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Preparation of composite paraffin / mineral powder as a novel form-stable phase change material for thermal energy storage

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***Abstract*— The aim of this research is to prepare a novel form-stable composite phase change material (PCM) for the latent heat thermal energy storage in buildings, by dispersion of expensed clay into molted paraffin through the technique of dispersion. The structure, thermal properties, thermal reliability and thermal conductivity of the composite PCM were determined by scanning electron microscope (ESEM), Fourier transformation infrared (FTIR), differential scanning calorimetry (DSC) and hot disk analysis technique. The results show that the composite stabilized form prevents leakage of the material phase change from the matrix. The surface of the clay matrix is completely charged with paraffin by a physical attraction with a mass ratio of 41%. The FT-IR analysis shows that there is no chemical reaction between the matrix and the MCP. From differential scanning calorimetry (DSC) analysis, the melting and freezing temperatures and latent heats of the form-stable PCM were measured as 55,92°C and 56,81°C and -66,42 J/g and 62,91 J/g, respectively. The thermal conductivity of the form-stable PCM composite increased gradually with the content of EG. Thermal conductivity of the material containing 10% EG was 0.55 W/m K. All of the conclusions indicate that the composite has a better thermal conductivity and good thermal and chemical stability.**

***Keywords*— Thermal energy storage, composite phase change materials, expended clay, paraffin, Thermal conductivity enhancement.**

Introduction

Thermal Protection and l insulation are two important problems in many fields such as industry, agriculture and medical. Thermal energy storage (TES) is a simple and effective technique for solution of these problems [1]. Among TES methods, latent heat thermal energy storage using a phase change material (PCM) is preferred due to high storage density and small temperature change from storage to retrieval [2–3]. These two important advantages led to small volume and less heat loss, which attract attention of researchers in many different fields.

Since the 1970s, a number of researchers have tried to apply PCMs into buildings to enhance the thermal comfort of lightweight constructions. Three general methods are proposed for the incorporation of organic PCMs into construction elements such as wallboards, gypsum boards, concrete, and so on [4-5]. The first one is the immersion of conventional wallboards into molten PCMs [6-8]. Although the method is simple and low cost, the impregnated wallboards are inflammable owing to leakage of the liquid PCMs to the surfaces of the wallboards, especially after the PCMs experienced several heating-cooling cycles. The second one is the integration of microencapsulated PCMs with ordinary building materials [9-11]. However, the method suffers from the complicated polymerization processes and the high costs related to the microencapsulation of PCMs [12]. The third one is the incorporation of a kind of shape-stabilized PCMs into building materials, which shape-stabilized PCMs can be prepared by blending PCMs with supporting materials [13-14]. This technique is reported in the literature as the most effective due to having excellent thermal properties but also to have prevented leakage of liquid MCP [15].

This study aimed to prepare the composites of paraffin /expanded clay with varying mass fraction of EG additive to obtain a form-stable composite PCM and to investigate the effect of EG addition on thermal conductivity of form-stable of PCM composite.

I. EXPERIMENTATION

A. *Materials*

Paraffin is made of the alkenes series and belongs to the organic PCMs (Fig. 1a). It has good storage density with respect to mass, as well as melts and solidifies correspondingly with little or no subcooling. Paraffin is not soluble in water and compatible with metals. Expended clay is used as a thermal storage medium. It is reduced to a fine powder in order to increase its capacity for absorption of paraffin (Fig. 1b).

B. *Preparation of PCM/expanded clay*

Before the preparation of the composite, the expanded clay is pounded, reduced to a powder then dried in an oven at 105 ° C for 24h. The procedure of sample preparation consisted of two steps. In the first dispersion step, Paraffin was placed into a water bath at 65 °C. When the paraffin was melted, the expanded clay powder is added in the molten paraffin wax. During this step, the temperature of the mixture is maintained above the melting point of the paraffin wax at 65 °C. In the second solidification step, the mixture is poured into a rectangular mould of the dimensions of 40 x 40x 4 mm^3, and is then allowed to freely crystalline at room temperature (21°C) to form solid composite samples. Complete solidification of the samples took about 1h. Order to improve the thermal conductivity of the composite made of expanded graphite is added with the mass fractions of 10% (Fig. 1c). At the end, the mixture undergoes a uni-axial cold compression.

Fig. 1 Sample images of a) PCM and b) expended clay

C. *Characterization of the form-stable composite PCM*

Laser particle size analyser (Malvern Instruments, Scirocco 2000 A) is used to test the size distribution of expanded clay. Differential Scanning Calorimetry (Mettler Toledo DSC, Co instrument) is used to test the thermal properties of the paraffin and the PCM/ expanded clay composite. The heating rates were 3°C/min in a nitrogen atmosphere from 20°C to 70°C and from 70 °C to 20°C. The morphology of PCMs was observed with a SEM (PHILLIPS ESEM XL 30 model.) at t he acceleration voltage of 20 kV under low vacuum. Infrared spectra of expensed clay and PCM / expended clay are obtained with a Fourier transform infrared spectrophotometer (8001M FTIR). The hot disk thermal constants analyzer (TPS 500, Perkin Elmer) is used in the present study to measure the thermal conductivity of the composite PCM, at room temperature (25°C).

II. TEST RESULTS AND DISCUSSION

A. *Size particles of expanded clay*

The size distribution of expanded clay is shown in Fig. 2 and its size parameter is listed in Table 1. Table 1 shows that the size distribution of expanded clay is between 0, 7 µm and 600 µm and the average size of expensed clay is 89, 717µm. The specific surface area of expensed clay is 367 cm^2 / g. Therefore, expensed clay has good absorption.

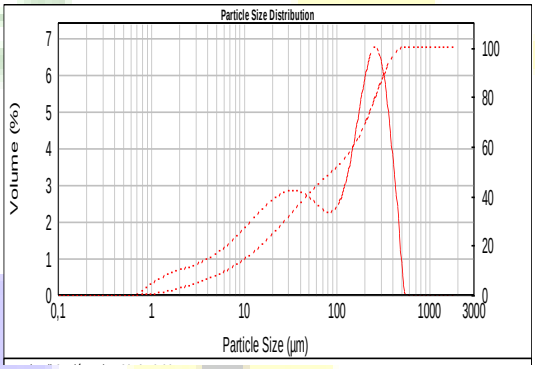

Fig. 1 Size distribution of expended clay

TABLE I
SIZE PARAMTERS OF EXPENSED CLAY

Samples	D_{10}(µm)	D_{10}(µm)	D_{10}(µm)	S/g (cm2/g)
expanded clay	6,594	89,717	327,50	367

Annotation: D50 means the corresponding particle size when the cumulative distribution percentage reaches 50%; D10 means the corresponding particle size when the cumulative distribution percentage reaches 10%; D90 means the corresponding particle size when the cumulative distribution percentage reaches 90%.

B. Microstructure and optimum percentage retained by form-stable composite PCM

SEM images were taken for the expanded clay and PCM / expanded clay, as presented in Fig. 4. It is clearly seen that individual expanded clay has multiple pores and their size distributions of are nearly uniform (Fig. 4a). The microstructure of the composite PCM is similar to that of the matrix sample except that the porous microstructure is thoroughly covered with paraffin as shown in Fig. 4b. The maximum mass percentage of LA absorbed into the pore of EP was determined as 41 wt%. There was no leakage of paraffin from the surface of the composite up to this mass ratio even when the temperature of the form-stable composite PCM was over the melting point of paraffin.

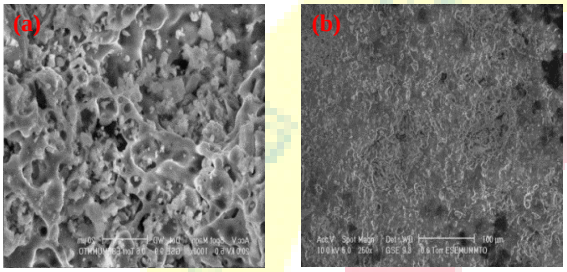

Fig. 3 ESEM images of PCM and PCM composite
a) expended clay, b) PCM/ expended clay

B. FT-IR analysis of form-stable composite PCM

The FT-IR spectrum provides useful information about the interactions between the components of the composite. From Fig. 5, it is obvious that there are principal peaks at the wave number 3458, 1633, 1045 and 773 cm^{-1}, respectively. The absorption band at 3458 cm-1 is the stretching vibration of the functional group of Si-OH. The peaks at 1045 and 773 cm-1 represent the asymmetric stretching vibration of Si-O -Si, and bending stretching vibration of functional group Si-O, respectively. The peak at 1633 cm−1 can be assigned to the vibration of OH.
In composite PCM, new peaks associated with adding of paraffin are present, in addition to peaks of expended clay. The absorption peaks of paraffin at 2917 and 2850 in composite PCM spectra, which signify the stretching vibration of C-H. The peak at 1166 cm-1 corresponds to asymmetric stretching vibration of C = O.

C. Thermal properties of the form-stable composite PCM

Fig. 5 displays the DSC curves of paraffin and PCM/expanded clay composite, respectively. The DSC curve of the composite PCM is similar to that of paraffin, exhibiting two peaks on both heating and cooling curves. The primary peak corresponds to the solid–liquid phase change, whereas the secondary peak occurs at a lower temperature represents the solid–solid phase change. For the paraffin wax that is a mixture of alkanes with different carbon numbers, phase change occurs over a relatively wide temperature span (more than 10°C). The two phases changes temperatures during melting and freezing are found to be nearly 36, 83 and 52, 23°C, respectively, whereas the phases changes temperatures during solidification are around 39,90 and 56, 35°C, respectively. The phase transition of the PCM/expanded clay composite took place in a melting temperature range between 52,23°C and 58,37°C, with 62, 20 J/g of thermal storage capacity, and a freezing temperature range between 56,35°C and 50,26°C, with 62, 98J/g of thermal releasing capacity. The quantity variation of thermal storage capacity and thermal releasing capacity was 0, 78 J/g, indicating the prepared composite exhibited stable heat storage.

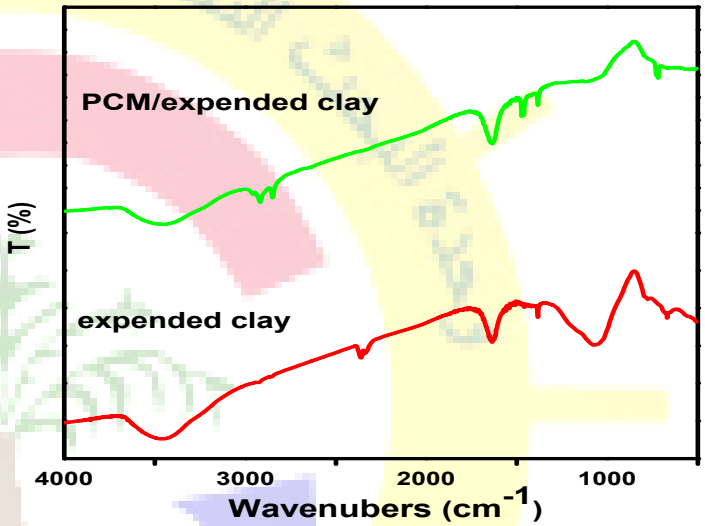

Fig. 4 FTIR analysis of expended clay and PCM/ expended clay composite

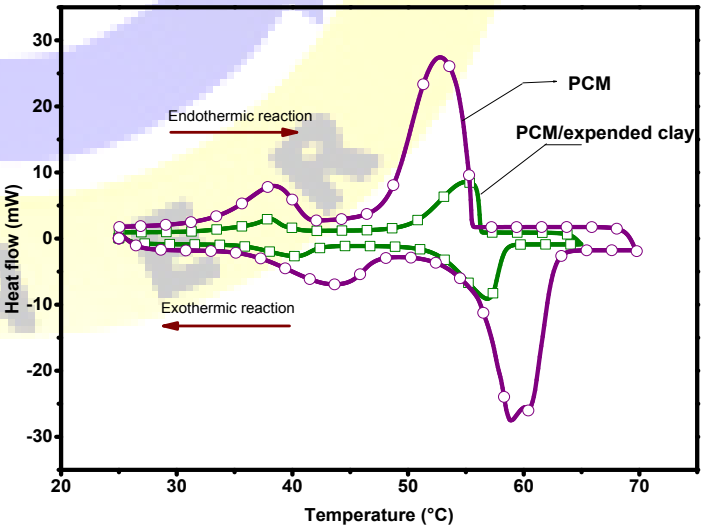

Fig. 5 DSC curves of PCM and PCM/ expended clay composite

D. Thermal conductivity analysis

The thermal conductivity analysis of paraffin, PCM/expended clay and PCM/expended clay composite containing 10% EG is shown in Fig. 6. Their thermal conductivity of materials showed 0, 1716, 0, 26, and 0, 55 W mK^{-1}, respectively. It shows that incorporating PCM into the structure of diatomite improves the thermal conductivity of PCMs. However, the rate of increase of thermal conductivity according to the sample is not high. It can be seen that the thermal conductivity of the PCM composite loaded with EG was 2 times higher than that of the PCM composite without EG.

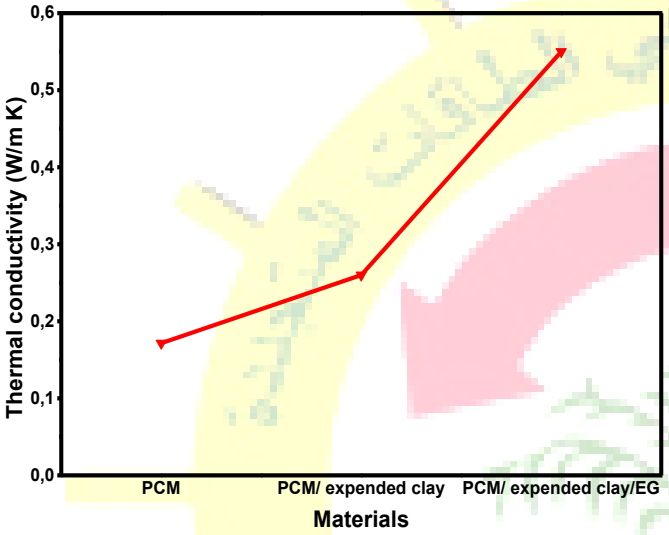

Fig. 6 Thermal conductivity of PCM/ expended clay composite

III. CONCLUSION

In this research, a novel form-stable composite PCM was prepared for latent heat storage application in buildings by incorporation of expended cay powder into paraffin wax using dispersion method. The maximum percentage of PCM contained by expended clay with-out leakage was found to be 41%. ESEM micrographs showed that paraffin was confined into the pores of supporting material through capillary and surface tension forces. FT-IR spectrum showed that the components of form-stable composite PCM are chemically compatible. The melting and freezing temperatures and latent heats of the composite PCM were measured as 52,23and 50, 26 °C, and 62, 20 and 62, 98 J/g, respectively, by DSC analysis. The thermal conductivity of the PCM composite loaded with EG was 2 times higher than that of the PCM composite without EG. It can therefore be concluded that the prepared form-stable composite PCM is a promising candidate for thermal energy storage applications.

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