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Synthesis and characteristics of composite phase change humidity control materials

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Abstract

A new kind of phase change humidity control material (PCHCM) was prepared by using PCM microcapsules and different hygroscopic porous materials. The PCHCM composite can regulate the indoor hygrothermal environment by absorbing or releasing both heat and moisture. The PCM microcapsules were synthesized with methyl triethoxysilane by the sol–gel method. The vesuvianite, sepiolite and zeolite were used as hygroscopic materials. The scanning electron microscopy (SEM) was used to measure the morphology profiles of the microcapsules and PCHCM. The differential scanning calorimetry (DSC) and the thermal gravimetric analysis (TGA) were used to determine the thermal properties and thermal stability. Both the moisture transfer coefficient and moisture buffer value (MBV) of different PCHCMs were measured by the improved cup method. The DSC results showed that the SiO₂ shell can reduce the super-cooling degree of PCM. The super-cooling degrees of microcapsules and PCHCM are lower than that of the pure PCM. The onset temperature of thermal degradation of the microcapsules and PCHCMs is higher than that of pure PCM. Both the moisture transfer coefficient and MBV of PCHCMs are higher than that of the pure hygroscopic materials. The results indicated the PCHCMs have better thermal properties and moisture buffer ability.

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Keywords: Microencapsulated phase change material; Humidity control material; Energy efficiency; Passive hygrothermal design

1. Introduction

Climate change is happening; and it is mainly caused by the increase of greenhouse gas emissions. Since most of this emission increase is a result of burning fossil fuels for energy, it's critical to improve the energy efficiency to

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tackle the climate change. Many technologies are utilized to reduce fossil energy consumption. For example, the development of green energy, improving energy efficiency and the use of innovative passive materials are feasible methods [1-3]. The energy consumption of the heating, ventilation and air conditioning (HVAC) system accounts for 1/3 of building energy consumption. So it's essential to improve the building energy efficiency and reduce the energy consumption of HVAC systems. Using new type of building materials to passively control the indoor temperature and humidity to at a relatively stable and comfortable level is a possible way of energy saving [4, 5].

Building materials with large specific heat capacity can reduce indoor temperature fluctuations. Phase change materials (PCM) can absorb or release large amount of thermal heat, and the temperature of the materials maintain constant in phase change process. So phase change materials can be used to regulate indoor temperature and cut down the energy consumption [5].

The moisture transfer process may cause moisture damage to construction materials. And indoor relative humidity affects the comfort and health of human body. For example, low relative humidity ($RH < 30\%$) is related to mucous membrane, dryness of skin and throats, sensory irritation of eyes, and high relative humidity ($RH > 70\%$) may cause rheumatic, rheumatoid arthritis, respiratory discomfort and allergies by promoting mold growth [6-9]. Previous studies [10] show people feel most comfortable when the indoor relative humidity is ranging from 50% to 60% [10]. In order to maintain a stable and comfortable indoor relative humidity, HVAC system is used to dehumidify/humidify the supply air in most building applications, which consumes a lot of energy to remove the latent heat of the moisture. Hygroscopic humidity control materials can absorb and release large account of moisture from indoor air, which means that these materials may be used to control the relative humidity.

The main purpose of the study is to develop a new kind of passive phase change humidity control material (PCHCM), which can moderate both the indoor temperature and moisture. Several PCHCMs were prepared in the paper. The thermal properties, moisture transfer coefficient and moisture buffer value of different PCHCMs were tested, analyzed and compared.

2. Experimental

40g PCM and 5g sodium dodecyl sulfate (SDS) were added into 150ml distilled water in a beaker. The temperature of the solution was kept at 35 °C to melt the PCM, and then the solution was stirred at a rate of 600 rpm for 0.5 h with a magnetic stirrer. And then the temperature of the solution was maintained at 23 °C, and the solution was stirred for 0.5h. 40g Methyl triethoxysilane (MTES), 40g ethanol and 75ml distilled water were mixed in a beaker to form the solution. The pH of the solution was adjusted to 2–3 by adding hydrochloric acid. Then the temperature of the solution was maintained at 50 °C, and the solution was stirred at a rate of 500 rpm for 20 min by a magnetic stirrer. After the hydrolysis reaction of the MTES, the sol solution as the microencapsulation precursor was obtained.

The temperature of the prepared PCM Oil/Water emulsion was controlled at 35°C and stirred at a rate of 400 rpm. And then the PH degree of the prepared PCM Oil/Water emulsion was adjusted to 9-10 by adding ammonia solution. Then, the sol solution was dropped into the PCM Oil/Water emulsion. The mixture was kept reacting and being stirred for 2 h. The SiO_2 was formed by condensation reactions between the methyl silicate and methyl silicate. After the polymerization process of the sol mixture, the SiO_2 shell was formed on the surface of the PCM droplet. Then, the microcapsules were collected by filter paper and washed with distilled water. Then the microcapsules were dried in a low temperature vacuum oven at 0 °C for 24 h. The microencapsulated PCM with SiO_2 shell were gained, and then named as CPCM. The vesuvianite, sepiolite and zeolite are typical hygroscopic porous materials, which are often used as humidity control materials for indoor environment. We chose these three materials as the base material for the preparation of PCHCM. Firstly, the vesuvianite, sepiolite and zeolite were dried in a vacuum oven for 10 h at 100 °C. Then the CPCM was added into the vesuvianite, sepiolite and zeolite with the mass ratio of 1:4, respectively. The CPCM can influence the mechanical properties of the hygroscopic materials, which may make the bricks too loose to be formed. In this experiment, in order to obtain bricks, the mass ratio of the CPCM and hygroscopic materials was tested repeatedly. The mixtures and water with mass ratio 1:2 were stirred at a rate of 200 rpm at the room temperature for 5 min, and were formed as bricks. Then the bricks were dried in a low temperature vacuum oven at 0 °C for 48 h. The CPCM/vesuvianite, CPCM/sepiolite and CPCM/zeolite composites were acquired, and then were named as VCPCM, SCPCM and ZCPCM, respectively. The hygroscopic materials and water with mass ratio 1:2 were stirred at a rate of 200 rpm at the room temperature for 5 min, and were formed as bricks. The bricks formed by pure vesuvianite, sepiolite and zeolite will be as the control samples for the PCHCMs.

3. Characterizations of the CPCM and PCHCMs

The microstructure and morphology of the CPCM and PCHCMs are shown in Fig.1. As seen in Fig. 1a, the microcapsules have a compact SiO₂ shell to encapsulate the PCM, and the SiO₂ shell can keep the PCM from leaking when the PCM is melted. The microcapsules have a spherical shape, and the size of the microcapsules is about 100μm. The SEM profiles of VCPCM, SCPCM and ZCPCM are shown in Fig.1b-d. It can be seen that the CPCM was been dispersed in the hygroscopic materials.

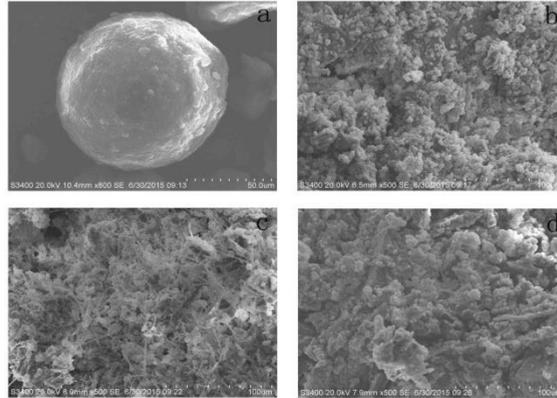


Fig.1 SEM photographs of the (a) CPCM; (b) VCPCM; (c) SCPCM; (d) ZCPCM

Fig.2 and Fig.3 showed the DSC results of the PCM, CPCM, VCPCM, SCPCM and ZCPCM. The PCM melting process is shown in Fig.2, and the PCM solidifying process is shown in Fig.3. As can be seen in, the melting temperature and solidifying temperatures of the PCM are investigated to be 28.3°C and 24.8°C, the melting latent heat and solidifying latent heat are measured to be 146.2kJ/kg and 148.7kJ/kg, and the super-cooling degree is 3.5°C. The melting temperature of the CPCM, VCPCM, SCPCM and ZCPCM are measured to be 27.2°C, 26.9°C, 26.8°C and 27.1°C. The solidifying temperatures of the CPCM, VCPCM, SCPCM and ZCPCM are measured to be 25.0°C, 25.2°C, 25.2°C and 25.1°C respectively. The super-cooling degrees of the CPCM, VCPCM, SCPCM and ZCPCM are 2.2°C, 1.7°C, 1.6°C and 2.0°C, respectively. It can be seen that the super-cooling degrees of CPCM, VCPCM, SCPCM and ZCPCM are lower than that of the PCM. The reason is that the SiO₂ shell of the microcapsules acts as nucleation agent, which can improve the phase change process. The lower super-cooling degree is conducive to the stability of the temperature.

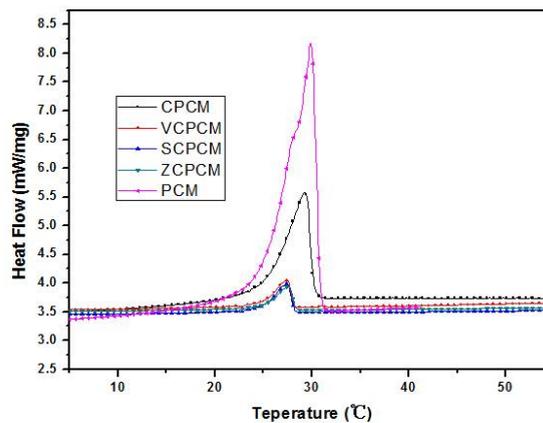


Fig.2 Melting DSC curve of PCM, CPCM, VCPCM, SCPCM and ZCPCM

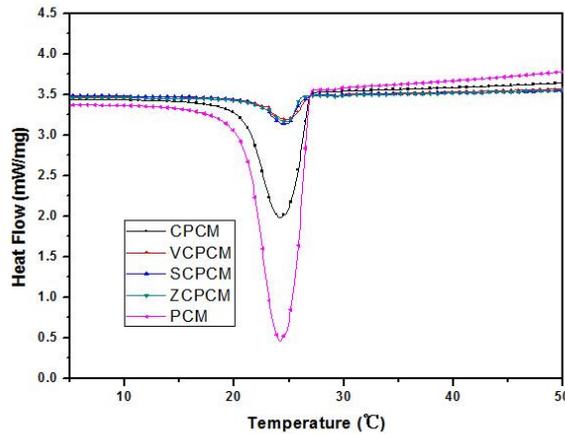


Fig.3 Solidifying DSC curve of PCM, CPCM, VCPCM, SCPCM and ZCPCM

The melting latent heat of the CPCM, VCPCM, SCPCM and ZCPCM are 77.4kJ/kg, 14.1kJ/kg, 15.4kJ/kg and 12.9kJ/kg respectively. The solidifying latent heat of the CPCM, VCPCM, SCPCM and ZCPCM are 79.5kJ/kg, 14.4kJ/kg, 15.9kJ/kg and 13.2kJ/kg respectively. The hygroscopic materials have no phase change process, so the latent heat of the composites is lower than that of PCM.

Fig.4 showed the TGA results of the PCM, CPCM, VCPCM, SCPCM and ZCPCM. When the temperature is up to 130 °C, the thermal degradation process of the PCM occurs, and the residual weight of the PCM at 230 °C is close to zero. When the temperature is up to 175 °C, the thermal degradation process of the CPCM and PCHCMs occurs. Hence the SiO₂ shell is advantageous to form a physical protective barrier on the surface of the PCM. The protective barrier can hinder the transfer of flammable molecules to the gas phase, which means that the SiO₂ shell can protect the PCM, improve the stability of the composites and acts as a flame retardant to improve the kindling point.

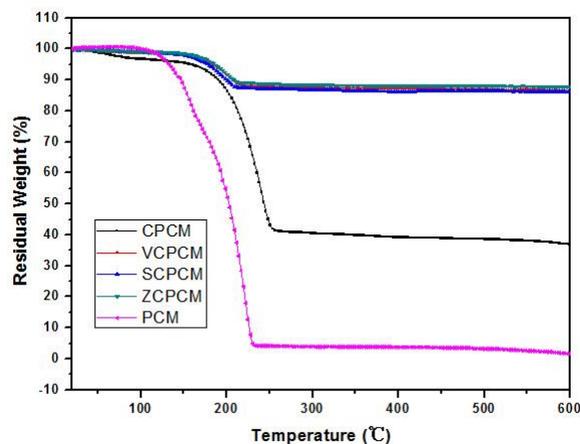


Fig.4 TGA curve of PCM, CPCM, VCPCM, SCPCM and ZCPCM

The moisture transfer coefficient was measured with classic cup method. The samples with areas of 4*4cm² were fixed in the outlet of containers, which filled with saturated NaCl solution. The saturated NaCl solution kept the RH of the air in container as 75%. And the RH outside is maintained at 54%. The difference between the RH made the water vapor transfer from one side to the other side of the sample.

The moisture transfer coefficients of vesuvianite, sepiolite, zeolite, VCPCM, SCPCM and ZCPCM are shown in Table 1. As seen in Table 1, the moisture transfer coefficients of the PCHCMs are all higher than those of the pure hygroscopic materials. The moisture transfer coefficient of VCPCM is 1.47 times higher than that of vesuvianite, the moisture transfer coefficient of SCPCM is 1.68 times higher than that of sepiolite, and that of ZCPCM is 1.83 times higher than that of

zeolite. And the moisture transfer coefficients of the PCHCMs are all higher than the gypsum. The result indicates that the CPCM can improve the moisture transfer in hygroscopic materials.

Table 1 Moisture transfer coefficient of vesuvianite, sepiolite, zeolite, VCPCM, SCPCM and ZCPCM

Samples	Moisture transfer coefficient ($10^{-8}\text{kg/m}^2\cdot\text{s}\cdot\text{RH}$)
Vesuvianite	8.25
Sepiolite	5.42
Zeolite	4.11
VCPCM	12.12
SCPCM	9.11
ZCPCM	7.54
Gypsum	2.4

The moisture buffer value (MBV) is defined as a characteristic of a material based on a period of moisture uptake/release [11, 12]. The practical MBV presents the amount of water vapor that is transport in or out a material per open surface during a certain period of time, when it is subjected to relative humidity variations of surrounding air. The practical moisture buffer value can be measured with an experimental set up. The samples are exposed to cyclic variations in high RH and low RH for 8h and 16h. the high RH is controlled at 75% with saturated NaCl solution, and the low RH is controlled at 33% with saturated KCl solution. The moisture uptake/release process was alterative operated for at least 7 days, which ensure the process was stable. And the mass of the samples were measured with analytical balance.

Table 2 shows the MBV of the samples. It can be seen that the MBV of the PCHCMs are all higher than those of the pure hygroscopic materials. The MBV of VCPCM is 1.45 times higher than that of vesuvianite, the MBV of SCPCM is 1.44 times higher than that of sepiolite, and the MBV of ZCPCM is 1.46 times higher than that of zeolite. And the MBVs of the PCHCMs are all higher than the gypsum. The results show that adding CPCM can improve the moisture buffer ability of hygroscopic materials.

Rode [12] used five different categories to classify the MBV. The good class ranges from 1 $\text{g/m}^2\text{RH}$ to 2 $\text{g/m}^2\text{RH}$, the moderate class ranges from 0.5 $\text{g/m}^2\text{RH}$ to 1 $\text{g/m}^2\text{RH}$, and the limited class ranges from 0.2 $\text{g/m}^2\text{RH}$ to 0.5 $\text{g/m}^2\text{RH}$. It can be seen that the MBV of VCPCM is within good class and higher than that of the other two PCHCMs. The MBV of SCPCM and ZCPCM are within moderate class.

Table 2 MBV of vesuvianite, sepiolite, zeolite, VCPCM, SCPCM and ZCPCM

Samples	MBV ($\text{g/m}^2\text{RH}$)
Vesuvianite	0.788
Sepiolite	0.542
Zeolite	0.351
VCPCM	1.145
SCPCM	0.78
ZCPCM	0.514
Gypsum	0.26

4. Conclusion

A new kind of phase change humidity control material was synthesized by using microencapsulated PCM and different hygroscopic porous materials. The results showed that the SiO_2 shell can reduce the super-cooling degree of PCM. The super-cooling degrees of CPCM, VCPCM, SCPCM and ZCPCM are lower than that of the pure PCM, which is advantageous to make temperature stable. The onset temperature of thermal degradation about the CPCM is higher than that of PCM, which can improve the stability of the composites and acts as a flame retardant to improve the kindling point. The CPCM also can improve the moisture transfer performance and moisture buffer ability of hygroscopic materials. The moisture transfer coefficients of PCHCMs are all higher than that of the pure hygroscopic materials, ranging from 1.47 times for CPCM/vesuvianite composite to 1.83 times for CPCM/zeolite composite. The moisture buffer values of PCHCMs are averagely 1.45 times higher than that of pure hygroscopic materials. The results also indicate that the

CPCM/vesuvianite composite has a better hypothermal performance than other two PCHCMs. It has the potential to be a good energy saving material.

Acknowledgments

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