PREPARATION AND CHARACTERIZATION OF SHELL-FUNCTIONALIZED MICROCAPSULE

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Introduction

Microcapsules have been applied to many fields such as pharmaceutical, biomedical applications, phase change material, coating, catalysis and environmental engineering. These microenvironments provide protection for core materials from deteriorating environment such as oxidation, moisture, release and sustained-release under a controlled condition. Recently, a new application of poly(urea-formaldehyde) microcapsules filled with dicyclopentadiene, which are prepared by in situ polymerization technology, has been developed to fabricate self-healing polymeric composites[1-2].

However, the interface between microcapsule's shell and polymer matrix directly influences the mechanical performance and self-healing efficiency of the self-healing materials[3]. In order to improve interface action, we focus on the research of functionalization for microcapusule's shell. In this paper, we adopted chitosan as the shell materials, then added hydroxyl-terminated urea-formaldehyde prepolymer to crosslink the shell chitosan via situ-polymerization.

Chitosan is positively charged polyelectrolyte，especially, which can adsorb with negatively charged polymer to form complex[4]. Therefore, we utilize electrostatic adsorption between negatively charged sodium dodecyl sulfate (SDS) and chitosan in an oil-in-water emulsion to form combination, crosslinking the combination to make the shell rigid.

Experimental

Materials

Chitosan was obtained from Shanghai Zhanyun Chemical co. Ltd. and dissolved in 1w% acetic acid solution.

Dicyclopentadiene(DCPD) (Hangzhou Yangli chemical company, China) is used as core material.

Urea (U) and 37wt% formaldehyde (F) was obtained from Tianjin Chemical Plant, China.

Triethanotamine (TEA) (Harbin Chemical Plant, China) is used to control the pH of solution.

sodium dodecyl sulfate(SDS) is purchased from Tianjin Kemeng Chemical co. Ltd..

10 wt% hydrochloric acid solutions were prepared to control the pH value of emulsion. All the materials are commercial products and were used without further purification.

Preparation procedure of hydroxyl-terminated urea-formaldehyde(UF) prepolymer: urea and 37 wt% formaldehyde were mixed in a 250 ml three-neck round-bottomed flask with mechanical stirring at room temperature. The weight ratio between urea and formaldehyde was 1:2. The pH of mixed solution was adjusted to 8–9 with TEA. The temperature of system was raised to 70℃ and kept for 1 h, then the UF prepolymer solution was obtained.

Preparation procedure of chitosan-(urea formaldehyde) (CUF) microcapsules: 20g DCPD was added into 40g deionized water. 0.039g SDS was added into solution under the agitation ratio of 500 rap for 15-30 min. 10g 1w% chitosan solution (1w% acetic acid) was slowly added by drop funnel under agitation ratio of 100 rap. 8.4g UF prepolymer solution and 0.5g resorcinol as solidify promoter were added. The pH of the solution was adjusted slowly to 3.0-4.0 by 10 wt% hydrochloric acid solution, then the solution was heated to 60℃ and kept for 3 h. The microcapsules were rinsed with deionized water and acetone, filtered and air-dried for 24 h.

Apparatus and Procedures

Surface morphology and size distribution of the microcapsules were observed by scanning electron microscopy (QUANTA 200 ESEM, FEI). The average size of microcapsules was measured on data sets of at least 200 measurements. Samples were prepared on an aluminium slice, dried in a vacuum oven, and sputtered a coat with gold-palladium.

The infrared spectrometric analyzer (AVATAR 370 THERMO NICOLET) was used to identify the chemical structure of microcapsule shell materials which were prepared by grinding the sample with a potassium bromide (KBr).

Results and Discussion

Microcapsules surface morphology

Figure 1 shows the SEM micrograph of microcapsules. The microcapsules surface are rough, which can increase surface area of microcapsules and enhance surface

adhesion.

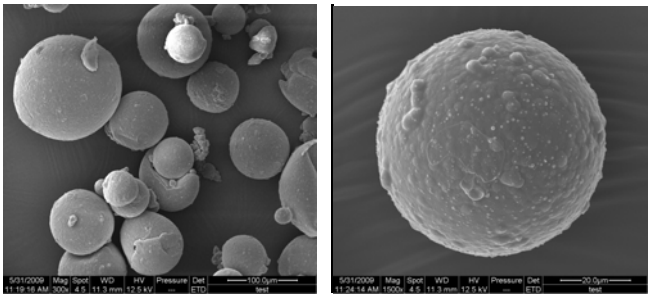

Fig. 1 SEM micrograph of microcapsules.

Microcapsules size analysis

Figure 2 shows the size distribution of microcapsules samples. The microcapsules size is in a wide range of 10–160μm and the mean diameter is 40μm, which depends on the fluid flow around the propeller. Larger microcapsules exist in the region of flow away from the propeller and smaller microcapsules exist in the vicinity of the propeller blades. Therefore, the microcapsule size can be controlled by the adjusting the agitation rate.

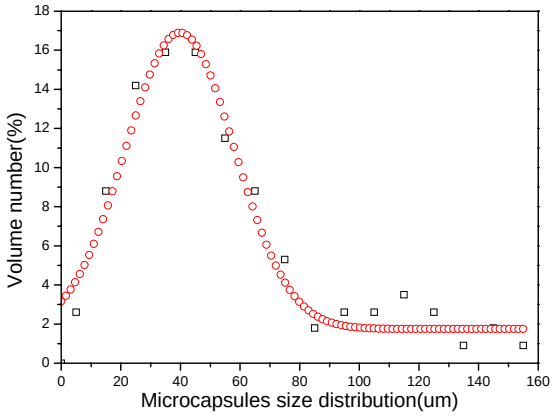

Fig. 2 Size distribution of microcapsules.

Chemical structure analysis of CUF shell materials

Figure 3 shows Fourier-transform infrared spectrometer(FTIR) spectra of chitosan and CUF. Absorptions peak at 3373 cm^{-1} represents the stretching modes of -OH and -NH, and the peaks at 2968cm^{-1} is the characteristic of –CH. Absorption peaks at 1641 cm^{-1} and 1559 cm^{-1} respectively represent the stretching vibrations of –C=O and –CN group of CUF, which indicates that characteristic of UF prepolymer is existent in the shell. It implies that copolymerization has occurred between UF prepolymer and chitosan. For the CUF, there are absorption peaks at 1153 cm^{-1} and 1022 cm^{-1}, which are characteristic for C-O-C and C-OH stretching vibrations from the carbohydrate ring of chitosan and demonstrates that hydroxyl groups of chitosan are contained in the chemical structure of shell materials. It proves that CUF as the microcapsules' shell have been formed.

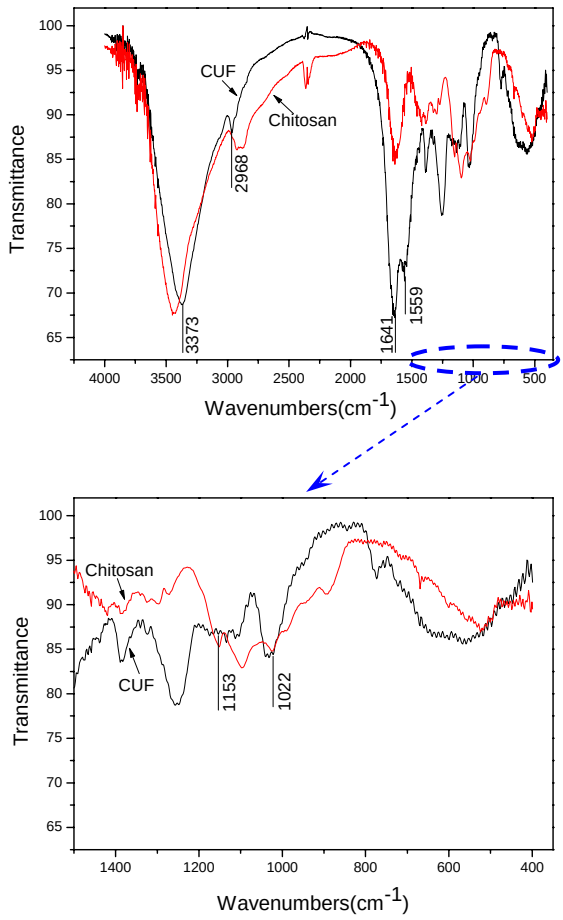

Fig. 3 FTIR spectra of shell materials and chitosan.

Conclusion

CUF microcapsules were successfully prepared. The surface, size distribution and shell chemical structure of the microcapsules were investigated. Massive hydroxyl groups and amine groups existing in the CUF shell will be advantageous for the interface performance between microcapsules and epoxy matrix.

References

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