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# Effects of Surface Modification on the Properties of Microcapsules for Self-healing

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**Abstract:** Poly (urea-formaldehyde) (UF) microcapsules with epoxy resin E-51 as core material used as self-healing materials were prepared by interfacial polymerization method. The surface of UF microcapsules was modified by γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH-560). The interfacial interactions between UF microcapsules and KH-560 were studied by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectrometric analysis (XPS) of microcapsules. The surface topography of microcapsules was characterized by scanning electron microscopy (SEM). The thermal stability and mechanical properties were evaluated. FTIR and XPS results showed that there were physical and chemical combinations between the silicon coupling agent and the microcapsules surface. The thermal stability and mechanical property analysis showed that the addition of KH-560 could greatly improve the thermal stability, tensile property and elastic property. SEM results indicated that the addition of KH-560 could improve the bonding between the surface of microcapsules and resin matrix and improve the ability of self-healing.

**Key words:** microcapsule; KH-560; surface modification; interfacial polymerization method

## 1 Introduction

Polymeric materials always inevitably have cracks and damages due to the effect of external environment during their long-term use, which causes substantial financial losses and requires extensive efforts to limit its impact. Composites with self-healing ability have been developed rapidly in recent years[1-8]. The healing agent is embedded into microcapsules and as soon as the cracks destroy the capsules, the healing agent will be released to respond to the stimulation and achieve the purpose of repair. Studies[9] showed the self-healing system prepared by in-situ emulsion polymerization with melamine-formaldehyde and epoxy resin as wall material and healing agent separately and the mean particle size of microcapsule was about 93 μm.



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However, There is weak interfacial adhesion between self-healing microcapsules and the matrix, which can affect the mechanical properties of the composites. Surface modification is the common method used to improve the properties of composites. The use of KH-550 and KH-560 can improve properties of high temperature resistance of epoxy resin.

Li H[10] *et al* studied the self-healing system with cyclopentadiene as core material and the surface of microcapsule was modified with organosiloxane KH-550. The results showed that the amino groups on the microcapsule surface could increase the binding force between microcapsules and epoxy resin substrate. Wang[11] *et al* studied the self-healing component of composites and the surface of microcapsules was modified by γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH-560). The results indicated that KH-560 played an important role in improving the interfacial performance between the microcapsules and the matrix, as well as the mechanical properties of the composites, such as the tensile fracture strength and tensile modulus.

In this the paper, the microcapsules were prepared by interfacial polymerization with urea formaldehyde resin and epoxy resin E-51 as wall

material and core material separately. The surface of microcapsules was modified by silane coupling agent KH-560. The interfacial interactions between UF microcapsules and KH-560 were studied by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectrometric analysis (XPS) of microcapsule. The surface topography of microcapsules was characterized by scanning electron microscopy (SEM). The thermal stability and mechanical properties were evaluated.

## 2 Experimental

### 2.1 Raw materials

Epoxy resin (E-51) was supplied by SanMu Group Corporation of Jiangsu, China; KH-560, urea, 37% formaldehyde and sodium dodecylbenzenesulfonate were supplied by Guangzhou Chemical Reagent, China; Triethanolamine, sodium chloride, hydrochloric acid, acetone, resorcinol and n-octanol were supplied by Damao Chemical Reagent of Tianjin, China. All commercial chemicals were used without further purification in this study.

### 2.2 Preparation of epoxy resin microcapsule by interfacial polymerization process

2.2.1 Prepolymer preparation

Urea (U) and 37wt% formaldehyde (F) were mixed in a 250 mL three-necked round-bottomed flask and stirred at 70 ℃ for 90 minutes. The mass ratio between urea and formaldehyde was 1:2. After the urea was dissolved, the pH value of the mixed solution was kept at about 8-9 by adding triethanolamine.

2.2.2 Synthesis of microcapsules

E-51 was dissolved into the solution of thinner and emulsifier and dispersed by ultrasonic equipment for 20 minutes, and then stirred by mechanical stirring equipment for 20 minutes; the oil-in-water emulsion (*O/W* emulsion) was obtained. U-F pre-polymer was added into the above *O/W* emulsion with 500 r/min continuous mechanical agitation at 50 ℃. Resorcinol (0.5 g) and NaCl solution (4wt%) were added into the solution. After the solution was stirred for 20 min at the agitation ratio of 500 r/min, the pH of solution was adjusted slowly to 3.0 by 10wt% hydrochloric acid solutions, and then the solution was heated to 60 ℃ and kept at this temperature for 3 h. The microcapsules were rinsed with deionized water and acetone, filtered and air-dried for 24 h.

2.2.3 Surface modification of UF microcapsules with KH-560

Pre-modification method (PMM): Urea (U), 37wt% formaldehyde (F) and a certain amount of silane coupling agent KH-560 were mixed in a 250 mL three-necked round-bottomed flask and stirred at 70 ℃ for 90 minutes. The weight ratio between urea and formaldehyde was 1:2. After the urea was dissolved, the pH value of the mixed solution was kept at about 8-9 by adding triethanolamine. The prepolymer was prepared and used to prepare microcapsules.

Conventional modifying method (CMM): a certain amount of silane coupling agent KH-560 water solution was prepared and 5 g UF microcapsules were added into 100 g of the above solution. Then, the pH value of the solution was adjusted to about 7.0. The system was stirred for 1 h and heated up to 80 ℃. The obtained suspension was filtered and the modified microcapsules were obtained. The microcapsules modified were dried at room temperature for 24 h.

### 2.3 Manufacture of epoxy specimen filled with self-healing microcapsules

The resin mixture was prepared by E-51 and amine curing agent and the mass ratio between E-51 and amine curing agent was 2:1. The specimens were prepared by mixing 10% self-healing microcapsules with the resin mixture described above. To obtain the cured sample, the composites were degassed, poured into a closed polyvinyl fluoride mold, and cured for 7 h at room temperature.

### 2.4 Performance test and structure characterization

2.4.1 Molecular structure identification

An FTIR(FT-IR, Nicolet Avatar 360) spectrometer was used to identify the molecular structure of microcapsule. The samples were ground and dispersed in KBr, followed by compression to consolidate the formation of the pellet. FTIR spectra were obtained in the wave number range from 400 to 4 000 $cm^{-1}$.

2.4.2 Analysis of microcapsule size and shell morphology

The surface topography of microcapsules was analyzed by an optical microscope (OM) and scanning electron microscope (SEM).

2.4.3 Thermal analysis of microcapsule

Microcapsules were analyzed using thermal analysis (DTA-TG, ZRY-2P) in nitrogen environment with a sample weight of about 8.0-10.0 mg. Heating rate was maintained at 10 ℃/min in the temperature range of 25-600 ℃. The flux of nitrogen of the method is 60 mL/min.

2.4.4 Mechanical property analysis of microcapsule

Mechanical property of microcapsule was analyzed using tensile testing machine (DL-1000B) at room temperature in the crosshead speed of 5 mm/min.

2.4.5 X-ray photoelectron spectrometric analysis (XPS) of microcapsule

X-ray photoelectron spectrometric analysis was carried out on PHI ESCA 5700. The instrument used Al Ka (1486.6 eV) as the radiation source and the vacuum was maintained at $10^{-6}$ Pa. The data was processed by PC-ACCESS ESCA-V6.0E software.

# 3 Results and discussion

## 3.1 FTIR of microcapsules

FTIR spectra of microcapsules before and after modified (prepared by PMM and CMM methods) by KH-560 are shown in Figs.1-3.

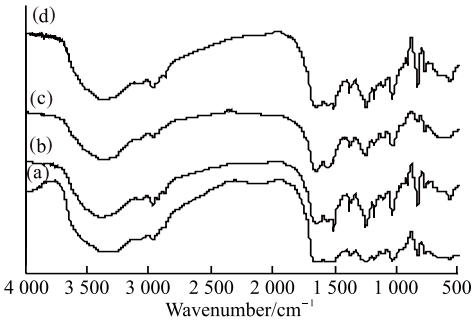


Fig.1 FTIR spectra of microcapsules prepared by PMM (the amount of KH-560: a-0%, b-1%, c-2%, d-3%)

Fig.1 shows the FTIR spectra of microcapsules before and after modified by KH-560 prepared by PMM. In Fig.1, the peaks at 3 375, 2 970, 1 650, and 1 560 $cm^{-1}$ are the characteristic absorption peaks of -NH or -OH, -CH, -C=O, and -CN, respectively. The four primary peaks indicate the formation of urea-formaldehyde polymer. In addition, the peaks at 910 and 837 $cm^{-1}$ are the absorption peaks of epoxy ring, which shows that the core materials are successfully encapsulated in urea-formaldehyde shell. Compared with the result of Fig.1(a), the peaks at 1000 $cm^{-1}$ (attributed to the absorption peaks of -OH) in Figs.1 (b, c, d) become stronger which indicates that the content of -OH is higher. The higher content of -OH indicates that there is linear structure in the urea-formaldehyde polymer of microcapsules prepared by PMM. The existence of linear structure has an adverse effect on the stability of the microcapsules. In addition, the stronger absorption peaks at 1 250, 1 180, 1 020, and 910 $cm^{-1}$ are the characteristic absorption peaks of KH-560 in Figs.1 (b, c, d), which indicates that KH-560 was adsorbed on the surface of the microcapsules.

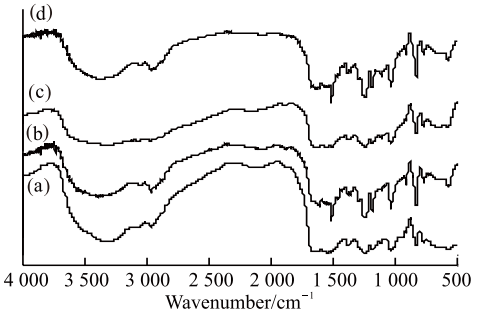


Fig.2 FTIR spectra of microcapsules prepared by CMM (the amount of KH-560: a-0%, b-1%, c-2%, d-3%)

Fig.2 shows the FTIR spectra of microcapsules before and after modified by KH-560 prepared by CMM. In Fig.2, the four peaks at 3 375, 2 970, 1 650, and 1 560 $cm^{-1}$ were the characteristic absorption peaks of -NH or -OH, -CH, -C=O, and -CN, respectively which indicated the formation of urea-formaldehyde polymer. The absorption peaks of epoxy ring at 910 and 837 $cm^{-1}$ indicated that the core materials had been successfully encapsulated in urea-formaldehyde shell. Compared with Figs.2 (b, d), the characteristic absorption peaks of KH-560 at 1 250, 1 1801, 1 020, and 910 $cm^{-1}$ became weaker in Figs.2 (a, c), which indicated that the adsorption of KH-560 on the surface of the microcapsules became weaker.

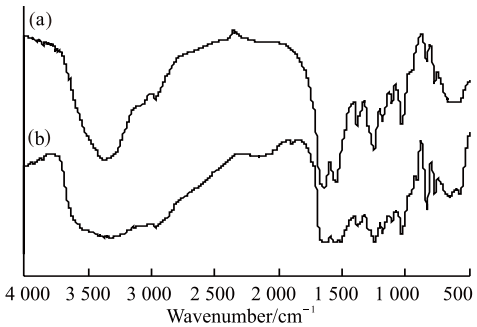


Fig.3 FTIR spectra of microcapsule prepared by PMM and CMM: (a) PMM; (b) CMM. Here, the amount of KH-560 is 2%

Fig.3 shows the FTIR spectra of microcapsules prepared by PMM and CMM. Compared with the FTIR spectra of microcapsules in Fig.3(a), the characteristic absorption peaks of urea-formaldehyde shell, KH-560 and -Si-OH at 1 100 $cm^{-1}$ become weaker and the absorption peaks of epoxy ring become stronger in Fig.3(b). These indicate that silane coupling agent may be chemically attached on the surface of microcapsule prepared by CMM.

## 3.2 XPS of microcapsules

In order to further confirm the interfacial binding between silane coupling agent and microcapsules, XPS test was used. Fig.4 shows the XPS of microcapsule prepared by CMM (the amount of KH-560 is 2%). With the increasing of each etching level, etching

depth increases by 20 nm. According to the result of Fig.4, the rapid decline of Si2p atomic percent in the first etching level occurs. This indicates that silicon coupling agent forms a layer of organic coating on the surface of the microcapsule, which is the main feature of silane coupling agent. With increasing etching level, the Si2p atomic percent decreases slowly, which indicates that there are physical and chemical combinations between the silicon coupling agent and the microcapsule surface.

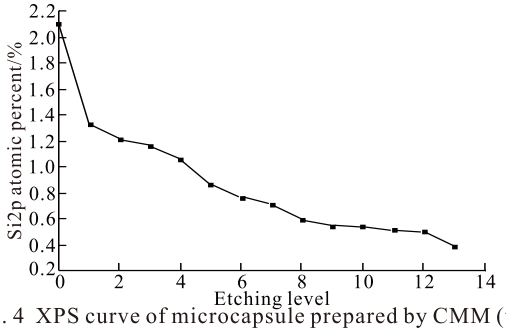


Fig. 4 XPS curve of microcapsule prepared by CMM (the amount of KH-560 is 2% )

### 3.3 Mechanical properties of microcapsules

The addition of microencapsulated healing agent in matrix can potentially change its mechanical properties. Tables 1-3 show the mechanical properties of matrix with microcapsules before and after modified by KH-560 (prepared by PMM and CMM methods).

Table 1 shows the mechanical properties of matrix with microcapsules before and after modified by KH-560 (prepared by PMM method). The results of Table 1 indicated that the addition of microcapsules modified by KH-560 (prepared by PMM method) could decrease all the mechanical properties. According to the results of FTIR, KH-560 was adsorbed on the surface of the microcapsules prepared by PMM method and the adsorption of KH-560 on the surface of the microcapsules resulted in the poor binding force between microcapsules and resin.

Table 2 shows the mechanical properties of matrix with microcapsules modified by KH-560 (prepared by CMM method ). The results of Table 2 show that the addition of KH-560 has a significant influence on the mechanical properties of microcapsules prepared by CMM method. When the amount of KH-560 was 1%, the tensile property and elastic property increased. When the amount of KH-560 increased to 2%, there was a significant increase in elastic property. When the amount of KH-560 was 3%, the tensile property and elastic property all decreased.

According to the results of Figs.1-4 and Tables 1-2, we modified the microcapsules by CMM method and the amount of KH-560 was 2%.

**Table 1 Mechanical properties of matrix with microcapsules before and after modified by KH-560 (prepared by PMM method )**

| Amount of KH-560 | Maximum load/N | Tensile strength /MPa | Tensile load/N | Tensile stress/MPa | Tensile yield stress/MPa | Offset yield stress/MPa | Modulus of elasticity/MPa |
|---|---|---|---|---|---|---|---|
| 0% | 886.5 | 29.5 | 323.2 | 10.8 | 29.0 | 3.7 | 870.6 |
| 1% | 692.5 | 19.2 | 214.0 | 5.9 | 19.2 | 1.2 | 6.8 |
| 2% | 594.4 | 16.5 | 184.5 | 5.1 | 16.5 | 0.2 | 6.8 |
| 3% | 440.0 | 12.2 | 140.8 | 3.9 | 8.8 | 3.1 | −487.4 |

**Table 2 Mechanical properties of matrix with microcapsules modified by KH-560 (prepared by CMM method )**

| Amount of KH-560 | Maximum load/N | Tensile strength /MPa | Tensile load/N | Tensile stress/MPa | Tensile yield stress/MPa | Offset yield stress/MPa | Modulus of elasticity/MPa |
|---|---|---|---|---|---|---|---|
| 0% | 886.5 | 29.5 | 323.2 | 10.8 | 29.0 | 3.7 | 870.6 |
| 1% | 995.3 | 27.6 | 484.3 | 13.5 | 21.1 | 0.2 | 891.2 |
| 2% | 627.8 | 17.4 | 268.8 | 7.5 | 10.9 | 2.3 | 1 046.2 |
| 3% | 622.3 | 17.3 | 233.2 | 6.5 | 16.2 | 0.1 | −410.0 |

**Table 3 Mechanical properties of matrix with different amount of microcapsules**

| Amount of KH-560 | Maximum load/N | Tensile strength /MPa | Tensile load/N | Tensile stress/MPa | Tensile yield stress/MPa | Offset yield stress/MPa | Modulus of elasticity/MPa |
|---|---|---|---|---|---|---|---|
| 10% | 627.8 | 17.4 | 268.8 | 7.5 | 10.9 | 2.3 | 1 046.2 |
| 30% | 117.5 | 3.3 | 45.3 | 1.3 | 1.8 | 0.7 | 5.7 |
| 50% | 69.9 | 1.9 | 33.6 | 0.9 | 1.0 | 0.4 | 7.6 |

Table 3 shows the mechanical properties of epoxy matrix with different amount of microcapsules. When the amount of microcapsules is 10%, the epoxy matrix shows better mechanical properties. When the amounts of microcapsules decrease to 30% and 50%, the mechanical properties of epoxy matrix decrease rapidly. The results of Table 3 show that the amount of microcapsules has great influence on the mechanical properties of the epoxy matrix and the optimum amount of microcapsules mixed in epoxy matrix is 10%.

### 3.4 Thermal stability of microcapsules

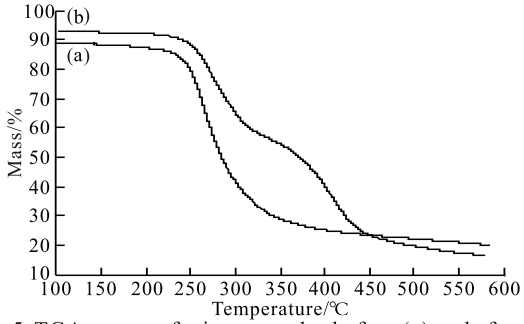


Fig.5 TGA curves of microcapsules before (a) and after (b) modified with KH-560(prepared by CMM method and the amount of KH-560 is 2%)

The thermal stability of microcapsules plays an important role in their applications in self-healing composites materials. Fig.5 shows the TGA diagrams of microcapsule before and after modified with KH-560. According to the Ref.[12], the thermal decomposition temperature of core material epoxy resin is 200 ℃. The weight loss could be seen as the surface adsorption of water and formaldehyde in initial stage before 250 ℃, which indicates that the core material is well coated by shell material. There is a quick decomposition process between 250-450 ℃ due to the shell material being cracked or destructed, resulting in the rapid release of the core material. The TGA curves of the microcapsules show that the decomposition temperature of the microcapsules exceeds the decomposition temperature of the core material 200 ℃, which indicates that the decomposition temperature of the microcapsules is improved because of the protection of the shell material. Then there is a further weight loss between 450-600 ℃ because of the decomposition of shell material. In view of the above results, it is established that the core materials are successfully encapsulated in urea-formaldehyde. The decomposition temperature of microcapsules is about 250 ℃ and the microcapsules can be safely stored and used below this temperature.

Comparing Fig.5(a) and Fig.5(b), the decomposition temperature of the microcapsules modified with KH-560 is higher than that of the microcapsules unmodified, but the decomposition rate is lower than that of the microcapsules unmodified. $T_{50}$ of the microcapsules modified with KH-560 is 400 ℃, which is higher than that of the unmodified (275 ℃). According to the above result, it is indicated that the addition of KH-560 could greatly improve the thermal stability of microcapsules.

### 3.5 Morphology characterization of microcapsules

The morphology of the microcapsules before and after modified with KH-560 was characterized by SEM and the results are shown in Fig.6. Fig.6 (a) shows that microcapsule shows uniform round and smooth surface, which guarantes that the microcapsules can be uniformly dispersed in the matrix in a certain extent. Fig.5(b) shows that the shells of the microcapsules modified with KH-560 are thickened and the outer surfaces of these microcapsules become rougher. The result shows that KH-560 is bounded to or chemisorbed on the surfaces of the microcapsules.

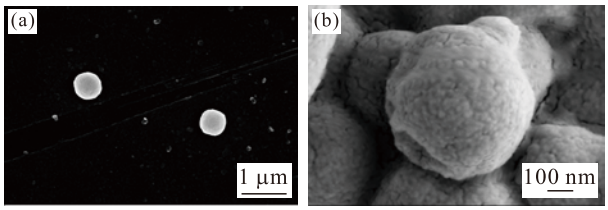


Fig.6 SEM images of microcapsules before (a) and after modified with KH-560 (b)

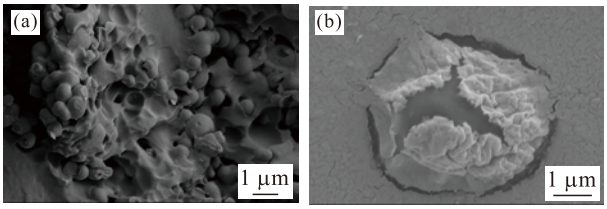


Fig.7 SEM images of microcapsules embedded into epoxy matrix before (a) and after modified with KH-560 (b)

Fig.7 shows the SEM images of microcapsules before (a) and after modified with KH-560 (b) embedded into epoxy matrix. When the microcapsules were incorporated into an epoxy matrix, the exterior shells of the microcapsules led to the formation of a three-part interphase region. The ability of the exterior epoxy matrix to partially penetrate the rough exterior shell of the microcapsules is advantageous for promoting bonding to the surrounding polymer material, and therefore increasing healing agent delivery[12]. Fig.6 (a) shows that there are obvious

cavities on the connection between the surface of the unmodified microcapsules and the resin matrix. Compared with the result of Fig.7 (a), Fig.7 (b) shows that the surface of the microcapsules modified with KH-560 is connected closely with epoxy matrix and the crack between the surface of the modified microcapsules and the resin matrix obviously decrease. This indicates that the silane coupling agent has great effect on the interface between the surface of microcapsules and resin matrix, which could improve the bonding between the surface of microcapsules and resin matrix and improve the ability for self-healing.

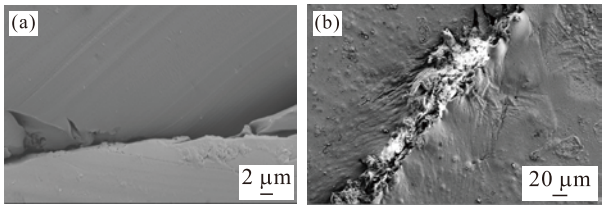


Fig.8 SEM images of fractured surface of microcapsules (20wt%) embedded into epoxy matrix before (a) and after self-healing (b)

When the microcapsules containing the self-healing agent were ruptured, the self-healing agent was delivered to the cracks. Fig.8 shows the SEM images of fractured surface of microcapsules (20wt%) embedded into epoxy matrix before (a) and after self-healing (b). Compared with the result of Fig.8 (a), the crack regions are shown to be healing agent deposited from the microcapsules in the epoxy matrix.

# 4 Conclusions

Poly (urea-formaldehyde) (UF) microcapsules used as self-healing materials were prepared by interfacial polymerization method using epoxy resin E-51 as the core material. The surface of UF microcapsules was modified by KH-560. The effects of KH-560 on the properties of microcapsules were studied by FTIR, XPS, TGA, and SEM and the mechanical properties were evaluated. The experimental results showed that the silane coupling agent had great effect on the properties of the microcapsules prepared by CMM. FTIR and XPS results showed that there were physical and chemical combinations between the silicon coupling agent and the microcapsule surface. TGA and mechanical property analysis showed that the addition of KH-560 could greatly improve the thermal stability, tensile property and elastic property. SEM results indicated that the addition of KH-560 could improve the bonding between the surface of microcapsules and resin matrix and improve the ability for self-healing when the amount of microcapsules embedded into epoxy matrix was 20wt%.

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