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Research Paper

Enhanced thermal conductivity of phase change nanocomposite in solid and liquid state with various carbon nano inclusions

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HIGHLIGHTS

- Thermal conductivity of lauric acid with various carbon additives are measured.
- Contrasting thermal conductivity enhancement in solid and liquid state is noticed.
- For 1 vol% CNTs, enhancement in solid and liquid state is 171% and 20%.
- For 1 vol% graphene, enhancement in solid and liquid state is 223% and 37%.
- Thermal interface resistance is an order of magnitude higher in liquid state.

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ABSTRACT

We report contrasting enhancement in the solid state and liquid state thermal conductivity of phase change nanocomposite seeded with various carbon nano inclusions. Phase change nanocomposites were prepared using *n*-Dodecanoic acid as the host matrix. Single-walled carbon nanohorns, multi-walled carbon nanotubes and few-layer graphene nanosheets were considered as the nano inclusions. Thermal conductivity measurements were carried out using a custom built transient hotwire technique. The thermal conductivity enhancement significantly depends on the shape and aspect ratio of the nano inclusions. Maximum thermal conductivity enhancement was obtained in the presence of graphene nanosheets as the nanofiller candidate followed by carbon nanotubes and carbon nanohorns. The thermal conductivity enhancement was significantly higher in the solid state than the liquid state of the material for all the nano composites. Thermal conductivity enhancement results were compared with the effective medium theory calculations and Yamada-Ota model calculations considering the role of interfacial thermal resistance between the nanomaterial and the surrounding host matrix. The model calculations show that that the interfacial thermal resistance significantly limits the thermal conductivity enhancement in the liquid state compared to the solid state. The model calculations also show that interfacial thermal resistance is an order of magnitude higher at the solid-liquid interface compared to that of solid-solid interface which leads to a contrasting thermal conductivity enhancement in liquid and solid state of the nanocomposites.

1. Introduction

Solid-liquid phase change materials (PCM) due to its excellent energy storage capabilities, low cost, abundance in natural resources are frequently used for thermal energy storage applications in concentrated solar power plants [1,2], passive electronics cooling [3] and waste heat recovery systems [4]. Among numerous PCMs, organic PCMs, have proved to be desirable for latent heat storage purposes due to its high stability, negligible super cooling and low cost. Especially organic fatty acid based PCMs possess many favourable properties such as high phase change enthalpy, low vapour pressure and wide range of melting point which makes it ideal for several applications [5,6]. Unfortunately, organic PCMs suffer from inherently low thermal conductivity which limits its application in energy storage systems and passive electronic

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cooling. Henceforth, recent research focus on the development of novel nano materials to significantly enhance the thermal conductivity of PCMs.

Traditional techniques to enhance the thermal conductivity of PCM is to include metallic fins [7] and utilization of metallic foams [8,9]. Such techniques often have manufacturing constraints and porous foams despite offering significant thermal conductivity enhancement suppress the natural convection rate during the melting process in energy systems [10]. Another potential alternative to enhance the thermal transport is the inclusion of high thermal conductive nano materials in the PCM matrix [11–13]. The increase in thermal conductivity of organic PCMs using different nanomaterials is a subject of recent interest [14–18]. Nanomaterials of different metals, metallic oxides and carbon allotropes with higher thermal conductivity have been investigated for this purpose. Carbon allotropes such as carbon nanotubes and graphene nanosheets are attractive nano inclusions primarily due its high intrinsic thermal conductivity (as high as $\sim$5000 W m^{-1} K^{-1}) [19,20].

Yavari et al. [21] utilized graphene nanosheets and reported a thermal conductivity enhancement by a factor of $\sim$1.8 for 1-octadecanol/graphene nanocomposites at a loading of 1 vol%. Similar thermal conductivity enhancement by a factor of 1.5–2.3 was reported for PCM/graphene and CNT based nanocomposites in the literature [22–25]. Recently, Zheng et al. [26] reported a large contrast in the electrical and thermal conductivity enhancement in graphite/hexadecane suspensions. Harish et al. [27] reported a large enhancement in the solid phase ($\sim$250%) for 0.25 wt% of single-walled carbon nanotube/octadecane nanocomposite compared to a nominal enhancement in the liquid phase ($\sim$10%). Similarly, Sun et al. [28] using acid treated multi-walled carbon nanotube/hexadecane nanocomposite showed that at room temperature the thermal and electrical conductivities can be tuned by a factor of $\sim$3 and $\sim$5 respectively. Schifferes et al. [29] with 1 vol% of graphene/hexadecane nanocomposites demonstrated that by varying the cooling rate of nanocomposites from 10^{-3} to 10^{2} °C/min, electrical and thermal conductivities can be significantly varied due to the change in aspect ratio of crystalline structures of the PCM.

Despite the high intrinsic thermal conductivity of carbon nanostructures, the magnitude of thermal conductivity enhancement reported in the literature is quite limited. The physical reasons behind these under-whelming performance is not completely understood yet. Moreover, potential mechanisms behind the contrasting thermal and electrical conductivity enhancements in the solid and liquid state of nanocomposites is yet to be understood.

Hence, in this work we systematically investigate the effect of nanomaterial dimensionality in enhancing the thermal transport of PCMs using single walled carbon nanohorns (SWCNH), multi-walled carbon nanotubes (MWCNT) and graphene nanoplatelets (GnP). We show that thermal conductivity enhancement significantly depends on the material aspect ratio and dimensionality of the nano inclusions. Using effective medium theory and Yamada-Ota theoretical models, we extract the interfacial thermal boundary resistance between the nano inclusions and the surrounding PCM matrix. The model calculations show that the thermal conductivity enhancement is significantly limited by the poor interfacial thermal conductance between the nanomaterials and the PCM despite the high intrinsic thermal conductivity of carbon nanostructures. The interfacial thermal conductance is at least an order of magnitude higher in the solid state compared to the liquid state of the nanocomposites irrespective of the nanomaterial dimensionality. The present work helps to understand the mechanism behind the contrasting thermal conductivity enhancements observed in the solid and liquid state of nano composites.

2. Materials and methods

2.1. Sample preparation

In the present work, we made use of *n*-dodecanoic acid (Lauric acid, $C_{12}H_{24}O_2$) as the phase change material with a phase transition temperature of $\sim$43 °C. We made use of carbon based nanostructures namely single-walled carbon nanohorns (SWCNH), multi-walled carbon nanotubes (MWCNT) and few-layer graphene nanoplatelets (GnP) as the nano filler candidates to enhance the thermal conductivity of phase change material. Oxidized single walled carbon nanohorns were purchased from NEC Corporation, Tokyo with a diameter (d) of 2–5 nm, length (L) of 40–50 nm, density of 1.1 g/cm^3 and specific surface area of $\sim$1300 m^2/g. Multi-walled carbon nanotubes were purchased from Sigma Aldrich with outer diameter (d) of 6–13 nm, mean length (L) of 10 μm and density of 2.2 g/cm^3. Liquid phase exfoliated few layer graphene nanoplatelets were purchased from XG Sciences (Grade M) with an average thickness (d) of 5–10 nm mean particle diameter (L) of 15 μm and density 2.2 g/cm^3. Fig. 1(a–c) shows the scanning electron microscopy (SEM, FEI Versa 3D dual beam, LoVac detector) visualization of SWCNH, MWCNT and GnP respectively.

SWCNH samples were directly used in the nanocomposites preparation without any further treatment. CNTs and GnP nanoplatelets were pre-treated as follows: 0.5 g of the nanomaterial was dispersed in 25 mL of concentrated nitric acid (68 wt%) and then refluxed at a temperature of 100 °C for 2 h. The mixture was filtered, then washed with deionized water and dried at 150 °C in vacuum for 6 h.

The nanocomposite samples were prepared by adding the nano-inclusions with molten lauric acid kept on a hot plate at a temperature of 100 °C under vigorous (250 rpm) stirring by a magnetic stirrer for 30 min. After that, the samples were subjected to intensive sonication using an ultrasonic processor (Hielscher GmbH, UP-400S with H3/Micro Tip 3) for 60 min at 50% amplification.

2.2. Thermal conductivity measurements

In this work, we made use of a custom built transient hot wire technique in-order to measure the thermal conductivity of the nanocomposites. The suitability of hot wire technique to measure the thermal conductivity of nanocomposites is generally questioned due to the possibility of settling of nanoparticles on the wire surface. A recent benchmark study [30] on nanoparticle suspensions show that the measurement technique does not have any significant impact on the thermal conductivity results. In addition, we look into the Pt wire prior and after the thermal conductivity measurements using SEM, and no deterioration or deposition of the nano-fillers were found. Details of the experimental setup are reported elsewhere [18,25]. In brief, a platinum wire of diameter 25.4 μm (AM systems) with an electrically insulating isonel coating of 2.5 μm and length 50 mm were used in the experiments. In this technique, platinum hot wire acts as both the heating element and the electrical resistance thermometer. The measurement method involves heating the transient hot wire by a constant DC power supply and measuring its electrical resistance change as a function of time. The hot wire temperature is calculated based on its temperature dependent electrical resistance variation [31]. The thermal conductivity (k) of the nanocomposite is calculated from the Eq. (1) as follows.

$$k = \frac{q}{4\pi}\left(\frac{d\ln t}{dT}\right) \tag{1}$$

In Eq. (1), q is the heat flux per unit length, T and t are temperature and time respectively. From a known volumetric heating per