Synthesis and Characterization of Phase Change Material Microcapsules Using Different Emulsifiers

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Abstract: In this study, a series of phase change material microcapsules (MicroPCMs) were synthesized by a core-shell-like emulsion polymerization method using different emulsifiers. The interactions between core material, shell material and dispersed medium were investigated in detail. The copolymer (PS-MAA) of styrene and methylacrylic acid and paraffin were used as wall materials and core materials respectively. High temperature interfacial tensiometer was employed to measure the interactions between different materials. Fourier transformed infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Thermogravimetry (TG), Differential scanning calorimeter (DSC) and laser particle size analyzer were used to characterize the chemical structure, morphology, thermal properties, particles size and size distribution of the MicroPCMs. The results indicated that alkylphenol polyoxyethylene (OP-10) is the optimal emulsifier in this method. The MicroPCMs prepared by using OP-10 as emulsifier displayed smooth and compact surface, the productivity was as high as 93.35%. The melting enthalpy and crystallization enthalpy were -84.6J/g and 83.5J/g, respectively. The mean particle size was 16.33μm.

Keywords: Phase change material; Microcapsules; Core-shell-like emulsion polymerization.

1. Introduction

Materials used for thermal-energy storage and release by phase change are called Phase change materials (PCMs). PCMs are very attractive energy storage materials due to the fact that they can store thermal energy nearly isothermally by undergoing a phase change and the ability to provide high energy storing density [1,2]. The most common used PCMs are paraffin waxes, eutectic materials, salt mixtures, and salt hydrates [3,4]. Organic PCMs have caused the extensive concern due to higher chemical stability, thermal stability, lacking of segregation, little supercooling and almost no corrosion problems [5]. As a typical kind of organic PCMs, paraffin waxes are safe, reliable, long-lasting, higher melting heat, chemically inert, non-corrosive, non-toxic, no phase segregation, commercial availability and low cost [3,6]. However, paraffin waxes are not easy to handle during using because of the leakage and volume change caused by solid-liquid phase change [7]. In addition, these bulk PCMs have an interfacial combination problem with matrix materials and they also suffer from a low thermal conductivity [8]. Those shortcomings reduced the performance of heat energy storage and thermal regulation during the melting and solidification cycles and restricted their applications.

Microencapsulation of PCMs is an effectively method to broaden their applications [9,10]. Microencapsulation can not only solve the problem of volume change during solid-liquid phase transition [11], but also prevent PCMs from being exposed to the external environment. Up to now, some attempts have been done to develop a cheap and technically easy process for the encapsulation of PCMs. The most common used methods including interfacial polymerization [12,13], emulsion polymerization [14,15,16], situ polymerization [17,18], spray drying [19], coacervation [20,21], sol-gel [22,23] and suspension polymerization [24 25].

The polymer shell materials play an important role in controlling the surface morphologies, thermal storage capacities, thermal stabilities and temperature-regulated properties of MicroPCMs [26]. Copolymer shells have more research values because the properties can be regulated by changing their macromolecule [27]. Qiu et al. [24,26,28,29], employed the copolymer of butyl acrylate (BA), butyl methacrylate (BMA), lauryl methacrylate(LMA) and stearyl methacrylate(SMA) and MMA as shell materials to fabricate MicroPCMs. They prepared MicroPCMs with p(n-butyl methacrylate-co-methacrylic acid), acrylic-based polymer and different n-butyl methacrylate-based copolymer as shell materials and n-alkane, n-octadecane as core materials, respectively. The results indicated that MicroPCMs with MMA-based copolymer, acrylic-based copolymer and BMA-based copolymer as shells, especially crosslinked copolymer shells, showed excellent potentials thermal energy storage. J.Giro-Paloma et al.[14] synthesized two different types of microcapsules employed poly (styrene-co-ethylacrylate) (PScEA) as shell materials via an emulsion polymerization. Mechanical characterization of the prepared microcapsules was performed exhaustive by using the Atomic Force Microscopy. The results confirm that when paraffin was used as core material, the Young 's modulus and force applied to break the microcapsules are similar at different temperatures. The microcapsules prepared by using palmitic acid as core material have different mechanical behavior at different temperatures. From aforementioned we can see the present studies are focused on the modification of core and shell material, and the optimization of process conditions. Seldom researches pay attention to the interaction between core material, shell material and phase medium.

In this paper, we took a facile method to encapsulate paraffin with copolymer PS-MAA using a core-shell-like emulsion polymerization, and investigated the influence of emulsifier on the productivity, morphology, structure, enthalpy, and particle size distribution on the prepared MicroPCMs by measured the interactions between core materials and disperse medium, shell material and disperse medium accurately. On the other hand, we tried to wrap the paraffin in solid state. The liquid paraffin dispersion was first prepared and then cooled down to room temperature to form water-based latex containing solid paraffin particles coated with emulsifier. The shell monomers mixture was added to the disperse system and enriched on the surface of the paraffin particles under the mechanical agitation. In this study, we also tried to research the interactions between core materials and disperse medium, shell material and disperse medium accurately. In order to achieve this aim, alkylphenol polyoxyethylene (OP-10), Tween80, sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium chloride (CTAC) were chosen as emulsifiers.

2. Experiment

2.1 Materials

Styrene (St, AR) alkylphenol polyoxyethylene (OP-10, CP) were purchased from Tianjin Fuchen Chemical Reagent Co., Ltd.. Methyl acrylic acid (MAA, AR), Sodium dodecyl sulfate (SDS, CP), Tween80 (AR), Cetyl trimethyl ammonium chloride (CTAC, CP) and Paraffin waxes (melting point is between 48 and 52) were purchased from Sinopharm Chemical Reagent Co.,Ltd and used as received without further purification. Azodiisobutyronitrile (AIBN, CP) was also supplied by Sinopharm Chemical Reagent Co.,Ltd and it was purified before using.

2.2 Preparation of MicroPCMs

The microencapsulated paraffin was fabricated through core-shell-like emulsion polymerization. The procedure included three steps. First, the emulsion of core material, 0.5g emulsifier was dissolved in 60ml deionized water and stirred well, transferred them to a three neck flask which was equipped with a agitator, add 15g paraffin and heat them to 75℃, after the paraffin melted, emulsified them mechanically with a stirring rate of 1000rpm for half an hour. Second, shell monomers wrapped on the surface of the core material, transferred the emulsion paraffin to a four neck flask equipped with an oil thermostat bath, a reflux condenser and a nitrogen gas inlet tube and continued mechanical raking with a stirring rate of 1000rpm for a moment until the paraffin solidification with the protection of nitrogen, added the mixture of 10g of St, 3g of MAA and 0.195g of AIBN drop-wise to the emulsion paraffin. Last, the polymerization of the shell materials, after added the shell materials, heated up the system to 75° to initiate the polymerization and adjusted the stirring rate to 400rpm, the polymerization maintained for 6h. The oil bath was then switch off and allowed to cool down naturally to room temperature. After cooling, the suspension of MicroPCMs were transferred to a clean glass beaker and washed three times with boiling water to remove the unreacted monomers and the uncoated paraffin. The separated MicroPCMs were spread on a tray and placed in an oven at 40℃for 24h for drying. The dried MicroPCMs were then collected for testing.

2.3 Characterization of MicroPCMs

High temperature interfacial tensiometer (Bruker DSA100, Bruker Co., Ltd.,Germany) was used to measure the contact angle and interfacial tension, the contact angle measured by sessile drop method and interfacial tension measured by pendant drop method.

Fourier Transform Infrared Spectroscopy (FTIR, Bruker Tensor27, Bruker Co., Ltd.,Germany)was used to determine the FTIR spectra of paraffin, PS-MAA and MicroPCMs. The samples were mixed with KBr and pressed into pellet. The FTIR spectra in absorbance mode were recorded among the range of 500-4000cm-1.

Scanning Electron Microscope (SEM, JEOL JSM-7500, Japanese electronics Co., Ltd.,Japan)was used to observe the morphologies and structures of MicroPCMs. All samples were coated with a layer of gold prior to the observation.

Thermogravimetric(TG, Netzsch TG209F1, Netzsch Instruments Ltd., Germany)was used to characterize the thermal stabilities of paraffin, PS-MAA and MicroPCMs. The heating temperature and rate were of 30-600℃

and 5℃/min in nitrogen atmosphere.

Differential Scanning Calorimeter (DSC, EXSTAR DSC6200, NSK LTD., Japan)was used to measure the thermal storage properties of paraffin, PS-MAA and MicroPCMs. The test temperature was in the range of 0-80℃ at a heating or cooling rate of ±5℃/min in a nitrogen atmosphere.

Laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd.,UK)was used to determine the particle size distribution (PSD) of MicroPCMs. In such analysis, a small sample of suspended MicroPCMs was dispersed into deionised water bath. The PSD curves were directly given by the instruments.

3. Results and discussion

3.1 The interfacial tension and contact angle

The fabrication schematic of the microcapsules is shown in Fig.1.The most important step is the shell mononers wrap on the surface of paraffin particles. The interfacial tension between shell monomers and disperse phase, the contact angle between disperse phase and paraffin will influence the wrap and then influence the encapsulation efficiencies, morphologies and thermal properties of MicroPCMs.

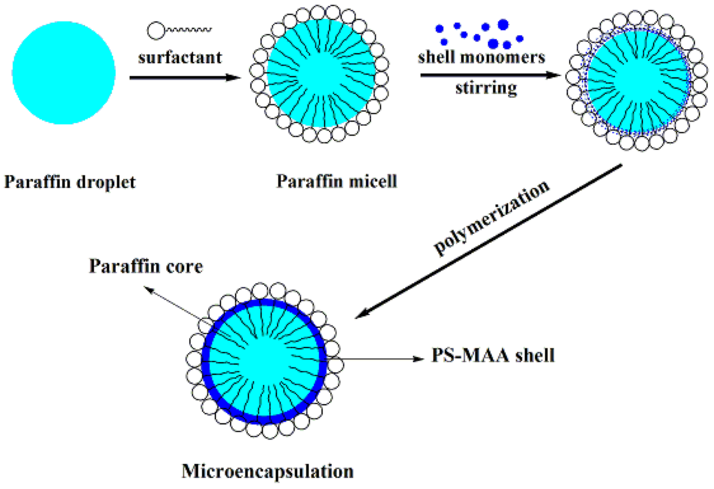

Fig.1.Formation schematic of the MicroPCMs

The interfacial tension between emulsifier aqueous solution and shell monomers, contact angle between emulsifier aqueous solution and paraffin and corresponding productivity are listed in Table 1. The productivity was calculated by the formula (1):

$$\text{Productivity} = \frac{m_{MicroPCMs}}{m_{Paraffin} + m_{St} + m_{MAA}} \quad (1)$$

Where $m_{MicroPCMs,}$ $m_{Paraffin,}$ m_{St} and m_{MAA} are mass of dried MicroPCMs, Paraffin, Styrene and Methyl acrylic acid, respectively.

Table: 1. The interfacial tension, contact angle and productivity

Aqueous solution	Contact angle	Interfacial tension	Productivity
SDS	51.0°	10.30mN/m	51.32
OP-10	43.2°	7.16mN/m	93.35
Tween80	58.5°	12.27mN/m	70.67
CTAC	66.4°	14.14mN/m	/

Note: / denotes the preparation is unsuccessful

The data in Table 1 indicates that the productivities of MicroPCMs were greatly influenced by the type of emulsifier. On the whole, the productivities are higher when the nonionic emulsifiers were used, when the anionic emulsifier SDS was used the productivity is lower and when the cationic emulsifier CTAT was used the encapsulation is unsuccessful. The SDS, as an anionic surfactant, can produce negative charge in the aqueous solution and adsorb to the surface of paraffin particles to form protective layer with negative charge, which are benefit to the dispersion between the particles. But the existence of negative charge on the surface of paraffin particles repelled the enrichment of monomers and oligomer of MAA and St to the surface of paraffin to form compact capsule wall because MAA and oligomer of MAA and St carried negative change in aqueous solution. And the initial enrichment of monomers to the surface of paraffin was more important to the forming of MicroPCMs. So more monomers polymerized in disperse phase and not on the surface of paraffin, this led to the lower productivity of MicroPCMs. In the system with cationic emulsifier CTAT, when the electronegative shell monomers were added and under the stirring the CTAT were attracted on the surface of shell particles. Therefore, the shell monomers polymerization and paraffin phase separated from the system. When the non-ionic emulsifiers were used, the encapsulation did not influenced by electric charge interaction, after the shell monomers were added they wrapped on the surface of the emulsified emulsion paraffin particles more easily. As can be seen from Table1, the contact angle and interfacial tension of OP-10 is smaller than Tween80, this indicates the emulsion efficiency of OP-10 is higher than Tween80 on the same content. Therefore, the productivity of OP-10 is higher than Tween80. From the above analysis we can say that the productivity was great influenced by the interaction between core material, shell material and dispersed phase.

3.2 Chemical characterization

FTIR spectra of Paraffin, PS-MMA and MicroPCMs were shown in Fig.2. The spectrum of paraffin has a typical multiple strong absorption peaks between 2850cm^{-1} and 2950cm^{-1}. The peaks are the symmetric and asymmetric stretching vibration of -CH$_2$ and -CH$_3$ groups [30,31]. The absorption peak appears at 1467 cm^{-1} representing the unsymmetrical bending vibration of -CH$_3$ and scissors bending vibration of -CH$_2$ in aliphatic chain. The absorption peak appears at 1378cm^{-1} corresponding to the symmetric stretching vibration of and -CH$_3$ in aliphatic chain. The strong absorption peak appears at about 720cm^{-1} corresponding to the in-plane bending vibration and characterizes that the alkane chains have more than four methylenes [22,32].

FTIR spectrum of PS-MAA has a typical multiple weak absorption peaks between 3100cm^{-1} and 2900cm^{-1} which indicates unsaturated C-H stretching vibration on the benzene ring. The strong absorption peaks appear at 699cm^{-1} and 758 cm^{-1} are out-plane deformation vibration of H on benzene ring, which is the characteristic peak of mono-substitution benzene ring. Strong peak appears at 1698cm^{-1} corresponding to the blue shift stretching vibration of C=O, and the weak absorption peak appears at 1400 cm^{-1} corresponding to stretching vibration of O-H. These peaks indicate the existence of carboxyl group [16,25,33]. From the above analysis we could surely come to the conclusion that the shell is the copolymer between St and MAA.

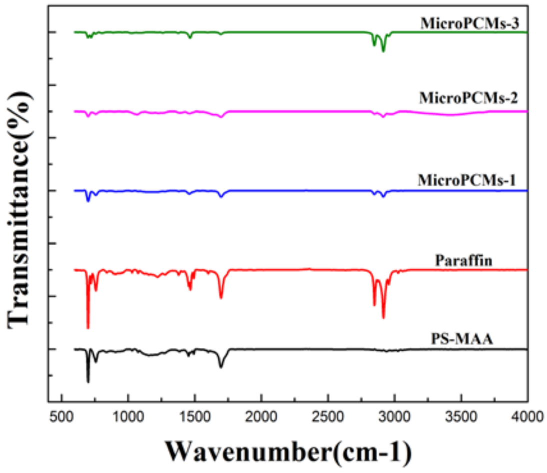

Fig.2. FTIR spectra of paraffin, PS-MMA and and MicroPCMs prepared with different emulsifier: MicroPCMs-1,OP-10; MicroPCMs-2,Tween80; MicroPCMs-3,SDS

All characteristic peaks of paraffin and PS-MAA can be found in the FTIR spectrum of MicroPCMs, and there is no addition peaks appear, therefore paraffin and PS-MAA are coexisted in the microcapsules and no chemical reaction between core materials and shell materials.

3.3 Morphology of MicroPCMs

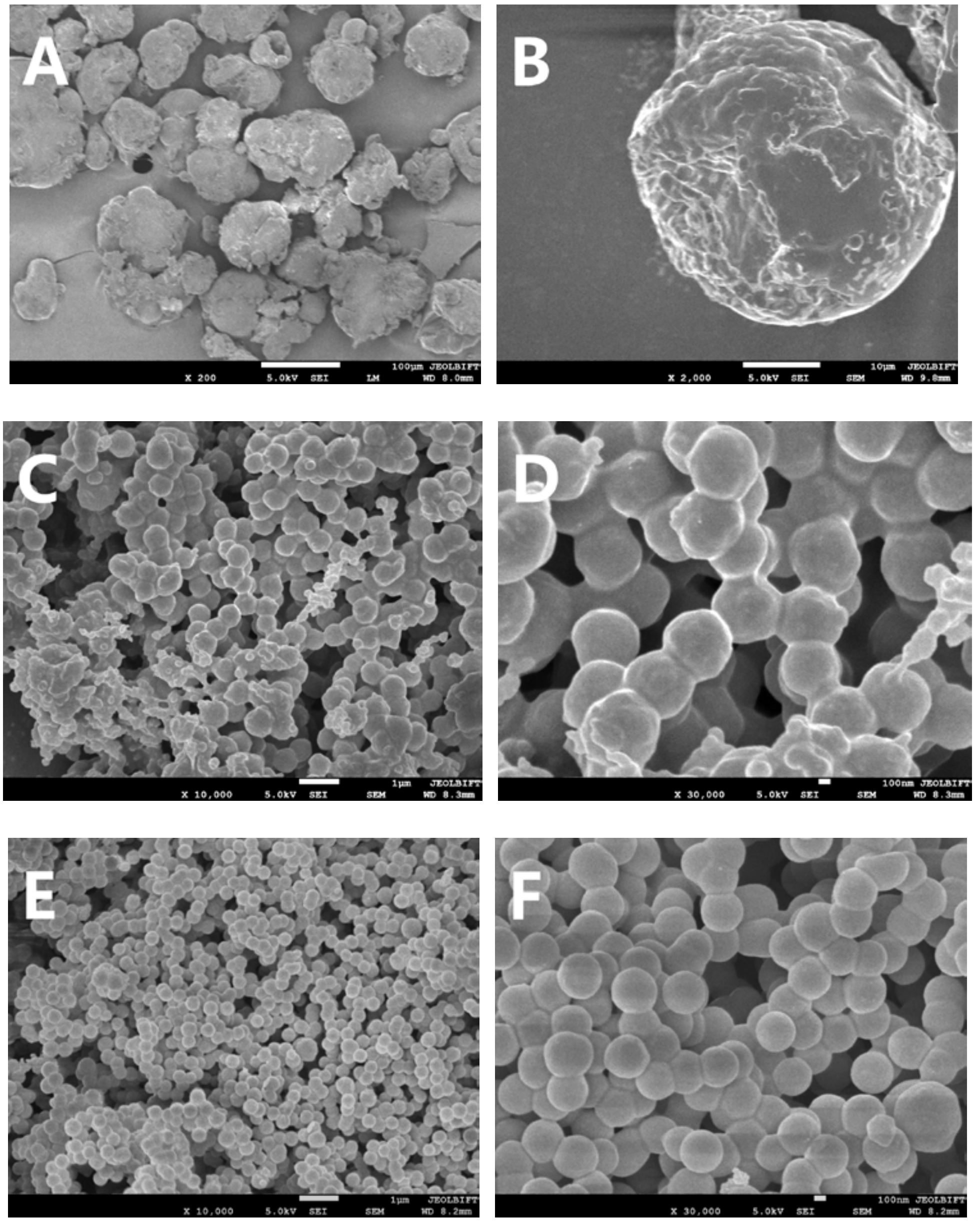

Fig.3. Morphologies of the MicroPCMs prepared with different emulsifier. A and B,SDS; C and D,Tween80; E and F,OP-10.

The SEM photographs of MicroPCMs prepared using different emulsifiers were illustrated in Fig.3. As can be seen from these images, the capsules prepared using SDS as emulsifier show irregular blocks profile, the capsules using Tween80 and OP-10 as emulsifiers have spherical profile with fairly uniform structure and compact surfaces, but adhered to each other and aggregated to some extent, which result in a large mean diameter in PSD curves. The capsules synthesized by using OP-10 as emulsifier have the most perfect surface morphologies, which maybe the result of stability of the emulsion system of OP-10 [18]. Combining with the above analysis of contact angle and interfacial tension, we induces that the when nonionic emulsifiers OP-10 and Tween80 were taken, the mixture of shell monomers spread on the surface of core materials and then polymerization. While SDS was taken as emulsifier, owing to the electronegativity and polarity between MAA and SDS, the polymerization between shell monomers occurred first and then the polymer adhered to the surface of core materials. When CTAC were used as emulsifier, the interfacial tension between shell mononers and disperse phase was the biggest, the monomer droplets were more easily separated from disperse phase, therefore under the mechanical agitation they were more easily miscibility to paraffin particles, after the polymerization the

PS-MAA separated from the paraffin and lead to the synthesis unsuccessful. When the contact angle and interfacial tension are big, shell materials are compatible to the core materials instead wrap on the surface of core materials.

3.4 Thermal stability of MicroPCMs

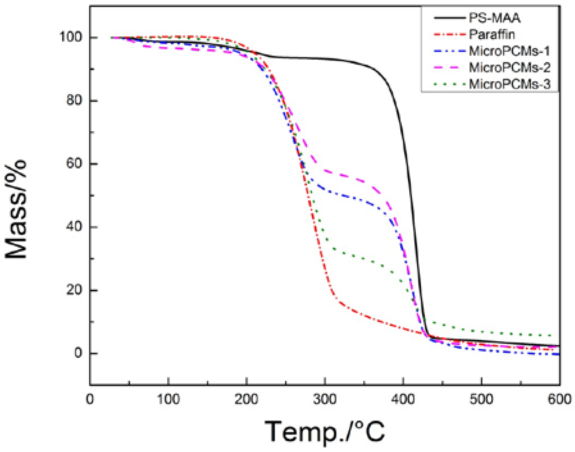

Fig.4. TG curves of paraffin, PS-MMA and MicroPCMs prepared with different emulsifier: MicroPCMs-1,OP-10; MicroPCMs-2,Tween80; MicroPCMs-3,SDS

TG degradation curves of the Paraffin, PS-MAA and MicroPCMs were shown in Fig.4. Paraffin starts to lose weight at approximately 190°C, and completely loses its weight at about 300°C. The TG curve of paraffin is sharp and one step because it is composed of linear alkane molecules with a lower decomposed temperature [16]. The degradation curve of PS-MAA is also one step between 350°C and 420°C. However, all curves of MicroPCMs are two step with quite similar. The first stage from 190°C to 300°Ccorresponding to the gasification of phase change material [33], and the second from 350°C to 420°C corresponding to the decomposition of PS-MAA.

Based on the first stage, the percentage of phase change materials in three different were approximately 45%, 50% and 70%, respectively.

3.5 Thermal properties of MicroPCMs

The content of PCM in microcapsules is an important factor for MicroPCMs, and it directly determines the phase change enthalpy and energy storage efficiency [34]. The DSC curves of paraffin, PS-MMA and MicroPCMs are shown in Fig.5 and the specific data are listed in table 2.

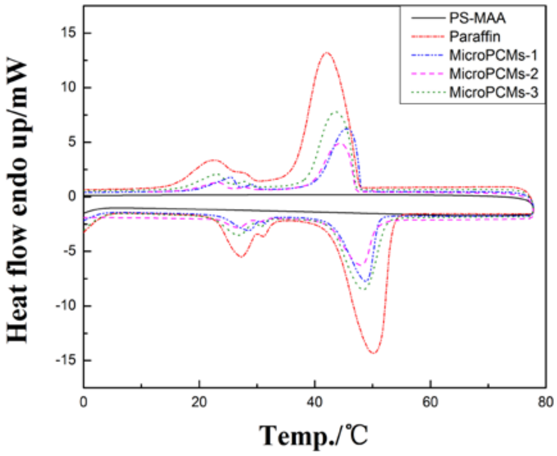

Fig.5. DSC curves of paraffin, PS-MMA and MicroPCMs prepared with different emulsifier: MicroPCMs-1,OP-10; MicroPCMs-2,Tween80; MicroPCMs-3,SDS

Table: 2. Thermal property of MicroPCMs

Sample	T_{pm}/°C	ΔH_m（J/g）	T_{pc}/°C	ΔH_c（J/g）	PCM content/%
paraffin	50.1	-161.0	42.4	159.1	100
MicroPCMs-1	48.4	-84.6	43.5	83.3	52.5
MicroPCMs-2	48.1	-62.2	44.5	58.6	37.7
MicroPCMs-3	48.8	-106.7	45.5	105.6	66.3

Note: T_{pm} is melting point, ΔH_m is melting enthalpy;T_{pc} is crystallization point, ΔH_c is crystallization enthalpy.

As Fig.5 shown, the PS-MAA has no phase change behavior in the test range. Therefore, the content of paraffin within the MicroPCMs can be calculated by the following formula [35]:

$$\text{paraffin contant} = \frac{\Delta H_{\text{m, MicroPCMs}} + \Delta H_{\text{C, MicroPCMs}}}{\Delta H_{m,\ PCMs} + \Delta H_{c,\ PCMs}} \tag{2}$$

Where $\Delta Hm_{,MicroPCMS}$ and $\Delta Hc_{,MicroPCMS}$ are melting enthalpy and crystallization enthalpy of MicroPCMs, respectively; $\Delta Hm_{,PCMS}$ and $\Delta Hc_{,PCMS}$ are melting enthalpy and crystallization enthalpy of PCMs, respectively.

As Fig.5 shown, all DSC curves have two peaks, the main peak represents solid-liquid phase change of paraffin and the minor peak may correspond to solid-solid phase transition of paraffin [36,37,6,38]. Therefore, the minor peak will be neglected in the following analysis. As can be seen from Fig.5, the MicroPCMs with OP-10, SDS and Tween80 as emulsifiers have the similar curves to pure paraffin, which indicates the encapsulation did not influence the properties of paraffin. Table 2 shows that the MicroPCMs prepared using SDS as emulsifier have the largest paraffin content 66.3. While for the Tween80, the paraffin content in the lowest, only 37.7%. The paraffin content of MicroPCMs prepared by using OP-10 as emulsifier almost the similar to its content in raw materials. The results indicate that the type of emulsifier has great influence on the process of encapsulation and the encapsulation efficiency of paraffin using PS-MAA as the shell material through core-shell-like emulsion polymerization. The enthalpy of and paraffin content of MicroPCMs-1 is the highest, but its productivity is the lowest. Therefore, OP-10 is the optimal emulsifier in this method.

3.6 Particle size distribution of MicroPCMs

The application of MicroPCMs strongly depends on the particle size and size distribution (PSD) [38]. The PSD of the microcapsules prepared by using different emulsifier distribution curves were shown in Fig.6 and the specific data are summarized in table 3.

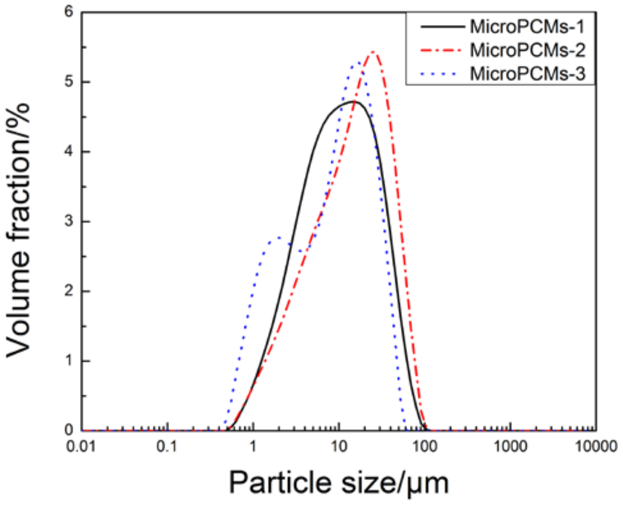

Fig.6. PSD curves of MicroPCMs prepared with different emulsifier: MicroPCMs-1, OP-10; MicroPCMs-2,Tween80; MicroPCMs-3,SD

Table: 3. PSD of MicroPCMs

	Particle size range/μm	Average particle size/μm	PSD index
MicroPCMs-1	0.48-104.71	16.33	1.01
MicroPCMs-2	0.51-112.54	21.47	0.888
MicroPCMs-3	0.41-54.12	12.95	0.949

As can be seen from Fig.6, all MicroPCMs show wide distribution, the size distribution curves of MicroPCMs-1 and MicroPCMs-2 are singlet and particle sizes are larger than single microcapsule, this indicates there exist sever aggregation among particles, which also can be seen from Fig.2. The particle size range of MicroPCMs-3 is the narrowest and average particle size is the smallest, but as Fig.2 shows there is little agglomeration among particle, therefore, the MicroPCMs prepared by using SDS as emulsifier distributed unevenly. Although the particle sizes are large and particle size ranges are wide, they can be applied to certain fields [39].

4. Conclusion

Microcapsules containing paraffin with PS-MAA copolymer shell were fabricated by a core-shell-like polymerization method. OP-10, Tween80, SDS and CTAC were employed as emulsifiers. The contact angle between dispersed medium and core material, the interfacial between shell material and dispersed medium were measured in detail. The emulsifier had great influence on the productivity, morphology and enthalpy of the prepared MicroPCMs, but had litter influence on the thermal properties and phase-transition temperature. The OP-10 was the optimal emulsifier in this method.

5. References

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