Study of Capric–Palmitic Acid/Clay Minerals as Form-Stable Composite Phase-Change Materials for Thermal Energy Storage

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Cite This: ACS Omega 2021, 6, 24650−24662

1. INTRODUCTION

In recent years, with rapid economic development and the shortage of fossil energy, energy storage and the effective use of new energy have attracted considerable attention. As an important method to effectively improve energy efficiency, thermal energy storage has become a key research topic.1−4 The thermal energy storage technology can be divided into sensible heat storage, chemical reaction energy storage, and latent heat storage, according to the form of energy storage.5 Sensible heat storage has certain shortcomings, such as a low energy storage density and large temperature changes associated with heat storage and release. The chemical reaction heat storage and its processes are relatively complicated, and its safety is difficult to guarantee. Chemical reaction heat storage is rarely used in practice. Latent heat storage, also known as the phase-change energy storage, has the advantages of nontoxicity and non-corrosiveness, a high energy storage density, and an almost constant phase-change temperature. It is widely used in building envelopes with solar energy utilization and in other heat storage and temperature control fields. The use of phase-change energy storage in buildings can improve the thermal comfort of the building environment and achieve an effective use of solar energy.6−7 During the day, when the temperature is high, the phase-change material (PCM) melts and absorbs heat, and at night, when the temperature decreases, the PCM releases heat through the solidification process to provide heat to the building.8,9

The key to phase-change energy storage is the choice of the PCM. According to their chemical properties, PCMs can be divided into organic, inorganic, and composite categories. Inorganic PCMs have problems with phase separation and undercooling. Organic PCMs have the advantages of good crystallization performance, good stability, a high latent heat of phase change, no phase separation, and low undercooling, making them the first choice for phase-change energy storage materials.10,11 Among them, fatty acids are considered as...
Table 1. Leakage Records of FSPCMs with Different PCM Proportions

| CA–PA content          | 25 wt % | 30 wt % | 35 wt % | 40 wt % | 45 wt % | 50 wt % |
|------------------------|---------|---------|---------|---------|---------|---------|
| CA–PA/ATP FSPCM        | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       |
| CA–PA/SPL FSPCM        | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       |
| CA–PA/VMT FSPCM        | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       |
| CA–PA/DM FSPCM         | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       |
| CA–PA/BT FSPCM         | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       |
| CA–PA/KL FSPCM         | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       | ⊘       |

“Key to the symbols in the table: “n” indicates leakage, and “⊙” indicates no leakage.”

potential PCMs. However, due to the high melting point of most single fatty acids, leakage occurs during the phase-change process, which limits their application in buildings. However, a variety of single fatty acids can be combined into binary or multiple fatty acid mixtures with a specific mass ratio chosen to reduce their melting point. These PCMs can then be encapsulated into form-stable PCMs (FSPCMs) to prevent leakage during the melting process. The encapsulation methods for PCMs used in buildings include direct impregnation, vacuum adsorption into porous materials, and microencapsulation. The porous material vacuum adsorption method is a simple and low-cost method; the produced material can be added to concrete as a fine aggregate, and there is essentially no leakage. The porous materials are often low-cost clay minerals, which have a large specific surface area and a rich porous structure. Clay minerals used for the preparation of clay mineral-based PCMs include diatomite, sepiolite, kaolin, vermiculite, bentonite, attapulgite, etc. Diatomite has the advantage of being a highly porous, lightweight, inert, and abundant in nature. Bentonite is a mineral composed mainly of montmorillonite, which exhibits good cation-exchange performance. In comparison, kaolin has a smaller interlayer spacing and a lower cation-exchange capacity; therefore, PCMs do not easily enter the kaolin interlayer spacing. However, kaolin can be modified to increase the interlayer spacing, which is then conducive to the entry of PCMs.

Fu prepared stable PCMs with stearic acid as a PCM and diatomite as a carrier by the vacuum adsorption method. The composite materials melted at 52.3 °C with a latent heat of 57.1 J/g, showing good thermal stability. Li prepared a paraffin/bentonite composite PCM by the sol-intercalation method and formed a stable composite PCM by organic modification. The latent heat capacity was 39.84 J/g, and the maximum adsorption of paraffin in the composite was 44.4%. In addition, bentonite can enhance the heat-transfer rate of paraffin/bentonite composites. Sari used kaolin as a carrier, with capric acid (CA), PEG600, and heptadecane (HD) as organic PCMs, and prepared three composite PCMs using the vacuum adsorption method. Leakage tests showed that the maximum mass fractions of CA, PEG600, and HD that could be added to kaolin were 17.5, 21, and 16.5%, respectively. The thermal reliability of the three composite PCMs was good after 1000 heating/cooling cycles. Moreover, the addition of 5% by mass of expanded graphite (EG) can significantly improve the thermal conductivity of the composite PCMs.

Attapulgite has a unique layer chain structure, vermiculite exhibits strong adsorption, which play a significant role in preventing the leakage of PCMs. Zhang successfully prepared a composite PCM of lauric–palmitic–stearic acid ternary eutectic mixture/vermiculite. The maximum mass fraction of the vermiculite-adsorbed ternary eutectic mixture was 50 wt %, without melting leakage. The scanning electron microscopy (SEM) results revealed that the ternary eutectic mixture was limited to the layer pore structure of vermiculite. The composite PCM exhibited a melting temperature of 34.4 °C and a phase-transition latent heat of 75.8 J/g, and its good thermal performance and reliability were deemed suitable for use in energy-saving building materials.

Sari studied a composite PCM composed of cement-based gypsum and its indoor temperature control performance. A eutectic mixture of capric–stearic acid was co-infiltrated with sepiolite by direct impregnation. The optimum mass fraction of the eutectic mixture into sepiolite was 42 wt %, and the cement plate containing the composite PCM displayed good temperature control performance in the laboratory.

In recent years, there have been many studies on the formation of FSPCMs by immersing different types of PCMs in clay minerals, with the prepared composite PCMs exhibiting excellent thermal stability. However, the maximum adsorption rate of a specific PCM in different clay minerals may vary significantly. Furthermore, the influence of the structure of the different clay minerals on the heat storage performance, thermal stability, and chemical structure of the final FSPCMs is still poorly understood and has rarely been reported in the scientific literature.

In this study, attapulgite, sepiolite, vermiculite, diatomite, bentonite, and kaolin were selected to stabilize a capric–palmitic acid (CA–PA) binary eutectic mixture. The maximum adsorption ratio of the CA–PA binary eutectic mixture in each of the six clay minerals was studied, and the thermal properties, pore structure, thermal stability, microstructure, and chemical structure changes of the resulting FSPCMs were analyzed. Finally, the heat storage efficiency of the FSPCMs was studied using a self-made heat-storage and heat-release measurement device.

2. RESULTS AND DISCUSSION

2.1. Determination of the Maximum CA–PA PCM Adsorption Capacity of the Clay Minerals. In theory, the higher the PCM content in the FSPCMs, the higher the latent heat of the composite. However, the adsorption capacity of the clay minerals for PCM is limited. When the PCM content in the FSPCM exceeds the adsorption capacity of the clay mineral, leakage will occur, affecting the performance of the FSPCM. The prepared composite PCM was placed on a filter paper and heated in a constant temperature heating box at 45 °C for 1 h. Leakage of the molten CA–PA was indicated by marks left on the filter paper, with the results presented in Table 1. As shown in Figure 1, no leakage was detected for a...
CA−PA content lower than 35 wt % in CA−PA/ATP, 30 wt % in CA−PA/SPL, 40 wt % in CA−PA/VMT, 40 wt % in CA−PA/DM, 35 wt % in CA−PA/BT, and 35 wt % in CA−PA/KL. The results show that the morphology of the composite PCMs is good when the amount of PCMs is below the maximum adsorption capacity of the clay minerals and that the various clay minerals provide good encapsulation of CA−PA. Among them, vermiculite and diatomite exhibit the highest adsorptivity for CA−PA, while sepiolite exhibits the lowest adsorptivity of only 30 wt %.

2.2. Thermal Properties of the FSPCMs. The phase-transition temperature and latent heat of the CA, PA, and CA−PA eutectic mixtures were analyzed using differential scanning calorimetry (DSC), with the results shown in Figure 2 and presented in Table 2. As evident in Figure 2, there is only one endothermic peak and one exothermic peak in the CA−PA mixture, indicating that the CA−PA mixture has reached a eutectic state when the mass fraction of CA is 85.3 wt %. The corresponding phase-transition melting temperature ($T_m$) and phase-transition freezing temperature ($T_f$) of the CA−PA eutectic mixture are 22.28 and 20.87 °C, respectively, which are close to the predicted phase-transition temperatures and lower than those of both CA and PA and thus suitable for low-temperature phase-change heat storage. It is worth mentioning that the CA−PA eutectic mixture also has a high latent heat and lower undercooling; the latent heat of melting ($H_m$) is 176.26 J/g, and the latent heat of freezing ($H_f$) is 175.78 J/g, which meets the requirements for energy saving applications.

The latent heat of phase change is an important parameter that affects the thermal storage performance of composite PCMs. Figure 3 shows the DSC curves of the six mineral-based composite PCMs. As shown in Figure 3, the phase-transition temperature of clay mineral-based PCMs is lower than that of the pure PCM, and the decrease in phase-change temperatures is due to the weak attractive interaction between CA−PA and the inner surface wall of the porous material. These results are in agreement with that reported by Radhakrishnan, Zhang et al., and Fu et al. In their research, they found that the interaction between PCMs and porous carrier materials plays an important role in determining the moving direction of phase-change temperature in porous media. In addition, this interaction affects the shape of the phase-transition peak of the composite, which is not sharp enough.

Clay minerals do not contribute to the latent heat of phase change of the FSPCM, so the latent heat of phase change of the FSPCM depends only on the CA−PA content; that is, a higher porous material content will lead to a lower latent heat of phase change of the FSPCM. The latent heats of melting of the CA−PA/ATP, CA−PA/SPL, CA−PA/VMT, CA−PA/DM, CA−PA/BT, and CA−PA/KL FSPCMs were determined to be 61.08, 51.67, 69.27, 69.48, 60.12, and 60.88 J/g, respectively. The phase-change latent heats of the six porous material-based FSPCMs were lower than the theoretical value.

| sample     | melting point (°C) | latent heat (J/g) | freezing point (°C) | freezing heat (J/g) |
|------------|--------------------|-------------------|---------------------|--------------------|
| CA         | 30.61              | 147.82            | 27.23               | 145.58             |
| PA         | 61.71              | 206.68            | 59.48               | 204.25             |
| CA−PA      | 22.28              | 176.26            | 20.87               | 175.78             |

Figure 1. Photographs of the FSPCMs exhibiting no leaks: 35/65 wt % CA−PA/ATP (a), 30/70 wt % CA−PA/SPL (b), 40/60 wt % CA−PA/VMT (c), 40/60 wt % CA−PA/DM (d), 35/65 wt % CA−PA/BT (e), and 35/65 wt % CA−PA/KL (f) after heating at 45 °C for 60 min.

Figure 2. DSC test curves of CA, PA, and the CA−PA eutectic mixture.

Table 2. Thermal Performance Data of CA, PA, and CA−PA

![Diagram showing DSC test curves of CA, PA, and CA−PA eutectic mixture.](https://doi.org/10.1021/acsomega.1c03344)
The theoretical latent heat of FSPCMs can be calculated using the following equation (eq 1):

\[ \Delta H_{lh} = \Delta H_{pure} \times \beta \]  

where \( \Delta H_{lh} \) and \( \Delta H_{pure} \) are the theoretical value of latent heat of the clay mineral-based FSPCM and pure CA–PA, respectively, and \( \beta \) represents the mass ratio of CA–PA in the FSPCM.

Figure 4 shows the comparison between theoretical and measured values of FSPCM. The latent heat is lower than the theoretical value, and the slight difference between the results could be due to the restriction of phase-change behavior of the PCMs retained into the porous network of the clay minerals. It can be seen from Figure 4 that the crystallization effect of the ATP-based FSPCM is better than that of the other clay-mineral-based FSPCMs, with the measured values of the phase-change latent heats during melting and freezing only 0.99% and 1.53% lower than the theoretical value, respectively. The results show that the crystallization effect of SPL-based FSPCM is poor, and the measured value of the latent heat of phase change during melting and freezing is lower than the theoretical value by 2.29% and 5.39%, respectively, and the error is still acceptable. Finally, FSPCMs still have high latent heat of phase transition, and they can be used for low-temperature thermal energy storage.

2.3. Thermal Stability of the FSPCMs. The thermal stability of various clay mineral composite PCMs was evaluated by thermogravimetry (TG) analysis. Figure 5 shows the TG and derivative TG (DTG) curves of CA–PA and various FSPCMs. As can be seen from Figure 5, only a decomposition stage exists for pure CA–PA. The decomposition of CA–PA starts at 136 °C and ends at 420 °C, when the maximum decomposition rate of CA–PA occurs at 250 °C. It can be clearly observed that the FSPCMs show a similar three-stage mass loss process, and the negligible weight loss from room temperature to 145 °C is attributed to the evaporation of a small amount of adsorbed water and pore water in FSPCMs. The obvious second weight loss at 145–260 °C is mainly caused by the decomposition of CA–PA adsorbed on the surface of clay minerals. It is worth noting that the decomposition rate of FSPCMs slows down after 260 °C, indicating that CA–PA is adsorbed in the pore structure rich in clay minerals, which delays the decomposition of some CA–PA and improves the thermal stability of FSPCMs. In addition, Figure 5 shows that the weight loss trajectories of PCMs in the six prepared FSPCMs are similar. After 480 °C, CA–PA in FSPCMs decomposes completely, and the remaining weight is...
the clay minerals; it corresponds to the results of the determination of the maximum CA−PA adsorption capacity of clay minerals. Based on the above analysis, we can conclude that FSPCMs prepared with different clay minerals as supports in this study have good thermal stability.

2.4. Chemical Structure Analysis of the FSPCMs. Figure 6 shows the changes in the functional groups before and after adsorption of CA−PA by the clay minerals, as characterized by Fourier transform infrared (FTIR) spectroscopy. Figure 6 (a) shows the infrared absorption spectrum of...
the CA−PA/ATP FSPCM, with the characteristic peak at 3644 cm$^{-1}$ attributed to the $\sim$OH stretching vibration and the characteristic peak at 1706 cm$^{-1}$ attributed to the carboxyl (C$\equiv$O) stretching vibration. Figure 6b shows the infrared absorption spectrum of the CA−PA/SPL FSPCM, with the characteristic peaks at 700 and 1710 cm$^{-1}$ attributed to the stretching vibrations of $\sim$OH and C$\equiv$O, respectively. Figure 6c shows the infrared absorption spectrum of the CA−PA/VMT FSPCM, with the characteristic peaks at 937 and 719 cm$^{-1}$ attributed to the bending vibration of the $\sim$OH bond, while the C$\equiv$O vibration causes a large characteristic peak at 1710 cm$^{-1}$. Figure 6d shows the infrared absorption spectrum of the CA−PA/DM FSPCM, with the characteristic absorption peak at 1093 cm$^{-1}$ attributed to the asymmetric vibration of the Si−O bond and the peak at 2927 cm$^{-1}$ attributed to the symmetric stretching vibration of $\sim$CH$_3$ and the sharp peak at 1712 cm$^{-1}$ is characteristic of the C$\equiv$O stretching vibration. Figure 6e shows the infrared spectrum of the CA−PA/BT FSPCM, with the characteristic absorption peak at 3621 cm$^{-1}$ corresponding to the typical $\sim$OH stretching vibration of bentonite, the peak at 912 cm$^{-1}$ corresponding to the bending vibration of the $\sim$OH bond, and the characteristic absorption peak at 2850 cm$^{-1}$ attributed to the stretching vibration of the−C$\equiv$H$_3$ bond. Figure 6f shows the infrared spectrum of the CA−PA/KL FSPCM, with the characteristic peaks at 2923, 2852, and 1710 cm$^{-1}$ attributed to the stretching vibrations of $\sim$CH$_3$, $\sim$CH$_2$, and C$\equiv$O, respectively. The infrared spectra of the CA−PA PCM and the associated clay mineral-based PCMs are also shown for comparison and indicate that no new characteristic absorption peaks appear. These results suggest that CA−PA impregnated into the pores of the clay minerals are only physically adsorbed and that no chemical changes occurred.

Table 3. Pore Parameters of Clay Mineral Materials

| samples  | before adsorption of CA−PA | after adsorption of CA−PA |
|----------|-----------------------------|---------------------------|
|          | $S_{BET}$/m$^2$ g$^{-1}$    | $V_t$/cc g$^{-1}$        | $d_{ave}$/nm | $S_{BET}$/m$^2$ g$^{-1}$ | $V_t$/cc g$^{-1}$ | $d_{ave}$/nm |
| ATP      | 55.6                        | 0.068                     | 4.90         | 12.0                       | 0.010            | 3.25         |
| KL       | 11.0                        | 0.016                     | 5.83         | 2.0                        | 0.009            | 1.77         |
| DM       | 53.6                        | 0.116                     | 8.67         | 2.4                        | 0.010            | 1.65         |
| SPL      | 8.0                         | 0.012                     | 5.87         | 0.7                        | 0.006            | 3.09         |
| BT       | 15.7                        | 0.065                     | 1.65         | 2.0                        | 0.010            | 2.10         |
| VMT      | 18.0                        | 0.061                     | 1.35         | 2.1                        | 0.018            | 3.43         |

The CA−PA/ATP FSPCM (a) and CA−PA/DM FSPCM (c) and the nitrogen adsorption−desorption isotherms for CA−PA/ATP FSPCM (b) and CA−PA/DM FSPCM (d).
2.5. Pore Structure of Clay Mineral Materials and FSPCMs. Before and after attapulgite and diatomite have absorbed CA−PA, the nitrogen absorption−desorption isotherms and BJH pore diameter distribution are shown in Figure 7. From Figure 7, we can find that according to IUPAC classification, the nitrogen absorption−desorption isotherms of attapulgite and diatomite belong to H2(b) hysteresis ring II isotherms. The low-pressure section protrudes to the Y-axis and has an inflection point, meaning that attapulgite, diatomite, and absorbate have a strong absorption effect. It can be seen from the BJH pore size distribution that the pore size is distributed in the range of 2−50 nm, and the hysteresis area is large, which indicates that the pore size distribution is wide. After attapulgite and diatomite have absorbed CA−PA, the nitrogen absorption−desorption isotherms present H3 hysteresis ring III isotherms and the convex X-axis of the low-pressure section, indicating that the adsorption of attapulgite, diatomite, and adsorbate becomes weaker, acting as mesopores with a layer structure.

From the data of Table 3, it can be seen that the specific surface area (S\text{BET}) (attapulgite decreases from 55.6 to 1.2 m² g⁻¹, with a range of 97.8%; diatomite decreases from 53.6 to 2.4 m² g⁻¹, with a range of 95.5%) and pore capacity (Vₚ) all decrease dramatically after the samples have absorbed CA−PA, which means that the pores of attapulgite and diatomite have absorbed a great deal of CA−PA, reducing nitrogen absorbing capacity. This is consistent with the change of the nitrogen absorption−desorption isotherms pre and post modification.

Before and after sepiolite, kaolin, bentonite, and vermiculite have absorbed CA−PA, the nitrogen absorption−desorption isotherms before and after the samples absorbed CA−PA belong to H3 hysteresis ring III isotherms. The low-pressure section protrudes to the X-axis, which indicates that the interaction between the sample and the adsorbate is weak. The area of the hysteresis loop is small, which indicates that the pore size distribution is narrow and it is a layered mesoporous material. After adsorption of CA−PA, the nitrogen adsorption−desorption isotherms of the four clay mineral materials are basically the same as those before adsorption, indicating that the pore structure of the materials has no obvious change.

From the data of Table 3, it can be seen that the specific surface area (S\text{BET}) (sepiolite decreases from 8.0 to 0.7 m² g⁻¹, with a range of 91.3%; kaolin decreases from 11.0 to 2.0 m² g⁻¹, with a range of 81.8%; bentonite decreases from 15.7 to 2.0 m² g⁻¹, with a range of 87.3%; and vermiculite decreases from 18.0 to 2.1 m² g⁻¹, with a range of 88.3%) and pore capacity (Vₚ) all decrease dramatically after the samples have absorbed CA−PA, which means that the pores of samples have absorbed a great deal of CA−PA, reducing nitrogen absorbing capacity.

2.6. Morphology and Microstructure Characterization of the FSPCMs. The surface morphology and microstructure of the CA−PA/ATP, CA−PA/SPL, and CA−PA/KL
FSPCMs were studied by SEM (Figure 10). The microstructures of attapulgite and sepiolite comprise a staggered distribution of fibrous rod crystals. Furthermore, it can be observed from Figure 10a−d that the fibrous rod crystals on the surface are bonded together. The unique layered chain structure can be used as a good PCM carrier that effectively prevents the melting leakage of PCMs. Figure 10e,f shows that the kaolin surface is composed of particles with irregular shapes and different sizes, and the interlayer spacing of the different particles is conducive to the adsorption of PCMs. It is worth mentioning that the leakage indicated on the surface of the CA−PA/KL FSPCM is due to the high voltage of the electron microscope; however, most of the interlayer spacing is filled by the PCM. The adsorption of the PCM by kaolin is slightly lesser as compared to those by attapulgite and sepiolite.

The surface morphology and microstructure of the CA−PA/DM, CA−PA/VMT, and CA−PA/BT FSPCMs are shown in Figure 11. These three types of mineral materials have high porosity. With the support materials of CA−PA, the leakage of the PCM is restrained by the capillary effect and surface effect of the porous material structure. Figure 11a,b shows that the shape of the original diatom remains almost unchanged after the diatomite adsorbs the organic PCM, which uniformly fills in the pores of the material to make its surface smooth. It can be observed from Figure 11d−f that the interlayer spacing of porous materials impregnated with CA−PA becomes smaller, and some PCM adheres to the surface of the porous material.
owing to surface tension, while the pores are uniformly filled with the PCM. The prepared FSPCMs exhibited strong morphological stability. Even when the above three types of mineral-based FSPCMs were used for SEM, CA–PA on the surface of clay minerals melts due to electron beam, but the FSPCMs maintained a stable shape, reflecting the good supporting effect of the porous material.

3.7. Thermal Storage Performance Analysis of the FSPCMs. The heat storage and release capacity of the FSPCM affect its effectiveness in practical applications. The heat storage and release performance of the clay mineral-based composite PCM was tested using a homemade experimental platform. The heat storage and release curves obtained from the experiments are shown in Figure 12. The initial temperature of all the samples was set at 10 °C, and the maximum heating temperature was set at 65 °C. It can be observed from Figure 12 that the temperature of CA–PA and the FSPCMs increases with increasing test time before the phase changes from solid to liquid (thermal storage process) and the mineral-based FSPCMs require a shorter time to reach the melting point than the pure CA–PA PCM. The melting process of PCMs absorbs a lot of heat, resulting in a significant constant temperature platform in a certain temperature range, which is still suitable for the cooling and exothermic process. It took 560 s for the pure CA–PA PCM during the melting process, while the six kinds of mineral-based FSPCMs only took 310 s (CA–PA/ATP), 376 s (CA–PA/SPL), 345 s (CA–PA/KL), 248 s (CA–PA/VMT), 267 s (CA–PA/DM), and 295 s (CA–PA/BT). In the solidification process, the pure CA–PA PCM took 670 s to solidify, and CA–PA/ATP, CA–PA/SPL, CA–PA/KL, CA–PA/VMT, CA–PA/DM, and CA–PA/BT respectively took 395, 420, 408, 348, 367, and 380 s. Compared with pure CA–PA PCMs, FSPCMs show higher heat storage and heat release efficiency.

3. CONCLUSIONS

In this study, six types of clay mineral-based composite PCMs were prepared by the vacuum adsorption method. The structure, thermal properties, thermal stability, and thermal storage performance of the FSPCMs were studied.

(1) Six clay minerals were used as supports to prepare FSPCMs. The adsorption capacity of vermiculite and diatomite is satisfactory, and sepiolite shows the worst adsorption capacity. TG analysis shows that six FSPCMs have good thermal stability, the abundant pore structure of clay minerals can delay the thermal decomposition rate of CA–PA, so the FSPCMs show a similar three-stage mass loss process.

(2) Microstructure shows that the six clay materials have a rich porous structure and large specific surface area, which can be used as good carriers of CA–PA. The BET results show that the specific surface area and pore capacity of clay minerals all decrease dramatically after the clay minerals have absorbed CA–PA.

(3) FSPCMs exhibit a higher heat storage and release efficiency and form an obvious constant temperature platform in the process of temperature rise and fall, which reflects a certain temperature control performance. In addition, only physical adsorption between CA–PA and the clay material occurred, and no chemical reaction occurred.

The research on the thermal conductivity and reducing the undercooling of clay mineral-based composite PCMs will be the research direction in the future.

4. EXPERIMENTAL SECTION

4.1. Materials. Capric acid (C10H20O2, 99% pure) and palmitic acid (C16H32O2, 99% pure) were purchased from Sinopharm Chemical Reagent Co., Ltd., and attapulgite, sepiolite, expanded vermiculite, diatomite, bentonite, and
kaolin clay minerals were provided by Yanxin Mineral Co., Ltd., Hebei Province, China. The clay minerals were dried for 12 h in a constant-temperature heating box at 250 °C.

4.2. Preparation of the CA−PA Eutectic Mixture. A eutectic mixture refers to a mixture of two different chemical substances or elements to form a single compound with a melting point lower than that of any of its constituents. As the melting temperature of a single fatty acid is high, it is generally not suitable for use as a PCM in low-temperature thermal energy storage. When two types of fatty acids are mixed in a certain proportion, their phase transformation "behavior" is similar to that of a eutectic, and so the mixture is called a quasi-eutectic system. The theoretical ratio of the two mono-fatty acids to the eutectic can be calculated using the following formula:

$$T_m = \frac{1}{T_i} - \frac{R \ln x_i}{H_i}$$

where $H_i$ is the molar melting heat of component $i$ at the melting point (J·mol$^{-1}$), $T_i$ is the melting point of component $i$ (K), $T_m$ is the temperature of the eutectic point (K), $x_i$ is the molar ratio of component $i$ in the eutectic mixture, and $R$ is the gas constant (8.314 J K$^{-1}$·mol$^{-1}$).

The melting temperatures of CA and PA at different ratios were calculated using the above formula. A binary phase diagram is shown in Figure 13. The intersection of the two liquidus lines in the figure is the quasi-eutectic point, indicating that when the mass percentage of CA is 85.3%, the predicted melting temperature of the CA−PA mixture is 24.85 °C.

4.3. Preparation of Form-Stable PCMs. Using attapulgite (ATP), sepiolite (SPL), expanded vermiculite (VMT), diatomite (DM), bentonite (BT), and kaolin (KL) as support materials and the CA−PA eutectic mixture as an additive, six types of clay mineral-based composite PCMs were prepared by the vacuum adsorption method. As shown in Figure 14, the six clay minerals were placed in a heating box at a constant temperature of 250 °C for 12 h to remove organic impurities. Next, the clay minerals were successively placed in a conical flask, which was then heated in a water bath at 80 °C and evacuated to a pressure of 0.01 MPa for 30 min to remove the air in the porous structure of the clay material during the vacuum pumping process. Subsequently, the prepared molten CA−PA eutectic mixture was added to the conical flask through a separation funnel, and the CA−PA eutectic mixture was vacuum-impregnated into the clay minerals over 1 h. After that, the vacuum process was ended, and air was allowed to enter the flask again to force the molten CA−PA to penetrate into the pore space of the clay minerals. Composite PCMs with various CA−PA PCM mass fractions of 25, 30, 35, 40, 45, and 50 wt % were prepared. The as-prepared composite PCMs were then set down on a filter paper and placed in a constant...
temperature heating box at 45 °C for 1 h. The leakage of molten CA–PA is detected by the mark left on the filter paper.

4.4. Characterization. The phase-change temperature and latent heat of the CA–PA mixture and clay mineral-based FSPCM were obtained under nitrogen by DSC using a Mettler DSC1 calorimeter (Switzerland) with a heating and cooling rate of 5 °C/min and a nitrogen scanning rate of 50 mL/min.

The thermal stability of various FSPCM samples was investigated using a thermogravimetric analyzer (Mettler-Toledo, Switzerland) under an atmosphere of nitrogen from 30 to 500 °C with a heating rate of 5 K·min⁻¹.

The surface morphology and microstructure of the clay mineral and clay mineral-based FSPCM were analyzed using field emission SEM (APREO, USA). Specific surface analysis (BET method, Autosorb iQ, USA) was used to characterize the porous structure of clay mineral materials and the clay mineral-based PCMs.

The functional groups of the CA–PA mixture and clay mineral-based FSPCM samples were analyzed by FTIR (Nicolet i550, USA). The experimental sample and KBr were fully ground to form tablets, and a scanning range of 500−4000 cm⁻¹ was used.

The heat storage and release properties of the clay mineral-based PCMs were tested using a self-made experimental platform. A schematic of the experimental device is shown in Figure 15, which includes a low-temperature refrigerator, high-temperature water bath, heat storage device, temperature inspection instrument, and computer. The heat storage device consisted of a glass container and a K-type thermocouple. The heat storage device was prepared by placing 30 g of the composite material in the glass container, and the K-type thermocouple was then positioned in the center of the container to measure the heat storage and release characteristics of the composite PCM. In step one, the heat storage device was placed in a high-temperature water bath with the temperature maintained at 65 °C such that the FSPCM was continuously heated from an initial temperature of 10 °C. When the temperature inside the container reached a constant 65 °C, heat storage was deemed completed. In step two, the heat storage device was placed in a low-temperature refrigerator with the temperature maintained at 10 °C to test the heat release performance. The computer recorded the temperature changes of the composite PCM during melting and solidification.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was funded by the National Natural Science Foundation of China, grant number 51774197.

**NOMENCLATURE**

FSPCMs form-stable composite phase change materials

PCM phase-change material
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