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Improving thermal conductivity phase change materials—A study of paraffin nanomagnetite composites

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ABSTRACT

Paraffin is a common organic phase change material (PCM) that finds many applications in thermal energy storage (TES) systems. One common characteristic of organic PCMs is their low thermal conductivities. This – in turn – causes a slow thermal response when paraffin is used in high power applications. In this study, paraffin–nanomagnetite (Fe_3O_4) composites (PNMC) were prepared by a dispersion technique to enhance their thermal properties. Nano magnetite prepared using the cost-effective sol–gel method was mixed into paraffin at two different mass fractions: 10% and 20%. Scanning electron microscope (SEM) was used to observe the morphologies of nanomagnetite and PNMCs during different stages of the composite production process. SEM analysis results showed that nanomagnetite particles of 40–75 nm in size were homogeneously distributed in the paraffin structure. The latent heat storage capacity of PNMC, measured by differential scanning calorimetry (DSC) at 1 °C/min, was found to be 8% higher than paraffin alone. Thermal conductivities and diffusivities of paraffin and PNMCs were determined by the "DICO" method. For 10% and 20% by weight PNMCs, the thermal conductivities were increased by 48% and 60%, respectively. These results clearly indicate that the addition of Fe_3O_4 nanoparticles is an efficient and cost effective method to enhance the heat transfer properties of paraffin, when they are incorporated into latent heat storage systems.

1. Introduction

Thermal energy storage (TES) is one of the key technologies incorporated into heating and cooling applications in order to better exploit renewable energy sources. Phase change materials (PCMs) with high storage capacities are especially useful in systems that require compact thermal energy storage [1]. There are numerous materials used – both organics and inorganics – that can become PCMs. The choice of the right PCM depends mainly on appropriate thermal properties for each application, as well as its stability and cost. Their studies can become even more challenging —considering the compatibility of materials, their containers, and heat exchanger selection. Inorganic PCMs—with their high latent heat storage capacities and thermal conductivities can be quite corrosive. On the other hand, organic PCMs have relatively high latent heat capacities and are more stable, nontoxic, and are not corrosive. Possessing these qualities, among the organic PCM**s**, paraffins are commonly preferred. Paraffin is a mixture of straight chain *n*-alkanes with the general formula of C_nH_{2n+2}. The melting points of alkanes increase with number of carbon atoms and are below 0 °C until $C_{14}H_{30}$ and may reach 100 °C for carbon numbers of more than 50. With their wide range of melting points, paraffin is used in various applications like buildings [2], solar energy systems [3], refrigeration [4] and in waste heat recovery [5]. However, their low thermal conductivities become a drawback in high power applications. In such cases, storage and recovery of thermal energy in very short durations like minutes or even in second is required [6]. To overcome this disadvantage, several methods have been used to increase thermal conductivity of organic PCMs. Most of these methods are based on dispersing high thermal conductivity particles, such as carbon, metals, or graphite within PCMs [7–11]. Earlier efforts tested stationary, highly conductive metal pieces as thermal enhancement additives into PCMs. In such a study, thermal enhancement of fatty acid was monitored using stainless steel, copper, or graphite pieces [12]. The results of this study have indicated that copper and graphite have both successfully increased heat flux, but stainless steel had only limited contribution. Another method proposed was to impregnate expanded graphite with PCM. In this study, PCM was absorbed by the voids within graphite which had been expanded through heat and strong acid treatment [13]. Thermal conductivity of paraffin could be increased by 20–130 fold with 10% expanded

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graphite in the composite matrix [13,14]. The anisotropy of graphite makes it highly conductive in one crystalline direction, whereas it acts as an insulator in another direction. This property needs to be considered carefully when graphite is used for thermal enhancement.

There is a recent trend of using different nanostructures as thermal enhancement additives in PCMs instead of bulky metal particles. This method is sometimes called nano-doping due to the very small amounts of nanostructures added. Nanostructures are already being used in several applications other than PCMs for different purposes including thermal enhancement [15,16]. In the review by Khodadadi et al. [17], nanostructures used are given as carbon-based (nanofibers, nano-platelets and graphene flakes), carbon nanotubes, metallic (Ag,Al,C/Cu and Cu) and metal oxide (Al_2O_3, CuO, MgO and TiO_2) nanoparticles and nano-wires. Generally, the thermal enhancements achieved with carbon based nanostructures are much better than that for metallic and metal oxide nano-additives. The thermal conductivities of various fatty acids as PCMs were increased by 336% and 166% with adding 5 wt% of exfoliated graphite nano-plates, and by 1 wt% carbon nanotubes, respectively [18]. The thermal conductivity of tetradecanol/copper nano-wire composite only increased 9 times higher than that for pure tetradecanol [19].

In more than 340 previous studies investigated, the maximum content of nanomaterial that was tested was never higher than 10% [17]. The reason for higher contents not being tested was most likely due to the high cost of nanomaterials, especially carbon based ones. Finding a cost-effective PCM is already a problem, nano-doping could be even more costly.

There are different measurement methods, such as hot wire [14], hot strip [20], laser flash [21], thermo reflectance [22], simple inverse [23], 3-ω methods [24,] that are used to determine thermal conductivities of materials. Each of these methods can also be used for measuring the thermal conductivity of PCMs. Depending on the form of the PCM samples, be it solid, liquid or a suspension, the method needs to be adjusted for these special experimental set-ups. In many laboratories in house experimental set-ups are developed based on these fundamental methods. Diffusivity and Conductivity (DICO) experimental set-up for solid samples was developed by CERTES based on the hot wire method based on transient measurements [25].

In this study, improving thermal conductivity of paraffin by adding nanomagnetite (Fe_3O_4), prepared by a very cost effective method was tested. Magnetite (Fe_3O_4) is a highly magnetic and conductive material with thermal conductivity of 9.7 W/m/K [26]. Magnetite particles – in normal sizes – are already used in the polymer industry to increase thermal conductivities. For example, thermal conductivity of polypropylene composite could be increased from 0.22 to 0.93 W/m/K for 44 vol% of magnetite [26]. Nanomagnetite with its low toxicity [26] and high corrosion resistivity [27] properties is suitable for PCM applications. There are limited studies that investigated the effects of nanomagnetite of thermal enhancement of PCMs. Moreover, the economic sol–gel method that was used in this study to produce nano magnetite allowed us to increase the presence of nanomaterial contents to higher than 10%. This was not done in previous studies mainly due to cost restrictions. Paraffin–nano magnetite composite (PNMC) was prepared by dispersion technique with nano magnetite at different mass fractions to enhance thermal properties of paraffin. The effects of adding nanomagnetite on latent heat storage capacities and phase change temperatures have been determined by Differential Scanning Calorimeter (DSC). The thermal conductivities and diffusivities of the PNMCs were measured by DICO experimental set-up developed by CERTES to measure the thermal enhancements achieved. Targeted applications for PNMC can be systems that require fast storage and recovery, such as waste heat management of appliances, electronics and batteries.

Table 1
The thermo physical properties of the block paraffin 46–48 °C Merck.

Form	Solid
Color	White
Melting point	~42–72 °C
Boiling point	> 350 °C
Flash point	~200 °C
Ignition temperature	> 300 °C at 1013 h Pa
Solubility in water	Insoluble (20 °C)
Density	~0.9 g/cm^3 (20 °C)

2. Experimental

2.1. Materials

A block technical grade paraffin with a nominal melting point around 46–48 °C was obtained from Merck company as PCM. The thermophysical properties of the paraffin (CAS-No. 8002-74-2) as given by the manufacturer are given in Table 1 [28]. Thermal conductivity of paraffin at 46–48 °C is 0.21 W/m/K/ [29].

Nanomagnetite used in this study has been synthesized from iron salts (($FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$-Sigma Aldrich), HCl(Sigma Aldrich) and NH_4OH(Sigma Aldrich) in technical grade by sol gel method [30]. Using technical grade materials with high yields [31] makes the production of nano magnetite very cost effective.

2.2. Preparation of paraffin nano magnetite composites (PNMC)

Synthesized nano magnetite was stabilized by oleic acid to prevent conglomeration of the particles. Oleic acid also served as an emulsifier to obtain more homogenous composites [32].

The emulsifier also provides the nano particles to stay in solution and prevents them from settling down during phase change. 1% oleic acid was added to the particles in this process. Fig. 1 shows the production steps of PNMCs with corresponding Scanning Electron Microscope –SEM (Zeiss Supra 55) images of particles. SEM analysis shows that size of nanoparticle starting with 40–75 nm increased at each step as layers were forming around the particles. At the final step, it can be seen that nano magnetite was homogeneously distributed in paraffin structure with particle sizes in the range of 55–120 nm.

PNMCs were prepared by adding nanomagnetite with dispersion technique as shown in Fig. 2. This technique consists of melting, stirring, sonication and solidification. Paraffin was first melted at 45 °C and nano magnetite was then added into the molten paraffin. Nano magnetite was added at concentrations of 10% and 20% by weight. Suspension was stirred by magnetic stirrer at 1000 rpm for 1 h. In the sonication process the suspension was stirred in ultrasonic bath for 2 h at 45 °C. Ultrasonic frequency of 35 kHz is applied in this process for uniform dispersion and avoiding precipitation of nano particles. In solidification step, suspension was poured into a plastic mold.

2.3. Thermal conductivity and diffusivity measurement

Diffusivity and conductivity (DICO) experimental set-up shown in Fig. 3 has been developed by CERTES for determining thermal conductivity and diffusivity simultaneously with a periodical method [28]. DICO has two parallel metal plates, which are made of brass and copper. The set-up is placed in a vacuum chamber connected to a pumping system. The temperature of the first plate (brass) is regulated by a thermoelectric device heated periodically and second plate is in contact with vacuum at ambient temperature. Samples are placed between the metallic plates.