Preparation and Performance Analysis of Form-Stable Composite Phase Change Materials with Different EG Particle Sizes and Mass Fractions for Thermal Energy Storage

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ABSTRACT: The low thermal conductivity and leakage of paraffin (PA) limit its wide application in thermal energy storage. In this study, a series of form-stable composite phase change materials (CPCMs) composed of PA, olefin block copolymer (OBC), and expanded graphite (EG) with different particle sizes (50 mesh, 100 mesh, and 200 mesh) and mass fractions are prepared by melt blending. OBC as a support material could reduce PA leakage during melting, and EG as a thermally conductive filler can improve the thermal performance of PCMs. The microstructure characteristics and chemical and thermal properties of prepared CPCMs are tested and analyzed. The results show that PA/OBC and EG have good compatibility, and there is no chemical reaction with each other to generate new substances. Thermal conductivity can be significantly improved by adding EG, and it is greatly enhanced with the increase in EG particle size at the same EG mass fraction. Simultaneously, the addition of EG increased the melting temperature of CPCMs and decreased the solidification temperature as well; meanwhile, the values of melting temperature and solidification are also reversed for CPCMs compared to PA/OBC. There is an optimal content of EG to balance the thermal conductivity and heat storage capacity for CPCMs. The addition of OBC can provide a stable geometric construction, and the leakage will be further improved with the increase in EG content. Finally, the melting time of CPCMs containing EG-50, EG-100, and EG-200 with 4 wt % EG is shortened by 52.9, 41.1, and 37.5%, respectively, compared with PCMs without EG in the heat storage and release experiments. Also, the CPCMs with EG-50 have better thermal performance compared with the CPCMs of EG-100 and EG-200.

1. INTRODUCTION

With the development of society, the energy shortage and environmental pollution problems caused by the massive consumption of fossil energy have become increasingly prominent, and it was more and more imperative to seek and utilize renewable clean energy such as wind energy and solar energy. Energy storage technology can not only solve the mismatch between time and space in continuous energy demand and the unsteady output of renewable energy but also efficiently recover energy and greatly reduce energy waste. Energy storage technology can be divided into sensible heat energy storage, latent heat energy storage, and thermochemical energy storage according to different ways of energy utilization. The phase change latent heat energy storage method has received extensive attention due to its high latent heat of phase change, stable performance, nontoxicity, low vapor pressure, and low cost. However, like other organic PCMs, PA has defects such as low

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thermal conductivity and leakage during phase change, which limits its popularization in thermal energy storage applications.\textsuperscript{11} To solve these defects, scholars have prepared different advanced composite PCMs (CPCMs) by encapsulating PCMs in shells or adding various functional matrices.\textsuperscript{12} However, the preparation of PCMs into phase change microcapsules has many limitations, such as low yield and high cost. At present, some scholars have focused more attention on confining PCMs in polymers to prepare form-stable CPCMs.\textsuperscript{2,3} Polymers such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), and triblock copolymer (stereylene-b-(ethylene-co-butylene)-b-styrene triblock copolymer, SEBS) have been widely studied in energy storage PCMs. As a support material, HDPE greatly improves the compressive strength of PA-Al\textsubscript{2}O\textsubscript{3}/HDPE CPCMs.\textsuperscript{14} As form-stable CPCMs, ASA/SEBS/PA can still maintain a complete shape after a 24 h accelerated leak test, which is because PA molecules have good compatibility with SEBS macromolecules; as a result, PA molecules can be firmly fixed on the molecular chain of SEBS.\textsuperscript{15} On the other hand, although the CPCMs prepared from these PAs and polymers have good shape stability, they also have high mechanical hardness and low tensile ability, which makes the prepared CPCMs brittle and difficult to process and apply to complex products. Therefore, polymers with good shape memory have attracted extensive attention. Olefin block copolymer (OBC) is a new type of thermoplastic elastomer with a crystallizable ethylene octene block with high melting point (hard segment) and an amorphous ethylene octene block (soft segment) with low glass transition temperature.\textsuperscript{16} PA molecules have good compatibility with OBC molecules. When the temperature is higher than the melting temperature of PA, the three-dimensional structure of OBC can inhibit the flow of PA, reduce leakage, and keep the CPCMs intact.\textsuperscript{17} In addition, the liquid-phase PA can change the fluidity of the OBC soft segment molecular chain, thereby giving the PCM a certain flexibility and reducing the contact thermal resistance with the product.\textsuperscript{18}

Although polymers as support materials reduce the leakage of PCMs, the low thermal conductivity of PCMs is another obstacle for the application of energy storage materials. Due to the low thermal conductivity of PA, it will prolong the heat storage and release time, thereby reducing the efficiency of the energy system. To solve this problem, researchers usually introduce different types of highly thermally conductive materials, such as metal foams, boron nitride, aluminum nitride, and expanded graphite (EG). They can greatly solve the problem of poor thermal conductivity of PCMs. For example, aluminum nitride was introduced into epoxy resin CPCMs to improve the thermal conductivity of PCMs.\textsuperscript{19} Boron nitride as thermal conductive nanoparticles can greatly shorten the overall heat storage and release time of capric-palmitic-stearic acid ternary CPCMs.\textsuperscript{20} Compared with carbon materials, the use of metal materials will inevitably lead to an increase in the weight and cost of the energy storage system. Compared with other carbon materials, EG has the advantages of good thermal conductivity, corrosion resistance, flame retardancy, nontoxicity, and low cost.\textsuperscript{21} EG is a worm-like substance with a rich pore structure, and its rich network structure can speed up the propagation of phonon groups and form tight heat conduction paths.\textsuperscript{22} At the same time, the porous structure can provide strong surface tension and capillary force so that EG can adsorb lots of PCMs. Zhao et al.\textsuperscript{23} used the porous adsorption properties of EG to prepare CPCMs containing different mass fractions of EG, and the results showed that with the addition of EG, the heat storage performance of the PCM was improved. Hua et al.\textsuperscript{24} studied the use of EG to enhance the thermal conductivity of PA, and their results showed a linear relationship between the thermal conductivity and the mass fraction of EG. Tian et al.\textsuperscript{25} found that when the ratio of large and small particle size EG is 9:1, PA can make full use of the spatial structure of EG, and the thermal diffusion coefficient of composite PCMs reaches $1.964 \times 10^{-8}$ m$^2$/s, nearly 22 times higher than that of pure PA. Li et al.\textsuperscript{26} studied the adsorption properties of EG with different particle sizes on NaNO$_2$−NaCl and found that EG with large particle size has a more complex layered structure, which can adsorb more PCMs in the porous framework. Chirtoc et al.\textsuperscript{27} studied the effect of different sizes of EG on the thermal conductivity, and they found that the larger the particle size of the EG, the higher the thermal conductivity and the smaller the interface thermal resistance. Zhao et al.\textsuperscript{28} studied the effect of EG particle size on PA/EG composite PCMs, and their results showed that compared with small size EG large particle size EG can bring higher degradation temperature to CPCMs, up to 31 °C. Deng et al.\textsuperscript{29} studied the thermal conductivity of polymer/EG composites from the perspective of the polymer chain structure, and their results showed that the interaction between the polymer matrix and EG and the crystallization process had a great impact on the thermal conductivity of the composites.

As summarized above, the thermal and mechanical properties of PCMs have been improved by adding higher thermal conductivity materials and polymer materials. Up to the present, the research on the effect of different sizes of EG on the thermal properties of composites mainly focuses on a single PCM. However, the mass fraction and particle size have a divergent effect on the properties and few research and explanation on the equilibrium relationship of the adding material properties, energy storage capacity, and thermal conductivity capacity of CPCMs with added polymer materials. In this study, a series of form-stable CPCMs composed of PA, OBC, and EG with different sizes and mass fractions were prepared by the melt blending method. OBC as a support material can reduce the leakage of PA during melting, and EG as a thermal conductive filler can improve the thermal properties of PCMs. The micromorphology, structure, and thermal performance of the prepared CPCMs were characterized. The effects of different particle sizes and different mass fractions of EG on the structure and properties of the polymer CPCMs were analyzed in detail. In addition, the heat transfer characteristics of pure PA and CPCMs based on different sizes of EG were evaluated through heat storage and heat release experiments. This study has an important reference value for the preparation and application of composite phase change energy storage materials based on EG.

2. EXPERIMENTAL SECTION

2.1. Materials. As a phase change energy storage material, phase change PA (OPE44, Luer new materials Co., Ltd., Hangzhou, China) has excellent latent heat capacity and phase change temperature of about 44 °C. OBC (INFUSE 9530, Dow Chemical, USA) has a density of 0.887 g/cm$^3$ and a melt index of 5 g/10 min (190 °C/2.16 kg). It has good compatibility with PA and plays a supporting role in CPCMs. The EG was purchased from Qingdao Jintao Graphite Co., Ltd., the mesh number is 50 mesh, 100 mesh, and 200 mesh, and the expansion ratio is 300 times. It plays a role in improving the thermal conductivity of the CPCMs.
2.2. Preparation of CPCMs. In this experiment, PA/OBC/EG CPCMs containing EG with different particle sizes were prepared. First, the EG was poured into a beaker and sealed with a film and then placed in a vacuum drying oven at 80 °C for 24 h. Then, the dried EG was put into an evaporating dish and heated in a microwave oven for 60 s to obtain EG that meets the requirements. The CPCMs were prepared by the melt blending method, and the specific preparation process is shown in Figure 1. The specific preparation steps are as follows: (1) an appropriate amount of solid PA was poured into a beaker and heated in a constant temperature oil bath at 80 °C for 30 min until it was completely melted; (2) the temperature of the constant temperature oil bath was slowly increased to 160 °C, and then, an appropriate amount of OBC was gradually added into the abovementioned PA solution in batches and stirred with magnetic force at 1300 rpm for 30 min to evenly dispersed OBC in the PA solution eventually. In order to maintain the morphological stability of CPCMs, the ratio of OBC to PA was maintained at 1:4; (3) the prepared EG was added to the abovementioned mixture in batches and mechanically stirred at 600 rpm for 30 min to make it uniformly dispersed in the PCM; and (4) the well-stirred mixture was poured into a stainless-steel mold with a diameter of 40 mm for molding and taken out after cooling to room temperature. The different components of the prepared CPCMs are shown in Table 1.

2.3. Characterization of CPCMs. Scanning electron microscopy (SEM, JSM-5600LV, JEOL, Japan) was used to characterize the microscopic morphology of the samples. The samples were fixed on the sample stage with double-sided tape. The chemical structure of the samples was investigated with a Fourier transform infrared spectrometry (FT-IR, Nexus 670, Thermo Nicolet, USA) instrument, which was mixed with potassium bromide (KBr) and pressed into small discs under a pressure of 5 MPa, and the scanning range was 400–4000 cm⁻¹. An X-ray diffraction (XRD, D8 Advance, Bruker, Sweden) instrument was used to analyze the crystal structure of PA, OBC, EG, and PA/OBC/EG composites with a scan range of 5°–80° and a rate of 5° (2θ) min⁻¹, the scanning mode is continuous scanning, the working voltage is 40 KV, and the working current is 40 mA. The thermal conductivity meter (TC3100, XIATECH, China) was used to analyze the thermal conductivity of PA/OBC and PA/OBC/EG CPCMs. Its measurement range and accuracy were 0.001–20.0 W/(m·K) and ±3%, respectively. The transient hot wire method was used for testing. Before the test, the sample was polished, the sensor probe was placed between the two samples, and then the sample and the sensor were pressed with a 500 g weight to reduce the contact thermal resistance. A differential scanning calorimetry (DSC, DSC200F3, NETZSCH, Germany) instrument was used to test the phase change temperature and latent heat of the sample. The mass range of the sample was 5–10 mg, the test temperature range was 0–120 °C, the heating rate is 10 °C/min, the test atmosphere was nitrogen, and the nitrogen flow rate was 30 mL/min. The thermal stability of the samples was analyzed by thermogravimetric analysis (TGA, STA449F3, NETZSCH, Germany). The loadage of the sample in TG test was 3–4 g, the sensitivity of the balance was 0.1 μg, the accuracy and precision of the balance were ±0.02 and 0.001%, respectively, the test temperature range was room temperature to 600 °C, the heating rate was 20 °C/min, and the atmosphere condition was nitrogen.

The leakage test was used to characterize the shaping ability of CPCMs. The process was as follows: each sample was placed with initial mass of M₀ on the filter paper. Then, the samples were put on the thermostatic heating plate and the temperature of the heating plate was set to 60 °C. After heating for 1 h, the samples were weighed and recorded with an electronic balance (FA2004, LICEN). Then, the samples were put on the new filter paper before putting them on the thermostatic plate again, and the operation was repeated. The mass of the samples heated n times on the thermostatic plate was recorded as Mₙ, then, the retention rate of the samples was calculated according to the following equation:

![Table 1. Sample of CPCMs with Different Compositions of PA/OBC/EG](image-url)
The heat transfer properties of PA, PA/OBC, and PA/OBC/EG were investigated by recording the temperature variations of pure PA and CPCMs during the melting and solidification process. As shown in Figure 2, the whole system consists of a computer, data acquisition unit, high- and low-temperature alternating test chamber, and heat transfer unit. The heat transfer unit consists of a beaker and a T-type thermocouple. First, 30 g of the sample was weighted and put in a 100 mL beaker; then, the T-type thermocouple was placed into the

\[
M \% = 100 - \frac{M_0 - M_a}{M_0} \times 100
\]  

(1)

Figure 2. Schematic diagram of the experimental setup.

Figure 3. SEM images of (a) EG-50, (b) EG-100, (c) EG-200, (d) PA/OBC/EG-50 CPCM, (e) PA/OBC/EG-100 CPCM, and (f) PA/OBC/EG-200 CPCM with 7% mass fraction.
middle position of the sample. During the experiment, the beaker was put into the high- and low-temperature alternating test chamber and cooled at 10 °C for 30 min to reach thermal equilibrium; then, the temperature of the test chamber was set to 80 °C. After the sample reached 80 °C, the test chamber was set to 10 °C to cool the sample. The computer and data acquisition unit recorded the temperature variations of the sample during the melting and solidification process.

3. RESULTS AND DISCUSSION

3.1. Micromorphology of EG and CPCMs. Figure 3 shows SEM images of three different particle sizes of EG and PA/OBC/EG CPCMs. It can be observed from Figure 3a−c that the microstructures of the three EGs with different particle sizes are loose and porous worm-like substances as a whole. When the SEM observation scale is 200 μm, the number of EG particles that can be observed in the view window decreases as the size of EG increased. On local magnification, EG is an irregular network structure formed by overlapping and intersecting many graphite flakes. As the particle size of the EG decreases, the network structure of the EG becomes more compact. At the same time, the dense thermal chain and crystalline stability of graphite flakes enable EG to provide good thermal conductivity for CPCMs. Under the action of surface tension and capillary force, the abundant pore structure endows EG with good absorption capacity for liquid-phase PA and OBC. Figure 3d−f shows the CPCM surfaces prepared by EG with different particle sizes and 7% mass fraction. The structures of PA/OBC and EG have good compatibility and appear flatter macroscopically. It is worth noticing that, microscopically, compared with EG-200, there is only a small amount of PCMs precipitated on the surface of the composite PCM prepared by EG-50, since the large-size EG has a better pore structure and can provide better adsorption capacity for PCMs.

3.2. FT-IR and XRD Analysis of CPCMs. In order to confirm whether there is a chemical reaction between the components of the CPCMs during the preparation process, FT-IR was used to characterize the chemical structure of the CPCMs. Figure 4 shows the Fourier spectra of samples PA, OBC, EG, and PA/OBC/EG with 7% mass fraction. It can be seen from Figure 4 that PA has four strong absorption peaks, of which 2919 cm$^{-1}$ corresponds to $\text{−CH}_2$ asymmetric stretching vibration, 2850 cm$^{-1}$ corresponds to $\text{−CH}_2$ symmetric stretching vibration, 1461 cm$^{-1}$ corresponds to $\text{−CH}_2$ bending vibration, and 721 cm$^{-1}$ corresponds to $\text{−CH}_3$ bending vibration. OBC has five strong absorption peaks at 2919, 2850, 1461, 817, and 717 cm$^{-1}$, of which 817 cm$^{-1}$ corresponds to $\text{−CH}_2$ bending vibration. The characteristic
peaks of EG appear at 3432 and 1619 cm\(^{-1}\), corresponding to the vibration absorption peaks of \(-\text{OH}\) stretching vibration and physical water absorption O–H, respectively. It can be seen from Figure 4b–d that the Fourier spectral curves of PA/OBC/

Figure 5. XRD patterns of pure materials and four different kinds of CPCMs: (a) PA/OBC, (b) PA/OBC/EG-50 CPCM, (c) PA/OBC/EG-100 CPCM, and (d) PA/OBC/EG-200 CPCM with 7% mass fraction.

Figure 6. (a) Thermal conductivity and (b) thermal conductivity performance enhancement of CPCMs with different mass fractions of EG.

EG show all the characteristic peaks of PA, OBC, and EG. There is no shift in the position of characteristic peaks and the generation of new characteristic peaks, but the intensity of characteristic peaks changes. It shows that the PA, OBC, and EG
in the CPCMs have good physical compatibility, and there is no chemical reaction with each other to generate new substances, just simple physical mixing.

XRD was used to analyze the crystal structure of the samples, and the XRD patterns of PA, OBC, EG, and PA/OBC/EG are shown in Figure 5. Pure PA has six strong diffraction peaks, which appear at 19.51, 19.84, 23.39, 34.83, 39.55, and 44.46°, which are attributed to the diffraction of (110), (200), and other crystal planes. The diffraction peak of OBC appears at 21.31°. The diffraction peaks of three different particle sizes of EG all appear at 26.34°, which corresponds to the characteristic peak (002) of EG. It is worth noticing that with the addition of OBC, the diffraction peaks of the PA/OBC/EG CPCMs are much lower than those of pure PA, which is because the PA crystals are restricted by OBC during the crystallization process. It can be seen from Figure 5b–d that the diffraction peaks of PA/OBC/EG CPCMs are related to the diffraction peaks of the above-mentioned materials, and there is no new diffraction peak and deviation of the diffraction peak, which indicate that the crystallization mode of PA has not changed. These results combined with FT-IR data prove that the components of PA/OBC/EG CPCMs are only simple physical mixing and there is no chemical reaction. Therefore, the effect of mass fraction and particle size on the properties of CPCMs cannot be presented by XRD and FT-IR research. As a result, the rest of XRD and FT-IR results of CPCMs with various mass fractions are not repeated in present research.

3.3. Thermal Properties of CPCMs. Due to the low thermal conductivity of organic PCMs, their heat transfer efficiency is limited, resulting in an excessively long time for PCMs to melt and solidify. Therefore, thermal conductivity is an important factor affecting the application of PCMs in energy storage.

In the CPCMs, the thermal conductivity of basis material PA is low. However, the thermal conductivity of the PA/OBC/EG composite is significantly higher than that of PA/OBC due to the addition of higher thermal conductivity of EG. Figure 6a shows the thermal conductivity of the CPCMs with different mass fractions of EG. It can be seen that the thermal conductivity of the CPCMs increases gradually with the increase in EG mass fraction. For example, the thermal conductivity of PA/OBC/EG-100 is 0.85, 2.53, and 3.92 W/(m·K), respectively, with the increase in mass fraction, and its thermal conductivity is 2.57 times, 7.67 times, and 11.87 times that of PA/OBC [0.33 W/(m·K)], respectively. The network structure of EG, as a high thermal conductivity matrix, forms a three-dimensional heat exchange path, which enhances the thermal

Figure 7. Phase transition properties of the produced samples. (a,c) DSC curves of pure PA and CPCMs with different mass fractions of EG and (b,d) DSC curves of pure PA and CPCMs with different particle sizes of EG.
bridge effect and improves the thermal conductivity of CPCMs effectively.

In order to better reveal the effect of EG on the thermal conductivity of CPCMs, the thermal conductivity performance enhancement ratio, \( K \), can be calculated according to the following equation \(^2\) :

\[
K = \frac{\lambda - \lambda_0}{\lambda_0} \times 100\%
\]

where \( \lambda \) is the thermal conductivity of the CPCMs and \( \lambda_0 \) is the thermal conductivity of sample S1.

It can be seen from Figure 6a that with the increase in EG particle size, the thermal conductivity of CPCMs is greatly enhanced under the same mass fraction. The thermal conductivity of CPCMs increases in the order EG-50 > EG-100 ≈ EG-200. For example, the thermal conductivity of PA/OBC/EG (10 wt %) is 4.96, 3.92, and 3.9 W/(m-K) with the increase in particle size of EG, respectively. The heat conduction of inorganic nonmetallic materials is realized by the lattice vibration wave in the microscopic mechanism.\(^3\)\(^4\) The phonon mean free path is the key parameter of heat transfer, and the thermal conductivity is proportional to the phonon mean free path. A large number of phonons collide with each other in the interface region between the two nonmetallic materials, which intensifies phonon scattering and shortens the average free path of phonons, which will significantly reduce the thermal conductivity.\(^3\)\(^4\) The greater the coupling strength between two nonmetallic materials, the higher the probability of phonons produced by two different frequencies passing through the interface.\(^5\) When CPCMs contain EG with smaller particle size, phonon scattering and boundary scattering in CPCMs are affected due to the large number of interfaces between EG and PCMs, resulting in larger interface thermal resistance and hindering heat transfer. Therefore, the thermal conductivity of CPCMs with small-sized EG is worse at the same EG content.

To sum up, for large-size EG particles, the thermal conductivity increases with the increase in EG mass fraction. The thermal conductivity decreases with the decrease in EG size, which is mainly due to the influence of interfacial thermal resistance. Therefore, when the EG size is 50 mesh, the PA/OBC/EG CPCM has the best thermal conductivity.

The thermal properties of PCMs, including phase transition temperature and latent heat of phase transition, are also critical to PCMs except for thermal conductivity. The phase transition characteristics of PA/OBC/EG were analyzed by the DSC curve. As shown in Figure 7, there are two obvious phase transition peaks on the DSC curves of PA and CPCMs. The smaller peak on the left is the solid–solid phase transition peak, and the larger peak on the right is the solid–liquid phase transition peak. Figure 7 shows the DSC curves of the melting and solidification process of pure PA and PA/OBC/EG CPCMs. Compared with pure PA, the phase transition temperature of CPCMs has changed. It is worth noticing that due to the addition of EG, the melting temperature and solidification temperature of the CPCMs have different changes compared to pure PA. For example, the melting temperature and solidification temperature of pure PA are 41.3 and 42.3 °C, respectively, and the melting temperature and solidification temperature of S2 are 42.8 and 41.1 °C, respectively. The melting temperature of most CPCMs is slightly higher than that of pure PA, and conversely, the freezing temperature of most composite PCMs is slightly lower than that of pure PA.

Meanwhile, the values of melting temperature and solidification are also reversed, that is, melting temperature of PA is lower than solidification temperature; inversely, it is higher than solidification temperature for CPCMs, as shown in Table 2.

| sample     | \( T_m \) (°C) | \( \Delta H_{m} \) (J/g) | \( T_s \) (°C) | \( \Delta H_{s} \) (J/g) |
|------------|----------------|--------------------------|----------------|--------------------------|
| PA         | 41.3           | 243                      | 42.3           | 241                      |
| S1         | 43.3           | 182.2                    | 41.2           | 183.9                    |
| S2         | 42.8           | 172.14                   | 41.1           | 170.4                    |
| S3         | 43.8           | 168.28                   | 41.1           | 167.28                   |
| S4         | 43.2           | 164.5                    | 40.9           | 164                      |
| S5         | 43.7           | 162.3                    | 40.9           | 161.6                    |
| S6         | 42.9           | 158.2                    | 40.9           | 157.8                    |
| S7         | 44.8           | 154.1                    | 40.2           | 153.4                    |
| S8         | 43.4           | 169.3                    | 40.8           | 168.9                    |
| S9         | 43.5           | 162.2                    | 40.7           | 161.6                    |
| S10        | 43.2           | 159.4                    | 40.5           | 158.8                    |

Table 2. Phase Change Temperature and Enthalpy of PA and S1–S10*.

The reason why phase transition temperature inversely changes can be explained according to the Clausius–Clapeyron equation \(^6\) :

\[
\ln \frac{T_1}{T_2} = \frac{\Delta V_m}{\Delta H_m} \times (P_2 - P_1)
\]

where \( T_1 \) and \( T_2 \) represent the phase transition temperature of pure PA and CPCMs, respectively, and \( \Delta V_m \) represents the volume change during the phase transition, m\(^3\). \( \Delta H_m \) represents the change in latent heat value during the phase transition, J/g. \( P_1 \) and \( P_2 \) represent the ambient pressure, MPa, during the phase transition.

In the process of endothermic melting of composite PCMs, the enthalpy of PA will be increased (\( \Delta H_m > 0 \)) due to the absorption of heat, the volume of PA increases in the melting process (\( \Delta V_m > 0 \)), the ambient pressure, namely, the pressure in the pore, increases (\( P_2 > P_1 \)) due to the limitation of the porous structure of EG, and the melting temperature of CPCMs moves to high temperature slightly. Similarly, the enthalpy of PA will be decreased (\( \Delta H_m < 0 \)) due to the heat release, the volume of PA shrinks during exothermic solidification (\( \Delta V_m < 0 \)), and the decrease in volume leads to the decrease in ambient pressure (\( P_2 < P_1 \)). Eventually, the solidification temperature of CPCMs moves to low temperature. Besides, the particle sizes of EG have a slight effect on the phase change temperature of CPCMs.

The experimental values of melting and solidification enthalpy of S4 (10 wt % EG-50) are 94.05 and 94.52% of the theoretical value, respectively, which has little difference from the theoretical value and has the best adsorption effect on PCMs since EG with large particle size has a better pore structure and can provide a better adsorption effect for PCMs.
the phase transition process. The theoretical enthalpy of CPCMs can be calculated according to the following equation

$$\Delta H_{p,\text{Th}} = \Delta H_{PA} \times \rho_{PA}$$

where $\Delta H_{p,\text{Th}}$ represents the theoretical enthalpy, $\Delta H_{PA}$ represents the enthalpy of PA, and $\rho_{PA}$ represents the proportion of PA in the CPCMs.

As Table 2 shows, the enthalpy of CPCMs is reduced with the content of EG, which is attributed to the decrease in PA. For example, the melting enthalpies of S1–S4 are 182.2, 172.14, 168.28, and 164.5 (J/g), respectively, with the increase in EG mass fraction. It can be seen from Table 2 that the test enthalpy of CPCMs is lower than the theoretical enthalpy. There are two main reasons for this error: on the one hand, the crystallinity of PA in CPCMs is limited by OBC, and on the other hand, the PA leakage caused by CPCMs during hot pressing. Among the three kinds of PA/OBC/EG composites, the melting enthalpies of S4, S7, and S10 are 164.5, 154.1, and 159.4 (J/g), respectively. Therefore, particle sizes have no obvious effect and tendency on the melting enthalpy of CPCMs.

### 3.4. Thermal Stability of CPCMs

Thermal stability was evaluated by the TGA curve, which is crucial for CPCMs. As shown in Figure 8a, the TGA curve shows that both PA and OBC have only one degradation platform. PA is mainly composed of straight chain alkanes. The initial decomposition temperature is about 150 °C, and it is completely decomposed at about 280 °C. OBC has almost no mass loss before 400 °C, and it is completely decomposed at 500 °C. For CPCMs, the TGA curve is divided into two decomposition platforms. The first stage occurs at about 150 to 290 °C. Due to the gasification and pyrolysis of PA, the mass loss rate is equivalent to the mass fraction of PA. The second stage occurs at 290 to 500 °C, which is similar to the decomposition process of OBC. After degradation at 500 °C, the residue that cannot be decomposed is EG. At the same time, it can be seen that as the mass fraction of EG added increases, the decomposition temperature of PA in the first stage also increases compared with that of pure PA. Because there is a physical bond between PA and EG, the network structure formed by the cross-linking of EG accommodates the PCM in it, making its phase change reaction resistance larger. The molecular thermal motion of the PCM is restricted, and a larger phase transition temperature is required to get rid of the restriction of EG, which has a certain inhibitory effect on the volatilization of the PCM, so the thermal stability of the PCM is improved.

The abovementioned results further show that PA, OBC, and EG are mixed uniformly, and the prepared CPCMs have good thermal reliability under high-temperature conditions.

When the ambient temperature is higher than the phase transition temperature of PA, the internal molecular structure of PA changes from the ordered crystal structure to the disordered amorphous structure. The increase in vibration energy will
destroy the supramolecular bond between single molecules and change the crystal arrangement into randomly oriented liquid.\textsuperscript{38}

Leakage may lead to equipment damage, so the leakage of PCMs is very important. Figure 9 shows the photographs of the samples before and after heating at 60 °C for the same time. It can be seen from Figure 9b that oil blots appear around the sample S1, but geometric construction of S1 remains almost intact, although the heating temperature 60 °C is much higher than its melting temperature 41.3 °C, which is since OBC has good compatibility with PA. When the ambient temperature is based between the phase transition temperature of PA and the phase transition temperature of OBC, the phase transition of PA occurs, while the OBC remains solid, and the three-dimensional structure of OBC can effectively wrap the PA to make it shape-stable. Therefore, the addition of OBC can effectively improve the thermal stability of CPCMs.

Additionally, EG has a rich pore structure and large specific surface area, which can also adsorb the PCM and decrease the leakage of PA further. When the PCM phase changes repeatedly, it can stabilize the shape of the PCM. Under the action of surface tension and capillary force, EG can evenly disperse the PCM in its pore structure and prevent the leakage of PCMs in the process of phase change. Different pore structures and mass fractions will lead to different adsorption properties of the EG matrix to PCMs. Therefore, the optimal content and particle size of CPCMs were selected through leakage experiments. The thermal stability of CPCMs with different EG-100 mass fractions (4, 7, and 10 wt %) were prepared, as shown in Figure 9. Figure 9a,b shows the leakage diagram of the sample before and after the static thermal cycle by placing on the constant temperature plate at 60 °C. It can be seen that there are oil blots of different sizes around the sample. The larger the mass fraction of EG, the smaller the size of the oil blots. However, PCMs still leaked out after the first thermal cycle for the CPCMs of the EG-100 matrix, which is mainly because the content of PCMs is greater than the adsorption capacity of EG. When the ambient temperature is higher than the phase change temperature, excess PCMs will leak around the filter paper.

As can be seen from Figure 10, with the increase in EG particle size in CPCMs, it can be observed that the leakage of PCMs gradually decreases. The shape of CPCMs containing the large particle size EG-50 matrix is stable after 10 thermal cycles, and the leakage of PCMs is less than 4 wt %, which reduces the leakage of PCMs by 3.97, 3.2, and 2.11 wt %, respectively, compared with CPCMs containing the EG-200 matrix (4, 7, and 10 wt %). Because the particle size of EG increases, the effect on the enhancement of the pore structure inside the EG is more obvious, resulting in the enhancement of the capillary force inside the EG matrix, which has a certain inhibitory effect on the leakage of the PCM.

Figure 10. CPCM mass ratio after 10 thermal cyclings: (a) 4 wt % EG-based CPCMs, (b) 7 wt % EG-based CPCMs, and (c) 10 wt % EG-based CPCMs with different particle sizes.
It can be seen from the abovementioned results that the content of EG is the decisive factor of CPCM leakage. The CPCM containing 7 wt % EG-50 remains almost unchanged in 10 thermal cycles, and the leakage of PCMs decreases significantly when the content increases to 10 wt %. The size of EG is another factor that affects the thermal cycling stability of CPCMs since large-sized EG has a better pore structure, which can provide better PCM adsorption and sealing ability. Therefore, EG-50 can be preferentially used as an additive material for CPCMs.

3.5. Heat Transfer Performance of CPCMs. Phase change energy storage materials are widely used in energy storage industry due to their large latent heat of phase change and almost stable temperature in the process of phase change. In order to further study the effect of EG particle size on the heat transfer performance of CPCMs, the heat storage and release experiments of CPCMs with different particle sizes of EG were carried out. First, all samples are put into the high-/low-temperature alternating test chamber, and then, the temperature in the chamber increased from 10 to 80 °C with an average rate of 0.3 °C/s. When a thermal balance between the samples and chamber was reached at 80 °C, the operating mode of the chamber was changed to the cooling mode and the temperature in the chamber decreased from 80 to 10 °C with a rate of −3 °C/s. Eventually, another thermal balance was built between the samples and chamber at 10 °C. The temperature variations of all samples and the ambient in real time are recorded through the data acquisition instrument. It can be seen from Figure 11a that the heat storage and release process of PCMs includes six stages (I–VI). The heat storage process can be divided into solid-sensible heat absorption, solid–liquid latent heat absorption, and liquid-sensible heat absorption. The heat release process can be divided into liquid heat release, solid–liquid latent heat release, and solid-state heat release. It can be seen from Figure 11a that the addition of EG can greatly improve the heat transfer performance of CPCMs. PA/OBC used 1114 s in the endothermic melting process, PA/OBC/EG-50 (4 wt %), PA/OBC/EG-100 (4 wt %), and PA/OBC/EG-200 (4 wt %) used, respectively, 524, 656, and 694 s, and it decreased by 52.9, 41.1, and 37.5% compared with PA/OBC, respectively. During the exothermic solidification process, PA/OBC took 920 s, PA/OBC/EG-50, PA/OBC/EG-100, and PA/OBC/EG-200 took 519, 612, and 661 s, and it decreased by 43.6, 33.47, and 28.15%, respectively. It demonstrated that EG can effectively improve the heat transfer performance of CPCMs and the EG particle size also has a significant influence on the heat transfer performance. For instance, the larger the EG particle size added to the sample, the shorter the time to reach thermal equilibrium with ambient. In order to further study the effect of EG particle size on the heat transfer performance of CPCMs, Figure 11b plots the real-time temperature variations ΔT between sample temperature and ambient temperature. It can be seen from the curve that the larger the EG particle size added to the sample, the smaller the ΔT between the sample and the ambient, which means the shorter the time for the sample to reach thermal equilibrium with the ambient. This result is consistent with that of thermal conductivity, which is the CPCM with large size EG has better thermal conductivity under the same EG content, as shown in Figure 6.

It is worth noticing that in the solid–liquid latent heat storage stage of stage II, the instantaneous temperature of PA exceeds that of PA/OBC, which is due to the fact that buoyancy generated by PA melting produces a thermal convection effect in liquid PA, thus enhancing the heat transfer performance of PA.\(^{(39)}\) In contrast, due to the addition of OBC, the liquid-phase PA is limited to the three-dimensional structure of OBC, which inhibits the flow of liquid-phase PA and remains solid under the macro. In the solid–liquid latent heat exothermic stage of stage V, different from stage II, PA shows a longer phase transition platform since the total phase transition enthalpy of PA is higher than that of the PA/OBC composite.

4. CONCLUSIONS

In this study, form-stable PA/OBC/EG CPCMs with different EG sizes and mass fractions were prepared by melt blending. The effects of EG sizes and mass fractions on the thermal and chemical performance of CPCMs were analyzed. The following conclusions can be drawn:

1. EG and PA/OBC were successfully physically mixed, and there was no chemical reaction occurrence among the components, which proves that the sample has good chemical structure stability.

2. The thermal conductivity of CPCMs increases with the increase in EG content. The influence of particle size on thermal conductivity is that the thermal conductivity is significantly enhanced with the increase in particle sizes, benefiting from the fact that the large-size EG has smaller interfacial thermal resistance at the same content of EG. Meanwhile, the addition of EG increased the melting temperature of CPCMs and decreased the solidification temperature as well; meanwhile, the values of melting temperature and solidification are also reversed for CPCMs compared to PA/OBC.

3. Due to the fact that the three-dimensional structure of OBC and the porous structure of EG limit the flow of PA, S4 with 10 wt % EG-50 has the best stability and the
leakage rate does not exceed 1 wt % under 10 thermal cycles.

(4) Benefiting from the excellent heat transfer performance of CPCMs with larger particle size EG, the melting time of PA/OBC/EG-50 (4 wt %), PA/OBC/EG-100 (4 wt %), and PA/OBC/EG-200 (4 wt %) significantly reduced by 52.9, 41.1, and 37.5%, respectively, compared with CPCMs without EG from heating to complete melting.

This study provides a strategy for the direct synthesis and application of polymer composite PCMs with different EGs in energy storage and thermal management industry. At the same time, we will deeply study the effect of the ratio between the polymer and EG on the mechanical and thermal properties of composite PCMs and further applied to the battery thermal management system.

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### Notes

The authors declare no competing financial interest.

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## NOMENCLATURE

### List of Symbols

- \( T \) temperature (K/°C)
- \( \Delta H \) latent heat (J/g)
- \( \Delta T \) temperature difference (K/°C)
- \( P \) pressure (Pa)
- \( V \) volume (m\(^3\))

### Subscripts

- \( m \) melting
- \( s \) solidification
- \( a \) ambient
- \( Th \) theoretical value
- \( Exp \) experimental value

### Greek Symbols

- \( \lambda \) thermal conductivity
- \( \rho \) mass fraction of pure paraffin

### Acronyms

- ASA acrylonitrile styrene-acrylate copolymer
- CPCMs composite phase change materials
- DSC differential scanning calorimetry
- EG expanded graphite
- FT-IR Fourier transform infrared spectrometry
- HDPE high-density polyethylene
- LDPE low-density polyethylene
- OBC olefin block copolymer
- PA paraffin
- PCM phase change material
- SEBS styrene-b-(ethylene-co-butylene)-b-styrene triblock copolymer
- SEM scanning electron microscopy
- TGA thermogravimetric analysis
- XRD X-ray diffraction

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