Mechanical Properties and Thermal Stability of Double-Shell Thermal-Energy-Storage Microcapsules

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ABSTRACT: Double-shell-structured microcapsules encapsulating phase-change materials (micro-PCMs) with an average diameter of 5–10 μm were successfully fabricated with a melamine–formaldehyde resin as the coating material. The mechanical properties of the obtained piled micro-PCMs, tested under compression, were evaluated with a pressure sensor. Typical stress–strain curves showed that both the single-shell- and double-shell-structured microcapsules had yield points and maximum point pressures. The morphological changes in the shell surface confirmed the existence of yield points by scanning electron microscopy. When the pressure was beyond the yield point, the microcapsules showed conventional plastic behavior, and the double-shell structure was more mechanically stable than the single-shell one. Differential scanning calorimetry analysis results revealed that the properties of the phase-change materials experienced no variation after coating with a single-shell- or double-shell-structured polymer. Thermogravimetric analysis showed that the double-shell-structured micro-PCMs experienced a weight loss of only about 5% from 86.3 to 232°C but did so more rapidly from 232 to 416°C. Thermoregulation was determined with periodical heating and cooling tests. The data showed that the micro-PCMs changed temperature in a narrow range of 20–25°C with a time lag of 20 min to reach the maximum or minimum temperature in comparison with a reference temperature of 18–28°C. J Appl Polym Sci 103: 1295–1302, 2007

Key words: mechanical properties; microencapsulation; thermal properties

INTRODUCTION

Microcapsules are usually small, core–shell-structured particles with an active agent as the core material and a polymer as the coating material. The core ingredient can be a solid or a liquid, whereas the polymer used for the protective shell can be natural or synthetic. To date, microencapsulation has been widely used in carbonless copying paper, functional textiles, liquid crystals, adhesives, insecticides, cosmetics, food, spices, pharmaceuticals, and so forth.[1]

Recently, the ever-increasing energy consumption problem has attracted many researchers around the world, and some energy-saving innovations and technologies thus have been made. Among them, phase-change materials (PCMs) have received much attention because they can absorb, store, and release large amounts of latent heat over a defined temperature range when experiencing a phase transition.[2–4] PCMs thus can be potentially used for thermal energy storage in many fields. In all these applications of PCMs, microcapsules encapsulating phase-change materials (micro-PCMs) offer an alternative measure for dealing with the supercooling problem and interfacial combination with environmental materials. This idea can be traced back to the 1990s,[5] and now a number of studies have shown that micro-PCMs are promising for practical use in functional fibers, solar energy utilization, heat-energy transfers, and building materials.[6–13]

For practical applications, micro-PCMs must possess considerable mechanical strength and thermal stability. For this reason, Sun and Zhang[14,15] established a micromanipulation technique to quantitatively measure the mechanical strength of microcapsules. During the measurements, a single microcapsule sample is compressed to a large deformation or even ruptured while the force being imposed on the sample is recorded simultaneously. However, this method requires a special apparatus, and it is difficult to straightforwardly observe the surface shape change during the course of compression. Very interestingly, Lulevich and coworkers[16,17] studied the deformation of both microcapsules and multilayered ones with atomic force microscopy. Through these methods, the strength of a single microcapsule can be obtained, but this value may not reflect the actual strength of micro-PCMs when they are put together for practical use. Thus, there is a need to find a sim-

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ple way of evaluating the mechanical properties for the latter case. Another aspect of micro-PCMs that must be evaluated is the thermal stability. Usually, it is examined by thermogravimetric analysis (TGA) without consideration of the effect of the encapsulated substance on the shell material. This consideration is probably true, as reflected by a recent study in which the authors demonstrated that the expansion space inside the microcapsules could be large enough for the capped *n*-octadecane to expand during the heating process and subsequently result in no force exerted on the shell, therefore keeping the shell intact and increasing the thermal stabilities of the microcapsules.[18]

In this work, micro-PCMs were prepared through an *in situ* polymerization of a melamine–formaldehyde (MF) prepolymer on the chosen PCM. To make the formed coating compact and thermally stable with excellent process durability, we established a two-step polymerization technique to form micro-PCMs with a double-shell structure, as detailed elsewhere.[19] In this work, the mechanical properties of the shells was studied by the evaluation of the morphological changes of the surface structure of piled micro-PCMs under pressurization by a pressure sensor. The morphologies of the changes were observed with scanning electron microscopy (SEM). Differential scanning calorimetry (DSC) and TGA were employed to investigate the thermal properties and thermal stability of the fabricated micro-PCMs, respectively.

EXPERIMENTAL

Materials

A solid–liquid composite PCM with lauryl alcohol as its main component was applied as the core material and was kindly provided by the Energy Sources and Low Emission Research Institute of Hebei University of Technology (Tianjin, China). The MF prepolymer was purchased from Shanghai JQ Chemistry Co. (Shanghai, China) with a solid content of 50 ± 2%; its dissociative formaldehyde concentration was less than 2% (wt %). A styrene/maleic anhydride copolymer (SMA) and poly(ethylene glycol) nonylphenyl (NP-10), obtained from Sigma Chemical, were used as a dispersant and an emulsifier, respectively. The other chemical reagents (analytical-grade) were supplied by the Tianjin Kermel Chemical Reagent Development Center (Tianjin, China).

Nowadays, formaldehyde residue has emerged as a health concern for living beings and is the main reason for many indoor air-pollution cases. For this reason, the MF prepolymer used in our work had a rather low free formaldehyde concentration. Moreover, urea and ammonium persulfate were introduced into the polymerization system to react with dissociated formaldehyde, leading to the thorough removal of formaldehyde from the final products. Besides, the micro-PCMs were tested and thus proved to be harmless to health, and they had no negative effect on interior air quality according to Chinese standards.[20]

Fabrication of the double-shell micro-PCMs

The procedure for preparing the double-shell microcapsules was similar to that reported in our previous study.[19] Its main feature was the addition of the MF prepolymer in two steps to control the polymerization behavior. The fabrication details were as follows. Initially, 10 g of SMA powder, 0.2 g of nonionic surfactant NP-10, and 0.8 g of NaOH were measured and put into a 200-mL beaker to dissolve in 100 mL of deionized water under agitation at 50°C. After 2 h, a clear surfactant solution was obtained with a pH value of 4–5. The PCM (32 g) was then added, and the resultant mixture was subsequently emulsified at a vigorous stirring rate of 3000 rpm for 10 min with a disperser (QSL1200 disperser, Shanghai Hongtai, Ltd., Shanghai, China). The resultant emulsion was transferred to a three-mouth bottle that was immersed in a steady-temperature bath stirred at a rate of 1500 rpm. The prepolymer (16 g) was subsequently added dropwise at a rate of 0.5 mL/min. The system was then heated by the temperature being slowly increased to 60°C for 1.5 h to form a one-layer shell. Later on, another 16 g of the prepolymer was introduced into the bottle drop by drop at the same rate to form a second layer, and this was followed by the addition of 0.5 g of urea and 0.1 g of ammonium persulfate to the reaction system to eliminate the remnant of formaldehyde. The reaction temperature was finally increased to 75°C and kept for 1 h to completely consume the reactants. The microcapsules thus prepared were washed with deionized water, filtered, and dried in a vacuum oven before property characterization.

Also, the single-shell micro-PCMs were fabricated in this work according to the aforementioned process by the addition of the same amount (32 g of the MF prepolymer) of the shell material at a rate of 0.5 mL/min in one step.

Characterization of the mechanical properties

The mechanical stability of the formed microcapsules was evaluated with a self-made design, which is schematically illustrated in Figure 1. Micro-PCMs samples of the same weight (4 g) were carefully and gently paved in the same area between two pieces of glass (4 cm × 2 cm), and the formed sandwich was then transferred to a high-resolution pressure sensor. After the addition of a force to the top glass, the sen-

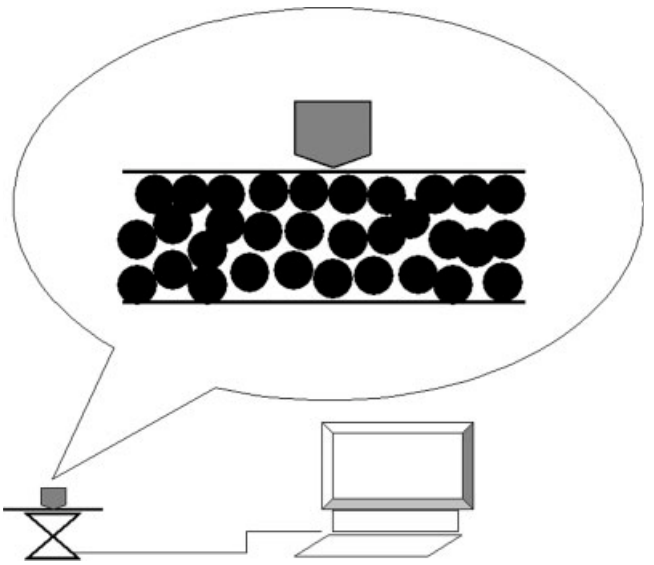

Figure 1 Schematic of a self-made design for measuring the mechanical properties of microcapsules.

sor under the bottom glass could simultaneously record the data. A typical curve of the stress–strain changes was seen automatically on a computer connected to the sensor. Each sample was tested five times to achieve the average values of the yield point and the maximum point (burst point) pressure. After pressurization, the shells were examined with a Philips XL30 SEM analyzer (The Netherlands) to investigate the morphological changes.

Characterization of the thermal properties

The phase-change properties of the PCM after and before microencapsulation were determined with a DSC analyzer (DSC7, PerkinElmer). The sample (10 mg) was tested at a heating rate of 10°C/min with nitrogen as the purging and protective gas. Each sample was analyzed at least twice, and the average value was recorded. The thermal stability characterization was performed on a Dupont SDT-2960 TGA analyzer at a scanning rate of 5°C/min in a flow of nitrogen (40 mL/min). A self-made design was applied to improve the understanding of the thermal properties of the dried microcapsules in practical applications. As shown in Figure 2, the design has the ability to simulate the real living environment by controlling the temperature in a hermetically sealed box, in which there are two bins. One bin is filled with dried microcapsules, whereas the other is full of atmosphere and is used as a reference. Through a connected thermocouple, the temperatures of both bins are recorded. Three heating–cooling cycles were carried out with temperatures ranging from 18 to 24°C (i.e., comfortable for human living), and the time used for each cycle was set to be 250 min.

RESULTS AND DISCUSSION

SEM morphologies of the micro-PCMs

During polymerization, a low stirring rate is used to better control the structure of micro-PCMs. It may be understandable that added prepolymer material may adhere to the core particles more easily at low stirring rates. Then, the subsequent polymerization brings well-compacted microcapsules. Figure 3 shows SEM images of micro-PCMs in different cases for mechanical testing. In Figure 3(a), the fresh double-shell micro-PCMs have a smooth appearance and a regular, spherical shape with a average diameter of about 5 μm. The arrows point out some polymer fillings present among the microcapsules. This occurs not only because the core material may not be encapsulated completely but also because the shell material may not fully cover the cores. It is of interest to us to find the shell deformation at the yield point and the burst point after mechanical measurements. Figure 3(b,c) shows typical surface morphologies of the microcapsules; the presence of a concave deformation on the shell after the yield point and shell pieces after bursting can be observed.

Mechanical properties of the double-shell micro-PCMs

The compactness of micro-PCMs is of importance to potential applications. Previously, we have discussed

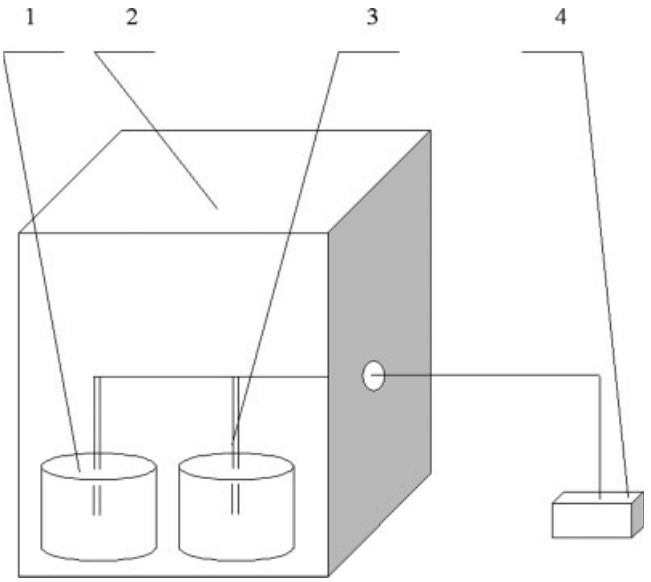

Figure 2 Design for evaluating the thermal regulation of dried microcapsules under numerous heating–cooling cycles: a hermetically sealed box with two bins inside, one bin with microcapsules and the other with air as the reference: (1) a bin filled with micro-PCMs, (2) a sealed box, (3) a bin with air as the reference, and (4) a high-resolution temperature sensor.

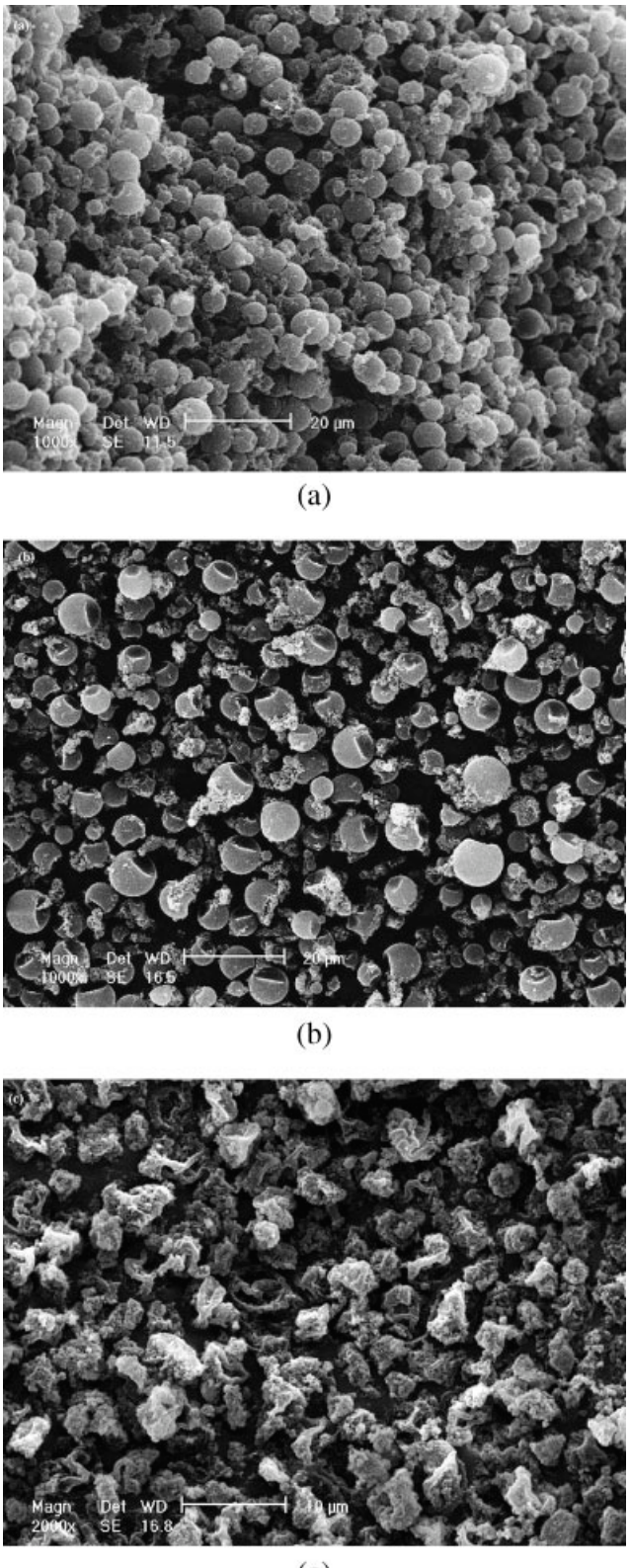

Figure 3 SEM images of micro-PCMs: (a) fresh double-shell micro-PCMs with the typical surface morphologies of microcapsules, (b) a concave deformation on a shell after the yield point, and (c) shell pieces after bursting.

that many factors, such as the core/shell mass ratio, microcapsule dimensions, and emulsifying agent content, can strongly affect the thickness of the shell, leading to variations in the compactness and mechanical features.[21] On the basis of our previous study, the shell/core mass ratio was 1:1 to make the shells possess suitable mechanical properties and prolong the staying time of the core material in the shells.

During the measurement of the mechanical properties, the microcapsules were compressed by a gradual increase in the loaded pressure until they all burst into pieces. After the yield point, the majority of the micro-PCMs may have burst much earlier at a much lower pressure. Figure 4(a) shows the typical curve stress–strain change of the single-shell and double-shell micro-PCMs under pressure. Obviously, each curve has a yield point, which reflects the fact that the shell has a plastic transformation. The result agrees with the SEM morphologies under increasing pressure, and this is helpful for understanding the evaluation of the shell deformation. The measurement of the stress–strain change was run at least five times for each sample to achieve average values. The data for the single-shell-structured microcapsules and double-shell ones are illustrated in Figure 4(b,c), respectively.

In Figure 4(b), there is a large difference in the mechanical data for tested single-shell micro-PCMs, such as yield points ranging from 3×10^4 to 4×10^4 Pa and maximum points (i.e., burst points) ranging from 9×10^4 Pa to 12×10^4 Pa. These data indicate that the fabricated single-shell micro-PCMs were not structurally uniform, so different values resulted for each test. On the other hand, double-shell micro-PCMs showed nearly the same mechanical data for several runs, as shown in Figure 4(c). The average maximum point and average yield point values were 13.5×10^4 and 5.5×10^4 Pa, respectively. Hence, it can be deduced that the two-step method to form the shell material may have a positive effect on the shell mechanical strength. In the meantime, the double-shell-structured micro-PCMs were found to be structurally homogeneous and have better mechanical stability.

As the aforementioned data indicate, both the yield point and maximum point of the double-shell-structured micro-PCMs were higher than those of the single-shell ones. With the improved mechanical properties of double-shell micro-PCMs, the PCM may have served for a longer time in the shells. This may be due to the fact that with the two-step addition of the MF prepolymer at a low stirring rate, the shell material could better precipitate onto the cores, and this resulted in better polymerization. Also, the two-step technique may have led to a higher degree of crosslinking, eliminating defects such as pores, cracks, and hair crackling in the shells.

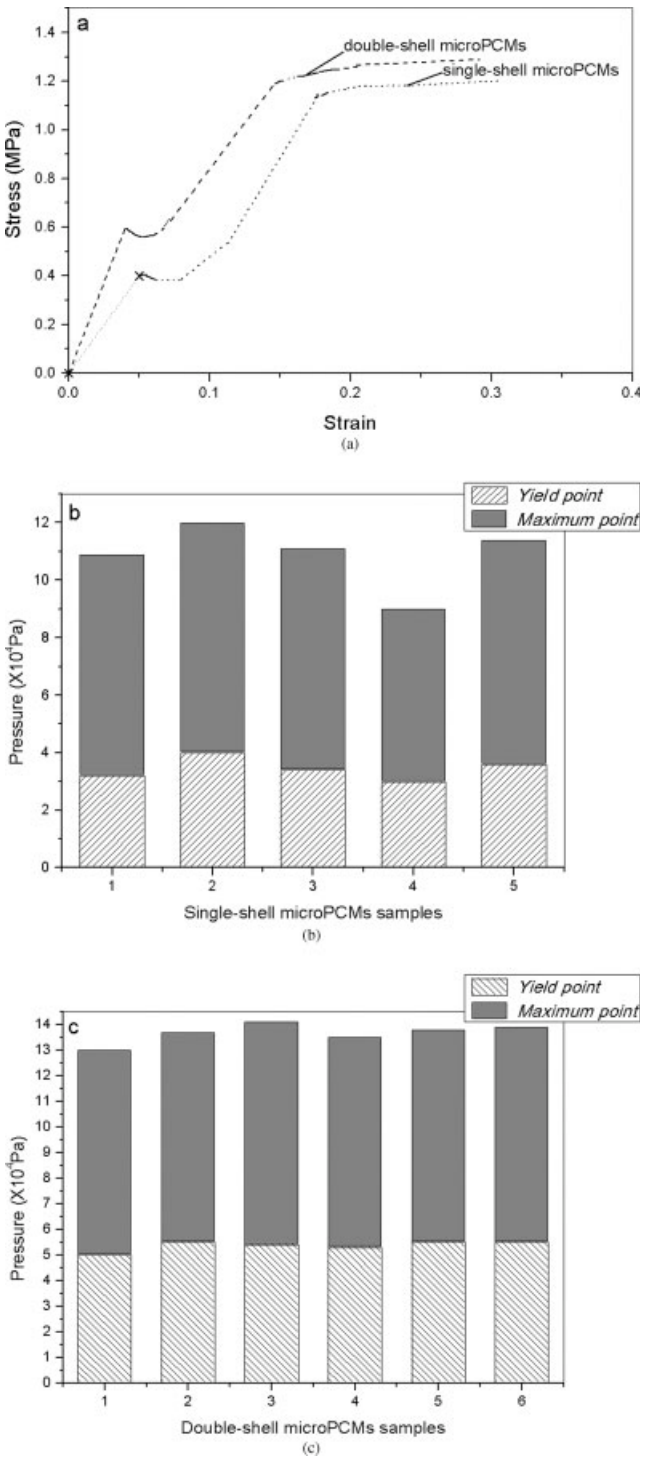

Figure 4 Mechanical properties of micro-PCMs: (a) typical stress–strain curves of micro-PCMs, (b) yield point and maximum point pressure of single-shell-structured micro-PCMs, and (c) yield point and maximum point pressure of double-shell-structured micro-PCMs.

Thermal properties of the micro-PCMs

Figure 5 shows DSC thermal curves for micro-PCMs. From these results, we can obtain information about the transition properties of the encapsulated PCM, such as the changes in the melting point and phase-transition heat. The pure PCM had a melting point of 24.0°C, and its phase-change heat was determined to be 225.5 J/g, as shown in Figure 5(a). For the double-shell micro-PCMs in Figure 5(b), the melting point was 24.7°C, nearly equal to that of pure PCM. The absorbed heat was 113.9 J/g, which was nearly half of that of pure PCM because the core and shell had a weight ratio of 1 : 1.

The DSC thermal absorption peak indicates that the polymeric shells nearly do not influence the thermal proprieties of the encapsulated pure PCM. Therefore, the microcapsules prepared in this study can be very promising for subsequent applications. However, DSC cannot confirm that the double-shell polymer structures protect the PCM safely. Thus, the thermal stability of TGA is necessary and may reflect the shell compactness preventing the release of the PCM.

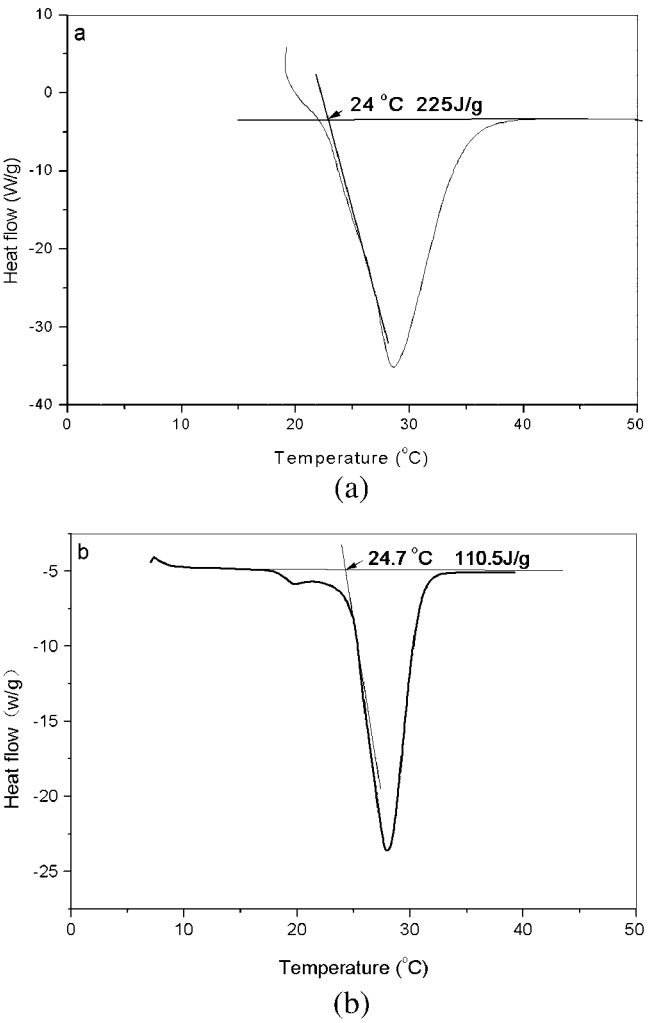

Figure 5 DSC analysis results for (a) pure PCM and (b) double-shell-structured micro-PCMs.

Thermal stability of the micro-PCMs

Figure 6 shows the TGA curves of PCM and micro-PCMs, which were obtained by the temperature being increased at a rate of 5°C/min from room temperature to 500°C. In Figure 6(a), pure PCM alone starts to lose weight at approximately 137°C, and it completely loses its weight at 207°C. The weight-loss speed of pure PCM is sharp because of its typical decomposition properties. However, for encapsulated PCMs, the TGA curves of single-shell and double-shell micro-PCMs are quite different, as shown in Figure 6(b, c).

Figure 6(a) shows that the single-shell micro-PCMs gradually lose their weight until the temperature is increased to 271°C, and this is followed by rapid decomposition. The weight loss around 100°C can be attributed to the evaporation of the water or solvent used for washing but trapped in the particles. The decomposition of the microcapsules begins at approximately 200°C. The weight loss of this sample is about 30% at 271°C, which reflects that single-shell micro-PCMs have appreciable thermal stability. To understand the particle dimension effect on the shell compactness, single-shell micro-PCMs, prepared at different emulsion stirring rates, were characterized with TGA.

The number-average diameters or weight-average diameters of microcapsules are strongly dependent on the process conditions, such as the emulsion stirring rate and emulsifier content. Zhang et al.[18] reported that the dimensions of microcapsules are exponentially dependent on the emulsion stirring rate, and a higher emulsion stirring rate consequently leads to smaller particles. Figure 6(b) presents the TGA results for single-shell micro-PCMs obtained at emulsion stirring rates of 1500, 2000, 2300, 2500, 2800, and 3000 rpm. The weight-loss temperature increases as the average diameter of the microcapsules decreases (corresponding to the increase in the emulsion stirring rate). All the samples lose nearly 10% of their weight at 125°C because of the evaporation of trapped water or solvent. The weight of the micro-PCMs (1500 and 2000 rpm) decreases quickly from 90 to 20% as the temperature increases from 100 to 250°C. At 2300 and 2500 rpm, the micro-PCMs thus fabricated lose their weight rapidly from 150 to 300°C in the same way. For emulsion stirring rates of 2800 and 3000 rpm, the micro-PCMs rapidly lose their weight from 200 to 300°C. These results indicate that single-shell micro-PCMs may protect the PCM, and the shell compactness is increased with a decrease in the particle diameter (i.e., an increase in the emulsion stirring rate).

On the basis of the aforementioned TGA properties of single-shell micro-PCMs, a 3000 rpm emulsion stirring rate was chosen to fabricate the double-shell ones with the expectation of preferable compactness. In Figure 6(c), the weight loss of double-shell ones is a two-phase process: about 5% weight loss from 86.3 to 232°C and a second rapid weight loss from 232 to 416°C. The curve of the first phase is nearly a level

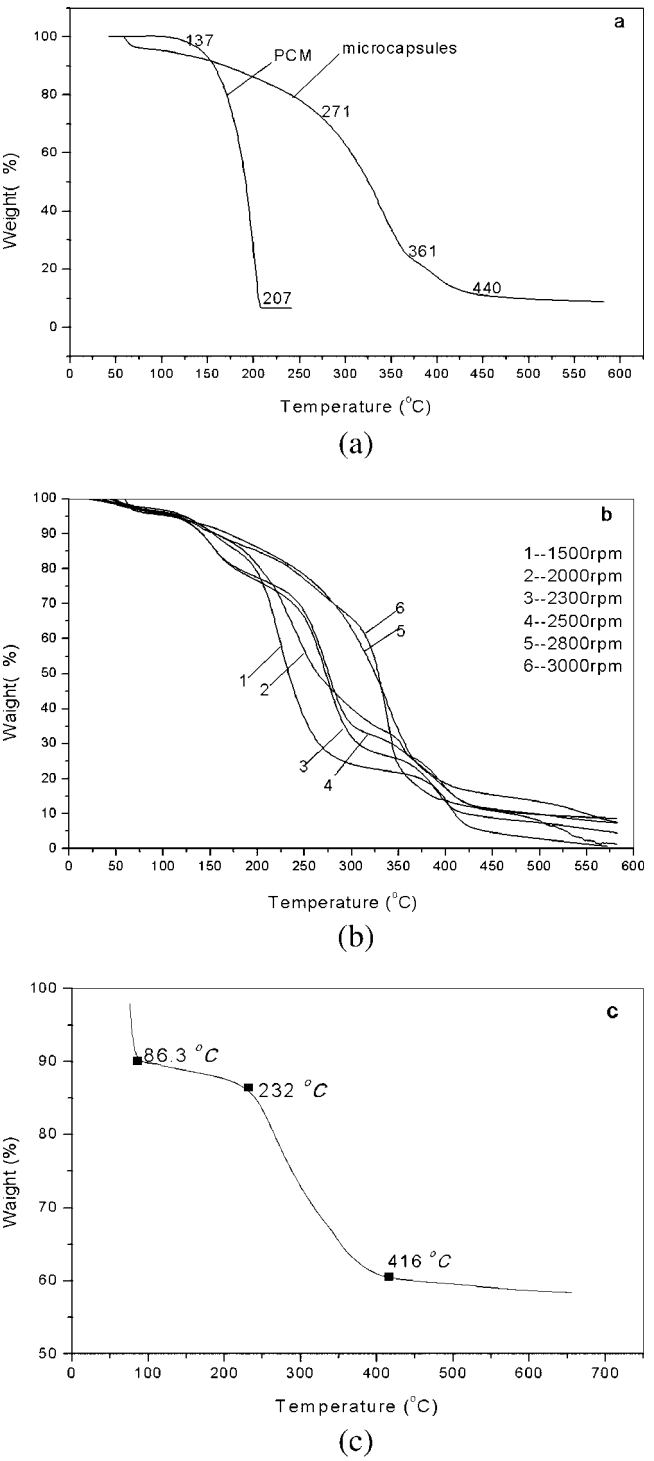

Figure 6 TGA curves of (a) pure PCM and single-shell micro-PCMs, (b) single-shell micro-PCMs prepared at different emulsion stirring rates, and (c) double-shell micro-PCMs prepared at an emulsion stirring rate of 3000 rpm.

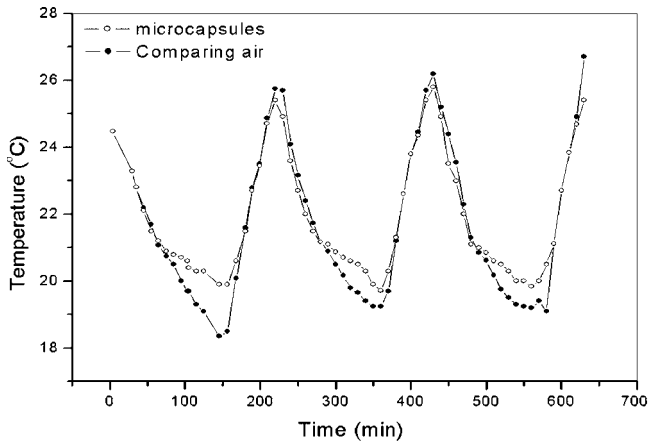

Figure 7 Evaluation of the thermal regulation of 500 g of micro-PCMs and reference air for three heating–cooling cycles.

line, which reflects that micro-PCMs can be protected safely without any leakage of the core material. Starting at the temperature of 232°C, the double-shell microcapsules cannot resist the thermal expansion, and some cracks may possibly occur in polymeric shells. Nearly 30% of the weight is lost very quickly because of the core material flowing out of the shells and then decomposing immediately. As the mass ratio of the core to the shell is 1 : 1 and the weight loss in the second phase is nearly half of the total weight loss, it can be imagined that the leakage of the core material started from 232°C.

The different TGA results for single-shell and double-shell structures indicate that the PCM is rather perfectly encapsulated by the double shell. However, it is necessary to analyze the thermal stability effectiveness of micro-PCMs for practical use. In this work, we evaluated the thermal stability by periodically increasing and decreasing the sample temperature and observing the thermal response with a home-made design, as shown in Figure 2. The box temperature can be controlled precisely, and the sensor can also measure the temperature in each bin momentarily.

Figure 7 shows the evaluation of the thermal regulation of 500 g of micro-PCMs and the reference air for three heating–cooling cycles with temperatures ranging from 18 to 28°C. The reference air changes its temperature in the range of 18.5–26.5°C, which is nearly uniform with the testing temperature range. The air temperature almost reaches the minimum point around 150 min for all runs. Because the reference air cannot effectively store or release energy, its temperature will rapidly change with the environment. Approximately, rapid weather changes usually make people feel uncomfortable. Comparatively, the micro-PCMs change temperature from 20 to 25°C in the periodic heating and cooling cycles. Interestingly, there is a time lag of 20 min for the micro-PCMs, compared with air, to arrive at their maximum temperature (25°C) or minimum temperature (20°C). Furthermore, after around 100 cycles, the SEM morphology shows there is no majority of leaking for the micro-PCMs. The double-shell structure still remains intact, and the core material retains its own solid–liquid phase properties without any changes as well.[22] Also, the results are identical to those of our previous study, which showed that leaked micro-PCMs may not give similar results; this is attributed to the fact that PCMs blending with shell materials do not show uniform heating–cooling curves.[23]

CONCLUSIONS

A serious of micro-PCMs were prepared to absorb, store, and release large amounts of latent heat for application in energy fields. Thus, we expected to encapsulate the core material as much as possible for a better effect. The shell strength had to be taken into account for prolonging the service time. The mechanical properties of single-shell-structured micro-PCMs and double-shell ones were dynamically investigated with a home-made compression design. Our experimental results showed that double-shell-structured micro-PCMs performed very well and seemed to provide a solution to the aforementioned concern. SEM analysis was successfully used to identify the typical process of the shell deformation. All the micro-PCMs were observed to have a yield point and a burst point, but the double-shell ones had higher values than the single-shell ones, indicating that the double-shell-structured micro-PCMs were more mechanically stable. The core material encapsulated in the double shell was found to not change its characteristic phase-transition temperature, and this is promising for practical applications.

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