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An ultrasonic-assisted direct impregnation method for preparation of diatomite-based phase change material nanocomposites

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Diatomite is an important natural raw material and the nanotube structures of diatomite are important in the preparation of composites. The nanotube structure of diatomite protects the phase change material from their environment. This work aims to develop leakage-free, thermally stable natural diatomite/phase change material nanocomposites (NanoCPCMs) by the ultrasonic-assisted direct impregnation method for thermal energy storage applications. This work uses diatomite and paraffin as the supporting and phase change materials, respectively. The diatomite-based form-stable nanoCPCMs were analyzed via scanning electron microscopy and differential scanning calorimetry. Paraffin leakage of nanoCPCMs was determined at 95˚ C by water bath for 45 minutes. At the end of test, thermal stability at 95˚ C evaluated with DSC analysis. The results show that the leakage-free NCPCMs were synthesized successfully for thermal energy storage applications.

Keywords: phase change material, diatomite, paraffin, thermal energy storage, latent heat

INTRODUCTION

Diatomite is an important natural raw material with significant reserves in Turkey (44.2 million tons). Although we have large reserves of this raw material, our use of diatomite is insufficient. The responsible use and evaluation of natural minerals has the potential to significantly augment the national economy. For the evaluation of natural reserves such as diatomite in recent years, the preparation of diatomite/phase change material nanocomposites (NanoCPCMs) research has gained momentum [1, 2, 3, 4]. The nanotube structures of diatomite are important in the preparation of composites. PCMs are moved into nanotubes in the construction of composites; channels and phase changes occur in these tubes and surface area increases as in microencapsulation which may lead to better heat transfer characteristics. The nanotube structure of diatomite also protects the sensitive materials from their environment [1].

Tang et al. (2015) prepared shape-stabilized fatty acid eutectics and diatomite composites by absorbing liquid fatty acid eutectics into diatomite [2]. The lauric acid (LA)/diatomite composite phase change materials (PCMs) were prepared using a direct impregnation method by Fu et al. (2015). The melting and freezing temperatures of composite PCM were 40.9 °C and 38.7 °C, respectively.

In Li et al. (2011), a series of binary fatty acids were absorbed in diatomite by the fusion adsorption method to prepare shape-stabilized PCMs. The microstructure and thermal property of the prepared shape stabilized PCMs were tested.

Paraffins can be used as energy storage materials due to their availability in a large temperature range [5]. In our previous studies we developed an easy and industrially applicable impregnation process for preparation of diatomite-based phase change material nanocomposites for thermal energy storage applications [1]. For this purpose, a series of nanoCPCMs with different paraffin: diatomite mass ratios were prepared. Proposed method for preparation of diatomite-based phase change material nanocomposites can be used in large scale industrial fabrication for latent heat thermal energy storage systems applicable at high temperatures [1]. In this study we add two new steps including ultrasonic treatment before and during impregnation in order to increase efficiency. To the best of our knowledge, among all available phase change material/diatomite studies, no study has been reported on the preparation of NanoCPCMs with an ultrasonic treatment before and after impregnation. In this study, a thermally stable diatomite/phase change material nanocomposite (NanoCPCMs) was prepared for thermal energy storage applications.

The properties of composites have been characterized by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).

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EXPERIMENTAL

Paraffin 42–44 with 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. Raw diatomite was in rock form including numerous consolidated individual shells. In order to separate each shell, raw diatomite was treated with ultrasonic probe in distilled water for 10 mins with 100% amplitude-1 cycle settings (UP400S, Hielscher, Germany).

The composite samples used in this work were manufactured by the direct impregnation method with ultrasonic bath. During the preparation of composites; firstly paraffin and diatomite were heated with a bain-marie method at 60 °C until the PCM was completely melted and mixed with hand. In the next step stirring and heating process were continued on a magnetic stirrer for 30 minutes. The final mixture was ultrasonically agitated for 30 minutes and at the end of process, composites were dried in an open air at 40°C for 48 h.

The morphological analysis of composites were analyzed using SEM (Zeiss EVO40). All samples were coated with a layer of gold prior to the observation. Thermal properties of core material and composites such as melting, crystallizing points and latent heats were measured by differential scanning calorimetry (DSC, Perkin Elmer Diamond) with a heating/cooling rate of 5˚C/min in the range of 10–60˚C. During DSC analysis, about 5 mg of sample was used.

In order to determine the leakage behavior and thermal properties of NanoCPCMs, PCMs and NanoCPCMs were heated to 95° C in a water bath for 45 minutes. At the end of 45 minutes, DSC analyses were performed.

RESULTS AND DISCUSSION

In order to analyse the morphological properties of NCPCMs SEM analysis was carried out, as reported in the micrograph (Fig.1). It can be seen that the paraffin is completely dispersed into the pores of diatomite used as the supporting material. Treatment with ultrasonic probe had a destructive effect on diatom frustules. However, porous frustule walls protected paraffin from environmental factors as a supporting matrix and phase changes occurred in nanopores of diatomite frustule walls even though the whole frustule structure was damaged due to sonication.

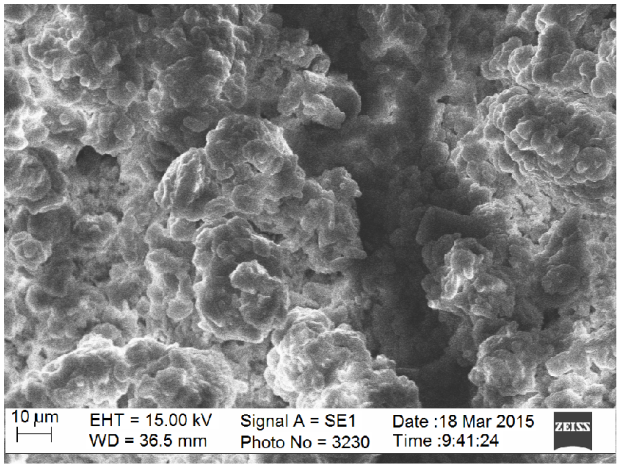


Fig.1. SEM images of CPCM

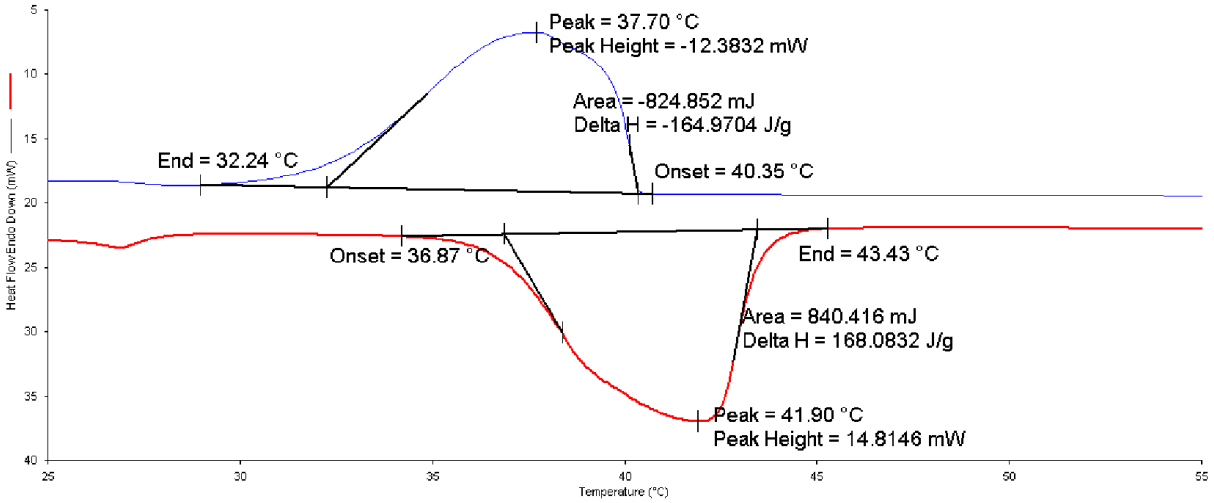
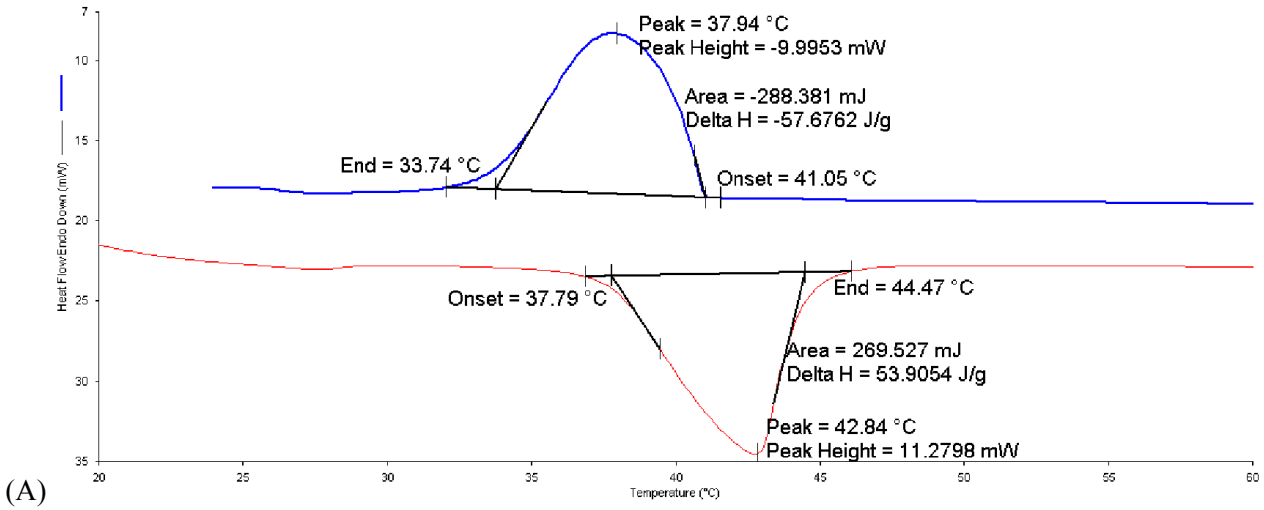


Fig.2. DSC Curves of paraffin

In order to investigate the presence of the PCM in the diatomite frustules, DSC analysis was carried out. The DSC curves of the paraffin and prepared NanoCPCMs are shown in Fig.2 to Fig.4. The

detailed melting and freezing temperatures and latent heat are presented in Table 1. The melting and freezing temperatures and latent heats of paraffin/diatomite nanocomposite were measured as 37,79 °C and 41,05 °C as well as 53,90 J/g and 57,67 J/g respectively. Based on obtained DSC results the prepared paraffin/diatomite composite could be a good alternative for solar thermal applications according to our previous studies for the studied temperature ranges [1].

In order to determine the leakage behavior and thermal stabilities of NanoCPCMs, PCMs and NanoCPCMs were heated to 95° C. Fig.4 shows DSC curve of NanoCPCMs treated at 95° C after 45 min. The DSC results are summarized in Table 1. We recommend prepared nanocomposites for thermally stable and leakage-free applications above 95 °C. The comparison of the energy storage capacity of NanoCPCMs prepared in this study and nanocomposites prepared in our previous study [1] are given in Table 2. Ultrasonic treatment didn't reduce paraffin content in diatomite mineral even though the whole frustule structure was damaged due to sonication. Pores on remaining walls of frustules from the whole structure were enough to protect the phase change material from environment. We recommend paraffin/diatomite composites prepared by an ultrasonic-assisted direct impregnation method as thermal energy storage materials.



(A)

Fig.3. DSC Curves of nanoPCMs

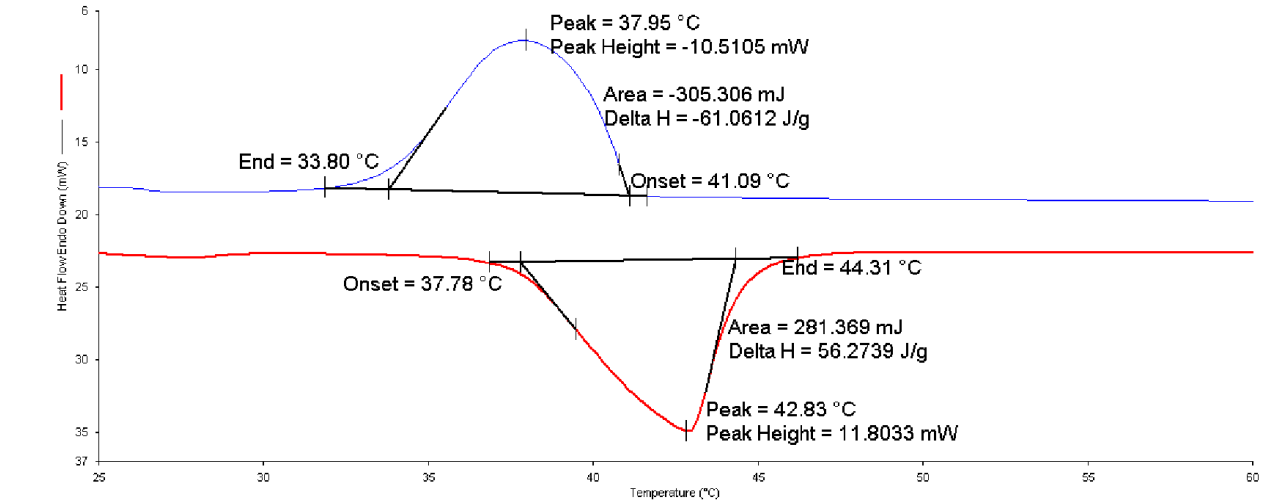


Fig.4. DSC Curves of nanoPCMs (95°C)

Table 1. Thermal properties of paraffin and microPCMs

Sample	Tom(^{o}C)	Tpm(^{o}C)	Tem(^{o}C)	Hm (J.g^{-1})	Toc(^{o}C)	Tpc(^{o}C)	Tec(^{o}C)	Hc (J.g^{-1})
paraffin	36,87	41,90	43,43	168,08	40,35	37,70	32,24	-164,97
NCPCM	37,79	11,27	44,47	53,90	41,05	37,94	33,74	-57,67
NCPCM(95^{0}C)	37,78	11,80	44,31	56,27	41,09	37,95	33,80	-61,06

T_{om}: Onset melting temperature of DSC curve. T_{oc}: Onset crystallizing temperature of DSC curve.
T_{pc}: Crystallizing peak temperature of DSC curve. T_{pm}: Melting peak temperature of DSC curve.
T_{ec}: Endset crystallizing temperature of DSC curve. T_{em}: Endset melting temperature of DSC curve.
H_c: Crystallization enthalpy of PCMs in DSC curve H_m: Melting enthalpy of PCMs in DSC curve.

Table 2. Comparison of thermal properties prepared diatomite/ paraffin composite with our previous study

Sample	Method	Tom (^{o}C)	Hm (J.g-1)	References
Diatomite/paraffin nanocomposite	Without ultrasonic treatment	36.55	53.15	Our previous study[1]
Diatomite/paraffin nanocomposite	With ultrasonic treatment	37.79	53.90	This study

T_{om}: Onset melting temperature of DSC curve.
H_m: Melting enthalpy of PCMs in DSC curve.

CONCLUSIONS

In this study paraffin/diatomite composite was prepared by an ultrasonic-assisted direct impregnation method as thermal energy storage materials. In the composites, the paraffin was used as PCMs for thermal energy storage, and the diatomite was used as supporting material. The structure and thermal properties of prepared nano composites have been characterized by SEM and DSC. The results indicate that treatment with ultrasonic probe had a destructive effect on diatom frustules. However, porous frustule walls protected paraffin from environmental factors as a supporting matrix and phase changes occurred in nanopores of diatomite frustule walls even though the whole frustule structure was damaged due to sonication. The ultrasonication treatment using different amplitude and cycle settings in order to protect the whole structure of frustules will be a subject of future research. Obtained from DSC results, the melting and freezing temperatures of paraffin/diatomite composite are 37,79 °C and 41,05 °C and the latent heats of paraffin/diatomite are 53,90 J/g and 57,67 J/g. We recommend paraffin/diatomite composites prepared by an ultrasonic-assisted direct impregnation method as thermal energy storage materials.

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