Study on stability of carbon residue/Sodium acetate trihydrate composite phase change material from sludge pyrolysis

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Abstract—In this paper, the pyrolysis carbon residue of sludge adsorbed sodium acetate trihydrate (SAT) of different quality to prepare composite phase change materials (CPCM). The thermal cycling performance of the prepared CPCM was tested to determine the optimal adsorption ratio of pyrolytic carbon residue to SAT. Multiple melt-solidification experiments were performed on pure SAT and CPCM to determine the improvement effect of pyrolytic carbon residue on SAT undercooling and phase separation phenomenon. The results show that the optimal adsorption ratio of pyrolytic carbon to SAT is 1:5, the undercooling degree of the CPCM is only -2.4, and the latent heat of phase change is 216.7 kJ/kg, which basically overcomes the undercooling degree and phase separation phenomenon of sodium acetate trihydrate. The composite phase change material still has high latent heat value and excellent heat storage capacity after many cycles.

1. Introduction
Sludge is a solid waste produced in the process of sewage treatment, containing heavy metals, pathogens and other harmful substances[1], in addition to the sludge contains organic substances, after pyrolysis of the sludge carbon residue, has certain adsorption properties, can be used as a carrier to adsorb other substances. Municipal sludge is a thick substance between solid and liquid[2]. It is difficult to separate solid and liquid by sedimentation method. If it is not properly treated, it will cause serious harm to the ecological environment and human health, resulting in profound influence[3]. Sludge pyrolysis is a thermal decomposition method under high temperature conditions, sludge decomposition under high temperature conditions, produce gas, solid and other products[4], the gas can be treated after discharge, the resulting sludge carbon can be used as adsorbent, catalyst and so on[5]. The pyrolysis residue can be used as a carrier to adsorb hydrated salts to prepare composite phase change materials.

Energy storage technology can address the spatial and temporal imbalance of power by storing energy at night for use during the day. Sodium acetate trihydrate is a typical inorganic phase change material with a phase change temperature of 58 ℃ and a latent heat value of 260kJ/kg[6-7]. By adding nucleating agent Na4P2O7ꞏ10H2O and thickening agent polyacrylamide, the composite prepared by Wang[8] et al. weakened the phase separation phenomenon, effectively reduced the degree of undercooling, and maintained a high heat storage capacity. Mao[9] and others on the trihydrate sodium acetate modified, the melt blending method is adopted to twelve water disodium hydrogen phosphate (DHPD) and carboxymethyl cellulose (CMC) as additive effectively reduces the super-cooling degree of SAT and suppress the phase separation phenomenon, by thickening agent to add the liquid viscosity increases, blocking water molecules emerge from salt hydrate, but also reduces the heat storage.
capacity. Kenji [10] et al. selected four kinds of crystals, NaCl, NaBr, Na₂HPO₄·2H₂O and Na₃PO₄·0.5H₂O, as nucleating agents to inhibit the supercooling of SAT from the perspective of homotype crystals, revealing the relationship between the arrangement of Na atoms in crystals and nucleation. Abdel et al. [11] used urea with melting point of 30 °C as additive and SAT as heat storage material to develop a new energy storage system with phase change temperature of 44.5 °C, which can store latent heat stably without phase stratification. Garay et al. [12] added polymer silica gel and CMC into SAT thermal storage material, which reduced the occurrence of phase stratification and increased the thermal cycling stability of composite phase change material. Hu et al. [13] adopted nano aluminum nitride as additive, which greatly reduced the undercooling of SAT solution during solidification. Meanwhile, due to its high thermal conductivity, it was evenly distributed in SAT and improved the thermal conductivity of SAT composite phase change material. Yuusuke et al. [14], in order to solve the problem of supercooling SAT as a heat storage material, adopted electron nucleation technology, adding compound sodium hydroxide into SAT melting liquid, inserting electrodes into the mixture, applying a certain voltage to promote nucleation, and achieved good results. Researchers often modify sodium acetate trihydrate by adding nucleating agent and thickening agent to reduce its undercooling and phase separation. This increases the preparation cost of composite phase change materials.

In this paper, municipal sludge was pyrolyzed in muffle furnace, and the pyrolytic carbon residue was adsorbed SAT to prepare composite phase change materials. Pyrolysis residues with different mass ratios were fused with SAT, and the resulting composite phase change materials were melted and solidified under multiple water baths to determine the optimal adsorption ratio between pyrolysis residues and SAT. The composite phase change material was compared with pure SAT for multiple cycles to judge the improvement effect of pyrolysis residue on SAT undercooling and phase separation. This is not only the resource utilization of sludge, but also provides a new way for the preparation of composite phase change materials.

2. Experimental materials and methods

2.1. Preparation of pyrolytic carbon residue/sodium acetate trihydrate composite phase change material

Municipal sludge (a sewage treatment plant in Qingdao) was heated and decomposed in muffle furnace without oxygen, and the reaction temperature was 500 °C. Industrial analysis of the carbon residue obtained after the decomposition of municipal sludge, Industrial analysis of sludge and pyrolytic carbon residues is shown in Table 1. The moisture content of sludge is high, and the volatilization grade of steam generated in the pyrolysis process will increase the number of micropores in the pyrolytic carbon residue, thus ensuring its excellent adsorption capacity.

| Table 1: Industrial analysis of sludge and pyrolytic carbon residues |
|---------------------------------|--------|------|-------|-------|
| proximate analysis (wt%)         | moisture | ash  | volatiles | fixed carbon |
| municipal sludge                | 78.7    | 8.3  | 11.6    | 1.4     |
| pyrolytic carbon residue        | 0       | 68.5 | 16.75   | 14.75   |

The pyrolytic carbon residue/sodium acetate trihydrate composite phase change material was prepared by melt blending method. Firstly, a certain mass of sodium acetate trihydrate (Shanghai Alpi Chemical Reagent Co., LTD) was placed in a beaker and melted in a water bath with the water bath temperature set at 70 °C. Then a certain mass of pyrolytic carbon residue was weighed and mixed. Finally, the mixture of carbon residue and sodium acetate trihydrate was stirred and mixed evenly using a thermostatic magnetic stirrer. Among them, the mass ratio of pyrolytic carbon residue to sodium acetate trihydrate is 1:5, 1:6 and 1:7, which are named CPCM5, CPCM6 and CPCM7 respectively. The preparation process of phase change materials is shown in Figure 1.
2.2. Thermal performance experiment of composite phase change materials

The melting and solidification heat cycle of pure SAT and three kinds of composite phase change materials was carried out in water bath. The composite phase change material is put into 15ml test tube, and the thermocouple is buried in the center of the test tube. The temperature change data of the composite material in the test tube is obtained through the data acquisition instrument, and the upper part of the test tube is sealed to prevent the loss of crystal water. The water bath temperature of CPCM during melting/solidification was set at 70/40°C. The experimental device is shown in Figure 2.

3. Results and discussion

3.1. Thermal cycling properties of composite phase change materials

The phase transition temperature of SAT was 58.2 °C and the latent heat value was 260kJ/kg by synchronous thermal analyzer. The phase transition temperatures of CPCM5, CPCM6 and CPCM7 were 57°C, 57.3°C and 56.8°C, respectively.
As can be seen from Figure 3-a, the maximum phase transition undercooling of CPCM5 in 30 thermal cycles is only 2.4℃, and its solidification exothermic section is stable and stable, and the exothermic temperature is around 55.7℃. As can be seen from Figure 3-b, the maximum undercooling degree of CPCM6 is 5℃, and its solidification heat release section is not stable. As can be seen from Fig. 3-c, the maximum undercooling degree(MUD) of CPCM7 is as high as 5.6℃, and its solidification exothermic section is extremely unstable, with almost no stable exothermic section. It can be concluded that the higher the proportion of SAT in the composite phase change material, the greater the latent heat value of the composite phase change material. Therefore, the optimal mass adsorption ratio of The pyrolysis residue to SAT is determined to be 1:5. In this case, the composite phase change material prepared has a low degree of undercooling and a relatively stable solidification exothermic section.

### 3.2. Improvement of SAT subcooling by pyrolysis residue

![Fig. 4 7 times melting - solidification temperature curve of SAT](image)
Figure 4 shows the temperature curve of pure SAT for 7 thermal cycles. As can be seen from the figure, the undercooling degree of pure SAT gradually increases with the increase of cycles, and the maximum undercooling degree in 7 cycles is as high as 6.7°C. It can be seen from Figure 4 that the solidification exothermic section of pure SAT is unstable. As can be seen from Figure 3-a, after the adsorption of SAT with a mass of 6 times, the pyrolytic carbon residue still has a low degree of undercooling (2.4°C) and a stable solidification exothermic section after multiple melting and solidification cycles. It can be seen that the addition of pyrolytic carbon reduces the supercooling degree of SAT.

3.3. Improvement of SAT phase separation by pyrolysis residue

Figure 5 shows the images of SAT after seven thermal cycles and CPCM5 after 30 thermal cycles. It can be seen from the figure that after the secondary thermal cycle, an obvious phase separation phenomenon occurs in SAT, which changes its chemical properties and makes it no longer suitable for storing energy as a phase change material. However, CPCM5 had no obvious phase separation after 30 cycles. It can be seen that the micropores of pyrolytic carbon remnant provide a stable phase transition space for the phase transition of SAT, which makes SAT still maintain chemical stability after multiple cycles.

![Fig. 5 Images of pure SAT and CPCM5 after repeated melting and solidification cycles](image)

3.4. Variation of latent heat value of CPCM5 after multiple cycles

Figure 6 shows the DSC curve of CPCM5 before and after 30 melting-solidification cycles. As mentioned earlier, the latent heat value of pure SAT phase change is 260kJ/kg, so the theoretical mass-weighted latent heat value of CPCM5 is 216.7kJ/kg. The latent heat values of the first and 30th phases of CPCM5 were 219.5 and 217.1kJ/kg, respectively. The difference from the theoretical value is only 0.2%-1.3%. It can be seen that CPCM5 still has a high and stable latent heat value after several thermal cycles.

![Fig. 6 DSC curves of composite phase change materials before and after 30 cycles](image)
4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

1) The optimal adsorption ratio of pyrolysis residue to SAT is 1:5, and the latent heat value of the prepared composite phase change material is as high as 216.7kJ/kg, the maximum undercooling is only 2.4℃, and the solidification exothermic section is stable.

2) CPCM5 overcomes the high supercooling degree and phase separation of SAT, and still has cyclic stability after repeated melting and solidification cycles.

3) CPCM5 is still stable after 30 cycles, and the difference between CPCM5 and theoretical latent heat value is only 0.2%-1.3%, which is suitable for energy storage material.

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