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Research paper

Easy and industrially applicable impregnation process for preparation of diatomite-based phase change material nanocomposites for thermal energy storage

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HIGHLIGHTS

- Diatomite-based phase change material nanocomposites were prepared.
- An easy and industrially applicable impregnation process was developed.
- Influence of diatomite: PCM mass ratio on thermal properties reported.

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ABSTRACT

The high porosity, high oil and water absorption capacity and low density of diatomite make it ideal for industrial applications. The porous structure of diatomite protects phase change materials (PCMs) from environmental factors as a supporting matrix and phase changes occur in nanopores of diatomite. Previous research on diatomite/PCMs composites aimed optimal composite preparation but many methods were feasible only in laboratory scale. In large scale industrial fabrication, easy, continuous and steady state methods are need to be performed. The main purpose of this study was to prepare leakage-free, thermally stable nanocomposite PCMs (nanoCPCMs) by an easy, continuous and steady state method for high temperature thermal energy storage applications. A series of nanoCPCMs with different paraffin:diatomite mass ratios were prepared. The properties of nanoCPCMs have been characterized via scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The leak (exudation) test was performed on prepared composites at higher temperatures (95 °C) in comparison with literature. As the optimum composite for thermal energy storage applications, thermal reliability of nanoCPCM was evaluated after 400 cycles of melting and freezing. NanoCPCM melted at 36.55 °C with latent heat of 53.1 J/g.

1. Introduction

The diatomaceous earth (diatomite) consists of the mineralised exo-skeletons of diatoms, which are microscopic (~1–500 mm in length) single-celled algae with characteristic rigid cell walls (frustules) composed of amorphous silica. They are ubiquitous organisms found in a wide variety of habitats and are thought to be responsible for up to 25% of the world's net primary production of organic carbon [1]. There are currently estimated to be over 100 000 different species, classified by their unique frustule morphologies. The frustule is created with 3D precision of tens of nanometers, in a hierarchical manner, and with multifunctional properties [2,3]. Frustules display an unparalleled diversity in structure and morphology, and this may be exploitable in nanotechnological applications [4]. The constant “rain” of dead diatom frustules to the bottom of the ocean and lake results in the accumulation in large fossil deposits of amorphous polymerized with silicic acid. These deposits are mined and used, for example, as an insulating material, abrasive, filter, paint filler, and pesticide carrier. The high porosity, high oil and water absorption capacity and low

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density of diatomite make it ideal for industrial applications; however, its full potential has far from been realized [5]. This biogenic source has a great potential because of its abundance and an inexpensive cost [6]. Research about preparation of PCM composites with diatomite draws attention in recent years. The high porosity and surface area of tubular frustules of diatomite are important in the preparation of composites. PCMs are moved into nanopores of diatomite in the course of preparation of composites and phase changes occur in these nanopores. Surface area increases as in microencapsulation which may lead to better heat transfer characteristics. The porous structure of diatomite also protects PCMs from environmental factors as a supporting matrix. Diatomite is biocompatible, do not cause harm to health, and do not cause environmental pollution. As a result, it has been stipulated that prepared composites can be used safely in many applications, which will provide significant energy savings.

Nomura et al. (2009) fabricated erythritol/diatomite composite PCM with onset melting temperature of 116.5 °C and latent heat of 237.4 J/g [7]. Li et al. (2011a) and Li et al. (2011b) prepared and characterized shape-stabilized fatty acids/diatomite composite PCMs [8,9]. Li et al. (2014) used three grades of diatomite particles, DP1, DP2 and DP3 to produce phase change material composites. This research group successfully loaded 47.9 wt% RT 21 into diatomite nanotubes [10]. The composite as form-stable thermal storage material melted at 15.7 °C with a latent heat of 63.98 J/g. Karaman et al. (2011) prepared polyethylene glycol (PEG)/diatomite composites with melting temperature and latent heat of 27.7 °C and 87.09 J/g, respectively [11]. Jeong et al. (2013a) used n-hexadecane, n-octadecane and paraffin wax as PCMs and prepared of PCM/diatomite composites using vacuum impregnation. The melting point of pure paraffin wax and paraffin wax/diatomite composite was 57.09 and 54.24 °C, respectively. The latent heat storage of paraffin wax/diatomite composite was 61.96 J/g [12]. Jeong et al. (2013b) enhanced thermal properties of composites of Jeong et al. (2013a) using exfoliated graphite nanoplatelets [13]. Sun et al. (2013) prepared a composite paraffin-based PCM by blending composite paraffin and calcined diatomite through the fusion adsorption method. The phase-transition temperature and the latent heat of the composite PCMs were 33.04 °C and 89.54 J/g, respectively [14]. Thermal energy storage cement-based composite (TESC) was developed by incorporating paraffin/diatomite composite PCM in Xu and Li (2013). Paraffin/diatomite composite PCM had melting temperature and latent heat of 41.11 °C and 70.51 J/g, respectively [15]. All these research suggest diatomite as an applicable, successful supporting matrix for PCMs.

The selection of suitable PCM plays an important role in terms of phase transition temperature, thermal efficiency, economic feasibility and utility life [16]. Paraffin is one of the main phase change materials (PCMs) for thermal energy storage systems and proved itself in energy storage applications. However, studies on preparation of diatomite/paraffin composites propose complicated procedures including pre-treatments to diatomite (heating to remove any water in pores or calcining at high temperatures) and paraffin (melting) before impregnation, gradually adding paraffin and diatomite, heat-mix runs during preparation of composites, impregnation in electric furnaces with vacuum pumps or vacuum impregnation on hot plate. Researches using all these treatments and methods aim optimal composite preparation but many processes are feasible only in laboratory scale. In large scale industrial fabrication, easy, continuous and steady state methods are need to be performed. Here, a direct impregnation method was proposed without any pre-treatment step which is easy and practicable in large scale applications. In addition, the leak (exudation) test was performed on prepared composites at higher temperatures (95 °C) in comparison with literature (e.g. 60 °C in Li et al. (2014) [10]). In this study, a series of leakage-free (at 95 °C), thermally stable diatomite/phase change material nanocomposites (nanoCPCMs) were prepared for thermal energy storage applications. The structure and properties of nanoCPCMs have been characterized via scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

2. Experimental

2.1. Material

Paraffin 42–44with purity above 98.0% (Merck, Germany; melting point; 42–44 °C) was used without further treatment as phase change material. Diatomite was used as supporting material for PCMs. The raw diatomite samples used in this study were taken from an abandoned diatomite quarry close to Nigde city, Turkey (38.23969°, 34.47785°) (Fig. 1). Diatomite in rock form was ground to particle size less than 250 μm by cross beater mill (SK100, Retch, Germany). The specific surface area of raw diatomaceous earth used in this study measured by nitrogen gas sorption analysis according to Brunauer, Emmett, and Teller (BET) theory with Micromeritics Gemini VII. The BET surface area of raw diatomaceous earth was 72 $m^2\ g^{-1}$. Macro pore volume and mean macropore diameter measured by mercury intrusion porosimetry (Quantachrome Corporation, Poremaster 60) were 0,42 $cm^3\ gr^{-1}$ and 1.2 μm, respectively. The chemical constituent of the raw diatomite sample was determined by XRF analysis, the results was given in Table 1.

No other treatments such as purification or heating was applied on received diatomite samples to avoid complicating the process although effects of purification and heat treatment on pore structure and composition of diatomite are known [17].

Diatomaceous earth deposits may contain opal, carbonate and detritic minerals due to their origin such as silica rich postvolcanic springs and silicate alteration [18]. In order to dissolve undesirable elements, the diatomaceous earth can be treated with acid solutions ([17,19]. Calcination also affects pore growth but decreases surface area [17]. Purification, sintering and processing may produce purer diatomaceous earth but all these processes are time-consuming, need qualified personel, cause hazardous chemical usage, and may be economically improper in larger scales in industrial applications.

Fig. 1. Picture of abandoned quarry where diatomite was taken for this study.