Polymer Bulletin 60, 725–731 (2008)
DOI 10.1007/s00289-008-0894-x

Polymer Bulletin

Preparation of Mono-Dispersed Polyurea-Urea Formaldehyde Double Layered Microcapsules

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Received: 3 October 2007 / Revised version: 30 December 2007 / Accepted: 30 December 2007

Summary

A new method to prepare a kind of double layered microcapsules was developed. Polyurea (PU) microcapsules were firstly fabricated by interfacial polymerization as inner layer, on which urea-formaldehyde (UF) resin was coated to form a protective outer layer by in-situ polymerization. Environmental scanning electron microscope, optical image analyzer, Fourier transform infrared spectrophotometer and thermo gravimetric analysis were employed to investigate their characteristics for the morphologies, particle size, materials structures and thermal properties. The prepared double layered PU-UF microcapsules are mono-dispersed with ultra-thick capsule wall and improved thermal stability.

Introduction

Microencapsulation is a technique to prepare nano-sized or micron-sized particles containing active materials for protection or delivery purpose. It has been widely used in carbonless copy papers, functional textiles [1], controlled release of drugs [2], insecticides [3], self-healing polymer composite [4], information materials like microencapsulated electrophoretic display system [5], and so on. In order to meet the requirements in certain circumstance, such microcapsules with special structures have been successfully prepared as multilayered microcapsules [6], thermoresponsive porous microcapsules [7], and hollow microcapsules with large voids [8]. Conventionally, multilayered microcapsules were fabricated by layer-by-layer technology which employs alternating assembly of oppositely charged species like polyelectrolytes, lipids [9] or inorganic particles. However, capsules consisting of different layers using combination of different encapsulation techniques were scarcely reported.

In this paper we have successfully developed a kind of layered microcapsules by condensing urea formaldehyde resin onto polyurea microcapsules. The inner PU layer was fabricated by interfacial polymerization. K. Hong et al studied the preparation and application of PU microcapsules from different isocyanates [10]. PU has some excellent properties like being flexible, optical transparent and hermetic. However, it is soft and deformable due to low mechanical strength. In addition, microcapsules obtained by interfacial polymerization tend to agglomerate because of the cross-linking between capsules by residual monomers inside. Consequently, the further application of the microcapsules is limited due to the difficulty of post-treatment, while mono-dispersed microcapsules are preferred in practical use [7]. This problem may be mitigated by adding some dispersants into the system to enhance the surface charge of the layer [11]. In this paper, we managed to solve the above problem by coating the polyurea microcapsules with another layer of non-sticky substance *i.e.* urea formaldehyde resin. Therefore, the UF pre-polymers could condense on the surface of the PU layer and then form a hard and stable protective shell.

Experimental

Materials

Tolyene 2,4-diisocyanate (TDI) and triethylene tetraamine (TETA) as inner wall materials, urea and 37 wt% aqueous solution formaldehyde as outer wall materials, polyoxyethylene octylphenyl ether (OP-10) as emulsifier, were obtained from Kewei Chemicals (Tianjin, China), without any further purification. Polyvinylpyrrolidone (PVP, K30) as protective colloid, triethanolamine, 50 wt% glutaraldehyde aqueous solution and tetrachloroethylene (TCE) were purchased from North Chemical Supplies (China). All the above chemicals used in this study were a reagent grade. Commercial grade Oil Red G as color indicator was supplied by Hoechst (Germany).

Synthesis of water soluble monomer

The water soluble monomer was synthesized by modifying TETA with glutaradehyde. The experiment was carried out in a 3-necked flask equipped with a reflux condenser, a stirrer, and a thermometer. 0.01M TETA and 10 mL of distilled water were charged into the flask at 90°C under vigorous stirring. 10 mL of 0.8 mol/L glutaradehyde was added dropwise into the system within 0.5 h. The reaction was kept for another 2 h to obtain the final monomer, a kind of transparent brown solution.

Preparation of the inner layer of the microcapsules

The inner layer was firstly fabricated by interfacial polymerization as illustrated by Figure 1a, b. 40 ml of aqueous solution containing 0.25 wt% PVP as a protective colloid was added into a 100 mL flask. Then 0.002M TDI and 3.2 mg Oil Red were dissolved into 4 ml of TCE to obtain internal phase, which was introduced into the reactor. Subsequently, the mixed solution was mechanically emulsified to yield an o/w emulsion by stirring at 800 rpm with OP-10 as emulsifier at 20°C. After stirring for 120 s, 0.01M modified TETA was added into the emulsion to initiate the interfacial polycondensation reaction and accordingly droplets of red solution were encapsulated to form the polyurea microcapsules. The stirring rate was decreased to 400 rpm after 3 min reaction. After another 10 min stirring, the microcapsules were separated from the aqueous phase and rinsed with distilled water to a pH of 7.

Preparation of the outer layer of the microcapsules

The outer layer was fabricated from urea-formaldehyde resin by in-situ polymerization method, as shown in Figure 1c, d. The above PU microcapsules as templates were introduced into a 100 mL flask with 60 mL water. 0.2 g PVP was added in the solution to prevent agglomeration between PU capsules. Then 1.0 g urea was added into the system and stirred moderately under 60°C. The pH of the system was adjusted to 1.5-2.0 by dropwise addition of hydrochloric acid (1M HCl) in 0.5 h. Then, 2.44 g 37 wt% formaldehyde aqueous solution was introduced to start the polymerization reaction. 1.5 h later, the slurry was cooled, filtered, washed and dried to obtain the resultant double layered microcapsules.

Characterization methods

The surface functional groups of capsule layers were observed with BIO-RAD3000 Fourier transform infrared (FTIR) spectrophotometer. The thermo properties of the capsules were studied by thermo gravimetric analysis (TGA) with TGA-50H (Shimadzu, Japan). Each time about 8 mg of sample was heated at the rate of 5°C /min in the temperature range of 30-600°C under constant nitrogen flow. The double layered structures, particle size distribution and morphologies of the microcapsules were observed using an image analyzer (53-XC Shanghai Forever, China) with CCD (Panasonic, Japan), and also using an environmental scanning electron microscope (ESEM, XC-30 TMP, Philips) after Au coating with ion sputtering for 180 s. The cross-sectional structures of the microcapsules were observed by cutting the microcapsules with a microtome knife.

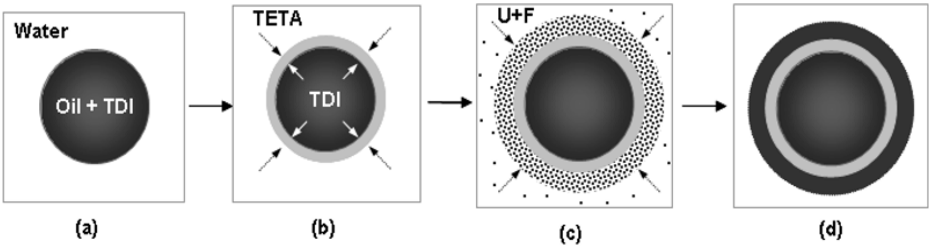

Figure 1: Schematic diagram of the process: (a) oil/water emulsion; (b) formation of the inner PU layer by adding TETA; (c) condensation of the UF resin; (d) consolidation of the outer layer.

Results and discussion

Morphology and size of microcapsules

Figure 2 shows the ESEM micrographs of the intermediate single layered and the final double layered microcapsules. From Figure 2a, it can be seen that single layered PU capsules are aggregated in clusters, and obvious defects like craters and shrinks are observed. This is due to the permeation of residual TDI through PU layer and causing cross-linking between adjacent microcapsules. And the single layered PU capsules have a wall thickness of about 2 μm with a smooth outer surface (Figure 1b). In contrast, the double layered microcapsules are well dispersed and spherical, as illustrated in Figure 1c. It can also be seen that morphological defects are dramatically eliminated due to the increase of mechanical strength by coating of UF resin layer. As shown in Figure 1d, the wall thickness is increased up to 7 μm, with a rough surface which is the typical morphology of UF-resin layer.

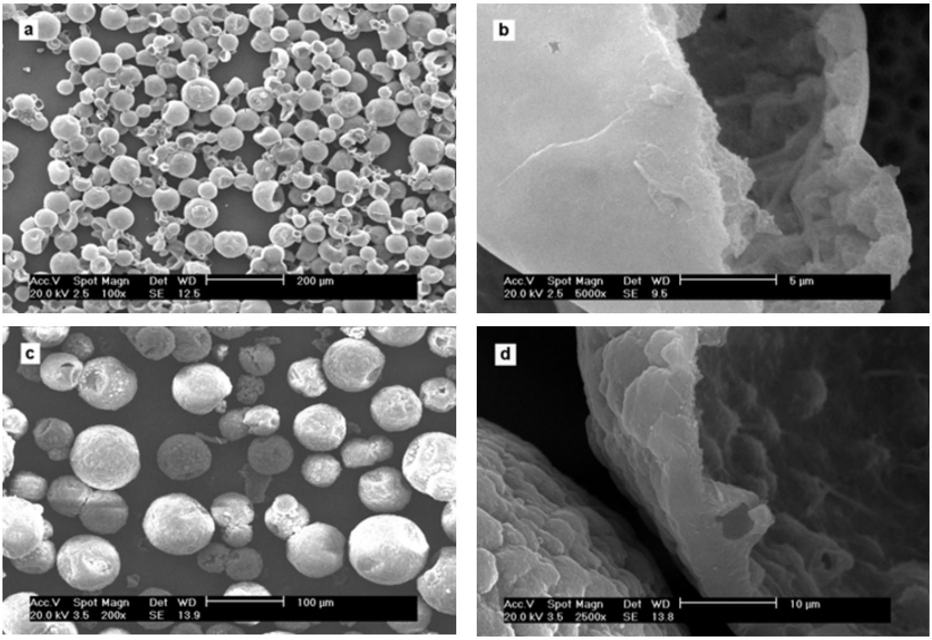

Figure 2: ESEM micrographs of (a) aggregated single layered PU microcapsules and (b) its cross-section view, (c) mono-dispersed double layered microcapsules and (d) its cross-section view.

Figure 3a shows the cross section of single layered PU microcapsules. The collapse phenomenon (arrow 1 in Figure 3a) indicates that the PU layer is flexible and not strong enough to keep the spherical morphology when the capsules dries up and tends to shrink. As mentioned above, the aggressive component TDI may permeate through the wall of PU capsules and cause cross-linking (arrow 2, 3 in Figure 3a). In Figure 3b, the inner PU layer has a red color while the outer UF-resin layer is almost achromatic and transparent. This means the core stuff Oil Red G can easily penetrate the inner layer but it is confined by the outer one. So the double layered microcapsules have

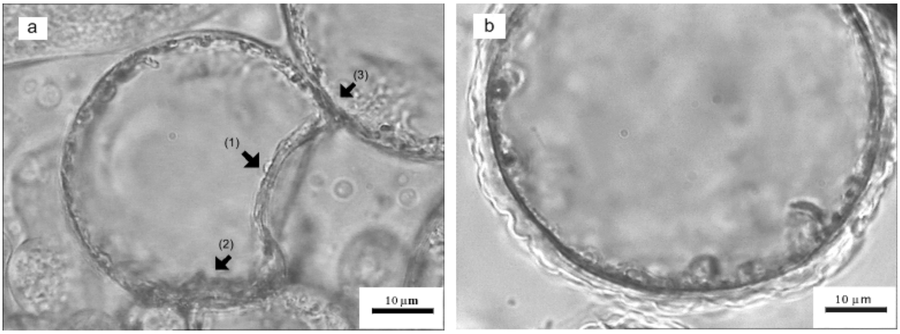

Figure 3: Cross-sectional micrograph of (a) single layered PU microcapsules and (b) double layered microcapsule under optical microscope (1000x).

a relatively lower permeability compared with the single layered ones and maybe have the potential for making products (e.g. medicine and pesticides) demanding longer release time.

Furthermore, the boundary line between the two layers can be clearly observed in Figure 3b by optical microscope. However, the boundary is not distinct in Figure 2d and what we can see is a solid and integral layer which indicates that the two layers are completely integrated. So it is found that the double layered microcapsules have formed.

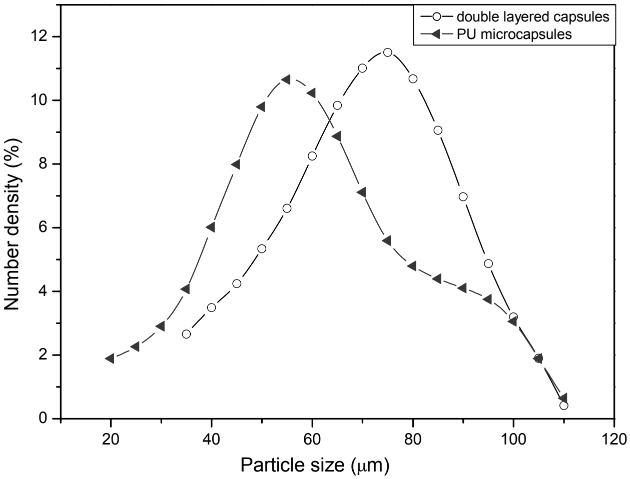

Figure 4: Particle size distribution of intermediate PU microcapsules and double layered PU-UF composite microcapsules.

Particle size distributions of the prepared microcapsules are displayed in Figure 4. All the microcapsules are in the size range of 20 μm ~ 110 μm, but the total particle size of double layered microcapsules is bigger than that of PU capsules. As we elaborated in the experimental section, PU microcapsules were prepared as templates and UF-resin layer was condensed on the templates to form the double layered capsules. So it is reasonable that the mean particle diameters are 59.5 μm and 70.9 μm for PU and double layered capsules respectively. The size distribution corresponds to the results of micrographs shown in Figure 2, 3 that the wall thickness of double layered microcapsule is around 5 μm bigger than that of PU capsule.

Characterization by FTIR

Figure 5 illustrates the FTIR spectra of single layered PU microcapsules, UF-resin, and double layered microcapsules. From IR spectra of PU (Figure 5a), a strong band known for hydrogen bonded N-H stretching vibration at 3302 cm^{-1} is observed. C=O stretching vibration is shown at 1645 cm^{-1}, and C-N stretching vibration combined with N-H bond is observed at 1544 cm^{-1}. The absorption peak at 1600 cm^{-1} is shown as the N-H bonded with benzene ring.

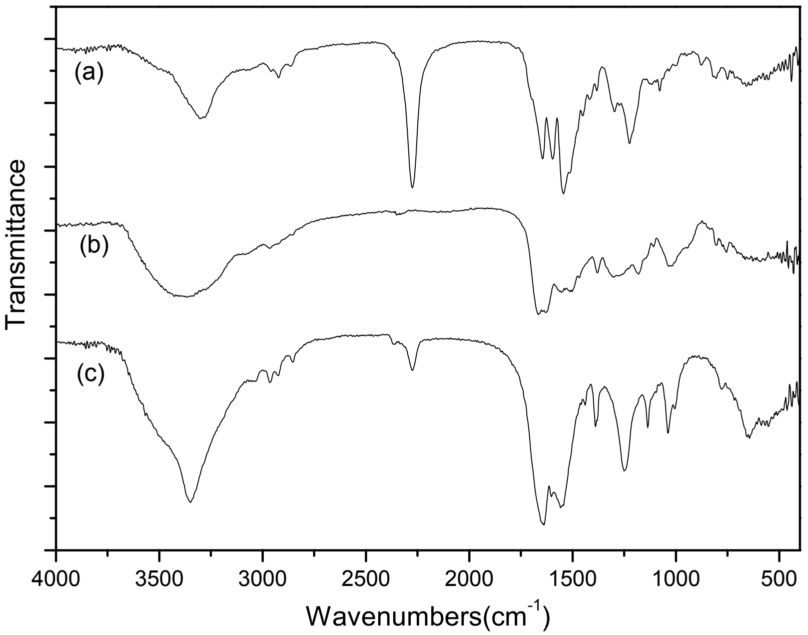

Figure 5: FTIR spectra of (a) PU microcapsule templates, (b) UF-resin, and (c) double layered microcapsules.

The sharp absorption peak of residual isocyanate groups in PU is shown at 2275 cm^{-1}. From the IR spectra of UF-resin (Figure 5b), three peaks of a N-H stretching vibration at 1555 cm^{-1}, a C=O stretching vibration at 1645 cm^{-1} and a C-N stretching vibration at 1286 cm^{-1} are observed. A broad absorption peak of O-H is shown at 3500-3250 cm^{-1}. In spectra c (Figure 5c), the structures of double layered microcapsules are clearly revealed. As illustrated by Figure 2, spectra c comprises the main characteristic of PU with peaks at 2275 cm^{-1}, 1645 cm^{-1}and 1600 cm^{-1}, and that of UF-resin at 1645 cm^{-1}, 1555 cm^{-1}and 1286 cm^{-1}. So it can be proved that the PU-UF double layered microcapsules have formed.

Characterization by TGA

The thermal properties of PU microcapsules and double layered PU-UF microcapsules containing TCE were investigated using thermo gravimetric analysis. As shown in Figure 6a, the first weight loss of about 42% was observed between 40 ~ 96°C, and the second one of 33.7% between 185 ~ 210°C. Correspondingly, the first weight loss is deemed to be due to release of hydrophobic core materials, and the second one is connected to the melting of PU wall and release of residual core materials. Whereas, the melting and thermal decomposition of double layered microcapsules were observed between 248 ~ 318°C with a weight loss of 60% as shown in Figure 6b. As a result, comparison between the two samples clearly demonstrates that double layered PU-UF composite microcapsule has higher thermo stability than single layered PU capsule, and the core materials (Oil Red G in this paper) are better preserved in the PU-UF capsules.

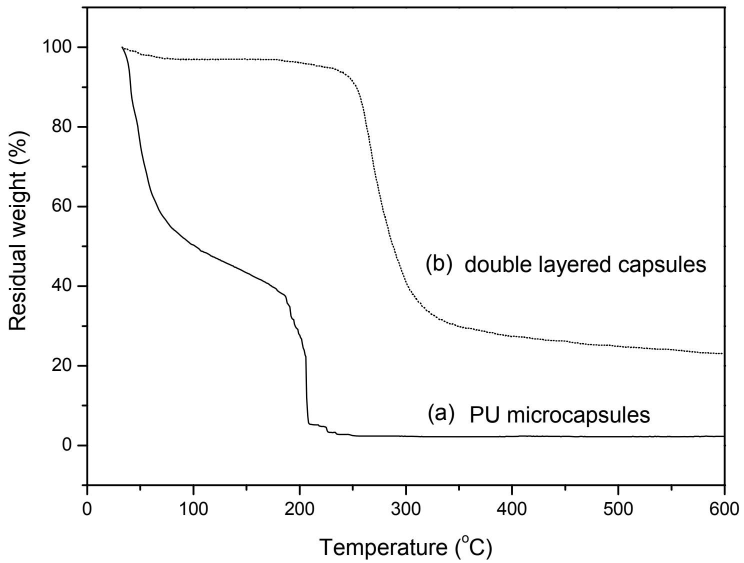

Figure 6: Thermal decomposition profiles of (a) PU microcapsules and (b) double layered PU-UF composite microcapsules.

Conclusions

A kind of mono-dispersed double layered microcapsules was prepared with Oil Red G solution as core, polyurea as inner layer and urea formaldehyde resin as outer layer. The double layered structure of the microcapsules was clearly observed by ESEM and optical microscope. Meanwhile its chemical structure and thermal stability was characterized by FTIR and TGA. The prepared microcapsules have obtained some significant properties: (i) easy handling as powder-like materials; (ii) ultra-thick capsule wall with good protection to core materials; (iii) double layered structure with higher thermal stability than single layered polyurea ones.

Acknowledgements. This project was supported by the National High Technology Research and Development Program of China (863 Program) (Grant No. 2004AA302010).

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