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# Thermal properties of myristic acid/graphite nanoplates composite phase change materials



Şeyma İnce <sup>a</sup>, Yoldas Seki <sup>a, \*</sup>, Mehmet Akif Ezan <sup>b</sup>, Alpaslan Turgut <sup>b</sup>, Aytunc Erek <sup>b</sup>

<sup>a</sup> Dokuz Eylul University, Department of Chemistry, Buca-İzmir, Turkey
<sup>b</sup> Dokuz Eylul University, Department of Mechanical Engineering, Buca-İzmir, Turkey

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## ABSTRACT

Myristic acid-graphite nanoplates (MA/Gr) composite phase change materials were prepared and thermal properties at various Gr loadings, 0.5%, 1% and 2%, were investigated. Melting and freezing temperatures, latent heats of melting and freezing, the extent of supercooling and the crystallization fraction were obtained with respect to the Gr loadings. It is observed that the Gr loading does not affect the crystallization fraction, but decreases the extent of supercooling. The effect of Gr loading on thermal stability and functional groups of myristic acid was determined by thermogravimetric and Fourier transform infrared analyses, respectively. Thermal conductivity of Myristic acid increased by 8%, 18% and 38% after Gr loadings of 0.5%, 1% and 2% into MA, respectively. Thermal cycling test was also conducted at various thermal cycles (1, 10, 40, 70 and 100 cycles). Repeated melting/freezing cycles have no significant effect on the thermal properties and chemical stability of MA/Gr composites.

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## 1. Introduction

Sustainability is one of the big challenges for using the environmental friendly energy resources, such as wind or solar energy, in industrial or domestic applications. In the case of solar energy, thermal energy storage (TES) is a key technology for reducing the mismatch between energy supply and demand for heating or cooling applications [1,2]. Solar energy can be charged while the energy sources are widely available (i.e. daytime), and then the stored energy can be discharged when the sources are limited (i.e. night time). This method can provide sustainable energy usage. Two types of TES methods are commonly in use for heating, ventilation, and air conditioning (HVAC) applications; sensible heat TES and latent heat TES. In comparison with the former one, latent heat TES (LHTES) can store great amount of thermal energy in a narrow temperature band [2,3].

Performance of a LHTES system is mainly designated by the design of a heat exchanger, thermal characteristics of the phase change material (PCM) and working parameters. Even though the design and working parameters significantly affect the rate of heat transfer for a particular LHTES, developing a new PCM with enhanced thermal properties will directly improve the performance

of a current system. In recent years, numerous studies have been conducted in order to increase some critical thermal properties of PCMs which are currently in use. According to Sharma et al. (2009) fatty acids are the most appropriate candidates as PCM, since they are cheap, widely available, thermally stable, mildly corrosive and most importantly they are not harmful for the nature [4]. However, the major drawback of fatty acids is to have lower thermal conductivity values [5]. Consequently, researchers try to overcome this drawback and improve the thermal conductivity of these substances with the aid of some novel additives. Different types of fatty acids were investigated as PCM for thermal energy storage. Hasan (1994) emphasized that myristic acid, palmitic acid and stearic acid are suitable materials for domestic water heating systems [6]. Sari and Karaipekli (2012) prepared fatty acid esters-based composite PCMs for thermal energy storage [7]. They observed that erythritol tetrapalmitate (ETP) and erythritol tetrastearate (ETS) are suitable candidates for thermal energy storage applications in buildings. They also added expanded graphite to increase thermal conductivity. Sari and Kaygusuz (2001) stated that myristic acid is a suitable PCM for energy storage for domestic solar water heating systems [8]. They also decided myristic acid has a suitable melting point of 49-51 °C and a high latent heat of 204.5 kJ/kg. Fauzi et al. (2013) identified myristic acid and palmitic acid as eutectic PCMs [9]. Recently, there is an increasing trend to use carbon-based materials into conventional PCMs in order to improve the thermal conductivity and shape stability. Mehrali et al. (2013a) investigated the palmitic acid/





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<sup>\*</sup> Corresponding author. Tel.: +90 232 3018656. *E-mail address:* yoldas.seki@deu.edu.tr (Y. Seki).

graphene oxide composite PCM. According to their findings, the thermal conductivity value of composite PCM are more than three times higher than the pure one, for both molten and solid states [10]. As a subsequent work, Mehrali et al. (2013b) applied graphene nano-platelets into palmitic acid to provide shape stability and enhanced thermal conductivity [11]. Based on the literature survey, there is no study on thermal properties, such as phase change temperatures, phase change enthalpies, the extent of supercooling and thermal conductivity, of Gr loaded myristic acid phase change materials.

In this study, we aimed to increase thermal conductivity of myristic acid, without any changes in the major properties such as melting and freezing temperatures, latent heats of melting and freezing of myristic acid, by loading graphite nanoplates (Gr) at different ratios (0.5%, 1% and 2%). Besides, the variations in the chemical and thermal stabilities of MA with loading of graphite nanoplates into MA were intended to examine during the thermal cycling process. For this purpose, myristic acid/graphite nanoplates (MA/Gr) composite was prepared and examined in terms of thermal conductivity, melting/freezing temperatures, and latent heat values of melting and freezing. The characterization of MA/Gr composites was carried out by using Fourier transform infrared spectroscopy (FT-IR), Differential scanning calorimetry (DSC). The chemical and thermal stabilities of MA/Gr composite PCMs were investigated at various thermal cycles (1, 10, 40, 70 and 100 cycles).

#### 2. Sample preparation and measurement methods

#### 2.1. Materials

Myristic acid (MA) was used as PCM in the preparation of the composite PCMs. The MA, with melting temperature range of 53–56 °C, has 98% purity. It was purchased from Alfa Aesar and used without further purification. Gr was used as an additive to improve the thermal properties of the MA. In the current study, Gr (GRAFEN<sup>®</sup>-iGP2) was obtained from Grafen Chemical Industries Company (Ankara, Turkey). The particle size, thickness and surface area of the Gr is 5  $\mu$ m, 5–8 nm and 120–150 m<sup>2</sup>/g, respectively.

### 2.2. Preparation of MA/Gr composite PCMs

Myristic acid-based composite PCM was prepared by adding Gr into molten MA. In order to examine the influence of Gr additive on the thermal conductivity of MA, the mass ratio of the Gr in the composite was varied to be 0.5, 1 and 2%. First, MA was heated to 60 °C in an incubator and Gr was added into liquid MA. The mixture was subjected to an ultrasonic homegenizator (Misonix, Sonicator 3000) for approximately 2 min to procure homogeneous distribution.

## 2.3. Analysis methods

TGA Analysis was operated by using Perkin–Elmer Diamond TG/ DTA Analyzer. The analysis was made between 25 and 600  $^{\circ}$ C at a heating rate of 10  $^{\circ}$ C/min under nitrogen atmosphere.

Measurements of phase change temperatures ( $T_m$  and  $T_f$ ) and latent heat values of melting ( $\Delta H_m$ ) and freezing ( $\Delta H_f$ ), for pure MA and the MA/Gr composites with different mass fractions were carried out with a differential scanning calorimetry (DSC; Perkin Elmer–Diamond). Samples between 5 and 10 mg were placed in an aluminum pan and sealed. The samples were scanned from 45 to 65 °C at the heating rate of 1 °C/min under nitrogen atmosphere. Then, the samples were held for 1 min at 65 °C. After cooling process from 65 to 45 °C at 1 °C/min, specimens were held for 1 min at 45 °C.

Fourier transform infrared spectroscopy (FTIR) analysis was carried out by using Perkin Elmer Spectrum BX-II FTIR spectrometer. After drying and grinding process of MA/Gr composite samples, 1 mg of MA/Gr was mixed with approximately 100 mg of high purity infrared-grade KBr. Then the mixture was compressed into pellets. FT-IR spectra of MA/Gr composite PCMs were recorded in between 4000 and 400 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> and 25 scans.

## 2.4. Thermal cycling test

Thermal reliability of MA/Gr composite PCMs was investigated by the thermal cycling tests via DSC. The variations in latent heat values and phase change temperatures were determined as a function of thermal cycling number. At the end of 10, 40, 70 and 100 thermal cycles, the chemical and thermal stabilities of MA/Gr composite PCMs were investigated by DSC and FT-IR analyses. DSC analyses were performed with a scan rate of 5 °C/min and for a temperature range between 45 °C and 65 °C under a constant stream of nitrogen.

#### 2.5. Measurement of thermal conductivity of MA/Gr composites

In the current study,  $3-\omega$  thermal conductivity measurement was utilized to determine the thermal conductivity of the molten PCMs. The method originates from conventional hot-wire



Fig. 1. Functional groups of pure MA and MA/Gr composites.

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