# Synthesis and Characterization of Chitosan/Urea-Formaldehyde Shell Microcapsules Containing Dicyclopentadiene

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**ABSTRACT:** Microcapsules containing healing agent have been used to develop the self-healing composites. These microcapsules must possess special properties during the use of composites such as stability in surrounding, appropriate mechanical strength, and lower permeability. A new series of microcapsules containing dicyclopentadiene with chitosan/urea-formaldehyde copolymer as shell materials were synthesized by *in situ* copolymerization technology. The microencapsulating mechanism was discussed and the process was explained. Also, the factors influencing the preparation of microcapsules were analyzed. The morphology and shell wall thickness of microcapsules were observed by using scanning electron microscopy. The size of microcapsules was measured using optical microscope and the size distribution was investigated based on data sets of at least 200 measurements. The chemical structure and thermal properties of microcapsules were characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis, respectively. The storage stability and isothermal aging experiment of microcapsules were also investigated. Results indicted that the chitosan/urea-formaldehyde microcapsules containing dicyclopentadiene were synthesized successfully; the copolymerization occurred between chitosan and urea-formaldehyde prepolymer. The microcapsule size is in the range of 10–160 μm with an average of 45 μm. The shell thickness of microcapsules is in the range of 1–7 μm and the core content of microcapsules is 67%. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2202–2212, 2011

**Key words:** chitosan; urea-formaldehyde; adsorption; copolymerization; microencapsulation

## INTRODUCTION

Microencapsulation processes are of vital importance to many industries because of their potential applications in the field of biomedical applications,[1] phase change material,[2] coating,[3] catalysis,[4] and environmental engineering,[5] etc. These microcapsules shells provide protection for core materials from deteriorating effects such as oxidation and moisture, release or sustained-release under a controlled condition. Recently, self-healing polymer using microcapsules as a healing key has drawn increased attention because it represents a new paradigm for active and responsive material.[6] The shell modification of microcapsules containing dicyclopentadiene (DCPD) was investigated to improve the interface performance between microcapsule and matrix through grafting epoxy functional group and using 3-aminopropyltriethoxy silane-coupling agent (KH550) recently.[7,8] The poly(urea-formaldehyde) (PUF) shell microcapsules containing healing agent were synthesized by *situ*-polymerization technology.[9,10] Polyurethane (PU) shell microcapsules containing reactive diisocyanate for use in self-healing polymers were fabricated via interfacial polymerization.[11] Microcapsules with melamine-formaldehyde (MF) resin as shell materials containing DCPD were also synthesized by *in situ* polymerization technology.[12] The potential application of microcapsules containing self-healing agent for polymeric composites is very large. Self-healing process is accomplished as soon as cracks start to propagate through the material and rupture embedded microcapsules, and the healing agent would be released into crack planes as a result of capillary effect and would heal the cracks. It demands higher performance for the shell materials in mechanical strength and chemical structure stability. Owing to the promising technical applications of microcapsules containing self-healing agents, the preparation of microcapsules containing self-healing agents have attracted more and more attentions.

Self-healing polymer composites can be used at different temperatures and pressures. The requirements for microcapsules containing healing agent are various according to the application environment of polymeric composites. The mechanical and

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thermal properties must be adequate to retain the intactness and lower permeability of microcapsules during the use of composites, and the microcapsules must rupture when the microcracks propagate through the material. Therefore, the shell materials play an important role in obtaining high physical property of microcapsules.

Chitosan is a reactive monomer and can be reacted with amine and hydroxy functional groups under the different pH condition because of its chemical structure. When pH value is lower than 7 in a solution, the main reaction is the polycondensation between amine and hydroxy. It extensively used in many applications such as pharmaceutical,[13] especially microencapsulation[14–16] due to the ability of electrostatic adsorption with negatively charged polymer. So it may be used as shell former for the fabrication of self-healing microcapsules. Shell materials consisting of copolymer of chitosan and UF prepolymer may possess higher storage stability, adequate mechanical properties, and lower permeability in the polymeric composites. Moreover, it can also provide more reactive dots in the chemical structure of the shell so as to be advantageous for improving the interface performance between microcapsules and matrix in the composite.

In this study, the method to prepare microcapsules is based on the followings: electrostatic adsorption between the cationic chitosan and negatively charged sodium dodecyl sulfate (SDS) forms a gel layer at the interface of oil-in-water emulsion; and subsequently, microcapsules' shells are synthesized by the copolymerization of chitosan and UF prepolymer at the interface. Detailed descriptions of the fabrication process and the fabrication conditions for UF prepolymer had been reported in many literatures.[17] The chitosan/urea-formaldehyde (CUF) shell microcapsules containing healing agent were characterized by Fourier-transform infrared (FTIR) spectroscopy, scanning electronic microscope (SEM), optical microscope (OM), and thermogravimetric analyzer (TGA) to investigate their chemical structure, surface morphology, size distribution and thermal stability, respectively. The epoxy samples containing CUF microcapsules were also fabricated and healing efficiency was investigated.

## EXPERIMENTAL

### Materials

DCPD (Hangzhou Yangli chemical company, China) is used as core material. Urea (U) and 37 wt % formaldehyde (F) was obtained from Tianjin Chemical Plant, China. Chitosan used as the copolymer monomer of shell material was obtained from Shanghai Zhanyun Chemical Co., Ltd. The chitosan solution was prepared by dissolving 1.00 g of chitosan flakes in 50 mL of 1% (v/v) acetic acid. Triethanotamine (TEA) (Harbin Chemical Plant, China) is used to control the pH of solution. SDS is purchased from Tianjin Kemeng Chemical Co., Ltd. Sodium dodecyl benzene sulfonate (SDBS) is purchased from Tianjin Kemiou Chemical Co. Ltd.. 10 wt % hydrochloric acid solutions were prepared to control the pH value of emulsion. Epoxy resin (diglycidyl ether of bisphenol A: DGEBPA, E-51) used as matrix was purchased from Wuxi Resin Plant, China. Triethylenetetramine(TETA) was purchased from Tianjin Yixin Tenglong Chemical Plant, China. Tungsten (VI) chloride $WCl_6$ (98.5%) used as catalyst of DCPD was obtained from Huajing Powder Material Science and Technological Co. Ltd., Changsha, China. Phenylacetylene used as effective coactivators with $WCl_6$ was purchased from Shandong Zibo HanKing Trading Co. Ltd. Nonylphenol used as a dissolution agent of $WCl_6$ was obtained from Chengdu Kelong chemical Plant, China. All the materials are commercial products and were used without further purification.

### Preparation of microcapsules

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

Preparation procedure of CUF microcapsules: DCPD was added into the mixture solution of deionized (40 g) water and emulsifier under the agitation for 15–30 min. Chitosan solution was slowly added by dropping funnel under agitation. Then UF prepolymer solution and resorcinol (0.5 g) as solidify promoter were added. The pH of the solution was adjusted slowly to 3.0 × 10 wt % hydrochloric acid solution, and then the solution was heated to 60°C and kept for 3 h. The microcapsules were rinsed with deionized water for several times, and collected in a centrifuge. Finally, the powder-like microcapsules were obtained after drying in an oven at 25°C for 48 h.

To optimize and evaluate the effect of the preparing conditions on the yield of microcapsules, an orthographic factorial design of four factors (i.e., weight ratio of DCPD/UF prepolymer, agitation rate, weight of chitosan solution, and emulsifier) and three level was used (Table I). The microcapsules' yield was calculated by[1]:

$$Y_{\text{microcapsule}} = W_m/W_0 \times 100\% \quad (1)$$

**TABLE I**
**Creation of an Orthographic Factorial Design of Four Factors and Three Levels for Microcapsules Preparation**

| | Factor | | | |
|---|---|---|---|---|
| Level | Weight ratio of DCPD/UF prepolymer (*A*) | Agitation rate (rpm) (*B*) | Chitosan solution (g) (*C*) | Emulsifier (*D*) |
| 1 | 3 : 1 | 200 | 15 | SDS |
| 2 | 2 : 1 | 300 | 10 | SDBS |
| 3 | 1 : 1 | 400 | 5 | None |

where $W_0$ represents the theoretical weight of the resultant microcapsules, i.e., the input weight of DCPD and shell-formers, $W_m$ represents the weight of the obtained microcapsules after removing the unreacted shell-formers, residual shell material and unencapsulated DCPD.

### Preparation of self-activated epoxy samples

The resin mixture was prepared by mixing 100 parts E-51 epoxide with 13 parts TETA curing agent. To prevent settling of $WCl_6$ particles in the resin mixture, epoxy resin mixture was degassed and allowed to react for 30 min. Then, the CUF microcapsules and 12 wt % $WCl_6$ were added to the resin mixture and mixed by hand carefully.[18] The resin mixture was poured into a closed silicone rubber mold, and cured for 48 h at room temperature, followed by postcuring at 50°C for 3 h.

### Characterization

FTIR spectrometer (AVATAR 370 THERMO NICOLET) was used to identify the chemical structure of microcapsule which was prepared by grinding the sample with a potassium bromide (KBr). Surface morphology and shell thickness of microcapsules were observed by SEM (QUANTA 200 ESEM, FEI). Samples were prepared on an aluminum slice, dried in a vacuum oven, and sputtered a coat with gold-palladium. The structure of microcapsules was observed using OM (BX51, OLYMPUS). Microcapsules size distribution was also investigated with OM, and size analysis of microcapsules was performed on data sets of at least 200 measurements. The storage stability under the condition of room temperature is crucial. The storage stability was characterized by the weight loss of microcapsules which were exposed to room temperature at periodic intervals. The thermal properties were analyzed using TGA (Pyris 6). Samples were combusted in $N_2$ at a heating rate of 10°C/min from 25 to 600°C. The isothermal aging experiment was characterized by weighting the microcapsules in an oven preset at 50°C for different time. The core content was characterized by weighing the microcapsules and the shell materials after extraction.

To evaluate self-healing ability of the polymeric materials, the protocol proposed by White et al.[6] was used, who carried out fracture tests on tapered double cantilever beam (TDCB) specimens. Five samples were tested for each case, calculating average healing efficiency. The healing Efficiency is defined as the ratio of fracture toughness, $K_{IC}$, of healed and virgin materials. Subsequently, the specimen was pin-loaded and tested under displacement control using a 1 mm/min displacement rate at room temperature (INSTRON 3344). The original specimens were tested to failure, giving the fracture toughness, $K_{IC}^0$. Load was then removed. The mixture solution of phenylacetylene and nonylphenol with weight ratio of 1 : 1 was then injected between the crack faces, allowing the crack faces to come back into contact and to be healed at room temperature for 24 h. The healed specimens were tested again and yielded the fracture toughness, $K_{IC}^1$. Accordingly, the crack healing efficiency $\eta$ can be calculated by[2]

$$\eta = \frac{K_{IC}^O}{K_{IC}^1} \tag{2}$$

## RESULTS AND DISCUSSION

### Microencapsulation process

For the method to fabricate microcapsule based on particle-stabilized emulsion, crosslinking of interfacial gel to make the shell rigid is the most challenging step. An interfacial gel layer is self-assembled by electrostatic adsorption using combination of oppositely charged surfactant SDS and polysaccharide chitosan in an oil-in-water emulsion. Subsequently, microcapsules' shells are formed on the surface of oil phase by *situ*-copolymerization of chitosan and UF prepolymer. Recently, Ao et al.[19] have developed a strategy based on particle-stabilized emulsion droplets as sacrificial templates and locking the interfacial particle to form a rigid polymer shell. In our study, gel layer is used to be an emulsion

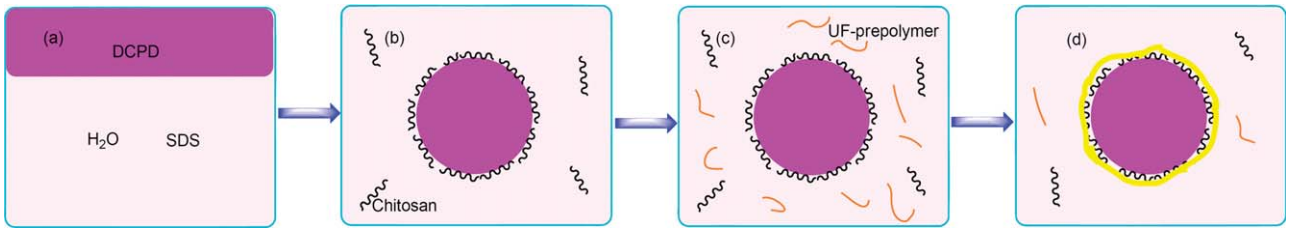


**Figure 1** Schematic showing the formation of microcapsule. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stabilizer, and subsequently copolymer layer forms on the gel layer.

For the route, our approach consists of three steps. The first is to emulsify a mixture of DCPD oil, deionized water, and surfactant SDS [Fig. 1(a)]. Hydrophobic dodecyl chains of surfactant insert into oil phase; negatively charged hydrophilic groups ($-SO_4^-$) immerge in water phase; the oil phase forms emulsion-droplets under surfactant's function. In the second step, with adding dropwise the positively charged chitosan solution [Fig. 1(b)], a gel layer is formed through automatical adsorption of chitosan with SDS.[20] The mechanism can be summarized in Figure 2. The resultant oil-in-water emulsion has a microencapsulated oil phase and saturated water as the continuous phase, and is stabilized by an interfacial monolayer of the chitosan-SDS gel. In the third step, a copolymer layer is gradually generated on the gel surface through polycondensation reaction between amidocyanogen of chitosan and hydroxyl of UF prepolymer (Figure 3 shows the reaction scheme of the formation of UF prepolymer), which can be controlled by the temperature of water bath and solution pH. The mechanism can be summarized in Figure 4. As a consequence, a rigid shell is formed to encapsulate the oil phase [Fig. 1(c,d)]. In addition, the possibility of polycondensation reactions which occur between UF prepolymers is not excluded.

To prove the adsorption between cationic chitosan and negatively charged surfactant SDS at the interface of oil-water, we carried out the verifying experiment. Figure 5 shows the OM photograph of chitosan-SDS gel microsphere containing DCPD in the water solution. For the convenience of observing sample, the chitosan-SDS gel microspheres were crosslinked by the use of glutaraldehyde, which only strengthened the strength of chitosan-SDS gel microspheres containing DCPD.[21,22] After that, the state of emulsion system changed from cloudy to clear. The Oil droplets in the solution decreased obviously because of the

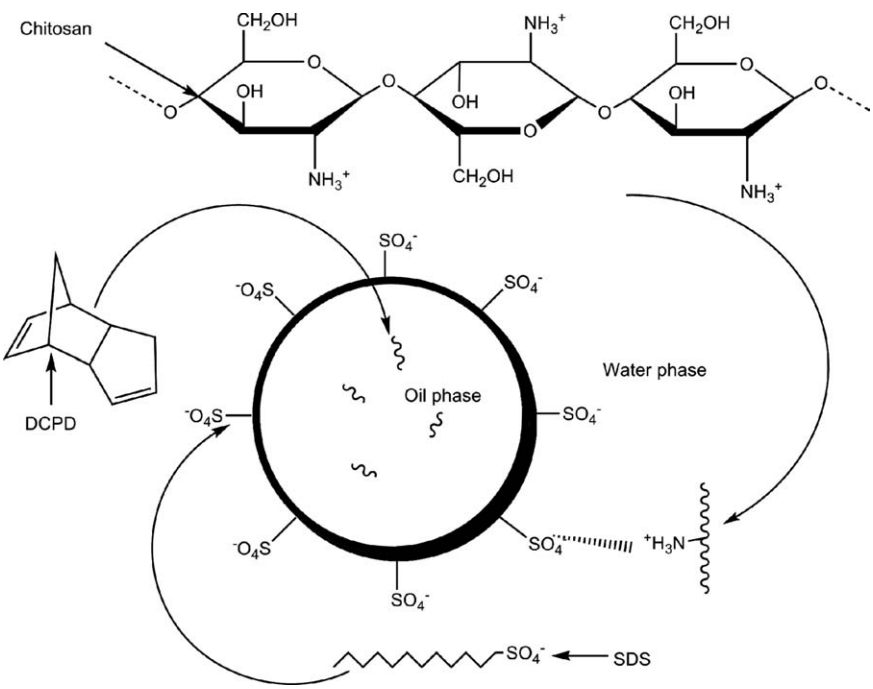


**Figure 2** Gel layer formation by electrostatic adsorption between chitosan and SDS.

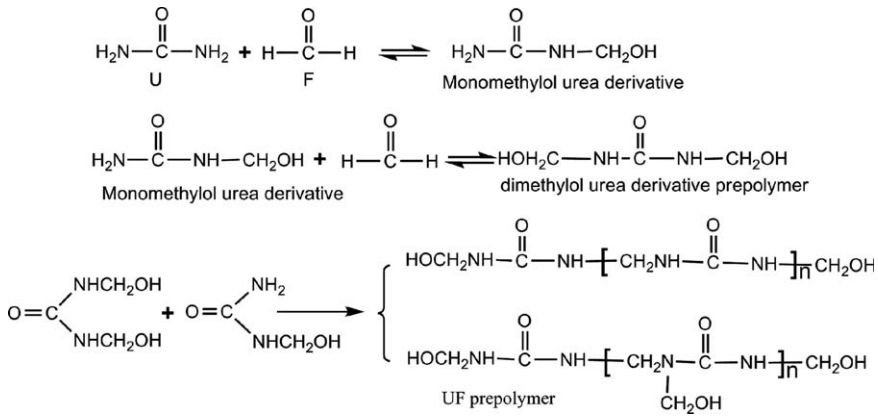


**Figure 3** The reaction scheme of the formation of UF prepolymer.

formation of chitosan-SDS gel microspheres containing DCPD.

### Influencing factors of preparation of the CUF microcapsules

As discussed above, the CUF microcapsules are fabricated via particle-stabilized emulsion and cross-linking *in situ* copolymerization of shell prepolymer. Therefore, the preparing condition such as weight ratio of DCPD/UF prepolymer, agitation rate, the weight of chitosan solution and emulsifier would influence on the yield of microcapsules. In this section, the influencing factors of preparation of the CUF microcapsules were investigated. For this purpose, orthographic factorial design was applied and the microcapsule yield was set as the response of the designed experiments. Tables II and III and Figure 6 show the results and analysis of the effects of the four factors at three levels (refer to Table I).

Table II shows the result analysis of the orthographic factorial design for microcapsules' preparation. Where the *P* value and *W* value was calculated by (3) and (4), respectively:

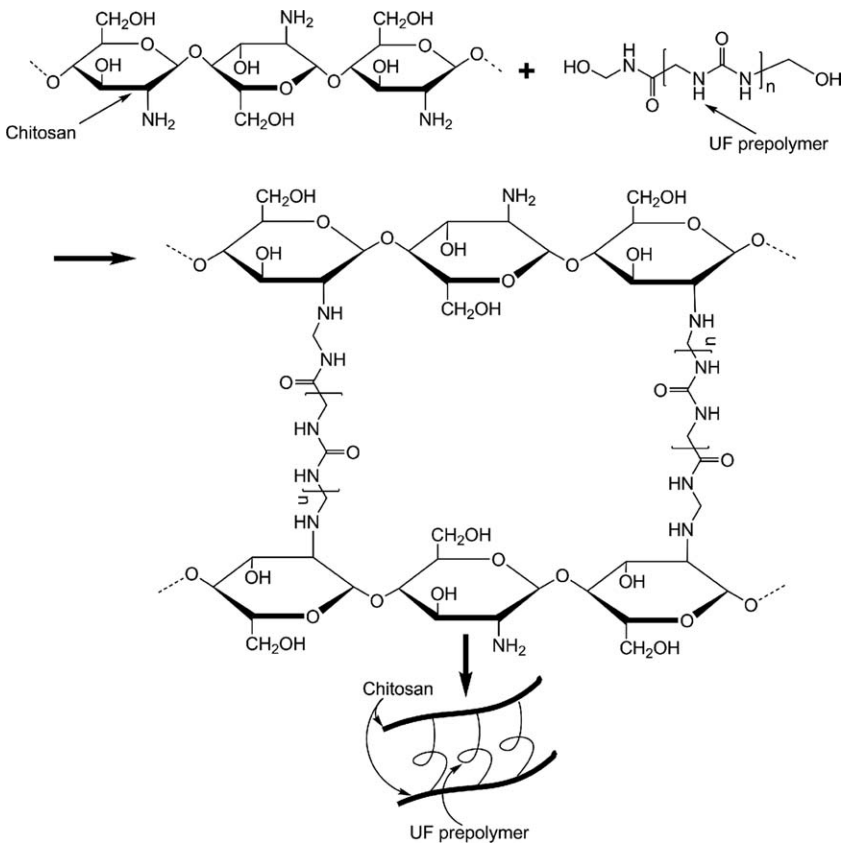


**Figure 4** The scheme of copolymerization reaction between chitosan and UF prepolymer.

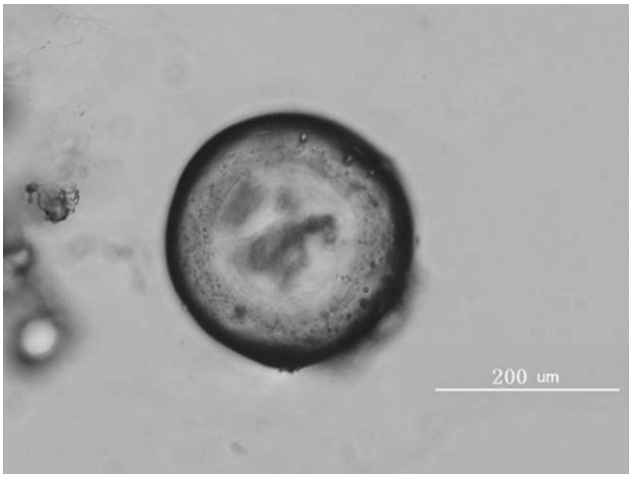


**Figure 5** OM photograph of chitosan-SDS gel microsphere containing DCPD in the water solution.

$$P = \frac{1}{n}\left(\sum_{x=1}^{n} Y_x\right)^2, \quad (n = 9) \tag{3}$$

$$W = \sum_{x=1}^{n} Y_x^2, \quad (n = 9) \tag{4}$$

Figure 6 shows the influence of different levels of the four factors (see Table I) on the averaged capsule yield (that was taken from the values of $R_{ij}$ listed in Table II). It is found that emulsifier has a very evident influence on the yield of microcapsules. This infers that the gel layer formed by electrostatic adsorption between the cationic chitosan and anionic emulsifier decreases the Gibbs free energy at the interface of oil-in-water emulsion and keeps stabilization of the emulsion. Comparing with no emulsifier, the stabler the emulsion is, the larger the microcapsules' yield is.

To distinguish the data's fluctuation, which caused by the change of experimental condition or experimental error, the resultant data of the yield is analyzed by variance analysis. Finally, the error and analysis precision are given and a criterion for estimating every factor influence on the microcapsules' yield is provided. Table III shows the analysis of variance of microcapsules' yield, where the $Q_i$ value was calculated by (5):

$$Q_i = \frac{1}{a_i}\sum_{j=1}^{b_i} Y_{ij}^2 \quad (i = A, B, C, D; j = 1, 2, 3) \tag{5}$$

When each column of orthogonal Table is saturated, the error of square sum of deviation equals the minimum of square sum of deviation, i.e., $S_e = S_{\mathrm{Min}(A,B,C,D)} = S_c$. This indicates that the influence of the weight change of chitosan solution can be approximately neglected.

From the results of Table III, according to the theory of analysis of variance, the bigger mean square's value is, the more important factor is. Therefore, the importance of factor from high to low in turn is emulsifier, agitation rate and weight ratio of DCPD/UF prepolymer. To estimate the influence of every factor on microcapsules' yield, $F$ value was introduced. $F$ value of factor $D$ is much larger than

**TABLE II**
**Result Analysis of the Orthographic Factorial Design for Microcapsules' Preparation**

| | Factor | | | | |
|---|---|---|---|---|---|
| Sample No. | *A* | *B* | *C* | *D* | Microcapsule yield(%), ($Y_i$) |
| 1 | 1 | 1 | 1 | 1 | 81.5 |
| 2 | 1 | 2 | 2 | 2 | 63.4 |
| 3 | 1 | 3 | 3 | 3 | 5.1 |
| 4 | 2 | 1 | 2 | 3 | 11.6 |
| 5 | 2 | 2 | 3 | 1 | 73.8 |
| 6 | 2 | 3 | 1 | 2 | 51.8 |
| 7 | 3 | 1 | 3 | 2 | 57.5 |
| 8 | 3 | 2 | 1 | 3 | 9.1 |
| 9 | 3 | 3 | 2 | 1 | 55.3 |
| Result analysis | | | | | |
| $K_{i1}$ | 150.0 | 150.6 | 142.4 | 210.6 | - |
| $K_{i2}$ | 137.2 | 146.3 | 130.3 | 172.7 | - |
| $K_{i3}$ | 121.9 | 112.2 | 136.4 | 25.8 | - |
| $R_1$ | 50.0 | 50.2 | 47.5 | 70.2 | - |
| $R_2$ | 45.7 | 48.8 | 43.4 | 57.6 | - |
| $R_3$ | 40.6 | 37.4 | 45.5 | 8.6 | - |
| $P$ | 18595.9 | | | | |
| $W$ | 25399.2 | | | | |

$K_{ij}$ denotes the sum of microcapsule yield with factor $i$ and level $j$.
$R_{ij}$ denotes the average of $K_{ij}$. $R_{ij} = K_{ij}/N_i$, $N_i$ is the number of level $j$ with the same factor $i$.

**TABLE III**
**The Analysis of Variance of Microcapsules' Yield**

| Variance source | Square sum of deviation ($S_i$) | Degree of freedom ($f_i$) | Mean square ($M_i$) | $F_i$ | $F_{0.01}(2.2)$ | $F_{0.05}(2.2)$ | $F_{0.2}(2.2)$ | Grade |
|---|---|---|---|---|---|---|---|---|
| *A* | 131.9 | 2 | 66.0 | 5.4 | 99 | 19 | 4 | Some influence |
| *B* | 295.1 | 2 | 147.5 | 12.1 | 99 | 19 | 4 | Some influence |
| *D* | 6351.9 | 2 | 3175.9 | 260.3 | 99 | 19 | 4 | Vital influence |
| Error | 24.4 | 2 | 12.2 | | | | | |
| Total | 6803.3 | 8 | | | | | | |

Square sum of deviation $S_i = Q_i - P$ ($i = A, B, C, D$), $S_{\text{total}} = W - P$.
When each column of orthogonal table is saturated, the error of square sum of deviation $S_e = S_{\text{Min}(A,B,C,D)} = S_c = 24.4$; Degree of freedom $f_i$ = number of the level with factor $i - 1(i = A, B, D)$; $f_{\text{total}}$=experiment times – 1, $f_e = f_{\text{total}} - f_A - f_B - f_D$; Mean square $M_i = S_i/f_i$, $F = M_i/M_e$.

$F_{0.01}(2.2)$. Therefore, the emulsifier has vital influence on microcapsules' yield, which is in accordance with the result of Figure 6. Similarly, *F* value of factor *A* and *B* is in the range of $F_{0.05}(2.2)$ and $F_{0.2}(2.2)$. Therefore, weight ratio of DCPD/UF prepolymer and agitation rate have some influence on microcapsules' yield. Presumably, after gel layer forming at the interface of oil droplet and water phase, intense stir would destroy the gel layer so that the yield is reduced. However, with the increase of the weight ratio of DCPD/UF prepolymer, the weight of the unencapsulated shell materials caused by self-polymerization of residual UF prepolymer decreases so that the yield is increased. As a result, the optimum conditions for preparing CUF microcapsules are: 3 : 1 for the weight ratio of DCPD/UF prepolymer, 200 rpm for the agitation rate, 5–15 g chitosan solution, and emulsifier SDS.

## Chemical structure of microcapsule

Figure 7 shows the FTIR spectra of core material DCPD, microcapsules, CUF shell material, chitosan, and PUF shell material. Table IV lists the detailed peak assignments of core material DCPD, CUF shell material, and chitosan. Obviously, the FTIR spectrum of CUF microcapsules containing the core material DCPD displays an absorption peak of =CH

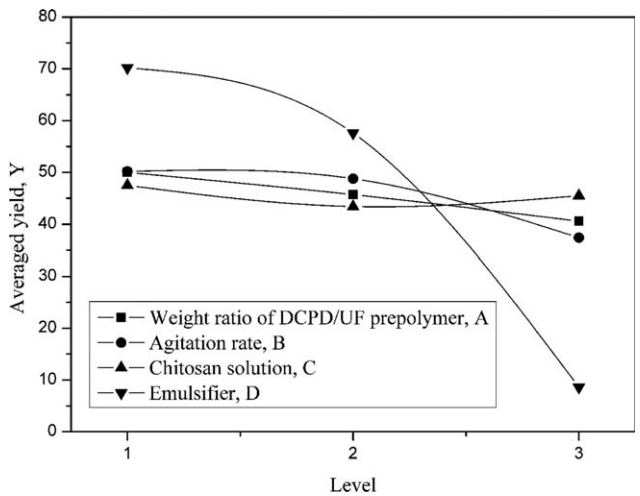


**Figure 6** Influence of different levels of the four factors (see Table I) on the averaged capsule yield (that was taken from the values of $R_{ij}$ listed in Table II).

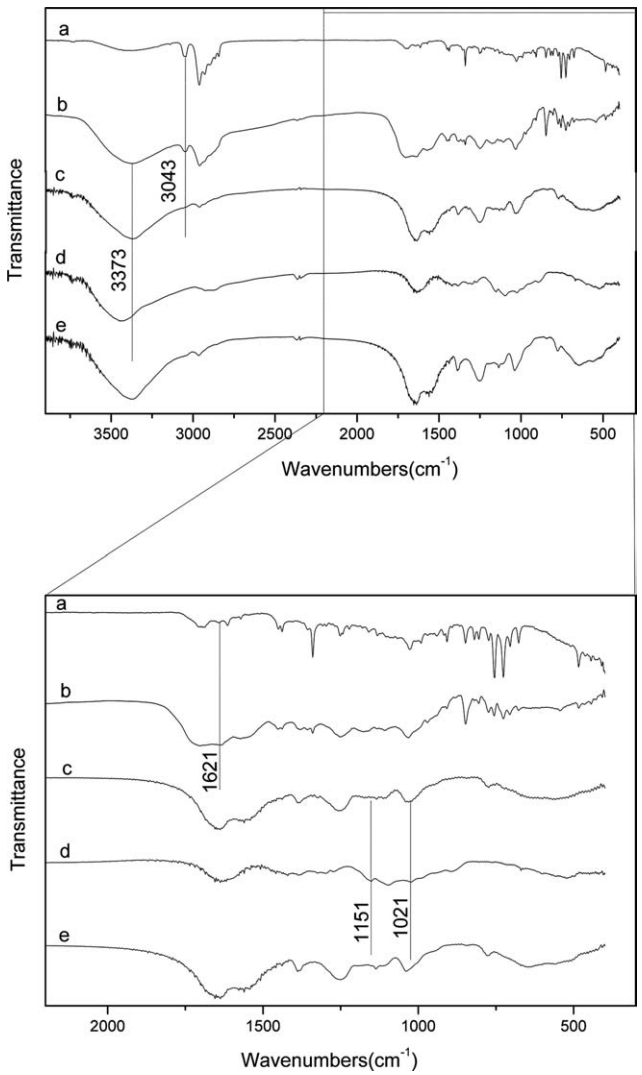


**Figure 7** FTIR spectra of (a) core material, (b) microcapsules, (c) CUF shell material, (d) chitosan, and (e) PUF shell material.

**TABLE IV**
**Wavenumbers ($cm^{-1}$) and Assignments of the FTIR Spectra of Core Material DCPD, CUF Shell Material, and Chitosan**

| DCPD | Approximate assignment | CUF shell material | Approximate assignment | Chitosan | Approximate assignment |
|---|---|---|---|---|---|
| 3043 | =CH(Cyclopentene double bond) | 3373 | O—H, N—H | 1151 | C—O—C C—OH |
| 1621 | | 1641 | —C=O | 1021 | (Carbohydrate ring) |
| | | 1559 | C—N | | |
| | | 1151 | C—O—C | | |
| | | 1021 | C—OH | | |

at 3043 $cm^{-1}$ and 1621 $cm^{-1}$, which indicates that the CUF microcapsules are filled with DCPD.

For the CUF shell material [curve (c) in Fig. 7], absorptions peak at 3373 $cm^{-1}$ represents the stretching modes of —OH and —NH, and the peaks at 2968 $cm^{-1}$ is the characteristic of —CH. Absorption peaks at 1641 $cm^{-1}$ and 1559 $cm^{-1}$ represent the stretching vibrations of —C=O and C—N group, respectively, which indicate that characteristic of UF prepolymer is existent in the shell. It implies that copolymerization has occurred between UF prepolymer and chitosan. There are absorption peaks at 1151 $cm^{-1}$ and 1021 $cm^{-1}$ of CUF shell material, which are characteristic for C—O—C and C—OH stretching vibrations from the carbohydrate ring of chitosan,[23] indicating that CUF shell materials have been formed via mechanism shown in Figure 4. Presumably, hydroxyl groups of UF prepolymer are scarcely existent in the formed shell because they are almost consumed by amine groups during the formation of polymer layer. Nevertheless, hydroxyl groups of chitosan are conserved owing to steric hindrance effect as a result of helical structure of polysaccharide.

Figure 8 shows the OM photo of microcapsule. According to optical theory, two different refractive index media microencapsulate each other, the diffraction ring will occur at the interface between the two different media. The diffraction ring can be observed evidently, which indicates that the CUF successfully microencapsulates DCPD.

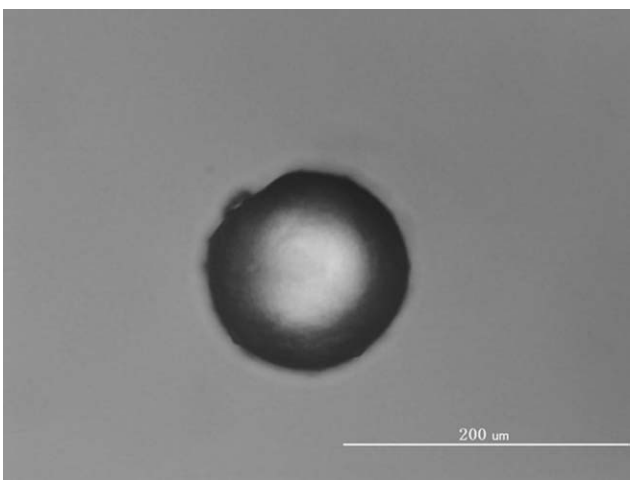


**Figure 8** OM micrograph of prepared microcapsule.

### Microcapsule surface morphology and shell thickness

Figure 9 shows the SEM micrograph of microcapsules sample. The outside surface of microcapsules is rough and it increases the surface areas of microcapsules and enhances surface adhesion. Thickness of shell determines the mechanical properties of microcapsules and the release model of core materials, largely depending on the manufacturing parameters such as the ratio of core-shell materials, agitation rate, and so on, which was measured directly from the SEM images of the fracture surfaces. Figure 10 shows the fractured microcapsules samples. Here, the shell thickness of the microcapsules sample is in the range of 1–7 μm.

### Size distribution

As shown in Figure 11, the microcapsules size is in a wide range of 10–160 μm and the mean diameter is 45 μm. Because the fluid flow around the propeller is turbulent, larger microcapsules exist in the region of flow away from the propeller and many smaller microcapsules exist in the vicinity of the propeller blades. The microcapsule size can be controlled by adjusting the agitation rate.

### Stability of microcapsules

Figure 12 shows the weight loss of microcapsules at periodic intervals under the condition of room temperature. The microcapsules can be well stored under the condition of room temperature in 50 days with the weight loss about 0.9 wt %. The weight loss of microcapsules in the first 0–10 days is much larger than other stages, which is mainly due to the elimination of free-formaldehyde. As the exposed time increasing, the weight loss of microcapsules evidently becomes larger owing to the diffusion of core material throughout the shell.

Figure 13 shows TGA curves of DCPD, microcapsules and CUF shell materials. The curve of shell

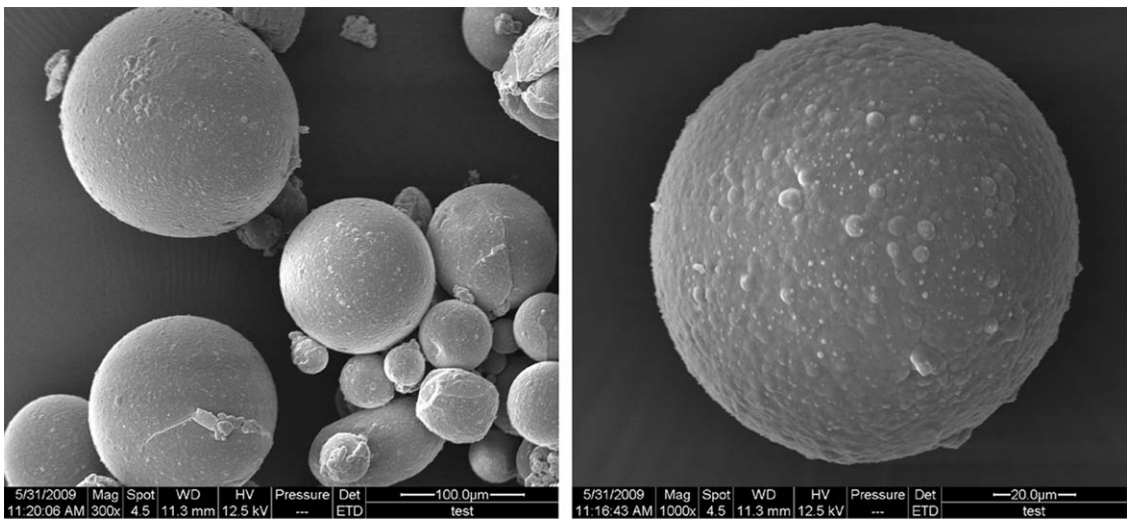


**Figure 9** SEM micrograph of microcapsules.

materials indicates that the weight loss before 230°C is mainly due to the elimination of formaldehyde and decomposition of small molecule. The weight loss at temperatures 230–350°C is mainly due to the decomposition of CUF. The weight loss of DCPD is in the range of 105–165°C. The curve of microcapsules consists of two stages of weight loss. In the first stage from 155 to 230°C, the decomposition of shell materials causes the microcrack, which leads to decomposition of little DCPD. The second stage from 230 to 255°C falls faster than the first stage, which infers that damage of CUF shell induces a large number of weight loss of DCPD. As a consequence, thermal stability of the DCPD in the microcapsules is evidently increased owing to the protection of shell materials, and core materials are successfully contained in the microcapsules.

The isothermal aging experiments of CUF microcapsules were also carried out. Figure 14 shows the curve of weight loss of microcapsules at different time under the condition of 50°C. The weight loss of microcapsules exposed to 50°C for 0.5 h is about 3.67 wt %, and as the exposed time increases further, the weight loss of microcapsules obviously tends to decrease and the slope of curve becomes small, indicating that the CUF microcapsules exposed to 50°C can maintain well in 5 h. The weight loss before 0.5 h is mainly due to the removal of entrapped residual water and the elimination of free formaldehyde, and the weight loss of microcapsules after 0.5 h is mainly owing to slow diffusion of little core material throughout the wall shell. The weight loss of microcapsules heat-treated increases with the enhancement of time, indicating that the microcapsules cannot be exposed to heat surrounding timelessly, which cause the larger weight loss of microcapsules.

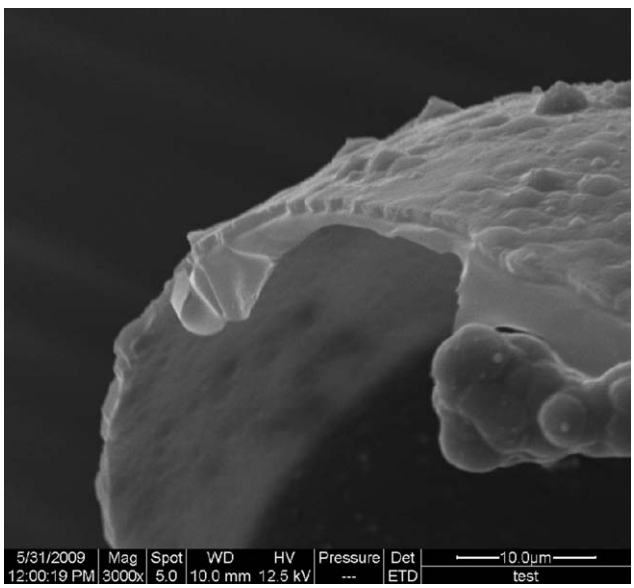


**Figure 10** SEM micrograph of fractured microcapsule.

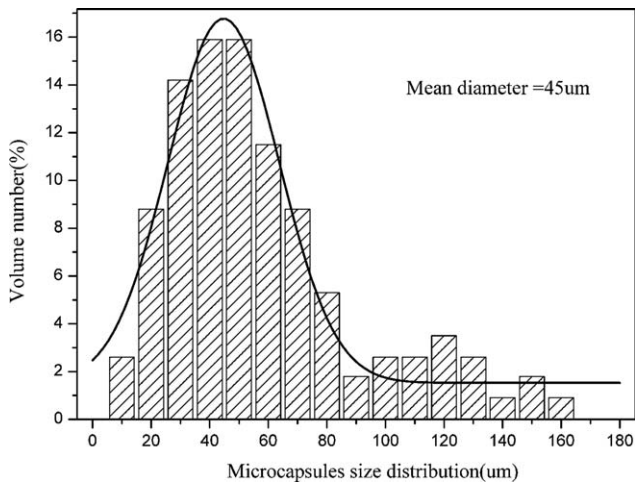


**Figure 11** Size distributions of microcapsules.

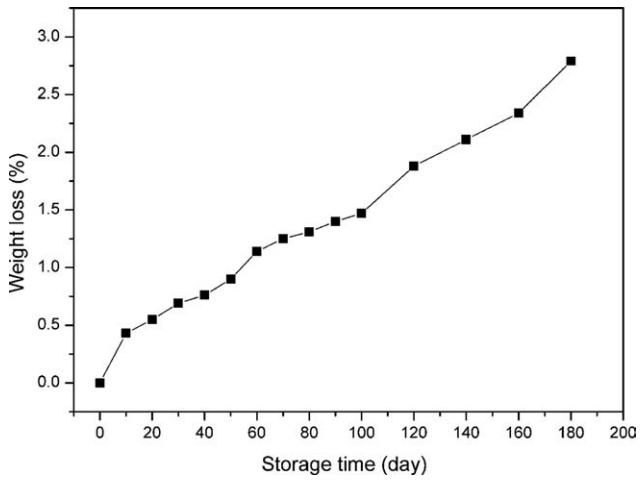


**Figure 12** Weight loss of microcapsules at periodic intervals at room temperature.

### Core content of microcapsules

The core content of resultant microcapsules was measured by acetone extracting method. Microcapsules samples were crushed in a mortar with pestle and washed with acetone three times, and then dried at room temperature. The core content of microcapsules can be calculated through the initial weight of intact microcapsules $W_{\text{microcapsules}}$ and the weight of residual shell $W_{\text{shell}}$ of microcapsules using the following Eq. (6):

$$W_{\text{core}} = \frac{W_{\text{microcapsule}} - W_{\text{shell}}}{W_{\text{microcapsule}}} \quad (6)$$

In this study, the core content of microcapsules with 45 μm mean size and 1 to 7 μm shell thickness is 67%. The core content of microcapsules depends on the size and shell thickness of resultant microcapsules. Bigger microcapsules with thinner shell thickness will possess a larger portion of core. Therefore, the content of the healing agent DCPD of microcapsules can be adjusted by the control of core/shell proportion and agitation rate during the preparation process.

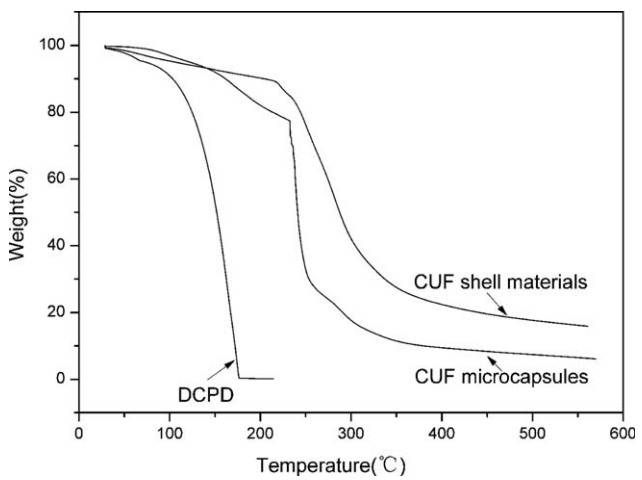


**Figure 13** TGA curves of CUF microcapsules, CUF shell materials, and core materials DCPD.

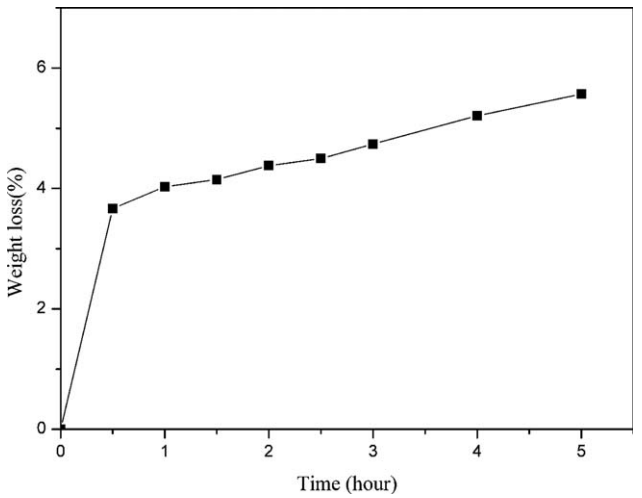


**Figure 14** Weight loss of microcapsules at different time under the condition of 50°C.

### Self-healing performance of epoxy samples containing CUF microcapsules

To evaluate self-healing ability of the CUF microcapsules containing DCPD applied to the polymeric materials, the microcapsules with different concentration were embedded in epoxy matrix to fabricate self-healing materials. Figure 15 shows influence of CUF microcapsule's content on self-healing ability of epoxy with 12 wt % $WCl_6$, average diameter of the microcapsules: 45 μm; content of the DCPD healing

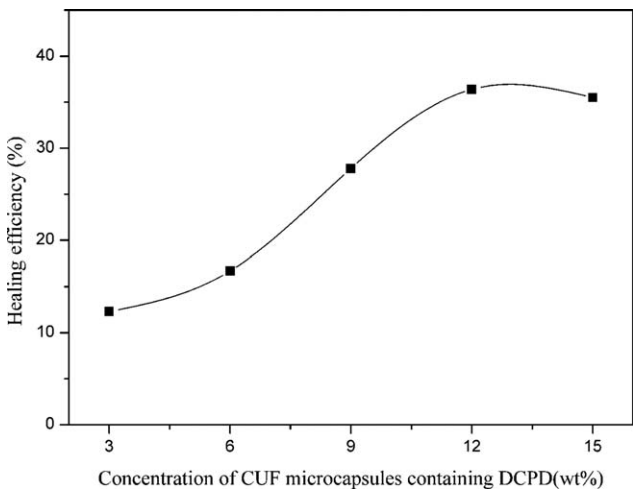


**Figure 15** Influence of CUF microcapsule's content on self-healing ability of epoxy with 12 wt % $WCl_6$. Average diameter of the microcapsules: 45 μm; content of the DCPD healing agent inside the microcapsules: 67%.

agent inside the microcapsules: 67%. Obviously, as the concentration of microcapsules increase, healing efficiency obviously becomes larger. It is worth noting that although healing efficiency increases with a rise in microcapsules content in the regime of low microcapsules content, the former is nearly independent of microcapsules content above a certain value. This coincides with the rule of curing of DCPD catalyzed by $WCl_6$. That is, the requirement of stoichiometric composition at every inch of repair region is unnecessary. Therefore, the distribution of microcapsules and catalyst greatly influences the healing efficiency. This phenomena is in accordance with the results reported by Kamphaus et al.[18] In this study, the average self-healing efficiency is in the range of 12.3%–35.5%.

## CONCLUSIONS

CUF shell microcapsules containing healing agent DCPD were synthesized successfully. This is achieved by a gel layer as emulsion stabilizer self-assembled at the oil-water interface, and forming a rigid shell around the oil phase through situ-copolymerization between chitosan and UF prepolymer. By analyzing the results of orthographic factorial design with respect to the effects of preparing conditions on microcapsules' yield, emulsifier was found to be the most important influencing factor, while weight of chitosan solution had nearly no influence on the yield. Microcapsules diameter is in a wide range of 10–160 μm and the mean diameter is 45 μm, and shell thickness is in the range of 1–7 μm, which can be adjusted by ratio of core-shell materials and agitation rate. The microcapsules may have a good storage at room temperature with a weight loss about 0.9 wt % in 50 days and basically exhibit a good chemical stability below 230°C, which can withstand the moderate or high temperature during the use of polymeric composites such as epoxy resins. Additionally, the epoxy samples containing CUF microcapsules possess the self-healing function, and the distribution of microcapsules and catalyst greatly influences the healing efficiency. In general, this study provides novel microcapsules for the self-healing composites, and the effects of microcapsules in the composites will be further examined in the future research.

## References


1. Aiedeh, K.; Gianasi, E.; Orienti, I.; Zecchi, V. J Microencapsul 1997, 14, 567.
2. Chang, C. C.; Tsai, Y. L.; Chiu, J. J.; Chen, H. J Appl Polym Sci 2009, 112, 1850.
3. Cho, S. H.; White, S. R.; Braun, P. V. Adv Mater 2009, 21, 645.
4. Parthasarathy, R. V.; Martin, C. R. J Appl Polym Sci 1996, 62, 875.
5. Wan Ngah, W. S.; Fatinathan, S. Chem Eng J 2008, 143, 62.
6. White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. Nature 2001, 409, 794.
7. Wang, R. G.; Li, H. Y.; Hu, H. L.; He, X. D.; Liu, W. B. J Appl Polym Sci 2009, 113, 1501.
8. Li, H. Y.; Wang, R. G.; Hu, H. L.; Liu, W. B. Appl Surf Sci 2008, 255, 1894.
9. Brown, E. N.; Kessler, M. R.; Sottos, N. R.; White, S. R. J Microencapsul 2003, 20, 719.
10. Yuan, L.; Liang, G. Z.; Xie, J. Q.; Li, L.; Guo, J. Polymer 2006, 47, 5338.
11. Yang, J. L.; Keller, M. W.; Moore, J. S.; White, S. R.; Sottos, N. R. Macromolecules 2008, 41, 9650.
12. Yuan, L.; Liang, G. Z.; Xie, J. Q.; He, S. B. Colloid Polym Sci 2007, 285, 781.
13. Chen, X. C.; Song, H.; Fang, T.; Bai, J. X.; Xiong, J.; Ying, H. J. J Appl Polym Sci 2010, 116, 1342.
14. Devi, N.; Maji, T. K. J Appl Polym Sci 2009, 113, 1576.
15. Wang, C.; Ye, W.; Zheng, Y.; Liu, X.; Tong, Z. Int J Pharm 2007, 338, 165.
16. Wang, B.; Zhao, Q. H.; Wang, F.; Gao, C. Y. Angew Chem Int Ed 2006, 45, 1560.
17. Asua, J. M. Prog Polym Sci 2002, 27, 1283.
18. Kamphaus, J. M.; Rule, J. D.; Moore, J. S.; Sottos, N. R.; White, S. R. J R Soc Interface 2008, 5, 95.
19. Ao, Z.; Yang, Z.; Wang, J. F.; Zhang, G. Z.; Ngai, T. Langmuir 2009, 25, 2572.
20. Babak, V. G.; Merkovich, E. A.; Desbrieres, J.; Rinaudo, M. Polym Bull 2000, 45, 77.
21. Monteiro, O. A. C.; Airoldi C. Int J Biol Macromol 1999, 26, 119.
22. Gupta, K. C.; Jabrail, F. H. Carbohyd Res 2006, 341, 744.
23. Lawrie, G.; Keen, I.; Drew, B.; Chandler-Temple, A.; Rintoul, L.; Fredericks, P.; Grondahl, L. Biomacromolecules 2007, 8, 2533.