Preparation and Characterization of Self-Healing Microcapsules with Poly(urea-formaldehyde) Grafted Epoxy Functional Group Shell

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ABSTRACT: Microcapsules were prepared by *in situ* polymerization technology with poly(urea-formaldehyde) (PUF)-grafted γ-glycidoxypropyltrimethoxy silane (KH560) copolymer as a shell material and dicyclopentadiene (DCPD) as core materials. The aim was to improve the interfacial bond between microcapsules and epoxy matrix in composites through the epoxy functional group in KH560. The microcapsulating mechanism was discussed and the process was explained. 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, X-ray photoelectron spectra, and thermogravimetric analysis. Results indicted that the PUF-graft KH560 microcapsules containing DCPD can be synthesized successfully; the epoxy functional group was grafted on the wall material. The microcapsule size is in the range of 40–190 μm with an average of 125 μm. The wall thickness of microcapsules sample is in the range of 2–5 μm and the core content of microcapsules is about 60%. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1501–1506, 2009

Key words: poly(urea-formaldehyde); γ-glycidoxypropyltrimethoxy silane; graft copolymer; micro-capsules; epoxy functional group

INTRODUCTION

Microencapsulation has been widely used in many fields such as phase change material,[1–3] drugs,[4–6] textile printings,[7] coating,[8] etc. because the core materials can be protected by the shell of microcapsules from the damages of environment or can be released under a controlled condition. Self-healing microcapsules were first introduced by White et al.[9] to recover the fracture properties of thermosetting polymers. Healing is achieved by incorporating a microencapsulated healing agent and a catalytic chemical trigger within a polymer matrix. Thus microcapsulated liquid healing agent for self-healing composites has been paid more attention. Self-healing was obtained with a healing agent based on the ring-opening metathesis polymerization reaction. Dicyclopentadiene (DCPD), a highly stable monomer with excellent shelf life, was encapsulated in urea-formaldehyde microcapsules.[10–13] Poly(urea-formaldehyde) (PUF) microcapsules containing epoxy resins healing agent were also proposed.[14,15] All these microcapsules filled with healing agent offer tremendous prospect of long-lived structural materials.

However the mechanical performance of the composite will be affected due to the addition of microcapsules. The weak interfacial adhesion between self-healing microcapsules and resin matrix is one of the major factors. There are no chemical bands on the interface when PUF microcapsules are added to the epoxy matrix. Therefore, the composites are susceptible to damage at the interface and the self-healing will decay at the same time.

In this study, γ-glycidoxypropyltrimethoxy silane (KH560) was introduced to offer epoxy functional groups that can be grafted on PUF microcapsules through *in situ* polymerization technology in an oil-in-water emulsion. The interfacial performance was subsequently improved through the formation of chemical bonds at the interfaces by the reactions of epoxy functional groups between microcapsules wall materials and epoxy matrix. The mechanics of polymerization was studied and the chemical structure, surface morphology, size distribution, and thermal stability of the microcapsules were characterized.

EXPERIMENTAL

Materials

DCPD (Hangzhou Yangli Chemical, Hangzhou, China) is used as core material. Urea (U) and 37 wt % formaldehyde (F) (Tianjin Chemical Plant, Tianjin,

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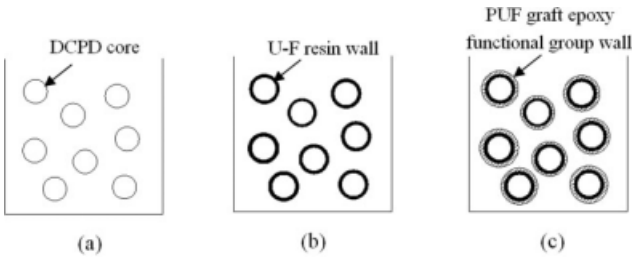

Figure 1 Schematic of the preparation of microcapsules. (a) Uniform dispersion of DCPD in U-F prepolymer; (b) primary shell formation of U-F resin; (c) the formation of microcapsules with the shell PUF-grafted epoxy functional group.

China) are used as shell materials. KH560 (Heilongjiang Institute of Petrochemistry, China) is used as the third monomer and the modification of shell materials. Triethanolamine (TEA; Harbin Chemical Plant, Harbin, China) is used to control the pH of solution. Sodium dodecylbenzene sulfonate (DBS; 99% purity) and octane (Tianjin Chemical Regents Factory, Tianjin, China) are used as emulsifier and dispersant agent. Ten weight percent hydrochloric acid (HCI; Harbin Chemical Plant, Harbin, China) solution was prepared to control the pH value of the emulsion. All the materials are commercial products and were used without further purification.

Preparation of microcapsules

PUF graft epoxy functional group microcapsules were prepared by a two-step approach. First, 5 g U and 10 g 37 wt % F were mixed in a 250-mL three-necked round-bottomed flask with the thermometer and mechanical stirred equipment at room temperature. The weight ratio is m (U) : m (F) =1 : 2. The pH of mixed solution was adjusted to 8–9 with TEA. The temperature of the system was kept at 70°C for 1 h, and then the U-F prepolymer solution was obtained. Second, under agitation, 50 mL 1 wt % aqueous DBS and 0.5 g resorcinol were added to the as prepared prepolymer solution, and then 20 mL DCPD was compounded with above prepolymer to dissolve the latter in the water phase of the former. One to two drops of Octane was added to the DCPD as a co-stabilizer to increase the hydrophobicity of the inner phase. After stirring for 20–30 min with a 500–600 rap stir rate, the pH of the emulsion was adjusted slowly to 3–4 by 10 wt % hydrochloric acid solutions and the solution was slowly heated to the target temperature of 60–65°C. After 1 h, the third monomer KH560 (4–5 g) was added into the solution, with the pH adjusted to 2.0–3.0, and kept for 2 h; then the reaction was ended. Finally, the obtained suspension of microcapsules was cooled down to ambient temperature and rinsed with deionized water, then filtered, and air-dried for 24 h.

Characterization

Microcapsules size distribution was investigated with optical microscope and the average size of microcapsules was measured on data sets of at least 200 measurements. Surface morphology and wall thickness of microcapsules were observed by SEM (XL 30 ESEM-FEG, Philips). Samples were prepared on an aluminum slice, dried in a vacuum oven, and sputter coated with gold-palladium. The infrared spectrometric analyzer (EQUINOX-55) was used to identify the chemical structure of microcapsules, which was prepared by grinding the sample with potassium bromide (KBr). The chemical elemental information on the surface of microcapsules was further studied by using an XPS. In the XPS analysis (surface analysis PHI5600, Physical Electronics), a monochromatic Al Ka X-ray was used at 14 kV. The XPS curve fitting of Si 2p was accomplished by MultiPak V6.0 A (Physical Electronics).The thermal properties were analyzed by using thermal gravimetric analysis (TGA; Pyris 6), during which microcapsules samples were combusted in N_2 at a heating rate of 10°C/min from 25 to 600°C. The core content was characterized by weighing the microcapsules and the wall materials after extraction.

RESULTS AND DISCUSSION

Microencapsulation process

Microcapsules containing DCPD monomer were prepared by *in situ* polymerization of urea, formaldehyde, and KH560 by using a modified process of Brown et al.[11] The mechanism can be summarized in Figure 1. DCPD was first uniformly dispersed in U-F prepolymer, which then has polycondensation for the formation of primary shells. After the addition of KH560, the microcapsules with the PUF-grafted epoxy functional group shells are obtained. Figure 2 shows the chemical structures of U, F, and KH560. The formation of U-F prepolymer and the condensation reaction scheme of U, F, and KH560 are shown in Figure 3(a,b), respectively.

Microcapsules surface morphology and shell wall thickness

Figure 4 shows the SEM micrograph of microcapsules sample. The outside surface of microcapsules

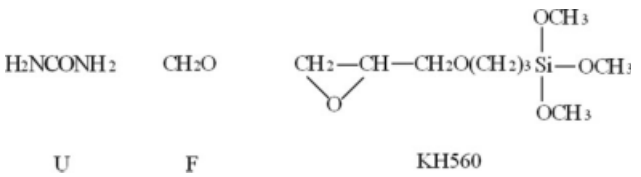

Figure 2 Chemical structure of the materials used in this work.

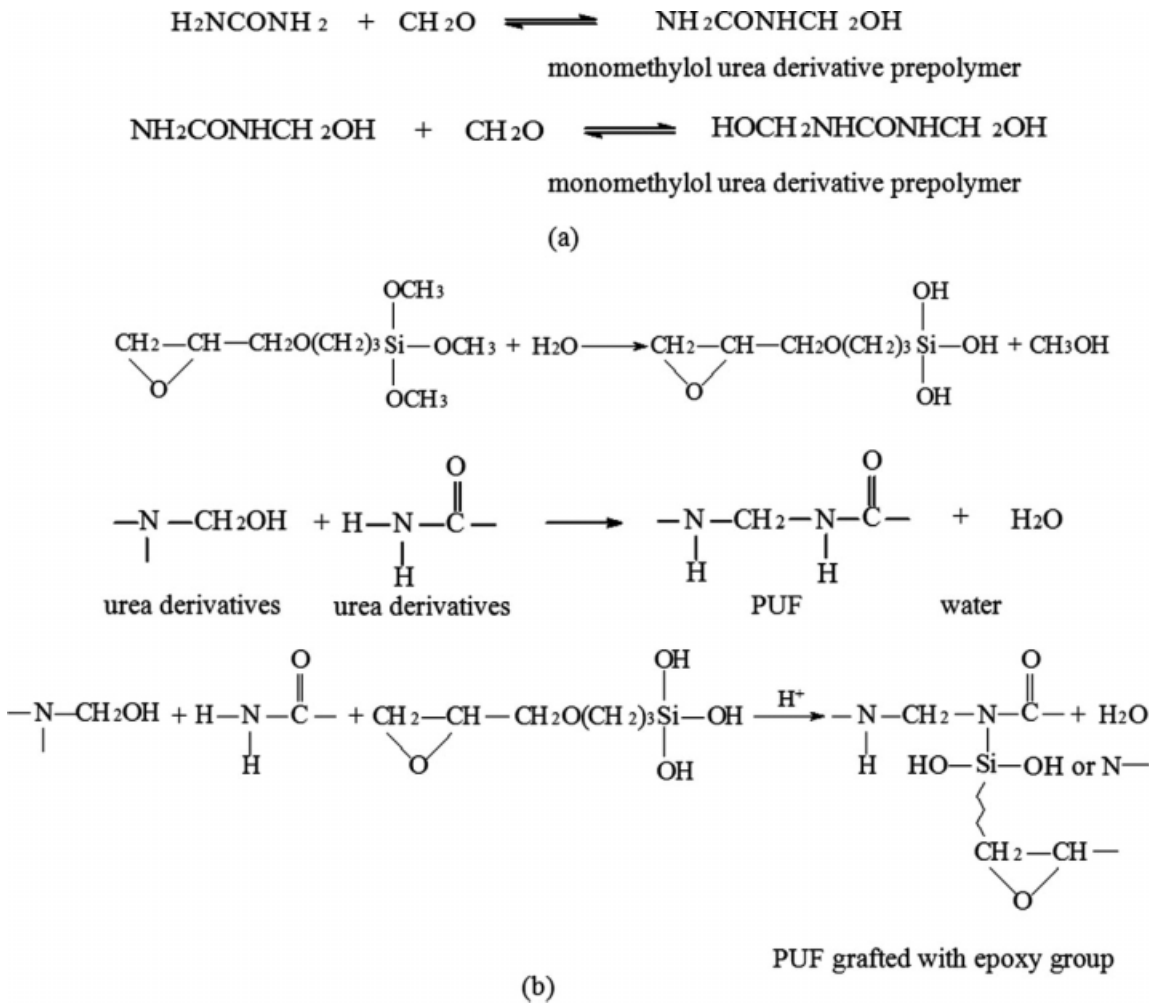

Figure 3 The reaction scheme of U-F resins and KH560. (a) The formation of U-F prepolymer. (b) The formation of PUF-grafted epoxy functional group.

are rough and it increases the surface areas of microcapsules and enhances surface adhesion. Thickness of shell wall 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 5

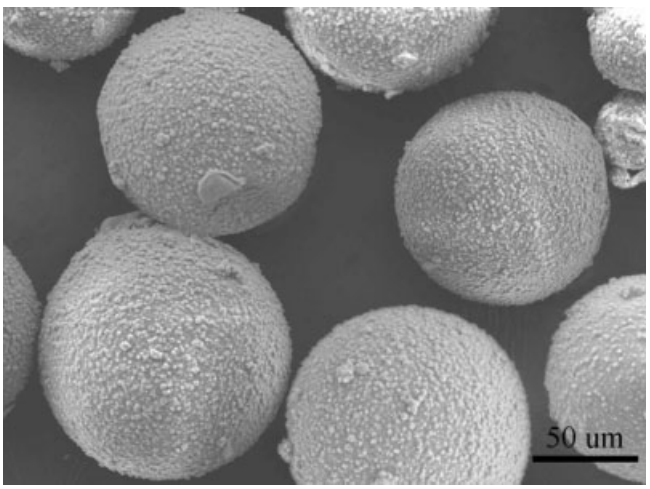

Figure 4 SEM micrograph of microcapsules.

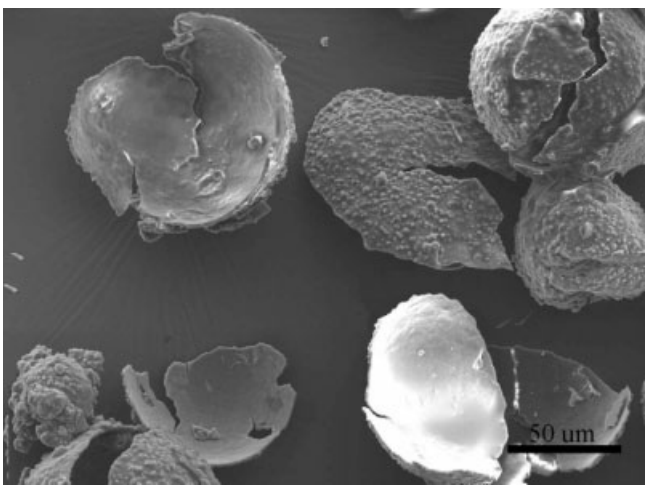

Figure 5 SEM micrograph of fractured microcapsule.

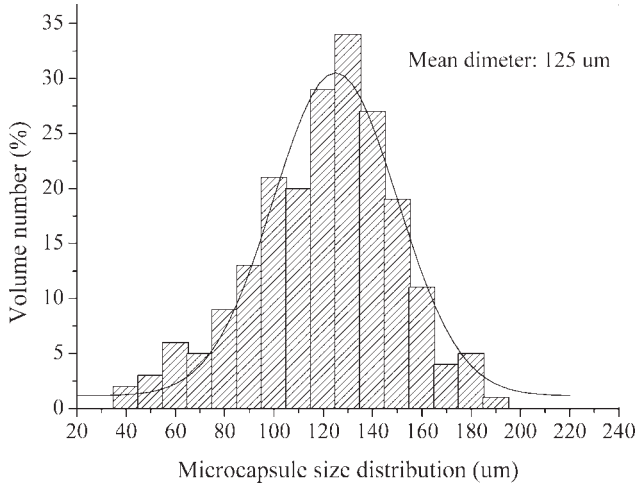

Figure 6 Size distribution of microcapsules.

shows the fractured microcapsules samples. Here, the wall thickness of the microcapsules sample is in the range of 2–5 μm.

Microcapsules size analysis

Figure 6 shows the size distribution of microcapsules samples. The microcapsules size is in a wide range of 40–190 μm and the mean diameter is 125 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 the adjusting the agitation rate.

Chemical structure of microcapsules

Figure 7 shows the FTIR spectra of PUF wall shell material and PUF-graft epoxy functional group wall shell material. There are strong absorptions peaks at 3365 and 3050 cm^{-1}, which represent the stretching modes of —OH and —NH; the highlighted peaks at 2961,1649, and 1563 cm^{-1} are characteristic of —CH, —C=O, and —CN group, respectively. The five primary peaks indicate the formation of U-F. The absorption peaks of epoxy functional group at 910–950 and 820 cm^{-1} indicate that the epoxy functional groups are successfully grafted on the PUF microcapsules shell wall materials.

XPS characterization

To confirm further the fact that the epoxy functional group has been grafted on the wall materials, the Si 2p XPS spectra of the microcapsules surface was

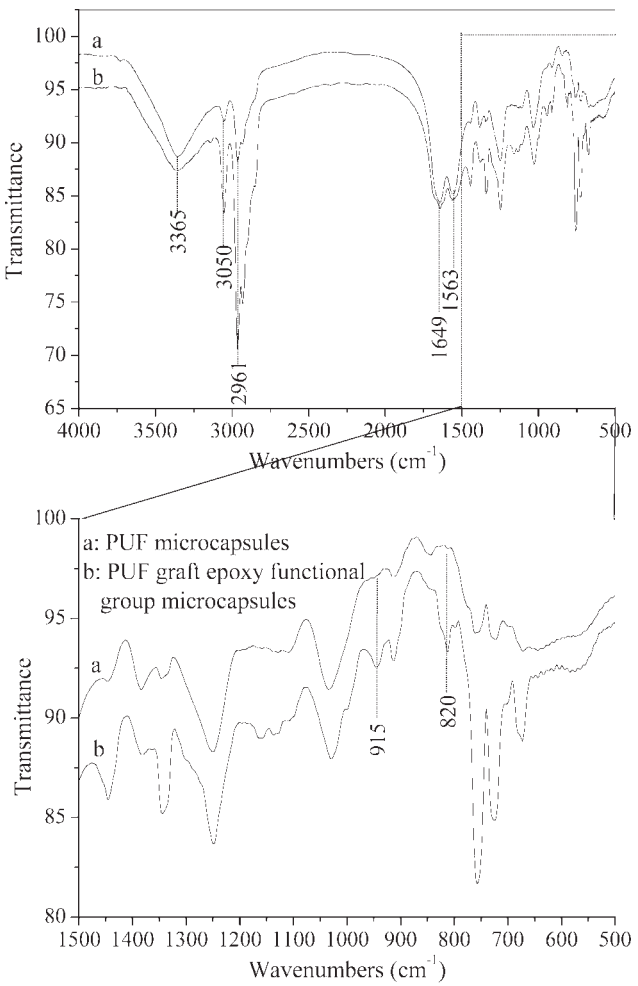

Figure 7 FTIR spectra: (a) PUF microcapsules; (b) PUF-grafted epoxy functional group microcapsules.

characterized as shown as in Figure 8. The binding energy of C 1s (284.8 eV) is used as the reference. The peaks at 100.8, 101.9, and 103.0 eV are the

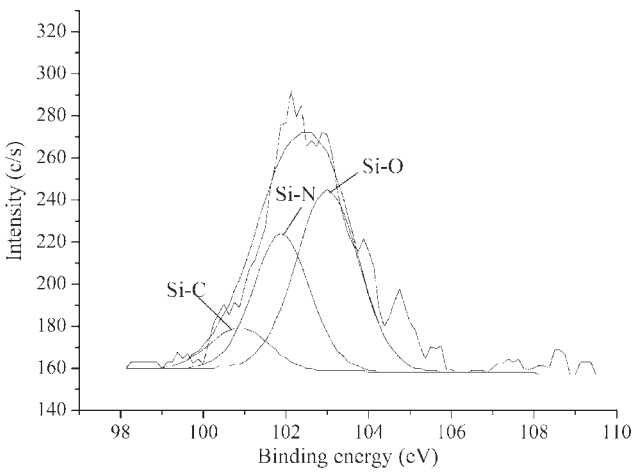

Figure 8 Si 2p XPS spectrum of microcapsules.

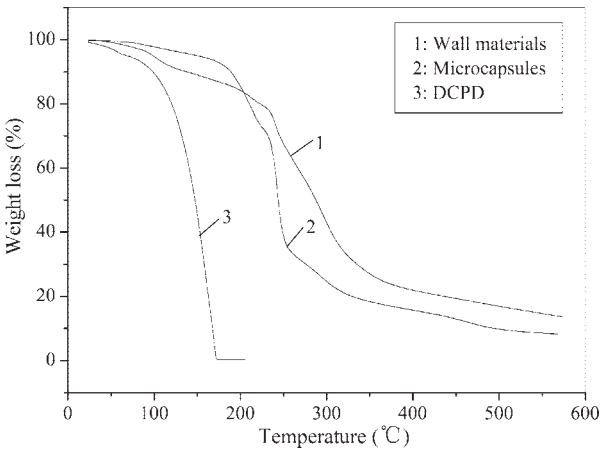

Figure 9 TG diagrams: (1) wall materials, (2) microcapsules, (3) DCPD.

binding energy of Si—C, Si—N, and Si—O, respectively. It is concluded that the chemical bond (Si—N) is formed and the silane is grafted on the shell wall.

FTIR spectra and the XPS analysis results indicted that the third monomer KH560 was grafted successfully on the surface of microcapsules, as shown as the reaction scheme in Figure 3(b).

Thermal stability of microcapsules

The thermal stability of microcapsules plays an important role in their applications. Figure 9 shows a TG diagram of the microcapsules, wall materials, and DCPD. The weight loss curve of wall shell is similar to the PUF wall shell reported by Yuan et al.[14] and Yin et al.[15] As illustrated in Figure 8, the TG curve of wall shell materials indicates that the weight loss before 245°C is mainly due to the elimination of F and decomposition of small molecule minor product. The weight loss at temperatures 245–342°C is mainly due to the decomposition of the crosslink wall shell materials. The decomposition temperature of DCPD is in the range of 110–150°C. The curve of microcapsules consists of two stages of weight loss with a rise in temperature (i.e., 185–245°C and 245–255°C, respectively). In the first stage of 185–245°C, the decomposition of wall materials causes the crack of microcapsules, which results in decomposition of little of the DCPD. The curve of the second stage from 245 to 255°C falls faster than the first stage. This is because they have reached the decomposition temperature 245°C of crosslink wall shell materials, and damage of wall materials induced a large number of weight loss of DCPD. Compared with the DCPD thermal degradation temperature of 110–150°C, the thermal stability of the DCPD in the microcapsules is evidently increased, owing to the protection of the shield of the wall material.

Core content of microcapsules

The core content of microcapsules was determined by acetone extracting method. Microcapsules samples were ground and washed with acetone several times, and then dried at room temperature. Knowing the initial weight of intact microcapsules $W_{\text{microcapsules}}$ and the weight of residual wall shell W_{wall} of microcapsules, we can calculate the core content of microcapsules from the following equation:

$$W_{\text{core}} = \frac{W_{\text{microcapsule}} - W_{\text{wall}}}{W_{\text{microcapsules}}}$$

In our study, the core content of microcapsules with 125 μm mean size and 2- to 5-μm wall thickness is about 60%. The core content of microcapsules is decided by microcapsules size and wall thickness. Bigger microcapsules with thinner wall thickness will possess a larger portion of core. Hence, the concentration of the healing agent can be adjusted.

CONCLUSION

KH560 encapsulated DCPD healing agent can be prepared by *in situ* polymerization. The epoxy functional group was successfully grafted on the wall materials, which develop the self-healing composites. In this study, the microcapsules were manufactured by three steps, the preparation of urea-formaldehyde prepolymer, the polycondensation of the prepolymer in DCPD emulsion, and the polycondensation of prepolymer and KH560. The size was measured and it can be controlled by adjusting agitation rate. The surface morphology and the wall thickness were observed by SEM. The epoxy functional group was grafted on the wall materials, which will be advantageous for the interface performance between microcapsules and epoxy matrix. The microcapsules thermal stability was analyzed. In general, this research provides novel microcapsules for the self-healing composites, while the effects of microcapsules on the polymeric composites and the interface performance will be further examined in our future studies.

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