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Preparation of Microencapsulated Phase Change Materials by the Sol-gel Process and Its Application on Textiles

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Abstract

A kind of microencapsulated phase change materials (PCMs) based on a paraffin core and inorganic silica shell was designed to enhance thermal conductivity and phase change performance. These silica microcapsules were synthesised by using tetraethoxysilane (TEOS) as an inorganic source through the sol-gel process. Scanning electronic microscopy images suggested that the silica microcapsules exhibited a spherical morphology with a well-defined core-shell microstructure. The particle size and distribution showed the microcapsules were uniform and dispersed evenly. It was confirmed by Fourier transform infrared spectra that the silica shell material was successfully fabricated onto the surface of the paraffin core. The DSC curve illustrated that the microcapsules with a silica shell had a higher melting temperature and enthalpy. The thermo-regulating properties of the coated fabric changed with the microcapsule weight added.

Key words: microcapsules, fabric, sol-gel, phase change materials, silica.

Introduction

Phase change materials (PCMs) have been used to manufacture thermo-regulated textiles to improve the thermal comfort of the wearer [1, 2]. PCMs are entrapped in a microcapsule to prevent their leakage during their liquid phase. These compounds possess the ability to absorb and store large amounts of latent heat during the heating process as well as to release this energy during the cooling process [3 - 5].

There are many methods to encapsulate the core materials, such as in-situ polymerisation, interface polymerisation, emulsion polymerisation and so on [6 - 8]. Currently sol-gel technology has attracted much attention and is used widely in many fields [9 - 13]; we have even used it to improve the fabric light property using titanium and silicane hydrosol [14 - 16].

For PCM selection, the most widely adopted are paraffin waxes, consisting of a mixture of mostly straight-chain n-alkanes: $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$. Paraffin waxes can absorb, store and release a great amount of heat repeatedly during phase conversions between solid and liquid phases. They are chemically inert, noncorrosive, odourless, long lasting, inexpensive, easily available, ecologically harmless and nontoxic [17, 18].

To encapsulate the core materials, some research groups have proposed the use of silica as the inorganic shell material of PCM microcapsules [19, 20]. The silica microencapsulated PCMs can achieve good phase change performance and high

encapsulation efficiency. Therefore in this paper, paraffin wax was taken as the core material, and silica was used as the shell of the microencapsulation through the sol-gel process.

Experimental part

Materials

Tetraethoxysilane (TEOS) and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co. Ltd, paraffin from Shanghai Huayong Paraffin Co. Ltd., and Emulsifier XP as emulsifying agent was bought from Shanghai Dijin Chemical Co., Ltd. Absolute ethyl alcohol was purchased from Changshu Yangyuan Chemical Co. Ltd.

Preparation of microcapsules

A series of microencapsulated paraffins with a silica shell were synthesised with different paraffin/TEOS weight ratios through the sol-gel progress at various pH values. The encapsulation of paraffin was derived from the hydrolysis and condensation reactions of TEOS in an O/W emulsion in the presence of an acidic catalyst. A typical synthetic procedure is described as follows:

In one beaker, paraffin wax was added to deionized water at 60 °C. Then emulsifier XP was added to this solution, and contin-

uously stirred at a speed of 10000 r.p.m. for one hour to form a stable emulsion using a High Shear Emulsifying Machine (BME-100LX). In another beaker, a mixture of TEOS and HCl aqueous solution with the desired pH value was stirred at 35 °C with a magnetic stirrer (IKA C-MAG HS7) for around one hour until a homogeneous solution was obtained, indicating that the hydrolysis of the TEOS was complete and the silica-sol solution as encapsulation precursors were formed. Subsequently the sol solution was added drop wise to the emulsion prepared with stirring for 24 hrs to complete the gel process. Some white powders were collected by filtration and washed with deionised water. Finally silica-microencapsulated paraffin powder was obtained by washing with alcohol to effectively remove the residual emulsifiers and other residuals after being dried at 50 °C.

Experimental scheme

During the preparation, we set different experimental parameters to obtain an optimised result, listed as the follows in **Table 1**.

Microcapsule treatment of fabrics

Woven cotton fabric samples (40S×40S, 91.63 g/m²) were treated with the silica-microencapsulated paraffin wax solution at a pick-up of 60 - 70%. The fabric

Table 1. Different experimental schemes of PCM preparation.

Sample	Paraffin wax, g	Deionized water, ml	Emulsifier Xp, g	TEOS, g	Alcohol, ml	Deionized water, ml	pH	Temperature, °C
1#	11.7	28.6	23.4	5.0	10.7	10.7	3.5	80
2#	10.0	57.2	20.0	10.0	21.4	21.4	2.3	70
3#	5.0	67.0	10.0	11.7	25.0	25.0	2.3	80

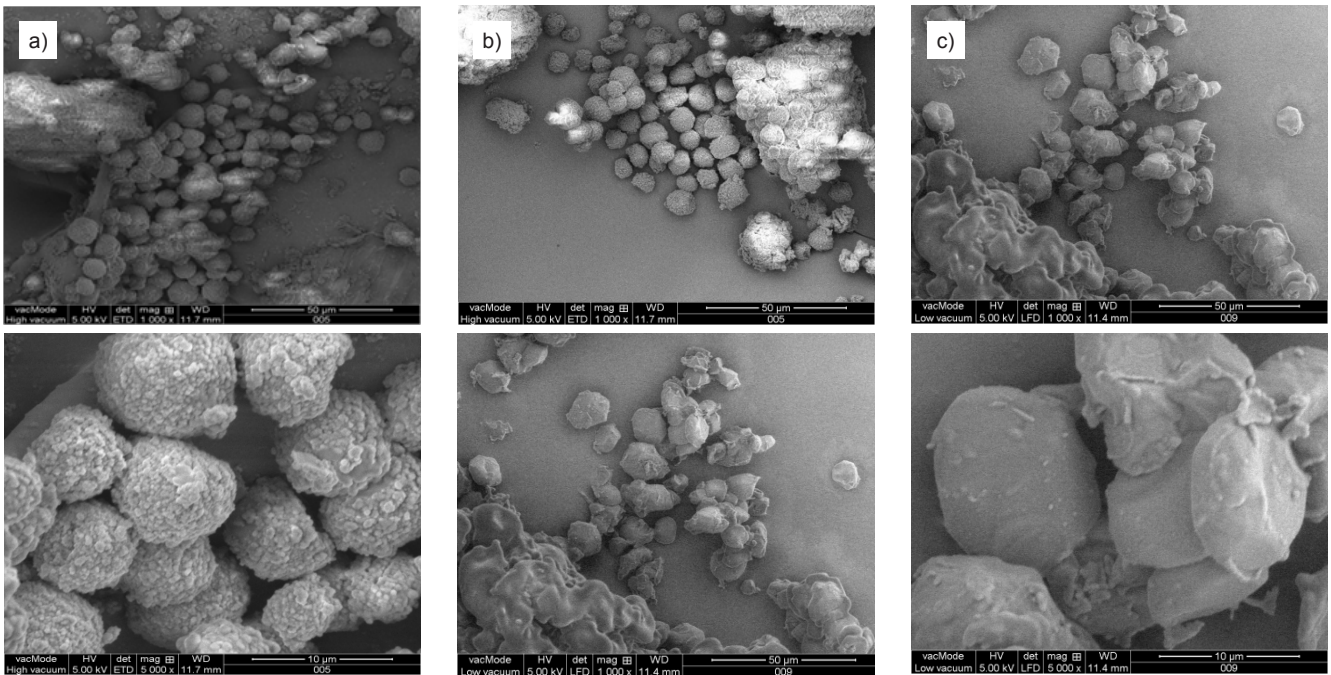


Figure 1. Morphology of microcapsules under different experimental parameters SEM of; a) sample 1#, b) sample 2#, c) sample 3#.

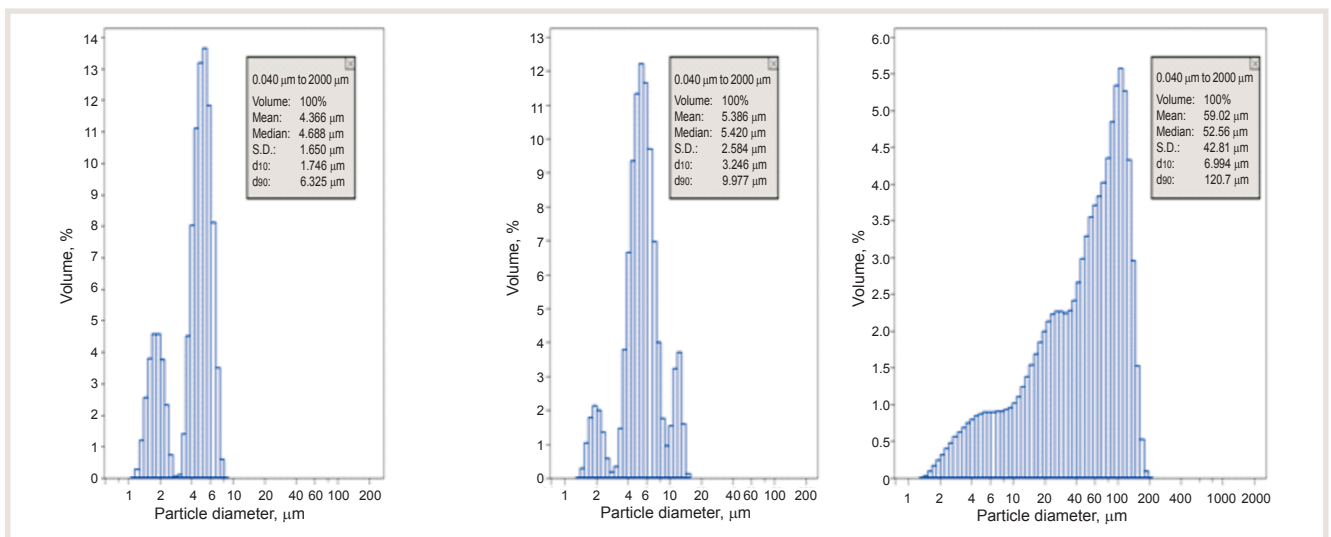


Figure 2. Size distribution of the microencapsulation particle; a) sample 1#, b) sample 2#, c) sample 3#.

treated was firstly dried at 80 °C and then cured at 150 °C for 2 mins.

Characterization

Morphologies of the microcapsules were investigated by a DXS-10A scanning electron microscope (SEM). Particle size distributions of the microcapsules were determined using an Ls13320 Laser Particle Size Analyser. Fourier transform infrared (FTIR) spectra of the samples were obtained by a Nicolet 6700. A DSC test was conducted on a Perkin-Elmer tester. During the DSC analysis, the specimens were heated and cooled within a certain temperature interval ranging from 0 to 60 °C at 2 °C per min. At the same time,

different weights of the microcapsules (5, 10, 15%) were treated on the sample fabric, then their temperature change was recorded, respectively. The fabric thermo-regulating effect was also carried out by means of a fabric heat property tester (SFJJ-606PC), including the clo value, thermal transmittance coefficient and warmth retention rate parameters.

Results and discussion

SEM of microcapsules

SEM images of the silica microcapsules synthesised according to **Table 1** are shown in **Figure 1**.

For the microcapsule samples synthesised at different weight ratios of paraffin wax/TEOS and pH, the regular spheres can be seen in **Figure 1**, but their surfaces were rough and loose. A typical core-shell structure is observed, and a thin shell can be distinguished (**Figure 1.c**). It was noteworthy that the microcapsules synthesised at pH 2.3 (sample 2#) exhibit a compact surface without any disfigurements and possess a well-defined core-shell structure. Moreover their particles were uniform in size, being less than 10 μm (**Figure 1.b**).

When the microcapsules were synthesised at a pH of around 2.3, the conden-

sation rate appropriately matched the self-assembly of the silica oligomers and the subsequent condensation continued among the silanol groups. However, the synthesis of the microcapsules failed at $\text{pH} < 2.0$ or > 3.0 , because the condensation rate was so fast that the silica oligomers did not have enough time to deposit onto the surface of the paraffin wax before condensation. This led to the self-condensation of the silica precursors, could not be encapsulated effectively.

Compared with these pictures, there was less assembling for samples 1# and 2#, and their microcapsules had a smoother and more compact surface. There was an assemble for sample 3#, and there were some gel residuals in the end. Therefore it is probable sample 2# will be taken into further consideration.

Particle size and distribution

The particle size and distribution of silica microcapsules of the above samples were determined using a laser particle size analyser, shown in *Figure 2*.

From the particle diameter distribution curve in *Figure 2*, the encapsulated particles displayed a scatter feature. Sample 3# of *Figure 2.c* showed an obvious difference from the former two: not a normal distribution. While *Figures 2.a* and *2.b* showed a similar distribution shape. There was a uniform Gaussian distribution for themicrocapsules of 1# and 2#, and one can also note major differences existing in the mean particle sizes for the different conditions.

Combined with the SEM pictures and particle size distribution above, the optimised experimental method of 2# was adopted.

FTIR spectra

The silica-microencapsulated paraffin wax was characterised by FT-IR spectra, shown in *Figure 3*.

In the spectrum of tu paraffin wax, the C-H bonding vibrations at 1463 and 1373 cm^{-1} were due to methylene bridges, and alkyl C-H stretching vibrations of methyl and methylene groups can be observed at 2920 and 2847 cm^{-1} . In addition, the characteristic absorption peak at 720 cm^{-1} corresponded to the in-plane rocking vibration of the methylene group.

The spectra of the silica microcapsules showed peaks at 1085 cm^{-1} , attributed

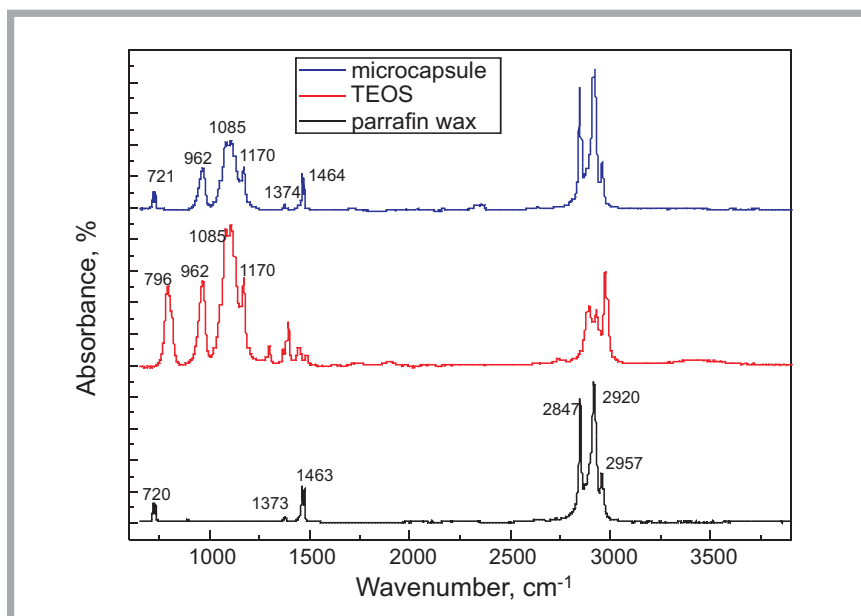


Figure 3. FT-IR spectra of the microencapsulation prepared.

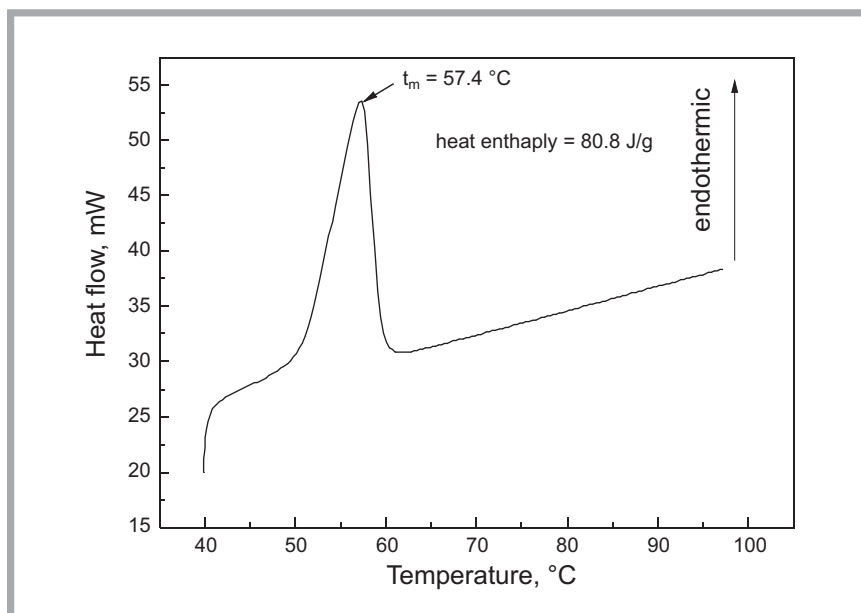


Figure 4. DSC curve of microcapsule.

to asymmetric Si-O-Si stretching vibrations of the silica shells. An intense absorption band at 962 cm^{-1} was attributed to Si-OH bending vibrations.

It is noteworthy that all the characteristic peaks of paraffin wax can be distinguished in the spectra of the microcapsules, which confirmed the successful encapsulation of paraffin wax within the silica shell. As the microcapsules were synthesised through condensation of the silica precursors via a so-gel route, it was expected that the silica sol groups could be detected on their silica shells.

DSC curve of silica-microencapsu Latino

The DSC curve of the microcapsule is shown in *Figure 4*, where the upward peak indicated the endothermic process, while the downward corresponded to the exothermic one.

It was easily found that the sample had exhibited a single and well-resolved endothermic peak during the heating process, corresponding to the melting behaviour of the microcapsule. It showed that the melting point of the microcapsule was about 57 °C, and the enthalpy was about 80.8 J/g. Compared with the

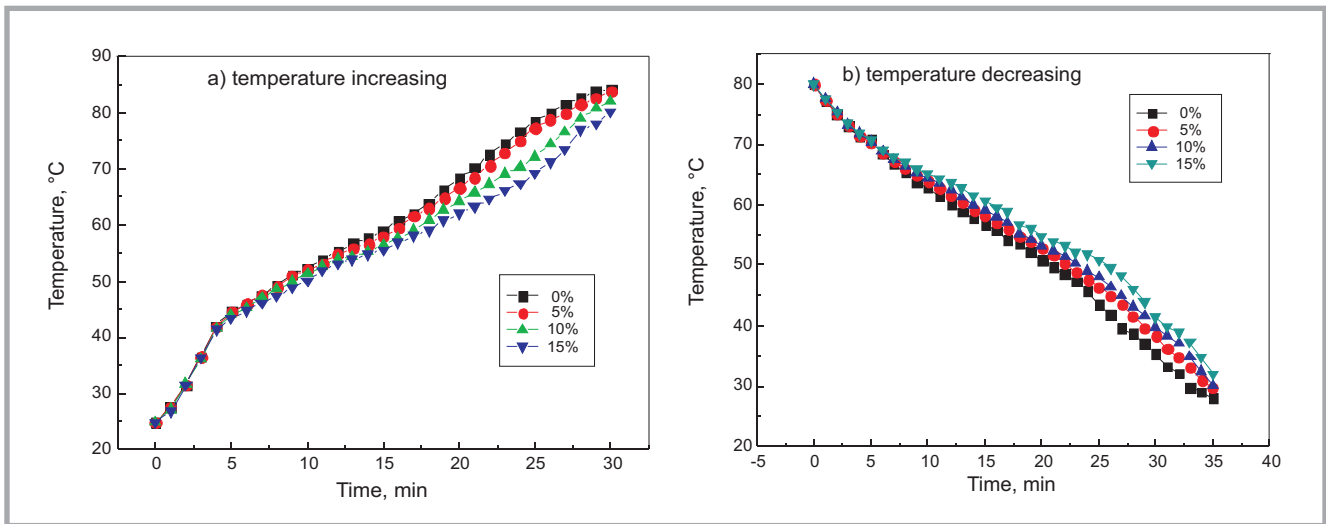


Figure 5. Heat regulation behaviour of treated fabric.

data of paraffin from the manufacturer: $T_m = 60\text{ }^\circ\text{C}$ and heat enthalpy 112.6 J/g , the T_m of the microencapsulated paraffin wax tended to decrease slightly. It was understood that the silica shell can generate a confinement effect on the crystallisation of paraffin when encapsulated, which restricted the motion of paraffin molecules during the crystallisation process and thus led to some defects in the crystals. The presence of these defects obviously resulted in a decline in the T_m of paraffin wax.

The thermo-regulating effect

To further test the thermo-regulating effect of the fabric with different microcapsule weights, the temperature behaviour of the sample was tested.

To detect the heating effect, the samples were heated from room temperature (about $20\text{ }^\circ\text{C}$) to $85\text{ }^\circ\text{C}$ in an oven, and the related temperature was recorded every 60 seconds. For the cooling effect, the fabric was firstly heated to $80\text{ }^\circ\text{C}$, then placed in a room, and next the tem-

perature was decreased and recorded every 60 s. The thermo-regulating effect at different microcapsule weight ratios is shown in Figure 5.

Figure 5.a shows that the temperature rising rate decreased with the microcapsule weight. At a temperature of $20 - 40\text{ }^\circ\text{C}$, there was no obvious temperature change among these samples. But from $40\text{ }^\circ\text{C}$, the temperature curves began to show deviation, especially in the range of $55 - 80\text{ }^\circ\text{C}$, where there were some big differences. The samples without microcapsules had the largest temperature increasing rate, whereas those with microcapsules increased temperature slowly. For the largest microencapsulation content of 15%, the temperature increased the slowest, indicating that the fabric treated with microcapsules has a thermal regulating effect and can change the temperature gradually.

Figure 5.b shows that the temperature curves were similar and with no difference at the beginning of $80 - 75\text{ }^\circ\text{C}$. But when the temperature decreased to $75\text{ }^\circ\text{C}$, the samples had a different thermo regulating rate, implying that the microcapsules began to have a thermo-regulation effect, especially at $65 - 20\text{ }^\circ\text{C}$. The microcapsules can delay the temperature descent, with the decrease being slowest with the maximum microcapsules weight.

The heat retention of the fabric treated with different microcapsule weights (5, 10, 15%) was also evaluated using an SFJJ-606PC instrument, where the clo value, thermal transmittance coefficient and warmth retention rate were described.

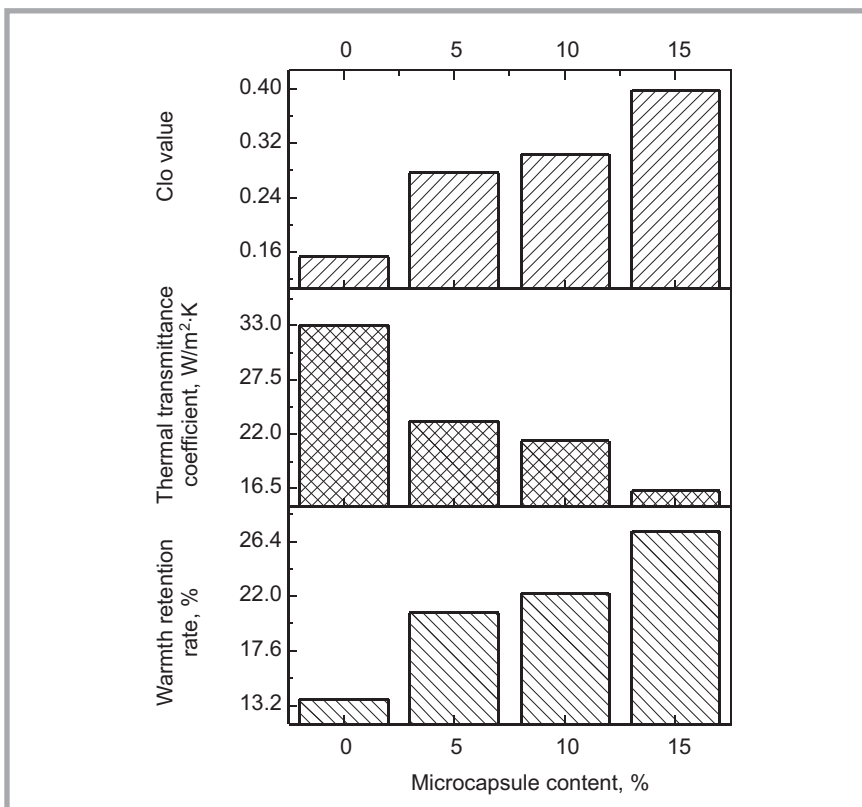


Figure 6. Clo, heat transfer coefficient and warmth rate of thermostat fabric.

Figure 6 shows that the clo value and warmth retention rate were positive in relation to the microencapsulation content, while the heat transfer coefficient was negative with respect to the microencapsulation content. With microcapsules used to treat the fabric, it improved its warmth retention.

■ Conclusions

In this paper, novel microencapsulated PCMs based on paraffin as the core and silica as the shell were designed and achieved via sol-gel technology. These silica microcapsules showed spherical morphology with a well-defined core shell structure. They also showed a particle size mostly distributed in the range of 4 - 10 μm . The FTIR spectra confirmed that paraffin was successfully encapsulated within the silica shell material. The DSC indicated that the melting temperature of the silica microcapsules changed due to the presence of the silica shell.

To investigate the thermo regulation effect of the microcapsules, fabric with different weights of silica microcapsules was tested while subjected to temperature change. It was found the fabric with more microcapsules had a slower increasing and decreasing temperature rate. And the heat retention of the fabric, including the clo value, thermal transmittance coefficient and warmth retention rate, was also related to the microencapsulation content. The fabric has higher warmth retention with more microcapsules



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Institute of Textile Engineering and Polymer Materials



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