Enhancing the Heat Storage Performance of a Na$_2$HPO$_4$·12H$_2$O System via Introducing Multiwalled Carbon Nanotubes

Cong Ding, Liqiang Liu,* Fukun Ma, Fuzhou Chen, Shuo Zhang, and Tao Sun

ABSTRACT: The hydrated salt disodium hydrogen phosphate dodecahydrate (DHPD, Na$_2$HPO$_4$·12H$_2$O) has a suitable phase transition temperature and high latent heat of phase transition. Still, there are problems such as supercooling, phase separation, and low thermal conductivity. In this paper, DHPD, sodium carboxymethyl cellulose (CMC), aluminum oxide (Al$_2$O$_3$), and poly(vinylpyrrolidone) (PVP) are used to configure DHPD-CAP to suppress supercooling and phase separation successfully. Multiwalled carbon nanotubes (MWCNTs) are used to stabilize DHPD-CAP phase-change materials and improve the thermal conductivity of pure DHPD. Further studies show only a physical interaction between MWCNTs and DHPD, and no new phases are generated. The addition of MWCNTs can also promote the nucleation of the DHPD-CAP composite, and the corresponding latent heat of phase change shows a trend of increasing and then decreasing with the increase of MWCNT content. Compared with DHPD after one cycle, the latent heat of DHPD-CAP/MWCNT$_4$ increases by 36.19%. With the addition of MWCNTs, the thermal stability of the composites is improved compared to pure DHPD. The DHPD-CAP/MWCNT$_4$ composite has good stability after many cycles.

1. INTRODUCTION

Currently, with the rapid development of science and industry, fossil energy consumption has become more intense. Correspondingly, negative impacts and environmental pressures are increasing. Finding a clean, renewable, and pollution-free way to produce and store energy has become an urgent challenge for scientists.1–5 Energy storage technology is one of the effective ways to deal with these problems. Generally speaking, energy storage methods mainly include sensible heat storage,6 latent heat storage,7,8 and chemical heat storage.9 Compared with the other two forms of energy storage, latent heat storage (LHS) has the advantages of high energy storage density and small temperature fluctuations during phase transition.10–12 Phase-change materials (PCMs) absorbing or releasing vast heat energy through a phase change process can be considered as an excellent LHS medium for thermal energy storage.13–16 PCMs can be divided into organics, inorganics, and eutectics, according to their chemical structures.17 Among them, a hydrated inorganic salt, as a typical inorganic phase change material, has the advantages of large heat storage density, comprehensive sources, low cost, and good thermal conductivity.18 It has broad application prospects in many fields, such as industrial waste heat recovery and reuse, power “peak shaving, and valley filling,” solar energy utilization, civil and industrial building heating, air conditioning and energy-saving, aerospace, greenhouse insulation, textile industry, battery thermal management, infrared stealth, horticultural greenhouse, cold storage logistics, and electronic information field.19–30

Disodium hydrogen phosphate dodecahydrate (Na$_2$HPO$_4$·12H$_2$O, DHPD) is a typical low-temperature hydrated salt phase change material with good heat storage performance (melting point is 35 °C and the phase change latent heat value is 256.60 KJ Kg$^{-1}$).31 However, like other hydrated salts, there are problems with supercooling, phase separation, and poor cyclic stability.32–34 Supercooling prevents the phase change material from undergoing a phase change in time when it is cooled to the freezing point, causing the crystallization point to shift back, reducing the nucleation effect, even unable to release heat in severe cases, and adversely affecting the use of phase-change materials.35 Phase separation means that when the hydrated crystalline salt is dehydrated, the metal salt cannot be completely dissolved in free water, and sedimentation occurs due to the high density. The energy storage
capacity of the hydrated salt is continuously lost during the freeze–thaw cycle. Cyclic stability refers to the properties of phase-change materials that remain stable after repeated melting and solidification cycles, which directly affects the energy storage effect of phase-change materials. A lot of work has been done by scientists to address the inherent defects of PCMs mentioned above. For example, Yu et al. prepared shape-stable graphene-modified hydrated salt/UV-curable urethane acrylate resin composites by the limiting effect of graphene, and the phase transition temperature of the copolymers could be continuously adjusted by the effect of graphene on the entropy of the hydrated salt PCM system. Yang et al. prepared a new shape-stable eutectic hydrate/self-curing acrylic resin composite (EHS/SCR), with good shape stability properties for thermal energy storage. Gao et al. through the mechanical mixing method prepared a novel multiwalled carbon nanotube-modified hydrated salt/sodium polycrylate copolymer hydrogel (MWCNT-GS/PAAS). The composite maintained good thermal and chemical stability after 500 thermal cycles. Liu et al. reported the size effect of rutile TiO2 nanoparticles on the latent heat of recovery of eutectic hydrate PCM. The results showed that the best latent heat recovery was obtained by incorporating TiO2 nanoparticles with a diameter of 25 nm in nanoparticle-modified EHS composites. Lu et al. prepared a new environmentally friendly PCM using agricultural solid waste rice husk ash (RHA) as the support material and organic paraaffin (PA) as the core material for thermal storage by mechanical mixing and impregnation. The prepared composite PCM maintained good thermal cycling reliability and withstood 200 thermal cycles. In addition, Peng et al. conducted relevant studies on the abovementioned defects of PCMs and obtained specific results.

In addition, most of the PCMs suffered from low thermal conductivity during the application, which directly affects the heat transfer performance of the energy storage system. Therefore, it is necessary to improve the thermal conductivity of PCMs. The usual approach is to add nanomaterials to the PCM matrix, and among various nanomaterials, multiwalled carbon nanotubes (MWCNTs) are considered as a good candidate for improving thermal conductivity. MWCNTs are mainly composed of hexagonally arranged carbon atoms and can be seen as curled-up sheets of graphene. Due to their very large aspect ratio, multiwalled carbon nanotubes have a high thermal conductivity due to their high heat exchange properties along their length. Liu et al. modified hydrated salt/sodium polycrylate copolymer hydrogels with MWCNTs. The heat transfer properties showed that the thermal conductivity and thermal diffusion coefficient of MWCNT-GS/PAAS composites were improved by 141.7 and 167.1%, respectively, compared to pure GS. Avid et al. doped paraaffin with MWCNT modified with an organosilane and showed that the thermal conductivity of PCM nanocomposites in the solid and liquid phases increased with increasing MWCNT content, independent of the type of MWCNTs, up to 30%.

However, most of the aforementioned studies have only partially addressed the inherent defects of PCMs, and their application requirements remain unmet. Therefore, in this work, we used the addition of certain amounts of aluminum oxide (Al2O3), sodium carboxymethyl cellulose (CMC), and poly(vinylpyrrolidone) (PVP) to Na2HPO4·12H2O to synthesize DHPD-CAP polymers, where CMC was added to the hydrated matrix as a thickening agent to significantly improve the solution viscosity and prevent phase separation. Also, PVP can further improve the dispersibility of the polymer. Then, MWCNTs were applied to modify the DHPD-CAP polymer to enhance the heat transfer properties of the system and, at the same time, to further promote the crystallization of the polymer. The resulting PCM composites can meet the practical application requirements of Na2HPO4·12H2O.

2. EXPERIMENTAL SECTION

2.1. Materials. Na2HPO4·12H2O, Al2O3, CMC, and PVP were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai). MWCNTs were purchased from Tanfeng Tech. Inc. All reagents were used as received.

2.2. Preparation of DHPD-CAP and DHPD-CAP/MWCNT Composites. To solve supercooling and phase separation, DHPD-CAP was prepared by mixing Na2HPO4·12H2O, CMC, Al2O3, and PVP in a mass ratio of 95:8:2:0:2. After mixing uniformly, the mixture was placed in a plastic tube. The tube was placed in a constant temperature water bath at 55 °C and allowed to remain for 30 min after melting to ensure complete melting to prevent unfused solid particles from acting as crystal nuclei during the solidification process. Then, the DHPD-CAP can be obtained.

The as-obtained DHPD-CAP was poured into a beaker, immersing MWCNTs in the molten DHPD-CAP. Then, the beaker was stirred vigorously for 5–10 min and placed in a constant temperature water bath for 30 min. Finally, the DHPD-CAP/MWCNT composite material was obtained. Five composites with different MWCNT contents (0.25, 0.5, 0.75, 1, 1.25%) were synthesized using the above method in this work, and they were denoted as DHPD-CAP/MWCNT, DHPD-CAP/MWCNT1, DHPD-CAP/MWCNT2, DHPD-CAP/MWCNT3, DHPD-CAP/MWCNT4, and DHPD-CAP/MWCNT5.

2.3. Analytical Testing. The thermal cycling experimental setup used a constant temperature heating bath and a low-temperature thermostat. A PT100 RTD (error ±0.1 °C) was inserted into the test tube containing the composite phase change material, which was heated in a constant temperature water bath at a constant temperature of 55 °C after being numbered separately. To ensure that the phase change material had melted completely, the sample temperature was allowed to increase to 55 °C and held for more than half an hour. Finally, the sample was placed in a low-temperature constant temperature sink at 20 °C, cooled, and solidified until the temperature was constant. The whole heating–cooling thermal cycles were observed using a recorder to record the temperature every 4 s and transmitted to the computer to obtain a graph of the temperature rise and fall of the sample. The crystallization analyses of the samples were done using a Rigaku MiniFlex II X-ray diffraction (XRD) analyzer. A TA DSC25 differential scanning calorimeter and a TA DSC–DTA Q600 simultaneous thermal analyzer were used to analyze the thermophysical properties. A Bruker Vertex 70 Fourier transform infrared spectrometer was used to get FT-IR spectra of the samples. A Hitachi Flex1000 SEM was used to analyze the morphological features of the samples.

3. RESULTS AND DISCUSSION

3.1. Morphological Analysis of MWCNTs, DHPD, DHPD-CAP, and DHPD-CAP/MWCNT Composites. The morphologies of MWCNTs, DHPD, DHPD-CAP, and
DHPD-CAP/MWCNT composites were investigated by scanning electron microscopy (SEM). Figure 1a shows the SEM image of MWCNTs, which are hair-like structures and prone to agglomeration. Figure 1b shows the microscopic morphology of DHPD. It can be seen from the SEM image that the morphology of pure DHPD varies after crystallization and agglomeration still exists. Figure 1c is the SEM image of DHPD-CAP composites, and it can be seen that DHPD-CAP composites show a stick-like shape with a length of around 6 μm. Compared to the pure DHPD, the addition of CAP is beneficial to the crystallization of DHPD but the agglomeration issue still exists. Figure 1d shows the SEM image of DHPD-CAP/MWCNT composites, from which it can be seen that the hydrated salts can be adsorbed and closely anchored on MWCNTs with uniform distribution after the composite formation of DHPD-CAP with MWCNTs. Owing to their unique structural stability, MWCNTs can greatly alleviate the agglomeration compared with DHPD and DHPD-CAP. This result indicates that MWCNTs can be used as an effective carrier matrix for hydrated salts, promoting their crystallization.

3.2. Crystal and Chemical Structures of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT Composites. Figure 2a shows the XRD patterns of pure DHPD, DHPD-CAP, and DHPD-CAP/MWCNT composites. The characteristic peaks of pure DHPD locate at 14.7, 17.1, and 32.8° corresponding to the (−2 0 2), (−1 1 2), and (0 0 4) facets, respectively. MWCNTs have a broad peak in the range of 20°−30°, corresponding to the (0 0 3) facet, and the characteristic peak is at 25.8° (the characteristic peak of MWCNTs locates at 25.8° and the broad peak indicates that MWCNTs have a
small morphology, which fits the SEM image). Compared with pure DHPD, DHPD-CAP has a strong diffraction peak at 31.4°, but there is no such diffraction peak in pure DHPD. The strong peak in the DHPD-CAP sample is due to the good crystal structure of Al2O3, which is maintained after composite formation. After immersion of MWCNTs in DHPD-CAP, no new diffraction peaks are observed. Compared with DHPD and DHPD-CAP, the diffraction peaks have a slight shift, which is due to the lattice distortion of the DHPD introduced by the surface tension of MWCNTs. XRD diffraction results show that only physical interactions occur between DHPD and MWCNTs with no new phases produced.

The infrared spectra of pure DHPD, DHPD-CAP, and DHPD-CAP/MWCNT composite materials are shown in Figure 2b. According to the infrared spectrum results of pure DHPD, there are two absorption peaks located at 985.6 and 1080.1 cm⁻¹ corresponding to the symmetric and asymmetric tensile vibration peaks of PO₃, respectively. The characteristic absorption peak of P−OH can be found at 866.0 cm⁻¹. The symmetrical tensile vibration peak corresponding to PO₄ appears at 526.6 cm⁻¹ owing to the presence of impure PO₄³⁻ in DHPD. MWCNTs have a very weak absorption peak at 1634.5 cm⁻¹, which is the vibration absorption peak of the C−C skeleton of MWCNTs. The absorption bands of DHPD-CAP and DHPD-CAP/MWCNT composites at 3464.0 and 3462.1 cm⁻¹ are caused by the humidity in the air during the test, respectively. In contrast, the infrared spectrum of DHPD-CAP/MWCNT composites contains all of the characteristic absorption peaks of pure DHPD, MWCNTs, and DHPD-CAP with no new absorption peaks appearing, indicating that there is no chemical interaction between DHPD, MWCNTs, and other materials. The result also indicates that there are no impurities during the synthesis process.

Figure 3. Phase separation of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT composites after melting (a) and crystallization (b); DSC curves of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT composites (c); DSC curves of DHPD-CAP/MWCNT systems with different MWCNT contents (d).

3.3. Phase Separation of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT Composites. Figure 3a,b shows the phase separation of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT composites after melting and crystallization. It can be seen that apparent phase separation occurred after crystallization of pure DHPD with a white precipitate at the bottom of the tube and a little clear liquid in the upper layer, while no apparent phase separation was observed in the DHPD-CAP and DHPD-CAP/MWCNT composites. The DSC test was carried out to get the melting latent heat of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT during the melting−cooling cycle process, and the results are shown in Figure 3c. Figure 3c shows two endothermic peaks in the DSC curve of pure DHPD. The starting point of the first peak is 33.42 °C, and the starting point of the second peak is 45.85 °C. From the reported results, the Na₂HPO₄/H₂O system has three stable states: Na₂HPO₄·12H₂O, Na₂HPO₄·7H₂O, and Na₂HPO₄·2H₂O. As pure DHPD undergoes phase separation during melting, it loses some of its crystal water when it solidifies and crystallizes, during which time Na₂HPO₄·12H₂O and low-grade salt Na₂HPO₄·7H₂O are produced. The lower melting point of Na₂HPO₄·12H₂O melts first and the higher melting point of Na₂HPO₄·7H₂O melts later, so two endothermic peaks appear in the DSC curve. Figure 3c shows that Na₂HPO₄·12H₂O removes five crystal water becoming Na₂HPO₄·7H₂O at about 33.42 °C, and then Na₂HPO₄·7H₂O removes five crystal water becoming Na₂HPO₄·2H₂O at about 45.85 °C. The latent heat of melting is 159.76 J g⁻¹, which is much lower than 256.60 J g⁻¹. This is because the samples undergo melting−cooling cycle experiments and severe phase separation occurs. The latent heat of melting is 159.76 J g⁻¹, which is lower than that of pure DHPD at 256.60 J g⁻¹, due to the different thermal effects of melting of the generated Na₂HPO₄·12H₂O and Na₂HPO₄·7H₂O (the
thermal effects depend mainly on the type and amount of water of crystallization and the nature of anions and cations) and incomplete dehydration.

While the latent heat of fusion of DHPD-CAP and DHPD-CAP/MWCNT composite phase change energy storage materials are 175.71 and 217.57 J g\(^{-1}\), respectively, the cyclcd latent heat was greater than the former 159.76 J g\(^{-1}\), which was due to the improvement of phase separation of DHPD by the CMC increasing the practical components and the latent heat. The latent heat of phase change increased 10% compared with pure DHPD. The increased latent heat in the DHPD-CAP/MWCNT system was owing to the porous structure of MWCNTs confining to DHPD during the melting and crystallization process, avoiding the leakage of the phase transition material. Furthermore, the porous structure adsorbed more DHPD and modified the phase separation, maintaining the effective phase transition component. The latent heat of DHPD-CAP/MWCNT was elevated to 36.19% compared to the pure DHPD material, which indicated that the addition of MWCNTs can restrain the phase separation of DHPD.

Compared with pure DHPD, the phase transition temperatures of DHPD-CAP and DHPD-CAP/MWCNT composite phase-change materials are 33.47 and 35.44 °C, respectively. The phase transition temperature of the DHPD-CAP system is increased due to the even dispersion of DHPD in the system, which is caused by the addition of the thicker CMC. The increased total heat transfer path in the composite leads to an elevation in the phase transition temperature. The increased phase transition temperature in the DHPD-CAP/MWCNT system is caused by the different degrees of interaction between DHPD and MWCNTs including surface tension and capillary force.\(^{53–55}\) In addition, the pure DHPD in Figure 3c shows two endothermic peaks, while the DHPD-CAP and DHPD-CAP/MWCNT composites have only one endothermic peak, which is because with the addition of CAP and MWCNTs, the phase separation of pure DHPD is inhibited and the formation of the low-grade salt Na\(_2\)HPO\(_4\)\(_7\)H\(_2\)O is prevented, so the DSC curves of DHPD-CAP and DHPD-CAP/MWCNT composites have only one endothermic peak. Figure 3d shows the DSC curves of the DHPD-CAP/MWCNT composite phase-change materials with different MWCNTs contents, and the detailed thermal properties are listed in Table 1. It can be seen from Figure 3d that the latent heat of fusion of DHPD-CAP/MWCNT\(_1\), DHPD-CAP/MWCNT\(_2\), DHPD-CAP/MWCNT\(_3\), DHPD-CAP/MWCNT\(_4\), and DHPD-CAP/MWCNT\(_5\) composite phase change energy storage materials are 190.99, 210.96, 217.17, 217.57, and 216.32 J g\(^{-1}\), respectively. When the content of MWCNTs is less than 1.25%, the latent heat of melting of the DHPD-CAP/MWCNT system increases with the increase of MWCNT content, and when the content of MWCNTs is greater than 1.25%, the latent heat of melting of the DHPD-CAP/MWCNT system decreases instead. This is because when the content of MWCNTs is sufficient, the phase separation of the system is completely suppressed, and MWCNTs do not provide latent heat. It can be seen that the DHPD-CAP/MWCNT\(_4\) system with a 1% MWCNT content has the best suppression of DHPD phase separation. Its phase transition temperature was 35.44 °C, and the latent heat of phase transition was 217.57 J g\(^{-1}\). In addition, the higher phase transition temperature of 44.32 °C for the DHPD-CAP/MWCNT\(_3\) system can be seen in Table 1. This may be due to the higher content of MWCNTs when the MWCNTs stick together to form a network structure, which prevents the heat transfer process of DHPD during melting, thus increasing the melting temperature.

3.4. Supercooling of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT Composites. The step cooling curves of pure DHPD, DHPD-CAP, and DHPD-CAP/MWCNT composites are shown in Figure 4a. Figure 4a shows the supercooling degrees of pure DHPD, DHPD-CAP, and DHPD-CAP/MWCNT are 7.4, 4.0, and 0.8 °C, respectively. This indicates that the DHPD-CAP composites with the addition of 2% Al\(_2\)O\(_3\) and 2% CMC and the DHPD-CAP/MWCNT system with the addition of MWCNTs can reduce the supercooling of DHPD. The addition of MWCNTs promotes the nucleation of DHPD-CAP composites by providing more nucleation crystallization centers for DHPD-CAP, which reduces the interfacial surface energy between the liquid and solid phases and decreases the phase transition resistance, thereby decreasing the supercooling degree.\(^{35,56–58}\) The step cooling curves of DHPD-CAP/MWCNT systems with different MWCNT contents are shown in Figure 4b. Figure 4b shows that the DHPD-CAP/MWCNT\(_1\), DHPD-CAP/MWCNT\(_2\), DHPD-CAP/MWCNT\(_3\), DHPD-CAP/MWCNT\(_4\), and DHPD-CAP/MWCNT\(_5\) systems have almost no supercooling phenomenon. The results show that the composite systems can greatly restrain the supercooling phenomenon in the pure DHPD.

3.5. Heat Transfer Performance of DHPD and DHPD-CAP/MWCNT Composites. During the experiment, we found that the DHPD-CAP composite had little effect on the heat transfer of pure DHPD. Therefore, to explore the effect of the DHPD-CAP/MWCNT composite on the heat transfer performance of pure DHPD, melting–cooling experiments were conducted on the samples using a constant temperature heating bath and a low-temperature constant temperature bath. The experimental details are given in the Experimental Section.

As shown in Figure 5, during the warming process, the temperature of the DHPD-CAP/MWCNT composite increased faster compared with pure DHPD, and with the increase of time, the inflection point and phase transition plateau of the DHPD-CAP/MWCNT composite appeared between 32 and 36 °C, and the inflection point and phase transition plateau of pure DHPD appeared between 34 and 36 °C. The DHPD-CAP/MWCNT composite had significantly shorter phase transition plateaus than pure DHPD, i.e., the addition of MWCNTs accelerated the heat transfer rate of the samples. The heat storage time of pure DHPD and DHPD-CAP/MWCNT composites were 1908 and 1684 s, respec-

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Table 1. Phase Change Properties of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT Composites

| samples         | content of DHPD (%) | melting temperature (°C) | latent heat of melting (J g\(^{-1}\)) |
|-----------------|---------------------|--------------------------|--------------------------------------|
| DHPD            | 100.00              | 33.42/45.85              | 159.76                               |
| DHPD-CAP        | 95.80               | 33.47                    | 175.71                               |
| DHPD-CAP/MWCNT\(_1\) | 95.55            | 33.68                    | 190.99                               |
| DHPD-CAP/MWCNT\(_2\) | 95.30            | 36.26                    | 210.96                               |
| DHPD-CAP/MWCNT\(_3\) | 95.05            | 38.07                    | 217.12                               |
| DHPD-CAP/MWCNT\(_4\) | 94.80            | 35.44                    | 217.57                               |
| DHPD-CAP/MWCNT\(_5\) | 94.55            | 44.32                    | 216.32                               |
tively, and the heat storage time of the latter was reduced by 11.74%.
In the cooling process, compared with pure DHPD, the temperature of the DHPD-CAP/MWCNT composite material decreases faster. The composite phase change material first exhibits a liquid–solid phase change and releases the latent heat, so the temperature is higher than that of pure DHPD, and the curve is above the pure DHPD curve. Then, pure DHPD also begins to emit latent heat, but the phase transition plateau is longer. The temperature drops faster when the heat release ends due to the more significant thermal conductivity of the DHPD-CAP/MWCNT composite. The curve is below the pure DHPD curve until the two temperatures approach the same, and the heat release time of pure DHPD and DHPD-CAP/MWCNT composites are 1284 and 1072 s, respectively, and the heat release time of the latter is reduced by 16.51%; in addition, the heat release time of pure DHPD and DHPD-CAP/MWCNT composites is less than the heat storage time. Therefore, the addition of MWCNTs accelerates the phase change rate of the phase change material and significantly improves the heat transfer properties of the phase change material.

3.6. Thermal Stability Analysis of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT Composites. The thermal stability of DHPD, DHPD-CAP, and DHPD-CAP/MWCNT composites is analyzed. In Figure 6, crystalline water in DHPD gradually evaporated as the temperature increased, and when the temperature reached 118 °C, almost all of the crystalline water in DHPD was lost, while the DHPD-CAP and DHPD-CAP/MWCNT composites still retained some of the crystalline water at the temperature of complete dehydration of DHPD. In addition, when the temperature reached 270 °C, the weight loss of DHPD-CAP and DHPD-CAP/MWCNT composites was caused by the carbonization of CMC. When the temperature attained 330 °C, the weight loss of DHPD was due to the decomposition of disodium hydrogen phosphate. In addition, the thermogravimetric curves of DHPD showed that the dehydration of DHPD was carried out in steps during the temperature rise. When the temperature reached 350 °C, the weight loss of pure DHPD was 71.57%, while the weight losses of DHPD-CAP and DHPD-CAP/MWCNT composites were 67.85 and 62.21%, respectively, which were 5.20 and 13.07% lower than that of pure DHPD. Among them, the DHPD-CAP/MWCNT composites had the best thermal stability. The phase-change materials were adsorbed and immobilized in the pores due to the porous structure increasing the surface tension and capillary force. As the temperature increased, the
thermal dehydration process of the phase change material underwent a phase change, which increased the difficulty of dehydration due to the reversible hydrogen bonds formed between the material and the porous material, and its thermal stability was improved. Furthermore, from the figure, the weight loss of the DHPD-CAP/MWCNT composite phase change energy storage material is greater compared to those of the pure DHPD and DHPD-CAP composites due to the incorporation of MWCNTs with high thermal conductivity. The improved thermal conductivity can be verified from Figure 5.

3.7. Cycle Stability Analysis of the DHPD-CAP/MWCNT4 Composite. Solid—liquid stratification occurred after the repeated melting—cooling process decreases the heat storage performance by reducing the effective component. Therefore, to determine the thermal cycle stability of the composite material, thermal cycling tests were carried out. The thermal cycling curves and latent heat of phase change after the test cycle are shown in Figure 7. The step cooling curves of the

![Figure 7. DHPD-CAP/MWCNT4 composite material cycle curve.](https://pubs.acs.org/10.1021/acsomega.1c04317)

first, tenth, twentieth, thirtieth, fortieth, and fiftieth cycles overlapped well, indicating the outstanding thermal stability of DHPD-CAP/MWCNT4. The DHPD-CAP/MWCNT4 possessed a stable melting temperature of 35.4 °C and latent heat of 214.65 J g⁻¹, almost no attenuation compared to the first cycle (217.57 J g⁻¹). The outstanding thermal stability of DHPD-CAP/MWCNT4 made it a promising material for energy-saving buildings and greenhouse heat preservation.

4. CONCLUSIONS

Pure DHPD suffers from severe phase separation and supercooling and cannot be directly used as a thermal storage material. CAP/MWCNTs can effectively improve the phase separation of DHPD and reduce the supercooling phenomenon. Compared with pure DHPD, the latent heat of melting of the DHPD-CAP/MWCNT composite was improved by 36.19%, while the supercooling was only 0.8 °C. Meanwhile, MWCNTs can improve the thermal conductivity and thermal stability of phase change composites. After 50 cycles, the melting temperature of the DHPD-CAP/MWCNT4 composite was stabilized at about 35.4 °C. The designed DHPD-based phase change composite has good thermal stability and broad application prospects. This work also illuminated the function of CAP and MWCNTs in the phase change energy storage materials realms.

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### Notes

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