



# Thermal characteristic of nanocomposite phase change materials during solidification process<sup>☆</sup>



Aziz Babapoor<sup>a</sup>, Gholamreza Karimi<sup>a,\*</sup>, Samad Sabbaghi<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, Shiraz University, Shiraz 7134851154, Iran

<sup>b</sup> Department of Nano Chemical Engineering, Shiraz University, Shiraz, Iran

## ARTICLE INFO

### Article history:

Received 8 February 2016

Received in revised form 22 March 2016

Accepted 11 May 2016

Available online xxx

### Keywords:

Phase change material  
Nanocomposite-enhanced phase change materials (NEPCMs)  
Nanocomposite  
Nano PCM  
Solidification

## ABSTRACT

Phase change materials are widely used in various thermal management applications. Conductive nanoparticles can be added to phase change materials to improve their thermal conductivities. The selection of suitable nanoparticles and weight percent is important from thermal performance point of view. In this study, various nanoparticles (e.g. SiO<sub>2</sub> (11 nm, 20 nm), Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO) and their combinations at different concentrations (2, 4, 6 and 8%wt) were used as thermal conductivity promoters to produce modified paraffin samples. Thermal properties of the synthesized nanocomposites were characterized by differential scanning calorimetric technique. Experimental measurements showed that the presence of nanoparticles can improve thermal conductivity of the nanocomposite (by a maximum of 150%) but the specific heat may be degraded (by a maximum of 39% max). Experimental results have indicated that considering all parameters involved, composite samples with 8 wt% ZnO offer optimum thermal properties. Therefore, it is very important to identify the type and optimum amount of the nanoparticles which are added to the phase change materials. The results of this study can be used to improve thermal performance of nanocomposites phase change materials.

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## 1. Introduction

Energy demand is continuously increasing due to global population growth and improved living standards [1,2]. As a result there has been an increasing mandate for convenient and efficient thermal energy storage to mitigate the environmental concerns over the past few years. An environment-friendly new energy saving technique is the storage and retrieval of thermal energy by using phase change materials (PCMs). Latent heat storage by PCMs has received much attention due to PCMs' high storage density and small temperature variation from storage to retrieval process. In a latent heat storage system, energy is stored by phase change of the storage medium, i.e. solid–solid, liquid–solid or gas–liquid. The PCM also presents the advantage of cumulating sensible heat corresponding to the temperature difference between charge and discharge steps. Various phase transitions for the charge/discharge process can be considered [3–5].

Thermal conductivity of PCMs is considerably low hence, in order to enhance heat transfer highly conducting materials (e.g. metal oxide nanoparticles) can be added to the phase change material [6–11]. Other thermal properties can be affected by the presence of nanoparticles. Zeng et al. [12] synthesized an organic PCM/Ag nanoparticles composite material and measured the effect of Ag nanoparticles on the thermal conductivity of the composite. The thermal conductivity of the nanocomposite PCM was found to increase with the loading of Ag nanoparticles. Valan Arasu et al. [13] studied melting performance of paraffin wax loaded with Al<sub>2</sub>O<sub>3</sub> as in an enclosure using the enthalpy-porosity formulation. Also, the effect of orientation of the heat transfer surface of a square enclosure and the volumetric concentration of Al<sub>2</sub>O<sub>3</sub> in paraffin wax on the melting performance is examined and reported. The fluid flow and the interface shape depend on the liquid layer thickness during the progress of melting. The melting rate decreases with the increase in the volumetric composition of Al<sub>2</sub>O<sub>3</sub> for both horizontal wall and vertical wall heating cases. The results showed that the effective thermal conductivity of a paraffin wax latent heat storage medium can be significantly increased by using smaller volumetric concentration of alumina particles in paraffin wax. Liu et al. [14] showed that addition of 20–60 wt% Al<sub>2</sub>O<sub>3</sub> to paraffin wax decreases the melting temperature by 7 °C. Teng and Yu [15] reported the production of nanocomposite-

<sup>☆</sup> This article is the 100th accepted paper in Journal of Energy Storage.

\* Corresponding author.

E-mail addresses: [gkharimi@shirazu.ac.ir](mailto:gkharimi@shirazu.ac.ir), [karimi1342@gmail.com](mailto:karimi1342@gmail.com) (G. Karimi).

## Nomenclature

$C_p$	Specific heat capacity ( $\text{J g}^{-1} \text{C}^{-1}$ )
$T$	Temperature ( $^{\circ}\text{C}$ )
$\rho$	Density ( $\text{g cm}^{-3}$ )
wt	Weight percentage

enhanced phase change materials (NEPCMs) using the direct-synthesis method by mixing paraffin with various nanoparticles as the experimental samples. The experimental results demonstrate that  $\text{TiO}_2$  compared to other additives, is more effective than the other additives in enhancing both the heat conduction and thermal storage performance of paraffin for most of the experimental parameters. Fethi et al. [16] modeled the graphite/paraffin composite as a two dimensional system. Three modes of graphite addition were analyzed. Graphite was added as fibers, as fins or as foam. For every case, the thermal heat storage/release cycle is evaluated versus different graphite mass fraction. The results indicate a noticeable improvement in the effective thermal conductivity of composites compared to the PCM. Gossard et al. [17] used experimental device in order to characterize the phase change material thermal properties (thermal conductivity, sensible and latent heat thermal energy storage, specific heat capacity) in the solid phase, during the solid–liquid transition and in the liquid phase. It allows to measure cylindrical samples of maximum 60 mm radius and 10 mm thick. A typical measurement consists in imposing a vertical temperature gradient through the PCM sample driven by a heat source, monitoring during the experiment time all the boundary conditions (temperatures and heat fluxes) and measuring temperature evolution in three locations within the PCM sample. These experiment data are used to solve the inverse heat conduction problem by applying the conjugate gradient method and finally, to determine the PCM thermal properties.

The thermal conductivity of such loaded nanoparticles must be higher than that of the PCM if they are to enhance the thermal conductivity and promote heat transfer. On the other hand, a poor combination of additives to PCMs can increase interface thermal resistance and particles sedimentation; as a result, thermal performance of the thermal storage material can be degraded. With the recent advances in nanotechnology, the size of additives can be reduced to nanometer scale, and this reduced size can enhance the suspension performance, specific surface area, and heat transfer performance of the PCMs [18,19].

Despite a large number of studies on PCM thermal conductivity, a detailed comparison of thermo-physical properties of various nanocomposite PCM containing different nanoparticles (type and weight percentage) during solidification is not available. To shed further light on the subject, in the present study, various metal oxide nanoparticles were loaded into paraffin mixture and the composite thermal behavior including phase change temperatures and heat capacity in solidification process are investigated. In fact, no previous study has done such a comprehensive study on the subject.

**Table 1**  
Thermo-physical properties of PCM.

Material	Melting temperature of paraffin ( $T_m$ )	Specific heat ( $\text{J/g}^{\circ}\text{C}$ )	Thermal conductivity ( $\text{W/mK}$ )	Density ( $\text{g/cm}^3$ )	Kinematic viscosity ( $\text{mm}^2/\text{s}$ )	Latent heat ( $\text{kJ/kg}$ )
Paraffin wax (solid)	53–57 $^{\circ}\text{C}$	2.384	0.41	0.895 (20 $^{\circ}\text{C}$ )	4.27	184.48
Liquid paraffin	Not available	3.046	0.148	0.867	52.20 (40 $^{\circ}\text{C}$ )	240

## 2. Experimental description

### 2.1. Materials

Liquid paraffin and paraffin wax were purchased from Merck and Sigma Aldrich companies respectively.  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  (11 and 20 nm) nanoparticles were purchased from US Nano Company and ZnO nanoparticles were provided from Neutrino Nanovation. Characteristics of these materials are presented in Tables 1 and 2.

### 2.2. Sample preparation

A mixture of 60 wt% solid and 40 wt% liquid paraffin was prepared as PCM. Paraffin wax is heated to a temperature above its melting point before it is blended with liquid paraffin. The mixture is kept in a sonicator bath (Ultrasonic Cleaner Soner 203H, Laftech, Australia) at a temperature above the melting point of the paraffin wax for 45 min to ensure that a uniform blend is obtained. Then, the nanoparticles and melted paraffin wax are mixed in a strong shear mixing condition using a magnetic stirrer for about 75 min. The resulting suspension is kept in room temperature for a while in order to be crystallized and converted to a uniform solid composite. Table 3 lists the compositions of the synthesized samples. It should be mentioned that blank (pristine paraffin) is the sample made of pure paraffin without nanoparticles and samples containing combination of five nanoparticles is labeled as “Five” in all manuscript (For instance, the weight of nanoparticles were 0.887 g in every 8 wt% samples.). Also, the abbreviation “F” is used for these samples.

### 2.3. Characterization of the particles and composites

Morphological properties identifying the components that make up the sample and dispersion of nanoparticles in paraffins mixture were characterized using scanning electron microscopy (MIRA3 FEG-SEM, Tescan, Czech, resolution  $<2$  nm). In this work, thermal properties of paraffin waxes including solidification temperatures and heat capacities were measured by differential scanning calorimetry (DSC) technique (Mettler Toledo DSC 822E/400, Switzerland, resolution 0.04 mW at RT (temperature range), temperature accuracy  $\pm 0.2$   $^{\circ}\text{C}$ ). The test temperature range was from 20  $^{\circ}\text{C}$  to 100  $^{\circ}\text{C}$  and the heating rate was 10  $^{\circ}\text{C}/\text{min}$ .

## 3. Results and discussion

### 3.1. Nanostructure of nanoparticles and composites

The morphology and structure of the samples are examined by SEM as shown in Figs. 1 and 2 for typical samples.

Fig. 1 shows the SEM images of  $\text{SiO}_2$  nanoparticles (20 nm) and a sample containing  $\text{SiO}_2$  nanoparticles (20 nm, Si20-4). These images indicate that the original morphology of the particles is approximately spherical. Fig. 2 shows the ZnO nanoparticles and the sample containing ZnO nanoparticles at the concentration of 6 wt%. This figures show nanoparticles doped and dispersed in

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