



Research Paper

Improving thermal characteristics and stability of phase change material containing TiO₂ nanoparticles after thermal cycles for energy storage



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HIGHLIGHTS

- Thermal characteristics and stability of TiO₂/paraffin with surfactant were improved.
- Thermal conductivity of TiO₂/paraffin/SSL composite (3 wt%) was increased 47.85%.
- TGA results showed that thermal stability of the nanocomposite with SSL was improved.
- There is no significant variations in thermal properties of nanocomposites after thermal cycles.
- Latent heat of composites showed an optimal value with increasing TiO₂ mass ratio.

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ABSTRACT

In this study, thermal characteristics and stability of TiO₂/paraffin composites with and without sodium stearyl lactylate (SSL) as a surfactant were evaluated. The TiO₂/paraffin composites with 0.5, 0.7, 1, 2, 3, 4 wt% were prepared in two series, with and without the SSL. FE-SEM micrographs illustrated that adding the surfactant to the paraffin matrix could improve the dispersion of the nanoparticles efficiently. DSC analysis showed that the maximum latent heat of 165.1 and 167 J/g for nanocomposites occurs in 1 and 3 wt% for samples of TiO₂/paraffin without and with the SSL, respectively. The thermal conductivity coefficient was enhanced with adding nanoparticles, considerably. An increase of 47.85% in the thermal conductivity was found for the paraffin containing 3 wt% of nanoparticles with the surfactant. TiO₂/paraffin composite with 3 wt% was chosen as an optimal sample to consider the physical and thermal stability after several thermal cycles. TGA thermograms showed that thermal stability of the TiO₂/paraffin/SSL composite (3 wt%), as compared to pure paraffin and TiO₂/paraffin (3 wt%), was improved. It was found that the melting temperature and the latent heat of nanocomposites had inappreciable changes after several thermal cycles. The thermal conductivity of the nanocomposites approached the initial thermal conductivity of the pure paraffin, after several thermal cycles, while a marked decrease in thermal conductivity of pure paraffin was apparent.

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1. Introduction

Energy storage is a useful tool for increasing energy efficiency and energy saving. The efficient use of the energy and utilization of the renewable energies increase because limited fossil fuel resources and environmental pollutions created by this type of fuel. Solar energy is one of the types of renewable energy. The non-uniform and time-dependent nature is the main obstacles in the use of solar energy. The intensity of sunlight varies during the day and does not exist energy during the evening. The energy

storage in various forms such as thermal, chemical and mechanical during the day can overcome these problems [1].

Phase change materials (PCMs) are considered as one of the best energy storage methods. The paraffins are selected as a suitable candidate for use in thermal energy storage systems because of the appropriate latent heat, the good stability and the low cost at the specific temperature range [2]. Low thermal conductivity of the paraffins is one of the limited properties of them and reduces their performance. For this reason, in the recent years many efforts were conducted to improve the thermal conductivity of the phase change materials, particularly paraffin [3,4]. Increasing the thermal conductivity causes to increase the heat transfer rate in the phase change materials and improve the energy storage efficiency. The thermal conductivity can be improved by using the metal fins,

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the porous matrix and the fibrous materials [5–8]. These methods are not desirable due to increase in weight and volume of the energy storage devices. Dispersing fine particles with high thermal conductivity in the phase change material has been introduced as a convenient method to increase the effective thermal conductivity. The thermal conductivity of PCM composites has been improved by adding the low amount of the metal or the metal oxide nanoparticles to PCMs in some studies [9,10].

Sohan et al. [11] reported an enhancement of 48% and 60% in the thermal conductivity for the paraffin containing 10 wt.% and 20 wt.% of iron nanoparticles, respectively. In literature, several studies show that there is not necessarily a linear relationship between the mass fraction of nanoparticles and the improvement in the thermal conductivity [12,13].

Teng and Yu [14] studied on thermal storage properties of the paraffin including different metal oxide nanoparticles. Alumina, Titania, silica and zinc oxide were dispersed into three concentrations of 1.0, 2.0, and 3.0 wt%. Their results showed that TiO₂ has more effect on the heat conduction performance and the thermal storage characteristics of the paraffin. The highest decrement ratio of the melting latent heat is only 0.46%, compared with that of the pure paraffin.

Harikrishnan and Kalaiselvam [15] investigated the thermal characteristics of palmitic acid contain TiO₂ during energy storage and release processes. The results showed, the melting and solidification times of composites were reduced by 6.43, 14.62, 21.05% and 6.18, 12.37, 20.11% for 0.1, 0.2 and 0.3 wt% of TiO₂ respectively.

In the most previous studies the effect of nanoparticles on the thermal properties of the PCM has been investigated, while stability and the dispersion of nanoparticles in the PCM matrix had not been considered. Wang et al. [16] synthesized anatase titanium oxide nanoparticles in 20 nm of diameter and examined the influences of dispersing of TiO₂ on the thermal properties of TiO₂/paraffin composites without surfactant. The dispersion of TiO₂ nanoparticles in the samples were examined using the polarizing optical microscope (POM). But the sustainability of the produced samples after the heating cycles has not been evaluated. Motahar et al. [17] performed laboratory studies on the thermal and the rheological properties of the n-octadecane with the TiO₂ nano-additive. The maximum improvement in thermal conductivity occurred in 3 wt% of nano-particle and the reduction was seen greater than 4 wt%. They discussed more about the rheological properties of PCM composites in their study.

Ho and Gao [18] prepared the composite by dispersing Al₂O₃ nanoparticles with 5 wt% and 10 wt% in n-octadecane by means of non-ionic surfactant. Thermo physical properties of samples, such as latent heat of fusion, density, dynamic viscosity, and thermal conductivity, were investigated experimentally. The amount of nanoparticles and surfactant are the affecting factors on the stability of nanoparticles in the PCM matrix.

Nourani et al. [19] studied thermal behavior of paraffin containing Al₂O₃ nanoparticles. Sodium stearoyl lactylate (SSL) has been used as the surfactant to increase stability of Al₂O₃/PCM samples. Their results showed that thermal conductivity of composite is higher than that of pure PCM at phase change temperature of sample, while heat fusion and melting temperature of obtained composite has no significant variations. In this study, stability of nanoparticles dispersion in the obtained nanocomposites and their thermal properties has not been investigated after thermal cycles.

A review of the previous research shows that there is a lack of studies regarding the effect of adding nanoparticles to paraffin on the thermal properties of the composites, stability and dispersion of nanoparticles in the paraffin matrix. Therefore, in this work, titanium oxide nanoparticles were added to paraffin in a wide range of mass fractions, in the presence and the absence of sodium stearoyl lactylate (SSL) as an effective surfactant. In addition, the thermal

properties of composites, such as melting temperature, latent heat and thermal conductivity, were evaluated. Also, the changes in the thermal properties were considered after the alternative thermal cycles. The thermal stability of the samples was investigated by the thermogravimetry analysis. The physical stability and the dispersion of the nanoparticles in the composites were evaluated for the first time using the scanning electron microscopy, after and before the alternative thermal cycles.

2. Materials and methods

2.1. Materials

Paraffin with the melting point about 54–58 °C (Merck, Germany) as phase change material. Sodium stearoyl lactylate (SSL) with the chemical formula C₂₄H₄₃NaO₆ was used as a surfactant were purchased from Merck Company (Germany). Titanium oxide nanoparticle was purchased from PlasmaChem Company (Germany) with average particle size of 5–20 nm and 50 ± 10 m²/g of specific surface area.

2.2. Preparation of the samples

Paraffin nanocomposites containing different mass fractions of the titanium oxide nanoparticles were prepared; weighted amount of nanoparticles was added to liquid paraffin in several steps and used magnetic stirrer and ultrasonic processor (Hielsher up 400 s) alternatively for appropriate dispersion in samples. Two series of samples; I) without the SSL and II) with the SSL as a surfactant with mass ratio 1:4 for SSL/TiO₂, were prepared in different mass fractions of TiO₂ 0, 0.5, 0.7, 1, 2, 3 and 4 wt%. Mass ratio of SSL to TiO₂ was selected based on experimental observations in three mass ratio 1:3.5, 1:4 and 1:4.5.

2.3. Characterization

Differential scanning calorimetry (DSC), Manufacturing BAHR Thermoanalyse GmbH Germany with the relative standard uncertainty of ±7% was used to determine the thermal characteristics of the samples such as melting point and the latent heat under nitrogen, with heating rate of 5 °C/min in the range temperature of 30–90 °C. Thermal stability in measurable temperature range was performed by Thermal Gravimetry Analysis (TGA). Thermal analyzer TGA/DTA Pyris Diamond model was used under nitrogen from room temperature to 450 °C temperature for thermal analysis of the samples. The relative standard uncertainty of thermal analyzer is ±10%. The Field-Emission Scanning Electron Microscope (FE-SEM), Mira 3-XMU model was used to evaluate the dispersion of nanoparticles in phase change material. The thermal conductivity was measured by KD2 Pro Manufacturing Co. Decagon America with the relative standard uncertainty of ±3%.

3. Results and discussion

3.1. Evaluation of dispersion of nanoparticles in the samples

Fig.1 shows FE-SEM images of 1 wt% and 3 wt% of TiO₂/PCM samples with (A, B) and without (a, b) the surfactant of SSL. As seen in the Figs. 1-a and -b, the nanoparticles in the paraffin without surfactant tended to aggregate together and dispersion of nanoparticles was less significant, while in the presence of SSL (Fig. 1-A and -B), dispersion of the nanoparticles appropriately occurred due to reduction in the surface energy of the particles.

It should be noted that TiO₂ nanoparticles in mass ratios up to 1 wt% are barely visible in the microscopic images. Wang et al.

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