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SHORT COMMUNICATION

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Preparation and mechanical properties of thermal energy storage microcapsules

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Abstract A series of heat energy storage microcapsules was prepared using melamine-formaldehyde resin as the shell material and the mechanical properties of the shell were investigated. A phase change material whose melting point was 24 °C was used as core and the quantity of heat involved in phase transition was 225.5 J/g. Average diameter of the microcapsules varied from 5 to 10 μm, and the globular surface was smooth and compact. The mechanical properties of the shell were evaluated by observing the surface morphological structure change after application of pressure by means of scanning electron microscopy. When the mass ratio of the core and shell material is 3:1, a yield point of about 1.1×10^5 Pa was found and when the compression was increased beyond this point the microcapsules showed plastic behavior. This has been attributed to the cross-link density and to the high degree of reaction of the shell material. Different yield points subsequently reflected differences in the mechanical behavior. It was also found that the mechanical intensity of double-shell microcapsules was better than that of single shelled ones.

Keywords Microcapsule · Thermal energy storage · Preparation · Mechanical properties · Yield point

Introduction

Phase change materials (PCMs) can absorb, store, and release large amounts of latent heat over a defined temperature range while undergoing phase changes, and its application in thermal energy storage is well-known in many fields. Microcapsulation of PCMs (microPCMs) provides a means to solve the super-cool problem and interfacial combine with circumstance materials. MicroPCMs have been used in functional fibers [1, 2], solar energy utilization [3], heat energy transfers [4], agriculture [5], and building materials [6]. However, they require considerable intensity in practical use and it is not easy to get accurate results. Sun and Zhang [7, 8] had investigated the strength of microcapsules made of three different shells using a micromanipulation technique. A single microcapsule was compressed to obtain a large deformation or rupture and the force applied was measured simultaneously. This method required the use of a special apparatus as it was difficult to see the surface shape changes straightaway. More recently, Lulevich et al. [9, 10] have studied deformation of microcapsules and multiplayer microcapsules with an atomic force microscope. Also when microPCMs were used in practice, the strength of a single microcapsule could not reflect the actual strength as the microcapsules were all piled together.

Thus, there is a need for a simplified method to evaluate the mechanical properties of microPCMs. The objective of this study is to synthesize microcapsules containing composite PCMs of size 5μm for application in controlling indoor wall temperatures, which would save energy and make indoors comfortable. MicroPCMs were prepared using insitu polymerization with the prepolymer of melamine-formaldehyde and their rigidity was characterized. Microcapsules were placed between two pieces of glass and were compressed. The rigidity of the shell was evaluated by observing the surface morphological structure change by means of scanning electron microscopy after application of pressure.

Experimental

Materials

The prepolymer of melamine-formaldehyde was obtained from Shanghai JQ Chemistry Co., China, and its solid content was 50%. The composite PCMs, whose main constituent was lauryl alcohol (prepared by Energy Sources and Low Emission Research Institute of Hebei University of Technology), was applied as core material. The phase change temperature was 24 °C and the quantity of heat involved in phase change was 225.5 J/g. Styrene maleic anhydride copolymer solid (Scripte-520) was used as a dispersant. Nonionic surfactant, NP-10 [poly (ethylene glycol) nonylphenyl] obtained from Sigma Chemical, was used as an emulsifier.

Preparation of microcapsules

The encapsulation was carried out in a 500 ml three-neck round-bottomed flask equipped with a condensator and a tetrafluoroethylene mechanical stirrer. First, 10 g of styrene-maleic anhydride and 0.8 g of NaOH were dissolved in 100 ml of water at 50 °C, the pH value being 4–5 after 2 h. To the aqueous surfactant solution 32 g of the core was added and the mixture was emulsified mechanically at a stirring rate of 2,500 rpm for 10 min using QSL high-speed disperse machine. The emulsition was immersed in the bottle dipping in steady temperature flume and stirred at the rate of 1,500 rpm while 16 g of the prepolymer was being immersed at a rate of 0.5 ml min^{-1}. The shell was produced after 1.5 h by increasing the temperature to 60 °C slowly. Then 16 g of the prepolymer in the bottle was immersed at the same rate. The temperature was then increased to 75 °C and after 1 h it was decreased to the atmospheric temperature. The resultant microcapsules were filtered and washed with water and dried in a vacuum oven.

Characterizations

Microcapsules were placed between two pieces of glass, 4 cm×2 cm, and compressed. The intensity was measured by a pressure sensor under the bottom glass and data were directly obtained. The rigidity of the shell was evaluated by observing the surface morphological structure after application of pressure by means of a XL30 PHILIPS scanning electron microscope.

Results and discussion

Shape of the microcapsules

After the microcapsules were dried in a vacuum oven at 40 °C for 24 h, their morphologies could be observed from the SEM photographs in Fig. 1. Most of the microcapsules have a smooth surface and the shape is often rounded with an average diameter of about 5 μm. There is no coaglutination between particles and the diameter of the microcapsules has a considerable size distribution. As the core material could not be encapsulated completely and the shell material also could not absolutely be covered on the cores, Fig. 1 shows minimal polymer piling between microcapsules.

The rate of immersion of the shell material could control the morphology of microcapsules. Microcapsules, both magnified 20000 times by SEM in Fig. 2a, b, were obtained by an immersion rate of 1 and 0.5 ml min^{-1}. With the increase in the immersion rate of the shell material, the surface was rougher. The reason is probably due to the prepolymer of melamine-formaldehyde will not capsulated on core slowly and tightly at rapid dropping speed.

Shell strength of the microcapsules

Microcapsules containing PCM required a certain intensity in practical use. In this study, we adapted a new method to obtain the intensity. As Fig. 3 shows, microcapsules were placed between two pieces of glass and were compressed. The rigidity of the shell is evaluated by observing the surface change after pressure application by means of scanning electron microscopy. The average diameter of the microcapsules was found to be 5 μm and the globular surface was smooth and compact.

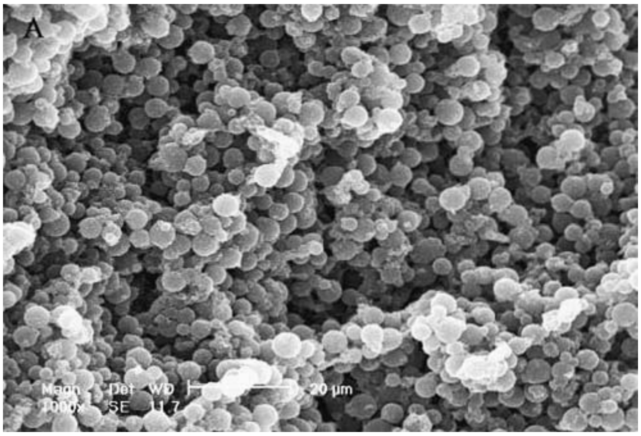


Fig. 1 SEM photograph (×1000) of microcapsule morphology, which dried in a vacuum oven at 40° for 24 h

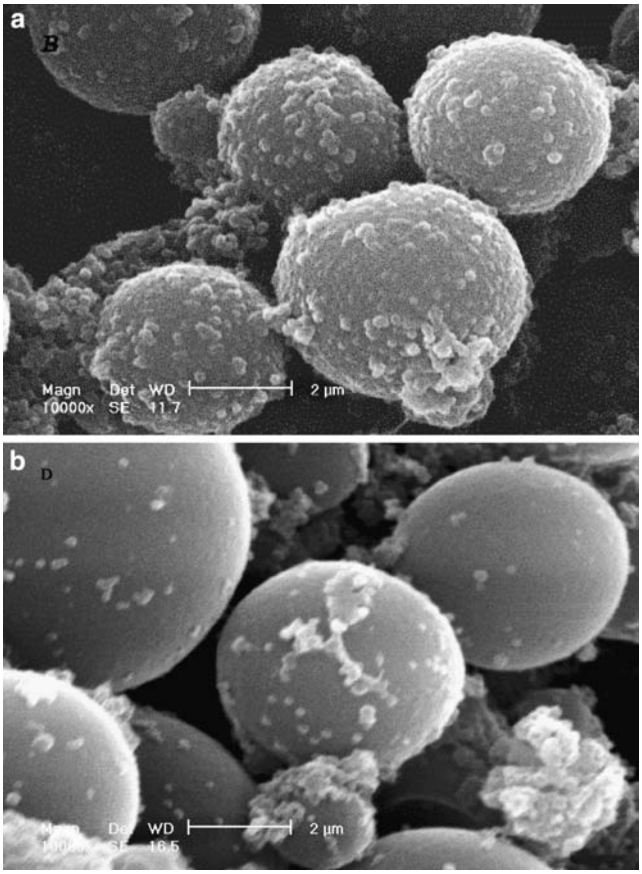


Fig. 2 SEM photographs (×10000) of microcapsules obtained by shell material immersion speed of **a** 1 ml min^{-1} and **b** 0.5 ml min^{-1}. With the increase of immersion rate, the surface was rougher

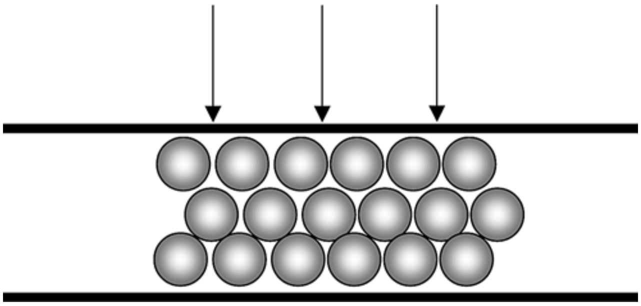


Fig. 3 Sketch map of microcapsules placed between two pieces of glass and compressed. The rigidity of the shell is evaluated by observing the surface change after pressure application by means of scanning electron microscopy

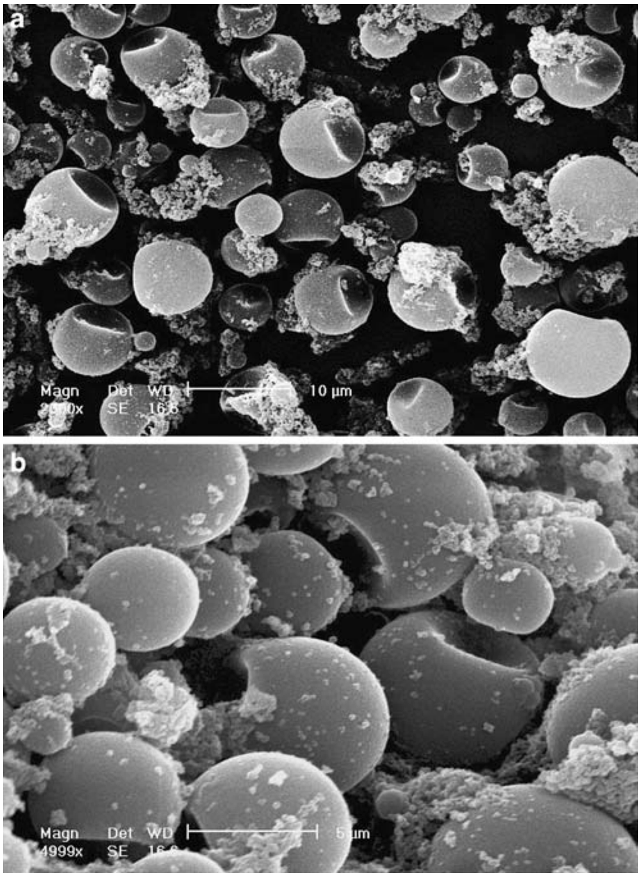


Fig. 4 SEM photographs of microcapsules whose mass ratio of core and shell materials was 3:1 after compression. As **a** ×2000 shows, there were concaves on microcapsules. As compression increased, some small microcapsules caved-in on large ones **b** ×4999

The microcapsules whose mass ratio of core and shell material was 3:1, after compression as Fig. 4a shows, demonstrated concaves on microcapsules. When the microcapsules were compressed to before a certain point, there was no change on the surface. However, when the deformation was beyond a ‘yield point’, there was profound hysteresis and the microcapsules showed a plastic behavior.

A yield point of about $1.1{\times}10^5$ Pa was found and when the compression exceeded this the microcapsules showed plastic behavior. As the compression increased, some small microcapsules caved-in on large ones as is seen in Fig. 4b. However, no rupture occurred. From SEM micrographs of the surface of microcapsules following compression, a yield point, just as the deformation needed mixture force, could be observed. It was also found that the mechanical intensity of double-shell microcapsules was better than that of single shells.

Obviously, there was an influence of core material on the yield point, but this was not considered in this study. The microcapsules were representative of the core-shell structure. Thus from the global strength formulae we know that the main factors affecting the strength of the shell are thickness and tightness. Therefore, the yield point is expected to be induced by the relationship of the core and shell. If the emulsification speed of the core material is uniform, then the core has the same average diameter; so the thickness is determined by the mass ratio of the core and shell. Tightness reflects the reaction temperature and velocity. These two factors, which were a result of piled cross-link molecules, can be regulated in the preparation process by controlling the parameters. Our ultimate goal is to establish relationships between mechanical features of the microcapsules and the encapsulation process control parameters. In order to know the effects of yield point on mechanical properties, three tests have been carried out at room temperature in a universal mechanical testing device. These tests evaluate the effects of the immersion rates of shell material, different mass ratio of core and shell material and single-shell and double-shell.

Figure 5 shows the variation of yield point of the shell for different immersion rates of the shell material, 0.5, 1.0 and 2.0 ml min^{-1}, during the encapsulation process. The values decrease as the mass ratio of core and shell increases. The reason is that the shell is not closely knit and there are lacuna or capillaries in the shell at high immersion rates. At lower rates of immersion, the smooth, orbicular shell increases the strength. Preceding microcapsulation, the core material was dispersed by mechanical stirring. The diameter of the dispersed core determined the average diameter of the microPCMs. Thus the same stirring speed, same immersion rate and different mass ratio of core and shell material result in different thicknesses of the shell and a different penetration property. The different mass ratios of core and shell microPCMs intensities are shown in Fig. 5. A mass ratio of 1:1 was slow that of 3:1 and 4:1.

The microcapsule used in the above study was composed of double melamine-formaldehyde resin shell, which was produced by the slow immersion of the shell polymer material twice. In contrast, we used single-shell microencapsulations with different mass ratios of core and shell materials by immersing the shell material continuously at the same speed, 0.5 ml min^{-1}, and obtained the yield point as shown in Fig. 6. Obviously, the yield point of single-shell microencapsulates was less than that of double-shelled ones. When the mass ratio of the core and shell is 1, the value of the single-shell is half of that of the double-shell. From Fig. 6 we also observe that the strength of the shell decreased rapidly. However, when the mass ratio of core and shell is close to 4, there is little difference between the two. MicroPCMs were produced to absorb, store and release large amounts of latent heat, and thus we expect to encapsulate as much more core material to get a better effect. At the same time, the shell strength has to be taken into account in practical use. Thus it is crucial to balance both sides. In our experimental study, a mass ratio of 3:1 was found to yield the best results.

Conclusions

We have successfully evaluated the mechanical properties of the shell using this new method by observing the surface morphological structure change after pressure application by means of scanning electron microscopy. From the SEM photographs we can easily observe the transformation and evaluate the structure of the shell. The optimal encapsulation process can be used to obtain a high yield point of the shell. The crucial point, though, is to form an intact core-shell structure. Double-shell will make the intact easier.

Fig. 5 Variation of the yield point of the shell for different shell material immersion rates, 0.5, 1.0 and 2.0 ml min^{-1}, during the encapsulation process

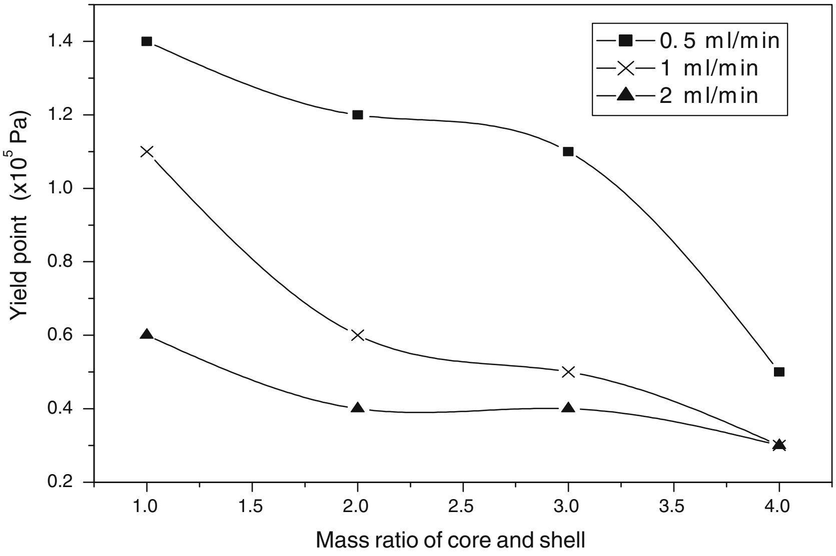
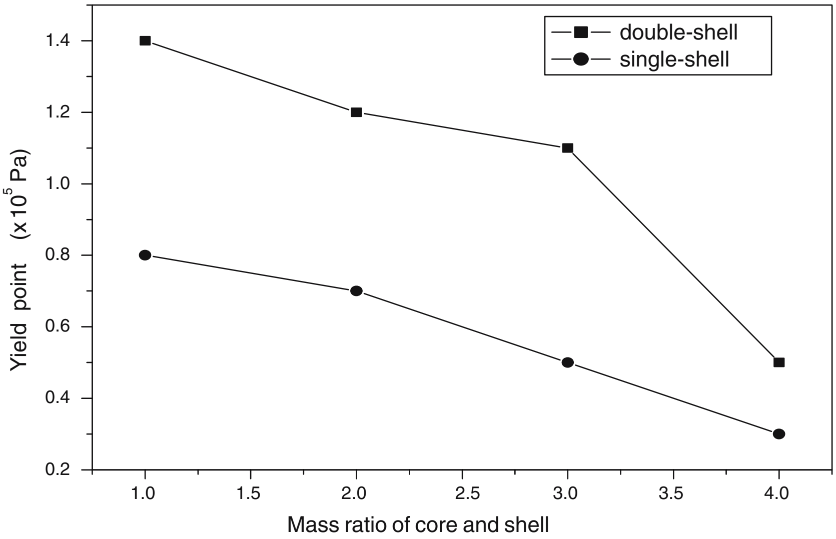


Fig. 6 Single-shell and double-shell microencapsulations with different mass ratio of core and shell materials obtained by immersing the shell material continuously at the same speed 0.5 ml min^{-1} and thus obtaining the yield points



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References

1. Jeong-Sook Cho, Aehwa Kwon, Chang-Gi Cho (2002) Microencapsulation of octadecane as a phase-change material by interfacial polymerization in a emulsion system. Colloid Polym Sci 280:260
2. Holman Mark E (1999) Use of microencapsulated phase-change materials to enhance the thermal performance of apparel. Am Soc Mech Eng 44:235
3. Mulligan JC, Colvin DP, Bryant YG (1996) Microencapsulated phase-change material suspensions for heat transfer in spacecraft thermal systems. J Spacecr Rockets 33(2):278
4. Inaba Hideo, Kim Myoung-Jun, Horibe Akihiko (2002) Heat transfer characteristics of latent microcapsule-water mixed slurry flowing in a pipe with constant wall heat flux. Trans Jpn Soc Mech Eng B 68(665):161
5. Cartwright DK, Bryant YG, Colvin DP (1999) Use of microPCMs in agricultural applications. Am Soc Mech Eng 44:241
6. Hawlader MNA, Uddin MS, Zhu HJ (2000) Preparation and evaluation of a novel solar storage material: microencapsulated paraffin. Int J Solar Energy 20(4):227
7. Sun G, Zhang Z (2001) Mechanical properties of melamine-formaldehyde microcapsules. J Microencapsul 18(5):593
8. Sun G, Zhang Z (2002) Mechanical strength of microcapsules made of different wall materials. J Microencapsul 242:307
9. Lulevich VV, Radtchenko IL, Sukhorukov GB, Vinogradova OI (2004) Deformation properties of nanadhesive polyelectrolyte microcapsules studied with the atomic force microscope. J Phys Chem B 107(12):2735–2740
10. Lulevich VV, Andrienko D, Vinogradova OI (2004) Elasticity of polyelectrolyte multiplayer microcapsules. J Chem Phys 8(120):3822–3826