

Article

Form-Stable Phase Change Material Integrated with PVA/CMC-Na Hydrogel for 5 °C Cold Chain Logistics

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Abstract

The rapid development of cold chain logistics has generated a strong demand for high-performance phase change materials (PCMs). In this study, a composite PCM (CPCM) applicable to 5 °C cold chain logistics, integrated with PVA/CMC-Na hydrogel to maintain form stability, is developed. N-Tetradecane and water are employed as the primary cold storage media in the composite. Span 80, Tween 80 and borax are introduced into the composite as homogenizing agents and supercooling depressant, respectively. The main preparation steps of the CPCM include aqueous phase preparation, emulsifier compounding, oil-phase preparation, blending, homogenization, and molding, in sequence. Experimental results demonstrate that the CPCM exhibits a phase transition temperature of 0–5 °C, a latent heat of 236.2 J/g, a supercooling degree of no more than 0.5 °C, and a volume expansion ratio of 3%. Therefore, the CPCM is able to satisfy the cold storage demand for cold chain transportation with a target temperature of approximately 5 °C, and can serve as a superior-performance alternative to the PCMs currently used for similar applications in the market.

Keywords: phase change material; water; n-tetradecane; form-stable; cold storage

1. Introduction

Phase change materials (PCMs) have garnered significant interest for thermal energy storage (TES) across various sectors, including cold chain logistics and building climate control [1,2]. For the cold chain, temperature control is crucial for preserving the quality and safety of perishable goods like food and pharmaceuticals [3,4], and sustaining a low-temperature environment between 0 °C and 10 °C is often essential for most fresh foods like fruits and vegetables [5,6]. PCM-based TES systems offer a promising solution for stabilizing temperatures in refrigerated compartments and transport vehicles, reducing energy consumption, and preventing temperature fluctuations [7,8].

PCMs suitable for the 0–10 °C range are broadly categorized into organic and inorganic types. Organic PCMs, such as paraffin waxes, are widely used due to their favorable properties like chemical stability, negligible supercooling, and good compatibility with container materials [9,10]. However, they suffer from disadvantages like low thermal conductivity (typically below 0.3 W/(m·K)) and significant volume changes during phase transition [11–13].



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Inorganic PCMs, including salt hydrates, eutectic solutions and water, generally possess higher latent heat and thermal conductivity compared to organics [14,15]. Nevertheless, inorganic PCMs often face challenges such as phase segregation, supercooling, and corrosion potential towards metallic containers [16,17]. Meanwhile, the phase change temperature of a single water/ice system is mainly concentrated at 0 °C. Therefore, in scenarios such as refrigerated transportation at 2–8 °C, its temperature-buffering range is relatively limited. In addition, problems such as flow, leakage, and volume variation may occur during the melting process. N-Tetradecane, as a typical organic phase change material, exhibits good chemical stability and a phase change temperature close to the refrigerated temperature-control range, thereby providing additional latent-heat buffering against temperature fluctuations in cold chain packaging. Therefore, compounding water with n-Tetradecane is expected to enable construction of a cold storage material system with high latent heat, good compatibility with the target temperature range, and thermal-buffering capability over a broader temperature range.

In the present study, a novel composite phase change material (CPCM) was developed for cold chain transportation and temperature-controlled packaging at 2–8 °C. Compared with conventional cold storage materials, the proposed CPCM improves stability, heat retention capacity and leakage resistance during freeze-thaw cycling, thereby enhancing its suitability for container-level cold storage units, such as insulated refrigerated boxes, cold storage plates, and modular cold storage components. Water and n-Tetradecane were selected as the primary phase change components, while the PVA/CMC-Na hydrogel was employed as the thickener. Span 80 and Tween 80 were introduced as emulsifying stabilizers to improve the dispersion stability of the composite system, and borax was incorporated as a nucleating agent to reduce the degree of supercooling. Thermophysical properties of the CPCM were tested, and an experimental study on application of the CPCM in a Cold Storage Container was conducted.

2. Materials and Methods

2.1. Materials

The raw materials used in this study include: n-Tetradecane (purity: 98%), polyvinyl alcohol (PVA, purity $\geq$ 98%), sodium carboxymethylcellulose (CMC-Na, purity $\geq$ 92%), anhydrous borax (purity $\geq$ 99.5%), and Span 80 (purity $\geq$ 98%) purchased from Tianjin Zhonglian Chemical Reagent Co., Ltd. (Tianjin, China); Tween 80 (purity $\geq$ 98%) obtained from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China); and deionized water complying with the National standard GB/T 6682-2008 (Water for analytical laboratory use—Specification and test methods, China, 2008) [18]. N-Tetradecane and water are adopted as the primary cold storage media in the CPCM, integrated with PVA/CMC-Na hydrogel to maintain form stability. Borax serves as supercooling depressant, while Span 80 and Tween 80 are introduced into the composite as homogenizing agents.

2.2. Preparation Steps

The preparation of the CPCM was carried out according to the following steps (all preparation procedures were independently repeated three times, and stirring was performed using a 10 mm $\times$ 70 mm high-temperature-resistant magnetic stir bar):

- (1) Weighing of components: The raw materials were precisely weighed according to the designated mass fractions (totaling 100.0 g): 55.0 g of deionized water, 39.0 g of n-Tetradecane, 1.5 g of Span 80, 1.5 g of Tween 80, 1.5 g of CMC-Na, 1.0 g of PVA, and 0.5 g of borax.
- (2) Preparation of the aqueous solution: Deionized water, CMC-Na, PVA, and borax were added into a 500 mL beaker. The mixture was placed in a 50 °C water bath and

stirred at 400 r/min for 20 min until the solutes were completely dissolved, forming a homogeneous aqueous phase.

- (3) Preparation of the compound emulsifier: Span 80 and Tween 80 were mixed in another 500 mL beaker.
- (4) Preparation of the oil solution: N-Tetradecane was added into the composite emulsifier to form the oil solution mixture. The mixture was heated in a 60 °C water bath and stirred for 20 min at 800 r/min to ensure the complete dissolution of the emulsifier.
- (5) Emulsification: The aqueous solution was stirred at 800 r/min, with the oil solution slowly dripped into it. The mixture was continuously stirred for 1.5 h to yield a stable, milky-white emulsion.
- (6) Homogenization: The obtained emulsion was processed by a high-pressure homogenizer twice at a pressure of 20 MPa.
- (7) Molding and solidification: The homogenized emulsion was poured into a sealed mold, which was then cooled in an environment at a constant temperature of 10 °C for 1 h, followed by a solidification period of 24 h in a 5 °C environment.

The final prepared CPCM is shown in Figure 1, and the detailed preparation process of the CPCM is illustrated in Figure 2.



Figure 1. The materials and CPCM.

2.3. The Ratio of the Relevant Components in the Material

To achieve the required phase transition temperature, the ratio of water to n-Tetradecane was adjusted. Calculations showed that a ratio of 11:9 between water and n-Tetradecane yielded the desired phase transition temperature. The emulsifier enables n-Tetradecane and water to form a uniform emulsion state. The emulsion stability of n-Tetradecane and water depends on the hydrophile-lipophile balance (HLB) value of the emulsifier. When the HLB value is approximately 10–12, n-Tetradecane and water can generate an oil-in-water (O/W) emulsion. In this study, Span 80 (HLB = 4.3) and Tween

80 (HLB = 15) were selected to form a compound emulsifier [19]. The HLB value of the compound emulsifier is calculated using the following equation [17]:

$$HLB = \frac{\omega_{Span} \times 4.3 + \omega_{Tween} \times 15}{\omega_{Span} + \omega_{Tween}} \quad (1)$$

where ω_{span} (g) is the mass of Span 80, and ω_{Tween} (g) is the mass of Tween 80.

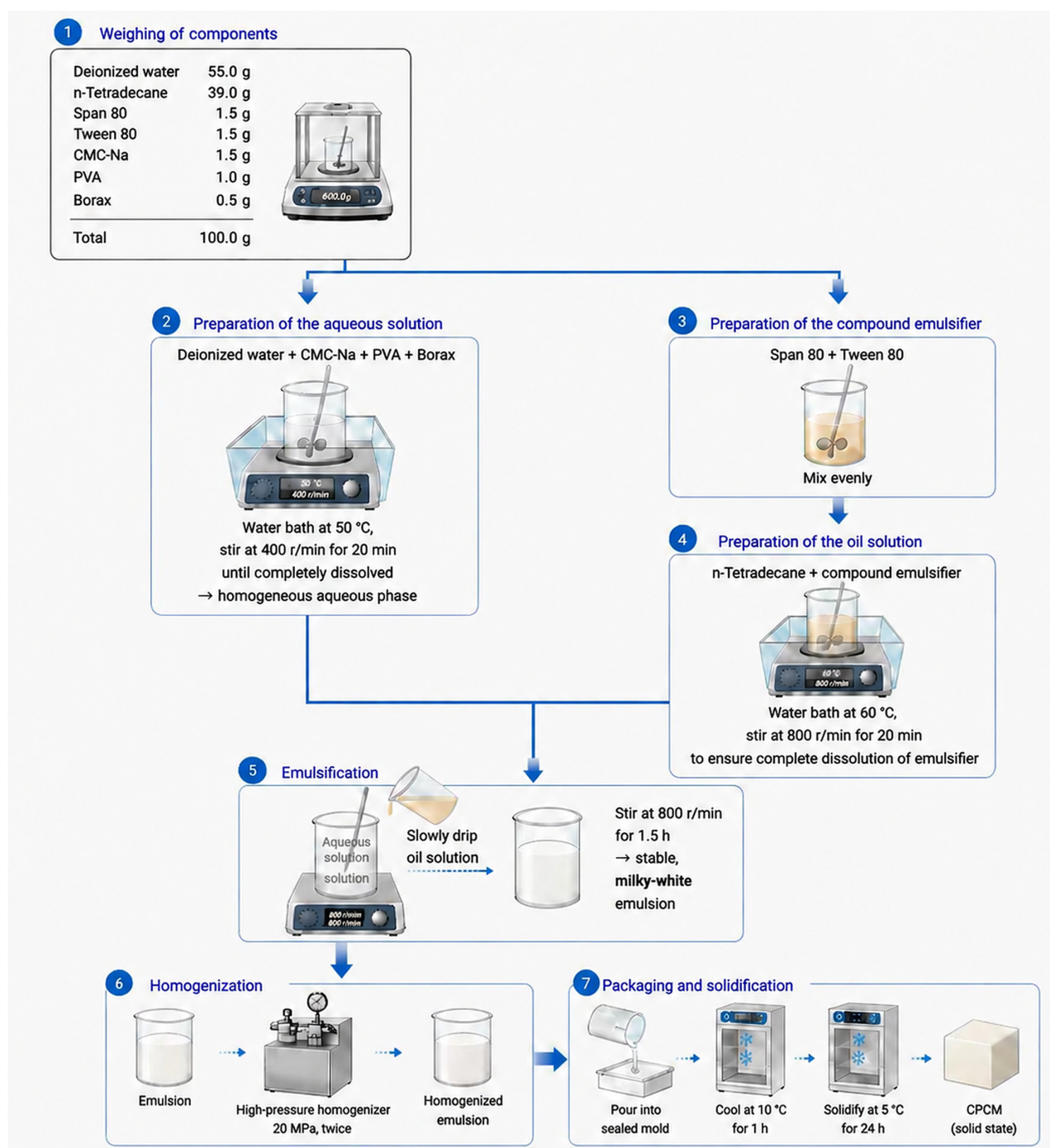


Figure 2. The preparation process of the CPCM.

When the mass ratio of Span 80 to Tween 80 is 1:1, the HLB value of the compound emulsifier is 10.5, which is suitable for the emulsion of n-Tetradecane and water. The initial mass ratio of the compound emulsifier (Span 80 and Tween 80) was 1%, and the proportion

was gradually increased. When the ratio reached 3%, no significant emulsion stratification was observed. In order to balance the emulsification performance and cost, the compound emulsifier ratio was finally determined to be 3% of the CPCM.

CMC-Na and PVA were employed as thickeners [20]. The relationship between the relative viscosity η_r and the continuous phase concentration ratio λ of the aqueous solutions can be described by the Huggins equation [21,22]:

$$\eta_r = 1 + \left[\frac{5\lambda + 2}{2(\lambda + 1)} \right] \phi \quad (2)$$

where the relative viscosity η_r is the ratio of the apparent compound emulsion viscosity η (Pa·s) to the continuous phase viscosity η_c (Pa·s):

$$\eta_r = \eta / \eta_c \quad (3)$$

ϕ is the volume fraction of the oil solution, and λ is the ratio of the dispersed oil-phase viscosity η_d (Pa·s) and the continuous phase viscosity η_c (Pa·s).

$$\lambda = \eta_d / \eta_c \quad (4)$$

To suppress the oil-water separation of the emulsion during the phase change process, the CPCM viscosity is typically required to be maintained within the range of 100–500 Pa·s. The initial mass ratio of CMC-Na and PVA in total was 1%, and the proportion was gradually increased. When the ratio reached 2.5%, the material presented as a uniform gel state. In order to balance the gel performance and cost, the CMC-Na and PVA in total accounted for 2.5% of the proposed CPCM. To avoid relying solely on theoretical equations for inference, the emulsion formation and oil leakage behavior were statistically evaluated at different CMC-Na/PVA ratios while maintaining the total mass fraction of CMC-Na and PVA at 2.5%. The detailed results are presented in Table 1.

Table 1. Statistical summary of CMC-Na/PVA systems with different mass ratios.

CMC-Na/PVA Ratio	Macroeconomic Outlook	Oil Leakage Rate %
9:1	High-viscosity emulsion	5
8:2	High-viscosity emulsion	3
7:3	High-viscosity emulsion	3
6:4	High-viscosity emulsion	1
5:5	High-viscosity emulsion	2
4:6	High-viscosity emulsion	4
3:7	High-viscosity emulsion	5
2:8	High-viscosity emulsion	5
1:9	High-viscosity emulsion	6

Therefore, the mass fractions of CMC-Na and PVA were set to 1.5% and 1%, respectively.

Furthermore, borax was utilized as a nucleating agent to reduce the supercooling degree of the aqueous solution. When the mass fraction of borax was in the range of 0.1–1%, the supercooling degree of the CPCM decreased with the increasing mass ratio of borax, and when the borax mass ratio exceeded 0.7%, the supercooling degree remained unchanged, as shown in Figure 3. However, when the borax mass fraction exceeded 0.5%, the CPCM exhibited significant stratification. Therefore, a borax dosage of 0.5% was determined for the final formulation.

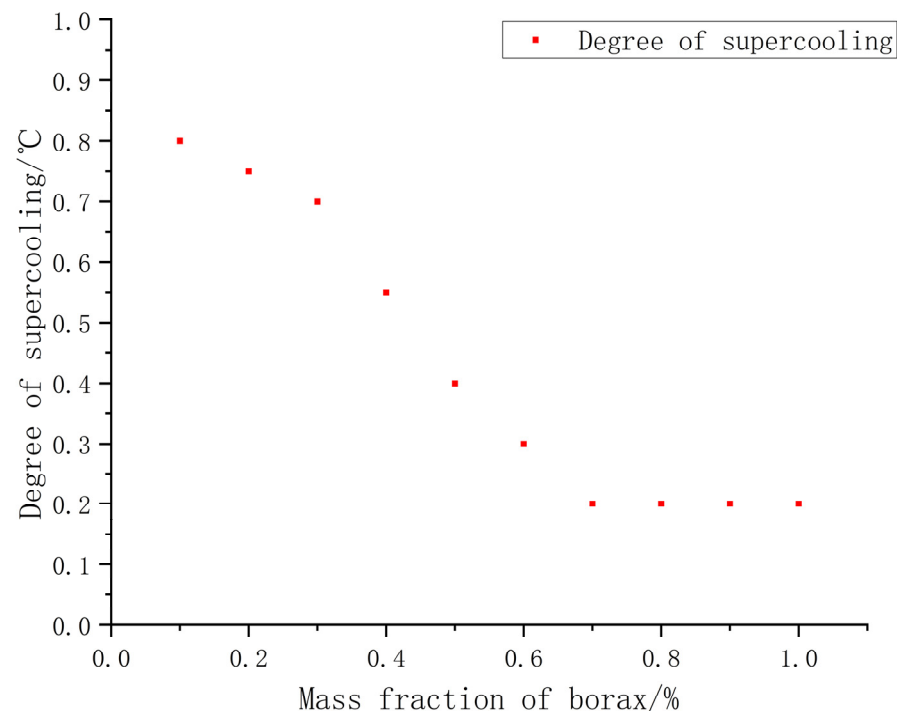


Figure 3. Supercooling degree of CPCM at different borax mass fractions.

3. Thermophysical Property Tests of CPCM

3.1. Instruments

The thermal conductivity and specific heat capacity of the CPCM at 25 °C were measured using a thermal conductivity meter (KD2 Pro, Decagon, San Francisco, CA, USA) by immersing the probe of the instrument into a test vial containing 50 g of CPCM. The temperature variation of the material during the freezing and melting processes was monitored using a JK3000 multi-channel temperature data logger (JINKO, Changzhou JinAiLian Electronic Technology Co., Ltd., Changzhou, China) at a sampling interval of 30 s, in order to evaluate the degree of supercooling of the material. The volumetric change ratio of the material was determined using the classical volumetric method.

3.2. Thermophysical Properties of the CPCM

Phase transition temperature and latent heat are the most critical thermodynamic parameters determining the application potential of cold storage materials in cold chain logistics [21]. The thermophysical properties of the prepared CPCM were characterized using Differential Scanning Calorimetry (DSC).

The thermophysical properties were characterized by DSC 8500 (TA Instruments, New Castle, DE, USA) under a nitrogen atmosphere over a temperature range of −20 °C to 30 °C, with a heating/cooling rate of 10 °C/min. In addition, the thermal reliability of the samples was evaluated after multiple DSC freeze-thaw cycles.

The DSC curve presented in Figure 4 indicates that the CPCM exhibits distinct phase transition peaks during the melting process. The phase transition temperature of the sample ranges from 0 °C to 5 °C, which can meet the temperature requirement of the cold chain transportation for fresh food. Meanwhile, the DSC results reveal that the latent heat of the CPCM is 236.2 J/g, which is mainly from the contributions of the two primary thermal storage mediums (n-Tetradecane and water) [7].

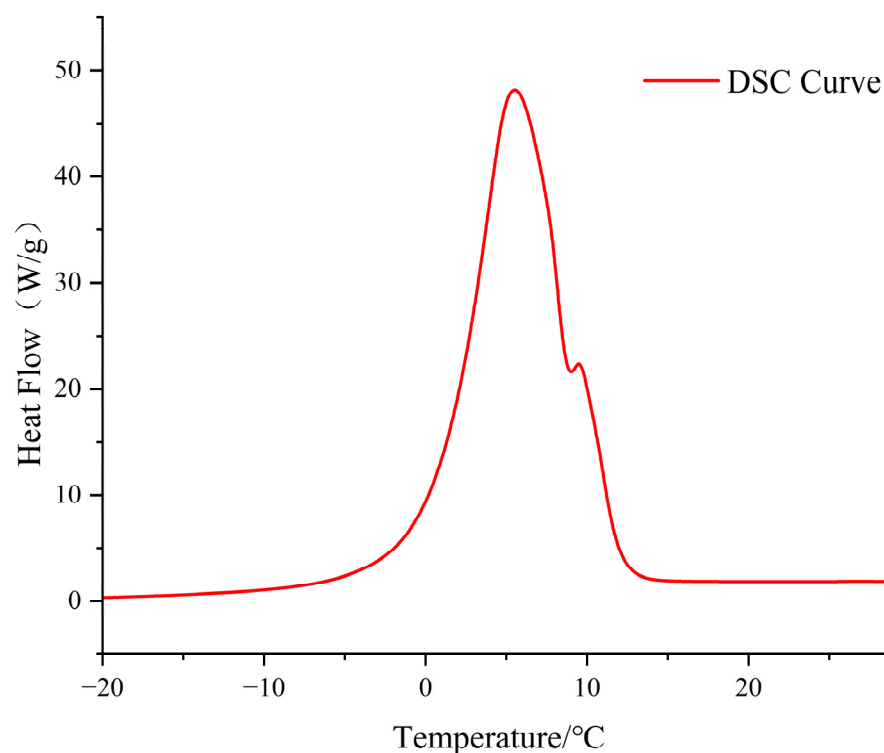


Figure 4. DSC curve of CPCM.

The freeze-thaw curve of CPCM sample (50 g), as shown in Figure 5, was recorded using a multi-channel temperature data logger. With 0.5 wt% of borax introduced into the aqueous solution as a nucleating agent, the crystallization barrier of water molecules is effectively reduced. The results demonstrate that the supercooling degree of the CPCM is no more than 0.5 °C. Since n-Tetradecane and water cannot form a eutectic state, the freeze-thaw curve in Figure 5 exhibits two phase transition points.

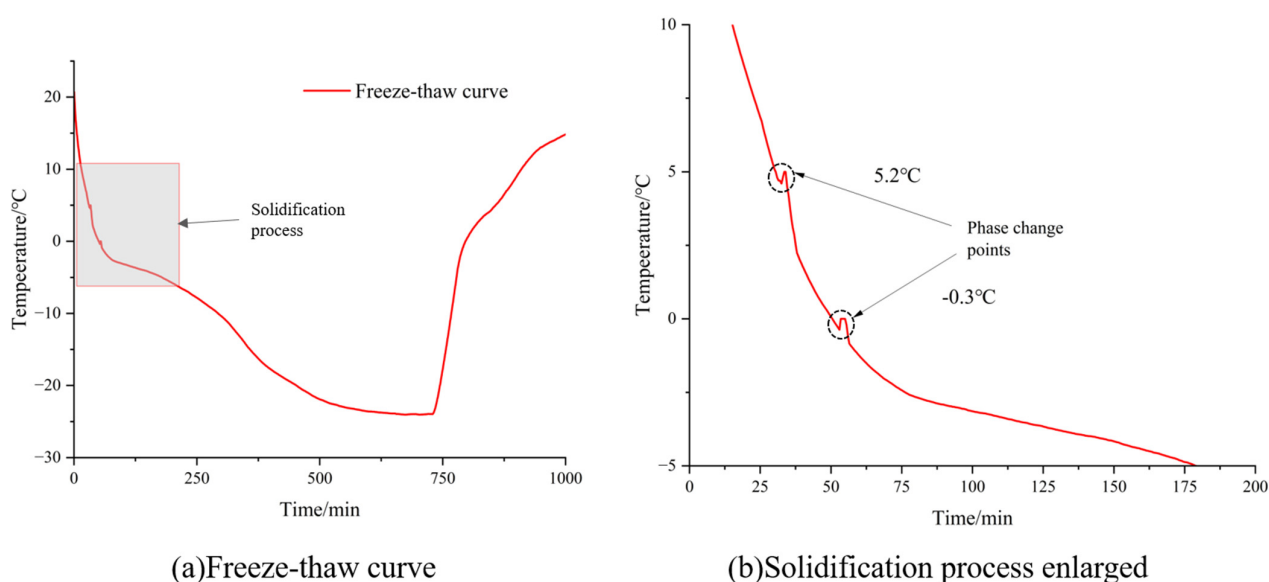


Figure 5. The freeze-thaw curve of CPCM.

To further validate the reliability of this formulation, samples were prepared independently in three groups. All measurements for each batch were repeated three times. The measurement data obtained from repeated tests on the three batches of samples were

statistically analyzed, and the results are presented in Table 2. The repeated measurements indicated acceptable reproducibility within the investigated experimental range.

Table 2. Sample data measurement and statistics.

Group Number	Sample Size mg	Latent Heat J/g	Heat Conductivity W/(m·K)
Group-1	7.6	271.2	0.317
		267.9	0.322
		267.8	0.338
Group-2	7.9	265.3	0.295
		266.3	0.341
		266.6	0.333
Group-3	7.0	262.2	0.333
		261.2	0.378
		259.7	0.330

To verify the stability of the thermophysical properties across multiple tests of materials from different batches, multiple DSC measurements were conducted and the results are shown in Figure 6. Meanwhile, the test curves of the raw cooling cycle from different batches in Figure 6 verify the robustness of the material.

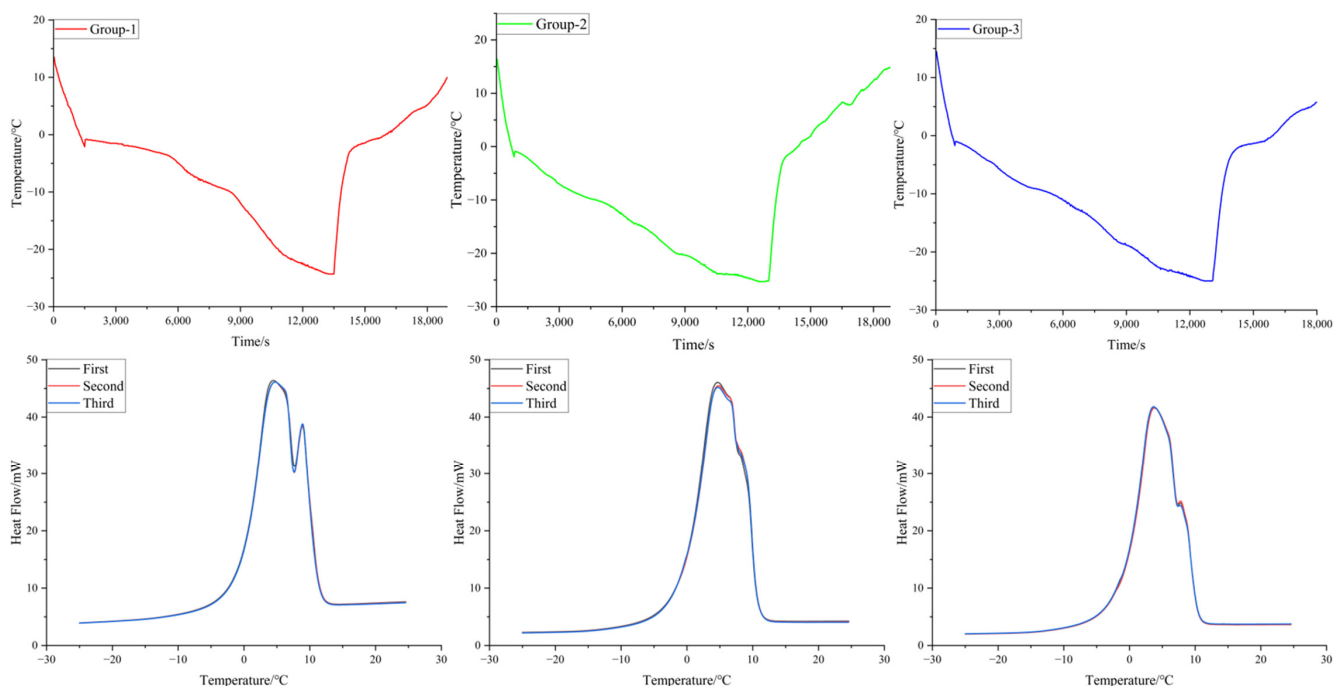


Figure 6. DSC measurements and freeze-thaw curves from different groups.

The results demonstrate that the positive CPCPM exhibits good repeatability and stability. Finally, traditional water-based PCMs face severe volume expansion issues during freezing [23]. The volume expansion rate of pure water upon freezing is approximately 9%, which may cause high-density polyethylene (HDPE) ice packs to deform or even rupture, triggering contamination risks. Meanwhile, the volume expansion rate of the CPCPM prepared in this study is merely 3% measured by the classical volumetric method, as shown in Figure 7. The significantly reduced expansion rate is attributed, on the one hand, to the mutual compensation of the volume change characteristics between the oil solution (n-Tetradecane) and the aqueous solution during the phase transition [24]; on the other

hand, the flexibility of the hydrogel network provides a certain buffer space for the growth of ice crystals. The low volume expansion rate of the CPCMs mitigates the mechanical stress damage to the packaging shell caused by phase change expansion, substantially enhancing the safety and reliability of the cold storage units in insulated containers.

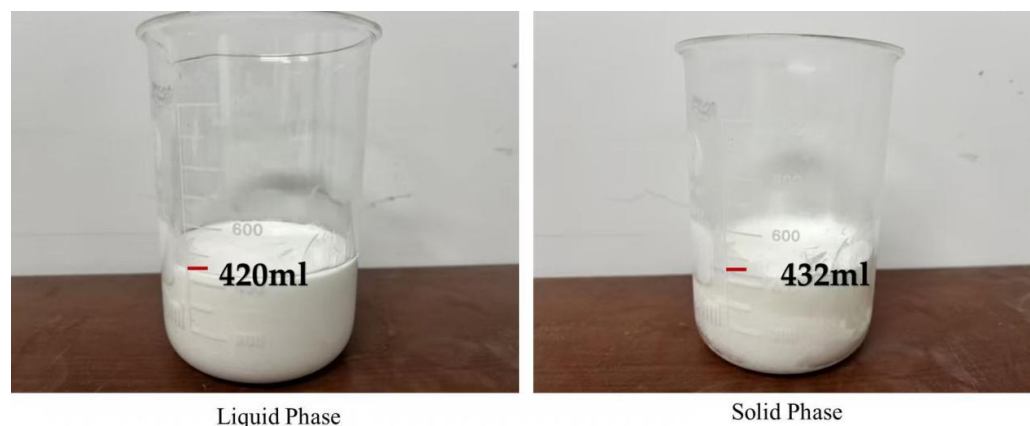


Figure 7. Volumes of CPCMs before and after freezing.

3.3. Stability of Form and Phase Transition Temperature

Phase separation and melting leakage are major engineering challenges for traditional solid-liquid PCMs. Meanwhile, in this study, by introducing the PVA/CMC-Na thickening system, a dense three-dimensional hydrogel network is formed via physical entanglement and hydrogen bonding among the polymer chains. This network skeleton utilizes strong capillary forces and surface tension to firmly anchor the emulsified n-Tetradecane oil droplets and free water within the microscopic pores.

In order to evaluate the morphological stability of the CPCMs, melting experiments and mass loss tests were conducted. As shown in Figure 8, solid-phase CPCMs at 2 °C were put on a piece of paper, which was placed in a temperature-controlled environment at 20 °C for 4 h. Results show that the sample remains form-stable in a melted state, with no obvious oil-water separation or liquid leakage observed; at 0 min, the sample mass was 1.6 g, while after 240 min, the sample mass decreased to 1.5 g, corresponding to a mass loss rate of 6.25%, which confirms that the blended emulsifier (Span 80/Tween 80) coupled with the hydrogel network endows the emulsion system with exceptionally high structural stability, enabling it to easily withstand frequent thermal shocks and load fluctuations in mobile cold chains [25,26].

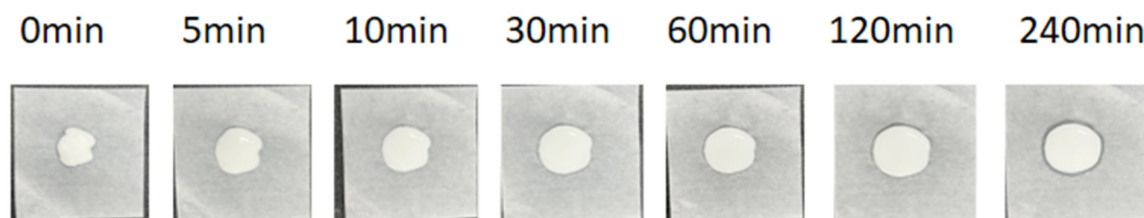


Figure 8. Optical images of the CPCMs during the melting process.

In addition, the long-term thermodynamic stability is an essential indicator for evaluating the reusability of the PCM [10]. Accelerated thermal cycling tests comprising 100 freeze-thaw cycles were performed on the samples using DSC to investigate the variations in phase transition temperature and latent heat of the CPCMs with the number of cycles. Figure 9 illustrates the variation in DSC curves after multiple cycles. The results indicate that after multiple freeze-thaw cycles, the phase transition temperature range of the CPCMs

exhibited no significant shift, and after 100 cycles, the latent heat of the phase transition decreased from 236.2 J/g to 224.0 J/g, with a decay rate of only 5.2%, indicating that the material maintained good thermal cycling stability within the tested cycling range.

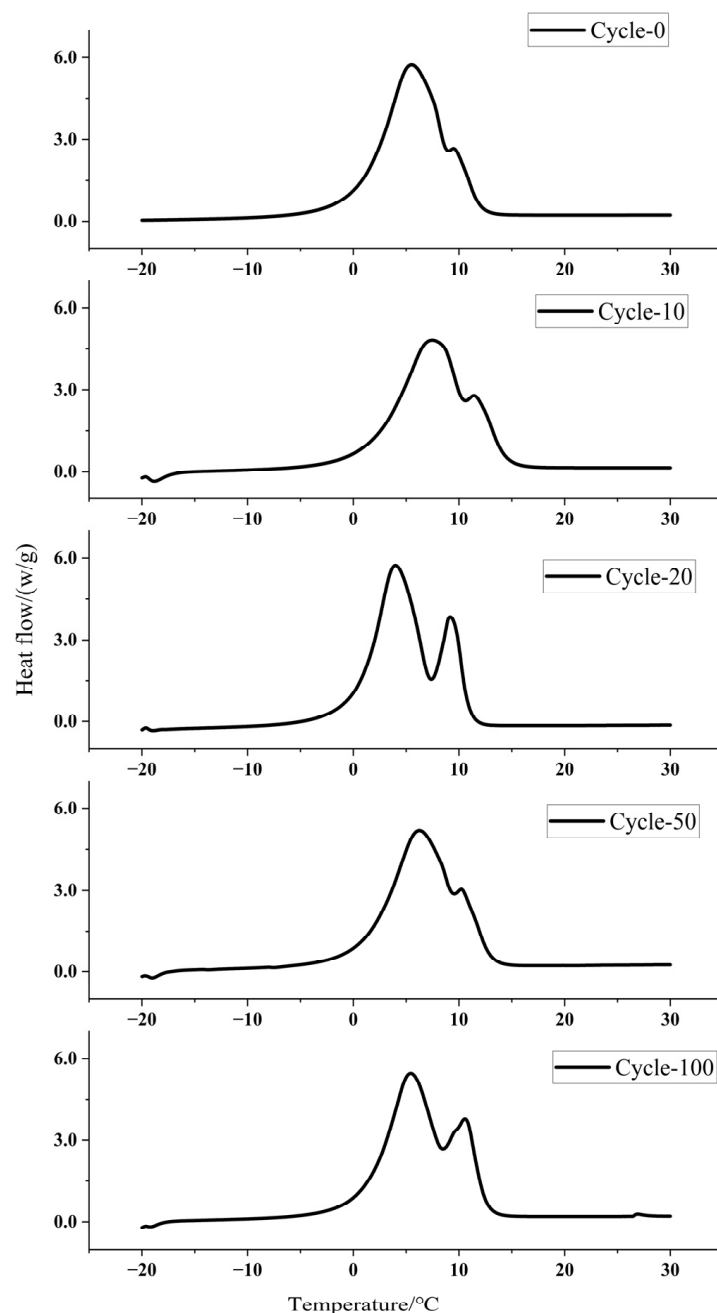


Figure 9. DSC measurements after different numbers of cycles.

To further validate the stability of the CPCPM, its performance was compared with that of commercial cold storage materials after 100 freeze-thaw cycles regarding phase change latent heat. As shown in Table 3, the CPCPM exhibits minimal attenuation in phase change latent heat, demonstrating stable properties.

The measurement accuracies of directly measured parameters, such as mass, temperature, latent heat and heat conductivity, were provided by the instruments manufacturers, while the error range of indirect measurement data was determined based on the calculation formula. The error table is provided below in Table 4.

Table 3. Comparison of CPCM and commercial materials after 100 freeze-thaw cycles.

Materials	Cycles	Latent Heat (J/g)	Attenuation Rate %
CPCM	Cycles-0	236.2	5.2
	Cycles-100	224.0	
PCM-1	Cycles-0	102.0	14.1
	Cycles-100	87.6	
PCM-2	Cycles-0	158.2	15.7
	Cycles-100	133.4	

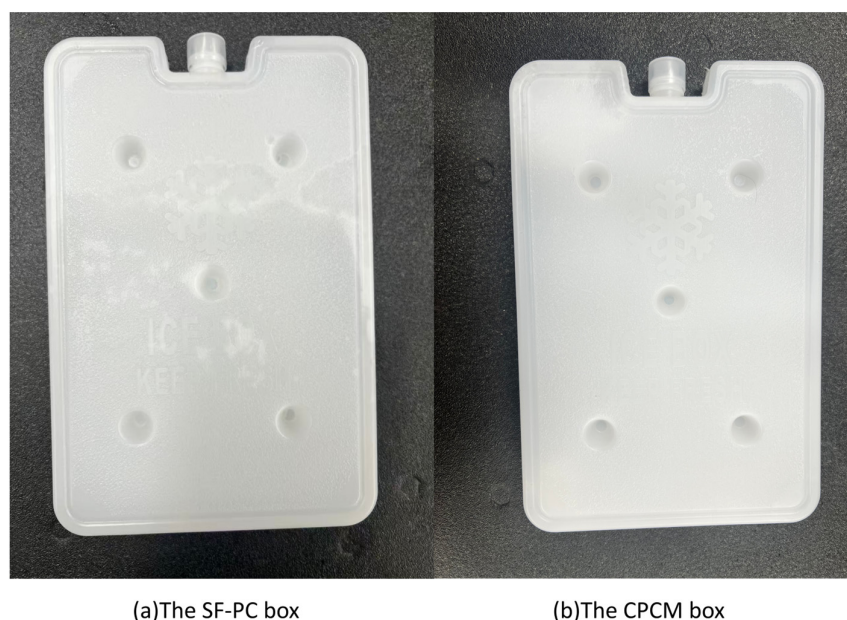
Table 4. Estimated maximum errors.

Parameters	Estimated Maximum Errors
Mass	± 0.0002 g
Temperature	± 0.1 °C
Latent heat	$\pm 10\%$
Heat conductivity	$\pm 5\%$
Degree of supercooling	± 0.2 °C

4. Application of the CPCM in a Cold Storage Container

To evaluate the performance of the prepared CPCM in practical cold chain logistics, an experimental study was conducted to test the temperature maintenance ability of the material in a thermal insulated container. A type of commonly used commercial PCM (SF-PC) was tested for comparison.

In total, 400 g of CPCM was packaged in a high-density polyethylene (HDPE) box. For comparison, 400 g of SF-PC (a type of PCM commonly used in commercial cold storage) was packed into a box identical to the previous one, as shown in Figure 10.

**Figure 10.** The packaged PCMs.

The thermal insulation of containers is crucial for maintaining product quality during cold chain transportation. The internal dimensions of the box were $360 \times 270 \times 225$ mm, as shown in Figure 11.

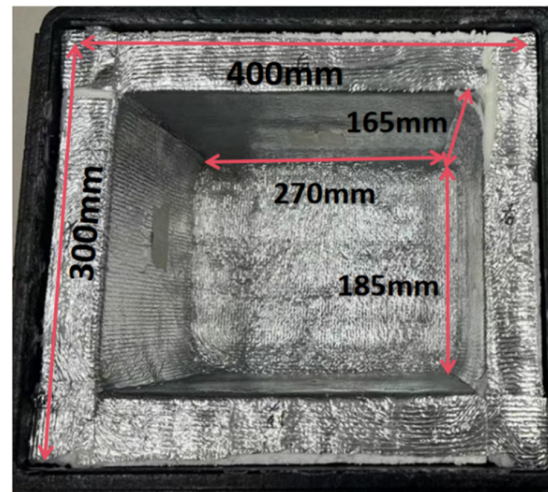


Figure 11. The insulated container.

The packaged PCM at a temperature of $-5\text{ }^{\circ}\text{C}$ was placed into the insulated container and the temperature at the center of the container was recorded in real time using a JK3000 multi-channel data logger. The entire setup was placed in an environment maintained at a constant temperature of $20\text{ }^{\circ}\text{C}$, as shown in Figure 12.

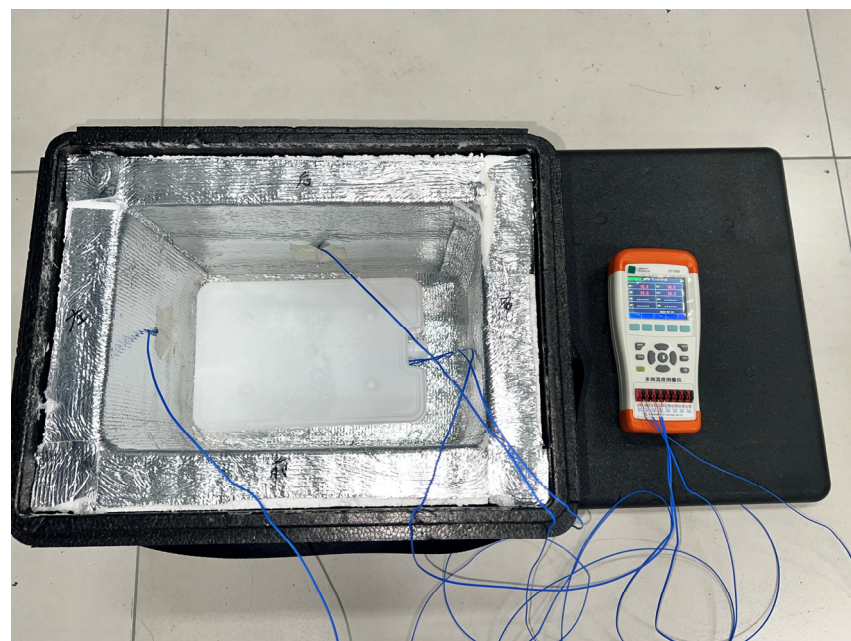


Figure 12. The experimental setup.

As illustrated in Figure 13, the inside temperature of the container increased with time. Since a temperature range of $2\text{--}8\text{ }^{\circ}\text{C}$ is demanded by cold storage for fresh foods like fruits and vegetables [27,28], in this study, the duration for which the temperature inside the chamber was maintained below $8\text{ }^{\circ}\text{C}$ was adopted as the evaluation criterion for the performance of the PCM.

Results indicate that, with the CPCM as the cold storage medium, the inside temperature of the container increases more slowly. The SF-PC package keeps the inside temperature below $8\text{ }^{\circ}\text{C}$ for about 2.9 h (173.95 min), while the CPCM package keeps the inside temperature below $8\text{ }^{\circ}\text{C}$ for up to about 8.3 h (498.53 min), which is an increase of 187% compared to the former.

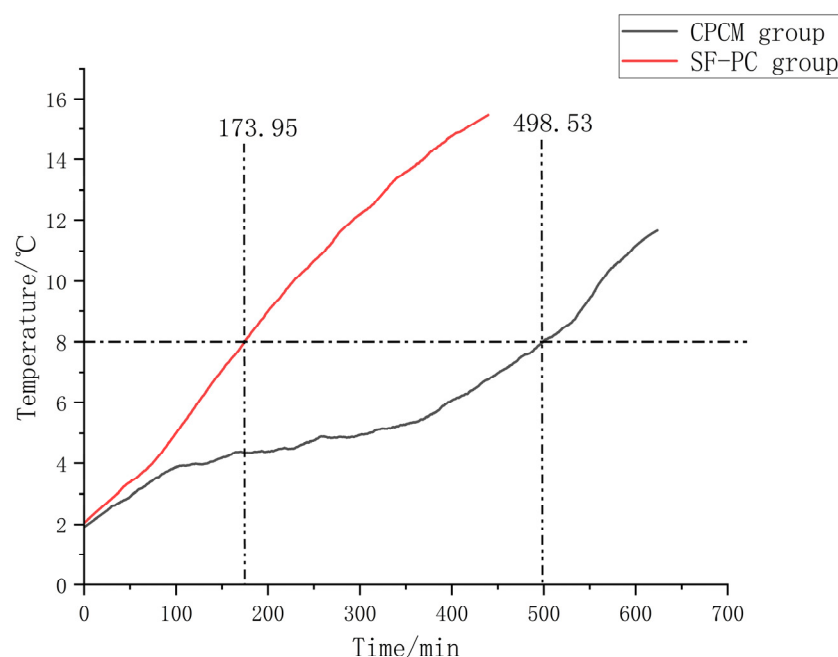


Figure 13. Variations in container temperature with SF-PC and CPCM as cold storage mediums.

From the perspective of large-scale preparation, the fabrication route adopted in this study mainly involves aqueous-phase polymer dissolution, oil-phase emulsification, crosslinking-induced gelation, and cooling-assisted shaping. The overall process does not involve high-pressure reactions or complex chemical synthesis, and is theoretically compatible with conventional emulsification/mixing and gel-forming equipment. Therefore, this system shows certain potential for scale-up production. To preliminarily evaluate its economic feasibility, the theoretical raw material cost of the material was estimated based on the mass fraction of each component and the corresponding unit price of the raw materials:

$$C_{\text{material}} = \sum_i \omega_i C_i \quad (5)$$

where ω_i represents the mass fraction of component i , and C_i denotes the corresponding unit price of the raw material. The estimated results are presented in Table 5.

Table 5. Estimated material cost of the CPCM.

Component	Mass Fraction wt%	Unit Price RMB·kg ^{−1}	Cost Contribution RMB·kg ^{−1}
Water	55.0	1.5	0.8
N-Tetradecane	39.0	247.0	96.3
PVA	1.0	48.0	0.5
CMC-Na	1.5	44.0	0.7
Span-80	1.5	38.0	0.6
Tween-80	1.5	99.6	1.5
Borax	0.5	45.8	0.2
Total	100.0	100.6	100.6

It should be noted that this estimation only considers the raw material cost and does not include expenses associated with processing energy consumption, equipment depreciation, packaging and encapsulation, quality control, transportation, or waste disposal. Therefore, the result can only serve as a preliminary economic analysis at the laboratory stage. In terms of cost composition, components such as water and borax are relatively inexpensive, whereas n-Tetradecane, surfactants, and polymeric components are likely

to be the major contributors to the overall material cost. For applications targeting cold chain logistics products, further optimization of the n-Tetradecane content, emulsifier dosage, and encapsulation structure will be required to achieve a balance among cold storage performance, stability, and cost. The cost of commonly commercial cold storage materials for cold chain applications is approximately 40 RMB/kg. In this study, a detailed cost analysis of the prepared CPCM was conducted, and the total cost was calculated to be 100.6 RMB/kg. The relatively high cost is mainly attributed to the high purity of n-Tetradecane used in the experiment. In conventional industrial production, high-purity n-Tetradecane is not necessary, and the material cost is therefore expected to be much lower than the laboratory-scale cost.

Furthermore, although the components of the CPCM, except water, may exhibit slight toxicity, the CPCM is intended to be used in a sealed container during practical cold chain applications and will not come into direct contact with food products. In addition, the CPCM is non-corrosive and has good fluidity, allowing it to be encapsulated in containers made of metals, plastics, or other suitable materials; under proper encapsulation and normal use conditions, leakage and related safety risks can be effectively avoided.

5. Conclusions

In this study, a type of composite PCM (CPCM) applicable to cold chain logistics is proposed. N-Tetradecane and water are adopted as the primary cold storage media in the composite, integrated with PVA/CMC-Na hydrogel to maintain form stability. Span 80, Tween 80 and borax are introduced into the composite as homogenizing agents and supercooling depressant, respectively. Thermophysical property tests and application experiments were conducted, and results indicate that the CPCM exhibits favorable thermal properties and good performance in application. The main conclusions can be drawn as follows:

- (1) The phase transition temperature of the proposed CPCM ranges from 0 °C to 5 °C, with a latent heat of 236.2 J/g and a supercooling degree of no more than 0.5 °C. The volume expansion rate during the liquid-solid phase transition is 3%, and the CPCM in the liquid phase remains form-stable without any liquid leakage.
- (2) After 100 freeze-thaw cycles, the latent heat of the CPCM decreases from 236.2 J/g to 224.0 J/g, with a decay rate of 5.2%, while the phase transition temperature shows no significant variation.
- (3) To evaluate the performance of the CPCM in practical cold chain application, the ability of the CPCM to maintain a low-temperature environment in a container is tested. The results show that the CPCM could extend the temperature maintenance duration by 187% compared to conventional materials (SF-PC).

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

PCM	phase change material
CPCM	composite phase change material
PVA	polyvinyl alcohol
HDPE	high-density polyethylene
SF-PC	a phase change material commonly used in markets
HLB	Hydrophile-lipophile balance
O/W	oil-in-water
CMC-Na	sodium carboxymethylcellulose
DSC	differential scanning calorimetry

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