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Effect of MUF/Epoxy Microcapsules on Mechanical Properties andFractography of Epoxy Materials

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Abstract: Melamine-urea-formaldehyde (MUF) microcapsules were synthesized, morphology, shell thickness, average diameter and interface morphology were studied by scanning electron microscope (SEM). The spherical MUF microcapsules are size normal distribution without adhesion and accumulation, being compact, rough and uneven with a thickness of 3.2μm and a core contents is approximate 70%. A latent imidazoleas the curing agent for a cross-linking chemical reaction for cracking repairing .A good dispersion of MUF microcapsules and a good interfacial bonding are obtained. Effects of MUF microcapsule size and content on bending property and dynamic mechanical propertywere investigated. Both bending strength and storage modulus of the composite are considerably reduced with an increasing addition of the microcapsules whereas the glass transition temperatures are almost not influenced. Significant toughening effects of MUF microcapsules on the epoxy composites are observed at the conditions of different content and size of microcapsule especially at low microcapsule contents and small microcapsule sizes.

1. Introduction

In this paper, MUF microcapsules with a core of modified epoxy adhesive were synthesized. A latent imidazole catalyst with heat sensitivity and stability was used as curing agent for a design of self-repairing system, which was added together with MUF microcapsules into epoxy matrix in order to fabricate applicable microcapsule/epoxy self-healing composite. Morphology, shell thickness, average diameter of the MUF microcapsules and fracture morphology of the microcapsule/epoxy composite material were studied by SEM. Effects of microcapsule size and content on the bending property, the dynamic mechanical property and toughness for the microcapsule/epoxy composite material were investigated by bending testing and DMA testing.

2. Experimental Section

2.1. Preparation of MUF Microcapsule

At room temperature, melamine (Analytical-grade, Sigma-Aldrich China), urea (Analytical-grade, Sigma-Aldrich China) and formaldehyde (37 wt.%, Analytical-grade, Tianjin Chemical Plant, China) in a molar ratio of 0.05:1:2 were added into three-necked round-bottomed flask fitted with a stirrer. After a fully mixing, pH of the mixed solution was adjusted to 8-9 bytriethanolamine (Analytical-grade,Merck China). The three-necked flask was suspended in a temperature-controlled water bath. The temperature

of the system was raised to 70°C. and kept for 1 hour under stirring and refluxing until a transparent viscous MUF prepolymer was obtained. At this stage, the viscous MUF prepolymer was emulsified by Sodium dodecyl benzene sulfonate (SDBS) (0.5% wt%, 99% purity, Merck China). The emulsion was used to form shell material after cooling to room temperature. The MUF prepolymer and diglycidyl ether of bisphenol A epoxy E-51 (density is 1.20 g·ml-1 and epoxide equivalent weight is 196 g·mol-1,Shanghai Resin Plant, China) which was previously diluted by 17.5 wt% n-butyl glycidyl ether (BGE) (Analytical-grade, Sigma-Aldrich China) were together added into a three-necked round-bottomed flask fitted with stirrer in a molar ratio of 1:1. The O/W emulsion was obtained after stirring for 20-30 minutes at a agitation rate of 200-1000rpm. Various sizes of MUF microcapsules were prepared by the adjustment of agitation rates. The pH of the mixed chemicals was adjusted to 2–3 by drop-wise addition of dilute sulphuric acid (0.05 wt%, Analytical-grade, Sigma-Aldrich China). When the walls of microcapsules were fully formed after a curing reaction of 70°C. for 2 hours, the mixture was cured further at 60°C. for 2 hours under continuous agitation. Finally, MUF capsules were filtered and rinsed three times with ethanol and deionized water respectively and vacuum dried at 40°C. for 10 hours.

2.2. Preparation of Microcapsule /Epoxy Self-Healing Composite

Epoxy was added into suction flask and vacuum filtrated for 10 minutes in order to remove bubbles in the resin. BGE diluent, MC120D curing agent(Industrial product, Guangzhou Chuanjing Electronic Material Corporation, China) and MUF microcapsules with different sizes (Average diameters are 90μm,200μm and 550μm respectively) and various contents (2wt%, 5wt% and 10wt% respectively) were mixed with epoxy resin in beakers. The mixture was evenly blended until a uniform mixture was achieved. Diethylenetriamine (DETA) (Analytical-grade, Sigma-Aldrich China) of a curing agent for the epoxy matrix was blended into the mixture with a mass ratio for curing agent to epoxy resin of 15:100. The mixture was stirred for 5-10 minutes and vacuum filtrated for 10-30 minutes in order to remove bubbles. The blended resin was injected carefully into polytetrafluoroethylene mould (Mould dimension: 65×14×2mm) , following cured at a room temperature in vacuum drying oven for 24 hours. The specimens were taken out from the oven and demoulded, measured by vernier caliper and polished by rough and fine sandpapers to ensure that each batch of specimen has identical thicknesses, smooth edge surfaces and no visible defects.

MC120D chemicals used in this work is an imidazole compound, 6-(2-(2-methyl-1H-imidazol-1-yl) ethyl)-1, 3, 5-triazine-2, 4-diamine, white powder, thesoftening point is 95-115°C., particle diameter is less than 10μm. The stoichiometric ratio of curing agent to epoxy used is 20:100. The curing temperature is 100°C. for 40 minutes as the supplier suggests[1].

2.3. SEM Study

SEM (S-3400N(II), HITACHI, Japan) is used with an acceleration voltage of 15-20kV. The microcapsules and the fractured composite specimen were placed on conductive carbon tapes attached to a mounting piece, then sputter-coated with an approximate 10 nm conductive gold layer. MUF microcapsules ruptured using sharp razor blade were analyzed for measuring the average shell thickness for broken microcapsules varied at least 10 locations.

2.4. Testing Sample

At least ten MUF microcapsule/epoxy composite specimens were selected to form a batch of MUF microcapsule/epoxy self-healing sample. Nine specimens were divided into three groups including virgin sample (Type I), damage-controlled sample (Type II) and self-healing sample (Type III). The tenth specimen was used for DMA test. Because these specimens may occur post curing reaction during heat process that interfere with evaluation of the self-healing efficiency, the needed thermal preprocessing conditions were discussed in the relevant DSC measurement.

The Type II and the Type III samples were subjected to a controlled constant strains using three-point bending fixture with deformation of 90% bending fracture strains of the specimens which

produce cracks within the materials based on the bending deformation vertical distance of the specimens in the fixture. The specimens were clamped at this bending deformation distance for 24 hours. After the cracks observed, the specimens were removed off and flattened under a loading, then tested by universal tensile machine for bending properties and DMA instrument for the dynamic mechanical property.

The Type III samples after subjection to constant strain damaging were heated in vacuum drying oven at 100°C. for 1 hour. After the self-healing process, bending properties of these specimens and the dynamic mechanical property were measured through bending tests and DMA test.

2.5. Bending Test

Bending properties for three types of samples were measured by universal tensile machine (model AGX, Shimadzu, Japan). The Type I samples were directly measured without any treatment. In this three-point bending test, bending span was 30 mm and bending speed was 5mm/min. Force-displacement curves were recorded for data analysis. The average value of three specimens data was taken as corresponding type bending strengths (I) and bending fracture strains (ε) calculated.

2.6. DMA Test

Storage modulus (E'), loss modulus (E'') and mechanical loss factor (Tanδ) of the tested specimen were measured via DMA temperature sweep experiment (Q800, TA Instruments, UK). DMA test was performed using a double cantilever beam, heating from 25°C.to 140°C at a heating rate of 5°C/min and an oscillator frequency of 1 Hz under nitrogen atmosphere.

3. Results and Discussions

3.1. MUF Microcapsule and Epoxy Composite

The applications of microcapsules in self-healing material are significantly influenced by stability, mechanical performance and interfacial property of the microcapsules. Many problems including low water-resistance, formaldehyde emission and short shell-life exist in previous used urea-formaldehyde (UF) microcapsules. UF resin modified with melamine can improve thermal stability, water resistance, durability, roughness and shell strength of the microcapsule, and simultaneously reduce its formaldehyde emission content[2]. The surface features, geometry and properties of microcapsules depend on the experimental core/shell ratio, reaction temperature, agitation speed, and surfactant, etc. The prepared MUF microcapsules have been optimized at various parameters of chemicals ratio and synthesis condition , etc, as described in our previous work[3]. Various diameters of the MUF microcapsules were obtained at different agitation rates, typical at 250rpm, 600rpm and 1000rpm respectively, and average sizes of MUF microcapsules were 550μm, 200μm and 90μm correspondingly. Surface morphology and shell thickness for MUF microcapsules are shown in Figure 1, indicating that size distribution of the microcapsules is a typical normal distribution and the spherical MUF microcapsules surfaces are rough and uneven. There is little adhesion each other and MUF resin accumulation among the microcapsules. The shell which was formed by MUF resin during the polymerization deposition is compact with thickness of 3.2μm. Additionally, there is no significant difference in the shell thickness among the several sizes microcapsules.

Core content of the microcapsule was obtained by extracting method using acetone. Microcapsules were ruptured adequately in agate mortar and socked in acetone for 24 hours, then treated by ultrasonic apparatus for 30 minutes and continuously socked in acetone for 24 hours to fully dissolve the core material. After a final filteration, the residual was the shell material, which was vacuum dried and weighed. The core contents of MUF microcapsules were obtained according to Equation. The core contents of MUF microcapsules with diameters of 550μm, 200μm and 90μm are 74.52%, 70.15% and 68.71% respectively.

$$\text{Microcapsule core content}\,\% = \frac{M_0 - M}{M_0} \times 100\% \quad (1)$$

Where, M0(g) is weight of MUF microcapsules, M(g) is weight of the shell material.

As seen in Figure 2, the dispersity of MUF microcapsules in the epoxy material is relatively uniform. Good interfacial bonding between microcapsules and matrix is achieved due to the rough surface of MUF microcapsules increasing the contact area with epoxy substrate.

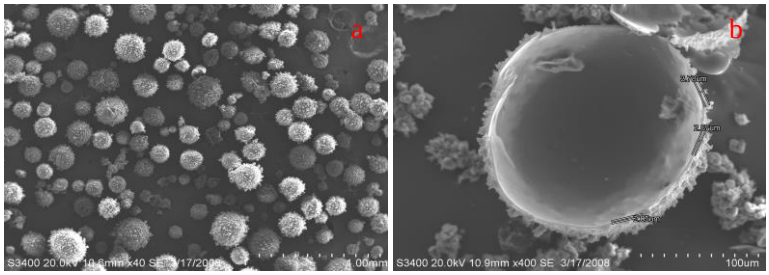

Figure 1. Morphology of MUF microcapsules. a) Surface characteristic; b) Shell thickness.

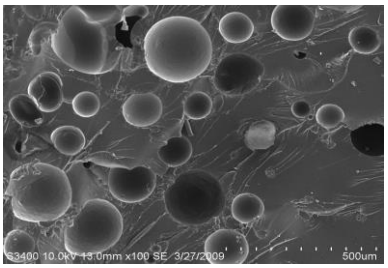

Figure 2. MUF microcapsule distribution in epoxy matrix (5wt% microcapsule content)

3.2. Bending Testing

Tensile performance and bending performance are important mechanical properties of material. Fracture elongation is a crucial parameter to evaluate fracture toughness. The previous results indicated that the microcapsules reduce tensile performance of polymer composite, but toughen the composite by 2-5% contents of microcapsule addition. With an increase of microcapsule content, tensile strengths of microcapsule/polymer self-healing materials are reduced while the elongations are increased. From 5% to 10% microcapsule content, the elongations decline further[4].In tensile testing, fracture location of the material is often unexpected due to imprecisely controlled damages introduced, thus affecting the testing accuracy. Three-point bending experiment is therefore used to make stress more concentrated on central area of material specimen along longitudinal direction where cracks are more likely to be produced rapidly, which facilitates the damaging process with an accurate control. As shown in Figure 3 (a), compared with the bending strength of epoxy specimen, those of microcapsule/epoxy specimens are drastically reduced. The microcapsules embedded in epoxy matrix may play a function of the material defects as stress concentration points inducing micro-cracks around the MUF microcapsules on the loading region where stress was introduced by three-point bending, decreasing mechanical strength of the material. When microcapsule content is 2wt%, the bending strengths of specimens whose MUF microcapsule diameters are 90μm, 200μm and 550μm are reduced to 90%, 81% and 53% value of the epoxy specimen respectively. The microcapsule size is a crucial factor affecting the descend range of bending strength for the material with this microcapsule content. The smaller microcapsules size, the better microcapsules dispersity exists in the matrix. The specific surface areas are bigger which increase the contact areas between microcapsules and epoxy substrate, thereby being capable of bonding the epoxy matrix more effectively and bearing bigger stress. When the content exceeds 2wt%, the difference is not so significantly affected by microcapsule size in the descend range of bending strength for the material. At the same condition of microcapsule mass fraction, although the larger size microcapsules lead to greater stress concentration degree on themselves, the smaller amounts microcapsules are contained in the matrix so fewer locations for stress concentration exist. Thus, the

numbers of induced micro-cracks are relatively less exhibited. In contrast, more micro-cracks are produced by smaller size microcapsules throughout the specimen, but the degree of stress concentration for the material is relatively lower by the small size microcapsules. Therefore, microcapsule numbers and sizes of the epoxy material with the condition of high microcapsule mass fraction together affect the descending bending strength for the epoxy composite.

Bending fracture strain is the other important parameter to evaluate fracture toughness. The larger strain of bending fracture, the better toughness of material indicates. The effects of microcapsule content and size on bending fracture strain of the epoxy composites are seen in Figure 3(b). When the epoxy is subjected to an external force, matrix itself bears the load, so the lower toughness of material is shown. When the microcapsule content is 2wt%, the bending fracture strain of the specimen is visibly increased which demonstrates a toughening effect of MUF microcapsules on epoxy material. With the increase of MUF microcapsule content, bending fracture strains of the specimens embedded MUF microcapsules, whose diameters are 90μm and 200μm, are slightly increased at a low microcapsule content, reaching a maximum strains at 2wt% microcapsule content, then that of the specimens are gradually decreased at high microcapsule contents. Particularly, within whole range of microcapsule content, the bending fracture strain of epoxy specimen embedded microcapsule whose diameter is 90μm is larger than that of epoxy specimen with 200μm microcapsules, showing a significant toughening effect of microcapsules on epoxy specimen. In contrast, the epoxy specimen embedded 550μm microcapsules have obviously negative effect on both the bending fracture strain and the bending strength. Additionally, when microcapsule content increases to 10wt%, a large amount of MUF microcapsules are served as stress concentration points and defects within the material, the bending strength and fracture strain of the epoxy specimens embedded different size microcapsule especially 550μm microcapsule are deteriorated significantly. Therefore, the MUF microcapsule/epoxy composites embedded 2wt% and 5wt% microcapsule contents whose diameters are 90μm and 200μm were studied in the following.

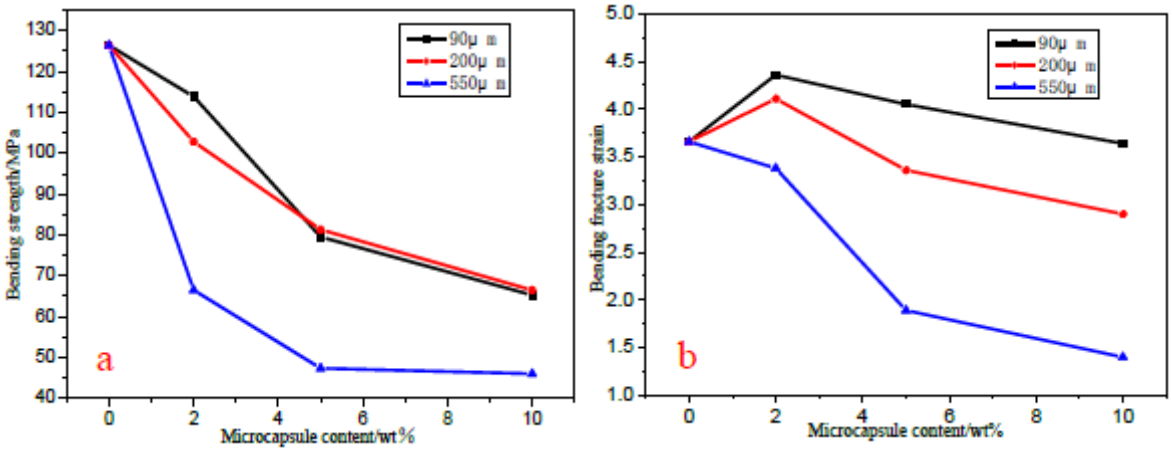

Figure 3. Effect of MUF microcapsules on bending properties for epoxy composites. (a) Bending strength comparison; (b) Bending fracture strain comparison

3.3. Dynamic Mechanical Properties

Dynamic mechanical analysis is non-destructive to the measured material and sensitive to the mechanical relaxation transition for chain segments and molecular motion of polymeric material. The structural factors of dynamic modulus and mechanical loss factor of polymer with temperature under fixed frequency are simultaneously obtained to analyse microscopic movements within material. Storage modulus is a measure of material stiffness to characterize the ability to resist deformation of material. The higher storage modulus material, the stronger resist deformation ability has. Polymer mechanical performance is relative to the crosslink density of polymeric network. The higher crosslink

degree of polymeric network, the shorter length of chain segment between cross-link points and the more compact cross-link networks exist within polymer, forming high strength of cured substance. The temperature corresponding to the peak of Tanδ is defined as glass-transition temperature[5].

As shown in Figure 4(a), compared to epoxy specimen, the storage modulus of epoxy composite specimen declines because crosslink density and resist deformation ability for the composite is reduced due to the addition of MUF microcapsules. With an increase of microcapsule content, initial storage moduluses of epoxy composites with 2wt% and 5wt%microcapsule content are respectively decreased to 93% and 84% value of the epoxy, which is consistent with the changes of bending strength in the bending performance discussed before. The distance between molecular chains and free volume in crosslink network of epoxy resin are increased with the rise of MUF microcapsule content, thus decreasing the storage modulus and improving the epoxy material toughness. In Figure 4(b), two or more transition peaks are not appeared in Tanδ curves of the three specimens, which indicates a good compatibility and interfacial adhesion between MUF microcapsules and epoxy matrix. The glass-transition temperatures of the epoxy specimens with 0wt%, 2wt% and 5wt% microcapsule are 80.2°C, 77.4°C and 77.5°C respectively. The cross-linking density of the epoxy material is decreased by microcapsule addition, causing the Tg of the epoxy composite specimens embedded MUF microcapsules is slightly lower than that of the epoxy specimen. Besides that, there are few differences in both the peak values of Tanδ and the Tg for the epoxy composites specimens with 2wt% and 5wt% MUF microcapsules, indicating that compared to the epoxy specimen with 2% MUF microcapsule content, the addition of 5% MUF microcapsule content into the epoxy specimen is not capable of obviously reducing the thermostability for the material[6].

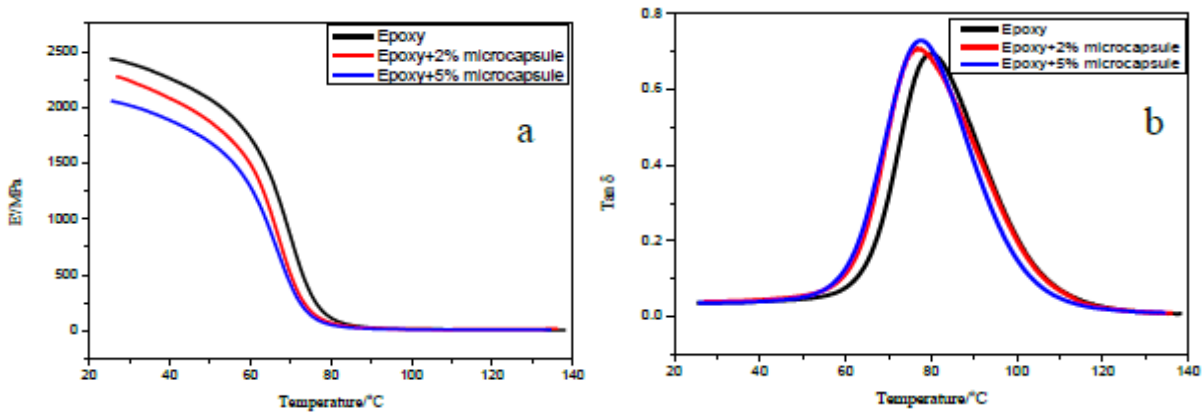

Figure 4. Effect of MUF microcapsule content on dynamic mechanical properties for epoxy composites.
(a)storage modulus (E'); (b)mechanical loss factor (Tanδ) .

3.4. The Toughening Effect of Microcapsule on Epoxy Composite

In the previous discussion, bending properties and dynamic mechanical performances indicated that the MUF microcapsule/epoxy composite materials were toughened by the addition of MUF microcapsules. Besides these data, morphology analysis on the fractured surface of the composites reveals this toughening effect.

Typical features of the epoxy composites with different MUF microcapsules size were shown in Figure 5. As seen in Figure 5(a) and 5(b), the smaller microcapsules size contained in epoxy specimen, the rougher fracture surfaces on the epoxy surrounded with microcapsules appear. Figure 5(c) shows a typical brittle fracture surface of the epoxy specimen embedded 550μm size microcapsules. In toughening materials, the distance between two toughening particles is important to affect the toughness. With a decrease of this distance between poly(acrylonitrile-butadiene-styrene) copolymer (ABS) particles within polycarbonate (PC) matrix, the stress fields around ABS particles occur overlap

leading to the generations of more crazings and shear yielding, thus improving the material toughness[7]. For the case studied here, at a same level of microcapsule content, the smaller microcapsule size, the greater microcapsules spatial density and the shorter distance between microcapsules are within matrix, resulting in larger toughening areas which consume more surface energy. This observation also explains the increase of bending fracture strain for the epoxy composites by the small size microcapsules addition.

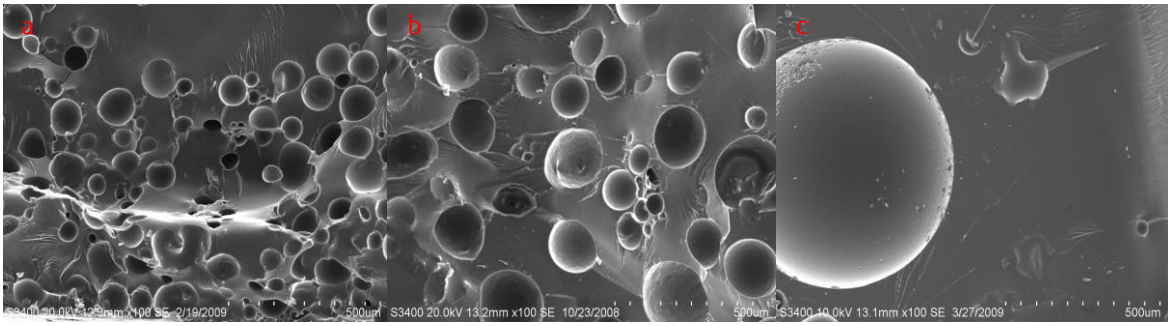

Figure 5. Effect of MUF microcapsules size on fracture morphology of epoxy composites (5wt% microcapsule content).
(a) specimen with 90μm microcapsules diameter; (b) specimen with 200μm microcapsules diameter; (c) specimen with 550μm microcapsules diameter.

Several types of toughening effects for MUF microcapsules/epoxy composites are shown in Figure 6. Caudiform structure appears around the surrounding microcapsule in Figure 6(a), which can be attributed to shear band within matrix initiated by the microcapsules as stress concentration points. A number of crazings are induced at the end of shear bands to absorb stressing energy[8]. When fracturing occurs in the material, deformation area may be enlarged by the microcapsules incorporated in epoxy matrix. This consumes an extra energy, which in fact toughens the epoxy material. Besides, a multilevel fracture path is exhibited within the matrix indicating a good fracture toughness can be realized by this rough fracture surface which is initiated by the microcapsules producing stress concentration, guiding cracks to pass through microcapsules at different spatial locations, further extending on multilevel fracture paths to delay the process of crack propagation[9]. Figure 6(b) shows the morphology of fracturing and debonding for MUF microcapsules. The crack is finally terminated by fractured MUF microcapsules, which reveals that addition of the microcapsules into epoxy is effectively prevent the crack propagation. A destruction of the interface between microcapsules and epoxy matrix consume considerable extra energy, which also toughens the epoxy materials.

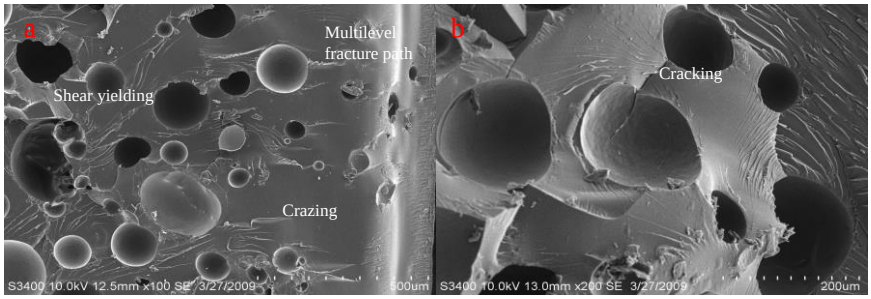

Figure 6. Toughening effects of MUF microcapsules/epoxy composites.
(a)multilevel fracture plane; (b)fracturing and debonding microcapsules

4. Conclusion

MUF microcapsules composed of a shell of MUF resin and a core of modified epoxy healing agent

were adopted together with imidazole chemical for designing a self-healing MUF microcapsule/epoxy composite material. The spherical microcapsule shell is compact, rough and uneven with a thickness of 3.2μm, having normal size distribution. There is no adhesion and accumulation between MUF microcapsules. Core contents of the MUF microcapsules for the diameters of 550μm, 200μm and 90μm are 74.52%, 70.15% and 68.71% respectively. There is a good dispersion of MUF microcapsules in epoxy composite and a good interface between the microcapsule and epoxy matrix as designed. Both bending strength and storage modulus of the microcapsule/epoxy composite are considerably reduced with the increasing addition of the microcapsules, whereas the glass transition temperatures of microcapsule/epoxy composites are not visibly influenced. Significant toughening effects of MUF microcapsules on the epoxy composites are obtained at the conditions of different content and size of microcapsule especially at low microcapsule contents and small microcapsule sizes and observed several toughening morphologies including shear yielding, crazing effect, micro-cracking, multilevel fracture path, microcapsule fracture and debonding. Toughening effect of the shear yielding is the most effective.

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6. References

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