ABSTRACT: In this study, a capric acid (CA)-stearic acid (SA)/expanded graphite (EG) composite phase change material (PCM) was prepared, and the optimum mass ratio of CA-SA is 0.84:0.16. The composite PCM was characterized by scanning electron microscopy, differential scanning calorimetry, and X-ray diffraction. It can be concluded that the CA-SA mixture was found to possess good compatibility with EG, the thermal conductivity of the CA-SA/10 wt % EG composite PCM was 3.28 times higher than that of the CA-SA mixture, and the PCM thermal stability was satisfactory; no leakage occurred in the CA-SA/10 wt % EG composite PCM. The PCM has good thermal reliability after 500 thermal cycles. Finally, it is shown that the CA-SA/10 wt % EG composite PCM showed excellent performance, and therefore, it can be used for low-temperature thermal energy storage.

1. INTRODUCTION

In recent years, with the rapid development of economy and the continuous exploitation of fossil fuels, opinions on energy and environmental issues have become a hot issue of social concern. Thermal energy storage technology (TES) has been proven to be a low-cost and highly promising energy-saving technology.\textsuperscript{1–6} Heat storage technology can be divided into sensible heat storage, chemical reaction energy storage and latent heat storage according to energy storage forms.\textsuperscript{7} Sensible thermal energy storage can realize energy storage by heating the energy storage material to make its temperature rise and internal energy increase. Sensible heat storage has the advantages of high heat storage efficiency and low cost, but it has the disadvantages of low energy storage density and great change of heat storage/heat release temperature. Chemical reaction energy storage uses reversible chemical reactions to convert chemical energy and heat energy to each other to achieve energy storage. The process of chemical reaction energy storage is complicated, and its safety is difficult to guarantee, which leads to the few practical applications of this method. The latent heat energy storage uses the latent heat absorbed and released during the phase change process of the material to store energy, which has the advantages of high energy storage density, compact structure of the heat storage device, and almost constant temperature during the phase change process. In recent years, latent heat energy storage has become a research hotspot of energy storage technology and has been widely used in the fields of energy storage and temperature control, such as the “peak cut” of electric power, building envelopes, air conditioning energy storage systems, solar energy utilization, textiles and clothing, etc.\textsuperscript{5,9} The core of latent heat energy storage is phase change energy storage materials (PCM). In a certain temperature range, phase change energy storage materials melt and absorb ambient heat for storage. When the ambient temperature drops, phase change energy storage materials begin to solidify and release heat to the surrounding environment, so as to realize the storage and release of heat.\textsuperscript{10–13} According to the chemical properties, phase change materials can be divided into organic phase change materials, inorganic phase change materials, eutectic phase change materials, and composite phase change materials.\textsuperscript{14–16} Organic phase change energy storage materials mainly include paraffin, fatty acids, sugar alcohols, and polyethylene glycol, whereas inorganic phase change energy storage materials mainly include molten salts, hydrated salts, metals, and alloys.\textsuperscript{17} The advantages of inorganic phase change materials include high thermal conductivity, small volume change of the phase transformation process, and lower cost; however, there are problems of phase separation and supercooling. Compared with inorganic phase change materials, organic phase change
materials have become the preferred materials in thermal energy storage due to the advantages of nontoxicity, non-
corrosion, good crystallization performance, good stability, high latent heat of phase change, no phase separation, and small supercooling. Researchers have investigated the latent heat of phase change, crystallization performance, and thermal stability of organic phase change materials. Li prepared a eutectic salt solution by ultrasonic mixing of 6 wt % K$_2$HPO$_4$, 3H$_2$O, 6 wt % NaH$_2$PO$_4$, 2H$_2$O, 6 wt % Na$_2$SO$_4$, 3H$_2$O, and 82 wt % deionized water. To reduce deionized water undercooling, the effect of a nucleating agent on its undercooling was explored. The experimental results show that when 1 wt % Na$_2$B$_4$O$_7$·10H$_2$O (borax) is added, the undercooling degree of a eutectic salt can be effectively reduced, and the phase transition enthalpy is 161.8 J·g$^{-1}$; however, the phase transition temperature is very low. Sari et al. studied the thermal stability of an LA-SA eutectic mixture by thermal cycling experiments. The experimental results show that when the mass ratio of LA:SA = 75:5:24.5, the melting temperature of the LA/SA eutectic mixture is 37 °C, and the melting latent heat is 182.70 J·g$^{-1}$. After 360 thermal cycles, the melting temperature and enthalpy of the LA/SA eutectic mixture changed by 0.36 K and 0.2%, respectively, compared with that before thermal cycling. The fatty acid eutectic mixture showed good thermal stability. Zhang prepared a ternary eutectic mixture with a mass ratio of lauric acid (LA), palmitic acid (PA), and stearic acid (SA) of 62.2:24.6:13.2 and prepared a shape-stabilized composite phase change material with an expanded perlite (EP) matrix by a vacuum infiltration method. DSC test results show that the melting temperature of the LA-PA-SA/EP composite phase change material is 31.6 °C, and the melting latent heat is 81.50 J·g$^{-1}$.

Among the several organic phase change materials, fatty acids are considered as a potential PCM. However, due to the high melting point and low thermal conductivity of most of the fatty acids, a liquid flow occurs during phase change, which limits their application. The thermal conductivity of the composites can be enhanced by adding high-thermal conductivity particles to the fatty acid phase change materials. Expanded graphite (EG) is a porous structure material with several advantages such as high thermal conductivity, light weight, tastelessness, nontoxicity, and low cost. Zhang et al. improved the thermal conductivity of the composite phase change material by varying the amount of EG in paraffin. The study found that the thermal conductivity of the composite phase change material increased by 3.2 times compared with that before the addition of EG, and the maximum mass percentage of paraffin absorbed in the composite PCM sample was up to 92%. Hu et al. prepared a series of palmitic acid/EG composite phase change materials by melt blending. The addition of EG weakened the natural convection of phase change materials in the endothermic process and enhanced the temperature control effect in the exothermic process.

In this study, a novel PCM of a CA-SA binary eutectic mixture with suitable phase change temperature and high latent heat of phase change is obtained. To improve the thermal conductivity of the CA-SA binary eutectic mixture and prevent the phase change material from leaking, the CA-SA eutectic mixture/10 wt % EG composite PCM with the best absorption mass ratio was prepared. The microstructure and thermal properties of the CA-SA/EG phase change material were characterized by SEM, DSC, BET, and XRD. Finally, the thermal cycle experiment was carried out to determine the thermal reliability of the CA-SA eutectic mixture/10 wt % EG composite PCM.

2. RESULTS AND DISCUSSION

2.1. Determination of the Best Mass Ratio of the CA-SA Mixture. Figure 1 shows the DSC test curves of a series of CA-SA binary mixtures in an endothermic process.

![Figure 1. DSC test curves of a series of CA-SA binary mixtures in an endothermic process.](image)

As shown in the figure, the DSC curve only shows a solid—liquid phase transition peak, and it can be considered that CA and SA are mixed uniformly and only one solid—liquid phase transition occurred. The phase transition temperature of CA-SA binary mixtures with different mass ratios is different. The mass fraction of SA increased from 16 to 22%, and the corresponding phase transition melting temperature ($T_m$) increased from 24.81 to 28.91 °C. The melting latent heat of phase change ($H_m$) increased from 165.82 to 168.44 J·g$^{-1}$. The corresponding phase transition freezing temperature ($T_f$) increased from 22.62 to 26.22 °C, and the freezing latent heat of phase change ($H_f$) increased from 164.01 to 167.15 J·g$^{-1}$. When the SA mass fraction was 14%, the corresponding phase transition melting temperature is 25.83 °C, and the melting latent heat data of the binary mixture are recorded in Table 1.

| samples | $T_m$ (°C) | $H_m$ (J·g$^{-1}$) | $T_f$ (°C) | $H_f$ (J·g$^{-1}$) | $T_w$ (°C) |
|---------|------------|----------------|------------|----------------|------------|
| CA-SA16% | 25.83 | 160.21 | 23.52 | 159.82 | 2.31 |
| CA-SA18% | 24.81 | 165.82 | 22.62 | 164.01 | 2.19 |
| CA-SA20% | 25.70 | 166.14 | 22.81 | 165.33 | 2.89 |
| CA-SA22% | 27.25 | 167.51 | 24.73 | 165.90 | 2.52 |
| CA-SA24% | 28.91 | 168.44 | 26.22 | 167.15 | 2.69 |

Table 1. Phase Transition Data of the Melting and Freezing Process of the CA-SA Eutectic Mixture
the theoretical calculation results, so choose a eutectic mixture with a mass ratio of CA:SA = 0.84:0.16 for follow-up research.

2.2. Test Results of Thermal Conductivity. Low thermal conductivity is a common defect of fatty acid compounds for both CA and SA. Thermal conductivity has a significant effect on the energy storage and release efficiency of phase change materials.33,34 This work improved the thermal conductivity of the composite by adding different mass fractions of EG to the CA-SA eutectic mixture. The average value of three experiments was taken as the final value of the thermal conductivity. The average values with error and the increment in thermal conductivity of the CA-SA eutectic mixture after adding different mass fractions of EG are shown in Figure 2. The data error is due to the uncertainty factors in the measurement process and the slight difference in the adsorption capacity of EG to CA-SA in different samples. The standard deviation of seven samples is less than 1%, which can be considered that the measurement results are more accurate. Before adding EG, the thermal conductivity of the CA-SA eutectic mixture was only 0.1577 W·m⁻¹·K⁻¹. However, when the mass fraction of EG increased from 2 to 10 wt %, the thermal conductivity of the mixture increased from 0.2055 to 0.5218 W·m⁻¹·K⁻¹, and the increase in thermal conductivity was almost linear; this can be attributed to the nature of high thermal conductivity of EG. Among them, the thermal conductivity of the mixture with 10 wt % EG added was 3.28 times higher than that before the addition of EG. When the mass fraction of EG increased from 10 to 12 wt %, the rate of increase in thermal conductivity is only 7.7%. It is shown that the addition of EG can significantly increase the thermal conductivity of the CA-SA eutectic mixture. However, EG is not added unlimitedly. Once the composite material has formed heat transfer pathways, even though there is a continuous increase in the addition of EG at the same degree, the increase in thermal conductivity of the composite material slows down.35

2.3. Optimum Absorption Ratio of the CA-SA Eutectic Mixture and EG. The addition of EG can significantly improve the thermal conductivity of the composite PCM. However, EG can be added only in a limited quantity. Figure 3 shows the images of the CA-SA/EG composite PCM with different EG contents (0, 2, 4, 6, 8, 10, and 12 wt %) after heating for 1.5 h at 45 °C. Figure 3 shows that the leakage in P1 is the highest because this sample does not include EG. Samples P2 to P5 leaked because the content of the CA-SA mixture exceeded the adsorption capacity of EG. As the mass fraction of EG increased (from 2 to 8 wt %), the imprint area on a filter paper gradually decreased, indicating that the leak degree gradually decreases. The images of P6 and P7 samples showed no leakage, indicating that EG in these two samples completely absorbed the CA-SA eutectic mixture. To calculate the mass loss rate of the sample before and after heating, the sample was weighed. The weighing results of the samples before and after heat treatment are shown in Table 2. When EG added to the mixture exceeds 8 wt %, the mass loss rate of the sample after heating drops rapidly, and it shows that the EG and CA-SA mixture has good adsorption effects.

2.4. Chemical Structure Analysis of the CA-SA/EG Composite PCM. Figure 4 shows the FT-IR spectra of EG and the CA-SA eutectic mixture with different EG mass fractions, the peaks at 2850 cm⁻¹ are assigned to the C–H stretching vibration absorption band, the C=O stretching vibration peak is observed at 1708 cm⁻¹, and the peaks at 1115 cm⁻¹ are assigned to the C–O stretching vibration band. The peak at 936 cm⁻¹ is due to the bending vibration of C=OH. Due to the presence of carboxyl groups in fatty acids, strong hydrogen bonds can be formed between carboxylic acid molecules to affect the position of the C=O absorption band in fatty acids, causing the C=O absorption band to shift to a low wavenumber and no effect on the chemical structure of the overall eutectic. It is shown that the FT-IR spectra of CA-SA mixtures with different EG contents are almost the same. In short, between the CA-SA mixture and EG, no chemical interaction occurred.

2.5. Thermal Stability of the CA-SA/EG PCM. Thermal stability is an important index to verify the stability of the composite phase change materials in the application temper-
ature range; because EG will not be thermally decomposed in the temperature range below 500 °C, when the thermal decomposition of the CA-SA eutectic mixture is completed, the remaining mass is the mass of EG in the sample. The actual loading rate (\(\lambda\), wt %) of the CA-SA eutectic mixture in the PCM was calculated using formula 1,\(^3\) and their calculation results are listed in Table 3.

\[
\lambda = 1 - \frac{m_{\text{em}}}{m_{\text{cpcm}}} \times 100\%
\]  

where \(\lambda\) (wt %) is the actual load rate of the CA-SA eutectic mixture in the PCM, \(m_{\text{em}}\) (in grams) is the weight of EG after heat treatment, and \(m_{\text{cpcm}}\) (in grams) is the weight of the CPCM.

Table 2. Weight of the CA-SA Mixture/EG Composite PCM before and after Heat Treatment

| samples          | P1   | P2   | P3   | P4   | P5   | P6   | P7   |
|------------------|------|------|------|------|------|------|------|
| EG content (wt %)| 0    | 2    | 4    | 6    | 8    | 10   | 12   |
| before thermal treatment (g) | 1.794 | 1.783 | 1.802 | 1.750 | 1.725 | 1.723 | 1.702 |
| after thermal treatment (g)    | 1.198 | 1.289 | 1.356 | 1.470 | 1.496 | 1.611 | 1.617 |
| quality loss rate (%)           | 33.2  | 27.7  | 24.8  | 16.0  | 13.3  | 6.5   | 5.0   |

Figure 5 shows the TG curves of the CA-SA mixture with different EG mass fractions. As shown in the figure, the masses of all samples did not change before 100 °C, indicating that the prepared composite materials were in the range of 25–100 °C, no thermal decomposition occurred, and the thermal stability was satisfactory. The mass of the sample begins to decrease in

Table 3. Comparison of the Theoretical Load Rate and the Actual Load Rate of the CA-SA Eutectic Mixture

| samples          | CPCM1 | CPCM2 | CPCM3 | CPCM4 | CPCM5 | CPCM6 |
|------------------|-------|-------|-------|-------|-------|-------|
| theoretical load rate (%) | 98    | 96    | 94    | 92    | 90    | 88    |
| actual load rate (%)   | 97.60 | 95.74 | 93.81 | 92.14 | 89.90 | 87.66 |
the range of 100–300 °C, indicating that the fatty acid mixture thermally decomposes, the final curve is stable, and the remaining mass is the mass of EG in the sample. As shown in Figure 5a, the TG curves of the three samples CPCM1, CPCM2, and CPCM3 have similar downward trends, and the temperatures at the time of complete decomposition are also very close. As shown in Figure 5b, the maximum mass loss rates in the DTG curves corresponding to samples CPCM4, CPCM5, and CPCM6 occurred at 240, 207, and 185 °C, respectively. It is possible that the EG content added to the PCM within a certain range will have a certain strengthening effect on the thermal decomposition process of the composite material. In addition, as shown in Table 3, the deviation between the theoretical load rate and the actual load rate of the CA-SA eutectic mixture in the sample with an EG mass fraction of 10% is the smallest, and it shows that the eutectic mixture of EG and CA-SA is most evenly mixed.

### 2.6. Thermal Storage Performance of CA-SA/EG Composite PCM

Figure 6 shows that the melting phase transition temperature of the CA-SA/EG composite phase change material is slightly lower than that of the CA-SA mixture, and the solidification phase transition temperature is slightly higher than that of the CA-SA mixture. It can be considered that the mixing of EG and CA-SA has a positive effect on the enhancement of heat transfer, with EG as thermally conductive pathways between the PCM layers, resulting in a faster phase transition.35,37 As the mass fraction of EG increases, there is a corresponding reduction of the latent heat of the PCM, which indicates that the addition of EG does not contribute to the latent heat of phase change of the CA-SA mixture. When EG increases from 0 to 10 wt %, the average change rate of the latent heat of phase change during the endothermic melting process of the composite phase change material is 1.93%. The latent heat values of phase change during endothermic and exothermic processes of the composite PCM with 12 wt % EG are 146.71 and 145.23 J·g⁻¹, which are 2.47 and 3.40% lower than that with 10 wt % EG (detailed data are shown in Table 4). This shows that when the addition of EG exceeds 10 wt %, the phase change latent heat of the composite PCM will be significantly inhibited.

In addition, the addition of EG has a positive effect to the suppressed supercooling of the PCM. In addition, the CA-SA/10 wt % EG composite PCM reflects the lowest supercooling degree, but when the loadings of EG increase to 12 wt %, the supercooling degree of the PCM becomes worse. This may be caused by the uneven distribution of EG in the PCM due to an excessive EG content.39 Combining the heat storage performance of the CA-SA/EG composite PCM, TG tests, and the analysis results of the leakage experiment, the CA-SA eutectic mixture/10 wt % EG composite PCM was selected for follow-up research. In addition, Table 5 shows the comparison of thermal properties between the CA-SA eutectic mixture/10 wt % EG composite PCM and the composite PCM reported in the literature. The latent heat capacity of the PCM in this paper is better than that of other composite PCM, so it can be used for low-temperature phase change heat storage.

Figure 6. DSC test curves of the CA-SA/EG composite PCM with different EG mass fractions: (a) melting process and (b) freezing process.

### Table 4. Thermal Performance Data of the CA-SA/EG Composite PCM with Different EG Mass Fractions in the Process of Heat Absorption and Heat Release

| samples | melting | freezing |
|---------|---------|----------|
|         | T_m (°C) | H_m (J·g⁻¹) | T_f (°C) | H_f (J·g⁻¹) | T_i (°C) |
| CPCM0   | 24.81    | 165.82    | 22.62    | 164.91    | 2.19     |
| CPCM1   | 24.58    | 162.61    | 22.45    | 161.21    | 2.13     |
| CPCM2   | 24.61    | 160.23    | 22.56    | 159.50    | 2.05     |
| CPCM3   | 24.70    | 156.94    | 22.74    | 156.43    | 1.96     |
| CPCM4   | 24.52    | 152.80    | 22.80    | 152.24    | 1.72     |
| CPCM5   | 24.47    | 150.42    | 22.82    | 150.35    | 1.55     |
| CPCM6   | 24.40    | 146.71    | 22.62    | 145.23    | 1.78     |

### Table 5. Comparison of Thermal Properties of the CA-SA/10 wt % EG PCM with those of the Composite PCM Reported in the Literature

| samples                          | T_m (°C) | H_m (J·g⁻¹) | ref. |
|----------------------------------|----------|--------------|-----|
| capric acid—palmitic acid/expanded graphite | 23.05    | 131.8        | 41  |
| decanoic acid-palmitic acid-stearic acid/expanded graphite | 28.93    | 137.38       | 42  |
| stearic acid-palmitic acid/diatomite | 52.93    | 106.70       | 43  |
| quinary fatty acid eutectics/hollow SiO2 nanofibers | 17.83    | 123.80       | 44  |
| capric acid-stearic acid/sepiolite | 22.86    | 76.16        | 45  |
| capric acid-stearic acid/expanded graphite | 24.47    | 150.42       | this work |
2.7. SEM Analysis of EG and the CA-SA Eutectic Mixture/10 wt % EG Composite PCM. The surface morphology and microstructure of raw EG, the CA-SA eutectic mixture, and the CA-SA eutectic mixture/10 wt % EG composite PCM were studied by SEM, as shown in Figure 7. It can be observed from Figure 7a that EG showed a wormlike structure. In addition, a large number of well-developed reticular pores at a microscale in wormlike EG can be clearly observed (Figure 7b), and it is shown that raw EG has a large specific surface area, thereby presenting an excellent absorption ability. Upon comparing Figure 7a−f, there is a clear indication that the pore structure of the EG surface is filled with the eutectic mixture. The CA-SA eutectic mixture and EG are closely connected at their two-phase interfaces due to the high infiltrating capacity of the CA-SA eutectic mixture, thereby showing good compatibility. The energy-dispersive spectroscopy (EDS) analysis is shown in Figure 7g−i, and the composition and content of elements were obtained by surface scanning. The EDS spectrum of EG shows that the content of atomic C is 93.58%, including 6.05% atomic O and a few Al and Si elements, and it shows that there are trace impurities in EG used in the experiment, which does not affect its adsorption performance. Only C and O elements were detected in the CA-SA mixture, which was consistent with the chemical formula of fatty acids. CA-SA/EG PCM analysis has detected four elements common to EG and the CA-SA mixture, and the atomic content of the C element is higher than that of the CA-SA mixture, indicating that EG has been fused with the CA-SA mixture.

2.8. XRD Analysis of EG and the CA-SA Eutectic Mixture/10 wt % EG Composite PCM. The crystal structures of EG, the CA-SA eutectic mixture, and the CA-SA/10 wt % EG composite PCM were characterized by XRD, and the characterization results are shown in Figure 8. EG has a strong diffraction peak at 2θ = 26.38°, and the CA-SA eutectic mixture/10 wt % EG composite PCM has four strong diffraction peaks at 2θ = 12.12°, 2θ = 21.57°, 2θ = 23.95°, and 2θ = 26.43°. The above strong diffraction peaks can be observed in the XRD pattern of the CA-SA mixture. Since the CA-SA eutectic mixture is adsorbed by EG, the increase in the diffraction peak of the composite PCM at 2θ = 26.43° is not obvious. The diffraction peaks of EG and the CA-SA eutectic mixture can be found in the diffraction patterns of the CA-SA/10 wt % EG composite PCM, and no new strong diffraction peaks appear. The results show that the addition of EG does not change the crystal structure of the CA-SA eutectic mixture. It is only a simple physical adsorption, which meets the preparation requirements of the composite PCM.

2.9. Pore Structure Analysis of the CA-SA/10 wt % EG Composite PCM. The nitrogen adsorption–desorption isotherms of EG and the CA-SA/10 wt % EG composite PCM are shown in Figure 9a. Figure 9a shows that the
nitrogen adsorption–desorption isotherms of the two materials are all type-III isotherms. In the low-pressure zone, the adsorption capacity of nitrogen is small. At this time, the force between nitrogen and the CA-SA/10 wt % EG composite PCM is weak. In the high-pressure zone, the nitrogen adsorption curve rises, nitrogen condenses in the pores, and almost no desorption hysteresis occurs, indicating that a large amount of CA-SA is filled in the EG pores, and the porosity drops rapidly.

Figure 9b shows that the pore size distribution curve of expanded graphite exhibits double peaks below 10 nm. The pore diameters corresponding to the two peaks are 3.78 and 6.60 nm, the specific surface area is 2.492 m$^2$·g$^{-1}$, and the total pore volume is 0.0724 cm$^3$·g$^{-1}$. The pore size distribution curve of the CA-SA/10 wt % EG composite PCM is a single-peak curve. The pore size corresponding to the peak is 3.81 nm, the specific surface area is 0.356 m$^2$·g$^{-1}$, and the total pore volume is 0.02192 cm$^3$·g$^{-1}$. EG is similar to a worm structure, with a larger specific surface area and pore structure. EG is used as a support material for the CA-SA/10 wt % EG composite PCM. After vacuum adsorption of the eutectic mixture, the specific surface area is 2.492 m$^2$·g$^{-1}$ and drops to 0.356 m$^2$·g$^{-1}$, and the total pore volume is greatly reduced. The results show that the pore structure of EG in the composite PCM is filled with the CA-SA eutectic mixture.

2.10. Thermal Reliability of the CA-SA/10 wt % EG Composite PCM. Figure 10 shows the DSC curves of the CA-SA eutectic mixture/10 wt % EG composite PCM after 500 thermal cycles at a heating and freezing rate of 5 K·min$^{-1}$. The relevant data are listed in Table 6. As shown in Figure 10, after 500 thermal cycles, the melting temperature ($T_m$) and freezing temperature ($T_f$) of the composite PCM change by 0.04 and $-0.15 \, ^\circ$C. The melting latent heat ($H_m$) of the CA-SA/10 wt % EG composite PCM decreased from 150.42 to 148.58 J·g$^{-1}$, and the solidification latent heat ($H_f$) decreased from 150.35 to 146.80 J·g$^{-1}$. The data fluctuation was within 1.22 and 2.36%, which was in the acceptable range. After 500 thermal cycles, the FT-IR spectrum and the XRD curve maintained a stable curve, and the crystal structure and chemical structure of the composite material did not change. The experimental results show that the CA-SA/EG composite PCM can maintain good thermal stability after 500 thermal cycles.

3. CONCLUSIONS

In this study, the CA-SA binary mixture was prepared by the vacuum impregnation method, and the best mass ratio was determined to be 0.84:0.16 through DSC. To improve the thermal conductivity of the binary mixture, the CA-SA/EG composite PCM was prepared by adding different mass fractions of EG to the mixture, and the optimal addition amount of EG was 10 wt %. SEM, XRD, and BET showed that the pore structure of EG was filled with the CA-SA eutectic mixture. After 500 thermal cycles, the phase change temperature of the CA-SA/10 wt % EG composite PCM did not change significantly, the latent heat of phase change was not significantly reduced, and the FT-IR spectrum and the XRD curve maintained a stable curve, indicating that the PCM has good thermal reliability. In conclusion, the CA-SA/10 wt % EG composite PCM has excellent performance and can be used for heat storage in low-temperature phase change materials.

4. MATERIALS AND METHODS

4.1. Materials. Here, we used the following materials: capric acid (CA, also known as decanoic acid, chemically pure, purity of $\geq 98\%$, produced by the Sinopharm Chemical Reagent Company in China), stearic acid (SA, chemically pure, purity of $\geq 98\%$, produced by the Tianjin Beilian Fine Chemicals Development Company in China), and EG predried in an oven at 75 $^\circ$C to ensure dryness (purity of...
≥98%, produced by the Qingdao Tengshengda Carbon Machinery Company in China).

4.2. Preparation of the CA-SA Eutectic Mixture. The eutectic mixture of two or more fatty acids has a lower melting temperature, and its theoretical molar ratio and phase transition temperature can be calculated using the Schroeder theory prediction formula (eq 2).46

\[
\ln x_i = \frac{H_i}{R \left( \frac{1}{T_i} - \frac{1}{T} \right)}
\]

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); \( T \) is the temperature of the eutectic point (K); \( x_i \) is the molar ratio of component \( i \) in the eutectic mixture; \( R \) is the gas constant (8.314 J·K\(^{-1}\)·mol\(^{-1}\)). The theoretical phase diagram of the CA-SA binary mixture is shown in Figure 11. To verify the reliability of the calculation formula, a series of CA-SA mixtures with different mass fractions were prepared. First, CA and SA with mass fractions of 86 and 14%, respectively, were mixed in a 150 mL beaker, and then, the mixture was heated in a 75 °C constant-temperature water bath and stirred magnetically for 1 h until the CA and SA were completely mixed. Then, the molten mixture was put on a laboratory bench to cool to room temperature and labeled as CA-SA\(_{14\%}\). Other mixtures with different mass ratios were prepared in accordance with the above method and were marked as CA-SA\(_{16\%}\), CA-SA\(_{18\%}\), CA-SA\(_{20\%}\), and CA-SA\(_{22\%}\).

4.3. Preparation of the CA-SA/EG Composite PCM. EG was used as the supporting material, and the CA-SA binary eutectic mixture was used as the additive.47 A series of CA-SA/EG composite phase change materials (CPCM) were prepared by the vacuum impregnation method. As shown in Figure 12,
EG was placed in a conical flask, placed in a water bath at 75 °C, and vacuumed to 0.01 MPa, and air was discharged for 30 min. The prepared molten CA-SA eutectic mixture was then added to a conical flask through a separation funnel. The CA-SA was vacuum-impregnated into EG for 1 h. After that, the vacuum process was over, and air was allowed to enter the flask again to force the molten CA-SA full access to EG. Two weight percent EG, 4 wt % EG, 6 wt % EG, 8 wt % EG, 10 wt % EG, and 12 wt % EG were added to the Erlenmeyer flask in turn, the composite was denoted as CPCM1—CPCM6, and the mixture without EG was used as a control group (denoted as CPCM0).

After obtaining six kinds of composite phase change materials with different EG mass fractions, they were pressed into a disk sample with a radius of 10 mm and a thickness of 2 mm using a tablet press. Then, they were placed on a filter paper and placed in a constant-temperature heating box with the temperature controlled at 45 °C. After heating for 1 h, the leakage in the composite phase change material was observed, and the quality of the sample before and after heating was compared.

4.4. Characterization. The phase change temperature and latent heat of the CA-SA mixture and the CA-SA/EG composite PCM were obtained by differential scanning calorimetry (DSC) using a Mettler DSC1 calorimeter (Switzerland), with heating and cooling rates of 5 °C/min and a nitrogen scanning rate of 20 mL/min. After cooling the CA-SA/EG composite material with liquid nitrogen for 30 min, the sample mold pressed the test object into a test piece with a ϕ of 12 mm and a thickness of 2 mm, and then, we used a laser thermal conductivity measuring instrument (Netzsch LFA457, Germany). The thermal conductivity of the test piece was measured. The surface morphology and microstructure of EG and CA-SA/EG composite phase change materials were analyzed by field emission scanning electron microscopy (FESEM, APREO, USA).

To analyze the changes in the crystal structure of the composite phase change material, an XRD (Rigaku Utima IV, Japan) was used to analyze the crystal structure. The crystal structures of EG, CA-SA, and the CA-SA/EG PCM were characterized, and the radiation source was a Cu target with a diffraction angle of 0–50°. The functional groups of EG and CA-SA eutectic mixture/EG composite phase change material samples were analyzed by Fourier transformation infrared spectroscopy (FT-IR, Nicolet iSS50, USA). The mixture of the two substances and KBr was ground, and tablets were prepared. The scanning range was from 500 to 4000 cm⁻¹. The thermal stability of these CA-SA eutectic mixture samples with different EG mass fractions was investigated by thermogravimetric analysis (Mettler Toledo, Switzerland) under an atmosphere of nitrogen from 25 to 500 °C with a heating rate of 5 K·min⁻¹. Specific surface analysis (BET method, ASAP2460, USA) was used to characterize the porous structure of EG and the CA-SA/EG composite PCM.

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**Notes**

The authors declare no competing financial interest.

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