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Study on performance optimization of sodium sulfate decahydrate phase change energy storage materials

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Abstract

In this paper, sodium sulfate decahydrate (SSD) with a phase transition temperature of 32 °C was selected as the phase change energy storage material. However, SSD has the problems of large degree of supercooling, obvious phase stratification, and low thermal conductivity. To address these issues, a new SSD composite phase change energy storage material was synthesized by adding certain amounts of nucleating agents, thickeners, and high thermal conductivity agent to SSD. The results showed that when the addition of nucleating agent $Na_2B_4O_7 \cdot 10H_2O$ and thickener carboxymethyl cellulose (CMC) reached an optimal formulation ratio of SSD:$Na_2B_4O_7 \cdot 10H_2O$:CMC = 100:5:3, the supercooling degree of the SSD composite phase change material was only 1.5 °C. Moreover, the heat release time of the phase change process was 25 min, and no phase stratification occurred. When expanded graphite with high thermal conductivity was added with the mass ratio of 9%, the effect on the supercooling degree of the SSD composite energy storage material was small, and the thermal conductivity increased by 3.9 times, reaching 2.13 W m^{-1} K^{-1}. Differential scanning calorimetry method and step cooling curve method were used to test the decay rate of the thermal properties of the new composite phase change energy storage material, and the results were relatively close.

Keywords Sodium sulfate decahydrate · Energy storage material · Supercooling degree · Phase stratification · Thermal conductivity

Introduction

Since the end of the last century, numerous researchers have extensively investigated phase change materials. In particular, phase change energy storage materials have gained much interest in the fields of aerospace, energy utilization, materials science, engineering, thermal physics, and other research areas [1]. The development and exploration of phase change energy storage materials began with inorganic hydrated salt phase change materials. Telkes et al. [2–4] conducted extensive research on phase change energy storage materials and first established the energy storage solar house with $Na_2SO_4 \cdot 10H_2O$ as a phase change energy storage material. The research field of phase change material (PCM) has gradually expanded from inorganic materials to organic materials, and then to a wide range of metal materials, which has greatly promoted the theoretical research and practical application of phase change energy storage materials. Inorganic hydrated salts are very popular as medium- and low-temperature phase change energy storage materials. Their phase transition temperature is between 8 and 117 °C, and their melting enthalpy is about 116–377 J g^{-1} [5]. Inorganic hydrated salt phase change energy storage materials are widely used because of their broad application range, low price, and large latent heat of phase change. In most cases, inorganic hydrated salts are neutral.

Although inorganic hydrated salts have many advantages, they also have two significant disadvantages, namely supercooling degree and phase stratification, which have a great influence on their performance and service life. Therefore, researchers at home and abroad have focused on reducing the degree of supercooling, preventing phase stratification and

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enhancing the thermal conductivity of inorganic hydrated phase change materials [6–10].

Based on the above research background, sodium sulfate decahydrate (SSD) with phase transition temperature of 32 °C was selected as phase change energy storage material in this work. However, it has the common disadvantages of inorganic hydrated salts, that is, the problems of large degree of supercooling [11, 12], obvious phase stratification [13, 14], and low thermal conductivity [15]. Therefore, this paper investigated the performance optimization of SSD-based phase change energy storage materials by adding a nucleating agent, a thickener, and a thermal conductivity improving agent. The composite material with the optimized formula of SSD and additives exhibited excellent phase change and energy storage performance.

Experimental

Selection of nucleating agent and thickener

Five nucleating agents and three thickeners were initially screened by the "Scientific Method" and "Edison Method" to improve the supercooling degree and phase stratification in the phase transformation of sodium sulfate decahydrate (SSD) crystal. The nucleating agents were: $Na_2SiO_3 \cdot 9H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $(NH_4)_2S_2O_8$, $Na_2HPO_4 \cdot 12H_2O$, and $Na_2CO_3 \cdot 10H_2O$, which were all in a crystalline state, as white or beige granules. The thickeners were: carboxymethyl cellulose (CMC), polyacrylamide (PAM), and activated clay, all of which are white or beige powders. The materials selected were all analytically pure.

Experimental procedure: (1) A total of 15 groups of experiments were designed. The amount of SSD in each group was 10 g, the mass percentage of nucleating agent was 5%, the mass percentage of thickener was 3%, and the mixture was evenly mixed by grinding; (2) the mixed material was added to a test tube with diameter of 25 mm, and a thermocouple was inserted. The test tube was then placed in a constant temperature water bath at 50 °C for heating and melting; (3) after the melting was complete, the test tube was quickly taken out and placed in an air bath (20 °C) to cool down. By measuring the phase change temperature of the phase change heat storage system and the duration of the phase change, the optimal addition formula was determined to solve the problem of large supercooling degree of SSD. Each group of samples was subjected to three repeated experiments.

The step cooling curve of samples with CMC as thickener and different nucleating agents after completing a heat storage and discharge cycle is shown in Fig. 1. When the nucleating agent was $Na_2B_4O_7 \cdot 10H_2O$, the supercooling degree of the material was about 1.5 °C. Also, the heat release process of the phase change was obvious and the heat release time was 25 min. When the nucleating agent was $Na_2HPO_4 \cdot 12H_2O$, the supercooling phenomenon was very obvious. The supercooling degree was 4 °C, and the heat release time of the phase change process was only 8 min. When the nucleating agents were $Na_2SiO_3 \cdot 9H_2O$, $(NH_4)_2S_2O_8$, and $Na_2CO_3 \cdot 10H_2O$, there was no heat release platform in the phase transformation process, and the nucleation effect of the material was very poor.

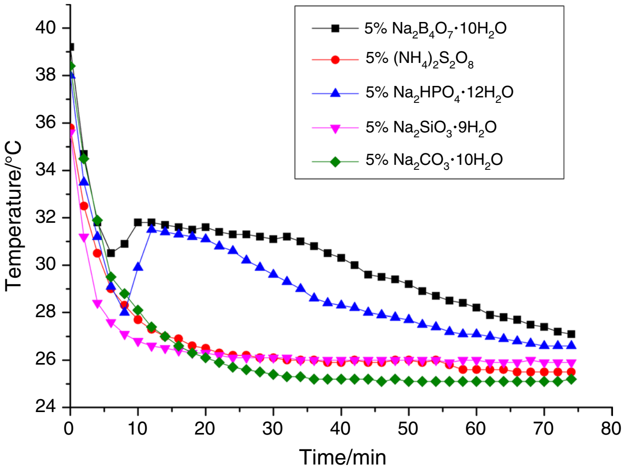


Fig. 1 Step cooling temperature curve of samples with CMC as thickener and different nucleating agents

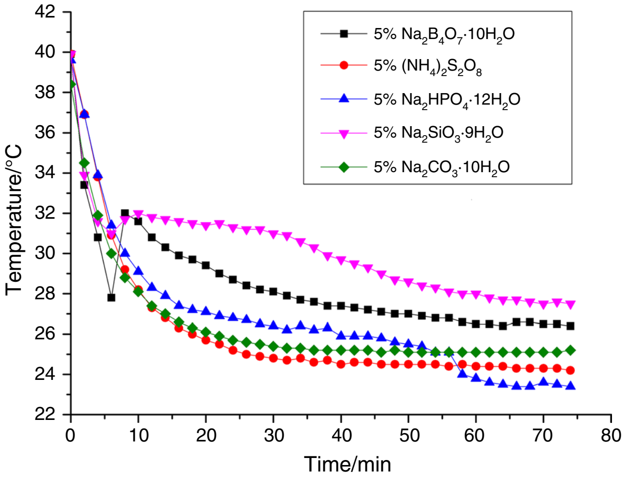


Fig. 2 Step cooling temperature curve of samples with activated clay as thickener and different nucleating agents

The step cooling curve of samples with activated clay as thickener and different nucleating agents after completing a heat storage and discharge cycle is shown in Fig. 2. When the nucleating agent was $Na_2SiO_3 \cdot 9H_2O$, the nucleation effect of the material was very obvious. Its supercooling degree was only 1 °C, the heat release platform of the phase change process was remarkable, and the time of heat release was about 23 min. When the nucleating agent was $Na_2B_4O_7·10H_2O$, the supercooling phenomenon was very obvious, there was a supercooling degree of 5 °C, and there was no exothermic platform in the phase transition process. When the nucleating agents were $Na_2HPO_4·12H_2O$, $(NH_4)_2S_2O_8$, and $Na_2CO_3·10H_2O$, the heat release platform did not appear in the phase transition process, and the nucleation effect of the material was not good.

The step cooling curve of samples with PAM as thickener and different nucleating agents after completing a heat storage and discharge cycle is shown in Fig. 3. When the nucleating agent was $Na_2B_4O_7·10H_2O$, the supercooling degree of the material was only 1 °C, and the heat release time of the phase change process was about 25 min. When the nucleating agent was $Na_2HPO_4·12H_2O$, the supercooling phenomenon was very obvious. There was a supercooling degree of 3.5 °C, and the heat release time of the phase change process was only 5 min. When the nucleating agents were $Na_2SiO_3·9H_2O$, $(NH_4)_2S_2O_8$, and $Na_2CO_3·10H_2O$, no heat release platform occurred during the phase transformation, and the nucleation effect of the material was not significant.

From the above 15 compositions, the experimental formulas of three groups of composites with low supercooling degree and long phase change heat release time were selected, as shown in Table 1.

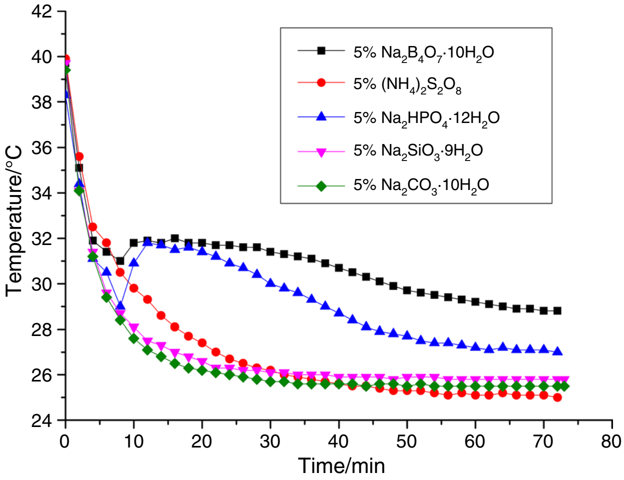


Fig. 3 Step cooling temperature curve of samples with PAM as thickener and different nucleating agents

According to the three selected groups of formulas that meet the requirements, as shown in Table 1, the optimization experiment of different dosages of nucleating agent and thickener was carried out. When the amount of thickener was kept constant, the effect of the amount of nucleating agent on the properties of SSD composite phase change material was studied, and vice versa.

Experimental study on improving thermal conductivity of SSD composite

The thermal conductivity of the composite phase change energy storage material was enhanced by adding a substance with high thermal conductivity. At present, the most commonly used additives for this purpose are metal wire mesh, metal powder, expanded graphite, and activated carbon fiber. There are two main requirements for the selection of this additive: (1) The selected material should have a high thermal conductivity; (2) the selected material should be dispersed very stably inside the inorganic hydrated salt phase change heat storage material, and delamination should not occur after repeated use. In this experiment, iron powder, activated carbon particles, and expanded graphite were selected as additives.

A solution blending method was used to select materials that enhance the thermal conductivity. The main steps were: (1) According to the optimized ratio of added nucleating agent and thickener, three identical composite phase change materials were placed into three identical plastic test tubes with diameter of 35 mm; (2) the three samples were placed in a water bath at 50 °C for heating and melting; (3) in a completely molten state, 5% iron powder, 5% activated carbon particles, and 10% expanded graphite were, respectively, added to the three test tubes, and then stirred and uniformly mixed; (4) heating was continued for about 1 h, and then the test tube was taken out and allowed to stand in an air bath at 18 °C for 10 min to observe changes in its state.

Experiments were conducted to determine the choice and amount of thermal conductivity improver, so that the composite achieved optimal phase change performance. The dosage optimization experiment of thermal conductivity

Table 1 Formulas that meet the requirements

Plan number	Formula	Supercooling degree/°C	Phase transition temperature/°C	Phase change heat release time/min
1	SSD, $Na_2B_4O_7·10H_2O$, CMC	1.5	32	25
2	SSD, $Na_2SiO_3·9H_2O$, Activated clay	1	32	23
3	SSD, $Na_2B_4O_7·10H_2O$, PAM	1	32	25

performance improver was performed in the same manner as the nucleating agent and thickener optimization experiments.

Results and discussion

Effect of different amounts of nucleating agent and thickener on the energy storage performance of SSD phase change material

The amounts of nucleating agent and thickener have a great influence on the experimental results. When the amounts of additives are insufficient, the problems of supercooling degree of phase change materials and phase stratification cannot be solved, but the additive amounts should not be excessive. When the amount of the thickener added is too large, the thickener is easily wrapped on the outside of the nucleating agent, so that it does not sufficiently contact the matrix material of the melt. Consequently, it is difficult for the material to form a crystal nucleus and the heat released by the phase change process is also reduced. In addition, if the amounts of additives blended in SSD are too large, the solidification temperature and the storage density of the system would be lowered, thereby affecting heat transfer. The results measured by the step cooling temperature curve method can be used to measure the quality of the material's heat storage performance.

The amount of nucleating agent directly affects the crystallization effect of the phase change material. In this work, experiments were used to determine the optimum addition amount of nucleating agent. The amount of the thickener (active clay, PAM and CMC) was set at 3 mass%, and the amount of SSD was 10 g.

Figure 4 shows that when 3 mass% of CMC was used as the thickener and the mass percentage of $Na_2B_4O_7 \cdot 10H_2O$ was 5%, the supercooling degree of the phase change composite was only 1.5 °C, and the heat release time of the phase change process was 25 min. Thus, the phase change performance of the composite was optimal. Similarly, Fig. 5 shows that when 3 mass% of activated clay was used as the thickener and 4% of $Na_2SiO_3 \cdot 9H_2O$ was added, the phase transformation property of the phase change composite was optimal and the heat release time of the phase change process was 26 min. Figure 6 shows that when 3 mass% PAM was used as a thickener and the mass percentage of $Na_2B_4O_7 \cdot 10H_2O$ was 4% and 5%, the supercooling degree of the phase change composite was relatively low, only 1 °C. The heat release time of the phase change process was almost 25 min, and the phase change performance of the composite material was better. Through three repeated experiments, it was found that when the mass percentage of the nucleating agent $Na_2B_4O_7 \cdot 10H_2O$ was 5%, the phase transition performance was the most stable. Therefore, the nucleating agent selected was 5% $Na_2B_4O_7 \cdot 10H_2O$.

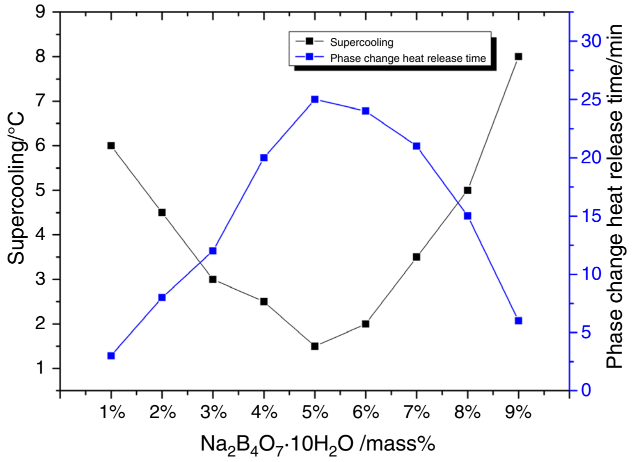


Fig. 4 Supercooling degree and phase change heat release time of samples with CMC as thickener and different amounts of $Na_2B_4O_7 \cdot 10H_2O$

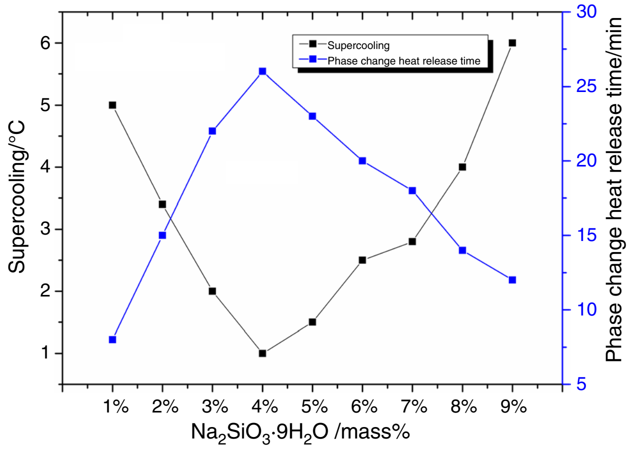


Fig. 5 Supercooling degree and phase change heat release time of samples with activated clay as thickener and different amounts of $Na_2SiO_3 \cdot 9H_2O$

In the next experiment, the optimal nucleating agent was set as 5% $Na_2B_4O_7 \cdot 10H_2O$, and different thickeners of CMC, activated clay and PAM were used, respectively. The thickener addition ratios were varied (2%, 3%, 4%, 5%, and 6%) to determine the optimum amount of thickener. In the same experiment, the sample supercooling curve was measured and the phase stratification was recorded.

Figure 7 shows that when the mass percentage of CMC addition was 3%, the supercooling degree was the smallest, only 1.5 °C, and the heat release time of the phase change process was 25 min. As shown in Fig. 8, the addition of 3%, 4%, 5%, and 6% thickeners all significantly improved

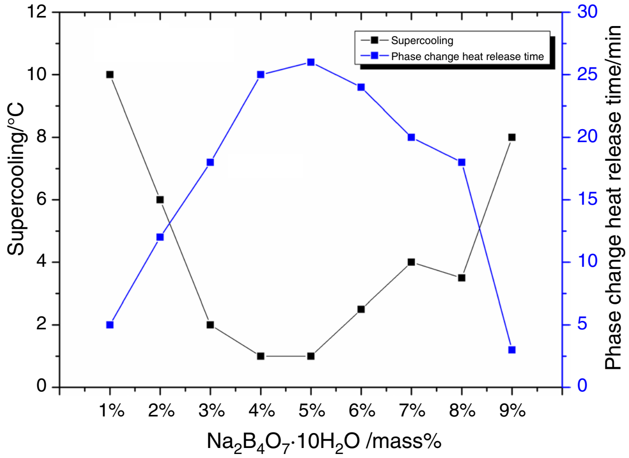


Fig. 6 Supercooling degree and phase change heat release time of samples with PAM as thickener and different amounts of $Na_2B_4O_7 \cdot 10H_2O$

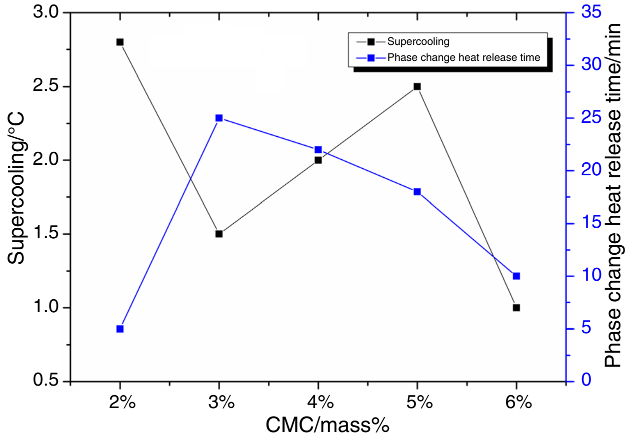


Fig. 7 Supercooling degree and phase change heat release time of samples with 5 mass% of $Na_2B_4O_7 \cdot 10H_2O$ as nucleating agent and different amounts of CMC

the phase stratification of the material, and the crystallization effect was obvious.

Figure 9 shows that when the mass percentage of activated clay was 5%, the supercooling degree was the smallest, only 3.5 °C, and the heat release time of the phase change process was 15 min. As shown in the photograph in Fig. 10, the addition ratios of activated clay in the test tubes from right to left were 3%, 4%, 5%, and 6%, respectively. When the proportion of activated clay was 3%, 4%, and 5%, the crystallization was better, with slight phase layering. When the addition ratio was 6%, the phase stratification phenomenon disappeared, but the supercooling degree reached 6 °C, and the phase transformation heat release time was only 12 min.

Fig. 8 Phase stratification of samples with 5 mass% of $Na_2B_4O_7 \cdot 10H_2O$ as nucleating agent and different amounts of CMC

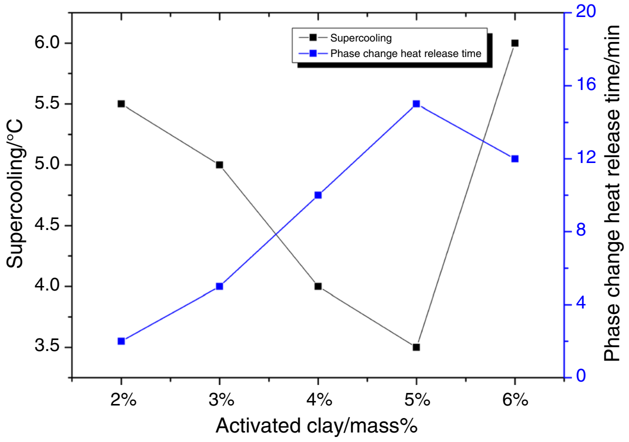


Fig. 9 Supercooling degree and phase change heat release time of samples with 5 mass% of $Na_2B_4O_7 \cdot 10H_2O$ as nucleating agent and different amounts of activated clay

Figure 11 shows that when the mass percentage of PAM addition was 3%, the supercooling degree was small, only 1 °C, and the heat release time of the phase change process was 25 min. As shown in Fig. 12, the PAM addition ratios in the test tubes from right to left were 3%, 4%, 5%, and 6%, respectively. When the PAM addition ratio was 3% and 4%, the crystallization phenomenon was not obvious, and there was severe phase stratification. When the addition ratio was 5%, the crystallization was better, and the phase stratification was obviously improved. When the addition ratio was 6%, there was maximum crystallization and slight phase stratification. After three repeated experiments, it was found that when PAM was used as a thickener, the phase transition property was very unstable.

According to the above optimization experiments, the three factors of supercooling degree, heat release time of the phase change process, and phase stratification were considered, and the optimal composition was found to be SSD:$Na_2B_4O_7 \cdot 10H_2O$:CMC = 100:5:3. With the optimized composition, the supercooling degree of the composite phase change

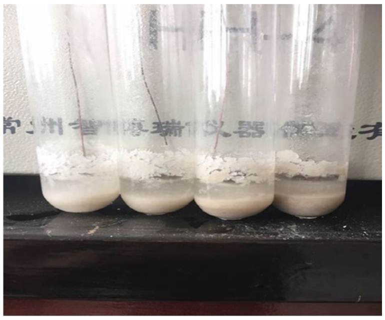


Fig. 10 Phase stratification of samples with 5 mass% of $Na_2B_4O_7 \cdot 10H_2O$ as nucleating agent and different amounts of activated clay

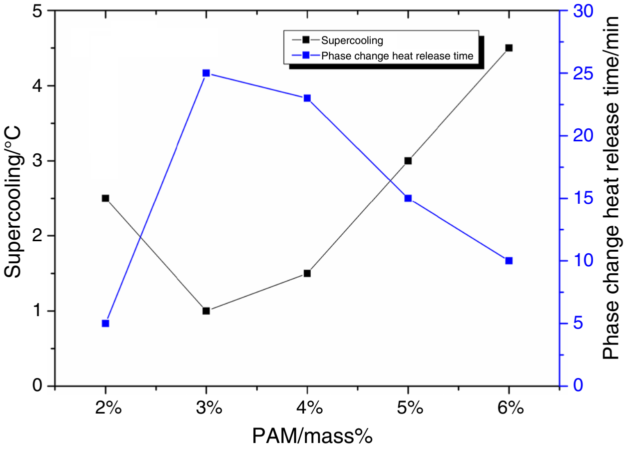


Fig. 11 Supercooling degree and phase change heat release time of samples with 5 mass% of $Na_2B_4O_7 \cdot 10H_2O$ as nucleating agent and different amounts of PAM

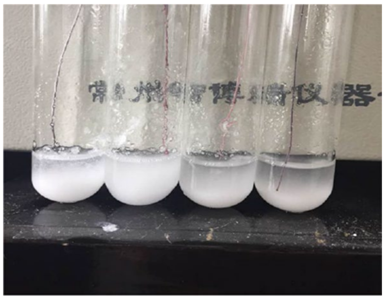


Fig. 12 Phase stratification of samples with 5 mass% of $Na_2B_4O_7 \cdot 10H_2O$ as nucleating agent and different amounts of PAM

material was only 1.5 °C, and the heat release time of the phase change process was 25 min. Moreover, there was no phase stratification phenomenon.

Thus, the problem of supercooling degree and phase stratification of phase change material SSD was solved by adding different proportions of additives. After screening different formulas and dosage optimization experiments, the following conclusions were obtained: A certain proportion of nucleating agent $Na_2B_4O_7 \cdot 10H_2O$ combined with thickener CMC or PAM had a good inhibitory effect on the supercooling degree of SSD, and the sample maintained a good heat storage capacity. The combination of nucleating agent $Na_2SiO_3 \cdot 9H_2O$ and thickener active clay also led to a significant improvement in the phase transformation effect of SSD. Thus, different amounts of nucleating agent and thickener had a great influence on the supercooling degree, phase stratification, and phase change heat release time of the material. Through multiple experiments, the optimal composition for storage performance of SSD composites was finally determined to be: SSD, $Na_2B_4O_7 \cdot 10H_2O$ and CMC in the mass ratio of 100:5:3.

The two important indicators for measuring the phase change performance of PCM are the supercooling degree and heat storage capacity. These two indicators are theoretically very complicated and diverse, related to the theory of dissolution of inorganic hydrated salts and the growth of crystals. Therefore, the experimental conditions, the temperature of the environment, the purity of the reagents, etc. would all have an impact on these indicators. Many researchers have conducted experimental studies on the amount of additives used, and the results were different, perhaps due to the diversity of influencing factors.

Effect of expanded graphite on phase transformation properties of SSD composites

To further improve the heat conductivity of the SSD composite, different agents were considered. It was observed that iron powder is difficult to be uniformly dispersed in the liquid state of inorganic hydrated salts because of its high density. Thus, iron powder was not selected in this work. Activated carbon particles float on the surface of the solution and are difficult to mix with the inorganic hydrated salt mixed solution. After considerable stirring and mixing, the delamination phenomenon could still not be eliminated. Therefore, activated carbon was also not used herein. Expanded graphite was uniformly dispersed in the hydrated salt composite solution system. After repeated cycles of experiments, no delamination occurred. Therefore, expanded graphite was selected as the heat conductivity improving agent for the composite.

Expanded graphite not only has the advantage of good thermal conductivity of natural graphite itself, but also has enhanced adsorption performance due to its increased surface area and surface energy. Natural graphite has a large density of about 2200 kg m^3. After puffing, the density was 3 kg m^3, which was less than 0.2% of natural graphite [16]. After mixing with the expanded graphite, the SSD phase change composite system can be easily embedded into the voids of the expanded graphite due to its porous adsorption characteristics. Moreover, the thickening effect of the CMC was good, and the expanded graphite with low density was difficult to separate from the inorganic hydrated salt composite solution. Thus, the prepared SSD/expanded graphite composite energy storage material exhibited stable performance.

Expanded graphite with mass fractions of 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, 11%, 12%, 13%, and 14%, respectively, was mixed in the SSD phase change composite. The supercooling change in the SSD/expanded graphite composite was obtained by the step cooling curve test. The results are shown in Table 2.

The addition amount of expanded graphite has a direct influence on the thermal conductivity of the composite material and affects its heat storage and release processes. Therefore, when investigating the effect of the amount of expanded graphite on the phase transformation properties of the material, it is necessary to focus on the effect of the supercooling degree of the composite. According to Table 2, three experiments were repeated, and the average supercooling degree was analyzed to obtain the relationship between the addition amount of expanded graphite and the supercooling degree of the composite material, as shown in Fig. 13. As can be seen, when the added mass percentage of expanded graphite was less than 9%, the supercooling degree of the composite phase change material was about 1.5 °C, and the addition of expanded graphite had little effect on the supercooling degree of the composite material. However, when the addition amount of expanded graphite exceeded 9%, the supercooling degree of the composite phase change material increased remarkably. This was because when the added amount of expanded graphite was increased to a certain ratio, it could easily surround the outer surface of the composite phase change material, thereby affecting the phase change properties of the material.

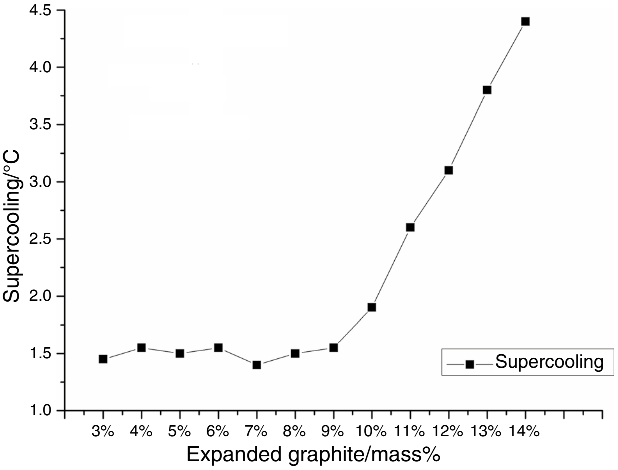


Fig. 13 Supercooling curve of composite phase change material with addition of different mass fractions of expanded graphite

From the analysis of the supercooling degree of the composite phase change material, addition of 9% mass fraction of expanded graphite was considered suitable.

Heat storage and release experiments were carried out for the phase change composites with and without the addition of expanded graphite to verify whether the expanded graphite can play a good role as a thermal conductivity improver.

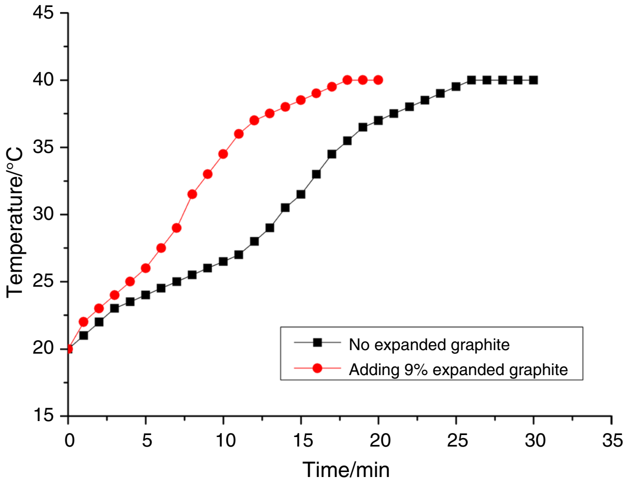
Figure 14 is a comparison chart showing the storage and release process of the SSD composite phase change material with and without the addition of 9% expanded graphite. Figure 14a shows that the temperature rise range of the composite phase change material was 20–40 °C, the time required for the composite material without the expanded graphite was about 26 min, and the time required for the composite material with the expanded graphite was about 18 min. The

Table 2 Supercooling degree of the composite phase change materials with different amounts of expanded graphite

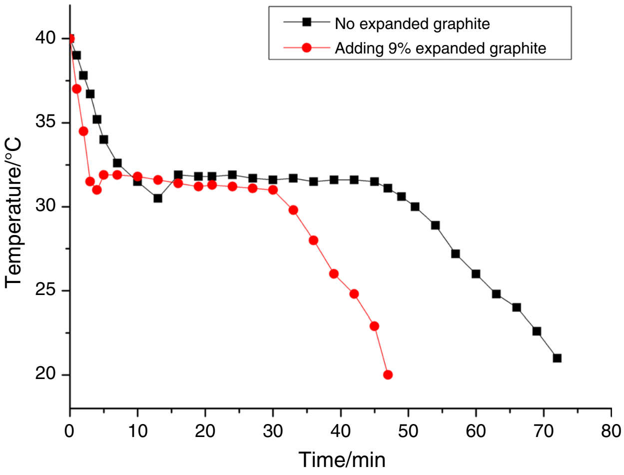
Mass fraction	First supercooling/°C	Second supercooling/°C	Third supercooling/°C	Average supercooling/°C
3%	1.45	1.4	1.5	1.45
4%	1.55	1.5	1.6	1.55
5%	1.4	1.55	1.6	1.5
6%	1.5	1.55	1.6	1.55
7%	1.35	1.4	1.45	1.4
8%	1.45	1.5	1.55	1.5
9%	1.6	1.65	1.4	1.55
10%	1.9	1.8	2	1.9
11%	2.5	2.8	2.5	2.6
12%	3.2	3.2	2.9	3.1
13%	3.8	3.6	4	3.8
14%	4.2	4.4	4.6	4.4

phase change heat storage process of the composite after the addition of expanded graphite was reduced by 30.8%. Figure 14b shows that the temperature reduction range of the composite phase change material was 40–20 °C. Moreover, the time taken by the SSD composite phase change material was about 75 min, while the SSD/expanded graphite phase change material only required 47 min. The phase change exothermic process of the composite after the addition of expanded graphite was reduced by 37.3%.

The time taken for SSD/expanded graphite composite material to store and release heat was significantly lower than that of SSD composite phase change material. This is because the thermal conductivity of expanded graphite is higher, which greatly improved the heat transfer rate of composite phase change material. Therefore, the time required for storing and releasing heat was shortened, confirming that expanded graphite had a good effect on enhancing the thermal conductivity of composite phase change materials.



(a) Heat storage process



(b) Exothermic process

Fig. 14 Step cooling temperature curve before and after adding expanded graphite

Measurement of thermal conductivity of SSD/expanded graphite composite phase change material

Thermal conductivity of the SSD/expanded graphite composite phase change material was measured by the transient planar heat source method. The mass ratio of the expanded graphite was 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, 11%, 12%, 13%, and 14%, respectively, in SSD/expanded graphite composite phase change material. The thermal conductivity was measured after cooling and solidification of the material into blocks. The results of the measurements are shown in Table 3.

According to the experimental data in Table 3, the relationship between the addition ratio of expanded graphite and the thermal conductivity of the material was obtained, as shown in Fig. 15.

As the addition amount of expanded graphite increased, the thermal conductivity of the SSD/expanded graphite composite increased. When the addition amount of expanded graphite was 9%, the rate of increase in the thermal conductivity of the composite began to slow down. The addition of expanded graphite not only affected the thermal conductivity of the composite, but also had a certain influence on the supercooling degree of the composite. Therefore, on the one hand, the thermal conductivity of the material can be improved by adding expanded graphite, and on the other hand, adverse effects on the phase transition property of the SSD composite phase change material should be reduced as much as possible to prevent the occurrence of supercooling and delamination. The results

Table 3 Thermal conductivity of composites after adding different mass percentages of expanded graphite

Expanded graphite/mass%	Thermal conductivity/W m^{-1} K^{-1}
3	1.32
4	1.48
5	1.62
6	1.75
7	1.88
8	2.01
9	2.13
10	2.19
11	2.25
12	2.3
13	2.38
14	2.42

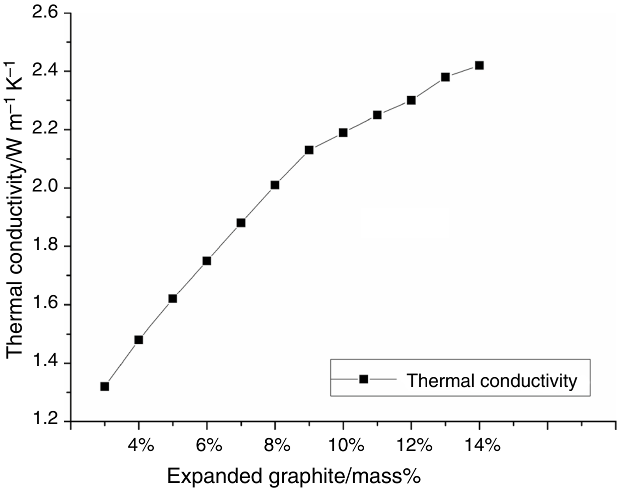


Fig. 15 Relationship between mass fraction of expanded graphite and thermal conductivity

of Figs. 13 and 15 were combined to give Fig. 16. As shown in Fig. 16, when the mass ratio of the expanded graphite added in the SSD composite phase change material was 9%, the influence on the supercooling degree of the material was not large, and the increase in the thermal conductivity was also ideal. Therefore, the optimum mass ratio of the expanded graphite added to the composite phase change material was set as 9%. It can be seen from Table 3 that when the addition amount of expanded graphite was 9%, the thermal conductivity of SSD/expanded graphite composite was 2.13 W m^{-1} K^{-1}. The thermal conductivity of $Na_2SO_4 \cdot 10H_2O$ was 0.544 W m^{-1} K^{-1}. Thus, the thermal conductivity of the composite phase change material was increased by 3.9 times after adding 9% of expanded graphite.

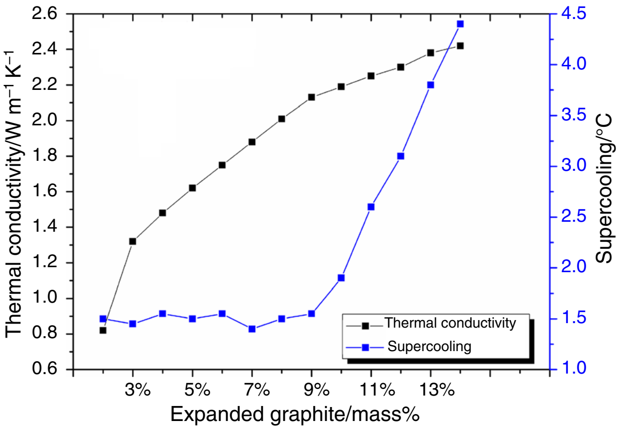


Fig. 16 Effect of expanded graphite addition on supercooling degree and thermal conductivity of composite phase change material

Thermal cycling stability test of SSD/expanded graphite composite phase change material

The degree of latent heat decay of the phase change was determined by melting–solidification cycles of the SSD/expanded graphite composite phase change material. The SSD/expanded graphite composite phase change material with the optimized formula was repeatedly tested. The temperature of the constant temperature water bath was 50 °C, and the temperature of the air bath was 20 °C.

Table 4 shows that as the number of thermal cycles increased, the supercooling degree of SSD/expanded graphite increased gradually. Moreover, the heat release time of the phase change process and the heat storage capacity of the composite phase change material both decreased. According to the phase transition theory of inorganic hydrated salt, after multiple melting–solidification cycles, the heat storage capacity of the material would be reduced due to the delamination of the material and the increasing particle size of the crystals [17]. When the SSD/expanded graphite composite phase change material was subjected to 500 melting–solidification cycles, the solution formed in the test tube began to show three layers. The uppermost layer was the unbound crystal water diluted solution, the middle layer was inorganic hydrated salt saturated solution, and the lowermost layer was the precipitated anhydrous salt. In fact, only the inorganic hydrated salt saturated solution in the intermediate layer had a latent heat of phase change in the heat storage and discharge cycle. Therefore, as the number of cycles increases, the latent heat value of the composite phase change material will continue to decrease, and the thickness of the intermediate layer will become thinner.

Characterization of SSD/expanded graphite composite phase change material

In order to test the thermal enthalpy of the SSD/expanded graphite composite phase change material, differential scanning calorimetry was used to determine the latent heat of phase change in the system. DSC tests were conducted on the samples after 1, 200, and 500 heat storage and release cycles, respectively, as shown in Figs. 17–19. The temperature control range of the experiment was 10–50 °C, the rate of temperature rise and fall was 3 K min^{-1}, and the sample

Table 4 Experimental results of thermal cycles for SSD/expanded graphite composite phase change material

Cycle index	1	200	300	500
Supercooling degree/°C	1.5	1.8	2.4	3.2
Phase change heat release time/min	25	22	20	17

Fig. 17 DSC curve of SSD phase change system after 1 heat storage and release cycle

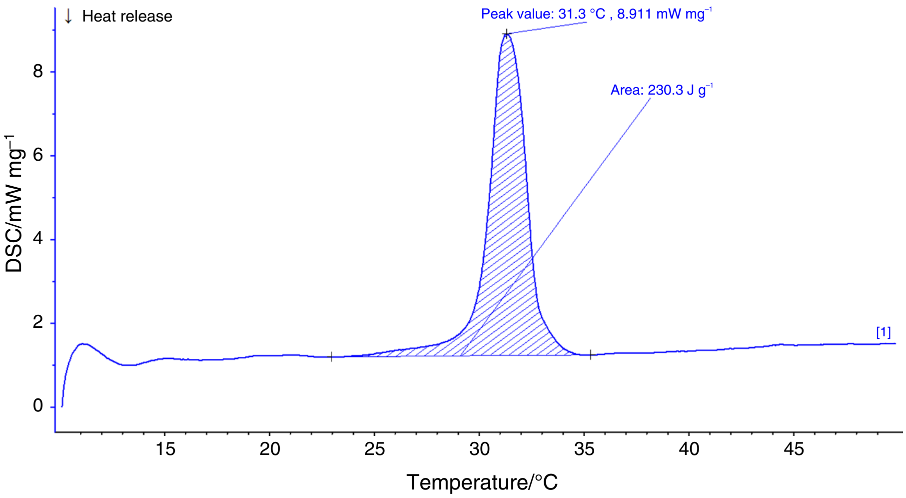


Fig. 18 DSC curve of SSD phase change system after 200 heat storage and release cycles

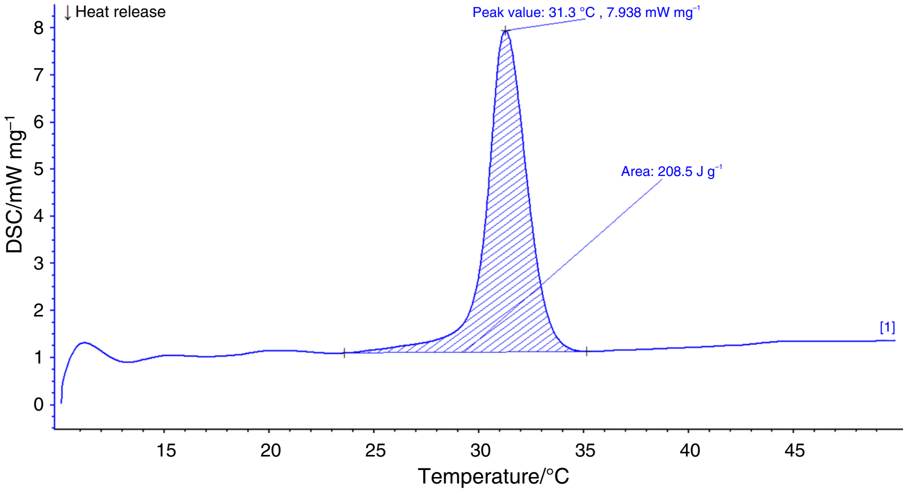


Fig. 19 DSC curve of SSD phase change system after 500 heat storage and release cycles

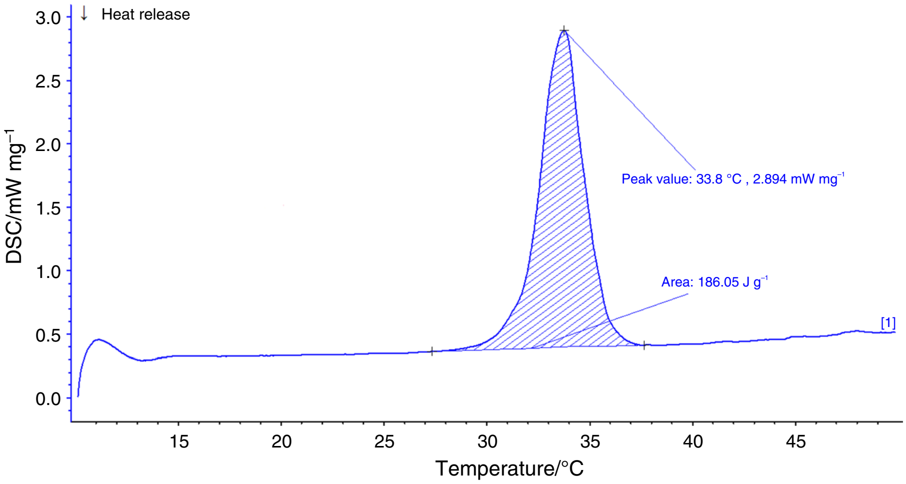


Table 5 DSC test results of SSD phase change system

Number of cycles for SSD phase change system	Peak value of the temperature rise curve/°C	Enthalpy of phase change/J g^{-1}
1 cycle	31.3	230.3
200 cycles	31.3	208.5
500 cycles	33.8	186.05

amount was 2–5 mg. The DSC test results for the SSD phase change system are shown in Table 5.

DSC test results of SSD phase change system are shown in Table 5.

Through the DSC test of the material, it was found that the latent heat of phase change in the SSD/expanded graphite composite phase change material gradually decreased with the increase in number of thermal cycles, which was similar to the result of the step cooling curve method. After 200 heat storage and discharge cycles, the phase transition enthalpy of the composite material was lowered by 9% compared with the first cycle. After 500 cycles of heat storage and discharge, the phase transition enthalpy of the composite was 19% lower than that of the first cycle. Combined with the step cooling curve method (as shown in Table 4), after 200 heat-discharge cycles, the heat release time of the composite phase change process was reduced by 12% compared with the first cycle. After 500 cycles of heat storage and discharge, the heat release time of the composite phase change process was reduced by 32% compared with the first cycle. After 200 heat storage and discharge cycles, the decay rate of the thermal properties of the materials in the two test methods was close, and the error of the results was 3%. After 500 heat storage and discharge cycles, the error of the test results of the two methods increased to 13%. Therefore, the thermal properties of the SSD/expanded graphite composite phase change material became very unstable as the number of heat storage–discharge cycles increased.

Conclusions

In this paper, the phase transition properties of SSD were studied. The problem of supercooling and phase stratification of SSD was solved by adding a nucleating agent and a thickener, and the thermal conductivity of the SSD composite phase change material was also enhanced by adding a thermal conductivity improver. Finally, a new composite phase change energy storage material was obtained with large phase change latent heat, high thermal conductivity, and stable phase change energy storage performance. The main conclusions of this work can be drawn as follows:

1. Through the step cooling temperature curve method, an optimal material composition was obtained, i.e., SSD :$Na_2B_4O_7 \cdot 10H_2O$:CMC = 100:5:3. The supercooling degree of the SSD composite phase change material obtained by the optimized formula was only 1.5 °C, and the heat release time of the phase change process was 25 min. Moreover, no phase stratification occurred.
2. When the mass ratio of expanded graphite reached 9%, the effect on the supercooling degree of the SSD composite energy storage material was small, and the supercooling degree was only 1.5 °C. However, the thermal conductivity was significantly increased by 3.9 times, reaching 2.13 W m^{-1} K^{-1}. At the same time, the heat storage time of the composite material was reduced by 30.8%, and the heat release time was reduced by 37.3%, thereby enhancing the heat exchange.
3. The SSD/expanded graphite composite heat storage material was subjected to multiple melting–solidification thermal cycle experiments. As the number of cycles increased, the supercooling degree gradually increased, and the heat release time and phase change latent heat of the phase change process decreased. The DSC test results showed that the phase transition enthalpy of the material decreased by 9% after 200 heat storage and discharge cycles compared with the first cycle. After 500 cycles of heat storage and discharge, the phase transition enthalpy of the material was lowered by 19%. After 200 heat storage and discharge cycles, the result of the DSC method was similar to that of the step cooling curve test method, and the decay rate of the thermal properties was relatively close. The error of the two test methods was 3%.

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