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Effects of Surface Modification of Self-Healing Poly(melamine-urea-formaldehyde) Microcapsules on the Properties of Unsaturated Polyester Composites

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ABSTRACT: Poly(melamine-urea-formaldehyde) (MUF) microcapsules used as self-healing component of composites were prepared by *in situ* polymerization. The surface of MUF microcapsules was modified by 3-aminopropyltriethoxy silane-coupling agent (KH550). The interfacial interactions between MUF microcapsules and KH550 were studied by Fourier transform infrared spectra (FTIR). FTIR results show that the silane-coupling agent molecule binds strongly to the MUF microcapsules surface. A chemical bond (Si—O—C) is formed by the reaction between the Si—OH and the hydroxyl group of MUF microcapsule. This modification improves the thermal properties of microcapsules. Optical microscope (OM) and scanning electron microscope (SEM) show that a thin layer is formed on the surface of MUF microcapsules. The interfacial adhesion effect between MUF microcapsules and unsaturated polyester matrix was investigated. MUF microcapsules disperse evenly in the composites. When crack propagated, the microcapsules were broken and the repair agent flowed from the microcapsules to react with the curing agent. Then the crosslinking structure was formed and the composite was repaired. The tensile properties, impact properties, and dynamic mechanical properties of composites have been evaluated. The results indicate that the silane-coupling agent plays an important role in improving the interfacial performance between the microcapsules and the matrix, as well as the mechanical properties of the composites. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: poly(melamine-urea-formaldehyde); (MUF); microcapsules; KH550; Surface modification; interfacial performance; mechanical properties

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INTRODUCTION

Composites with self-healing function have been developed rapidly in recent years.[1–3] Microcapsules filled with healing agent as self-healing component in thermosetting resin have attracted more and more attention. Poly(urea-formaldehyde) (PUF) self-repairing microcapsules containing dicyclopentadiene,[4–12] PUF microcapsules containing epoxy resin,[13–16] poly(melamine-formaldehyde) microcapsules containing epoxy resin[17–19] or curing agent,[20] and polyurethane[21] materials used to prepare microcapsules for self-healing applications have been reported. However, the applications of self-healing material are restricted due to the weak interfacial adhesion between self-healing microcapsules and the matrix, which has great effect on the mechanical properties and self-healing efficiency of composites.[22] As a result, surface modification of microcapsules is very important to improve the properties of composites.

To improve properties of polymer filled with microcapsules, silane-coupling agents have gained attention because of their special structures. The coupling process can be accomplished via the chemical reaction between the silane molecules and the hydroxyl groups on the substrates, which can improve the performance of composites. There has been considerable amount of work on the influence of coupling agents on the physical and mechanical properties of inorganic-filled composites.[23–26] However, there are few reports about the effect of silane-coupling agent on the properties of self-healing material filled with microcapsules. Thermosetting unsaturated polyester (UP) resin is widely used due to its excellent performance. The interface between the microcapsules and the matrix has great effect on

the mechanical properties of composites. Adhesion/bonding between the microcapsules and the matrix was controlled by using various coupling agents and little improvement in the mechanical properties was observed.

In this article, self-healing MUF microcapsules containing epoxy resin were prepared by *in situ* polymerization. The surface characteristics of microcapsules were modified by commercially available 3-aminopropyltriethoxy silane-coupling agent (KH550). The interfacial interactions between microcapsules and KH550 were studied by Fourier transform infrared spectra (FTIR). The thermal stability of microcapsules was studied by Thermogravimetric analysis (TGA). Then the microcapsules were added into the UP composites. The morphology of composites was observed by optical microscope (OM) and scanning electron microscope (SEM). The mechanical properties such as tensile properties, impact properties, and dynamic mechanical properties were measured. The results show that poly(melamine-urea-formaldehyde) (MUF) microcapsules disperse in the matrix evenly. When crack propagated, the microcapsules were broken and repair agent flowed from the microcapsule to react with the curing agent. The crosslinking structure was formed and the matrix was repaired. The amount of microcapsules has significant effect on the mechanical properties of the composites. The compatibility and the mechanical properties were significantly improved by the surface modification of microcapsules.

EXPERIMENT

Materials

MUF microcapsules containing epoxy resin were manufactured in our laboratory and the materials for preparing MUF microcapsules were listed in our previous study papers.[27,28]

3-Aminopropyltriethoxy silane (KH550) used as coupling agent in this research was supplied by Petroleum and Chemical Academy of Wuhan, China; UP resin 191 used as matrix was purchased from Xibei Chemical Institute, China; methyl ethyl ketone peroxide used as curing agent and corresponding curing accelerator were purchased from Tianjin Resin Plant, China. Polyamide used as hardener to react with the epoxy in the microcapsule was purchased from Tianjin Resin Plant, China. All commercial chemicals were used without further purification in this study.

Preparation of MUF Microcapsules

Microcapsules were prepared by *in situ* polymerization in an oil-in-water emulsion. At room temperature (20–25°C), E-51 (14.3 g), gum Arabic (2.2 g), sodium dodecyl benzene sulfonate (SDBS) (0.73 g), and deionized water (60 mL) were added in 250-mL three-necked round-bottomed flask fitted with stirrer, distillation head, and condenser. After stirring for 1 h at the agitation ratio of 600 rpm, the O/W emulsion was obtained.

Urea (U) (2.0 g), 37 wt % formaldehyde (F) (5.4 g), and melamine (M) (5–10 wt % of UF) were added in 100-mL three-necked round-bottomed flask with mechanical stirred equipment. The molar ratio of urea and formaldehyde was 1 : 2. The flask was suspended in a temperature-controlled water bath on a programmable hot plate with external temperature probe. After the urea dissolved, the pH of the mixed solution was adjusted to 8–9 by drop-wise addition of triethanolamine. The temperature of system was raised to 80°C and kept for 1 h. Transparent viscous prepolymer solution was obtained.

Prepared prepolymer was added into the above emulsion with 400 rpm continuous mechanical agitation by two-bladed stirring paddle, reacted at 70°C. The pH of solution was kept about 3 by adding batches of NH_4Cl and 10 wt % HCl for 3 h. After the mixture was agitated for 2 h, the hot plate was switched off. Once cooled to the ambient temperature, the resultant slurry counteracted by 10 wt % Na_2CO_3 solution. The microcapsules were rinsed with deionized water, filtrated, purified with acetone, and vacuum dried at 40°C for 24 h.

Surface Modification of MUF Microcapsules with KH550

One wt % silane-coupling agent water solution was prepared and 5 g MUF microcapsules were added into 100 g of the above solution. Then, the pH of the solution was adjusted to about 7.0. The system was stirred and heated up to 80°C using water bath. After stirring for 1 h, the obtained suspension was filtered and the modified microcapsules were obtained by washing repeatedly with acetone and deionized water. Finally, the microcapsules were dried for 2 h at 60°C. At the same time, a blank test was carried with MUF microcapsules at the same reaction time and temperature.

Manufacture of UP Composites Filled with Self-Healing MUF Microcapsules

The unfilled UP composites specimens were produced through mixing 100 parts UP 191 with 1 part curing agent methylethylketone peroxide and 1 part curing accelerator. The self-healing UP composites was prepared by mixing different concentrations of the microcapsules containing epoxy and its hardener polyamide. To obtain the cured sample, the composites were degassed, poured into a closed silicone rubber mold, and cured for 24 h at room temperature.

Performance Test and Structure Characterization

Molecular Structure Identification. FTIR spectrometer (Spectrum100, PerkinElmer, San Jose, CA) was used to identify the molecular structure of the microcapsule. Samples with weight of 0.9–1.0 mg were prepared by grinding the

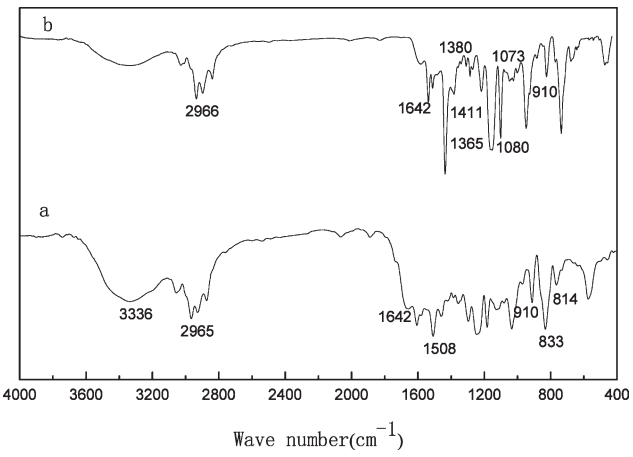

Figure 1. FTIR spectra of MUF microcapsules before (a) and after (b) modified with KH550.

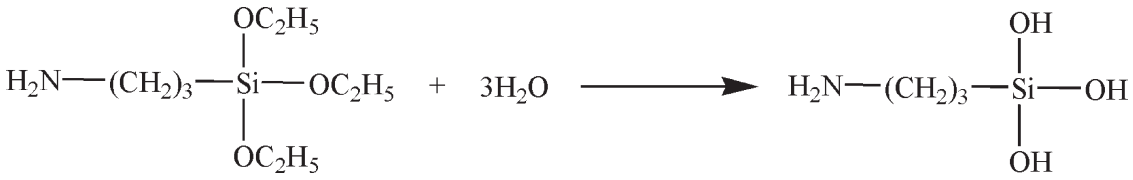

Figure 2. Molecular formulas of KH550 modifiers during hydrolysis.

microcapsules with potassium bromide (KBr) for qualitative analysis. FTIR spectra were obtained in the wave number range from 400 cm^{-1} to 4000 cm^{-1}.

Thermal Analysis of Microcapsules and Composites. TGA (Q500, TA; New Castle, DE) was used to discuss the thermal stability of microcapsule and composites. All experiments were carried out with a sample weight of about 5 mg, at heating rate of 10 °C/min, from 25°C to 600°C, under nitrogen atmosphere.

Analysis of Microcapsule Morphology Dispersed in UP Matrix. Microcapsules in the UP matrix were measured by OM (BK-POL, Auto optics Co., Chongqing, China) and SEM (Quanta 200, FEI; Oregon). The fractured surface morphology of UP matrix filled with modified MUF microcapsules was also observed by SEM. Before observation, samples were vacuum sputter coated with a thin layer of gold to provide electrical conduction.

Assessment of Mechanical Properties of Composites Filled with Microcapsules. Mechanical properties of UP and UP composites filled with microcapsules and hardener have been assessed by tensile and impact test. The tensile strength was measured according to GB/T 1040-96 on a testing machine (XWW-10A,Chengde Jinjian Testing Instrument Co., Ltd, Chengde, China). Samples with dimensions of 120 mm × 10 mm × 4 mm were used for all tensile tests, in the crosshead speed of 1 mm/min, with force sensor of 500 N.

The impact strength was performed according to GB/T1843 on a testing machine (XJU-22,Chengde Jinjian Testing Instrument Co.,Ltd, Chengde, China). Samples with dimensions of 100 mm × 10 mm × 4 mm were used for all impact tests; in the impact velocity of 3.5 m/s and impact energy of 11 J. At least 10 specimens for each system were tested.

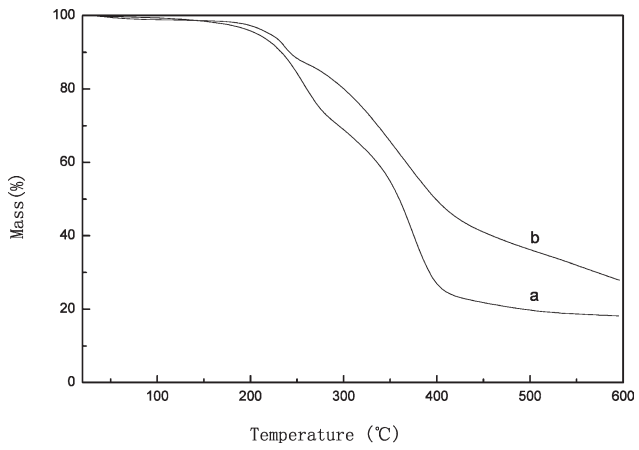

Figure 3. TGA curves of MUF microcapsules before (a) and after modified with KH550 (b).

Dynamic mechanical analysis (DMA) measurements were performed by Dynamic Mechanical Analyzer (Q800, TA Instruments, New Castle, DE). Sample dimensions of 35 mm × 10 mm × 4 mm were used for all tests. The samples were heated from room temperature to 230°C at heating rate of 3 °C/min and frequency of 3 Hz under nitrogen atmosphere.

RESULTS AND DISCUSSION

IR Spectra of MUF Microcapsules

Figure 1 shows the FTIR spectra of MUF microcapsules before and after modified by KH550. The peaks at 3336 cm^{-1}, 2965 cm^{-1}, 1642 cm^{-1}, and 814 cm^{-1} are the characteristic absorption peaks of —OH or —NH, —CH, —CO, and triazine ring, respectively. The four primary peaks indicated the formation of MUF material. The peaks at 910 cm^{-1} and 833 cm^{-1} are the absorption peak of epoxy ring, which showed that microcapsules containing epoxy resin has been formed with MUF resin as shell. There are —OH functional groups in the surface of MUF microcapsules. The stretching vibration peaks of Si—OH reach near 1100 cm^{-1}. Moreover, the peaks at 1380 cm^{-1}, 1080 cm^{-1}, and 1073 cm^{-1} are the characteristic peaks of organic groups of silane, C—Si—O and Si—O—Si, respectively.[22] The great change of adsorption peak at 1000–1050 cm^{-1} might be attributed to the —OH group. The stretching vibration peaks at 1365 cm^{-1} and 1411 cm^{-1} are the characteristic peaks of KH550. All the data suggest that silane-coupling agent is bound to or chemisorbed on the MUF microcapsules surface.

The silane-coupling agent undergoes chemical changes during hydrolysis and drying. During hydrolysis of the silane, the $SiOC_2H_5$ group will transform into Si—OH as shown in Figure 2.

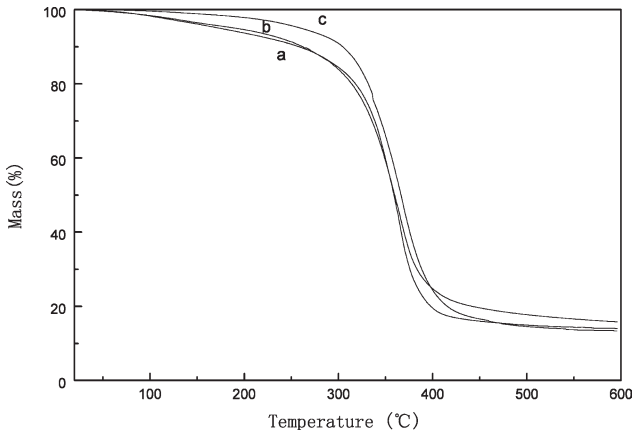

Figure 4. TGA curves of UP composites (a), UP composites filled with MUF microcapsules (b), and UP composites filled with MUF microcapsules modified by KH550 (c).

Table I. TGA Analysis of UP Composites

	$T_{5\%}$ (°C)	T_{50} (°C)
UP composites	174	359
composites filled with MUF microcapsules	190	359
composites filled with modified MUF microcapsules	260	366

In general, one Si—OH of coupling agent reacts with the hydroxyl groups of MUF microcapsules surface and forms the covalent bond. Other Si—OH either has condensation reaction with Si—OH of other silane-coupling agent or being free, thus it is possible to form the hydrogen bond in the interface simultaneously. Of course, there is the possibility of condensation reaction between terminal amino group of the silane and the methylol group of the MUF surface. This reaction might occur due to the reactivity of amino-methyol groups.

The Thermal Stability of MUF Microcapsules and UP Composites Filled with MUF Microcapsules and Hardener

Thermal stability is very important for the microcapsules and composites for their applications and processing. Figure 3 shows TGA diagrams of MUF microcapsules before and after the modification with KH550. There are two main stages. Weight loss in range of 200–290°C of MUF microcapsules was about 30%, mainly due to the decomposition of the shell and core proliferation through the shell. Weight loss in range of 290–450°C was about 50% due to the formation of the higher thermal stability of crosslinked polymer yielded by the core material. MUF microcapsules modified by KH550 started to decompose around 240°C. The heat resistance of microcapsules is improved by KH550 modification. The energy of molecular thermal motion increases.

The addition of MUF microcapsules has no significant effect on the reactivity of UP composites. The viscosity of the composites does not vary with the addition of the microcapsules at room temperature. Figure 4 shows that the thermal stability of the UP composites increased when composites were filled with MUF microcapsules, because MUF microcapsules have higher heat-resistance than UP composites. When UP composites filled with MUF microcapsules were modified by KH550, the heat-resistance has been improved further as Table 1. It is mainly because the coupling agent produced inorganic salts SiO_2 during decomposition. Furthermore, there are better compatibility and stronger intermolecular forces between microcapsules and the substrate, so the more dense material forms.

Morphology Characterization of Microcapsule Dispersion in UP Composites

In order to observe microcapsule rupture and self-healing in UP composites, the microcapsules dispersed in UP matrix and mixed with 1wt % curing agent. The mixture containing different amount of microcapsules was stirred and degassed to remove entrapped air, and then poured into molds. Having been left for 24 h at 25°C in the baking box, the sample was frozen and fractured to obtain a fracture plane.

Figure 5 shows the SEM micrographs of MUF microcapsules before and after modified by KH550. On comparing Figure 5(b) with Figure 5(a), there is a thin layer on the surface of MUF microcapsules. The result is in agreement with the analysis of FTIR. The outer surface of modified microcapsules is rougher.

Figure 6 shows the OM images of MUF microcapsules dispersion in UP matrix before and after modified by KH550. It can be very clearly observed that there is black region around the modified microcapsules in the matrix that is consequence of the presence of the silane coupling agent. When modified microcapsules are embedded into UP matrix, the —NH of KH550 could

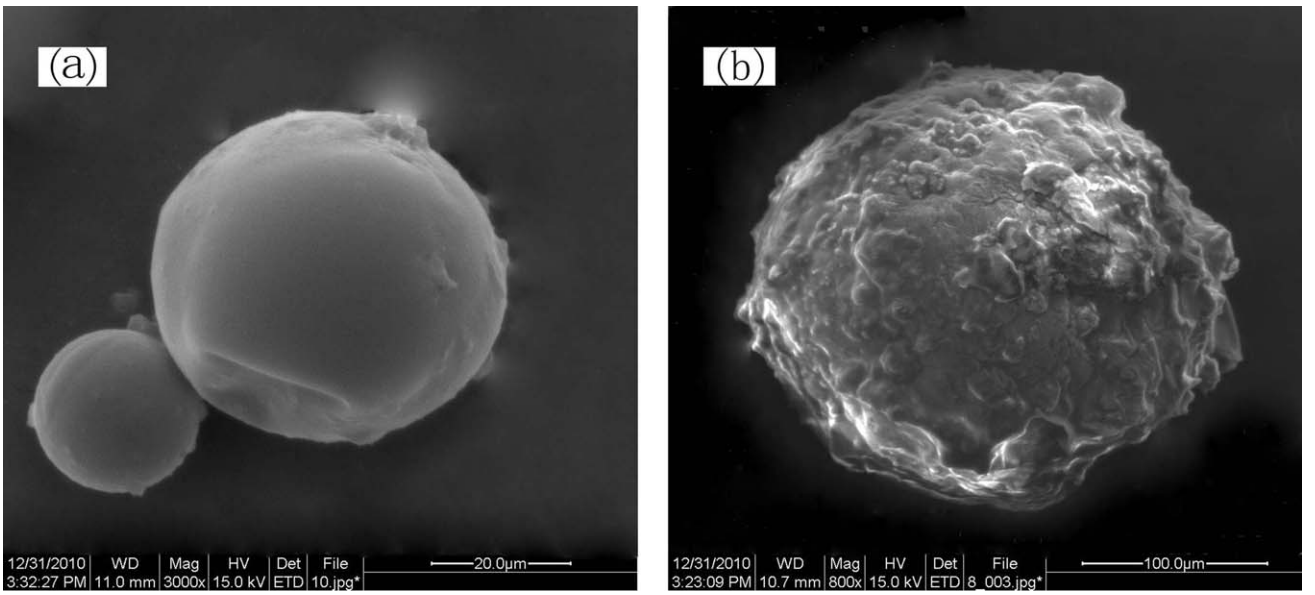

Figure 5. SEM images of MUF microcapsules before (a) and after (b) modification by KH550.

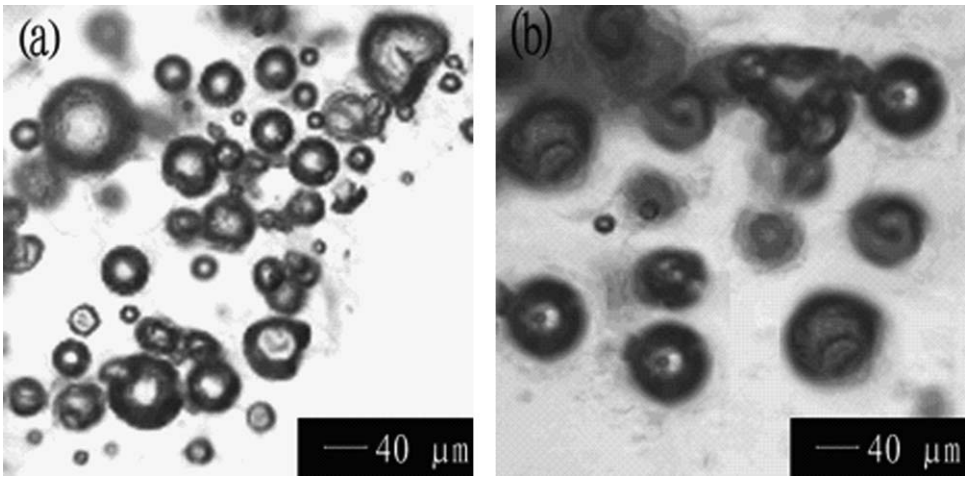

Figure 6. OM images of MUF microcapsules dispersion in UP before (a) and after (b) modification.

form the hydrogen bond with the ester group of UP resin. There is interaction between the substrate and the microcapsules. Therefore, the interfacial performance would be greatly improved. The compatibility of microcapsules with the substrate increased when the surface of microcapsule was modified with a transition layer. The interfacial adhesion is pronouncedly improved, and there is little dehiscence phenomena at the interface.

Figure 7(a) shows the SEM images of surface micrographs of MUF microcapsules embedded into UP matrix. Figure 7(b) shows the SEM images of surface micrographs of KH-550 modified MUF microcapsules embedded into UP matrix. Figure 7(c) shows the SEM images of the fracture surface of self-healing composite specimen, which contains 7 wt % of MUF microcapsules after modified by KH550. The specimen had been fractured during the first impact test, and there are obvious cracks on the surface. In regions where crack propagated there are multiple broken microcapsules. During this process, a few broken microcapsules are observed in the UP composite as shown in Figure 7(d). After healed at 25°C for 24 h, repair agent epoxy flowed from the microcapsule as Figure 7 (e) and reacted with the hardener polyamide to form the cross-linking structure, and then the material surface showed the wrinkles [Figure 7 (f)].

Mechanical Properties of UP Composites Filled with MUF Microcapsules

The addition of microencapsulated healing agent in matrix can potentially change its mechanical properties and processing characteristics. The amount of microcapsules has significant effects on the mechanical properties of UP composites. The extent of the change depends on the fraction of the microcapsules, the level of interfacial interaction, and the inherent properties of the microcapsules.

The specimen is easily pulled off at high tensile rate. The break elongation is too small to be measured and the tensile strength decreases seriously at high tensile rate. Figure 8 shows the dependence of the tensile strength of cured UP composites on the content of MUF microcapsules at lower tensile rate.

As the content of unmodified MUF microcapsules increases, the tensile strength increases first and then decreases [Figure 8(a)]. There is the maximum of tensile property. Seven weight percent is the suitable content for the system to have the maximum tensile strength. The improvement in tensile strength can be explained by the following reasons: Firstly, because microcapsules can be considered to be viscoelastic at smaller deformations and plastic at a larger deformation, the addition of microcapsules might act as fillers and reduce the stress of matrix during the curing process.[29] Secondly, during the cracks propagated, microcapsules might pin or blunt the crack progress according to the results reported in Ref. [30], and the deboning of microcapsules from the matrix or the cavitations of microcapsules could absorb more energy and thus stabilize the crack.

The tensile strength of UP composites decreased with higher content of microcapsules. The viscosity of UP matrix increases with the increasing amount of microcapsules at high temperature. The variation of molding process results in bubbles, holes, clusters, and many other defects in the composites. This defect is apt to cause cracks.Too many microcapsules in the molding process may easily lead to uneven dispersion, resulting in heterogeneous composites, so the tensile strength decreased. In addition, the higher content of microcapsules might cause too much interaction among microcapsules, which prohibits extra plastic deformation owing to the shorter distance of microcapsules.[31]

After modification, the tensile strength increased with the content of microcapsules, and maintained stability [Figure 8(b)].The reason is the compatibility between the microcapsules and substrate improved. The improvement of mechanical properties and their effects of microcapsules mutual reunion may interact.

Figure 9 shows the dependence of the impact strength of cured UP composites on the content of MUF microcapsules. The impact strength of UP composites with MUF microcapsules decreased significantly with the increasing amount of microcapsules [Figure 9(a)]. There are defect points between the microcapsule and the matrix. So the stress concentration points increased. Surface modification increased the impact strength, even more than the original properties [Figure 9(b)].The

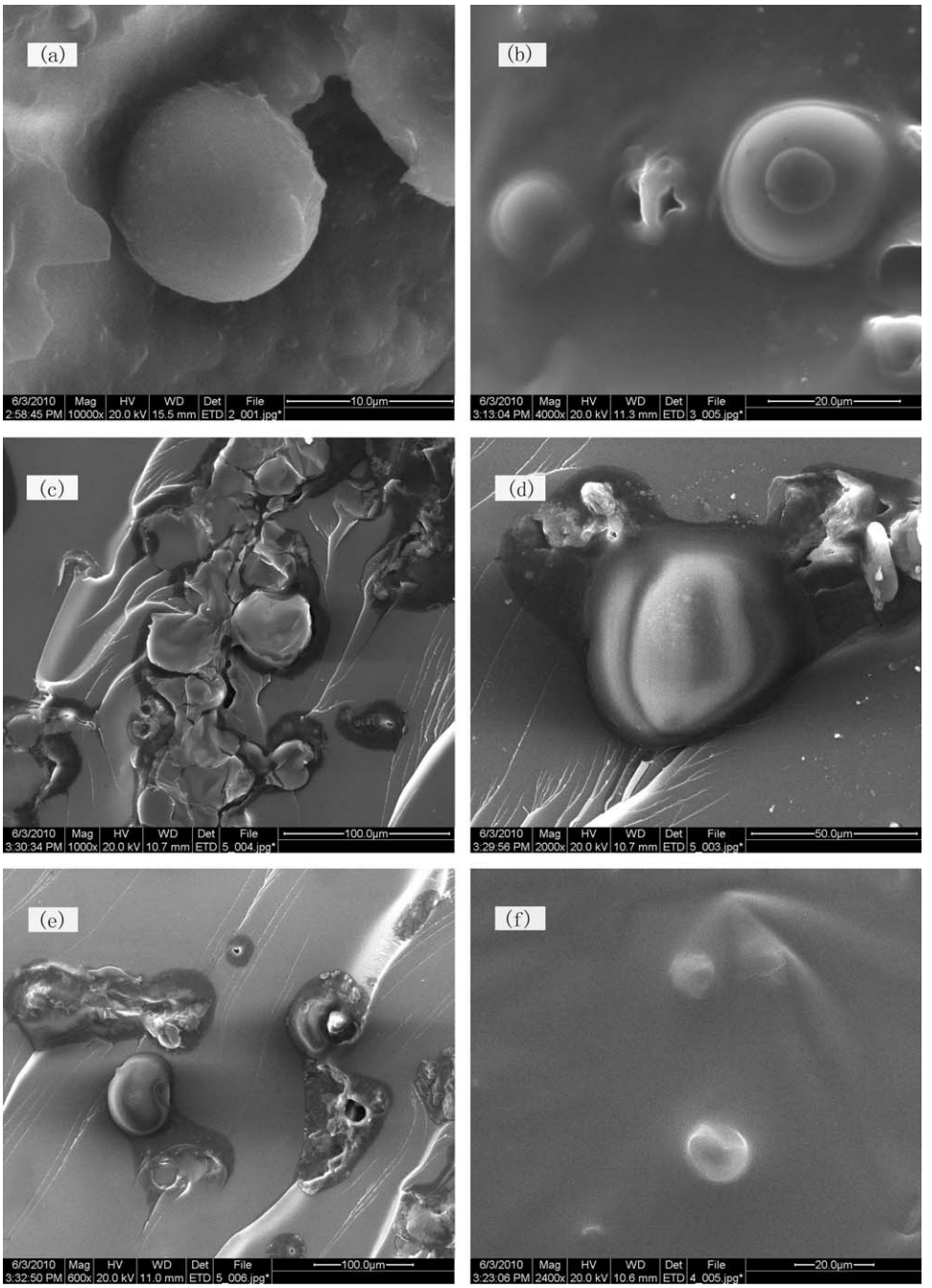

Figure 7. SEM images of MUF microcapsules before (a) and after (b) modification dispersion in UP, fractured surface micrographs of UP composites (c), microcapsules rupture during external force (d), rupture microcapsules self-repairing during healed at 25°C for 24 h (e), and formation of cross-section structure of damaged materials(f).

improvement of impact strength is due to the uniformity of the composites. Overall, the embedded microcapsules provide two independent effects: the increase in virgin fracture toughness from general toughening and the ability to self-heal.

DMA Analysis of UP Composites Filled with MUF Microcapsules Before and After Modification

The mechanical behaviors of composites can also be studied by DMA, a technique that the storage modulus (E') and loss modulus (E'') of the sample, under oscillating load, are monitored against time, temperature, or frequency of oscillation. The DMA curves of these cured resins are shown in Figure 10. In the lower temperature range, the storage modulus of UP composites filled with modification microcapsules is higher than that of unmodified microcapsules.Small and medium size microcapsules in UP composites can reduce stress. Under the action of dynamic forces and heating conditions, large size microcapsules broke and the repair agent flowed to react.

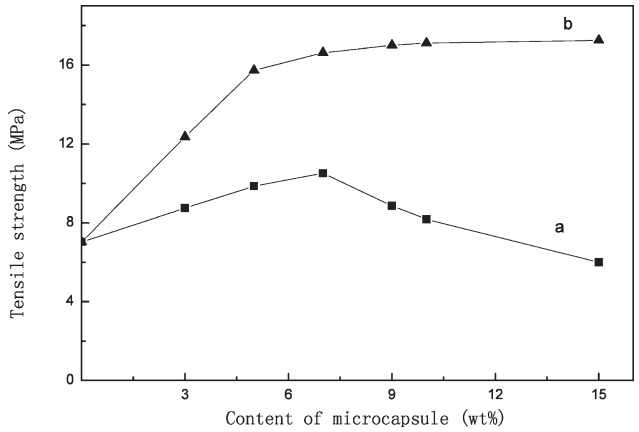

Figure 8. Dependence of the tensile strength of cured UP composites on the content of MUF microcapsules before modification (a) and after modification (b).

Microcapsules added to the composites reduces the crosslinking density. So the storage modulus is declined rapidly with the temperature. The breadth of the tan δ curve for surface-treated microcapsules becomes narrower than that of the unmodified microcapsules. The compatibility between the microcapsules and substrate improved the storage modulus and damping performance.

CONCLUSIONS

Poly(melamine-urea-formaldehyde) microcapsules filled with epoxy resin were applied to UP composites to develop a novel system. The effects of KH550 on the microcapsules were investigated. The silane-coupling agent plays an important role in improving the interfacial performance between the microcapsules and the matrix. So the mechanical properties of the composite can improve significantly. When cracks propagated, the microcapsules were broken and the repair agent flowed out to react with the curing agent. The crosslinking structure was formed and the composite was repaired.

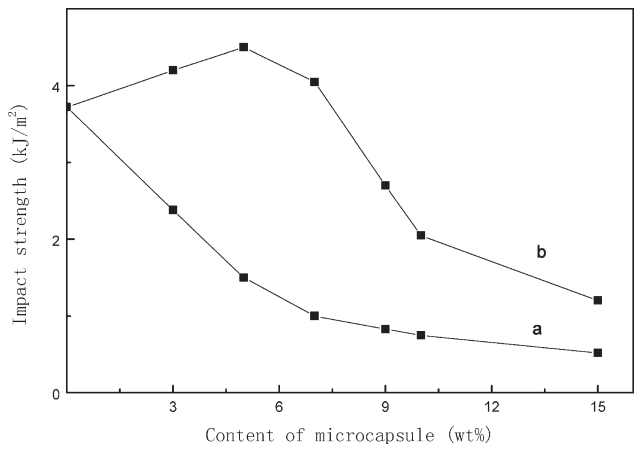

Figure 9. Dependence of the impact strength of cured UP composites on the content of MUF microcapsules before (a) and after modification (b)

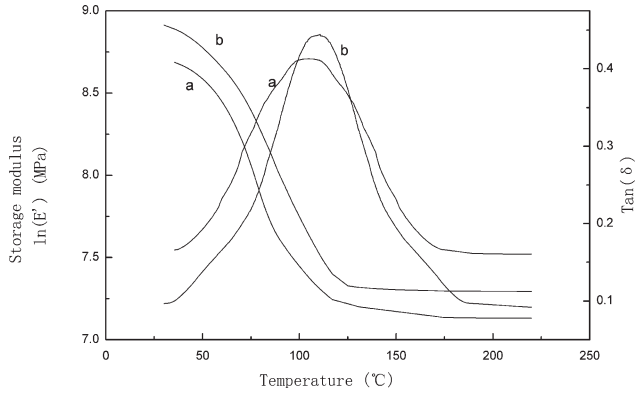

Figure 10. DMA curves of cured UP composites filled with MUF microcapsules before (a) and after (b) modification.

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REFERENCES

1. White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kesslser, M. R.; Sriram, S. R. *Nature* **2001,** *409*, 794.
2. Sottos, N. R.; White, S. R.; Bond, I. *J. R. Soc. Interface* **2007,** *4*, 347.
3. Kessler, M. R.; Sottos, N. R.; White, S. R. *Compos. A* **2003,** *34*, 743.
4. Mauldin, T. C.; Rule, J. D.; Sottos, N. R.; White, S. R. *J. R. Soc. Interface* **2007,** *4*, 389.
5. Brown, E. N.; Sottos, N. R.; White, S. R. *J. Microencapsul.* **2003,** *20*, 719.
6. Kessler, M. R.; White, S. R. *J. Polym. Sci. Part A: Polym. Chem.* **2002,** *40*, 2373.
7. Blaiszik, J.; Caruso, M. M.; McIlroy, D. A.; Moore, J. S.; White, S. R.; Sottos, N. R. *Polymer* **2009,** *50*, 990.
8. Brown, E. N.; White, S. R.; Sottos, N. R. *Compos. Sci. Technol* **2005,** *65*, 2466.
9. Brown, E. N.; White, S. R.; Sottos, N. R. *J. Mater. Sci.* **2004,** *39*, 1703.
10. Brown, E. N.; White, S. R.; Sottos, N. R. *J. Mater. Sci.* **2006,** *41*, 6266.
11. Rule, J. D.; Sottos, N. R.; White, S. R. *Polymer* **2007,** *48*, 3520.
12. Rule, J. D.; Sottos, N. R.; White, S. R.; Moore, J. S. *Educ. Chem.* **2005,** *42*, 130.
13. Cosco, S.; Ambrogi, V.; Musto, P. *Macromol. Symp.* **2006,** *234*, 184.
14. Cosco, S.; Ambrogi, V.; Musto, P. *J. Appl. Polym. Sci.* **2007,** *105*, 1400.
15. Yuan, L.; Liang, G. Zh.; Xie, J. Q.; Guo, J. *Polymer* **2006,** *47*, 5338.
16. Yuan, L.; Liang, G. Zh.; Xie, J. Q.; Guo, J.; Li, L. *Polym. Degrad. Stab.* **2006,** *91*, 2300.

17. Yuan, Y. C.; Rong, M. Zh.; Zhang, M. Q. *Acta. Polym. Sin.* **2008,** *5*, 472.
18. Yuan, Y. C.; Rong, M. Z.; Zhang, M. Q. *Macromolecules* **2008,** *41*, 5197.
19. Yin, T.; Rong, M. Z.; Zhang, M. Q.; Yang, G. C. *Compos. Sci. Technol.* **2007,** *67*, 201.
20. Yuan, Y. C.; Rong, M. Zh.; Zhang, M. Q. *Polymer* **2008,** *49*, 2531.
21. Yang, J.; Keller, M. W.; White, S. R.; Sottos, N. R. *Macromolecules* **2008,** *41*, 9650.
22. Li, H. Y.; Wang, R. G.; Hu, H. L.; Liu.W. B. *Appl. Surf. Sci.* **2008,** *255*, 1894.
23. Ukaji, E.; Furusawa, T.; Sato, M. *Appl. Surf. Sci.* **2007,** *254*, 563.
24. Xie, Y. J.; Hill, C. A. S.; Xiao, Z. F.; Militz, H.; Mai, C. *Compos. A* **2010,** *41*, 806.
25. Wu, D.; Liu, J. X.; Wang, Y. *Appl. Surf. Sci.* **2010,** *256*, 2934.
26. Vogel, B. M.; DeLongchamp, D. M.; Mahoney, C. M.; Lucas, L. A.; Fischer, D.A.; Lin, E. K. *Appl. Surf. Sci.* **2008,** *254*, 1789.
27. Tong, X. M.; Zhang, T.; Yang, M. Zh.; Zhang, Q. *Colloids Surf. A* **2010,** *371*, 91.
28. Zhang, T.; Zhang, M.; Tong, X. M.; Chen, F.; Qiu, J. H. *J. Appl. Polym. Sci.* **2010,** *115*, 2162.
29. Sun, G.; Zhang, Z. *Int. J. Pharm.* **2002,** *242*, 307.
30. Brown, E. N.; White, S. R.; Scottos, N. R. *J. Mater. Sci.* **2004,** *39*, 1703.
31. Bagheri, R.; Pearson, R. A. *Polymer* **2000,** *41*, 269.