Preparation and characterization of fatty acid eutectic/diatomite filter aid form-stable phase change material for thermal energy storage

Duo Meng¹ and Anqi Wang
School of Civil and Architectural Engineering, Liaoning University of Technology. Jinzhou121000, China
¹ Email:mengduo39@163.com

Abstract. The aim of this study is to prepare a form-stable phase change material (PCM) with capric and lauric fatty acid (CA-LA) eutectic as the heat absorption material and diatomite filter aid as the supporting matrix. The method of vacuum impregnation was conducted to prepare the composite PCM which has high thermal performance. Its characteristics such as microstructure, thermo-physical properties and thermal stability were investigated by SEM, FT-IR, DSC and TG technique. The adsorption capacity of diatomite filter aid to CA-LA eutectic was 49wt%, and the composite PCM kept solid in macro-level even when the CA-LA melted due to the capillary and surface tension forces of diatomite filter aid. DSC analysis showed that phase change temperature and latent heat of the form-stable PCM was 21.8°C and 75.45 J·g⁻¹ respectively. TG analysis indicated that the diatomite filter aid particles absorbed and constrained the CA-LA molecules in the pores and confirmed the form-stable property of the composite. After 100 times thermal cycling, the phase change temperature and latent heat of the form-stable PCM respectively decreased by 0.9% and 1.1%, which can be neglectable in the practical engineering application.

1. Introduction
Energy shortage is a severe long-term problem for human beings. Building energy consumption occupies 30 percent of the whole society energy consumption, thus, building energy conservation is an important part to implement the energy sustainable utilization and the sustainable development of the society. One of the key techniques for building energy conservation is to promote the thermal insulation property by using the efficient and economic building materials in the building envelope construction. The efficient thermal insulation materials can retard the response speed of the indoor temperature to outdoor temperature in order to reduce the traditional energy consumption caused by air-conditioning or heating for improving the living comfort[1]. Phase change materials (PCMs) can absorb and release heat by phase transformation temperature adjustment and energy storage. With the advantages of large latent heat and constant temperature during phase transition, PCMs can be applied in the building materials or envelope to absorb or release thermal energy to influence the ambient temperature in some degree and behave a few times thermal insulation effect of ordinary building thermal insulation materials. Moreover, PCMs can take part in the building energy storage and usage as well by rational design.

Form-stable phase change materials (PCMs) are a kind of thermal functional composites which can be applied in the latent heat thermal energy storage and prevent the flow and leakage of solid-liquid
PCM. Fatty acid as a kind of excellent PCMs with properties such as adjustable phase change temperature, proper latent heat, stable chemical property, low cost and etc. has been widely researched and applied in thermal energy storage system[2-5]. However, fatty acid would have leakage when it is used directly in building materials because it absorbs thermal energy by solid-liquid phase transition. This phenomenon will lead to the performance degradation of fatty acid and environmental pollution. To resolve this problem, form-stable PCMs which consist of encapsulated material as supporting matrix and PCM as heat absorbing core material have been researched and developed in recent years. Form-stable PCMs can keep solid phase even when the fatty acid melts at the ambient temperature above its melting point at the micro level. Inorganic porous materials are usually used as supporting matrix due to the good properties of high porosity and heat absorption capacity, small particle size, cheap price and etc.[6-9]. Diatomite is one of the inorganic porous materials with the above advantages. The form-stable PCMs based on diatomite have small particle diameter and stable chemical properties, so they can be mixed with ordinary building materials to construct the building envelope which will play a role in heat preservation and room temperature regulation by phase change heat absorb or release. Diatomite resources in China mostly have poor condition, high content of impurity and relatively low porosity resulting in the poor absorption capacity of the diatomite. To modify the diatomite can improve its absorption capacity, but the cost is higher and the production period longer. Thus, in this study, the diatomite filter aid owing high purity and porosity was chosen as the supporting matrix and binary fatty acid eutectic was as the core material to prepare the diatomite filter aid/fatty acid form-stable PCM by vacuum impregnation method. The morphology, thermo-physical and form-stable properties, thermal stability and thermal storage performance were investigated to prove the thermal potential energy conservation ability of the composite PCM.

2. Experimental

2.1. Materials
Diatomite filter aid as phase change core was obtained from Sinopharm Chemical Reagent Co., Ltd. Fatty acids including capric acid (CA) and lauric acid (LA) purchased in Sinopharm Chemical Reagent Co., Ltd were selected to be the phase change core material. According to the Schrader Formula and our previous research on the binary fatty acid eutectic[10], the mass fraction of CA and LA in CA-LA binary eutectic was calculated to be CA/LA=66/34. Its melting point and melting heat tested by DSC was 19.79℃ and 154.16 J/g.

2.2. Preparation of CA-LA/diatomite filter aid composite PCM
Diatomite filter aid was dried beforehand in the drying oven at 105 ℃ for 24 h in order to get rid of the water adsorbed in the pores and surface of the diatomite particles. The equal weight of solid CA-LA eutectic and dried diatomite filter aid was put in a filter flask and agitated evenly. Using the water circulation vacuum pumping, the inner space of the filter flask was vacuumized. Then the filter flask was fixed into the water bath of 50 ℃ to make the CA-LA eutectic melt. The melted CA-LA was absorbed into the pores of diatomite filter aid by negative pressure. After the adsorption ended, the filter flask was transferred into the drying oven at 50 ℃ for 12 h. The superfluous liquid CA-LA eutectic was removed through suction filtration for several times until the composite PCM particles dispersed easily and had no obvious seepage imprinting on the filter paper. The CA-LA/diatomite filter aid composite PCM was obtained and sealed in the drying oven.

2.3. Characterization
A Fourier Transform Infrared spectrophotometer (FT-IR, Sensor27) was used to analyze the chemical structures of the CA-LA/diatomite filter aid composite PCM. Apparent morphology observations on the diatomite filter aid and the prepared composite PCM were obtained by using the Scanning Electron Microscopy (SEM, Zeiss EVO18). The specific surface, pore size distribution and pore volume variation of the diatomite filter aid and CA-LA/diatomite filter aid composite PCM was characterized
by BET measuring instrument (Autosorb IQ). The phase change temperature and latent heat of PCMs was measured using the Differential scanning calorimetry (DSC, 200F) technique. The experimental measurements were carried out under a nitrogen atmosphere at a constant heating rate of 5 °C·min⁻¹. The scanning temperature ranged from 0 °C to 140 °C. Thermo-gravimetric analysis (TG, STA6000) was used for examining the thermal decomposition stability and composition of the composite PCM by analyzing the weight loss variation. The samples were heated under a nitrogen atmosphere from atmosphere temperature to 700°C at a heating rate of 10 °C·min⁻¹.

3. Results and discussion

3.1. FT-IR analysis of the composite PCM

The FT-IR spectra of CA-LA eutectic, diatomite filter aid and CA-LA/diatomite filter aid composite PCM were shown as Figure 1. As shown in Figure 1, the spectrum of the composite PCM was similar with the spectrum superposition of CA-LA eutectic and diatomite filter aid. In the spectrum of the composite PCM, there was an intense absorption peak at the wave number of 1707.68 cm⁻¹. It was the typical characteristic absorption peak of fatty acid which caused by the stretching vibration of carbonyl group (C=O) existing in the form of carboxylate dimmer. The absorption peaks at 2954.87 cm⁻¹ and 2922.25 cm⁻¹ were due to the asymmetric and symmetrical stretching vibration of the -CH₃ group, respectively. The peak at 2853.14 cm⁻¹ was the symmetrical stretching vibration peak of the group of -CH₂. Wave number 1411.86 cm⁻¹ is the out-of-plane bending of group O-H. These above absorption peaks improved the existence of CA-LA in the composite. Meanwhile, the typical absorption peaks of diatomite filter aid were observed in the spectrum of the composite PCM. The peak at 1066.16 cm⁻¹ was caused by the asymmetric stretching vibration of the group of Si-O-Si and the wave number of 787.80 cm⁻¹ and 474.59 cm⁻¹ was the symmetrical stretching vibration and bending vibration respectively. These absorption peaks coincided with those of diatomite filter aid whose main ingredient was silicon dioxide. In addition, there were no new absorption peaks in the spectrum of the composite PCM. The FT-IR analysis indicated that CA-LA eutectic and diatomite filter aid were physical combination and no chemical reaction happened between them.

![Figure 1. FT-IR absorption spectra of the samples.](image)

3.2. Exudative stability of the composite PCM

The exudative stability of the CA-LA/diatomite filter aid composite PCM was detected through the method of diffusion-exudation circle. A mount of the composite PCMs were dispersed in the centre of the standard filter paper and then moved into the drying oven at 40 °C for 2 h until the CA-LA in the composite PCMs melted completely. After this treatment, the abundant CA-LA eutectic on the surface
and weakly adsorbed in the pores of the diatomite filter aid particles would desorb and infiltrate the filter paper. The bigger the exudation circle, the more the seepage of the CA-LA eutectic is. The tested particles were dispersed on a new filter paper and heated to 40 °C once again. The exudation circle after every time heating was photographed. The heating experiment repeated for several times until no obvious seepage trace and the obtained composite PCMs were considered to be form-stable PCMs.

Figure 2 was the diffusion-exudation circle results of the prepared composite PCM. As shown in Figure 2(a), the exudation radius of CA-LA was large and the seepage amount was big, which revealed that there were still a certain amount of CA-LA adhered to the surface and pores of the diatomite particles after several times suction filtration. Figure 2(b) showed seepage phenomenon of the composite PCM endured 5 times heating and the diffusion-exudation circle changed slightly. According to the experiment results, the diffusion-exudation circle became smaller and smaller along with the increase of heating times. After heated for 10 times, the diffusion-exudation circle nearly disappeared which revealed that weakly adsorbed CA-LA eutectic had subtotally taken off the diatomite particles. As a result, the composite PCMs after 10 times heating was considered to be the form-stable PCMs and chosen as the samples in the subsequent property test.

![Figure 2. Seepage after heating melt of the composite PCM: (a) 1 time; (b) 5 times; (c) 10 times.](image)

3.3. Morphology and structure analysis of the composite PCM

The SEM images of diatomite filter aid and CA-LA/diatomite filter aid form-stable PCM were shown in Figure 3. It was seen in Figure 3(a) that the particle of diatomite filter aid was circinal and have favorable micropore structure. The pore structure was tiny and able to supply enough space for fatty acid molecules. In Figure 3(b) of the composite PCM, the pores in the diatomite filter aid disappeared totally and the filled material was just CA-LA eutectic testified be FT-IR analysis. So it was concluded that CA-LA eutectic had been filled into the pores of the diatomite filter aid. Micropore diameter and volume analysis curve of the diatomite filter aid and CA-LA/diatomite filter aid form-stable PCM by BJH method and the pore structure characteristic parameters were listed in Table 1. From the results, the cumulative micropore volume was 0.038 cm$^3$·g$^{-1}$ and the most probable pore size 4.306 nm. While the cumulative micropore volume of the CA-LA/diatomite filter aid form-stable PCM decreased to 0.018 cm$^3$·g$^{-1}$. It proved that most of the diatomite filter aid pores had been filled by CA-LA eutectic in accordance with the SEM analysis. The most probable pore size of the composite PCM was 0.893 nm which was so small that could strongly adsorb the CA-LA molecules by capillary force. Correspondingly, the specific surface area changed from 1.775 m$^2$·g$^{-1}$ to 1.166 m$^2$·g$^{-1}$. The surface adsorption energy declined with the increase of CA-LA eutectic, and this also improved that CA-LA had been absorbed in the particle pores of diatomite filter aid. Thus it can be inferred that the micropore structure supplied the space and were able to absorb the CA-LA eutectic by capillary force and surface tension. These forces immobilized the CA-LA molecules in the pores of diatomite filter aid even when the composite PCM had phase changed, so the composite can keep solid in micro-level.
Figure 3. SEM images of the samples: (a) diatomite filter aid; (b) form-stable PCM.

Table 1. Pore structure characteristic of the diatomite filter aid and the prepared form-stable PCM.

| Samples         | The most probable pore size /nm | Specific surface /m²·g⁻¹ | Micropore volume /cm³·g⁻¹ |
|-----------------|---------------------------------|--------------------------|--------------------------|
| Diatomite filter aid | 4.306                           | 1.775                    | 0.038                    |
| Composite PCM   | 0.893                           | 1.166                    | 0.018                    |

3.4. Thermo-physical properties of the composite PCM

Phase change behaviors of CA-LA/diatomite filter aid form-stable PCMs were evaluated by DSC technique and their thermograms were displayed in Figure 4. As seen in Figure 4, the phase change temperature of CA-LA/diatomite filter aid form-stable PCM was determined as 21.8°C which lowered 2.01°C than that of CA-LA eutectic. The probable reason may be that the CA-LA eutectic needed to overcome the effect of the diatomite pores in the process of melting. Latent heat of the form-stable PCM was measured to be 75.45J·g⁻¹ that was less than CA-LA eutectic. This indicated that the adsorption capacity of diatomite filter aid to CA-LA was limited. Latent heat value of the form-stable PCM was 49 percent of CA-LA eutectic. The adsorption and pore restriction of the inorganic matrix can hinder the phase change behavior of fatty acid in some degree and made the form-stable PCM have latent heat loss. As a result, the real adsorption mass of CA-LA by diatomite filter aid should more than 49wt%. Based on the results of diffusion-exudation circle experiment, the adsorption mass fraction of 49% was maximal which can endow the composite PCM with large latent heat storage capacity and shape stability, and keep well dispersibility and service performance.

Figure 4. DSC curve of the form-stable PCM.
3.5. Thermal stability of the composite PCM

TG analysis was used to examine the thermal decomposition stability of the CA-LA/diatomite filter aid form-stable PCMs and the results were shown in Figure 5. As shown in the TG curve of diatomite filter aid, the weight loss was only 0.85% at 700 °C. It illustrated that diatomite filter aid had no volatilization or decomposition ingredients. The TG curve of CA-LA eutectic showed that CA-LA had an obvious weight loss in the temperature range of 120 °C–195 °C as a result of the volatilization of CA-LA. At the temperature of 194 °C, CA-LA eutectic volatilized completely. Compared with CA-LA eutectic, the main weight loss temperature range of CA-LA/diatomite filter aid form-stable PCM was 120 °C–233 °C which was also caused by the CA-LA volatilization. The weight loss temperature range of CA-LA eutectic prolonged, and it indicated that diatomite filter aid particles separated the CA-LA molecules each other and restrained the volatilization of CA-LA. At the temperature of 233 °C, the weight loss of the form-stable PCM samples was 50.07% and the pure diatomite filter aid had a weight loss of 0.19% at 233 °C according to the TG curve. It can be inferred that the mass fraction of CA-LA in the form-stable PCM was about 49.88wt% that was a little lower than that obtained by DSC analysis. The result indicated that the relationship between CA-LA eutectic and diatomite filter aid was not simple absorption. Attributed to the small diameter and high porosity of the diatomite filter aid particles, the CA-LA molecules can be firmly adsorbed and immobilized in the pores. But the strong force will make a few fatty acid have no phase change and limit the adsorption capacity of diatomite filter aid to fatty acid. Thus, appropriate adsorption mass can ensure the foam-stable PCM higher latent heat and improve the thermal stability of the form-stable PCM.

In the practical engineering, form-stable PCMs should keep good thermal storage performance after subjected repeated melting-freezing cycling. Figure 6 showed the DSC curve of CA-LA/diatomite filter aid form-stable PCM after 100 times accelerated thermal cycling test. It was seen that the phase change temperature was 21.6 °C which was 0.2 °C lower than that of before thermal cycling and the latent heat was measured to be 74.6 J·g⁻¹ which decreased 1.1%. The variation in phase change temperature and latent heat can be neglectable in the thermal energy storage application engineering. From the thermal cycling test result, it was indicated that CA-LA eutectic hardly desorbed from the pore structure when melted above the phase change temperature and the form-stable PCM behaved good thermal reliability. The form-stable PCM had no leakage or loss of CA-LA eutectic in the heating absorption process which can satisfy the durability requirement from building energy conservation.
4. Conclusions
Vacuum impregnation method was conducted to prepare the CA-LA/diatomite filter aid form-stable PCM. The CA-LA eutectic was immobilized in the pores of the diatomite filter aid particles by the capillary force and surface tension. The composite PCM showed good exudation stability after 10 times diffusion-exudation circle test and the morphology observation result by SEM also proved that the CA-LA eutectic had filled into the pore structure of the diatomite filter aid. The DSC results indicated that phase change temperature and latent heat of the form-stable PCM was 21.8 °C and 75.45 J·g⁻¹ respectively, and the absorption mass fraction of CA-LA in the composite was about 49wt%. After combined with the diatomite filter aid, the main weight loss temperature range of CA-LA eutectic lagged from 120-195 °C to 120-223 °C, which illustrated that diatomite filter aid particles were able to absorb the fatty acid molecules effectively and strongly and then obstruct the volatilization of fatty acid. The phase change temperature and latent heat of the CA-LA/diatomite form-stable PCM hardly changed after 100 times thermal cycling test. TG analysis and thermal cycling test results indicated that the composite PCM has enough long term stability to satisfy the operating requirements of building energy conservation application. In sum, the CA-LA/diatomite filter aid form-stable PCM was supposed to be a potential thermal insulation and energy conservation material which can be applied in buildings to adjust the room temperature effectively.

Acknowledgements
This research was financially supported by the National Natural Science Foundation of China (No.51308275) and Science Foundation for Young Scientists of Liaoning Educational Committee (No. JQL201915403).

References
[1] Tyagi VV, BUDDHI DPCM 2007 Thermal Storage in Buildings: A State of Art [J] Renewable and Sustainable Energy Reviews 11(9) 1146-1166
[2] Meng Xin, Zhang Huanzhi, ZHAO Ziming, et al. 2013 Preparation, encapsulation and thermal properties of fatty aci/expanded graphite composites as shape-stabilized phase change materials [J] Chemical Journal of Chinese Universities 33(3) 526-530
[3] Huang Xue, CUI Yingde, ZHANG Buning, et al. 2014 Review on heat transfer and liquid phase leakage of fatty acids phasechange materials [J] Chemical Industry and Engineering Progress 33(10)2676-2680.
[4] Cemil Alkan, Ahmet Sari, Ali Karaipekli, et al. 2009Preparation, characterization, and thermal properties of microencapsulated phase change material for thermal energy storage[J]Solar Energy Materials and Solar Cells93(1)143-147
[5] Tumirah Khadiran, Mohd Zobir Hussein, Zulkarnain Zaina, et al.2015Encapsulation techniques for organic phase change materials as thermal energy storage medium: A review[J]Solar Energy Materials & Solar Cells143(12)78-98
[6] Li Min, Kao Hongtao, Wu Zhishen, et al.2011 Study on preparation and thermal property of binary fatty acid and the binaryfatty acids/diatomite composite phase change materials[J]Applied energy88(5)1606-1612
[7] Zhang Hong, Wu Xiaohua, Wang Xiaolei, et al. 2010Structure and properties of lauric acid/cetyl alcohol/silicon dioxide composite phase change material[J]Journal of Materials Science& Engineering28(5)672-675
[8] Wang Yi, Zhenghan, Feng Huixia, et al. 2012Effect of preparation methods on the structure and thermal properties of stearicacid/activated montmorillonite phase change materials[J]Energy and Buildings47(4)467-473
[9] He Yan, Zhang Xiong2016[J]Journal of Building Materials19(1)181-184
[10] Wang Lijiu, Meng Duo2010Fatty Acid Eutectic/Poly(methyl Methacrylate Composite as Form-Stable Phase Change Material for Thermal Energy Storage[J]Applied Energy87(2)2660-2665