Energy Reports 8 (2022) 2646–2655

Contents lists available at ScienceDirect

Energy Reports

journal homepage: www.elsevier.com/locate/egyr

Research article

Ternary composite phase change materials (PCMs) towards low phase separation and supercooling: eutectic behaviors and application

Xianghai Xing [a], Wei Lu [a,*], Guanhua Zhang [a], Yupeng Wu [b], Yanping Du [c], Zhibo Xiong [a], Li Wang [a], Kun Du [b], Hao Wang [a]

[a] *School of Energy and Power Engineering, University of Shanghai for Science and Technology, Shanghai, 200093, China*
[b] *Department of Architecture and Built Environment, Faculty of Engineering, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK*
[c] *China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai, 200240, China*

ARTICLE INFO

Article history:
Received 7 November 2021
Received in revised form 15 December 2021
Accepted 27 December 2021
Available online xxxx

Keywords:
Phase change materials
Ternary salt-water solution
Phase separation
Frozen food storage

ABSTRACT

Salt hydrates have been used as phase change materials (PCMs) for various types of Thermal Energy Storage (TES) especially for cold storage. In this project, a novel composite phase change material (PCM) consisted of mixed solution of inorganic salt and organic salt was developed and characterized. Firstly, the PCM solutions containing sodium formate, potassium chloride and water with various weight percentage were evaluated to understand their solidification temperature, melting temperature, the supercooling degree and the latent heat. Then a PCM with mass fractions at weight percentages of 22%/12%/66% with better performance was selected for further study to restrain the supercooling. Different gelling agents and nucleate agents were employed in this PCM. The results show that the addition of 0.6 wt% xanthan gum can effectively prevent the phase separation and leakage, while 0.6 wt% of nano-TiO_2 is the best nucleating agent since the supercooling can be reduced to 2.6 °C, which is 67.9% lower than that of the original PCM without any nucleating agent. Finally, the novel PCM was tested for frozen food storage application, in which the food temperature could be maintained below -18 °C for over 10 hours in the insulated box. This indicated the suitability of developed PCM for frozen food storage and transportation.

1. Introduction

As energy saving has become increasingly important in recent years, cold storage technology as a potentia solution for energy saving and energy load shifting has received significant attentions. Phase change materials (PCMs) have the capacity to store heat of fusion at a constant or near constant temperature, which corresponds to the phase transition temperature of the PCM (Mehling and Cabeza, 2008; Sharma et al., 2009). Currently, PCM has been widely applied in different fields including thermal energy storage for buildings (Wang et al., 2020), solar power plants (Prieto and Cabeza, 2019), solar air heating systems (Sharma et al., 2020), photovoltaic thermal system (Lu et al., 2018), refrigerators (Pirvaram et al., 2019), waste heat recovery (Ji et al., 2017; Lu et al., 2020) and domestic hot water systems (Seddegh et al., 2015; Du et al., 2018). Meanwhile, applications of PCMs for cooling and cold storage have been widely reviewed and studied by many researchers. Oró et al. (2013) mixed NH_4Cl with NaCl and AlF_3, respectively, and obtained a few samples of composite PCMs with a melting temperature in the range of −21 °C and −15 °C. Qin et al. (2020) analyzed the effect of phase-change material on hot water tank made of low melting point metal, and the results showed that phase-change material effectively improved the heat storage capacity of water tank and increased the thermal efficiency of hot water tank. Saline mixture is regarded as a potential composite in self-developed PCM for cold storage with larger latent heat and appropriate melting temperature. It was reported that inorganic salt solutions as PCMs were widely used in the temperature range from −20 °C to −10 °C (Yang et al., 2018). Li et al. (2013) studied PCMs with melting points lower than 0 °C for refrigeration systems. It was found that inorganic PCMs within these temperature ranges were cheap but with high latent heat of fusion. However, the current drawbacks for these PCMs include supercooling and phase separation during their phase change processes. In addition, Zalba et al. (2003) compared the advantages and disadvantages of organic and inorganic materials and found that the organic–inorganic composite PCMs could effectively overcome the shortcomings of a single inorganic or organic material to a certain extent, leading to a

* Corresponding author.
E-mail address: wei.lu@usst.edu.cn (W. Lu).

https://doi.org/10.1016/j.egyr.2021.12.069
2352-4847/

Table 1
Thermal properties of binary water-salt solutions.

Materials	Melting temperature (°C)	Latent heat of fusion (kJ/kg)
$HCOONa+H_2O$ (Chen et al., 2017)	−15.5	282
$KCl+H_2O$ (Yang et al., 2018)	−10.7	253

significant improvement of the thermal performance in practical applications. Therefore, the development of composite PCM has been widely investigated by many researchers. For example, Jia et al. (2019) developed a phase change composite material composed by trimethylolpropane (TMP) ammonium chloride and water with a thermal conductivity of 0.81 W/m·K. The measured phase change temperature and the latent heat of fusion were −19.9 °C and 246.8 kJ/kg, respectively. To overcome the phase separation and precipitation that affected the performance stability, Wang et al. (2021) made solutions by adding a gelling agent into the PCM mixtures. It was reported that the addition of hydroxyethyl cellulose (HEC) into the salt solution improved the recycling ability of the composite PCMs. Moreover, adding a nucleating agent can avoid supercooling phenomenon caused by the poor nucleation ability of salt hydrates and the use of nanomaterials as nucleating agents have been studied by many researchers. Eanest Jebasingh and Valan Arasu (2020) reported that the latent heat and thermal conductivity of phase change materials with nanoparticles dispersed in low-temperature applications, and analyzed the reasons for the increase or decrease of latent heat and the thermal conductivity of phase change materials. Hu et al. (2011) showed that Silicon carbide can effectively reduce the supercooling of sodium acetate trihydrate. The results showed that the maximum supercooling of the 2% SiC and 2% expanded graphite composite phase change material after 200 heat storage and release cycles was 1.1 °C. Fang et al. (2022) confirmed that AlN nanoparticles were proposed as the nucleating agent for sodium acetate trihydrate (SAT). Experimental results showed that the addition of 3–5 wt% AlN nanoparticles could reduce the supercooling of the thickened SAT to 0–2.4 °C. Fu et al. (2019) added silica (SiO_2) into sodium acetate trihydrate-urea non-eutectic mixture and observed a low supercooling. Moreover, Lu and Tassou (2013) found that the supercooling of water gel could be significantly reduced by adding AgI. With increasing of the AgI mass fraction from 0 to 0.8%, the supercooling temperature was gradually reduced.

In general, salt hydrates can be used as PCMs for many thermal energy storage (TES) applications especially for cold storage. However, most of previous researches focused on medium and high temperature PCM, and most of them cannot be used for cold storage for applications like frozen food transportation because the melting temperatures of most binary eutectic water-salt solutions are not far from 0 °C. There is only a few research carried out on low temperature PCMs (Oró et al., 2012; Lu et al., 2019). For low-temperature cold chain logistics applications below −23 °C, Jin et al. (2021) developed a new composite phase-change cooling material consisting of sodium acetate (HCOONa), ammonium chloride (NH_4Cl) and water, which can be used in a homemade insulation tank to keep frozen meatballs below −23 °C for more than 20 h, which can meet the requirements of short-distance cold chain transportation. In this study, a eutectic PCM solution containing Sodium formate, Potassium chloride and Water (SPW) was developed and optimized. When the salts used for the ternary eutectic water-salt solution (SPW composite) have binary water-salt solutions, their melting temperatures and thermal properties of the materials are presented in Table 1 (Yang et al., 2018; Chen et al., 2017). It shows their eutectic temperatures are −15.5 °C and −10.7 °C, so their binary water-salt solutions cannot be used to maintain product temperature below −18 °C for cold storage applications, but the ternary eutectic water-salt solution has lower phase change temperature, which can be subsequently used to maintain temperature below −18 °C for cold storage applications (Lu et al., 2019). In this study, the optimal mass ratio of each ingredient of the SPW (ternary water-salt solution) was determined according to the materials' thermal characteristics in cooling tests and the effects of mass fraction of stabilizer on phase separation reduction were investigated. Furthermore, the effects of nucleating agents on the inhibition of supercooling were studied by adding different nucleating agents with different mass fractions. Moreover, the energy storage performance of the optimized SPW gel composite was tested as phase change cold storage material in insulated box for frozen food storage and transportation. Finally, the layout of the PCM in the insulated box has been optimized to achieve the best insulation effect.

Table 2
SPW with fixed 70 wt% water.

Sample	A1	A2	A3	A4	A5
HCOONa	20%	21%	22%	23%	24%
KCl	10%	9%	8%	7%	6%
H_2O	70%	70%	70%	70%	70%

Table 3
SPW with fixed 22 wt% Sodium formate.

Sample	B1	B2	B3	B4	B5
HCOONa	22%	22%	22%	22%	22%
KCl	13%	12%	10%	8%	6%
H_2O	65%	66%	68%	70%	72%

Table 4
SPW with fixed 12 wt% Potassium chloride.

Sample	C1	C2	C3	C4	C5
HCOONa	20%	21%	22%	23%	24%
KCl	12%	12%	12%	12%	12%
H_2O	68%	67%	66%	65%	64%

2. Test facilities and experimentation

Determined by the Differential Scanning Calorimeter (DSC) in our previous work (Lu et al., 2019), the optimal mass fractions of the SPW eutectic solution for sodium formate, potassium chloride and water were 22%, 8% and 70%, respectively. However, the mass of DSC sample was as small as 15 mg, which might not be suitable to reveal the characteristics of these materials used in practical applications. Therefore, in this study, PCMs in bulk with different percentage of components were placed in a freezer to test their eutectic characteristics in charging processes.

2.1. Samples preparation

In this study, each sample was made following the procedure: distilled water was weighed in a beaker firstly, then, the weighed organic and inorganic salts were poured into the beaker. The liquid was stirred by a magnetic stirrer until the salts were completed dissolved within the distilled water at ambient temperature of 30 °C. All the samples were numbered from 1 to 5 according to the concentrations of the salts. Then, the samples were ready to be used for DSC and experimental tests. The details of ingredients and the measured percentages of SPW are listed in Tables 2–4.

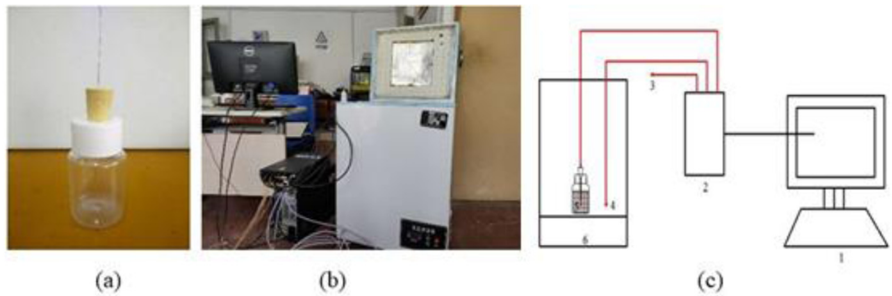

Fig. 1. (a) Photo of the plastic sample vial, (b) Photo of experimental equipment, (c) Schematic diagram of experimental system (1. Computer, 2. Data acquisition board, 3. Ambient temperature, 4. Temperature in freezer, 5. Sample temperature, 6. Freezer).

2.2. DSC measurements

DSC has been calibrated to ensure the accuracy of the measurement (temperature accuracy is ±0.1 °C for standard metal and ±0.6 °C in testing temperature range (−50 °C –30 °C) and calorimetric accuracy is ±2%). The PCM underwent cyclical measurements at temperature increase rate of 5 K/min and cooling rate of 5 K/min, ensuring that the PCM achieves stable and repeatable phase change behavior.

2.3. The cooling curve method and facilities

The cooling curve method was used to obtain the appropriate eutectic mass fraction in the experiments. The mass of sodium formate, potassium chloride and distilled water were weighed according to a preset ratio using a precision balance (accuracy: ±0.1 mg). Firstly, the weighed sodium formate, potassium chloride and water (40 g in total) were sequentially added to a beaker (100 ml) and mixed by a stirring rod. Then, each solution was selected with a weight of 20 g and numbered accordingly. These solutions were filled in plastic sample vials, shown in Fig. 1(a), to test their melting and solidification behaviors in a low temperature test chamber (Fig. 1(b)). The experimental device and layout are shown in Fig. 1(c). The low temperature test chamber was controlled at temperature of −40 °C (±5 °C). Meanwhile, the data was record with an interval of 60 s during the entire solidification–melting process. Calibrated T type thermocouples with an accuracy of ±0.2 °C were used to measure the ambient temperature, freezer temperature, and the temperature of the PCM solution, respectively.

3. Results and discussions

3.1. Eutectic composition

Firstly, the mass fractions had been changed slightly for both salts from the DSC selected SPW (22%/8%/70%) (Lu et al., 2019), which are numbered as A1–A5 in Table 2. Fig. 2(a) shows the temperature variation of these SPW composites in cooling process. Two clear turning points are observed for all tested samples, and the first one indicates the existence of the supercooling phenomenon in the discharging process. The second turning points mean the ingredients in these samples do not show crystallization simultaneously and there is no eutectic temperature for these ternary solutions, the phase transition process is unstable and the solidification temperature fluctuate significantly in the solidification process. Therefore, the appropriate concentration for each component in the SPW needs to be determined further to obtain a eutectic temperature for achieving the eutectic crystallization.

On the basis of the SPW mass ratio of 22%:8%:70% (Lu et al., 2019), the mass percentage of the sodium formate was maintained at 22% then. Fig. 2(b) shows the cooling temperature curves of different SPWs with proportions arranged by adjusting the proportion of Potassium Chloride and Water (shown in Table 3). It can be seen that the solution with SPW mass ratio of 22%:12%:66% shows only one turning point during its charging process, which indicates the existence of the eutectic temperature and the eutectic crystallization.

To further verify this ratio (22%:12%:66%) to obtain an appropriate eutectic concentration of SPW, the mass percentage of Potassium Chloride was maintained at 12% and the mass percentages of Sodium Formate and Water varied for the rest testing scenarios (samples in Table 4). It can be seen from Fig. 2(c) that only one turning point occurs in the phase transition process when the SPW mass fractions are 22%:12%:66% and 23%:12%:65%, respectively. The supercooling degree and the phased change temperature of the SPW with a mass fraction ratio of 22%:12%:66% are lower than that of the solution with ratio 23%:12%:65% for the same ternary components. Based on the above experimental results, it is implied that the appropriate eutectic SPW concentration is 22%:12%:66%.

Fig. 2(d) shows the cooling curve for SPW liquid (22%:12%:66%). The temperature of the curve from the point 1 to the point 2 gradually decreased until reaching the point 2 with supercooling. As there is no phase change, sensible heat release happened during this process. When the material temperature continuously decreased, the nucleus was generated, and then the thin-branched ice crystals were formed and rapidly diffused from the nucleation to the entire solution space. At the stage from the point 2 to the point 3, a portion of latent heat was released to heat up the material promptly until the phase change transition started at a temperature at point 3. In the stage from points 3 to 4, the ice layer formed gradually from the boundary layer to the whole space, in which process the latent heat was released at the phase change temperature and the temperature became stable. At point 4, the SPW liquid became solid completely. After point 4, the solid SPW released sensible heat below the solidifying temperature and the temperature continued to decrease approaching to the point 5, which was approximate to the ambient temperature in the test chamber. The whole process shows that the ternary solution solidified as pure substance and there is no phase separation happened as in other concentrations. According to Fig. 2(d), supercooling degree could be evaluated as over 8 °C, which needed to be reduced.

Fig. 3 shows the DSC results of cooling test-selected SPW with concentration of 22%:12%:66% and DSC-selected SPW (22%:8%:70% Lu et al., 2019), respectively. For the mass ratio of 22%:8%:70%, which shows clear phase separation in Fig. 2(a), the latent heat is 250.3 kJ/kg and the phase transition temperature is −23.8 °C (Lu et al., 2019). Comparatively, for the mass ratio of 22%:12%:66%, the latent heat is improved to 258.5 kJ/kg while the phase transition temperature is slightly changed to −23.6 °C. The figure also shows its melting area is slimmer. The above results

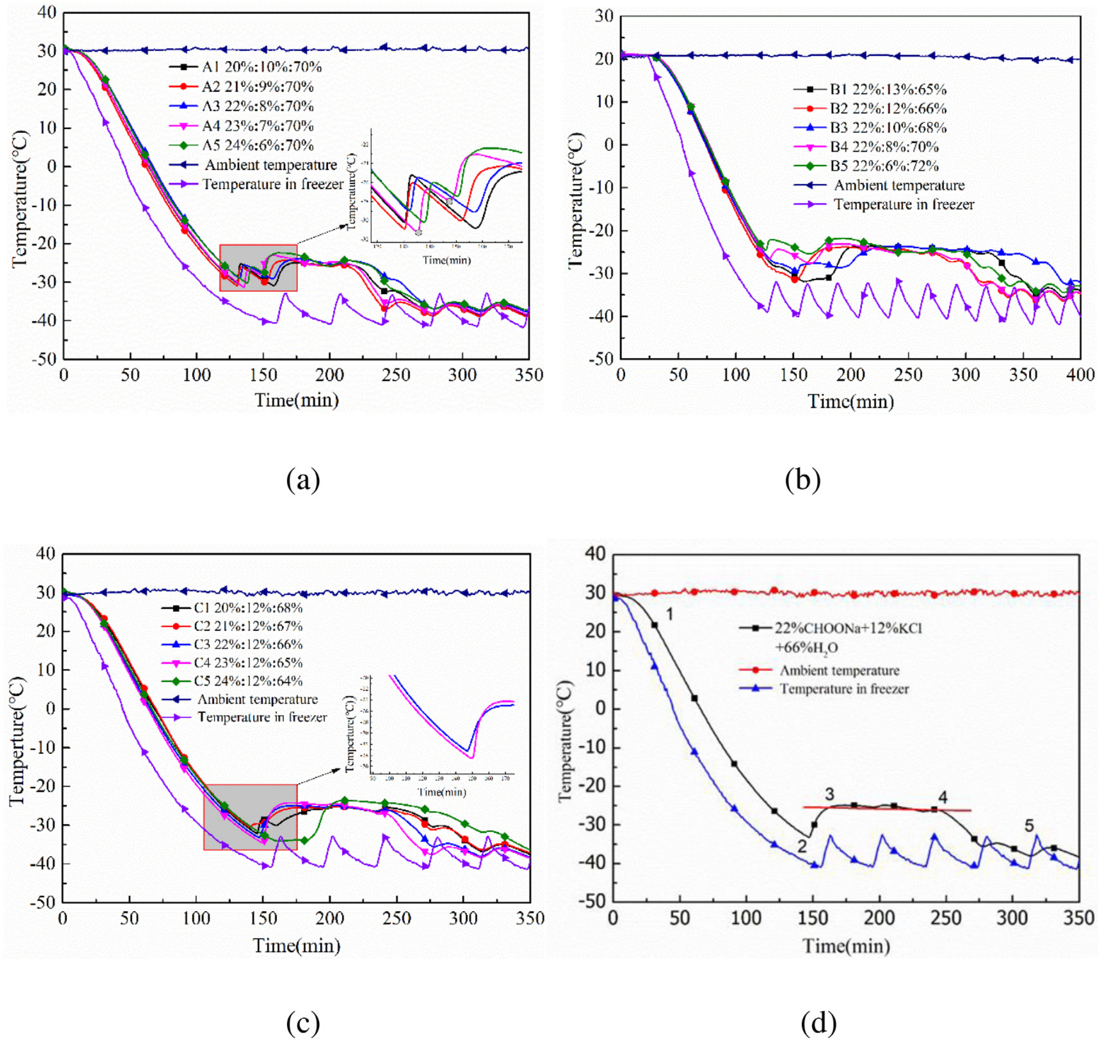

Fig. 2. The cooling curves of different proportions SPWs of (a) group A in Table 2, (b) group B in Table 3, (c) group C in Table 4, (d) C3 sample (22%:12%:66%).

verify applicability of the SPW solution (22%:12%:66%) for cold storage applications.

However, it is noted that the supercooling of the SPW solutions is still high, negating the thermal performance of the PCMs in various occasions. Nonetheless, this can be partly optimized by adding nucleate agent and/or gelling agent in the PCM solution, the effects of which on supercooling and phase separation are to be analyzed in the next subsection.

3.2. Effects of stabilizer on phase separation

To prevent phase separation phenomenon and leaking problems during phase change processes, a gelling agent is added to turn the salt hydrate PCM solution into a gel. Xanthan gum is selected as the gelling agent and added into the SPW liquid. Fig. 4 shows the temperature variation of SPW liquid and gels with different ratios of xanthan gum during the solidification process and their melting process. It can be seen that the phase transition processes of the SPW gels become more stable compared to that without xanthan gum.

Table 5 represents the thermal properties of the SPW liquid and gels, including the latent heat, phase change temperature, supercooling degree. There are no significant changes on phase change temperatures for SPW gels, which are at approximately −23.4 °C. This implies that the influence of adding xanthan gum on the phase change temperature is restricted. From the table,

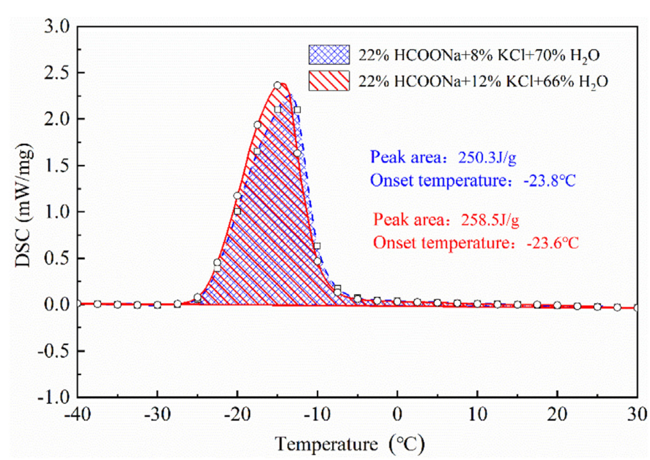

Fig. 3. DSC results of cooling test-selected SPW and DSC-selected SPW (Lu et al., 2019).

it is clear that the supercooling degree is lowered to 6.6 °C when the mass fraction of xanthan gum is 0.6%, which means the gelling agent has effects on reducing supercooling degree to some extent.

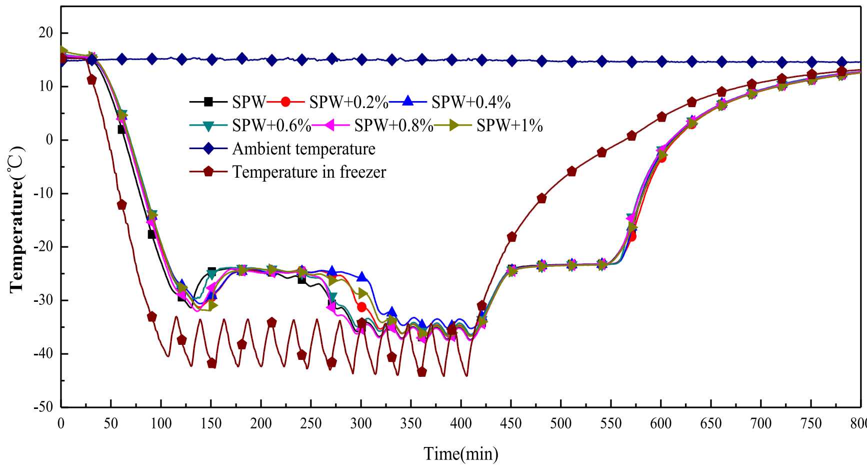

Fig. 4. Temperature variation of SPW composites with different ratios of xanthan gum during solidification process and melting process.

Table 5
Thermal properties of the SPW composites with different mass fraction of xanthan gum.

Serial number	Xanthan gum additive amount (wt%)	Latent heat of fusion (J/g)	The phase change temperature (°C)	Supercooling degree (°C)	Mobility
1	0	258.5	−23.3	8.1	Good
2	0.2	253.4	−23.4	7.8	Good
3	0.4	257.1	−23.3	7.2	Ordinary
4	0.6	257.2	−23.5	6.6	Little
5	0.8	258.1	−23.3	8.7	Little
6	1	253.4	−23.4	8.5	Little

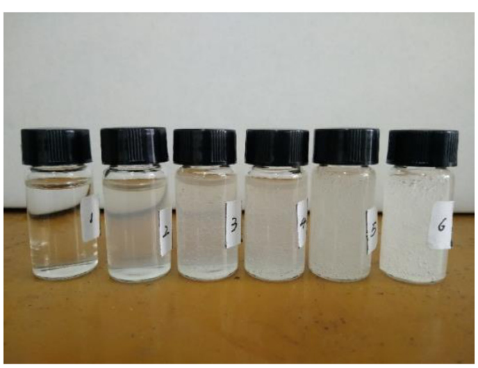

Fig. 5. Gel-type SPW solutions stored in bottles after 7 days.

All SPW liquid and gels with different mass fractions of xanthan gum were stored in bottles and left in the test chamber for over 7 days. The SPW liquid with no addition of xanthan gum was prepared as the benchmark in the experiments. As shown in Fig. 5, a little bit white powder appeared at the bottom of the SPW liquid without the xanthan gel (the left-most one). With the increase of xanthan gum concentration, the PCM changed from a clear liquid to a milky white gel without solid deposition.

To test this newly developed PCM composites, a filter paper is used to analysis flow performance of SPW added with different mass fractions of xanthan gum. In Fig. 6, the results show that the droplets without xanthan gum disappeared completely in 5 min. Comparatively, the SPW with 0.6% concentration of Xanthan gum does not penetrate in 250 min. It is evident that 0.6% xanthan gum is verified as a perfect gelling agent for the SPW liquid to form a gel type SPW.

The DSC tests were performed using the SPW liquids and the SPW gel, respectively. The comparative results are shown in Fig. 7, which shows that the latent heat of fusion and phase transition temperature of the SPW gel are changed very slightly from 258.5 J/g to 257.2 J/g and from −23.6 °C to −23.8 °C, respectively. Therefore, the addition of gelling agent brings nearly no change. In summary, the gelling agent is beneficial to suppress phase separation and leakage of the ternary solution without loss of cold storage ability and change of phase change temperature. However, although the gelling agent has effects on reducing supercooling degree to some extent, but the supercooling degree is still too high for applications. Therefore, it needs to be reduced further by using nucleating agents.

3.3. Effects of different nucleating agents on supercooling inhibition

By adding different types and mass fractions of nucleating agents, the nucleating agent's effects on the thermal performance of PCMs were specifically examined. Table 6 shows the additive of nucleating agents with different mass fractions investigated in this work. The effects of these nucleating agents with different mass fractions are different. Table 7 shows the optimum samples for different agents that have the lowest supercooling degree for each nucleating agent. It is found that nano materials as nucleating agents are superior to other nucleating agents for supercooling inhibition. The supercooling degree of SPW composites with 0.6 wt% of nano-Al_2O_3 and 0.6 wt% of nano-TiO_2 are reduced to 4.5 °C and 2.6 °C, respectively, which is 44.4% and 67.9% lower than that of SPW liquid without nucleating agent. The amount of nucleating agent addition should be within an appropriate range, in which case the nucleation agent meets the nucleation surface area required by the heterogeneous nucleation. However, the sample with the lowest supercooling degree is not the sample with the most mass fraction of nucleating agent.

Fig. 8 shows the temperature variation curve of the SPW composites with different mass fractions of nano-TiO_2. There are apparent latent heat release periods and latent heat absorption periods for all 8 samples (listed in Table 8). With the increase of the nano-TiO_2 mass fraction, the supercooling degree of the SPW composites decreases firstly and increases subsequently, showing an optimal concentration of the agent for the restraint of the

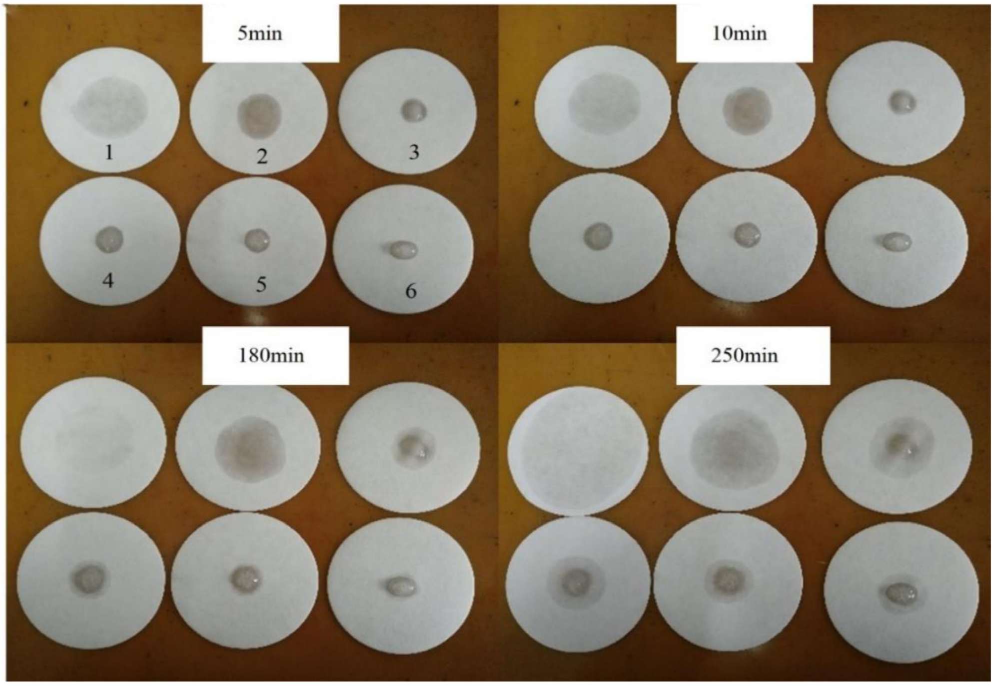

Fig. 6. Flow performance of SPW added with different mass fractions of xanthan gum.

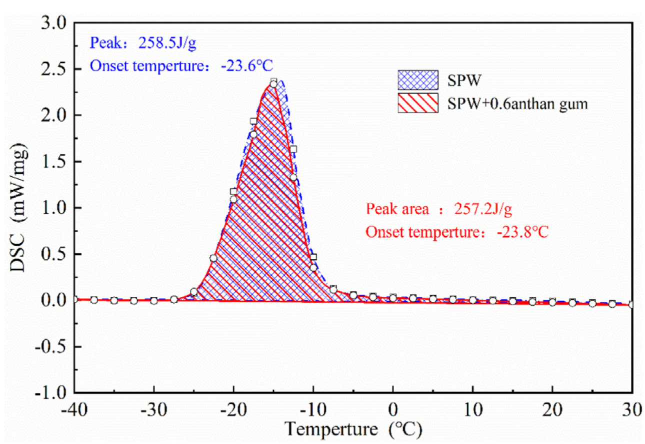

Fig. 7. Comparison of DSC tests for SPW fluid and SPW gel.

Table 6
Commonly used nucleating agents and their mass fractions.

Nucleating agents	Mass fraction (wt%)
$Na_2B_4O_7{\cdot}10H_2O$	0.2, 0.4, 0.6, 0.8, 1, 1.5, 2
SiO_2	0.2, 0.5, 1, 1.5, 2, 3
Nano Al_2O_3	0.08, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.5
Nano TiO_2	0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, 1

Table 7
Thermal properties of the SPW composites with different nucleating agents.

Nucleating agent	Mass fraction (wt%)	The phase change temperature (°C)	Supercooling degree (°C)
$Na_2B_4O_7{\cdot}10H_2O$	0.4	−23.7	6.3
SiO_2	3	−23.1	6.4
Nano Al_2O_3	0.6	−23.5	4.5
Nano TiO_2	0.6	−23.1	2.6

supercooling. Specifically, with 0.6wt% of TiO_2, the supercooling degree is the smallest (2.6 °C), which is 67.9% lower than that of the SPW liquid. But with the increase of the TiO_2 mass fraction, supercooling phenomenon becomes more severe. For example, when the mass fraction is 1%, supercooling degree is as high as 5.4 °C. It is explained that the content of nano-TiO_2 is difficult to be dispersed uniformly due to its large size, resulting in the precipitation group and the reduction of the nucleation effect.

Table 8
Thermal properties of the SPW composites with different mass fraction of TiO_2.

Nano TiO_2 additive amount (wt%)	The phase change temperature (°C)	Supercooling degree (°C)
0.06	−23.0	6.3
0.08	−23.1	6.1
0.1	−23.3	6.3
0.2	−23.1	5.3
0.4	−23.1	3
0.6	−23.1	2.6
0.8	−23.2	5.1
1	−22.9	5.4

3.4. Stability analysis of SPW composite after life cycles

Fig. 9 shows the temperature variations of the newly developed SPW gel with 0.6wt% of nano TiO_2 in the first and the fiftieth cycle tests. The temperature curve for the solidification process of the PCM after 50 solidification–melting cycles is similar to that of the PCM in the test of the first cycle, which indicates that the phase separation does not occur. Table 9 represents the thermal properties of the SPW composite before and after the life cycle test. It is shown that the phase change temperature is approximately constant, but the supercooling increases by 0.6 °C. The above experimental results imply the PCM composite with an addition of 0.6wt% of nano TiO_2 has reasonable stable thermal performance.

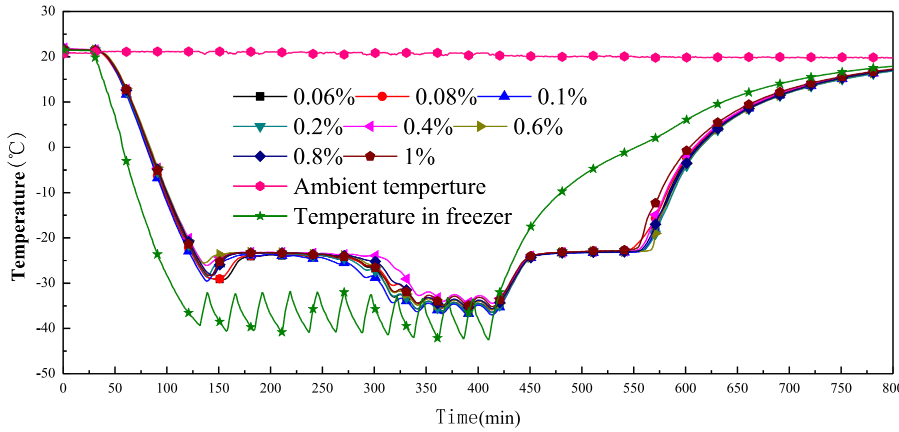

Fig. 8. Temperature variation of SPW gel added with different ratios of TiO_2 during solidification process and melting process.

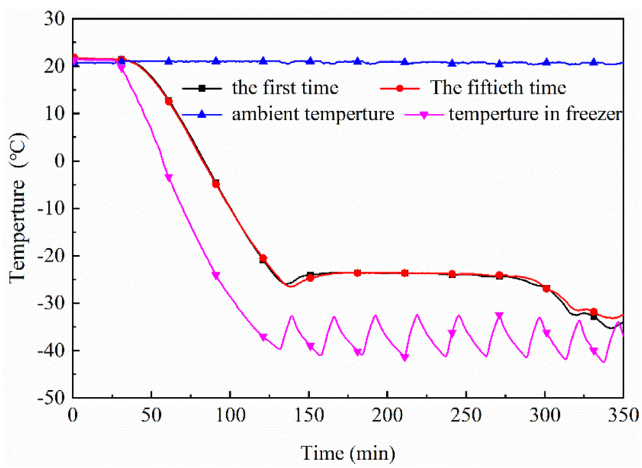

Fig. 9. Cooling curves of SPW composite before and after life cycles.

Table 9
Thermal properties of SPW in the 50 solidification-melting cycles.

Number of the cycle	The phase change temperature (°C)	Supercooling degree (°C)
1	−23.4	2.6
50	−23.3	3.2

4. Frozen storage investigation with developed PCMs

4.1. Design of the cold storage boxes filled with PCMs

Temperature is a crucial criterion for securing food quality during the storage and transportation processes. The self-developed SPW composite can be used to maintain a low temperature for frozen food. Experiments were carried out to investigate its thermal performance in a real cold storage application. Two insulated storage boxes were made, where one included SPW composite inside and the other is an enclosure of space without PCMs. T-type thermocouples were attached to the bottom, middle and top inner surfaces of the boxes, interior and surface of food store in the boxes, respectively. The designed insulated box can be seen in Fig. 10.

836 g of aforementioned SPW composite was prepared and packed into 6 bags equally, and then fully charged. An initial calculation indicated that it might take 8 h for the prepared SPW-PCM to be fully discharged with ambient temperature of 20.0 °C. The frozen food and 6 charged PCM bags were placed into a prepared insulated box. While for the other case, the frozen food was put into a similar box without PCM. The temperature variations inside the boxes, the food and room were recorded.

4.2. The temperature field in the insulated box

Fig. 11 shows the temperature variations in the insulated box without PCM. The frozen food absorbed heat transferred from the ambient air surround the box and then melted after 2 h when its temperature is higher than 0 °C. Fig. 12 shows the temperature variations at different positions in the insulated box with SPW composite as PCM. The temperatures at the inner surfaces of the bottom and top PCM layers were maintained below −18 °C for 11.2 h and 7.7 h, respectively. As a result, the temperature of the food in the insulated box with PCM was maintained below −18 °C for approximately 8 h. Therefore, the PCM has the effect of keeping food at a low temperature and can meet daily needs. However, the PCM bag at the top wall of the box melts faster and the temperature rises faster comparatively, while the bottom one has a lower temperature that is maintained for a longer period. The air flow due to natural convection inside the box makes the top PCM layer melting faster. In addition, the self-made phase change box has the problem of heat leakage due to insufficient sealing. This leads to stronger natural convection in the box, which further promotes the PCM in the top layer to be melted. As the melting process progresses, the top surface starts to absorb sensible heat, and the temperature difference between the top layer and the bottom layer is large. After the PCM in the bottom layer has been completely melted, only sensible heat transportation happens and the temperature difference decreases. It also can be seen that the thermal stratification is more severe at the end of the phase transition period. It is found that the temperature in the food has a temperature difference of around 2 °C or more to the top and bottom layers of the box, respectively.

From Fig. 12, it is clear that the food was maintained below −18 °C for approximately 8 h but the PCM in the bottom layer were melted completely 3 h later. This means that the initially planned arrangement (evenly distributed) may not be suitable for the insulation box. A different PCM loading arrangement used the same amount of PCM may improve the performance of the cold storage box.

4.3. Cold storage box optimization

Two representative schemes are proposed to improve the inhomogeneity of the temperature in the insulated box. Option

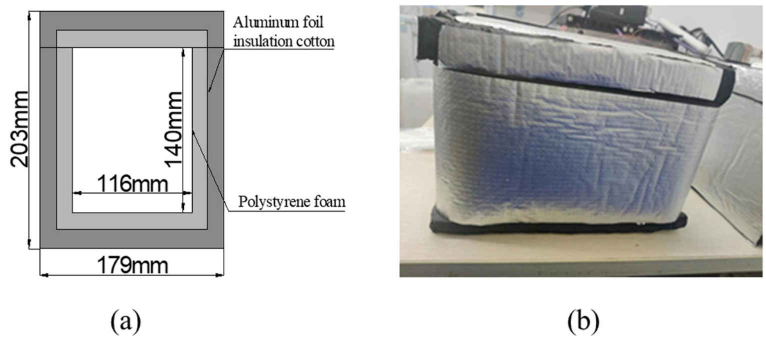

Fig. 10. (a) The cross section of box, (b) Photograph of the insulated box.

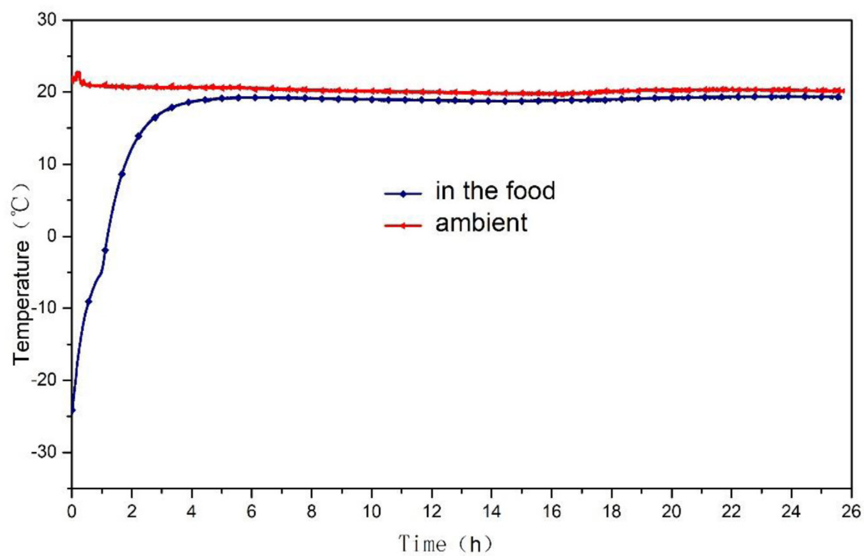

Fig. 11. Temperature varied with time for insulated box without PCM.

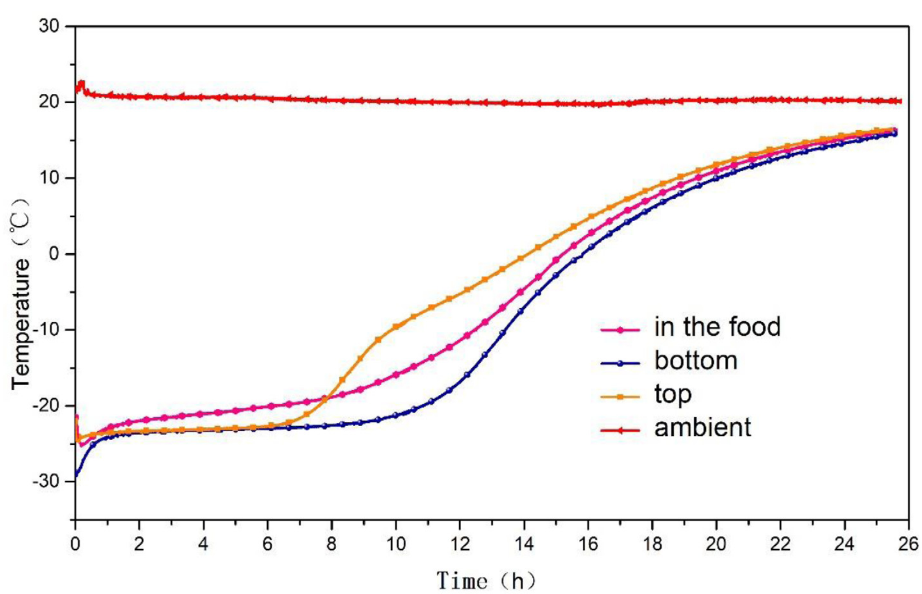

Fig. 12. Temperature varied with time for insulated box with PCM.

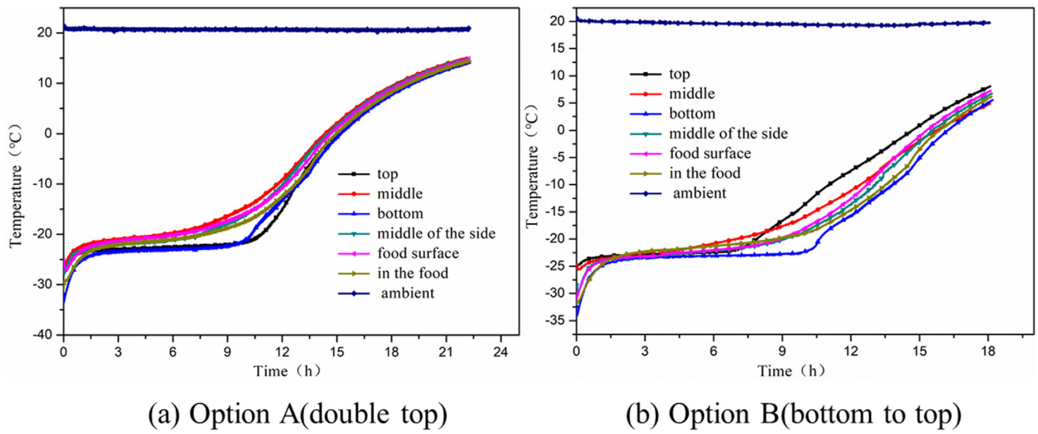

Fig. 13. Temperature distribution of each program.

A is to double the mass of the top PCM bag and reduce the mass of other 5 bags by 1/5 and Option B is to have 1/4 more for the top PCM layer and 1/4 less at the bottom PCM layer. The temperature variations of the cold storage boxes under these scenarios are shown in Fig. 13.

From the results shown in Fig. 13(a), it can be seen that the temperature of the top layer shows the same trend as that of the temperature of the bottom layer in Option A. Specifically, the top layer temperature can be maintained below −18 °C for 11.4 h, which is 3.7 h longer than that for initial evenly PCM distribution box shown in Fig. 12. The bottom layer temperature can be maintained below −18 °C for 10.7 h, which is 0.2 h less than the uniform distribution design. It is noted that the temperature of the middle layer is relatively uniform but higher than the temperatures at the top and bottom layers as there was less PCM loading in the middle walls to conquer the heat loss. It can be seen from Fig. 13(b) that the temperature durations below −18 °C for the top and bottom layers of the insulated box in Option B are 8.6 h and 11.1 h, which are shorter compared to those in Option A. It is found that the temperature difference is maintained within 2 °C for the first 8 h. It is examined that the temperature difference between two adjacent layers in Option B is around 1 °C, which reduces the temperature stratification. However, it increases after 8 h when the PCM in the top layer is fully melted in arrangement of the Option B, which means that it may be better to have more PCM in the top layer.

Table 10 summarizes the thermal insulation time for the top and bottom surfaces of the cold storage boxes, the cold preservation time of the food, and the maximum temperature difference in the phase change period. From this table, it can be concluded that the temperature distribution in the box with evenly distributed PCM is the most uneven case, which also has the shortest insulation time (8.4 h). Option A has a more uniform temperature distribution in the box and longer food insulation time (9.7 h). In this Option, the top and bottom surface insulation time is the closest. In option B, the natural convection temperature difference is slightly larger at the end of phase change process, but the Option B has smallest temperature difference inside the box during phase transition and the best food preservation performance. The cold preservation time of food in Option B is 10.6 h, which is 26% longer than that of the insulated box with evenly distributed PCM while its mass was unchanged. Therefore, Option B is the best arrangement.

5. Conclusions

In this work, eutectic ternary SPW composite was developed experimentally as PCM for cold storage applications. The optimized material (22% sodium formate, 12% potassium chloride and 66% water) showed the best eutectic performance and a proper phase change temperature (−23.6 °C) for frozen food storage and cold storage applications. Based on the optimal SPW solution, the effects of various additives on the thermal performance including the solidification and melting processes and supercooling were comparatively examined. 0.6wt% xanthan gum and 0.6wt% nano-TiO_2 were found to be the ideal candidates for minimizing the supercooling, phase separation and leakage and improving the thermal stability of PCMs in solidification and melting processes.

The self-developed PCM can be successfully applied in the storage and transportation of frozen food. This has been proven via comparative experiments of insulated boxes with or without PCMs. In addition, it was found that different layout of PCM materials can also have significant influence on the performance of cold storage devices. When 1/4 part of PCM at the bottom of the insulated box was moved to the top side, the temperature field in the insulated box turn into more uniform distribution, in which case the cold preservation time of food can be prolonged by 26% compared to that of the unoptimized insulated box with the same amount of PCM.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Engineering and Physical Sciences Research Council, UK [grant number EP/S030786/1]. This work was also supported by National Natural Science Foundation of China [No. 51976126 and No. 51406121].

Table 10
Temperature analysis of insulation boxes with different PCM arrangement.

PCM layout	Thermal insulation time on the top surface (<−18 °C)/(h)	Insulation time of the bottom surface (<−18 °C)/(h)	Cold preservation time of food (<−18 °C)/(h)	Maximum Temperature difference during phase transition/(°C)
Evenly distributed	7.7	11.2	8.4	3.8
Option A	11.4	10.7	9.7	3.3
Option B	8.6	11.1	10.6	1.7

References

Chen, W., Zhang, X., Huang, Y., Ren, Y., Ding, J., 2017. Sodium formate as low temperature phase change material in cold storage insulation box. J. Refrig. 38 (1), 68–72. http://dx.doi.org/10.3969/j.issn.0253-4339.2017.01.068.

Du, K., Calautit, J., Wang, Z., Wu, Y., Liu, H., 2018. A review of the applications of phase change materials in cooling, heating and power generation in different temperature ranges. Appl. Energy 220, 242–273. http://dx.doi.org/10.1016/j.apenergy.2018.03.005.

Eanest Jebasingh, B., Valan Arasu, A., 2020. A comprehensive review on latent heat and thermal conductivity of nanoparticle dispersed phase change material for low-temperature applications. Energy Storage Mater. 24, 52–74. http://dx.doi.org/10.1016/j.ensm.2019.07.031.

Fang, G., Zhang, W., Yu, M., Meng, K., Tan, X., 2022. Experimental investigation of high performance composite phase change materials based on sodium acetate trihydrate for solar thermal energy storage. Sol. Energy Mater. Sol. Cells 234, 111418. http://dx.doi.org/10.1016/j.solmat.2021.111418.

Fu, W., Zou, T., Liang, X., Wang, S., Gao, X., Zhang, Z., Fang, Y., 2019. Preparation and properties of phase change temperature-tuned composite phase change material based on sodium acetate trihydrate–urea/fumed silica for radiant floor heating system. Appl. Therm. Eng. 162, http://dx.doi.org/10.1016/j.applthermaleng.2019.114253.

Hu, P., Lu, D.-J., Fan, X.-Y., Zhou, X., Chen, Z.-S., 2011. Phase change performance of sodium acetate trihydrate with AlN nanoparticles and CMC. Sol. Energy Mater. Sol. Cells 95, 2645–2649. http://dx.doi.org/10.1016/j.solmat.2011.05.025.

Ji, C., Qin, Z., Dubey, S., Choo, F., Duan, F., 2017. Three-dimensional transient numerical study on latent heat thermal storage for waste heat recovery from a low temperature gas flow. Appl. Energy 205, 1–12. http://dx.doi.org/10.1016/j.apenergy.2017.07.101.

Jia, P., Wu, W., Wang, Y., Zhang, B., 2019. Preparation and thermophysical property optimization of a new composite phase change material for cold storage. CIESC J. 70 (7), 2758–2765.

Jin, Y., Wu, W., Fu, S., Jia, P., 2021. Research on optimization and application of phase change materials for low temperature cold chain logistics. J. Refrig. 1–8, http://kns.cnki.net/kcms/detail/11.2182.TB.20210914.1642.006.html.

Li, G., Hwang, Y., Radermacher, R., Chun, H., 2013. Review of cold storage materials for subzeroapplications. Energy 51, 1–17. http://dx.doi.org/10.1016/j.energy.2012.12.002.

Lu, W., Liu, Z., Flor, J.-F., Wu, Y., Yang, M., 2018. Investigation on designed fins-enhanced phase change materials system for thermal management of a novel building integrated concentrating PV. Appl. Energy 696–709. http://dx.doi.org/10.1016/j.apenergy.2018.05.030.

Lu, W., Liu, G., Xing, X., Wang, H., 2019. Investigation on ternary salt-water solutions as phase change materials for cold storage. Energy Procedia 158, 5020–5025. http://dx.doi.org/10.1016/j.egypro.2019.01.662.

Lu, W., Liu, G., Xiong, Z., Wu, Z., Zhang, G., 2020. An experimental investigation of composite phase change materials of ternary nitrate and expanded graphite for medium-temperature thermal energy storage. Sol. Energy 195, 573–580. http://dx.doi.org/10.1016/j.solener.2019.11.102.

Lu, W., Tassou, S.A., 2013. Characterization and experimental investigation of phase change materials for chilled food refrigerated cabinet applications. Appl. Energy 112, 1376–1382. http://dx.doi.org/10.1016/j.apenergy.2013.01.071.

Mehling, H., Cabeza, L., 2008. In: Mewes, D., Mayinger, F. (Eds.), Heat And Cold Storage With PCM. New York.

Oró, E., Barreneche, C., Farid, M., Cabeza, L., 2013. Experimental study on the selection of phase change materials for low temperature applications. Renew. Energy 57, 130–136. http://dx.doi.org/10.1016/j.renene.2013.01.043.

Oró, E., de Gracia, A., Castell, A., Farid, M., Cabeza, L., 2012. Review on phase change materials (PCMs) for cold thermal energy storage applications. Appl. Energy 99, 513–533. http://dx.doi.org/10.1016/j.apenergy.2012.03.058.

Pirvaram, A., Sadrameli, S., Abdolmaleki, L., 2019. Energy management of a household refrigerator using eutectic environmental friendly PCMs in a cascaded condition. Energy 181, 321–330. http://dx.doi.org/10.1016/j.energy.2019.05.129.

Prieto, C., Cabeza, L., 2019. Thermal energy storage (TES) with phase change materials (PCM) in solar power plants (CSP). Concept and plant performance. Appl. Energy 245, http://dx.doi.org/10.1016/j.apenergy.2019.113646.

Qin, Y., Wang, Z., Zhang, H., Dou, B., Zhang, G., Wu, W., 2020. The effect of phase change material balls on the thermal characteristics in hot water tanks: CFD research. Appl. Therm. Eng. 178, 115557. http://dx.doi.org/10.1016/j.applthermaleng.2020.115557.

Seddegh, S., Wang, X., Henderson, A., Xing, Z., 2015. Solar domestic hot water systems using latent heat energy storage medium: A review. Renew. Sustain. Energy Rev. 49, 517–533. http://dx.doi.org/10.1016/j.rser.2015.04.147.

Sharma, A., Chauhan, R., Kallioglu, M., Chinnasamy, V., Singh, T., 2020. A review of phase change materials (PCMs) for thermal storage in solar air heating systems. Mater. Today: Proc. http://dx.doi.org/10.1016/j.matpr.2020.10.560.

Sharma, A., Tyagi, V., Chen, C., Buddh, D., 2009. Review on thermal energy storage with phase change materials and applications. Renew. Sustain. Energy Rev. 13 (2), 318–345. http://dx.doi.org/10.1016/j.rser.2007.10.005.

Wang, H., Lu, W., Wu, Z., Zhang, G., 2020. Parametric analysis of applying PCM wallboards for energy saving in high-rise lightweight buildings in Shanghai. Renew. Energy 145, 52–64. http://dx.doi.org/10.1016/j.renene.2019.05.124.

Wang, T., Zhou, X., Liu, Z., Wang, J., Zhang, Y., Pan, W., 2021. Preparation of energy storage materials working at 20–25 °C as a cold source for long-term stable operation. Appl. Therm. Eng. 183, http://dx.doi.org/10.1016/j.applthermaleng.2020.116220.

Yang, T., Sun, Q., Ronald, W., Cheng, L., 2018. Review of phase change materials for Cold Thermal Energy Storage. J. Eng. Thermophys. 39 (3), 567–573.

Zalba, B., Marin, J., Cabeza, L., Mehling, H., 2003. Review on thermal energy storage with phase change materials, heat transfer analysis and applications. Appl. Therm. Eng. 23, 251–283. http://dx.doi.org/10.1016/S1359-4311(02)00192-8.