International Journal of Heat and Mass Transfer 67 (2013) 301–310

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Experimental determination of temperature-dependent thermal conductivity of solid eicosane-based nanostructure-enhanced phase change materials

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ARTICLE INFO

Article history:
Received 22 July 2013
Received in revised form 1 August 2013
Accepted 3 August 2013
Available online 7 September 2013

Keywords:
Copper oxide nanoparticles
Phase change materials
Thermal conductivity enhancement
Transient plane source method
Solid composites

ABSTRACT

The effective thermal conductivity of composites of eicosane and copper oxide nanoparticles in the solid state was measured experimentally by using the transient plane source technique. Utilizing a controllable temperature bath, measurements were conducted at various temperatures between 10 and 35 °C for the solid samples. In the course of preparation of the solid specimen, liquid samples with eight different mass fractions (0, 1, 2, 3.5, 5, 6.5, 8 and 10 wt%) of nanoparticles were poured into small diameter molds and were degassed within a vacuum oven. The molds were then subjected to one of the three solidification procedures, i.e. ambient solidification, ice-water bath solidification or oven solidification method. Measured thermal conductivity data of the composites were found to be nearly independent of the measurement temperature for a given loading of CuO nanoparticles regardless of the solidification procedure. Irrespective of the solidification method, as the melting temperature was approached, thermal conductivity data of the solid disks rose sharply for the three sets of samples. The ice-water bath solidification route for the eicosane–CuO samples consistently exhibited the lowest values of thermal conductivity, whereas the samples of oven solidification scheme exhibited to the highest values. This behavior is assumed to be due to the greater void percentage of ice-water bath samples and/or crystal structure variations due to the adopted phase transition method.

1. Introduction

Prior research effort on nanofluids (colloidal suspensions of nanoparticles) has focused on single-phase convective and liquid–vapor phase change (i.e. boiling) heat transfer (e.g. Das et al. [1]). Accordingly, experimental investigations of enhanced thermal conductivity of nanofluids were mainly conducted for water- and ethylene-glycol-based nanofluids as improved heat transfer fluids (Yu et al. [2]). In order to extend the applicability of such colloids, utilization of nanofluids as superior phase change materials (PCM) undergoing solid–liquid phase transition (i.e. solidification and melting) for thermal energy storage, referred to as nanoparticle-enhanced PCM (NePCM), was recently proposed by Khodadadi and Hosseinizadeh [3].

Various organic and inorganic materials with high values of the latent heat of fusion have been used as PCM for different thermal energy storage applications (Sharma et al. [4]), such as ice-water storage for thermal comfort in buildings, thermal management of electronic devices, industrial waste heat recovery, and solar thermal power generation. The proper PCM candidates for a specific application are usually chosen according to their melting/freezing points in regard to the desired temperature range. For example, *n*-alkanes (i.e. C_nH_{2n+2}, commonly called paraffin wax) with high carbon numbers have widely been used for the intermediate temperature range (0–100 °C). When it comes to high-temperature applications (>300 °C), molten salts have long been considered as the favored PCM candidates. Since 2007, a number of experimental efforts have been devoted to preparation and characterization, as well as application of NePCM composites of base PCM and nanostructured additives, such as metal and metal oxide nanoparticles, single- and multi-walled carbon nanotubes, and metal and carbon nanofibers (Khodadadi et al. [5]). Among the 20+ such studies reviewed by Khodadadi et al. [5], four investigations concerned combinations of nanoparticles and non-aqueous base PCM. Zeng et al. [6] prepared and characterized PCM composites made of 1-tetradecanol (TD) enhanced by silver (Ag) nanoparticles with a wide range of particle loadings. Ho and Gao [7] prepared NePCM made of *n*-octadecane ($C_{18}H_{38}$) and alumina (Al_2O_3) nanoparticles with two different mass fractions (5 and 10 wt%) and measured the important thermophysical properties. Phase change nanocomposites made of paraffin wax with γ-Al_2O_3 nanoparticles were prepared by Wang et al. [8] and the enhanced thermal conductivity

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http://dx.doi.org/10.1016/j.ijheatmasstransfer.2013.08.010

Nomenclature

k	thermal conductivity, W/mK
r	radius, m
T	temperature, K or °C

Greek symbols

ρ	density, kg/m^3
$\varnothing_{vol}$	volume fraction of the nanoparticles
$\varnothing_{wt}$	weight fraction of the nanoparticles

Subscripts

c	continuous phase
d	discrete phase
eff	effective
l	liquid
s	solid
vol	volume fraction
wt	weight or mass fraction

was investigated in both solid and liquid phases. Wu et al. [9] presented their experimental investigation on melting/freezing performance of paraffin enhanced by copper nanoparticles. Comparing to pure paraffin, faster melting and freezing rates by a factor of approximately 30% were observed for NePCM with 1 wt% nanoparticles. Fan [10] recently reported experimental data on temperature-dependent thermal conductivity of CuO-based colloids in both liquid and solid phases using the Transient Plane Source (TPS) technique. It was observed that in the liquid phase, the thermal conductivity of pure eicosane ($C_{20}H_{42}$ with a melting temperature of 35.1–38 °C, according to various sources) decreased as the measurement temperature was increased and the enhancement of thermal conductivity due to presence of the additives varied monotonically as the particle loading was increased. The observed enhancement was slightly more marked with increasing temperature, probably due to improved diffusion of nanoparticles at high temperatures. For the range of the loading of nanoparticles studied (mass fractions less than or equal to 10%), the relative monotonic enhancement of thermal conductivity in the liquid phase was in good agreement with the predictions based on the model of Maxwell [11]. Considering the data for the solid phase composites, the first attempt of Fan [10] to measure the thermal conductivity of a sample having solidified slowly from an initial temperature of 40 °C (liquid) to 20 °C (solid) over a period of about 30 min while the TPS sensor was submerged in the liquid gave rise to erratic information with high values of standard deviation (as high as 10%). Suspecting the greater degree of supercooling of eicosane and the long period of phase transition for the tested samples, Fan [10] proceeded to measure the thermal conductivity of a rapidly-quenched composite. The liquid composite was heated to 60 °C and then was poured into an empty cold glass sample container (kept at 10 °C) within which the TPS sensor was set in place. Despite improvements in the values of the standard deviation (less than 1%), a non-monotonic relation between the thermal conductivity and the mass fraction that was independent of the temperature range studied was exhibited, when the mass fraction was greater than 2%. For a given particle loading, the measured thermal conductivity values were generally insensitive to the measurement temperature (as observed for pure eicosane by Stryker and Sparrow [12]) except the data that were obtained near the melting point that exhibited a sharp rise.

Considering the limitations of the experimental work of Fan [10] having to do with lack of control over the phase transition, a new set of experiments were initiated. Moreover, no new thermal conductivity data have been reported for eicosane since the availability of data of [12] who utilized a steady-state thermal conductivity determination technique within the annular spacing of two concentric spheres maintained at constant temperatures. In the present study, the solid samples were prepared following three different approaches, namely: (i) ambient solidification, (ii) ice-water bath solidification, and (iii) oven solidification. The measurements were conducted using the TPS technique that is a transient method. Specifics of the preparation routes for the samples will be discussed below along with results of a detailed temperature-dependent thermal conductivity data of eicosane/CuO nanoparticles solid composites.

2. Preparation of the eicosane-based NePCM composites

Details of the preparation scheme of the NePCM liquid samples are discussed by Fan [10]. Similar steps were followed in the present study with deviations that will be outlined below. Eicosane ($C_{20}H_{42}$) that possesses a melting point of approximately 37 °C at the atmospheric pressure was selected as the base PCM. Copper (II) oxide (CuO) nanoparticles stabilized by sodium oleate ($C_{18}H_{33}O_2Na$) were synthesized and provided by chemist colleagues (Clary and Mills [13]). It was shown that the CuO nanoparticles were nearly spherical and most of them had a diameter within the range of 5–15 nm (Clary and Mills [13]). The NePCM samples with eight different mass fractions (0, 1, 2, 3.5, 5, 6.5, 8 and 10 wt%) of nanoparticles were prepared by dispersing the desired amounts of CuO nanoparticles into 99% pure eicosane (Sigma–Aldrich, St. Louis, MO) in liquid phase followed by rigorous stirring on a hot-plate magnetic stirrer (SP131325Q, Thermo Fisher, Dubuque, IA) at 80 °C for 30 min. A representative photo of five sample colloids with different mass fractions is shown in Fig. 1 (Fan [10]). Although it is seen that more nanoparticles tend to stick on the walls with increasing particle loading, no significant precipitation was visually found at the bottom of the containers, even for the most concentrated 10 wt% sample. Desirable long-term stability of NePCM samples prepared using the sodium-oleate-stabilized CuO nanoparticles in various alkanes (hexane, octane, dodecane, and eicosane) was studied by observing the absorbance spectra for mass fractions up to 20 wt% (Clary and Mills [13]). In the calculation of the required mass of nanoparticles for each concentration, it was assumed that the CuO nanoparticles are pure and the presence of sodium-oleate surfactant was ignored. There is no data in the

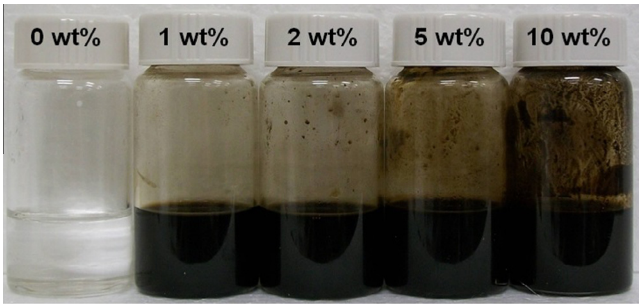

Fig. 1. Photograph of eicosane-based NePCM samples (in liquid phase) with different mass fractions of CuO nanoparticles [10].