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Surface Modification of Poly(urea-formaldehyde) Microcapsules and the Effect on the Epoxy Composites Performance

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The surfaces of poly(urea-formaldehyde) (PUF) were modified by γ-glycidoxypropyltrimethoxy silane (KH560) in order to improve the interfacial bonding between self-healing PUF microcapsules and epoxy matrix. The modification mechanism between PUF microcapsules and KH560 was studied. X-ray photoelectron spectra (XPS) analyses showed that the silane coupling agent molecular binds strongly to the surfaces of PUF microcapsules. Chemical bond (Si–O–C) and hydrogen bond were formed at interface by the reaction between Si–OH and the hydroxyl group of PUF microcapsules surface. The tensile and impact resistance tests revealed that strength and toughness of the composites was improved significantly. Furthermore, scanning electronic microscopy (SEM) photographs of the fractured surface confirmed that the silane coupling agent plays an important role in improving the interfacial performance between microcapsules and resin matrix.

Keywords: Poly(urea-formaldehyde) microcapsules, γ-glycidoxypropyltrimethoxy silane, surface modification, composites, mechanical properties

1 Introduction

Self-healing thermoset material has been widely researched in recent years. The most successful and extensively investigated self-healing system comprises the microcapsules with the healing agent that can release the healing agent into crack plane and heal the crack timely and automatically (1–5). However, the addition of microcapsules affects the mechanical properties of composites and restricts the applications of self-healing material due to the weak interfacial adhesion between self-healing microcapsules and resin matrix. Improvement of interfacial adhesion through surface modification becomes more and more important. Silane coupling agents have provided a simple route to modify the chemical and physical properties of surfaces and interfaces for a long period. Their method is ubiquitous in technologies from filled polymer with particles (6–10) to surface modification of metal that rely on surface coatings created from silanes (11,12). The coupling process can be accomplished via the chemical reaction between the trialkoxy groups of silane molecules and the hydroxyl groups on the matrix substrates, whereas other functional groups of silane molecules, which are generally ethylene, amine, epoxy, thiohydroxy, etc (13). There are few reports about the interfacial modification in the field of smart materials.

In this research, KH-560 (γ-glycidyloxipropyltrimethoxysilane) coupling agent containing an epoxy group was employed to modify the surface of self-healing PUF microcapsules containing the dicyclopentadiene (DCPD) healing agent. The interfacial interactions between microcapsules surface and KH560 were also studied. The performance of microcapsules (before and after modified by KH560)/epoxy composites were investigated.

2 Experimental

2.1 Materials

All commercial chemicals were used without further purification in this study.

$\gamma-$Glycidoxypropyltrimethoxy silane (KH560), supplied by Heilongjiang Institute of Petrochemistry, China, was used as coupling agent in this research. Poly(urea-formaldehyde) (PUF) microcapsules with average size of 200 μm and wall thickness of 2–5 μm were manufactured

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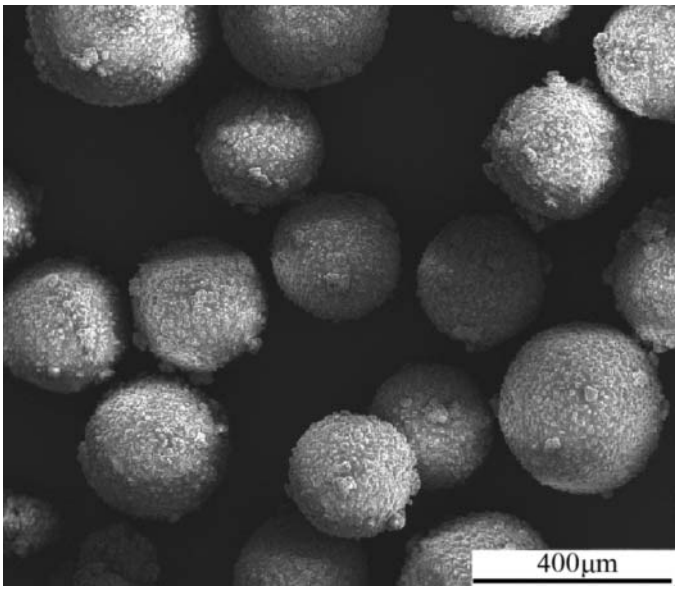

Fig. 1. The SEM micrograph of PUF microcapsules.

in our laboratory and the materials for preparing of PUF microcapsules were listed in our previous paper (14). Epoxy resin 4,5-epoxy cyclohexyl alkane-1,2 binary formyl glycidic ester condensation (TDE-85) and the curing agent m-phenylenediamine were purchased from Tianjin Resin Plant, China. Absolute ethyl alcohol, used as diluting agent, was purchased from Harbin Chemical Regents Factory, China.

2.2 Surface Modification of PUF Microcapsules with KH560

PUF microcapsules were prepared by *in situ* polymerization technique reported in our previous studies (14,15). The morphologies of microcapsules with averge diameter of 200 μm were shown in Figure 1. PUF microcapsules and deionized water were added into a 500 ml beaker equipped with a thermometer and stirrer. KH560 was added and the amount of coupling agent was 5 wt% in terms of PUF microcapsules. The pH of above solution was adjusted to 3.0–4.0 using 10 wt% acetic acid solution. The system was heated up to 80°C and reacted for 1 h. The modified microcapsules were obtained after the filtering of suspension and washing repeatedly with acetone and deionized water. Finally, the microcapsules were dried for 2 h at 60°C and 24 h at room temperature in a vacuum oven.

2.3 Manufacture of Self-Healing Microcapsules/Epoxy Composites

The m-phenlenediamine curing agent was dissolved in absolute ethyl alcohol, equal in quality. TDE-85 epoxy was added into this solution and the weight ratio between TDE-85 and curing agent solution is 100:36. The desired amount of treated or untreated PUF microcapsules was mixed with the above epoxy resin by stirring at room temperature for 10 min. Then, the mixture was poured into a steel mold that was surface treated with a mold-releasing agent, After cured at room temperature for 48 h and at 80°C for 2 h the composites samples were prepared.

2.4 Characterization and Performance Test of Samples

The interfacial interactions were studied using X-ray photoelectron spectrum (XPS). The tensile strength of the microcapsules/epoxy composites were measured on an Instron testing machine (model 1196), with a crosshead rate of 5 mm/min as per GB2561-81. Impact strength of PUF microcapsules/epoxy composites was determined by a falling dart impact tester with a hammer as per GB2571-81. The fractured surface morphology of epoxy matrix filled with the original and modified PUF microcapsules were also observed by scanning electron microscopy (XL 30 ESEM-FEG, PHILIPS).

3 Results and Discussion

3.1 Modification Mechanism

Silane coupling agent can be denoted as R–Si–$(OMe)_3$. Hydroxy group formed from the hydrolyzation of OMe can react with silane hydroxy on the surface of PUF microcapsules. For KH560, R is  , Me is CH_3.

When modified microcapsules are embedded into resin matrix, the epoxy organic group of KH560, which are adsorbed on the surface of modified microcapsules, can react with the epoxy function group of epoxy resin by the action of curing agent. Therefore, there are chemical bonds in the interface between microcapsules and resin matrix, and then the interfacial performance would be greatly improved. The modification mechanism was shown in Figure 2.

3.2 XPS Analyses

The XPS performance was characterized to confirm the interface bonding way between silane coupling agent and the PUF microcapsules. Figure 3 presents Si 2p XPS spectra of the modified PUF microcapsules wall material. The Si 2p peak can be fitted at three curves with peaks at 100.8eV, 102.8eV, 103.7eV, which are attributed to the Si-O-Si, Si-O-H and Si-O-C groups, respectively (16). The results indicated that the chemical bond (Si–O–C) and hydrogen bond (Si-O-H) are formed by the reaction between Si–OH of the

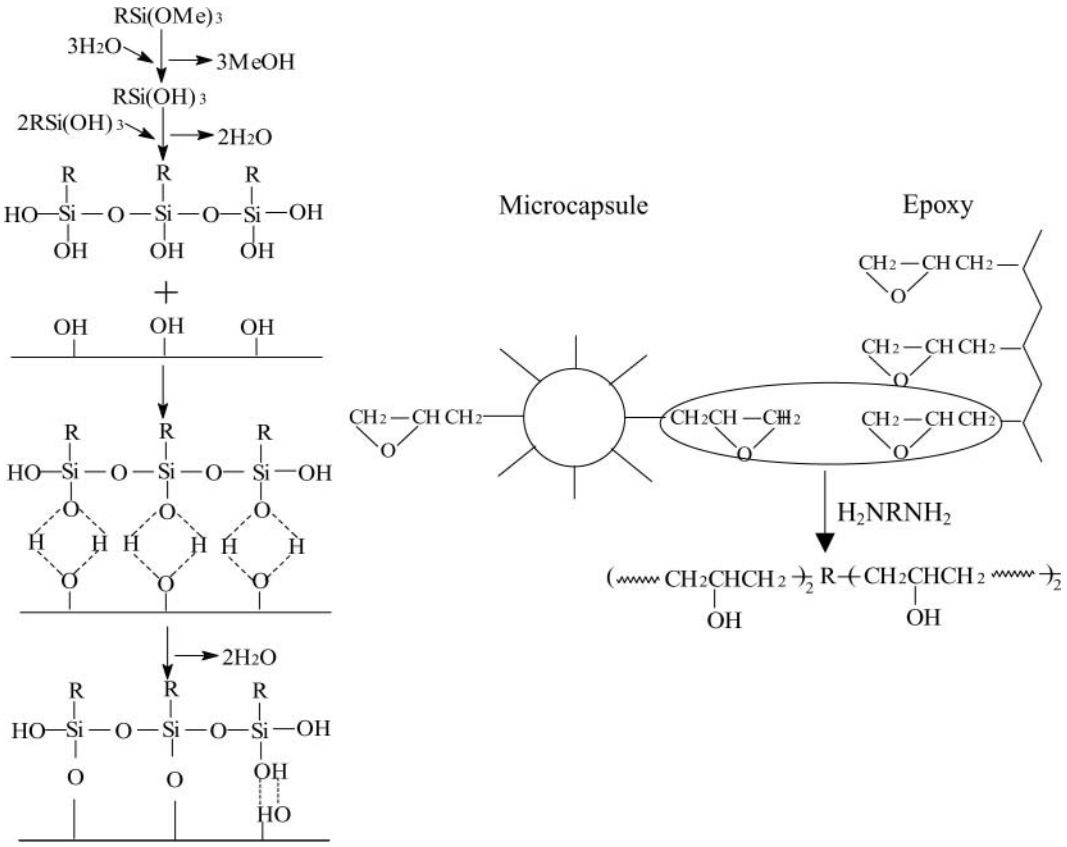

Fig. 2. The action mechanism of silane coupling agent on the PUF microcapsules surface and the action mechanism for modified PUF microcapsules and epoxy matrix.

coupling agent and the hydroxyl group of PUF microcapsules surface, the modifiers are well bonded to the surface of PUF microcapsules.

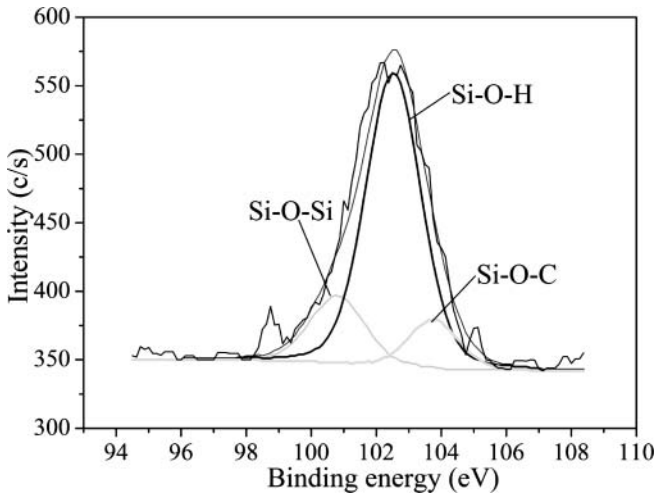

Fig. 3. Si 2p XPS spectrum of modified PUF microcapsules.

3.3 Tensile Strength and Impact Properties of Microcapsules/Epoxy Composites

Tensile strengths curves of microcapsules/epoxy composites were shown in Figure 4(a). It is seen that the tensile strength decreases with the increase of microcapsules concentration. This can be attributed to the large microcapsules diameter and the poor adhesion or bond at the interface between the matrix and the filler. In the systems with coupling agent, all the composites showed an improved strength. The result indicates that the silane coupling agent acts as a link between the filler and the matrix. Best mechanical properties can be achieved by using a coupling agent.

Impact strength is another important mechanical property parameter which is difficult to predict in a filled polymer. The impact strength of a filled polymer also depends on the degree of polymer-filler adhesion, but in a more complex manner than the tensile strength (8). The impact energy of the microcapsules/epoxy composites was plotted against weight percentage of the microcapsules filler in Figure 4(b). It is shown that the impact strength values increase linearly up to 10 wt% of microcapsules

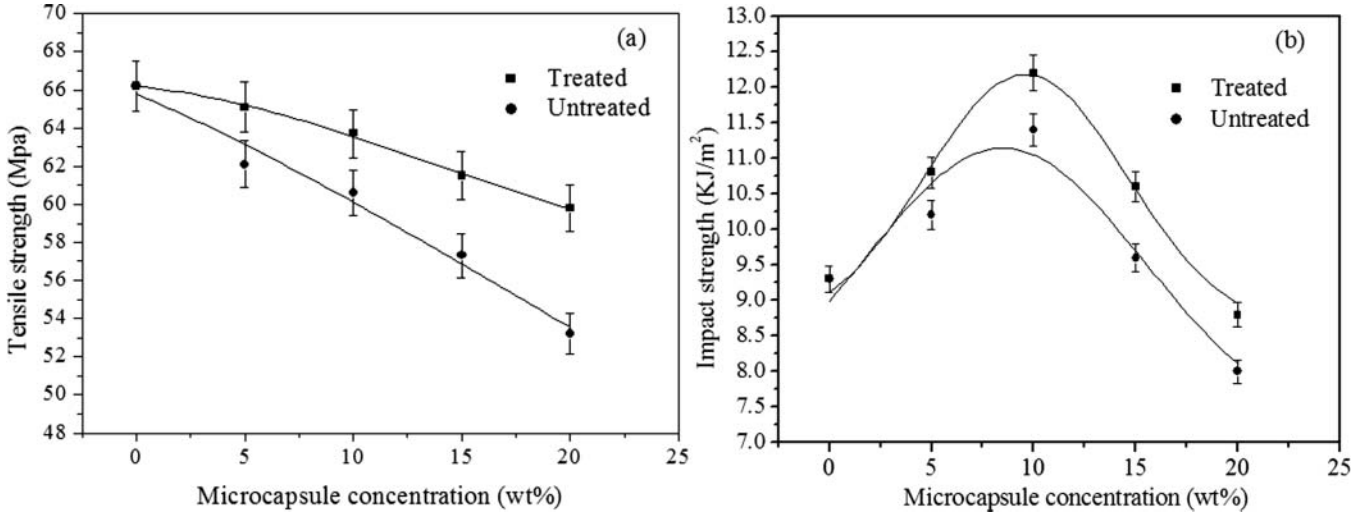

Fig. 4. Tensile strength (a) and impact strength (b) of the microcapsules/epoxy composites with and without the coupling agent.

concentration. As the microcapsules concentration increases further, the impact energy decreases. However, all the compositions of composites with silane coupling agent showed higher impact strength than the composites without coupling agent. For the composite systems containing modified PUF microcapsules, flexible interface layers were formed, and there was interfacial adhesion between the dispersed phase and the matrix. Therefore, the toughness of the composites could be improved (17). These results indicate that in the presence of the coupling agent, the interfacial bonding between the matrix and the filler increases and thus facilitates better transfer of stress.

3.4 Morphologies Studies

SEM micrographs of fractured surfaces of untreated and treated PUF microcapsules embedded into epoxy matrix were both observed. Bad interfacial adhesion and dehiscence at the interface between untreated PUF microcapsules and epoxy matrix is obviously seen from Figure 5(a). For the modified PUF microcapsules, the interfacial adhesion is pronouncedly improved and it have no dehiscence phenomena at the interface showed in Figure 5(b). It is suggested that a strong interfacial bonding between the PUF microcapsules and the matrix exists when the silane coupling agent was used. The result indicates that the coupling

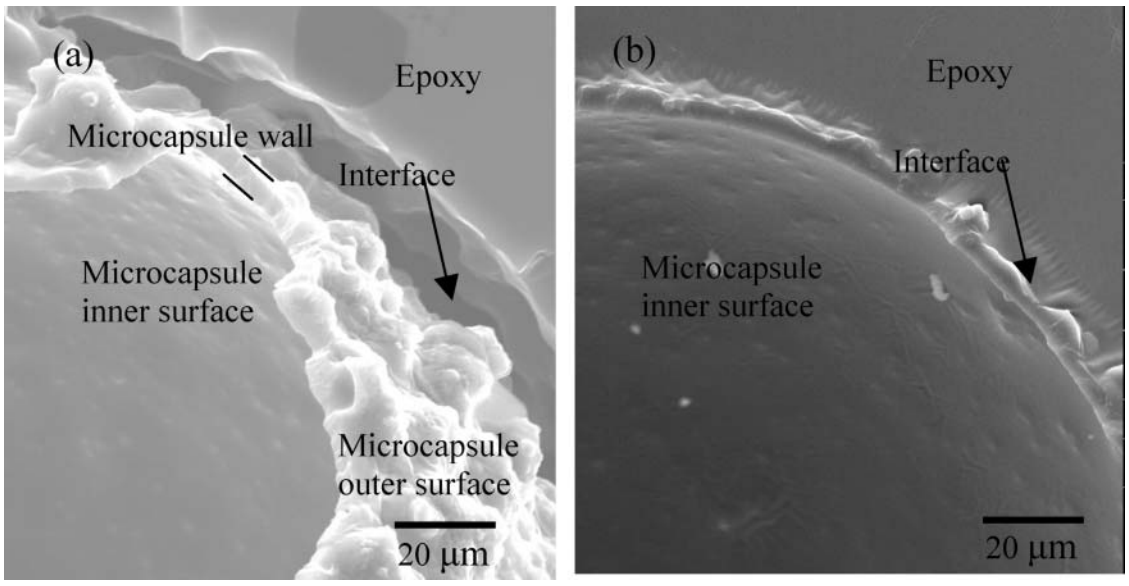

Fig. 5. SEM images of fractured samples of the composites without (a) and with (b) the coupling agent.

agent plays an important role in improving the interfacial performance.

4 Conclusions

PUF microcapsules were modified by silane coupling agent KH560. Based on the interfacial action, chemical bond and hydrogen bond in the interface between PUF microcapsules and KH560 have been built. The tensile strength and impact strength of composites was improved considerably with the modified PUF microcapsules by KH560 compared to untreated PUF microcapsules/epoxy composites. SEM results proved that the surface modification of PUF microcapsules has improved the interfacial adhesion performance of the PUF microcapsules/epoxy composites dramatically.

References

1. White, S.R., Sottos, N.R., Geubelle, P.H., Moore, J.S., Kessler, M.R., Sriram, S.R., Brown, E.N. and Viswanathan, S. (2001) *Nature*, 409, 794–797.
2. Kessler, M.R., Cottos, N. and White, S.R. (2003) *Compos. Part. A-Appl.*, 34(8), 743–753.
3. Brown, E.N., Kessler, M.R., Sottos, N.R. and White, S.R. (2003) *J. Microencapsul*, 20(6), 719–730.
4. Yin, T., Rong, M. Z., Zhang, M.Q. and Yang, G.C. (2007) *Compos. Sci. Techno.*, 67(2), 201–212.
5. Wu, D.Y., Meure, S. and Solomon, D. (2008) *Prog. Poly. Sci.,* 33(5), 479–522.
6. Tee, D.I., Mariatti, M., Azizan, A., See, C.H. and Chong, K.F. (2007) *Compos. Sci. Technol.*, 67(12), 2584–2591.
7. Hussain, M., Nakahira, A., Nishijima, S. and Niihara, K. (1996) *Mater. Lett.*, 26(6), 299–303.
8. Selvina, T.P., Kuruvillab, J. and Sabu, T. (2004) *Mater. Lett.*, 58(3), 281–289.
9. Li, X.H., Cao, Z., Zhang, Z.J. and Dang, H.X. (2006) *Appl. Surf. Sci.*, 252(22), 7856–7861.
10. Fu, W.Y., Yang, H.B., Hari-Bala, Liu, S.K., Li, M.H. and Zou, G.T. (2006) *Mater. Lett.*, 60(13–14), 1728–1732.
11. Vogel, B.M., DeLongchamp, D. M., Mahoney, C.M., Lucas, L.A., Fischer, D.A. and Lin, E.K. (2008) *Appl. Surf. Sci.*, 254(6), 1789–1796.
12. Huang, Y., Shi, K., Liao, Z.J., Wang, Y.L., Wang, L. and Zhu, F. (2007) *Mater. Lett.*, 61(9), 1742–1746.
13. Ma, P.C., Kim, J.K. and Tang, Z. B. (2006) *Carbon*, 44, 3232–3238.
14. Li, H.Y., Wang, R.G., He, X.D. and Liu, W.B., (2007) Proc. of SPIE, 6423, 64232T.
15. Li, H.Y., Wang, R.G., Hu, H.L. and Liu, W.B. (2008) *Appl. Surf. Sci.*, 255(5), 1894–1990.
16. Liao, J.G., Wang X.J., Zui, Y, Zhang, L.W., Ji, Q. and Li, Y.B. (2008) *J. Inorg. Mat.,* 23(1), 145–149.
17. Zhang, X.H., Xu, W.J. and Xia, X.N. (2006) *Mater. Lett.*, 60(28), 3319–3323.