# CLIMA 2016 - proceedings of the 12th REHVA World Congress

*volume 9*

Heiselberg, Per Kvols

*Publication date:*
2016

*Document Version*
Publisher's PDF, also known as Version of record

# Characteristics of Microcapsulated Phase Change Material Used in Auto Internally-Cooled Liquid Desiccant System

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**Abstract**
*To improve the performance of the liquid desiccant system, a novel method is proposed by adding microcapsulated phase change materials (MicroPCMs) in the desiccant solution, which is expected to restrain the temperature rise in the moisture-removal process, and then the auto internally-cooled dehumidification will be achieved. The MicroPCMs to be used in auto internally-cooled dehumidification, with melamine-formaldehyde polymer as shell and liquid solid mixture paraffin as core, was prepared by in-situ polymerization method in this paper. The effects of the types and contents of emulsifier on the diameter, morphology and phase change performance of the MicroPCMs were studied by using electron scanning microscopy (SEM) ,laser particle size analyzer and differential scanning calorimeter (DSC). The results showed that, when the compound emulsifier mixture of Span80 and Tween80 in proportion of 1:1 is used, and the content of the emulsifier is 60 % of the core material, the micro-shape of the prepared microcapsule with stirring rates of 1000 r/min in the synthesis process is the sphere with smooth surface and compact microstructure. Moreover, the sizes of the microcapsules are uniform, and the average diameter of the microcapsules is 0.45 μm, the phase change enthalpy is 51.41 J/g.*

***Keywords - liquid desiccant; internally-cooled; phase change material; microcapsule; emulsifier***

## 1. Introduction

In recent years, building energy consumption showing continued rapid growth, especially in some emerging developing countries. The energy consumption for air conditioning accounts for about 50% in the total energy consumed in building operation. Therefore, reducing the energy consumption for air temperature and moisture handling has great significance for the building energy conservation. Liquid desiccant technology can effectively utilize low-grade heat source to achieve the air temperature and humidity independent processing, and its advantages in energy efficiency has been recognized [1]. However, the efficiency of the key component in the liquid desiccant system - the dehumidifier is relatively low, thus, the energy-saving advantages of the liquid desiccant system can be

more fully exploited by improving the performance of the dehumidifier. Relevant researches mainly focused on improving the structure of the dehumidifier or the dehumidification process and improving physical properties desiccant [2,3].

The heat and mass transfer enhancement in the dehumidification process is critical to improving the efficiency of dehumidifier. The temperature rise phenomenon in the dehumidification process will lead to the less difference on the water partial pressures between the processed air and the liquid desiccant, which will greatly weaken the heat and mass transfer consequently. Control of the temperature rise effectively in liquid desiccant dehumidification process has become a research hotspot. A novel idea of auto-internally cooled liquid desiccant system was proposed to subdue the temperature rise in the dehumidification process, by adding phase change material microcapsules (MicroPCMs) in the liquid desiccant (such as lithium chloride desiccant solution), the isothermal heat absorption characteristics of phase change materials can be used to achieve auto-internally cooled dehumidification process, thus the performance of the dehumidification system will be improved.

MicroPCMs is the micro/nano-scale composite that the phase change material is encapsulated in the wall material, temperature adjustment and energy storage can be achieved when the MicroPCMs storages or releases heat, which is widely employed in many fields, including energy storage and building envelope system [4,5]. It has become the consensus that using the MicroPCMs is beneficial to building energy conservation [6]. However, in existing literatures, there is no related research on using MicroPCMs in liquid desiccant system to achieve building energy saving.

The MicroPCMs with suitable phase change temperature zone, good sealing/microstructure and the excellent thermal performance, is the foundation of the auto-internally cooled dehumidification related experimental research. Some researchers conducted MicroPCMs preparation related research. Zhang used n-octadecane as the core material, melamine - formaldehyde polymer as the wall material, studied the effect of some factors including stirring speed, emulsifier content and the content of cyclohexane on the performance of microcapsules [7]. Alkan conducted the preparation, characterization and thermal performance testing of MicroPCMs with positive eicosanedioic and n-dodecane as core materials. The results showed that the prepared MicroPCMs has good storage performance [8,9]. The influence of the emulsifier type, the amount and speed of the emulsifying on the properties of the microcapsules were studied by Yan et al.[10]. Zhang et al. compared the performance of MicroPCMs with different wall materials and various ratio of wall material [11,12]. The phase change temperature and phase change enthalpy of MicroPCMs with mixture of solid paraffin liquid and paraffin as core, were investigated by differential scanning calorimetry(DSC). The feasibility that obtains a suitable phase change

property by changing the composition ratio of paraffin mixture is proved [13].

However, there is no comparison study about the effect of types and contents of emulsifiers on the MicroPCMs morphology and phase change enthalpy. Based on this situation, the MicroPCMs used for auto-internally cooled liquid desiccant dehumidification, with compound liquid-solid paraffin as core and melamine - formaldehyde polymer (MF) as wall, were prepared in this paper, critical factors influence the morphology, particle size and phase change performance of the MicroPCMs, including the emulsifier type and amount of emulsifier were experimental studied.

## 2. Experimental Methods and Principles

In-situ polymerization used in this paper is the preferred method for MicroPCMs preparing, by which the morphology, thermal properties and density of the phase change microcapsules prepared are satisfactory and acceptable. The basic principle of in-situ polymerization is shown in Figure 1, the core material (solid-liquid paraffin compound) is dispersed into tiny droplets by the high-shear mulser. Then, the hydrophobic groups of emulsifier covers the surface of core material droplet, hydrophilic group locates in the periphery of the droplet outwardly and forms a negatively charged nature of the interface, the core material droplets is dispersed in water to form stable micelles. The wall material of positively charged melamine formaldehyde prepolymer (MF) is attracted to the core material droplet surface with negatively charged emulsifier, which leads to the polymerization reaction, and ultimately the core material droplet will be wrapped around uniformly by the MF prepolymer.

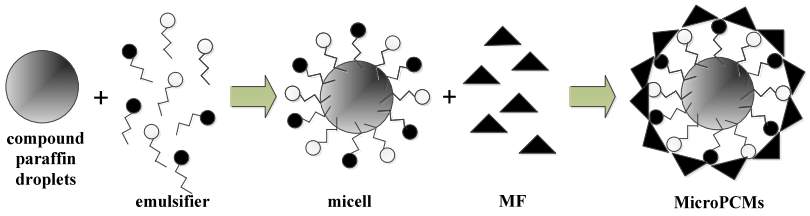



Fig. 1 The experimental principle of MicroPCMs prepared by in-situ polymerization

## 3. Experimental Procedure

Firstly, the MF prepolymer was prepared. 3g melamine and 6g formaldehyde solution (37% mass fraction) were dissolved in 15mL of deionized water. The pH value of the solution was adjusted to 8.5 ~ 9.0 by triethanolamine with mass fraction of 10%. Then, the solution was stirred at the rate of 500 ~ 600 r/min under constant temperature of 70 $^{o}$C. The clear and transparent MF prepolymer solution was obtained after 1h stirring.

Secondly, the paraffin emulsion was prepared. The solid and liquid paraffin were mixed with the mass ratio of 1:1. The melting point of the compound paraffin is 30.9 $^{o}$C, latent heat is 89.8 J/g. The mixture of paraffin and emulsifier was emulsification with 1000 r / min stirring speed in water bath at 80 $^{o}$C. A certain amount of the deionized water was added into the mixture after 15mins stirring. 30mins later, to adjust the pH value to 4.5 to 5.0 by acetic acid solution with concentration of 10%. Paraffin emulsion dispersion was obtained after 1 hour stirring consequently. Different types of emulsifiers used in this paper are shown in Table 1, the emulsifier used in sample A was the non-ionic emulsifier NP-10. The compound of anionic emulsifiers SDBS and nonionic emulsifiers NP-10 was used in sample B. In the preparation of sample C, the compound of anionic emulsifiers SDBS, nonionic emulsifiers Span80 and Tween80 was employed. Sample D~G adopted compound of the nonionic emulsifiers Span80 and Tween80.

Table 1. Composition of microcapsules

| Sample | Core material (Paraffin)/ g | Emulsifiers | | | |
|---|---|---|---|---|---|
| | | (NP-10)/g | (SDBS)/g | (Tween80)/g | (Span80)/g |
| A | 3 | 0.5 | | | |
| B | 3 | 0.2 | 0.2 | | |
| C | 3 | | 0.5 | 0.5 | 0.5 |
| D | 3 | | | 0.9 | 0.9 |
| E | 3 | | | 0.75 | 0.75 |
| F | 3 | | | 0.6 | 0.6 |
| G | 3 | | | 0.45 | 0.45 |

The paraffin emulsion obtained in the previous step was placed in a water bath at constant temperature of 70 $^{o}$C. Then the emulsion was stirred at 400 r / min stirring speed, meanwhile, the MF prepolymer was uniform dripped into the emulsion. The reaction lasted an hour. Finally, after filtration, washed with anhydrous ethanol and deionized water, and dried, the microcapsules was obtained.

## 4. Results and Discussion

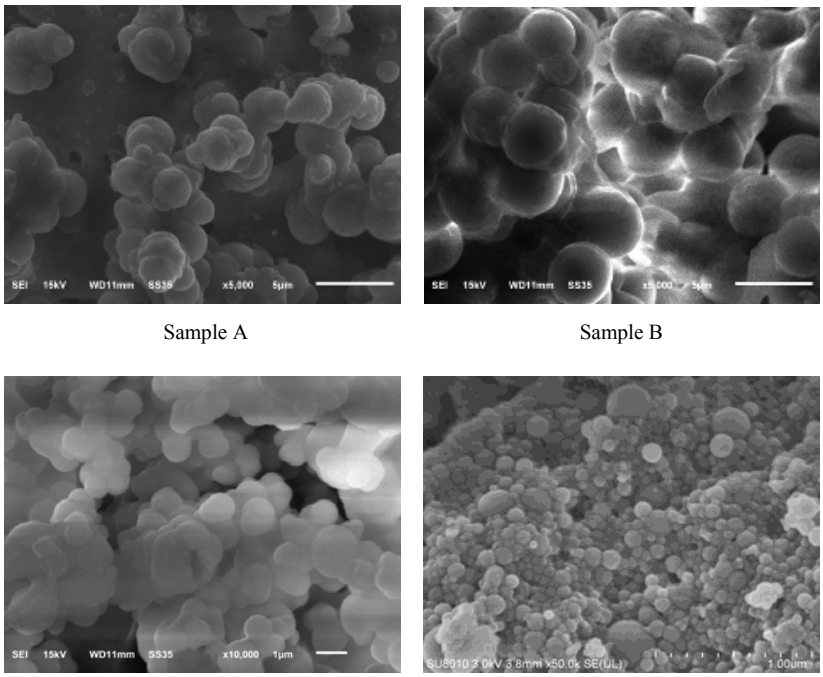
Scanning electron microscopy (SEM) was employed to observe the surface morphology of the prepared microcapsules, and the accelerating voltage was 15 kV. The phase change performance of the microcapsules was characterized by the differential scanning calorimeter (DSC) with heating/cooling rate of 5$^{o}$C/min. Besides, the particle size and diameter

distribution of the MicroPCMs was investigated by laser particle size measuring instrument with detection range of 400nm~2000μm. The average particle diameter is defined as follows:

$$D = \sum_{i=1}^{n} d_i n_i \tag{1}$$

Where $D$ is the average particle diameter of the microcapsules, $d_i$ is the i-th particle size of the microcapsules, $n_i$ is the percentage of the microcapsule with particle size $d_i$ in the total number of microcapsules.

### 4.1 Effect of the emulsifier type on microcapsule morphology




Sample A Sample B

Sample C Sample D

Fig. 2 Morphology of MicroPCMs synthesized by different types of emulsifier

The sample A ~ D listed in Table 1 used different types of emulsifier. The effect of the emulsifier types on the microcapsule morphology are shown in Fig.2. It can be seen in the figure, sample A prepared by the nonionic emulsifier NP-10 has the porous spherical surfaces, and obviously, there is the agglomeration among the microcapsules. Sample B was prepared

by compound of nonionic emulsifier NP-10 and anionic emulsifier SDBS, the appearance of the microcapsules sample B is the compact sphere with smooth surface, and there is few adhesions between the spheres, that is, the microcapsules has good dispersity. The sphere surface of sample C is smooth, which was prepared by the compound of nonionic emulsifier Span80, Tween80 and anionic emulsifiers SDBS. However, there is slight agglomeration among the capsules as seen in the figure. Sample D was prepared by the nonionic emulsifier Span80 and Tween80, the sample microcapsule is regular sphere with smooth surface and compact structure.

Among the four samples shown in Fig.2, only the sample A was prepared by a single emulsifier, the other three samples were all prepared by the compound of different emulsifiers. The morphology of sample A is the worst among the four samples, there is the most significant agglomeration. Therefore, compared to the compound emulsifiers, the interfacial film formed by single emulsifier has lower strength, and the dispersion and stability is relatively poor.

### 4.2 Effect of the emulsifier type on phase change performance

The phase change performance of the MicroPCMs prepared by different types of emulsifier was analyzed by DSC, the DSC curves are shown in Fig. 3. It can be found that, the tendency of DSC curves of samples A, C and D are relatively close, they all have obvious peaks, while the peak of curve of sample B is relatively insignificant. The phase change enthalpy of sample D is up to 51.41J/g, prepared by compound of non-ionic emulsifiers Tween80 and Span80, which is the highest among the four samples, and the corresponding paraffin content is 57.32%. The second highest phase change enthalpy belongs to the sample A microcapsules, which is prepared by single nonionic emulsifiers NP-10, the phase change enthalpy of which is 30.99J/g. The sample C, prepared by nonionic emulsifiers Span80, Tween80 and anionic emulsifier SDBS, has the phase change enthalpy of 21.01J/g. While the samples B, prepared by the compound of NP-10 and SDBS, its latent heat is only 1.38 J/g, which indicates that the MF prepolymer failed to wrap the core material paraffin adequately, and a stable wax emulsion can not be obtained by the emulsifiers mixture of SDBS and NP-10 with mass ratio of 1:1.

As shown in table 2, the initial melting temperature ($T_{om}$) of sample A ~ D was 34.78 $^{o}$C, 45.49 $^{o}$C, 37.72 $^{o}$C and 35.52 $^{o}$C respectively. The initial melting temperatures of sample B is higher than the other three samples of about 10 $^{o}$C, which is attributable to the few core materials encapsulated by microcapsule B. The melting peak temperature ($T_{pm}$) of samples A ~ D were 45.86 $^{o}$C, 48.62 $^{o}$C, 43.36 $^{o}$C and 44.41 $^{o}$C, which are relatively close. The pure core material - compound liquid and solid paraffin has the phase change enthalpy of 89.8 J/g, correspondingly, the paraffin contents of sample A ~ D were 34.51%, 1.53%, 23.40% and 57.25% respectively.

Table 2. Phase change properties of MicroPCMs

| Sample | $T_{om}$/ °C | $T_{pm}$/ °C | △$H$/(J/g) | Paraffin content (%) |
|---|---|---|---|---|
| A | 34.78 | 45.86 | 30.99 | 34.51 |
| B | 45.49 | 48.62 | 1.38 | 1.53 |
| C | 37.72 | 43.36 | 21.01 | 23.40 |
| D | 35.52 | 44.41 | 51.41 | 57.25 |

In the liquid desiccant dehumidification system using lithium chloride solution as desiccant, the heat of condensation of water vapor released in dehumidification will lead to the solution temperature rise, the temperature range is generally 30 ~ 50°C [14], the initial melting temperatures and melting peak temperatures of the above-mentioned four samples prepared in this article are all within this temperature range. Therefore, from the point of the phase transition temperature, the MicroPCMs with compound solid and liquid paraffin as core material prepared in this study is applicable to the auto-internally cooled liquid desiccant dehumidification process, which will effectively decrease the solution temperature rise, and then maintain a strong dehumidification capacity, the efficiency of the dehumidifying system will be improved.

### 4.3 Effect of the emulsifier type on the microcapsules' size

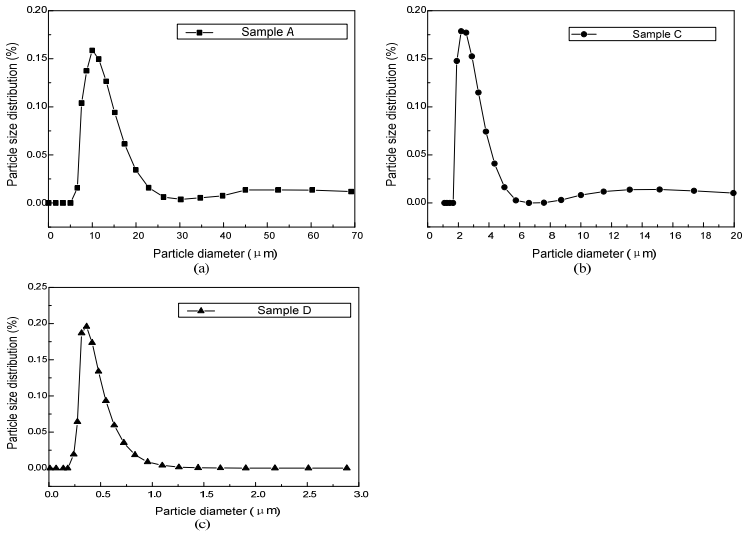



Fig. 4 Particle size distribution of sample A, C and D

The effect of emulsifier types on the size of the prepared microcapsules was investigated. Using a laser particle size analyzer, the microcapsules' particle size distribution of sample A, sample C, and sample D were

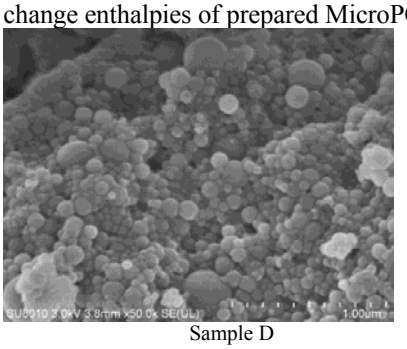
respectively measured. Since the phase change enthalpy of sample B was only 1.38 J/g, suggesting that few PCM be encapsulated inside, it has not be discussed in this section.

As shown in Fig.4(a), the sample A prepared by using a single NP-10 nonionic emulsifier exhibited the broadest particle size distribution and largest average particle diameter of 17.02μm. Most particles size of sample A is concentrated in the range of 8 ~ 25μm. Fig.4(b) shows the size distribution of microcapsule sample C prepared by using compound nonionic emulsifiers of Span80, Tween80 and anionic emulsifiers SDBS. It is seen that the average particle diameter of sample C was 4.16μm, smaller than that of sample A. By contrast, the microcapsules sample D prepared by using compound nonionic emulsifiers of Span80, Tween80 obtained the narrowest particle size distribution and smallest average particle size of 0.45 μm, as shown in Fig.4(c). Most of the microcapsules diameter concentrated between 0.2 ~ 1μm.

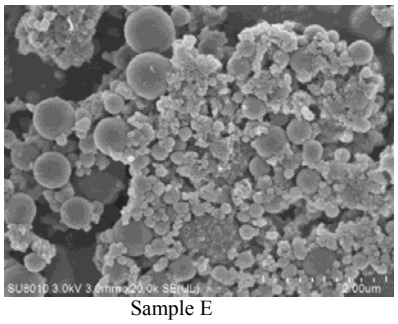
As the single emulsifier's interfacial film strength is relatively weaker, and has a poor stability, the repulsion between the core droplets is not enough to impede the droplets collide and merge together, consequently resulting in a larger particle size distribution. The use of compound emulsifiers can avoid this phenomenon, and hence the microcapsule size was more uniform and obtained a smaller average particle size. It suggested that the use of microcapsules sample D can achieve an improved delivery performance in a liquid desiccant system.

### 4.4 Effect of emulsifier content on the properties of microcapsules

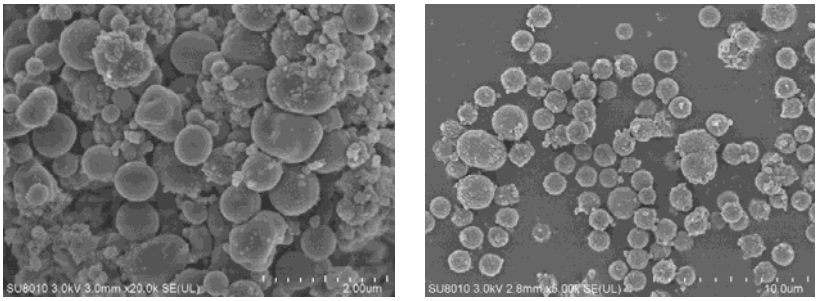
As mentioned above, the sample D was selected for relatively better morphology, particle size, dispersion and latent heat. To obtain the suitable added content of the emulsifier, microcapsules sample D, E, F and G was prepared when the added emulsifier Span80 and Tween80 content was 60%, 50%, 40% and 30%, respectively. Fig.5 showed the SEM photos of the prepared samples, and Table 4 listed the measured averaged size and phase change enthalpies of prepared MicroPCMs.



Sample D



Sample E



Sample F Sample G

Fig.5.Micrographs of microcapsules prepared by using different contents of emulsifier

Table 4 Diameters and phase change enthalpies of prepared MicroPCMs using different contents of emulsifier.

| Sample | Contents of emulsifier | $D$/μm | $\Delta H$/(J/g) |
|---|---|---|---|
| D | 60% | 0.45 | 51.41 |
| E | 50% | 3.2 | 27.05 |
| F | 40% | 4.4 | 17.62 |
| G | 30% | 12.7 | 8.65 |

## 5. Conclusions

In this paper, the MicroPCMs used for auto-internally cooled liquid desiccant dehumidification, with compound liquid-solid paraffin as core and melamine - formaldehyde polymer (MF) as wall, were prepared by in situ polymerization method. The effect of the emulsifier type and amount of emulsifier on the morphology, particle size and phase change performance of the MicroPCMs were investigated experimentally. The following conclusions can be drawn:

1) Among the four microcapsules samples prepared by using four different types of emulsifiers, the morphology of the sample prepared by compound emulsifiers Span80 and Tween80 with mass ratio of 1:1 is the best, which has uniform sphere size, smooth surface and compact structure. When the content of the emulsifier is 60 % of the core material and the stirring rates of emulsification is 1000 r/min, the prepared MicroPCMs has the highest phase change enthalpy, reaching 51.41J/g. Moreover, the microcapsule phase change temperature range is applicable to the auto-internally cooled liquid desiccant dehumidification process.

2) When the amount of emulsifier decreased from 60% to 30% of the core mass, the particle size of microcapsules prepared increased significantly, while its phase change enthalpy reduced significantly.

3) By using the compound emulsifier of NP-10 and SDBS, the stabilized paraffin emulsion can not be prepared.

4) The use of compound emulsifier is beneficial to improve the uniformity of the size of the microcapsules and obtain smaller microcapsules.

**Acknowledgment**

This work is financially supported by the grant from the National Natural Science Foundation of China (Grants No. 51406076) and by the Natural Science Foundation of Jiangsu Province (Grants No. BK20140942).

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