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The innovative application of phase change materials in heat storage products: warmer pads

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Abstract. As the issue of energy shortage becomes increasingly severe, energy storage technology has gradually attracted global attention, with the application of phase change materials (PCMs) being particularly widespread. This paper focuses on a common daily product: the warmer pad, and investigates the selection and ratio of suitable PCMs to achieve a recyclable heat storage solution. The study first outlines the research background, significance, and methods, then summarizes the basic principles of phase change and the role of differential scanning calorimetry (DSC) in the study of phase change heat storage. Finally, the properties of PCMs with different proportions were tested, and the DSC curves were analyzed. The results showed that the phase change material mixture with a ratio of paraffin: OBC: expanded graphite = 77:20:3 exhibits excellent performance in heat storage, with a thermal conductivity of 0.547 W/m·K, a phase change latent heat of 150 J/g, and a phase change temperature of 41.9°C. The warmer pad achieved a surface temperature close to 40°C and a heat release duration of nearly one hour. This study aims to promote the industry's transformation towards sustainable development and provide a reference for research in the field of daily-use products with phase change heat storage.

Keywords: Phase Change Materials, Applied Research, Warmer Pad, Differential Scanning Calorimeter.

1. Introduction

1.1. Research Background

The issue of global energy scarcity is becoming increasingly prominent, primarily due to the over-exploitation and consumption of fossil fuels. With the introduction of China's goals for ‘carbon peak and carbon neutrality’ and the construction of a new energy system, the development of new and renewable clean energy sources has become crucial. However, clean energy sources such as solar and wind power exhibit intermittency and discontinuity, leading to mismatched supply and demand in both time and space. Therefore, the development of energy storage technologies is becoming increasingly important. Thermal energy storage is a vital component of this, playing a significant role in the utilization of renewable energy. Heat storage materials typically come in two forms: chemical and physical. Chemical heat storage materials utilize chemical reactions or dissolution heat to store thermal energy, which can easily cause environmental pollution. Physical heat storage materials are divided into sensible heat and phase change types. Sensible heat storage materials store heat by increasing the

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temperature of the conductive medium, making it difficult to control temperature changes, resulting in lower heat capacity and larger volume. In contrast, phase change materials offer higher energy density, more stable temperatures, lower energy consumption, and longer service life. Consequently, phase change materials are gradually gaining attention in the field of heat storage [1]. As summarized by Wang et al [2], phase change thermal storage technology has been widely applied in building energy conservation, such as in air conditioning in summer and heating in winter. Jie et al [3] studied the application of phase change materials in shell-and-tube heat exchangers, demonstrating high energy storage efficiency. Tang [4] posits that the application of phase change technology in solar thermal storage systems can effectively improve energy utilization efficiency.

As people's living standards improve and their pursuit of a comfortable life intensifies, phase change materials also show a very broad prospect in daily life applications. Zhi [5] used a binary mixture of stearic acid and disodium hydrogen phosphate dodecahydrate as the phase change material for a heat storage pad. The heating temperature was around 55°C, with a heating time for up to 160 minutes. The final temperature during heat release was around 26°C, and the heat release time generally exceeded 500 minutes. Bin [6] developed a phase change heat storage electric floor heating system using paraffin and expanded graphite. After mixing the phase change material with concrete, the surface average temperature during heat storage was 1.35°C lower than that of ordinary concrete, and the heating time was extended by 1 hour and 41 minutes. During heat release, the surface average temperature was 1.49°C lower than that of ordinary concrete, and the cooling time was extended by 1 hour and 52 minutes. Meng et al [7] summarized the use of temperature-regulating clothing with phase change materials, which can be applied for medical cooling, heat protection, diving, polar exploration, and infrared camouflage.

Therefore, phase change warmer pads capable of heat storage and release hold significant research value. As a heating product, warmer pads have consistently been the top choice for individuals in winter or low-temperature settings. The market demand for these products is on the rise, as illustrated in Figure 1. However, widespread issues with currently available warmer pads, such as the risk of burns, the potential for liquid expansion, and environmental concerns, have prompted a shift in market expectations beyond basic heating functionality. There is an increased focus on the products' eco-friendliness, sustainability, and health safety. Phase change warmer pads can meet these market requirements by leveraging their recyclability, non-polluting nature, and safety features.

Figure 1. 2014-2020 China's warmer pad demand (in billions of pads).

1.2. Research Purpose and Significance

The core purpose of this study is to design a novel recyclable green warmer pad using phase change materials, aiming for a cycle of use that is pollution-free and safe. This study seeks to provide an efficient heat storage solution for warmer pads, reducing environmental impact while meeting the demands of modern society for high-efficiency, comfortable, and environmentally friendly heating products. This approach is intended to promote the industry's transformation towards sustainable development.

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1.3. Research Methods

This research endeavor incorporates a variety of methodological approaches, including theoretical analysis, empirical experimentation, and comparative evaluation. The theoretical analysis involved an exhaustive examination of pertinent literature and patent documentation, providing a comprehensive understanding of the internal mechanisms and performance criteria of warmer pads. This analysis laid the groundwork for conceptualizing a phase change material-based warmer pad framework. Subsequently, the empirical experimental method was pivotal in validating theoretical postulates and refining design parameters. A spectrum of materials was scrutinized through ratio experimentation, employing analytical instruments such as DSC and thermographic cameras to ascertain key thermal properties, including phase transition temperatures, latent heat, thermal conductivities, and surface temperature profiles. Furthermore, the comparative method was extensively utilized to juxtapose the performance of the prototype phase-change warmer pad against conventional warmer pads and analogous commercial products. This comparative analysis was instrumental in discerning areas for performance enhancement and ensuring the competitiveness of the proposed warmer pad design.

2. Experimental Principles and Methods

2.1. Basic Principles of Phase Change Materials

2.1.1. Thermodynamic Principles of Phase Change Processes

The basic principle of phase change materials is predicated on their capacity to absorb or release substantial quantities of latent heat during transitions between different phase states. As the material undergoes a phase transition from solid to liquid, it absorbs heat (melting), and when it reverts from liquid to solid, it emits heat (solidification). Given that this transition involves merely the transfer of energy without an accompanying change in temperature, it holds substantial applicability and broad scope for future applications within the realms of thermal energy storage and temperature regulation. The latent heat of fusion for phase change materials, which is the heat absorbed or released during the phase transition, as in equation (1),

$$\Delta H = T \cdot \Delta S \quad (1)$$

where ΔH represents the latent heat, T denotes the temperature of phase change, and ΔS signifies the change in entropy during the phase change process.

2.1.2. Classification and Characteristics of Phase Change Materials

Phase change materials can be differentiated based on the phase transition type into solid-solid, solid-gas, solid-liquid, and liquid-gas transitions. Solid-solid transitions primarily consist of materials such as polyols, while solid-liquid transitions encompass crystalline hydrates, metals and alloys, alkanes, and alcohols. When classified by material composition, PCMs are divided into organic, inorganic, and composite categories. The organic category includes paraffin waxes, fatty acids, polyols, etc.; the inorganic category comprises crystalline hydrates, molten salts, metals and alloys, etc and the composite category consists of mixtures of organic-organic, organic-inorganic, and inorganic-inorganic combinations. According to the temperature range, they are further categorized into low-, medium-, and high-temperature phase changes [8].

PCMs have the ability to absorb or release substantial latent heat during phase transitions. This feature enables warmer pads to deliver a stable output of thermal energy over an extended period without the need for additional energy input. Furthermore, by adjusting the proportions and selecting appropriate materials, the phase change temperature of PCM can be customized. This customization allows warmer pads to cater more effectively to the diverse requirements of various users and application settings, thus facilitating temperature regulation. Additionally, PCMs are associated with minimal environmental pollution and offer an extended lifespan.

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2.2. Experimental Materials

As shown in Table 1, the experimental materials selected include paraffin wax, OBC, foaming agent, expanded graphite, and SEBS.

Table 1. Experimental materials and their characteristics.

Material	Characteristics
Paraffin wax	Existing studies are abundant, the cost is relatively low, and the phase change temperature is suitable for warmer pads.
OBC	It serves as a supporting matrix to prevent paraffin leakage and enhance heat-induced flexibility[1].
Foaming agent	Fill spaces.
Expanded graphite	Utilizing a porous structure to match paraffin and enhance the thermal conductivity coefficient [9].
SEBS	Enhance shape retention, prevent leakage, and increase heat-induced flexibility.

Paraffin wax is produced by Donglin Plastics Business Department in Zhangmutou, Dongguan City, with a latent heat of 220.5 J/g, OBC is manufactured by Dow Chemical Company in the United States (Model 9530, characterized by a density of 0.887 g/cm³ and a melt flow rate of 190℃/2.16 kg). The foaming agent is produced by Hongzhi Network Information Technology Co., Ltd., and 80-mesh expanded graphite is produced by Qingdao Jintao Graphite Co., Ltd.

2.3. Differential Scanning Calorimetry

2.3.1. Principles of Operation and Experimental Procedure of DSC

DSC is a high-precision thermal analysis technique capable of accurately measuring the heat flow changes of materials during phase transitions. It measures the relationship between the heat flow rate of the sample and the reference material as a function of temperature or time, from which the phase change latent heat and the onset temperature of the material can be calculated [10]. DSC is characterized by programmable temperature control, simplicity, speed, minimal human factor influence, and good repeatability [11]. The sample and the reference material are placed in fixed positions in a common heating or cooling environment. When the sample undergoes a phase transition, such as melting or crystallization, it absorbs or releases heat, causing a temperature change in the sample container. The DSC instrument maintains temperature consistency between the sample and the reference material by controlling the heating or cooling rate. If the sample requires additional heat to maintain isothermal conditions (such as during melting), the instrument provides additional energy, the input of which is the DSC signal. The DSC curve is a graph of the heat flow as a function of temperature or time during the experiment.

Before performing DSC testing, first, weigh 5 to 10 mg of the sample using a precision electronic balance and seal it in a crucible, as shown in Figure 2. Then place the crucible into the DSC equipment for testing. Set an appropriate temperature range according to the characteristics of the sample and heat or cool at a constant rate. During the cooling phase, after reaching the preset lowest temperature, maintain an isothermal period of 2 to 5 minutes to ensure the sample is completely solidified. Then, heat to the highest temperature at the specified rate to complete the test. After the test is finished, the cooling or heating curve of the sample, phase change temperature, and latent heat value can be obtained through analysis software. Throughout the measurement process, liquid nitrogen is used as a refrigerant, while nitrogen gas serves as a protective gas and purge gas.

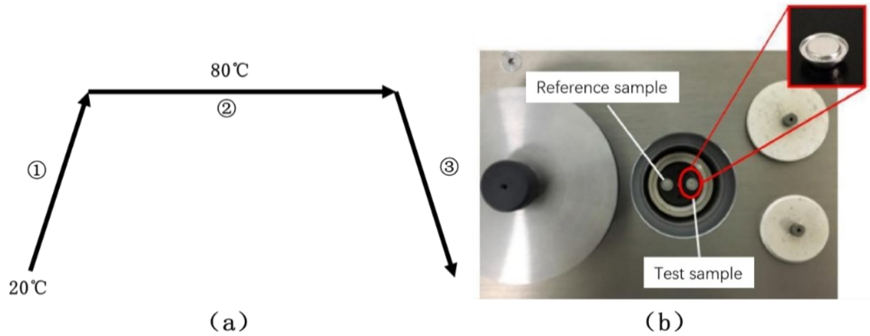

Figure 2.(a)①Melting: The solid turns into a liquid, causing the temperature to rise.;②Isothermal: 2 minutes.; ③Solidification: The liquid turns into a solid, causing the temperature to fall. (b)The positions of the reference and test samples in the Differential Scanning Calorimeter [12].

2.3.2. Application of DSC in the Study of Phase Change Materials

DSC serves a crucial role in the research of phase change materials. As a high-precision thermal analysis technology, DSC is capable of measuring the heat flow changes associated with temperature during the heating or cooling of materials. These measurements help scholars both domestically and internationally to better understand phase change materials, delve deeper into their thermal properties, and act as a vital link between fundamental research and practical applications. In this experiment, DSC is utilized for the identification of phase change temperatures, the measurement of the latent heat of phase transitions, and the optimization of material compositions.

2.4. Experimental Equipment

The primary equipment utilized in the experiment includes a DSC and a thermal conductivity analyzer, as shown in Figure 3. The DSC, manufactured by NETZSCH Instruments GmbH, model DSC200F3, is primarily used for measuring the temperature and latent heat of phase change materials. The thermal constant analyzer, produced by the Swedish Hot Disk company, model TPS500s, is mainly employed for determining the thermal conductivity coefficient of phase change materials. Additional auxiliary equipment is listed in Table 2.

Figure 3. (a)differential scanning calorimeter (b)thermal conductivity analyzer.

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Table 2. Experimental instrument information

Instrument	Manufacturer	Model	Precision
Precision electronic balance	Shanghai fangrui instruments co., ltd.	Fa2004	±0.1 mg
Digital temperature controlled water bath	Shanghai lichen bangxi instrument technology co., ltd.	Hh-4	0.1 °c
Thermocouple	Agilent Technologies	-	0.05 °C
Thermal conductivity analyzer	Swedish hot disk	Tps 500 s	0.01 °c
Differential scanning calorimeter	Netzsch instruments gmbh	DSC200f3	-
Vacuum drying oven	Shanghai qiao yue electronics co., ltd.	Dzf-6020	-
Beakers, Glass Rods, etc	Tmall Online Shopping Platform	-	-

3. Research

3.1. Warmer Pad Structural Design

The text of your paper should be formatted as follows: The overall structure, as shown in Figure 4, includes a Flexible soft shell, PCM, Isolated layer, Heating sheet, Circuit, Charging port, and Wire. In terms of energy supply, as depicted in Figure **5**, a lithium battery is chosen for its high energy density and stable power supply characteristics, serving as the storage and release device for electrical energy. Additionally, a temperature control circuit and heating sheet are integrated to ensure that the warmer pad provides a uniform and stable heat output during use.

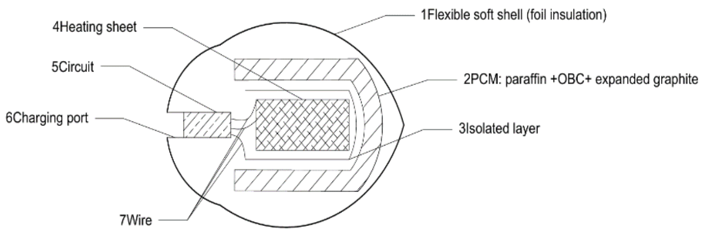


Figure 4. The overall design of the warmer pad.

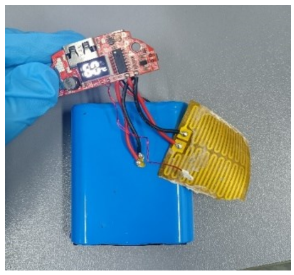
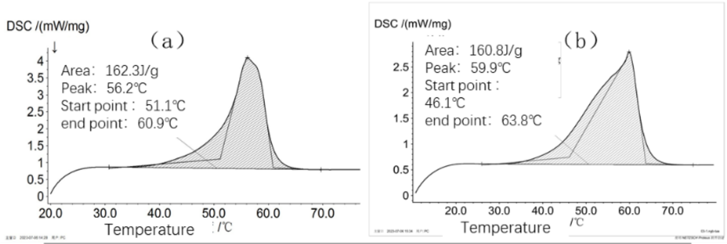


Figure 5. Circuit, heating element, and lithium battery.

3.2. Experimental Content

3.2.1. Comparison of DSC Curves for Phase Change Materials with Different Proportions

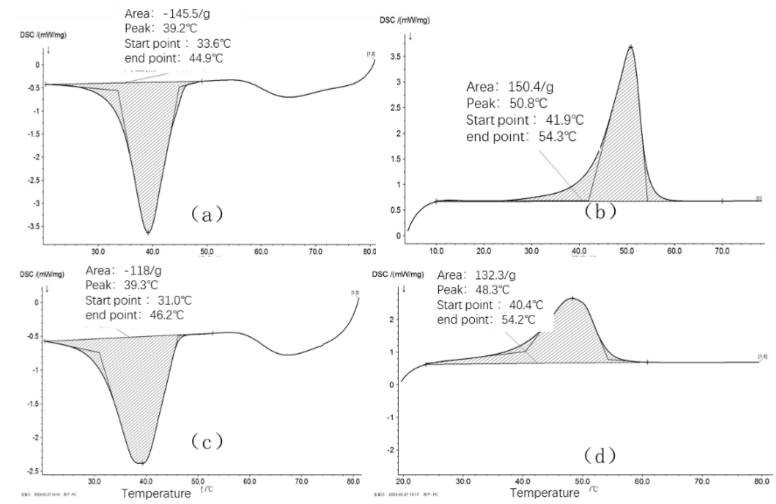
Three sets of experiments were conducted in total. The first set utilized a mixture of paraffin wax, OBC, and a foaming agent. Experiments were performed with mixture ratios of 66:33:1 and 65:27:6.7 for paraffin, OBC, and foaming agent, respectively. A meticulous analysis of the DSC curves, as depicted in Figure 6, revealed that an increase in the proportion of the foaming agent led to an expansion in the temperature range of the beginning and end of the phase transition. This suggests that the foaming agent facilitates better integration between paraffin and OBC. Nevertheless, due to a decrease in the overall quantity of paraffin, there was a reduction in the latent heat.



	paraffin wax (%)	OBC (%)	Foaming Agent (%)
(a)	66	33	1
(b)	65	27	6.7

Figure 6. The ratio of phase change materials consisting of paraffin wax, OBC, and foaming agent, as well as the DSC test results.

The second set of experiments involved a composite of paraffin wax, OBC, and expanded graphite. These were tested using DSC with mixture ratios of 77:20:3 and 65:30:5 for paraffin, OBC, and expanded graphite, respectively, as depicted in Figure 7. Studies show that incorporating expanded graphite results in a substantial decrease in latent heat, accompanied by variations in the temperature range of the phase transition. The difference in temperature between the initiation and termination of the phase change also widened, signifying a more extensive and gentle phase transition process[13]. This effect may arise from the thermal interaction between the expanded graphite and the phase change material, as well as the distribution of expanded graphite throughout the PCM matrix [14]. An excess of expanded graphite could lead to a drastic reduction in the phase change latent heat, whereas an insufficient amount might not deliver the anticipated improvement in thermal conductivity. The thermal conductivity of the material with the ratio of paraffin to OBC to expanded graphite at 77:20:3 was determined to be 0.547 W/(m · K).



	Paraffin wax (%)	OBC (%)	Expanded graphite (%)
(a) 、 (b)	77	20	3
(c) 、 (d)	65	30	5

Figure 7. Phase change materials: ratio of paraffin, OBC, and expanded graphite and DSC test results.

The third set of experiments involved a composite of paraffin wax, SEBS, and expanded graphite. SEBS effectively reduces the leakage rate and has excellent sealing performance [15]. The ratio chosen was 77:20:3 for paraffin, SEBS, and expanded graphite, respectively. However, under the conditions of

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a 160°C high-temperature oil bath, the composite material failed to fully melt into a liquid during the experiment, as depicted in Figure 8. This observation suggests potential issues with compatibility and thermal stability among paraffin, SEBS, and expanded graphite, which may be attributed to poor miscibility between SEBS and paraffin, or the thermal stability of expanded graphite at elevated temperatures. To resolve this issue, future studies could utilize additional characterization methods, such as Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM), to delve deeper into the thermal performance and microstructure of the materials [16].

(a) (b)

Figure 8. (a)Paraffin in a molten state; (b)Non-molten state after the addition of SEBS and expanded graphite.

3.3. Thermal Flow Analysis

During the melting process, materials absorb heat, leading to an endothermic peak on the heat flow curve; conversely, during the solidification process, materials release heat, manifesting as an exothermic peak. As the temperature increases during melting, the PCM absorbs heat, and an endothermic peak emerges on the DSC curve, with its peak position aligning with the material's melting point. The area under the endothermic peak expands as melting continues until the material is entirely in a liquid state. The heat flow variation during this phase, represented by the area under the curve, directly reflects the material's latent heat of fusion, indicating the energy required for the transition from solid to liquid. The rate of phase change influences the DSC curve's morphology. In DSC testing, the rate of phase change dictates the speed of heat exchange, subsequently affecting the shape and characteristics of the heat flow curve. When the phase change rate is rapid, heat is quickly absorbed or released, resulting in a sharp peak with a large area on the DSC curve. Conversely, a slower phase change rate leads to a more gradual heat exchange, resulting in a broader and flatter peak on the DSC curve. An increase in the cooling rate results in a broader and flatter shape, potentially due to altered crystallization behavior from rapid cooling, which disperses the heat release process [17].

3.4. Performance Testing

Tests can be conducted using an infrared thermal imager and thermocouples to evaluate the performance of the warmer pad. As depicted in Figure 9, the infrared imager demonstrates that with an ambient temperature of 26°C, the surface of the warmer pad can essentially achieve 40°C, offering users a warm and comfortable heating effect without causing high-temperature burns. Furthermore, this level of temperature performance can last for almost one hour, showcasing the warmer pad's outstanding thermal sustainability.

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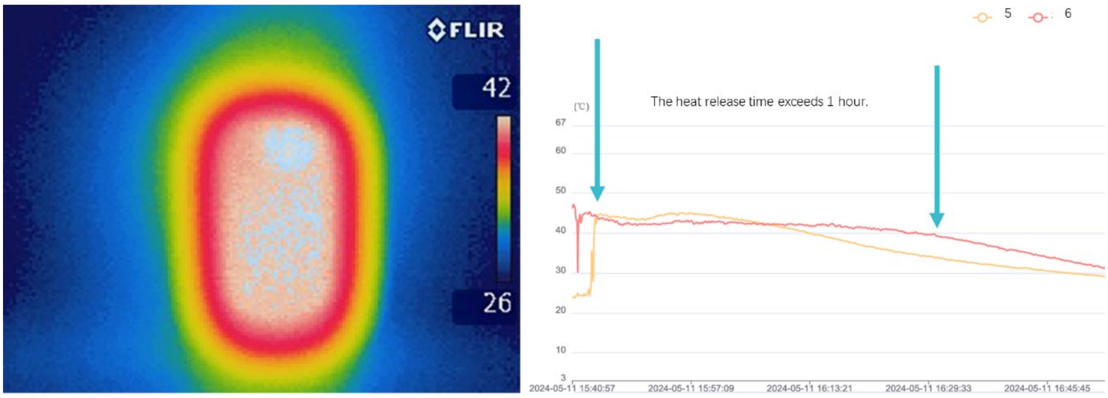

(a) (b)

Figure 9. (a)Infrared imager for measuring surface temperature (b)Thermocouple for testing the temperature variation curve on the surface of the warmer pad.

4. Conclusions

Through the research, the following conclusions have been drawn:

- Selection and proportioning of phase change materials: the selection and proportioning of phase change materials for the warmer pad were determined after extensive analysis. The precision of the equipment affected the accurate measurement of the foaming agent dosage in the first group. The third group, which included SEBS, did not exhibit a liquid state, while expanded graphite was found to enhance the thermal conductivity. Therefore, the second group's composition of paraffin wax, OBC, and expanded graphite was chosen as the phase change materials. Based on DSC and thermal conductivity analyses, the selected ratio of paraffin to OBC to expanded graphite was 77:20:3. this composition not only has a considerable thermal conductivity coefficient of 0.547 $w/(m \cdot k)$ but also possesses a suitable and stable latent heat of phase change of 150 j/g and a phase change temperature of 41.9°c. These characteristics are crucial for the performance of the warmer pad.
- Performance testing of the warmer pad: using an infrared thermal imager and thermocouples for assessment, the warmer pad was shown to maintain a surface temperature of 40°c and provide heat for approximately one hour, demonstrating its superior performance.

In the future, the development of phase change warmer pads will be expanded to advance alongside technological innovations and growing consumer awareness. With the integration of nanotechnology and artificial intelligence, these products will become more intelligent and exhibit enhanced thermal performance. Furthermore, as environmental and energy-saving consciousness strengthens, phase change warmer pads are anticipated to find widespread applications in fields such as healthcare, outdoor sports, and daily warmth. Through continuous technological innovation and market adaptation, these products are poised to become essential tools for energy conservation, emission reduction, and improving quality of life, contributing to the realization of a green, intelligent, and healthy lifestyle.

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