energies

Article

Preparation and Characterization of Microencapsulated Phase Change Materials for Solar Heat Collection

Hongbing Chen [1], Rui Zhao [2], Congcong Wang [1], Lianyuan Feng [3,4], Shuqian Li [3,4,*] and Yutong Gong [1]

[1] School of Environment and Energy Engineering, Beijing University of Civil Engineering and Architecture, Beijing 102616, China; chenhongbing@bucea.edu.cn (H.C.); wangcongcong@bucea.edu.cn (C.W.); yutonggong08@163.com (Y.G.)
[2] State Key Laboratory of Building Safety and Environment, China Academy of Building Research, Beijing 100013, China; 15630123571@163.com
[3] School of Civil Engineering, Hebei University of Water Resources and Electric Engineering, Cangzhou 061001, China; fengly@tju.edu.cn
[4] Hebei Technology Innovation Center of Phase Change, Thermal Management of Data Center, Cangzhou 061001, China
* Correspondence: lsqtcc@163.com; Tel.: +86-0317-7587223

Abstract: In this paper, a new type of microencapsulated phase change materials (MPCMs) with docosane as the core and titanium dioxide (TiO_2) as the shell was prepared by in situ polymerization. Its phase transition temperature was approximately 40 °C, and it can be used as a phase change material (PCM) in a low-temperature solar heat collection system. The properties of the new material were examined including the microstructure, the chemical elements on the surface of the microcapsules, and thermal conductivity. In addition, to obtain the optimized formula of the microcapsules, single-factor analysis on the emulsifier type, its mass fraction, ultrasonic oscillation time, pH, and core–shell ratio were performed. The results showed that the MPCMs prepared in this paper had a particle size of 2–5 μm and were spherical. Its surface was uniform and smooth without cracks, and the TiO_2 was well dispersed around the docosane, completely coating the docosane without impurities. The MPCMs had good performance in terms of thermal properties and heat storage when using 0.40% SDS as an emulsifier, 10 min ultrasonic, a 3.5 pH value, and a 1:1 core–shell ratio. However, the stirring method, time, and experimental reaction temperature also affected the properties of the material, which was not studied in this experiment. We will continue to study these factors in the future.

Keywords: microencapsulated phase change material; core–shell ratio; nanoparticles; thermal property

check for updates

Citation: Chen, H.; Zhao, R.; Wang, C.; Feng, L.; Li, S.; Gong, Y. Preparation and Characterization of Microencapsulated Phase Change Materials for Solar Heat Collection. *Energies* **2022**, *15*, 5354. https://doi.org/10.3390/en15155354

Academic Editor: Benedetto Nastasi

Received: 7 June 2022
Accepted: 20 July 2022
Published: 23 July 2022

1. Introduction

Phase change energy storage materials have been gaining popularity in the field of energy storage, and many scholars have conducted large amounts of research on phase change energy storage materials [1–3]. A phase change energy storage material absorbs or releases heat from the environment during its phase change process, which contributes to improving the efficiency of energy utilization. Some PCMs characterized by large volume changes, however, are beset by phase separation, supercooling, solidification, and other phenomena. Yuan et al. [4] investigated the thermal storage properties of erythritol-based phase change materials. It was found that this phase change material had high thermal density but low thermal conductivity and a subcooling of up to 75 °C, which seriously affected its thermal storage and discharge performance during energy storage. Yasushi. Y. et al. [5] conducted experiments on the thermal properties of phase change microcapsules and revealed that the phase change microcapsules showed supercooling and that the supercooling increased with a decreasing particle size in the range of 5–100 μm. P. Schossig et al. [6] applied phase change materials to buildings in order to solve the problem of overheating in summer. It has been concluded that unencapsulated phase change materials can alter the properties of a building's matrix material and that material leakage can occur during use. To overcome the above problems, MPCMs have been introduced into energy storage research. MPCMs use microcapsule technology to coat the PCM with a polymer or inorganic material in a physical or chemical method to form solid particles. In the process of external temperature changes, phase transformation occurs in the core of the PCM, while the wall of the PCM remains solid. This can not only effectively increase the specific surface area and thermal conductivity of the PCM but also improve the thermal stability and the prevention of leakage and corrosion of the PCM. Zhi et al. [7] used the sol-gel method to prepare stearic acid as a core material and silica as a shell material, which prevented the leakage of melted stearic acid. The results showed that the silica shell could improve the thermal stability of the microencapsulated stearic acid as a composite energy storage material.

At present, MPCMs have been widely used in building materials, textiles, solar heat collection, and other fields.

In terms of building materials, the addition of MPCMs can improve their heat storage performance. Cabeza et al. [8] investigated the performance of adding MPCMs to concrete walls and found that the addition of MPCMs could increase the thermal inertia and reduce the internal temperature. By adding commercial MPCMs (Inertek 23 °C) to the textile reinforced concrete panels, Bahrar et al. [9] analyzed the effect of MPCMs on textile reinforced concrete panels, and the results showed that the composite PCM improved the heat storage capacity and thermal inertia of textile reinforced concrete. In addition, Mankel et al. [10] made nine different mixtures of MPCMs that were composed of three water/cement ratios and three volume fractions of MPCMs, and they tested the heat storage performance of the MPCMs added to the cement slurry. The experimental results showed that the potential energy storage capacity largely depended on the volume fraction of the MPCMs, and the thermal conductivity decreased with the growth of the water/cement ratio and the volume fraction of the MPCM. Jessica et al. [11] evaluated the applicability of microcapsules in construction and other applications by studying the thermal and mechanical properties of microcapsules with paraffin as the core material and acrylic as the wall material. Compared with a commercial MPCM (Micronal DS5008 made by BASF, Berlin, Germany), the study found that the prepared sample had better thermal and mechanical properties than the traditional commercial MPCM DS5008.

In textile applications, the addition of MPCMs can accumulate or release heat under the influence of temperature changes to provide thermal comfort. Nejman et al. [12] studied the effects of n-octadecane as an MPCM on the thermal properties and air permeability of fabrics using three different application methods (i.e., printing, coating, and filling) and then the effects of different heating/cooling rates (i.e., 1, 5, 10, and 15 °C/min) on the thermal performance of textiles modified by MPCMs [13]. These studies provided data support for the better application of MPCMs in textiles. On the other hand, in the field of solar heat storage, the use of MPCMs make it possible to develop and utilize solar energy more efficiently. An MPCM with stearic acid as the core and silica gel as the shell was developed and designed by Lin et al. [14], and graphene oxide was adsorbed on the surface of the MPCM through a self-assembly process. The experiment tested the performance of the novel MPCM with 20 and 40 mg graphene oxide and non-graphene oxide and showed that the MPCM with 40 mg graphene oxide had the higher thermal conductivity and higher latent heat, substantiating MPCM's great potential as a solar thermal conversion storage material. With MPCMs prepared by wrapping paraffin wax in an inorganic shell of Cu_2O, Gao et al. [15] had shown that its microstructure and morphology were significantly affected by surfactants, alkali concentration, and copper content, proving that under optimal synthesis conditions, this microcapsule can realize the dual functions of solar photocatalysis and solar heat storage. Yang et al. [16] successfully synthesized a novel MPCM that can be applied to a low-temperature solar energy system, which took n-ocadecane as the core and polymethyl methacrylate as the shell, supplemented by modified Si_3N_4 powder. They also analyzed the latent heat, thermal conductivity, and thermal stability and concluded that the addition of Si_3N_4 particles reduced the latent heat of phase change and improved the thermal conductivity and thermal stability of the microcapsules.

Similarly, the use of MPCMs in solar collectors can improve the utilization of solar energy. Wang et al. [17] dispersed the paraffin@melamine resin/multiwalled carbon nanotube composite material into the water–ethanol mixture and tested the photothermal conversion performance of the nanofluid after adding an MPCM to the solar collector. The research found that covering the MPCM surface with nanolayer materials with high optical absorption capability can improve its photothermal conversion performance. Liu et al. [18] modified MPCMs with paraffin as the core and melamine-formaldehyde resin as the shell with graphite nanoparticles and synthesized an MPCM suitable for heat transfer fluid of a medium-temperature solar collector, and they analyzed its thermal conductivity and photothermal performance through experiments. In addition, Gao et al. [2] prepared a microcapsule with melamine-formaldehyde resin as the shell and octadecane as the core. Its shell was modified by reduced graphene oxide and the core was doped with oleic-acid-coated Fe_3O_4 magnetic nanoparticles, which improved the optical absorption and thermal conductivity. This kind of MPCM can not only directly convert solar energy into heat energy and store it, but it can also be directionally migrated or recycled under the action of an external magnetic field, which offer the prospects of wide application in solar collectors.

In the field of solar heat collection, low-temperature solar PV/T systems can be widely used to provide domestic hot water, domestic electricity, etc., and play a very important role in low-carbon energy conservation. By improving the heat storage capacity of the heat transfer medium in the solar PV/T system, the utilization rate of solar energy can be improved and the energy saving effect can be achieved. For the study of MPCMs, many researchers focus on the morphology, chemical composition, phase change properties and thermal stability, but the influence of preparation methods on the thermal properties of microcapsules. However, the thermal performance of the microcapsule was greatly affected by the synthetic methods.

The research objective was to study the heat transfer medium for low-temperature solar PV/T heat collection systems and took PCMs as the research object. In order to solve the problem of volatilization and leakage of PCMs during operation, the PCMs were encapsulated and a new type of MPCM was prepared by in situ polymerization with a core of docosane and a shell of titanium dioxide. In addition, the microstructure of the microcapsules was characterized, and the thermal conductivity was measured. The influences of the emulsifier type, mass fraction, ultrasonic oscillation time, solution pH value, and core–shell ratio on the thermal properties of the microcapsules were analyzed by changing single variables in the experiment, and the optimal ratio of the microcapsules was determined to achieve the optimal heat storage capacity of the microcapsules. The phase change temperature of MPCMs was approximately 40 °C, and the MPCMs can be applied in the field of low-temperature solar heat collection.

2. Experimental Method

2.1. Preparation Steps of MPCMs

The selection of wall materials and core materials can be found in Supplementary Material. Most preparation processes for microcapsules use deionized water as the reaction base fluid. However, because tetrabutyl titanate easily reacts with water, when the organic titanium dioxide precursor undergoes in situ polymerization in the emulsion, it exhibits fast hydrolysis and a high condensation rate during the sol-gel process. This is extremely unfavorable for the self-assembly of titania sol on the surface of PCM droplets. In view of this, in this experiment, formamide was used as the reaction base liquid, and a small amount of water was added to the solution to promote the hydrolysis and condensation reaction of tetrabutyl titanate. The rate of hydrolysis was controlled by the rate of drop acceleration to make the prepared core–shell structure more complete. Tetrabutyl titanate hydrolyzed in water, eventually generating hydroxide Ti(OH) and forming TiO_2 oligomer through a polycondensation reaction.

The raw materials and equipment involved in the preparation process are shown in the following Tables 1 and 2.

Table 1. List of experimental chemicals.

Raw Material Name	Chemical Grade or Purity	Manufacturer
Tetrabutyl titanate	98 wt%	Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.
Docosane	98 wt%	Shanghai Aladdin Bio-Chem., Shanghai, China.
Formamide	analytically pure	Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.
Hydrochloric acid	analytically pure	Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.
Anhydrous ethanol	99.8 wt%	Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China.
Deionized water	/	Produced in the Lab

Table 2. List of experimental equipment information.

Device	Model	Manufacturer
Magnetic stirrer	ZNCL-GS130*60	Gongyi Yuhua Instrument Co., Ltd., Henan, China.
Electronic balance	YH-A 10002	Ruian Yingheng Electric Co., Ltd., Zhejiang, China.
Ultrasonic cell crusher	SCIENTZ-IID	Ningbo Xinzhi Biological Technology Co., Ltd., Ningbo, China.
Intelligent peristaltic pump	STP-F01A Micro peristaltic pump	Carmel Fluid Technology Co., Ltd., Shanghai, China.
Oil-free diaphragm vacuum pump	YM-10A	Platinum Instruments Co., Ltd., Shanghai, China.

Figure 1 is a flow chart of the preparation method, and the steps for preparation are as follows:

1. Add a certain mass fraction of docosane to 100 mL formamide solution, put it in a water bath, and heat it at a constant temperature (75 °C) until it melts, Then, subjected it to ultrasonic oscillation so that it is evenly distributed in the form of small droplets in formamide solution, and obtain docosane emulsion;
2. Continuously stir the reaction solution kept at a constant temperature of 7 °C, and add a certain mass fraction of emulsifier to the fine emulsion of dodecane. Continuously stir magnetically for a certain amount of time at a rotational speed of 750 rpm and obtain a uniform and stable dodecane emulsion;
3. Drop hydrochloric acid into the reaction solution to adjust its pH value;
4. Continue to add a certain mass fraction of tetrabutyl titanate (TBT) solution to the reaction solution, and evenly disperse it around the emulsion droplets of doxyane by magnetic stirring;
5. Add 60 mL formamide solution containing 5 g deionized water (water mass fraction of 12%) to the reaction solution drop by drop, with a titration duration of 2–3 h. At the same time, conduct magnetic stirring, adjusting the speed to 600 rpm, which takes 5 h;
6. After the reaction, filter the solution with a vacuum pump to obtain the reaction precipitate, clean it with hot deionized water and hot anhydrous ethanol. After standing and drying for 24 h, titanium-dioxide-coated dodecane microcapsules can finally be obtained.

In this experiment, 18 samples were prepared with emulsifier type, ultrasonic oscillation time, pH, emulsifier mass fraction, and core–shell ratio as variables. All samples prepared are shown in Table 3.

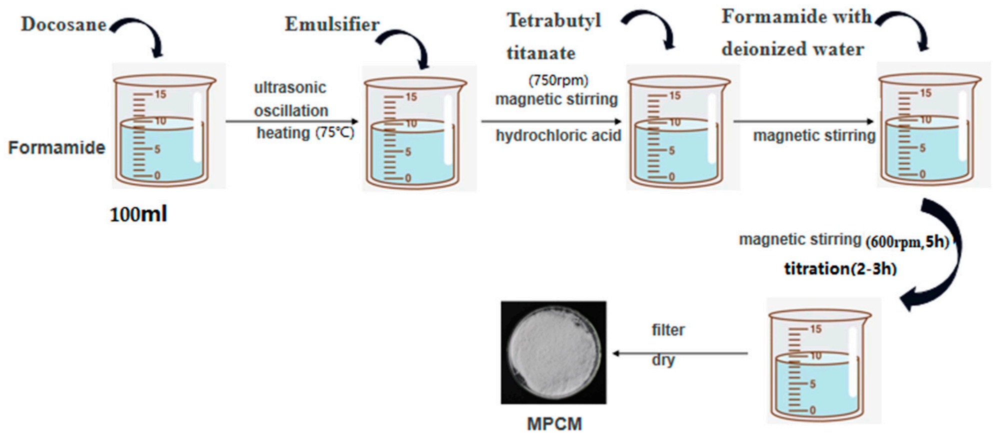


Figure 1. A flow chart of the preparation method.

Table 3. List of all samples.

Variables	Emulsifier Type	Ultrasonic Oscillation Time (min)	pH	Emulsifier Mass Fraction (%)	Core–Shell Ration
Emulsifier type	SDS/sodium alginate/OP-10	SDS	SDS	SDS	SDS
Ultrasonic oscillation time (min)	10 min	6/8/10/12	10 min	10 min	10 min
pH	4.5	4.5	2.5/3.5/4.5/5.5	3.5	3.5
Emulsifier mass fraction (%)	0.22	0.22	0.22	0.22/0.40/0.57/0.75	0.4
Core–shell ration	1:1	1:1	1:1	1:1	2:1/1:1/1:1.5

2.2. Microstructure Characterization

The success of the microcapsules' preparation mainly depends on the surface structure of the microcapsule. Consequently, it is very important to study the structure of the microcapsules. In fact, for microcapsules with excellent performance, the wall material in microencapsulation should be well-coated around the core material, which directly affects and determines the nucleation rate of the microcapsules. The most direct and effective way to judge the core material coverage rate is to observe its microscopic morphology through electron microscopy.

In this experiment, the microstructure of the microcapsules was observed by a scanning electron microscope (SEM), and the impurity and surface coating of the microcapsules were analyzed by an X-ray microanalysis system. Before testing, the surface of the MPCMs should be coated with a conductive layer. This is because the microcapsule particles are natural polymers and do not have conductive properties.

2.3. Thermal Conductivity Test

Thermal conductivity is an important indicator to assess the heat transfer performance and thermal response speed of MPCMs. If the thermal conductivity is too low, the thermal response of storing and releasing latent heat will be delayed. The application of phase change fluids prepared from materials with low thermal conductivity to solar collection systems may lead to incomplete heat absorption to reach the phase change temperature when flowing through the header, and then the incomplete phase change of the phase change fluids could reduce the energy performance of the solar collection systems. Therefore, it is of great significance to study the thermal conductivity of MPCMs.

A laser thermal conductivity instrument (LFA-427) manufactured by NETZSCH was used to test the thermal conductivity of the MPCMs. The instrument has the advantages of rapid measurement, high accuracy, and a rich variety of sample holders.

2.4. Measuring Method for Heat Storage Performance

The heat storage performance was measured with a DSC-200PC, developed by Netzsch. In this experiment, DSC tests were conducted on microencapsulated solid powder at the temperature interval −20 °C~80 °C~−20 °C at heating/cooling rates of 10 K/min. The purge and protective gas was N_2, with a flow rate of 60 L/min.

3. Results and Discussion

3.1. Microstructure of MPCMs

Figure 2 is the SEM micrograph of MPCMs observed from a macroscale perspective. The MPCMs here were prepared under the conditions of 0.40% SDS, an ultrasonic time of 10 min, pH of 3.5, and a core–shell ratio of 1:1. It shows that the MPCMs prepared in this paper were spherical with complete structures, uniform and smooth surfaces, no damage or large agglomerated particles, and well dispersed.

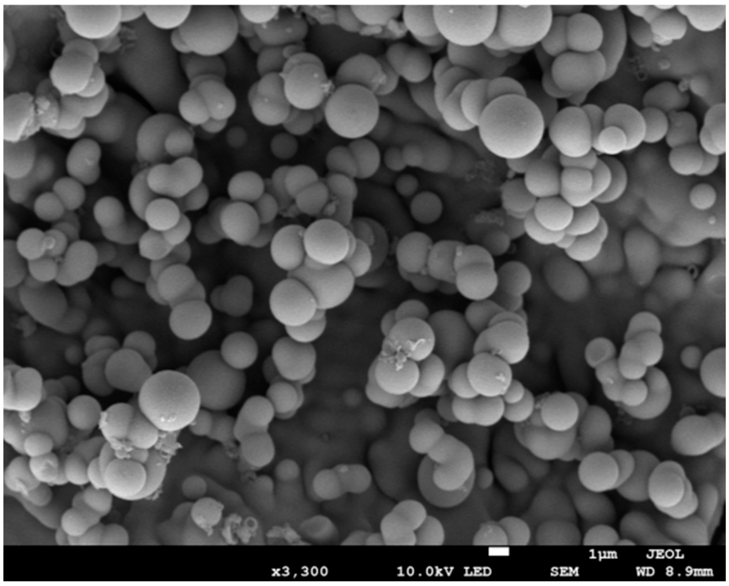


Figure 2. SEM micrograph of a macroscale perspective.

Figure 3 shows that the MPCMs had no surface unevenness with a uniform texture, and the particle sizes of the microcapsules were between 2 and 5 µm, which is in line with the particle size range of conventional microcapsules.

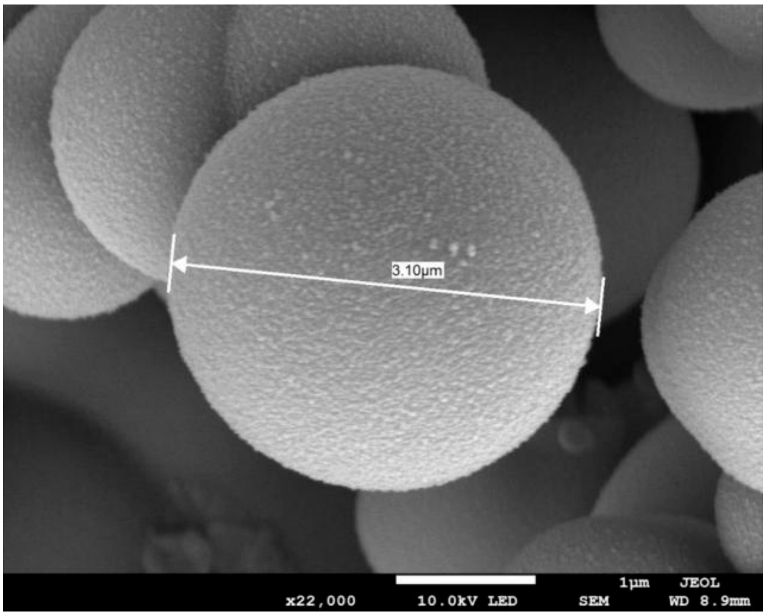


Figure 3. SEM micrograph from a microscale perspective.

Figure 4 shows the X-ray energy spectrum analysis of the MPCMs. According to Figure 4, the surface chemical elements of the MPCMs prepared only contained Ti and O. The MPCMs prepared in this paper were docosane coated with titanium dioxide, and the chemical elements contained in the titanium dioxide were Ti and O. Therefore, it can be concluded from the results of the energy spectrum analysis that the docosane in the MPCMs prepared in this paper was used as the core material and was completely coated with titanium dioxide.

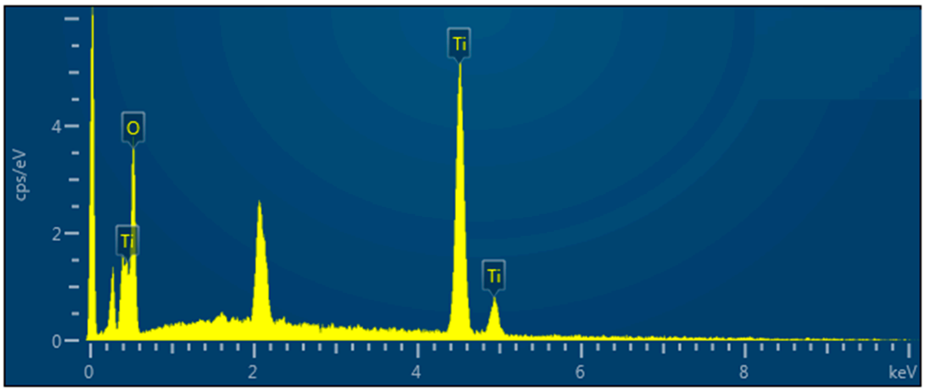


Figure 4. X-ray energy spectrum analysis of MPCMs.

3.2. Thermal Conductivity Test

Since the thermal conductivity of the prepared microcapsules is directly related to the core–shell ratio, the MPCMs with different core–shell ratios of 2:1, 1:1, and 1:1.5 were selected for testing in this experiment. The testing was conducted under three different temperatures of 25, 40, and 60 °C, respectively, corresponding to the three temperature stages before, during, and after phase change. The MPCMs here were prepared under the conditions of 0.40% SDS, an ultrasonic time of 10 min, pH of 3.5, and the results are shown in Table 4.

Table 4. Thermal conductivity of MPCMs.

Core–Shell Ratio (2:1)		Core–Shell Ratio (1:1)		Core–Shell Ratio (1:1.5)	
Temperature °C	**Thermal Conductivity W/(m·K)**	**Temperature °C**	**Thermal Conductivity W/(m·K)**	**Temperature °C**	**Thermal Conductivity W/(m·K)**
25	0.808	25	0.869	25	0.913
40	0.856	40	0.914	40	0.983
60	0.907	60	0.958	60	1.012

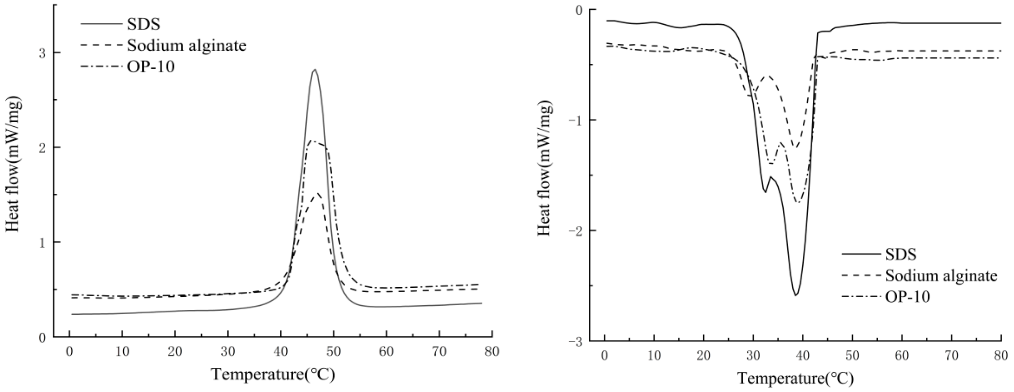
It can be seen from Table 4 that the thermal conductivities of these three MPCMs all performed well, ranging between 0.8 and 1.0 W/(m·K). The thermal conductivity of the MPCMs prepared in this experiment was significantly higher than that of several commonly used PCMs (0.1~0.3 W/(m·K) of paraffin wax, 0.22 W/(m·K) of lauric acid, and 0.20 W/(m·K) of decanoic acid). In addition, Table 4 shows that the higher the mass fraction of titanium dioxide, the higher the thermal conductivity of the prepared MPCMs. Under different temperature stages of the same MPCMs, the thermal conductivity showed a trend of increasing with an increase in the testing temperature.

3.3. The Influence of Different Variables on the Thermal Properties of MPCMs

3.3.1. Effect of the Type of Emulsifier on MPCMs

Emulsifiers are a class of compounds that can allow a mixed liquid of two (or more) immiscible components to form a stable emulsion. The principle of action is that during the emulsification process, the emulsifier is uniformly dispersed in the continuous phase in the form of nanoscale droplets. The addition of the emulsifier can reduce the interfacial tension of the components in the mixed liquid system and form a stronger film on the surface of the droplet. In addition, the electric charge of the emulsifier forms an electric double layer on the surface of the droplets to prevent the droplets from gathering together so that the droplets are evenly dispersed. To compare and test the latent heat of the phase change of MPCMs with different types of emulsifiers, the experiment uses the controlled single variable method. The types of emulsifiers added in the preparation process were (1) SDS (sodium dodecyl sulfate), (2) sodium alginate, and (3) OP-10; the mass fraction of the emulsifiers was 0.22% for all of them, the ultrasonic oscillation time was 10 min, the pH was 4.5, and the core–shell ratio was 1:1.

The samples are tested by DSC, and the results are shown in Figure 5. It can be seen from Figure 5 that the MPCMs prepared by adding three different emulsifiers all possessed the latent heat of the phase change. In the melting, the latent heat of the MPCMs with the addition of SDS, sodium alginate, and OP-10 were 91.1, 41.8, and 70.1 J/g, respectively. In the crystallization, the latent heat of the MPCMs with SDS, sodium alginate, and OP-10 added were 89.7, 42.5, and 69.8 J/g, respectively. The experimental results are shown in Table 5. From the perspective of the latent heat of the phase change, the value of latent heat is an important focus for the performance assessment of MPCMs. It can be concluded from the experimental results that the microcapsules prepared by adding SDS had higher phase change latent heat. Moreover, Figure 5 indicates that the DSC curves of the three MPCMs with different emulsifier types were basically the same. The phase change onset temperature in the melting was approximately 42 °C, and the phase change onset temperature in the crystallization was approximately 35 °C, with no obvious deviation. To summarize, SDS had a better effect as an emulsifier prepared by MPCMs. In the subsequent preparation process, all emulsifiers used were SDS.



(**a**) (**b**)

Figure 5. DSC curves of the MPCMs prepared with different emulsifiers in a ratio of 0.22%, ultrasonic oscillation time of 10 min, pH of 4.5, and core–shell ratio of 1:1. (**a**) Melting and (**b**) crystallization processes at a temperature rate of 10 K/min in a 60 L/min flow of N_2.

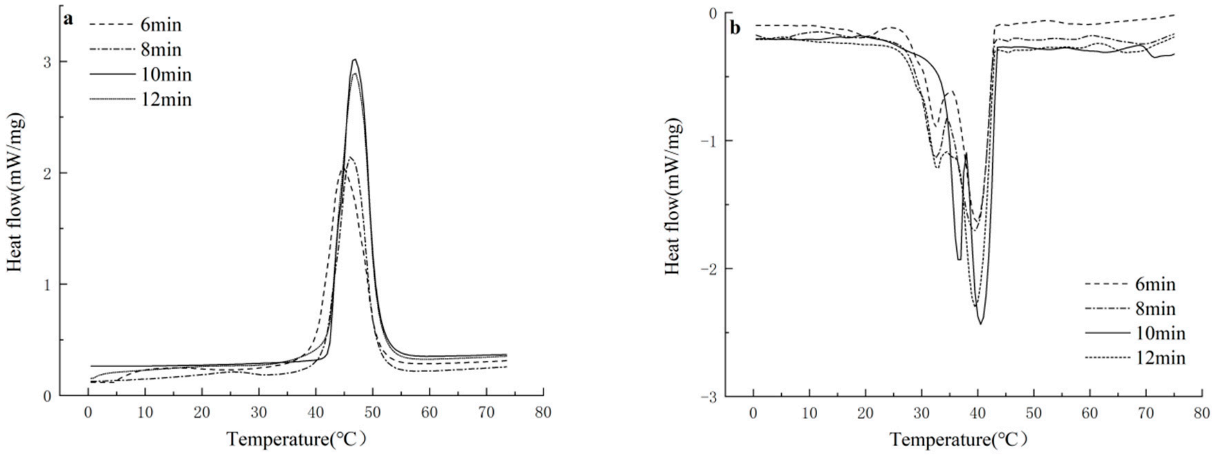
Table 5. Experimental results for changing type of emulsifier.

Variable Parameter	Melting		Crystallization	
Type of Emulsifier	**Latent Heat**	**Phase Change Onset Temperature**	**Latent Heat**	**Phase Change Onset Temperature**
SDS	91.1 J/g	42.3 °C	89.7 J/g	35.5 °C
Sodium alginate	41.8 J/g	42.1 °C	42.5 J/g	35.3 °C
OP-10	70.1 J/g	42.5 °C	69.8 J/g	35.1 °C

3.3.2. Effect of Ultrasonic Oscillation Time on MPCMs

Phacoemulsification refers to the process of mixing two (or more) immiscible liquids uniformly under the action of ultrasonic energy so that a specific liquid is evenly dispersed in another liquid. Compared with ordinary processes and other equipment, the solution after phacoemulsification is characterized by high emulsification quality, stable emulsification, stable emulsified product, and low power requirements. To determine the most suitable ultrasonic oscillation time, the ultrasonic oscillation time was changed in this study, and the ultrasonic time was tested at 6, 8, 10, and 12 min. Other experimental conditions remained the same. The type of emulsifier was SDS, the mass fraction of emulsifier was 0.22%, PH was 4.5, and core–shell ratio was 1:1.

The obtained samples were tested by DSC, and the results are shown in Figure 6. It shows that during the melting, with the extension of the oscillation time, the latent heat of the prepared microcapsules showed a growing trend. When the ultrasonic oscillation times were 6 and 8 min, the latent heat of the two MPCMs prepared were 46.2 and 66.8 J/g, respectively. When the ultrasonic oscillation time rises to 10 min, the latent heat of the phase change was 96.3 J/g, the maximum latent heat of the microcapsules obtained by four oscillation times. In addition, the latent heat of phase change with an oscillation time of 12 min was 90.3 J/g, which is basically the same as that of the microcapsule with an ultrasonic oscillation time of 10 min. The experimental results are shown in Table 6, which show that the phase change onset temperatures of the four kinds of MPCMs were also approximately 42 °C. In the crystallization, and the change rule of the phase change latent heat was basically the same as that of the melting. When the ultrasonic oscillation time was 10 min, the latent heat of the microcapsule was the largest, reaching 86.3 J/g, and the phase change onset temperature was approximately 32 °C. To summarize, when the ultrasonic time was 10 min, the latent heat of the obtained sample was higher, and the droplet size in the emulsion was ideal; not only did the emulsifier fully react to produce a better emulsifying effect, but it also had a higher nucleation efficiency, which could produce a microcapsule sample with better performance. Therefore, the ultrasonic oscillation time for the subsequent preparation processes was 10 min.



(**a**) (**b**)

Figure 6. DSC curves of MPCMs with different ultrasonic oscillation time in the SDS ratio of 0.22%, ultrasonic oscillation time of 10 min, pH of 4.5, core–shell ratio of 1:1. (**a**) Melting and (**b**) crystallization processes at a temperature rate of 10 K/min in a 60 L/min flow of N_2.

Table 6. Experimental results for changing ultrasonic oscillation time.

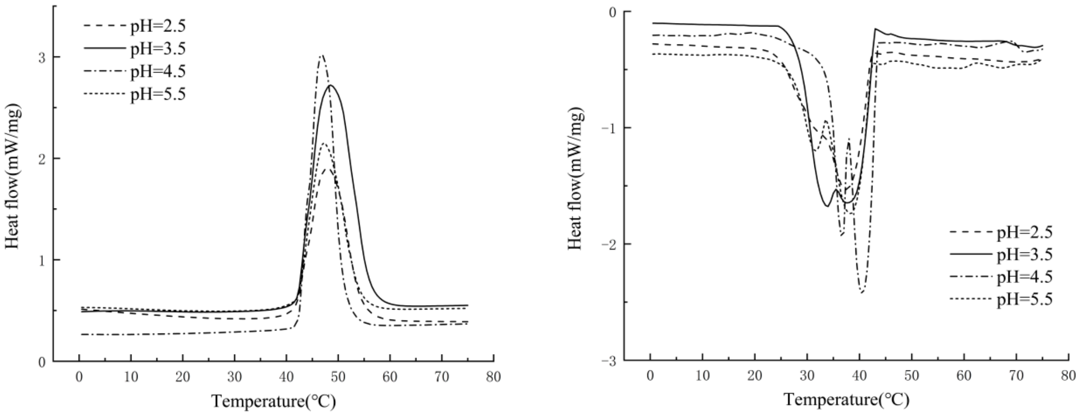
Variable Parameter	**Melting**		**Crystallization**	
Ultrasound Time	**Latent Heat**	**Phase Change Onset Temperature**	**Latent Heat**	**Phase Change Onset Temperature**
6 min	46.2 J/g	41.6 °C	45.1 J/g	31.8 °C
8 min	66.8 J/g	41.9 °C	61.3 J/g	31.6 °C
10 min	96.3 J/g	42.1 °C	86.3 J/g	32.2 °C
12 min	90.3 J/g	42.3 °C	75.1 J/g	32.1 °C

3.3.3. Effect of pH on MPCMs

The wall material of the microcapsule prepared in this experiment was titanium dioxide, and the titanium source was tetrabutyl titanate. However, due to the fact of its rapid reaction with water and intense hydrolysis reaction, tetrabutyl titanate formed n-butanol and titanium dioxide self-polymers before it had time to form the shell covering the surface of the microcapsule. Therefore, during the preparation of microcapsule samples, a large amount of white agglomerated precipitate often occurred in the solution, which led to the termination of the experiment. This may be due to the strong hydrolysis of tetrabutyl titanate during the reaction process. Titanium dioxide formed and agglomerated before it wrapped around the droplets. There are many ways to slow down the rate of hydrolysis such as by adding glacial acetic acid, ethanol, and diethanolamine. Most methods will increase the ethanol and then form titanium hydroxide and n-butanol. However, the docosane in this experiment was easily soluble in ethanol, which will affect the reaction. Therefore, this experiment adopted the method of adjusting the pH to inhibit the hydrolysis of tetrabutyl titanate using hydrochloric acid.

To study the pH of the reaction environment that can effectively control the hydrolysis of tetrabutyl titanate in this experiment, hydrochloric acid was added to the reaction solution to adjust the pH value of the reaction environment before the addition of tetrabutyl titanate and after the end of each phacoemulsification. The experimental conditions were as follows: the PH values were 2.5, 3.5, 4.5, and 5.5; the other experimental conditions were the same. The emulsifier was SDS, the mass fraction was 0.22%, the ultrasonic oscillation time was 10 min, and the core–shell ratio was 1:1.

DSC tests are carried out on the samples, and the results are shown in Figure 7, which shows that all four groups of MPCMs have phase change latent heat. In the melting, when the pH values were 2.5, 3.5, 4.5 and 5.5, the latent heat of the phase change values, respectively, were 68.4, 101.4, 96.3, and 68.8 J/g, and the onset temperatures of the phase change, respectively, were 41.9, 41.5, 41.6, and 41.8 °C. In the crystallization, when the pH values were 2.5, 3.5, 4.5, and 5.5, the latent heat of phase change values, respectively, were 68.3, 94.6, 86.3, and 69.1 J/g, and the onset temperatures of phase change, respectively, were 30.6, 31.2, 32.2, and 32.6 °C. The test data are shown in Table 7. It can be seen from Table 7 that the microcapsules showed good latent heat of the phase change when the pH values were 3.5 and 4.5, and the latent heat of the phase change was the largest when the pH was 3.5. This is because the acidic environment was not conducive to the deposition of titanium dioxide on the surface of docosane. As the concentration of hydrochloric acid increased, the shell structure covering the surface of the docosane became thinner. However, when the concentration of hydrochloric acid is too low, the morphology of the microcapsules will be affected, and the coating rate will decline. To summarize, the latent heat of the microcapsules prepared at a pH of 3.5 was high and had a complete shell structure.



(**a**) (**b**)

Figure 7. DSC curves of MPCMs prepared at different pH in the SDS ratio of 0.22%, ultrasonic oscillation time of 10 min, core–shell ratio of 1:1. (**a**) Melting and (**b**) crystallization processes at a temperature rate of 10 K/min in a 60 L/min flow of N_2.

Table 7. Experimental results for changing pH value.

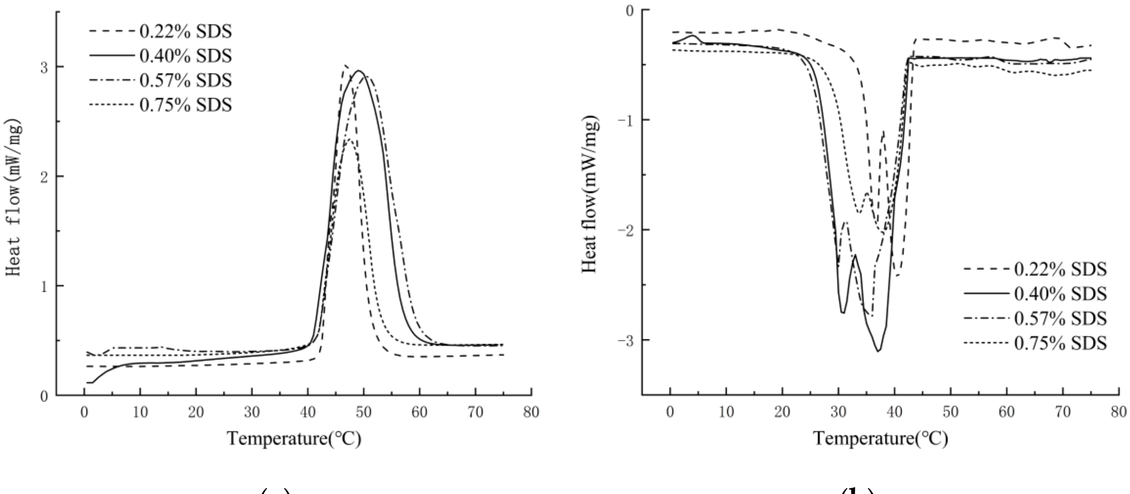
Variable Parameter	**Melting**		**Crystallization**	
pH	**Latent Heat**	**Phase Change Onset Temperature**	**Latent Heat**	**Phase Change Onset Temperature**
2.5	68.8 J/g	41.9 °C	68.3 J/g	30.6 °C
3.5	101.4 J/g	41.5 °C	94.6 J/g	31.2 °C
4.5	96.3 J/g	41.6 °C	86.3 J/g	32.2 °C
5.5	68.8 J/g	41.8 °C	69.1 J/g	32.6 °C

3.3.4. Effect of Emulsifier Mass Fraction on MPCMs

Emulsifiers can contribute to the formation of micelles in solution. The SDS activator, as an anionic activator, has two kinds of chains: oleophilic group—dodecyl chain; hydrophilic group—etheric sulfonic acid chain. The two branched chains can reduce the surface tension at the interface of oil-in-water emulsions. In addition, with the growth of emulsifier mass fraction, the surface tension of the oil-in-water emulsion decreases. Therefore, the concentration of the emulsifier in the solution has a great influence on the formation and performance of the microcapsules.

In this experiment, the emulsifier mainly adsorbs on the surface of the droplets to improve their dispersibility, so more titanium sources can be adsorbed on the surface of the droplets. When the tetrabutyl titanate undergoes a hydrolysis reaction, a uniform shell is formed to coat the docosane, which raises the nucleation rate of the microcapsules. At the same time, after dispersing the microemulsion droplets, the polymerization among the droplets can be reduced, the issue of the agglomeration of microcapsules resolved, and the particle size of microcapsules reduced. However, when the emulsifier mass fraction reaches a certain peak, the concentration in the solution also grows to the critical value of the micelle concentration. Even if the emulsifier mass fraction continues to grow, the micelle concentration will drop, instead of multiplying. In contrast, too much emulsifier may drive up the viscosity of the solution, resulting in uneven dispersion of microemulsion droplets and agglomeration. Hence, when the amount of SDS emulsifier reaches the critical value, the latent heat of the sample phase change gradually drops as its mass fraction continues to build up. To study the SDS mass fraction required to reach the critical micelle concentration, the emulsifier mass fraction was taken as the variable in this experiment. Adding 0.25, 0.45, 0.65, and 0.85 g SDS to 113.4 g of formamide solution, the mass fractions of emulsifier were 0.22%, 0.40%, 0.57%, and 0.75%, respectively. The other experimental conditions were the same. The ultrasonic oscillation time was 10 min, the PH value was 3.5, and the core shell ratio was 1:1.

The synthesized sample is tested by the DSC, and the results are shown in Figure 8 and Table 8, which hints that, when the emulsifier is added with a mass fraction of 0.22%, the prepared microcapsules have a lower latent heat of phase change compared with the other three groups. The latent heat of the phase change was 101.4 J/g during the melting, and the latent heat of the phase change during the crystallization was 94.6 J/g. Moreover, when the emulsifier mass fraction was between 0.40% and 0.57%, the latent heat of the phase change increased accordingly. When the addition amounts of SDS were 0.40% and 0.57%, the latent heat of the phase change of the microcapsules during the melting were, respectively, 166.7 and 159.7 J/g; the phase change temperatures were 42.4 and 41.9 °C, respectively; the latent heat of the phase change values during the crystallization were 119.4 and 113.4 J/g, and the phase change onset temperatures were correspondingly 31.2 and 30.4 °C. At this time, the solution almost reached the critical micelle concentration, the droplets were well dispersed, the particle size of the droplets was appropriate, the emulsifiers were all adsorbed on the surface of the droplets, the nucleation rate of the samples was high, and there was little agglomeration. After that, with the increase in the emulsifier mass fraction, the latent heat of the phase change of the microcapsules showed a decreasing trend. When the added amount of SDS was 0.75%, the latent heat of phase change in the melting and the crystallization were 97.2 and 84.6 J/g, respectively, and the phase change onset temperatures were, correspondingly, 41.9 and 31.95 °C. This is because when the emulsifier was added to the reaction solution, with the increasing mass fraction of the emulsifier, the surface tension of the docosane microemulsion droplets reduced, which in turn proliferated the coating rate of the phase change microcapsules. With the continuous growth of the mass fraction of emulsifier, when the solution reached the critical micelle concentration, the surface tension of the micelle no longer went up but dropped. Therefore, the concentration of emulsifier in solution is very important for the formation and performance of microcapsules. In summary, from the perspective of latent heat and phase change temperature, when the addition amount of SDS was 0.40%, the prepared MPCMs were optimal.



(**a**) (**b**)

Figure 8. DSC curves of MPCMs with different mass fractions of SDS emulsifier with an ultrasonic oscillation time of 10 min, pH of 4.5, core–shell ratio of 1:1. (**a**) Melting and (**b**) crystallization processes at a temperature rate of 10 K/min in a 60 L/min flow of N_2.

Table 8. Experimental results for changing the mass fraction of emulsifier.

Variable Parameter	Melting		Crystallization	
Emulsifier Mass Fraction	**Latent Heat**	**Phase Change Onset Temperature**	**Latent Heat**	**Phase Change Onset Temperature**
0.22%	101.4 J/g	41.5 °C	94.6 J/g	31.2 °C
0.40%	166.7 J/g	42.4 °C	164.2 J/g	31.2 °C
0.57%	159.7 J/g	41.9 °C	155.3 J/g	30.4 °C
0.75%	84.6 J/g	41.9 °C	79.1 J/g	31.9 °C

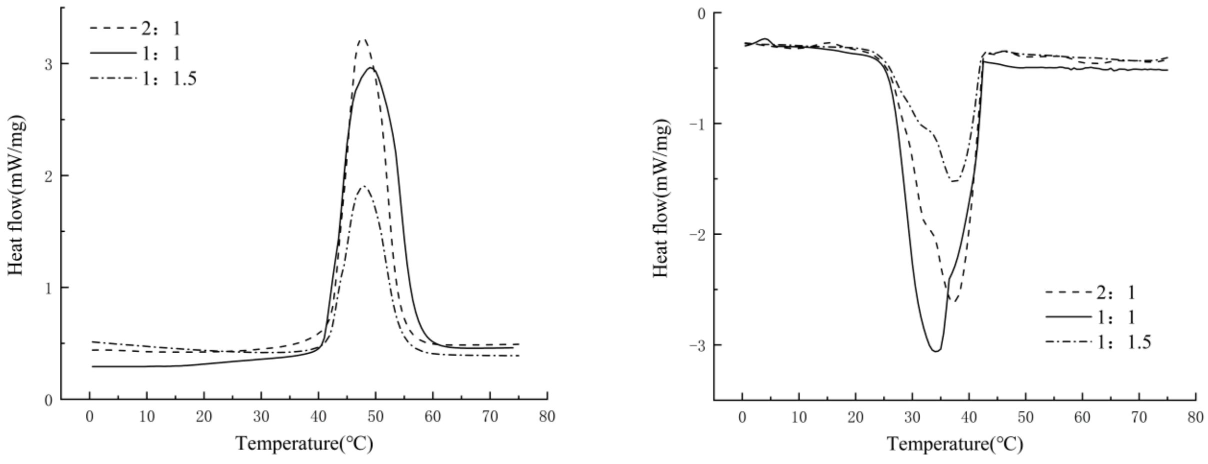
3.3.5. Effect of the Core–Shell Ratio on MPCMs

The core–shell ratio refers to the ratio of core material and wall material in the microcapsule, that is, the quality ratio of docosane and TBT added in this experiment. When the specific gravity of the shell material is high, the hydrolysis rate rises with the growth of the concentration of TBT in the solution, and the thickness of the shell material on the surface of docosane also escalates, which will inhibit the effect of the phase change material. In contrast, when the input amount of the titanium source is too low, there is not enough TBT to coat the surface of the docosane droplets, which means that the shell after the hydrolysis reaction is too thin and even may break during the preparation process, so that the nucleation rate of microcapsules is greatly reduced. Therefore, the matching scheme of the core–shell is particularly important for the preparation of microcapsules. To study the optimal core–shell ratio of microcapsules that could achieve higher nucleation rates, the core–shell ratio was used as a variable in the experiment, which were 2:1, 1:1, 1:1.5, and the other conditions were the same. The emulsifier was SDS with the mass fraction of 0.40%, an ultrasonic oscillation time of 10 min, and pH of 3.5.

As shown in Figure 9 and Table 9, the obtained samples were tested using DSC. When the ratios of docosane to titanium dioxide were 2:1, 1:1, and 1:1.5, the latent heat of the microcapsules are correspondingly 68.2, 166.7, and 132.9 J/g. The phase change onset temperatures of the three microcapsules were 41.9, 42.4, and 42.3 °C at the melting, while they were, respectively, 28.9, 31.2, and 32.9 °C at the crystallization. The obtained data demonstrate that when the core–shell ratio was 2:1, the phase change latent heat of the microcapsules was lower because there were fewer titanium sources that could hydrolyze, which led to a shortage of wall materials on the surface of the microemulsion drops. Under such conditions, the shell structure of the microcapsules easily leaks, which greatly reduces the latent heat of the PCM. When the core–shell ratio was 1:1, the latent heat of the sample grew significantly with the rising quality of TBT, indicating that with the rise of the titanium source content, the coating rate of the microemulsion droplet surface increased, the titanium source was fully utilized, and the nucleation rate of the sample improved. Moreover, when the core–shell ratio was 1:1.5, the phase change latent heat of the microcapsules showed a falling trend. This was because the high concentration of TBT in the solution accelerated the hydrolysis reaction rate of the solution, resulting in an insufficient reaction, a reduction in the microcapsule coating rate, and a decline in the latent heat. Therefore, a core–shell ratio of docosane to titanium dioxide of 1:1 was the best feeding ratio tested in this experiment.

Table 9. Experimental results for changing the core–shell ratio.

Variable Parameter	Melting		Crystallization	
Core–Shell Ration	**Latent Heat**	**Phase Change Temperature**	**Latent Heat**	**Phase Change Temperature**
2:1	68.2 J/g	41.9 °C	94.6 J/g	28.9 °C
1:1	166.7 J/g	42.4 °C	164.2 J/g	31.2 °C
1:1.5	132.9 J/g	42.3 °C	79.1 J/g	42.9 °C



(**a**) (**b**)

Figure 9. DSC curves of MPCMs with different core–shell ratios in the SDS ratio of 0.22%, an ultrasonic oscillation time of 10 min, and pH of 4.5. (**a**) Melting and (**b**) crystallization processes at a temperature rate of 10 K/min in a 60 L/min flow of N_2.

4. Conclusions

This paper reports the preparation of MPCMs suitable for low-temperature solar energy collection systems. The surface structure was observed by SEM, which showed that the MPCMs with docosane as the core and titanium dioxide as the wall material prepared by in situ polymerization had a complete structure and uniform and smooth surface. Its dispersibility was good and without impurities. The experiment tested the thermal conductivity of the phase change microcapsules. In addition, the effects of emulsifier type and quality, ultrasonic oscillation time, pH, and core–shell ratio on the thermal properties of MPCMs were studied by changing a single variable to determine the optimal ratio for better application in the heat carrying fluid of solar thermal collection system. The following conclusions are drawn:

1. The thermal conductivity of the MPCMs prepared in this experiment was significantly higher than that of several commonly used PCMs. It gradually increased with the increase in the specific gravity of the shell material and the increase in the phase change temperature;
2. Among the three groups of phase change microcapsules prepared with SDS, OP-10, and sodium alginate as emulsifiers, the MPCMs with SDS as a dispersant had better heat storage capacity. When the added amount of SDS was 0.45 g, the latent heat of phase change was 166.7 J/g;
3. The thermal properties of MPCMs prepared under four different ultrasonic oscillation times (i.e., 6, 8, 10, and 12 min) were tested. When the ultrasonic time was set to 10 min, the size of the docosane emulsion droplets was suitable, which could completely mix and react with the emulsifier, resulting in a good emulsification effect. The latent heat of phase change was 96.3 J/g, and the nucleation rate was better;
4. The effects of different pH values (i.e., 2.5, 3.5, 4.5, and 5.5) on the preparation of MPCMs were analyzed. When the pH value was 3.5, the latent heat of phase change was 101.4 J/g, and the MPCMs had a superior shell structure;
5. Three kinds of core–shell ratio (i.e., 2:1, 1:1, and 1:1.5) microcapsules were tested by DSC. When the core–shell ratio of docosane and titanium dioxide was 1:1, the latent heat of phase change was 166.7 J/g and had a good coating rate.

5. Discussion

The main objective of this study was to develop MPCMs suitable for low-temperature solar collector systems with a phase change temperature of approximately 40 °C, in addition to determining the optimal preparation conditions by studying the influence of the preparation methods on the thermal properties. In this paper, MPCMs with docosane as the core and TiO_2 as the shell were successfully prepared by in situ polymerization. Its microstructure was characterized by SEM, and its composition was analyzed by X-ray. In addition, the effects of emulsifier type, mass fraction, oscillation time, pH, and core–shell ratio on its thermal storage capacity were studied by DSC test.

The research shows that MPCMs with the required phase change temperature can be prepared by selecting suitable shell and core materials, and its thermal properties can be improved by changing the method of preparation of the material. When the emulsifier was SDS, the mass was 0.45 g, the ultrasonic time was 10 min, the pH was 10, and the core–shell ratio was 1:1, the MPCMs had better thermal conductivity and heat storage performance.

In addition, the study had some limitations. This paper only studied the effects of the emulsifier, ultrasonic time, pH, emulsifier mass fraction, and core–shell ratio on the thermal properties of microcapsules. However, the stirring mode time and experimental reaction temperature also have effects on the thermal performance [19,20], and these influencing factors were not studied in this experiment. The MPCMs have not been applied to the system for testing, and its stability and recyclable times during operation need to be further studied.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en15155354/s1. References [21–34] are cited in the supplementary materials.

Author Contributions: Conceptualization, H.C. and C.W.; methodology, L.F. and S.L.; validation, R.Z. and Y.G.; formal analysis, Y.G.; investigation, R.Z.; data curation, R.Z.; writing—original draft preparation, R.Z.; writing—review and editing, C.W.; supervision, S.L.; project administration, H.C.; funding acquisition, S.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science and Technology Project of Hebei Education Department (ZD2019032); the Basic Scientific Research Program in Colleges and Universities of Hebei Province Research projects (SYKY2001); the Key RESEARCH and Development Program Guidance Project of Cangzhou (213109007).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The work of this paper was fully supported by the projects of the National Key Research and Development Program (2016YFE0102300–08 and 2016YFC0700104) and the Beijing Advanced Innovation Center for Future Urban Design (UDC2016040200).

Conflicts of Interest: The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Li, G.; Zhao, X.; Ji, J. Conceptual development of a novel photovoltaic-thermoelectric system and preliminary economic analysis. *Energy Convers. Manag.* **2016**, *126*, 935–943. [CrossRef]
2. Alva, G.; Liu, L.; Huang, X.; Fang, G. Thermal energy storage materials and systems for solar energy applications. *Renew. Sustain. Energy Rev.* **2017**, *68*, 693–706. [CrossRef]
3. Hernandez, R.R.; Armstrong, A.; Burney, J.; Ryan, G.; Moore-O'Leary, K.; Diédhiou, I.; Kammen, D.M. Techno-ecological synergies of solar energy for global sustainability. *Nat. Sustain.* **2019**, *2*, 560–568. [CrossRef]
4. Yuan, M.; Ye, F.; Xu, C. Supercooling study of erythritol/EG composite phase change materials. *Energy Procedia* **2019**, *158*, 4629–4634. [CrossRef]
5. Yamagishi, Y.; Sugeno, T.; Ishige, T.; Takeuchi, H.; Pyatenko, A.T. An evaluation of microencapsulated PCM for use in cold energy transportation medium. In Proceedings of the 31st Intersociety Energy Conversion Engineering Conference, Washington, DC, USA, 11–16 August 1996.

6. Tan, P.; Lindberg, P.; Eichler, K.; Löveryd, P.; Johansson, P.; Kalagasidis, A.S. Effect of phase separation and supercooling on the storage capacity in a commercial latent heat thermal energy storage: Experimental cycling of a salt hydrate PCM. *J. Energy Storage* **2020**, *29*, 101266. [CrossRef]
7. Chen, Z.; Cao, L.; Shan, F.; Fang, G. Preparation and characteristics of microencapsulated stearic acid as composite thermal energy storage material in buildings. *Energy Build.* **2013**, *62*, 469–474. [CrossRef]
8. Cabeza, L.F.; Castellon, C.; Nogues, M.; Medrano, M.; Leppers, R.; Zubillaga, O. Use of microencapsulated PCM in concrete walls for energy savings. *Energy Build.* **2007**, *39*, 113–119. [CrossRef]
9. Bahrar, M.; Djamai, Z.I.; Mankibi, M.E.; Larbi, A.S.; Salvia, M. Numerical and experimental study on the use of microencapsulated phase change materials (PCMs) in textile reinforced concrete panels for energy storage. *Sustain. Cities Soc.* **2018**, *41*, 455–468. [CrossRef]
10. Mankel, C.; Caggiano, A.; Ukrainczyk, N.; Koenders, E. Thermal energy storage characterization of cement-based systems containing microencapsulated-PCMs. *Constr. Build. Mater.* **2019**, *199*, 307–320. [CrossRef]
11. Giro-Paloma, J.; Al-Shannaq, R.; Fernández, A.I.; Farid, M.M. Preparation and characterization of microencapsulated phase change materials for use in building applications. *Materials* **2015**, *9*, 11. [CrossRef]
12. Nejman, A.; Cieslak, M.; Gajdzicki, B.; Goetzendorf-Grabowska, B.; Karaszewska, A. Methods of PCM microcapsules application and the thermal properties of modified knitted fabric. *Thermochim. Acta* **2014**, *589*, 158–163. [CrossRef]
13. Nejman, A.; Cieslak, M. The impact of the heating/cooling rate on the thermoregulating properties of textile materials modified with PCM microcapsules. *Appl. Therm. Eng.* **2017**, *127*, 212–223. [CrossRef]
14. Lin, Y.; Zhu, C.; Fang, G. Synthesis and properties of microencapsulated stearic acid/silica composites with graphene oxide for improving thermal conductivity as novel solar thermal storage materials. *Sol. Energy Mater. Sol. Cells* **2018**, *189*, 197–205. [CrossRef]
15. Gao, F.; Wang, X.; Wu, D. Design and fabrication of bifunctional microcapsules for solar thermal energy storage and solar photocatalysis by encapsulating paraffin phase change material into cuprous oxide. *Sol. Energy Mater. Sol. Cells* **2017**, *168*, 146–164. [CrossRef]
16. Yang, Y.; Kuang, J.; Wang, H.; Song, G.; Liu, Y.; Tang, G. Enhancement in thermal property of phase change microcapsules with modified silicon nitride for solar energy. *Sol. Energy Mater. Sol. Cells* **2016**, *151*, 89–95. [CrossRef]
17. Wang, Z.; Qu, J.; Zhang, R.; Han, X.; Wu, J. Photo-thermal performance evaluation on MWCNTs-dispersed microencapsulated PCM slurries for direct absorption solar collectors. *J. Energy Storage* **2019**, *26*, 100793. [CrossRef]
18. Liu, J.; Chen, L.; Fang, X.; Zhang, Z. Preparation of graphite nanoparticles-modified phase change microcapsules and their dispersed slurry for direct absorption solar collectors. *Sol. Energy Mater. Sol. Cells* **2017**, *159*, 159–166. [CrossRef]
19. Xu, Y.L.; Han, X.G.; Wu, Y.B. Preparation and influence factors of microcapsules. In Proceedings of the Gansu Chemical Society Chemistry Teaching Experience Exchange Conference of Gansu Middle School, Lanzhou City College, Lanzhou, China, 23 December 2007.
20. Alberti, A.; Kappius, L.; Mantl, S. The effect of the reaction temperature on the thermal stability of polycrystalline $CoSi_2$ layers on Si (001). *Microelectron. Eng.* **2001**, *55*, 151–156. [CrossRef]
21. Gao, G.; Zhang, T.; Jiao, S.; Guo, C. Preparation of reduced graphene oxide modified magnetic phase change microcapsules and their application in direct absorption solar collector. *Sol. Energy Mater. Sol. Cells* **2020**, *216*, 110695. [CrossRef]
22. Sarı, A.; Alkan, C.; Karaipekli, A. Preparation, characterization and thermal properties of PMMA/n-heptadecane microcapsules as novel solid–liquid microPCM for thermal energy storage. *Appl. Energy* **2010**, *87*, 1529–1534. [CrossRef]
23. Delgado, M.; Lázaro, A.; Mazo, J.; Zalba, B. Review on phase change material emulsions and microencapsulated phase change material slurries: Materials, heat transfer studies and applications. *Renew. Sustain. Energy Rev.* **2012**, *16*, 253–273. [CrossRef]
24. Romero-Cano, M.; Vincent, B. Controlled release of 4-nitroanisole from poly(lactic acid) nanoparticles. *J. Control. Release* **2002**, *82*, 127–135. [CrossRef]
25. Salunkhe, P.B.; Shembekar, P.S. A review on effect of phase change material encapsulation on the thermal performance of a system. *Renew. Sustain. Energy Rev.* **2012**, *16*, 5603–5616. [CrossRef]
26. Jamekhorshid, A.; Sadrameli, S.M.; Farid, M. A review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium. *Renew. Sustain. Energy Rev.* **2014**, *31*, 531–542. [CrossRef]
27. Li, B.; Liu, T.; Hu, L.; Wang, Y.; Gao, L. Fabrication and properties of microencapsulated paraffin@ SiO_2 phase change composite for thermal energy storage. *ACS Sustain. Chem. Eng.* **2013**, *1*, 374–380. [CrossRef]
28. Zhang, H.; Sun, S.; Wang, X.; Wu, D. Fabrication of microencapsulated phase change materials based on n-octadecane core and silica shell through interfacial polycondensation. *Colloids Surf. A Physicochem. Eng. Asp.* **2011**, *389*, 104–117. [CrossRef]
29. Wang, L.-Y.; Tsai, P.-S.; Yang, Y.-M. Preparation of silica microspheres encapsulating phase-change material by sol-gel method in O/W emulsion. *J. Microencapsul.* **2006**, *23*, 3–14. [CrossRef]
30. Yu, S.; Wang, X.; Wu, D. Microencapsulation of n-octadecane phase change material with calcium carbonate shell for enhancement of thermal conductivity and serving durability: Synthesis, microstructure, and performance evaluation. *Appl. Energy* **2014**, *114*, 632–643. [CrossRef]
31. Cao, L.; Tang, F.; Fang, G. Preparation and characteristics of microencapsulated palmitic acid with TiO_2 shell as shape-stabilized thermal energy storage materials. *Sol. Energy Mater. Sol. Cells* **2014**, *123*, 183–188. [CrossRef]

32. Chai, L.; Wang, X.; Wu, D. Development of bifunctional microencapsulated phase change materials with crystalline titanium dioxide shell for latent-heat storage and photocatalytic effectiveness. *Appl. Energy* **2015**, *138*, 661–674. [CrossRef]
33. Zhao, A.; An, J.; Yang, J.; Yang, E.-H. Microencapsulated phase change materials with composite titania-polyurea (TiO_2-PUA) shell. *Appl. Energy* **2018**, *215*, 468–478. [CrossRef]
34. Cahill, D.G.; Allen, T.H. Thermal conductivity of sputtered and evaporated SiO_2 and TiO_2 optical coatings. *Appl. Phys. Lett.* **1994**, *65*, 309–311. [CrossRef]