Acid stuck in the surface of the MWCNTs. Ultimately, the final Stearic Acid@MWCNTs composite PCM was received after filtration and desiccation. Then the prepared Stearic Acid@MWCNTs composites were formed into several round blocks by dry pressing with a homemade cylindrical mold (3 cm inside diameter and 1 cm height) under the pressure of $100\ kg\ cm^{-2}$. Based on the volume of the mold we used, we calculated the masses of the composites needed for fabricating the blocks with the selected densities according to the formula $m = \rho \cdot V$. Then, we added the calculated amounts of the composite PCM powders into the mold to fabricate the blocks. Finally, we measured the actual volumes and masses of the formed blocks to calculate their actual packing densities, which were 900.0, 1000.0, 1100.0, 1200.0, and $1300.0\ kg\ m^{-3}$.

The stable nanofluids was obtained by high-speed stirring the Stearic Acid@MWCNTs composite aqueous solution added a little surfactant. The surfactant were composed of OP80 and SPAN80 with the mass ratio of 1:1, and the mass fraction of surfactant to Stearic Acid@MWCNTs composite was 1%. Three different nanofluids were prepared with different mass fraction of Stearic Acid@MWCNTs composite, which were 5, 10 and 15 wt%.

2.3. Characterizations of Stearic Acid@MWCNTs composite

The morphology and microstructure of MWCNTs and Stearic Acid@MWCNTs composite was observed by a transmission electron microscopy (FEI Tecnai G20). The structure of the composite was characterized by FT-IR spectra and X-ray diffraction. The FT-IR spectra were recorded on a Bruker 550 from 400 to $4000\ cm^{-1}$ using KBr pellets, the X-ray diffraction (XRD) patterns of the samples were carried out on X-ray diffractometer (D8 ADVANCE). The phase change temperature and latent heat of the samples were measured using a differential scanning calorimeter (Q20, TA). For DSC measurements, 5–8 mg for every sample was sealed in an aluminum pan for characterization at a heating rate of $10\ °C\ min^{-1}$ under a constant stream of nitrogen at flow rate of $50\ mL\ min^{-1}$. The thermal stability of MWCNTs and the Stearic Acid@MWCNTs composite PCM was investigated by the thermogravimetric analysis (TGA) using a thermal analyzer (Q600 SDT, TA, URT100). The measurements were conducted by heating the samples from room temperature to 600 °C at a heating rate of $10\ °C\ min^{-1}$ under nitrogen atmosphere with a flow rate of $100\ mL\ min^{-1}$.

The thermal conductivities of the obtained round blocks with