Types of Phase Change Materials and Encapsulated Methods for Microcapsules in Cold Storage: Review and One Case Study

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ABSTRACT

The preparation of phase change materials(PCMs) provides promising solutions for the technology implementation and popularization of renewable energy in both industries of thermal and refrigeration industries. This work focuses on the low temperature PCMs using in energy storage. The cutting-edge PCMs are expected to provide flexible temperature according to the preservation temperature of application systems. Moreover, the microencapsulated PCM (m-PCM) is potential to improve both the energy storage and refrigeration system performance by decreasing the leakage of the PCM and providing a better thermal conductivity.

In this regard, this paper provides a guided technological tour on the materials selection and the preparation methods for the m-PCMs, which remains elusive in the field of low temperature energy storage. Based on the comparative analysis on the existing researches, the effects and potential of different materials and preparation methods on the thermal properties of m-PCMs were summarized and demonstrated. At last, a novel m-PCM with the n-tetradecane as core and polystyrene as shell, as well as its corresponding efficient preparation method was preliminarily proposed and tested to verify its improvement.

Keywords: phase change material, microcapsules, encapsulated method, thermal conductivity, phase change temperature, latent heat of phase transition

NONMENCLATURE

Abbreviations

PCM	Phase change material
m-PCM	The microencapsulated PCM
Symbols	
T_m	The melting temperature
$\triangle H_m$	The latent heat of melting
K	Heat conductivity coefficient

1. INTRODUCTION

The overuse of fossil fuels leads to energy and environmental crisis of which all the world makes an effort to solve it[1]. China proposes an ambitious 3060 goal to peak carbon dioxide emissions before 2030 and to achieve carbon neutrality before 2060[2]. Under such backgrounds, renewable energy has received more attention than non-renewable energy sources, due to their long-term availability, ease of access and minimal harm to the environment. However, renewable energy has the disadvantage of being unstable and cannot be continuously supplied. In this regard, the development of energy storage technologies is an urgent task to guarantee the reliable and efficient utilization of renewable energy.

Energy storage includes thermochemical storage, latent heat storage, and sensible heat storage. Latent heat storage has attracted a lot of attention because of its higher energy density and safety. Phase change materials(PCMs) are typical materials that use latent heat for energy storage. It is able to undergo phase transitions at a certain temperature, while storing and releasing large amounts of energy. The existing

researches mainly focused on the field of thermal energy storage. However, the cold energy storage attained more and more attention as the rapid development of global cold logistics industry. It is expected to store temperature-sensitive crops to guarantee the quality[3].

PCMs includes solid-solid PCMs, solid-liquid PCMs, liquid-gas PCMs, etc. Solid-liquid PCMs have been widely applied due to their large heat storage capacity and small volume change during phase transition. However, solid-liquid phase change materials is restricted in practical application due to its disadvantages such as easy leakage, poor thermal conductivity, and easy to decompose and local cooling.

Therefore, the preparation of microcapsules has been implemented, which encapsulates the PCM in a shell with a smaller diameter, usually micro- or nano-size [4]. The Microcapsules are mainly composed of two parts: PCMs as core materials and polymers or inorganic materials as shells. Microcapsules can be made into regular shapes such as spherical, tubular and oval or irregular shapes. During this way, the leakage and low thermal conductivity of PCMs can be improve significantly. The structure of microencapsulated phase change material(m-PCM) is shown in fig 1. Then, the m-PCM is dispersed in the form of powder or granules in the base solution to achieve microcapsule phase change slurry. In this way, the heat transfer characteristics could be efficiently improved[5].

In practical application, the thermal properties of microcapsules, such as phase change temperature, latent heat of phase change, thermal conductivity and other parameters, mattered greatly[6]. These parameters are mainly affected by the type of PCM, the microencapsulation method, even the types of crosslinkers, which were mainly reviewed in this paper through literature research. The research intended give a reference on the preparation of efficient, safe and low-temperature m-PCM in the cold energy storage.
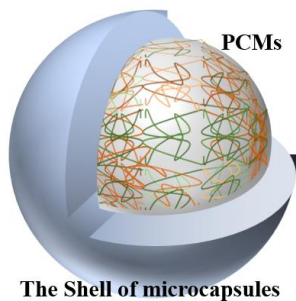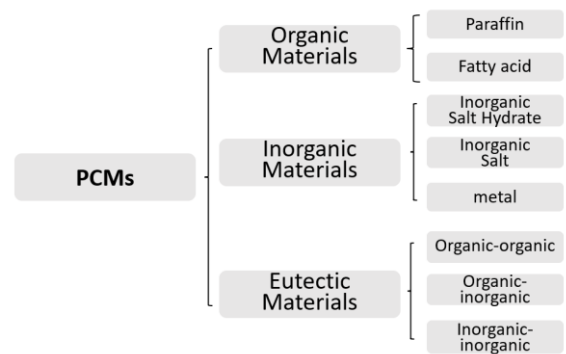

Fig. 1. The structure of m-PCM

2. TYPES OF PCM

Fig2 The types of PCM

The PCM as the core materials can be classified into organic, inorganic and eutectic materials. The specific classification situation is shown in fig 2. The classification detail is based on their ability to convert from liquid to solid. The most important feature of a PCM is that it must have a high heat storage capacity. Although inorganic materials are superior to organic materials in this respect, other disadvantages limit its use in Low temperature environment. [7].

2.1 Organic Materials

Organic PCMs are further divided into paraffin-based and non-paraffin-based. Non-paraffin bases are classified into fatty acids, sugar alcohols and polyethylene glycols respectively. Organic PCMs own a large number of advantages especially stable chemical and thermal properties. It is also non-corrosive, recyclable, able to self-nucleating in a fast rate. There is no problems with subcooling and phase separation in the application. It consequently possessed good compatibility with packaging materials, and unit weight can provide greater latent heat and lower air pressure[3]. However, they have the disadvantages of flammability, low thermal conductivity. At present, the most commonly used organic phase change materials in the market are paraffin waxes and fatty acids.

2.1.1 Paraffin

Paraffin wax (PW), as a typical medium and low temperature organic PCM, is composed of a single bond connecting carbon atoms and hydrogen atoms. Its general formula is $C_nH_{(2n+2)}$, where n represents the number of molecule C[3]. The melting point temperature of PW is related to the number of carbon atoms contained in paraffin. Usually the more carbon atoms in the paraffin chain, the higher its melting point [8]. Paraffin wax has the advantages of high latent heat of phase change. Meanwhile it has low subcooling, low vapor pressure during melting, good chemical stability. Although it is easy to occur self-nucleation, it rarely occurs phase separation and corrosiveness[9, 10]. It

usually has a melting temperature between 4.7-64 °C and a melting enthalpy of 200-220 J/g, which has been adopted as the core material of the m-PCMs. The latent heat value could reach 216.44 J/g with the gelatin and gum Arabic in water as the shell layer, when the core-shell ratio is 2: 1[11]. Sanchez-Silva et al.[12] prepared phase change microcapsules using Rubitherm RT-42 paraffin as core and polyurea formaldehyde as shell. The latent heat value of microcapsule reached the maximum 103.6 J/g.

However, pure PW has poor thermal conductivity and high leakage rate. As a result, in the actual application process, it is usually combined with expanded graphite and other nanomaterials, or encapsulated in the microcapsules with some shell materials which can offer high thermal conductivity. In order to make a high thermal conductivity PCM with better supportability and less leakage[2, 13]. Ji et al. [14] packaged PW in the titanium dioxide shell modified by graphene oxide nanosheets. The latent heat value of 160.75 J/g and the thermal conductivity of 0.297 W/m2/K were obtained. Compared to the pure paraffin wax as the phase change materials, thermal stability of the microcapsules was greatly improved.

2.1.2 Fatty Acid

Fatty acid is a long hydrocarbon chain consisting of 10-30 carbon atoms and hydrogen atoms. And its general formula is $CH_3(CH_2)_{2n}COOH$. Fatty acid is divided into saturated fatty acids and unsaturated fatty acids. Among them, the phase transition temperature of unsaturated fatty acids is lower[3]. The phase transition temperature and latent heat value of saturated fatty acids increase with the increase of carbon chain length[9] Though fatty acids have high phase transition temperature, it has high corrosion, bad smell and sublimation in the heating process. Therefore, derivatives of fatty acid esterified by alcohols and eutectic mixtures of fatty acids are used instead of pure fatty acid more. Though this method, the phase transition temperature can be regulated properly[9].

Fatty acids are divided into short chain fatty acids, medium chain fatty acids and long chain fatty acids further. Their phase transition temperature is usually related to the parity of the number of carbon atoms, arrows, double bonds and the distance of carbon chain. Common fatty acids contain heptameric acid, stearic acid, etc., with the melting temperatures of 61.3 °C and 69.6 °C, respectively. They are usually encapsulated in food microcapsules and rarely used in low-temperature energy storage applications. In this situation, the thermal property is unnecessary to be studied in this paper focused on low temperature microcapsules. A kind of new materials with silica as the shell and lauric acid as the core was prepared with a encapsulation rate of 78.6 %. The latent heat of phase transition of this microcapsules reached 186.6 J/g[15].

Table 1

Reference	PCM	Shell Material	Encapsulation efficiency(%)	T_m(°C)	ΔH_m (J/g)	K (W·m^{-1}·K^{-1})	Particle size
[16]	n-octadecane	TiO$_2$-PUA	77.3	29.66	181.1 ± 0.07	-	300 ± 100 μm
[17]	n-octadecane	SDB/MWCNT-NH$_2$	62.3 ± 0.6	30.5 ± 0.3	136.8 ± 0.8	0.285 ± 0.002	-
[18]	n-octadecane	Melamine-Formaldehyde Resin	-	26.5	160.0	-	0.1 nm to 12.3 μm
[19]	n-octadecane	polymethylmethacrylate	-	25.61	159.36	0.231570.0037	4 to 11 μm
[20]	n-tetradecane	PMMA and PS	54.5	5.0-14.8	116.9	-	20 to 250 μm
[21]	n-octadecane	Melamine–Urea–Formaldehyde	85.2	26.9	189.7	-	20.6μm
[22]	n-tetradecane	UF	85.6	2.94	171.9	-	43.2μm
[23]	Paraffin wax	Urea-Formaldehyde Resin	60.1	52	51.3	-	425.7 nm
[24]	Paraffin	polyurea Resin	91.3	-	86.6	-	32μm

2.2 Inorganic Materials

There are three types of inorganic materials: inorganic salt hydrate, inorganic salt and metal. Inorganic materials have higher latent heat per unit volume and better thermal conductivity than organic materials. Meanwhile they are often non-flammable in practical applications and usually cheaper to manufacture. However, most metals has strong corrosion, large supercooling, poor thermal stability. Worse still, phase separation tends to occur during the phase change process, which will damage the quality of the phase change process.

2.2.1 Inorganic Salt Hydrate

Hydrated salt hydrate is a crystalline, odorless, ionic substance. Inorganic salt hydrates are often described in terms of $X_nY_m \bullet aH_2O$, where X is cation, Y is anion, and a is the number of water molecules. At a certain temperature, the bond between the inorganic salt and the crystalline water will break, and at the same time, the salt will dissolve in the water, and when the inorganic salt does not melt, this temperature is also commonly referred to as the melting point of the inorganic salt hydrate.

Based on the actual situation, Li et al.[25] reviewed the methods to adjust the phase transition temperature of hydrated salts and improve the latent heat value. It is found that the main methods of controlling the temperature of phase transition are: the use of phase change temperature regulator, the encapsulation of hydrated salts, and the combination of these two methods. The main methods to control the latent heat of phase change are: adding excess water, combining hydrated salt with nanoparticles, using the limited range effect of porous matrix, etc. Both of them are regulated by changing the intermolecular and internal forces of the hydrated salt. However, because of many different functional groups on the surface of the matrix, they will have complex effects on the process of binding with hydrated salts, and this effect still has uncertain effects on the phase transition behavior.

2.2.2 Inorganic Salt

Molten salt is a molten liquid of salt, also known as an inorganic salt. Its general formula is A_xB_y, where A is a metal and B is a non-metallic or cationic complexing compound. Inorganic salt usually refers to nitrates, carbonates, chlorides, sulfates, fluorides and mixtures thereof or low eutectes. Phase transition of inorganic salt often happens at a higher temperature[3]. Meanwhile, the pure molten salt has problems of leakage and low thermal conductivity. So It is generally modified to improve its performance.

So, researchers widely used methods to make up for the flaws: core-shell encapsulation PCM and the preparation of shape-stabilized PCM by multi-skeleton materials[26]. It is found that both methods can provide better thermal performance while forming stable structure. The sol-gel method is the most promising microencapsulation technology at present. Meanwhile, the metal or alloy cannot be properly combined with the porous skeleton, so microencapsulation is a more appropriate approach.

2.2.3 Metals

Metals are made up of a large number of metal bonds that bind larger metal atoms together. Thus, it owns a higher thermal conductivity than organic materials and other inorganic materials. Because metal is usually of greater strength, more physical power is required to change the phase of the metal. Metallic phase change materials are commonly used in electronic systems. The melting temperatures of different metals vary greatly. It is mainly affected by the type of crystal. There is a decreasing relationship of the melting point between atomic crystals, ionic crystals, and molecular crystals.

The packaging of sodium nitrate was realized by using copper matrix as metal skeleton, and the performance of single metal PCM was improved[27]. At the same time, the thermal behavior of the stabilized PCM and the heat conduction of the liquid PCM through the metal matrix were numerically simulated. It was found that when sodium nitrate is in solid state, the heat transfer coefficient of stable PCM can be increased by 3.1 times compared with that in liquid state. This is because PCM with large porosity is subject to both natural convection and heat conduction, and heat conduction plays a much greater role in heat transfer than natural convection.

2.3 Eutectic Materials

A eutectic material is a group of mixtures or components with a single chemical structure[28]. Eutectic materials offer the performance advantages of combining organic and inorganic materials. Such as higher heat storage capacity per unit volume, and can be selected to meet higher latent heat values and lower subcooling. Eutectic materials' melting temperature is generally low, which can be calculated by the formula as follow. The phase transition temperature and latent heat can be regulated by selecting the appropriate PCMs[29].

$$T_m = \left[\frac{1}{T_i} - R \cdot ln \frac{X_i}{H_i} \right]^{-1}$$

where,
T_m is the melting temperature of mixture (K)
T_i is the melting temperature of the ith substance (K)
X_i is the molar fraction of the ith substance

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H_i is the latent heat of the ith substance (J·mol⁻¹)

R is gas constant (8.315 J·mol⁻¹·K⁻¹)

Wang et al.[30] prepared a low-eutectic temperature microcapsule material by encapsulating the lauric acid and stearic acid binary eutectic material as the core in the silica shell. When the encapsulation rate reached 80.98%, the phase transition temperature was 27.9 °C and the latent heat was 170.3 J/g. Compared with pure lauric acid and stearic acid binary eutectic materials, the m-PCM with silica shell coating has better thermal stability.

3. METHODS TO ENCAPSULATE PCMS

Solid-liquid PCMs are more widely used in cold chain transportation because they are more suitable for low temperature factories. However, when they appear in a molten state, the solid-liquid PCM is easy to leak because of its fluidity. In addition, PCM in this state is easy to be damaged under the action of external impact[1]. Encapsulating it in the shell structure can avoid these situation to a large extent. The selected packaging material cannot react with the PCM or interfere with its phase change process. At the same time, the shell should have good mechanical stability and good thermal conductivity. The method to encapsulate can be divided into chemical, physical and physical-chemical methods by the mechanisms of microencapsulation. Each method can be classified into different means, intended to form microcapsules with their own characteristics.

3.1 Chemical Methods

Chemical methods can provide phase-change microcapsules with higher encapsulation efficiency, smaller particle size and narrower distribution of average particle size. It is necessary to select the corresponding chemical method to complete the microencapsulation according to the mechanism of shell formation of monomer.

3.1.1 Suspension polymerization

Suspension polymerization is a kind of convenient, environmentally friendly, cost-effective and efficient polymerization method[31]. The principle of suspension polymerization is a polymerization reaction that is incompatible with water. The specific process is that one or more insoluble monomers are dispersed in a continuous aqueous phase. This process is reacting under the action of a high stirring homogenization rate and a small amount of suspension agent[32]. It is controlled by three simultaneous reaction mechanisms: particle aggregation and separation, secondary nucleation, and continuous diffusion of monomers towards the interface. The size, structure and morphology of microcapsules are affected by the interaction between monomers, polymers, phase change materials and initiators[32, 33].

Carreira et al. [34] synthesized acrylate-based microcapsules using octadecane as the core with suspension polymerization. This m-PCM was prepared by three types of initiators at different reaction temperatures. The high stability microcapsules owned melting enthalpy of 175 J/g, 70 % PCM and heat resistance temperature at 170 °C.

3.1.2 Dispersion polymerization

Dispersion polymerization is a conventional method to prepare polymer m-PCMs. The size of the resulting m-PCMs is often between a few hundred nanometers and a few microns. The dispersion polymerization reaction is restricted by different copolymers. Different copolymers will lead to different dispersion systems and different reaction behaviors.

By modifying dispersion polymerization method, a kind of polystyrene particles which can be dispersed in ethanol-water mixture at 70 °C were obtained. Then the hollow particles with bimetallic nanostructures were obtained by adding metal precursors. This material had good catalytic activity under low concentration conditions, and could be used repeatedly, which reduced the use cost while improving the efficiency[35].

3.1.3 Emulsion polymerization

The difference between emulsion polymerization and suspension polymerization is whether the initiator can dissove in the water phase. As a result, the polymerization reaction occurs in the water phase. The monomer in the droplet is first dispersed into the micelle, and then the surfactant in the water phase guides the polymerization reaction to form a microencapsulated micelle. Finally, the emulsifier need to be cleaned for removing the oil, turning out separate microcapsules[36].

Emulsion polymerization is more efficient than other chemical methods. It is mainly because the fine emulsion can be combined with ultrasonic treatment. During this way the small droplets can also be well encased in the shell material[37].

Wu et al.[37] synthesized a m-PCM with n-octadecane as the core and polymethyl methacrylate as the shell material with this method. After testing, the latent heat of phase transition of this material was 148.39 J/g, and the thermal stability temperature was 131 °C. Proving it had good performance and good heat storage performance.

3.1.4 In-situ polymerization

The PCM in the microcapsules prepared by this method does not need to add a reactive agent. The principle is that the shell is formed after the monomer is added to the reactor. Firstly, the oil-in-water emulsion is formed by mixing the oil core material with the water phase composed of the appropriate emulsifier and water-soluble shell material. Then, as the polymerization process continues, the monomer is fully consumed, the size of the prepolymer goes to grow until the solid shell is deposited[38]. Finally, the obtained m-PCMs is necessary to filtered, washed, and dried[37].

The effect of reaction temperature on the properties of m-PCMs with Rubitherm RT-42 paraffin as phase change material and polyurea formaldehyde as shell was studied[12]. It was found that the content of core material increased with the increase of reaction temperature until it reached the limit at 60-70 °C. Due to the excellent properties of paraffin, this material could be applied to different industrial scenarios, such as solar air conditioning systems.

3.1.5 Interfacial polymerization

In interfacial polymerization, hydrophilic monomers and hydrophobic monomers of the reaction system are dissolved in the water phase and the oil phase respectively. The polymerization reaction occurs at the interface of the two different phases. The hydrophilic and lipophilic monomers are rapidly polymerized to form walls at the interface of the water-in-oil emulsion. The dispersion phase is encapsulated by changes in reaction temperature and environmental PH value, thus forming m-PCMs[37].

Using lauric acid as PCM and silica as shell, a kind of phase change microcapsule with simple fabrication process, excellent thermal properties and wide application scenarios was obtained[15]. The melting enthalpy of 186.6 J/g and the encapsulation rate of 78.6 % were obtained, which improved the durability and cycle stability of PCM.

This method is mainly used to prepare m-PCMs with polyurea and polyurethane as shells. It has the advantages such as faster reaction speed and milder reaction process.

3.2 Physical Methods

The physical method is generally simple, cost-effective and suitable for large-scale manufacturing[39, 40]. Scholars have shown that spray drying method can be combined with other methods to obtain more stable mechanical properties and smaller particle size distribution. This kind of combination has a good effect on the heat dissipation performance of microcapsules in practical applications.

3.2.1 Spray drying

Spray drying is low-cost and the most commonly used physical method for encapsulating PCMs[37]. This process is consisted of three steps. It is produced by mixing the selected core material with the shell material firstly. Then spraying them into a drying chamber, the microcapsules are successfully prepared after rapid evaporation. The m-PCMs obtained by this method are uniform in size and do not have any dents or edges[11].

However, m-PCMs prepared by this simple method also have some disadvantages, such as easy agglomeration and poor coating rate[36].

Hawlader et al[11] synthesized m-PCMs by encapsulating paraffin wax with spray drying method and complex condensation method, respectively. Sets of comparative experiments shown that the m-PCMs prepared by the complex condensation method owns better thermal performance than spray drying. Follow the guidance given in this article, we can come to the conclusion that when selecting PCM from paraffins, physical methods will not be selected priority. However, why the phisical-chemical method can provide higher melting enthalpy than physical method has not been revealed from the mechanism.

3.2.2 Electrostatic method

Electrostatic method is when the polymer is forced through the spinneret under the action of an electric field to produce filaments. And then the fiber in the range of 10 mm-10 nm is produced because of the stretching action during the hardening and solidification process[41, 42].This method has the advantages of high encapsulation rate, excellent mechanical properties and easy to apply[3].

3.2.3 One-step Method

The one-step method has the advantages of simple process and easy operation. It is suitable for mass production of microcapsules.

3.3 Physical-chemical Method

Physical-chemical method is consisted of coacervation, sol-gel encapsulation and supercritical CO2 assisted method.

3.3.1 Coacervation

There are two kinds of coacervation processes: simple coacervation and complex coacervation. Both of them are the formation mechanisms of microcapsules, but they have different ways of phase separation[43].

Compared with simple coacervation, complex coacervation requires milder processing conditions. As a

result, it has lower cost and is widely used in protein gelatin and acacia polysaccharide. However, it usually leads to the dispersion of particles. Sometimes post-treatment (such as spray drying) is required. It has been proved by experiments that complex coacervation is often affected by ionic strength, PH value and charge distribution of macromolecules [44, 45].

3.3.2 Sol－gel encapsulation

Sol-gel method is a low cost, low consumables encapsulation with high functionality, durability and low pollution to the environment. It is a kind of process can produce high efficiency and high purity nano powder, fiber. Therefore, it is often used in medicine, construction and biotechnology. However, it is rarely used in the field of cold energy storage. The principle of the sol-gel method is that colloidal suspension and sol-gel are formed at the beginning. Forming a network in the continuous liquid phase later, so it can be called polycondensation as well[46].

3.3.3 Supercritical CO_2 assisted method

Supercritical CO_2 is a non-toxic, non-flammable, environmentally friendly gas with a low critical temperature at 31 °C and a critical pressure of 73.7 bar. Its property is between solid and liquid, and it can work at the temperature closing to ambient temperature. Because of its easy availability, high purity and high cost performance, supercritical CO_2 is the most widely used system in supercritical fluids. The supercritical CO_2 impregnation is to combine the oil phase and other solutes into the polymer matrix. So that it has a strong ability to dissolve different solutes and penetrate the polymer matrix.

4. CASE STUDY

Based on the literature research, a set of experiments on the effects of the crosslinking agents on the properties of m-PCMs were conducted. The in-situ polymerization was used to prepare phase change microcapsules. It is consisted of n-tetradecane as the core material and polystyrene after modified by silica sol as the shell material. The thermal properties of phase change microcapsules were adjusted by changing the proportion of crosslinker.

4.1 Materials

Tetradecane ($C_{14}H_{30}$, analytical reagent, purity $\geqslant$ 99%), Octylphenol polyoxyethylene ether (OP-10), AR, LTD. Tetraethyl silicate ($C_8H_{20}O_4Si$), 98%, LTD. Ethylene glycol dimethylallyl ester (EDMA), Gamma-methylacryloxy propyl trimethoxy-silane (KH-570), 98%, Ammonia ($NH_3 \cdot H_2O$), electronic grade, were acquired from Shanghai Macklin Biochemical Co., Methyl methacrylate (MMA), Azodiisoheptanitrile (AVBN), 98%; Sodium dodecyl sulfate (SDS), AR, sourced from Aladdin.

4.2 Synthetic method

The styrene after protreatment was mixed with copolymer, n-tetradecane, initiator and crosslinker to form oil phase, and then deionized water, SDS and OP-10 were mixed to form water phase. Then, homogenizing the oil phase with the water phase after mixing.

The white emulsion was transferred into a three-necked flask after deaeration and stirred it. After reacting for a period of time, silica sol was added. After the reaction, the white emulsion is transferred into the beaker, cooled to room temperature naturally, and sealed for storage. After the white emulsion was demulsified, the white solid obtained was phase change microcapsule after refrigeration, extraction filtration and cleaning respectively.
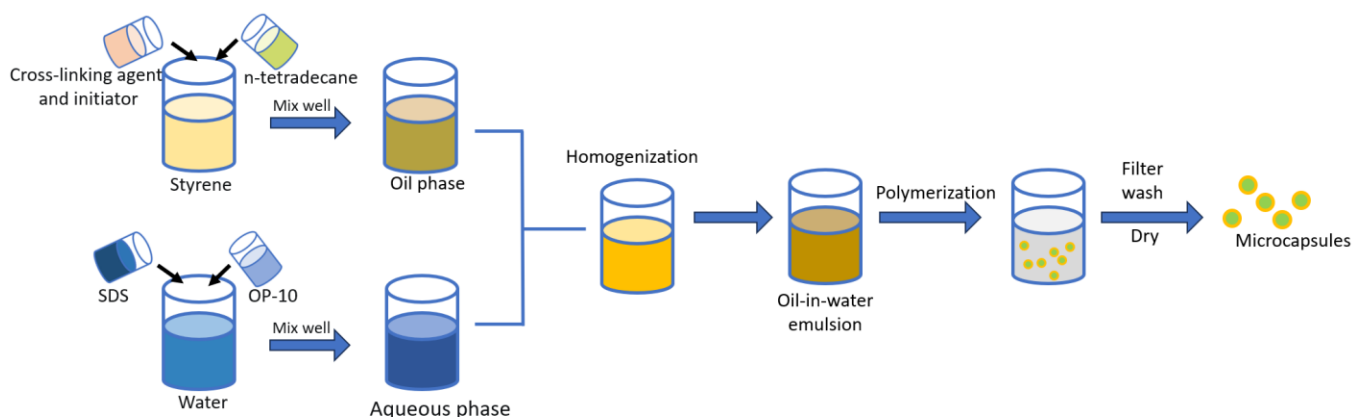

Fig. 3. The process of In situ polymerization process in case study

4.3 Results and discussion

The experimental result shows that m-PCMs could be aggregated successfully through this method. The preliminary DSC test showed that this kind of m-PCMs had melting temperature of 7.46 °C and latent heat above 130 J/g. Through investigation, it is found that this material could be used for the storage and transportation of low-temperature products. It could also be mixed with the base liquid to obtain phase change microcapsule slurry for solar cooling systems.

Through the SEM test, it could be found that tetradecane as core material can be well encapsulated in the polystyrene shell structure. The partial aggregation shown in the picture can be explained by the fact that some m-PCM is embedded in the composite polymer[47]. Meanwhile, its great static stability represented that there is almost no latent heat loss after 14 days.
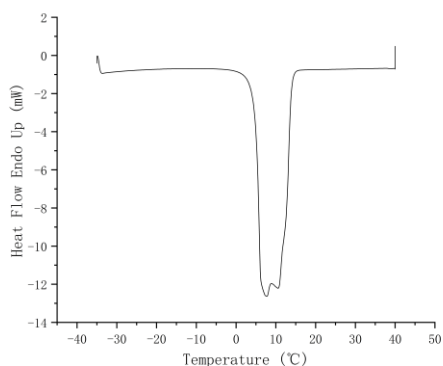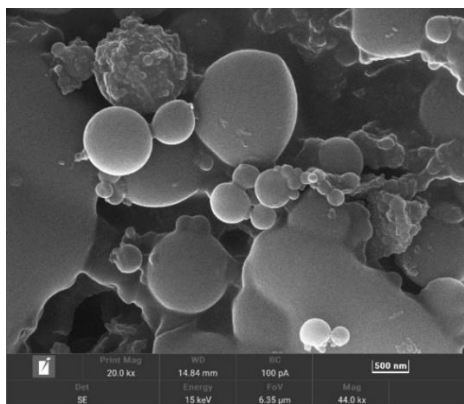

Fig. 4. The DSC curves of m-PCM

Fig. 5. The SEM observations of m-PCM

5. CONCLUSION

The preparation of phase change materials(PCMs) provides promising solutions for the technology implementation and popularization of renewable energy in both industries of thermal and refrigeration industries. Moreover, the microencapsulated PCM (m-PCM) is potential to improve both the energy storage and refrigeration system performance.

In this regard, this paper provides a guided technological tour on the PCM selection and the preparation methods for the m-PCMs, which remains elusive in the field of low temperature energy storage. PCMs can be organic, inorganic, or eutectic. Encapsulation methods are composed of physical method, physic-chemical method and chemical method. Each encapsulated method contains multifarious action mechanisms respectively. Physical method includes spray drying, electrostatic, one-step method. physical-chemical method includes coacervation, sol-gel method and supercritical CO_2 assisted method. And chemical method includes suspension polymerization, dispersion polymerization, emulsion polymerization, in-situ polymerization and interfacial polymerization.

Based on the comparative analysis on the existing researches, the effects and potential of different materials and preparation methods on the thermal properties of m-PCMs were summarized and demonstrated. At last, a novel m-PCM with the n-tetradecane as core and polystyrene as shell, as well as its corresponding efficient preparation method was preliminarily proposed and tested to verify its improvement.

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