




Self-healing isocyanate microcapsules for efficient restoration of fracture damage of polyurethane and epoxy resins

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Received: 21 September 2018

Accepted: 6 December 2018

Published online:

26 February 2019

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ABSTRACT

Isophorone diisocyanate-loaded microcapsules were synthesized with controllable size for self-healing of structural polymer materials. The obtained microcapsules showed good compatibility with polymer resins, e.g., one-component epoxy and multi-component polyurethane/water glass structural materials. During the processing of composite self-healing materials, the highly cross-linked composite capsule wall ensured the integrity of microcapsules and prevented the leakage and degradation of reactive liquid isocyanates effectively. A relatively larger amount of self-healing agent could be released to the local cracks with the increasing size and content of microcapsules in polymer matrix which improved the self-healing efficiency of the composites. Based on the microcapsules with a diameter of $\sim 96 \mu\text{m}$, the healing efficiency of epoxy composites containing 15 wt% of capsules and polyurethane/water glass composites containing 20 wt% of capsules could reach to 105 and 101% recovery of fracture toughness, respectively. The crack-healing effect was further verified by scanning electron microscopy. Meanwhile, a possible self-healing mechanism of microcapsules to the cracks of composite polymer materials was proposed.

Zhenglong He and Shuai Jiang contributed equally to this work.

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Introduction

Polymer materials exposed to environmental stress might arouse minor damages at nano- or micro-scale at initial stage which are difficult to be detected. The propagation of these damages would result in catastrophic failure to the whole system [1–4]. Therefore, it is essential to prevent the development of early damages and hence prolong the service life of the materials.

Various approaches have been explored to endow polymer coatings and structure materials with the autonomous damage-healing function [5–16]. Among these methods, self-healing strategy based on microencapsulation of liquid healing agents is one of the most successful and versatile approaches [17–30]. One representative example is the encapsulation of liquid isocyanates, which can easily react with water or moisture. Therefore, it can autonomously repair damage without additional catalysts which significantly extend the service life and reliability of the materials [31, 32]. Many efforts have been made to improve the physical and chemical properties of microcapsules to meet various requirements for practical application. In our previous work [33], microcapsules with good mechanical stiffness, reliable service life and water resistance were developed via a simple, cost-effective and efficient synthetic strategy. As a proof of concept, the microcapsules were introduced in epoxy resin. The resulting epoxy coatings could effectively protect metal substrates from corrosion through self-healing of cracks in the coating.

However, practical application of structural polymer materials requires the recovery of their mechanical properties instead of just the self-healing of cracks. Moreover, the preparation of structural materials usually involves the mixing of multiple components with different characteristics such as polarity, pH [34–38], as well as the harsh environment generated during the mixing process (e.g., highly exothermic reaction and high shear force) [39–44]. These factors may result in unpredictable effects on the microcapsules with respect to the leakage and degradation of reactive self-healing agents, the intactness of capsule structure and the dispersibility of capsules in polymer matrix.

In this study, liquid isocyanate-loaded microcapsules with different sizes were synthesized for the

preparation of microcapsule-based self-healing materials. One-component epoxy and multi-component polyurethane/water glass (PU/WG) structural materials were chosen as model polymer matrix here. The influence of size and content of microcapsules on the self-healing efficiency of the composites was systematically investigated by fracture toughness test. A possible self-healing mechanism of microcapsules to the composite polymer materials was proposed.

Experimental section

Materials

Isophorone diisocyanate (IPDI) and polymethylene polyphenylene isocyanate (PAPI) were obtained from Bayer. Diethylene triamine, polyvinyl alcohol (PVA, $M_n = 75,000$ g/mol, 95% hydrolyzed) and 1-octanol were purchased from Aladdin. Epoxy resin (WSR-618) was purchased from Bluestar New Chemical Materials Co., Ltd., China. Water glass was supplied by Dongyue Chemical Group Co., Ltd., China. The polyether polyol was supplied by Shanghai Gaoqiao Petrochemical Co., Ltd., China. Chlorinated paraffin-52 and dioctyl phthalate were provided by Shuanghong Chemical Technology Co., Ltd., China. All the other chemicals are analytical grade and purchased from TCI Shanghai Chemical Reagent Co., Ltd., China. The compositions of epoxy and PU/WG materials are shown in Table S1 and Table S2, respectively.

Synthesis and characterization of microcapsules

Microcapsules were prepared using a previously described procedure, followed by resulting core-shell microcapsules with a PVA-polyurea composite shell and liquid core containing IPDI (see Fig. 1a, b) [33]. Microcapsules with different sizes were synthesized by adjusting stirring rates of 400 rpm, 600 rpm, 800 rpm, 1000 rpm and 1200 rpm, respectively. The formation process of the microcapsules was observed by optical microscope (OM, Winner99, China). Average diameter of microcapsules was determined from datasets of at least 100 measurements obtained from OM images and analyzed using software Nano Measurer 1.2. The core contents of microcapsules

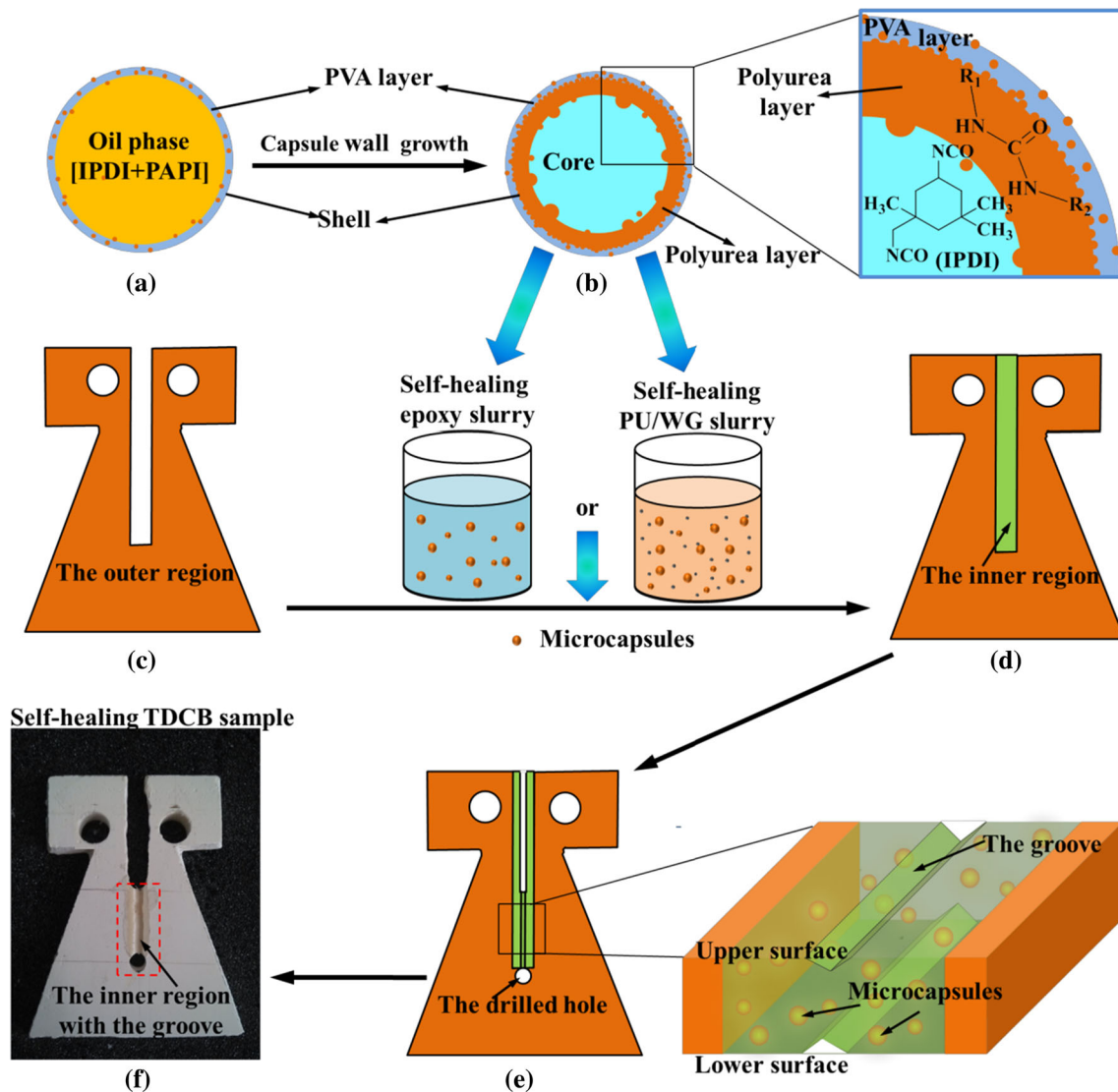


Figure 1 Schematic illustration of the preparation and the structure of microcapsules (a, b) and TDCB specimens: c the outer region of TDCB specimen, d the inner region of TDCB

were determined by ^1H NMR analysis (Bruker Avance 400 MHz) with maleic anhydride as a reference compound.

Preparation of tapered double-cantilever beam (TDCB) specimens

The preparation method and the structure of TDCB specimens are schematically illustrated in Fig. 1. And the geometry of TDCB specimens is shown in Figure S1 [8, 45–47]. The TDCB specimen was prepared in two parts. Firstly, components A and B of PU/WG materials were mixed well and poured into Teflon mold and cured at 45 °C for 3 days, obtaining a TDCB

specimen, e the pretreatment of TDCB specimen before test, drilled hole is designed for capturing the formed crack and f a real TDCB specimen with the short groove.

geometry specimen with a high toughness, defined as the outer region (Fig. 1c). Then, the middle blank area was filled with a mixed slurry of all components of epoxy (or PU/WG) and desired content of microcapsules, denoted as the inner region (Fig. 1d). The TDCB specimen was subsequently cured for 3 days at 45 °C to integrate the two regions.

Evaluation of self-healing efficiency

The self-healing properties of epoxy materials and PU/WG materials were studied by measuring the fracture toughness of TDCB samples. Fracture toughness test (test speed, 1 mm/min) of TDCB

specimens was carried out on an electron omnipotence experiment machine (SANS-CMT6503, Shenzhen Sans Testing Machine Co., China) at room temperature according to ISO-13586-2. As shown in Fig. 1e, two short grooves were created oppositely to each other on the upper and lower surface of the inner region, respectively. Moreover, a hole with a diameter of 5 mm was drilled into the specimen at the end of the grooves. The hole trapped growing cracks due to its high compliance and prevented the crack from growing to the end of the specimen. A pre-crack was created in the TDCB specimen by a razor blade above the grooves before testing. The specimen was loaded until the crack propagated along the groove to the drilled hole. Immediately afterward, the specimen was removed from the testing machine. After complete healing in an indoor environment at 25 °C for 7 days, the specimen was loaded again to assess healing efficiency. Healing efficiency was defined as the healed fracture toughness over the initial fracture toughness. The TDCB geometry allowed for fracture toughness to be directly proportional to the critical load at which the fracture propagates [46, 48]. This simplifies the equation of healing efficiency to

$$\eta_{\text{healing}} = \frac{K_{IC_{\text{healing}}}}{K_{IC_{\text{virgin}}}} = \frac{P_{\text{healed}}}{P_{\text{virgin}}} \quad (1)$$

where $K_{IC_{\text{virgin}}}$ is the fracture toughness of the virgin specimen, $K_{IC_{\text{healed}}}$ is the fracture toughness of the healed specimen, P_{virgin} is the critical fracture load of the virgin specimen, and P_{healed} is the critical fracture load of the healed specimen. Each of the reported values represents the average value of at least three specimens. Scanning electron microscopy (SEM, 2800B, KYKY, China) was operated at 25 kV to characterize the morphology of fracture surface of tested specimens. The specimens were coated with gold in a SBC-12 ion sputtering apparatus for 2 min.

Results and discussion

Synthesis of microcapsules with different sizes

Size and morphology of microcapsules depend on many physical factors such as agitation rate, properties and concentration of emulsifier, viscosity of the media, temperature as well as the design of the stirrer

[49–51]. Herein, a series of microcapsules containing liquid IPDI were synthesized using different concentrations of PVA (1–9 wt%). The other variables including core/shell ratio, oil/water phase ratio, emulsification time, agitation rate, DETA dose and reaction temperature were kept constant in this section. As shown in Fig. 2f, the average diameter of microcapsules decreased from 342 μm to 20 μm as the PVA concentration increased from 1 to 9 wt% at the agitation rate of 600 rpm. The decrease in diameter was aroused by the appearance of PVA in the aqueous phase which reduced the interfacial tension of organic and aqueous phase in an oil-in-water emulsion [52, 53]. With the increase in PVA concentration in the aqueous phase, the viscosity of aqueous phase increased and the interfacial tension reduced. Therefore, smaller microcapsules with narrower size distribution were obtained. Moreover, the wrinkling degree of the capsule shell was declined with the increase in PVA concentration (see Fig. 2a–e) which attributed to the thick PVA layers around the capsule. This thick layer would reduce the growth rate of the capsule wall through suppressing the diffusion of amine into the droplet. In addition, larger microcapsules could be collected more easily and afforded better self-healing effect [54]. In order to obtain capsules with a relatively uniform size and high yield [55, 56], the PVA concentration of 5 wt% was adopted for the synthesis of microcapsules in the following study.

The influences of agitation rate and emulsification time on the size of microcapsules were investigated with the other variables constant, such as core/shell ratio, oil/water phase ratio, DETA doses and reaction temperature. As shown in Fig. 3f, the mean diameter of microcapsules was significantly affected by the agitation rate and emulsification time. The droplet sizes at different agitation rates decreased in the first 4 min of emulsification and then kept at a relatively stable value, indicating the formation of a stable oil-in-water emulsion. Agitation rate effectively controlled the size of oil droplets in the emulsification system, and the average diameter of microcapsules decreased from 153 μm to 33 μm as the agitation rate increased from 400 rpm to 1200 rpm. Spherical microcapsules with a narrow-sized distribution were observed using optical microscopy (see Fig. 3b–f). Meanwhile, the increased agitation rate did not interfere with the integrity of the capsules.

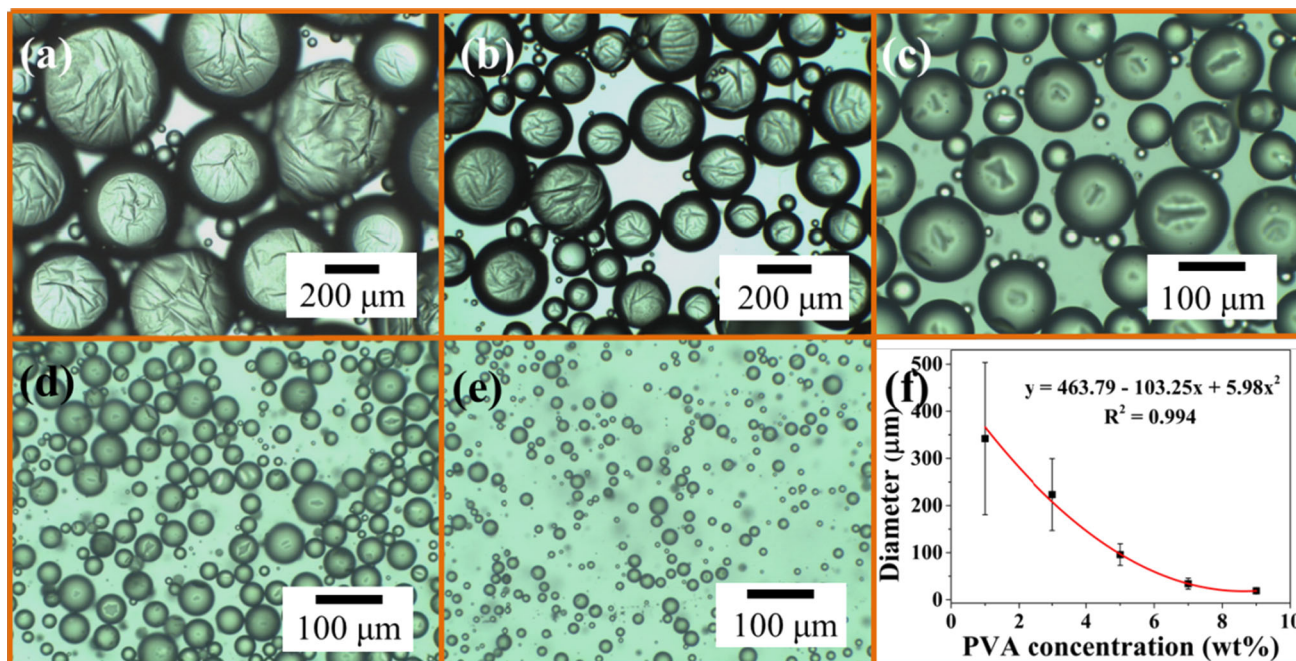


Figure 2 Optical microscopy photographs of microcapsules synthesized at different concentrations of PVA: **a** 1 wt%, **b** 3 wt%, **c** 5 wt%, **d** 7 wt% and **e** 9 wt%; **f** average diameter of microcapsules as a function of PVA concentration.

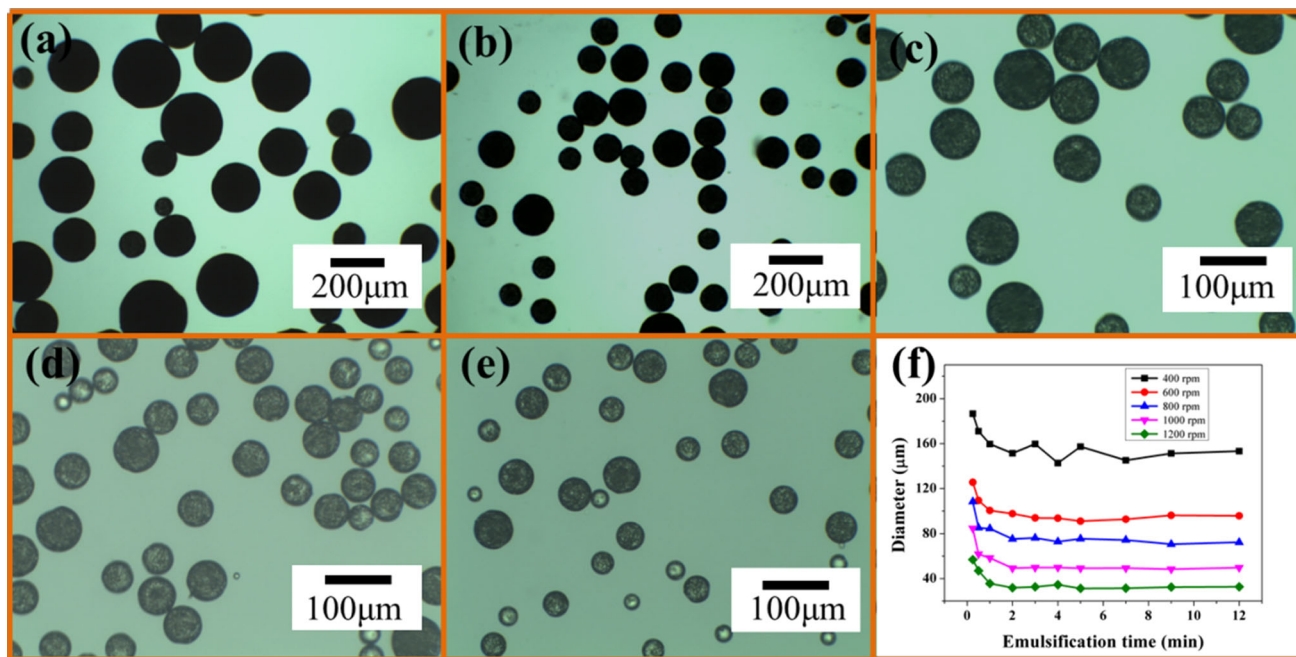


Figure 3 OM micrographs of microcapsules synthesized at different agitation rates: **a** 400 rpm, **b** 600 rpm, **c** 800 rpm, **d** 1000 rpm and **e** 1200 rpm; and **f** average diameter of microcapsules synthesized with different agitation rates and emulsification times.

A large amount of liquid payload released when the microcapsules were broken (see Fig. 4a). Moreover, shell fragments were not observed in released liquid, suggesting the completion of the synthesis

process [33]. The outer shell surface of the spherical microcapsules was relatively smooth, and the capsules were individually dispersed without adhering to each other (see Fig. 4b). By using SEM, it could be

observed that the microcapsules had a core-shell structure after being crushed (see Fig. 4c). In order to identify the composition of liquid core of the obtained microcapsules, ^1H NMR tests of IPDI, PAPI and core content were performed and the spectra are provided in Fig. 4d. The spectrum of core material was nearly identical to that of pure IPDI, indicating that IPDI was successfully encapsulated without PAPI (see Fig. 4d I, II and III). The core content of capsules was further determined by ^1H NMR (see Fig. 4d IV). As shown in Fig. 4e, the core content ranged from 69.3 to 83.7% for the capsules with sizes from 33 to 153 μm . Therefore, microcapsules with different sizes and high loading amount of self-healing agent IPDI have been successfully synthesized.

The dispersibility and integrity of microcapsules in epoxy and PU/WG composites

The dispersibility and integrity of capsules in polymer matrix are essential for the healing ability of self-healing materials. The dispersibility and integrity of capsules in the one-component and multi-component materials were first evaluated by mixing the capsules with epoxy resin or component A of PU/WG material. As shown in the red wireframe of Fig. 5a, d, light-yellow capsules were uniformly dispersed in the epoxy resin and component A of PU/WG, respectively. No aggregates were observed. The good dispersibility could be attributed to the polar groups ($-\text{OH}$, $-\text{NH}-$ and $-\text{NH}_2$) on the PVA/polyurea composite shell which improved the compatibility of capsules with the epoxy resin and component A of PU/WG [33]. The uniform distribution of capsules in final polymer composites was confirmed by the SEM micrographs of fractured cross sections of epoxy and PU/WG materials (see Fig. 5b, c, e, f). Moreover, SEM

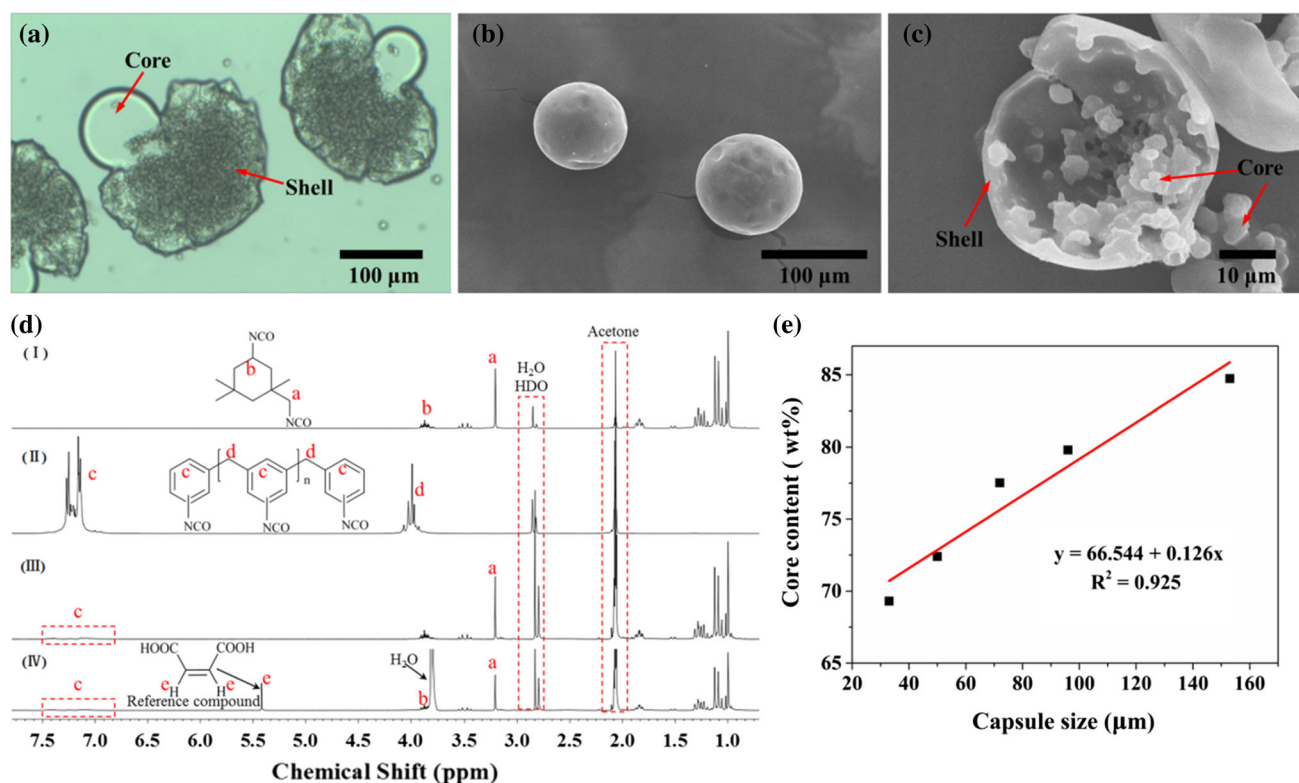


Figure 4 a OM image of microcapsules; SEM micrographs of microcapsules: **b** spherical microcapsules and **c** broken microcapsules; **d** ^1H NMR spectra of (I) IPDI in acetone- d_6 (II) PAPI in acetone- d_6 , (III) the extracted core of the resulting

microcapsules in acetone- d_6 and (IV) the extracted core of the resulting microcapsules with maleic anhydride as a reference compound; **e** core content of microcapsules prepared at different agitation rates.

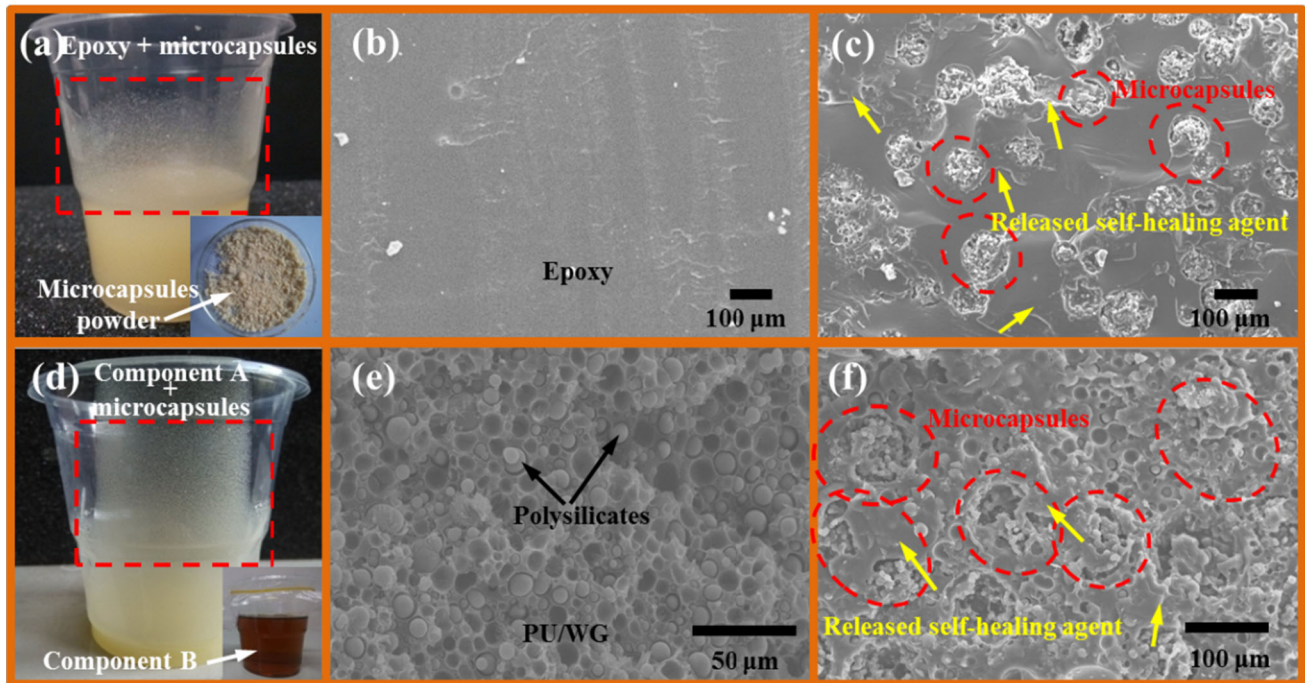


Figure 5 The photographs of **a** a mixed slurry of epoxy and microcapsules in the cup, **d** a mixed slurry of component A of PU/WG and microcapsules in the cup; SEM micrographs of fracture

surface of **b** epoxy and **e** PU/WG materials and their corresponding self-healing materials (**c**, **f**).

observation of capsule morphology in polymer matrix combined with the released large amount of liquid self-healing agent on the fractured cross sections indicated that the integrity of microcapsules was preserved during the synthesis and post-processing of the composite materials (see Fig. 5c, f).

Effect of capsule size on self-healing efficiency of epoxy and PU/WG materials

To evaluate the self-healing efficiency of IPDI-loaded microcapsules for epoxy and PU/WG materials, the TDCB specimen was employed [57]. Microcapsules with sizes ranging from 153 μm to 33 μm prepared at different agitation rates from 400 rpm to 1200 rpm were used to determine the impact of microcapsule size on self-healing efficiency of polymer materials. As can be seen from Fig. 6, the self-healing efficiency of the composite materials containing 15 wt% of microcapsules increased with the increase in capsule size. With a capsule size of 33 μm , the self-healing efficiency of microcapsules in both cases of epoxy and PU/WG materials was over 65%. The healing efficiency further increased to almost 100% when the capsule size increased to 153 μm . The self-healing efficiency was related to the amount of isocyanate

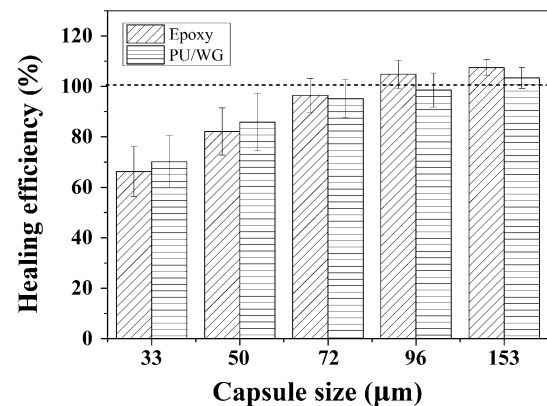


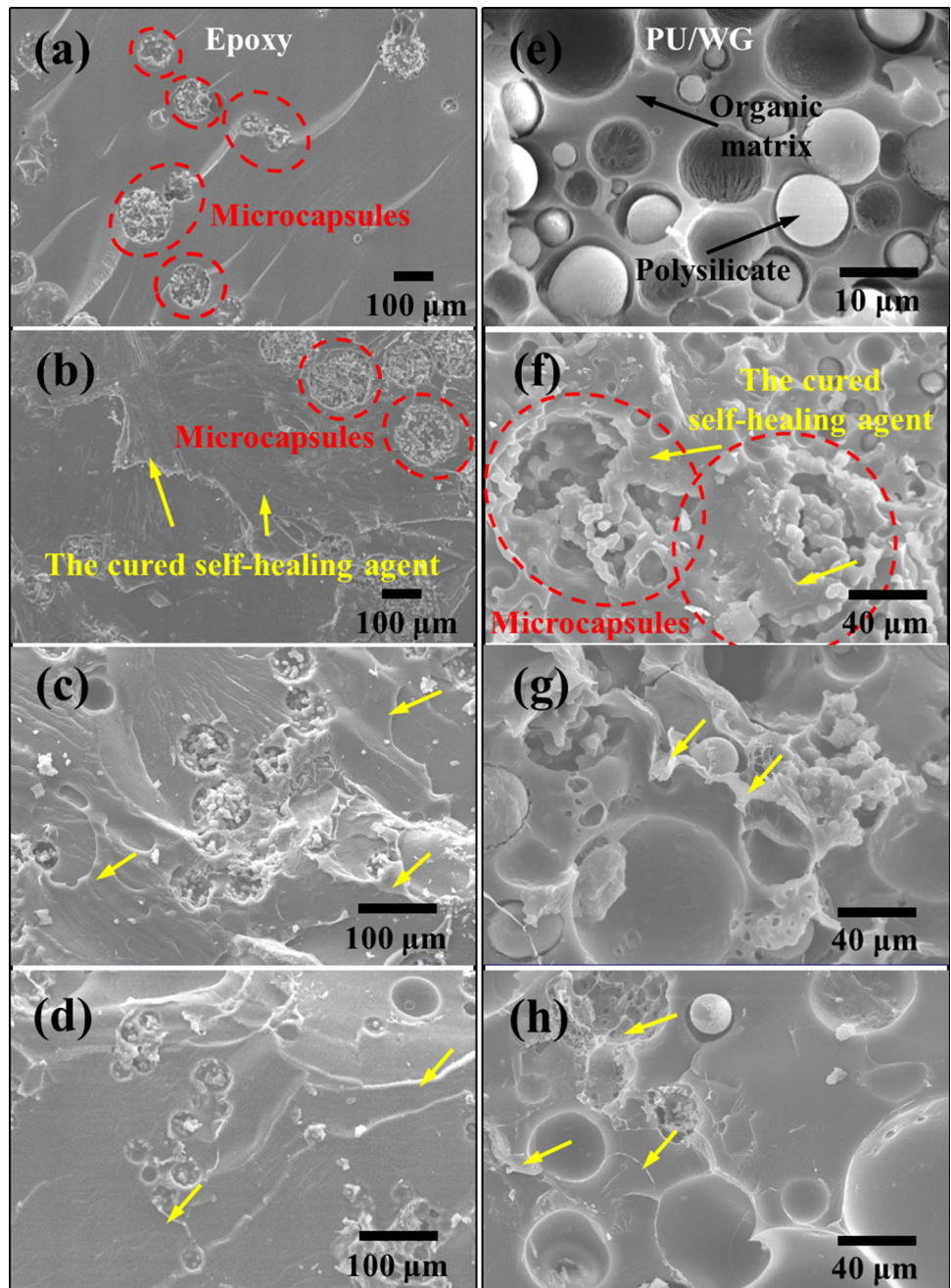
Figure 6 Self-healing efficiency of polymers with different sizes of microcapsules (the content of microcapsules in polymer matrix was kept at 15 wt%).

released from the broken microcapsules to the fracture plane [48]. A larger capsule meant a higher core content, which released more healing agent when the capsule was opened by the propagating crack. In addition, small capsules increased the inner surface area of the fracture plane, which might increase the consumption of the healing agents. Therefore, the cracks in the composites could be effectively healed by the larger capsules.

As shown in Fig. 7, microcapsules were uniformly distributed in the fractured cross section of the epoxy resin. The formation of tail lines that emanated from capsules along the direction of crack growth could be observed on the fairly flat fracture surface (see Fig. 7a). These tail lines were the result of the capsules impeding the growth of cracks in epoxy matrix, which led to crack front trapping. Therefore, addition of the capsules to epoxy material contributed to the improvement in fracture toughness of the thermosetting composites. In addition, a representative

set of SEM images of the fracture cross section of self-healing epoxy composites with different sizes of microcapsules after self-healing process is shown in Fig. 7b–d. For these samples, layers of cured self-healing agent apparently exhibited the fracture surface of epoxy composites. The coverage and thickness of the cured layers increased gradually with the growth of capsule size, indicating that large microcapsules were more conducive to be captured and release healing agent to the cracks. In summary, the embedded microcapsules not only improved the

Figure 7 SEM micrographs of self-healing epoxy composites containing capsules with different diameters: **a** non-healed cross section, **b** 153 μm , **c** 72 μm , **d** 33 μm ; and self-healing PU/WG composites containing capsules with different diameters: **e** without capsules, **f** 153 μm , **g** 72 μm , **h** 33 μm ; (the content of microcapsules in polymer matrix was kept at 15 wt%).



fracture toughness of epoxy matrix but also enhanced the self-healing ability of fracture event.

Similarly, a flat fracture surface of organic matrix appeared in the PU/WG materials, as shown in Fig. 7e. The coverage and thickness of the cured layer increased with the increasing capsule size (see Fig. 7f, g, h). Therefore, when the microcapsule content was constant, the larger the microcapsules were, the more the self-healing agent could be released to the fracture cross section, and thus the higher the self-healing efficiency of the material.

Effect of microcapsules content on self-healing efficiency of epoxy and PU/WG materials

The effect of capsule content in polymer matrix on the self-healing efficiency of composites was further investigated. As shown in Fig. 8, healing efficiency of the material increased as the capsule content increased in both cases of self-healing epoxy and PU/WG materials. A maximum healing efficiency of the epoxy and PU/WG materials was achieved at capsule content of 15 and 20 wt%, respectively, indicating that a sufficient content of microcapsules was required for releasing enough liquid healing agents to fill the fracture plane.

The fracture surface of self-healing composites with different contents of capsules was photographed using SEM. As shown in Fig. 9b–d, the capsules were uniformly distributed in epoxy matrix. The outflow of liquid from the capsules indicated that the integrity of the capsules was maintained during the synthesis and processing of the self-healing materials.

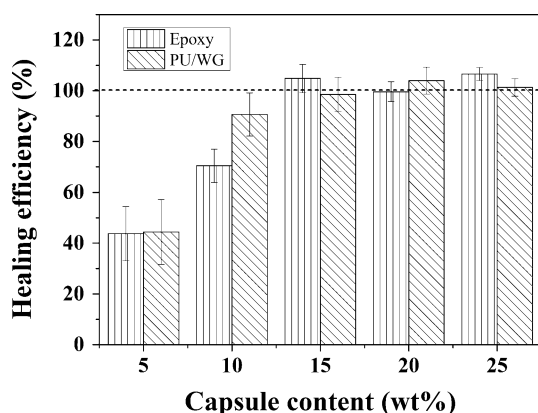


Figure 8 Self-healing efficiency of epoxy and PU/WG materials with different contents of microcapsules (the average size of microcapsules was kept constant at $\sim 96 \mu\text{m}$).

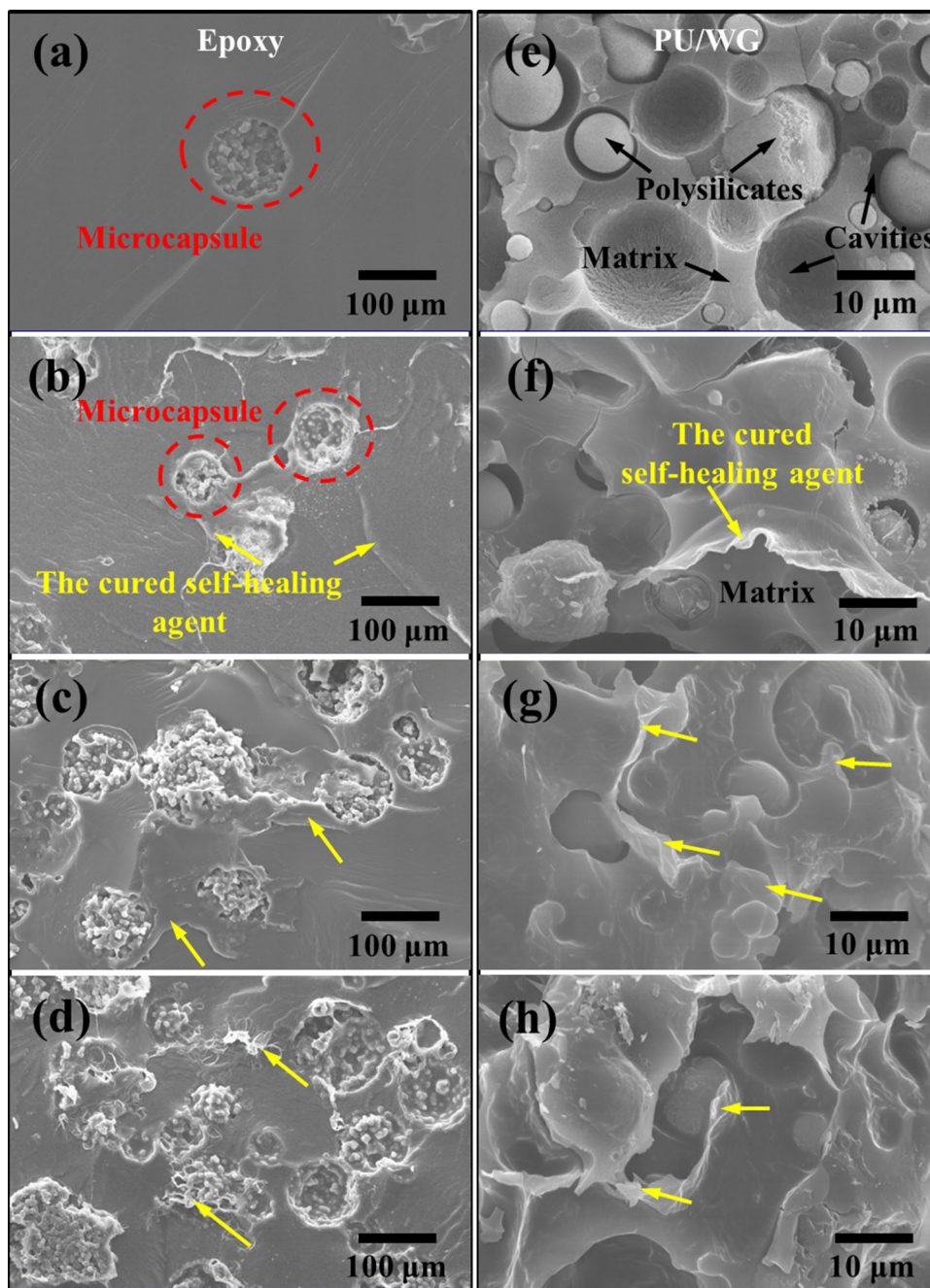
The increased amount and coverage area of released healing agent were observed with the increase in the capsule content in the epoxy composites (highlighted by yellow arrows in Fig. 9b–d). The surface of polysilicate particles on the fracture surface of PU/WG materials containing self-healing microcapsules (see Fig. 9f) was rougher than that of pure PU/WG materials (see Fig. 9e). The silicate particles were partially covered by layers of cured self-healing agent on the fracture surface. At a capsule content of 5 wt%, the cavities between spherical polysilicate particles and polyurethane matrix were not completely covered by the thin cured layer (see Fig. 9f). As the microcapsule content increased, the coverage of cavities enhanced (see Fig. 9g, h). Indeed, the presence of large number of cavities on the fracture surface of PU/WG materials aggravated the consumption of liquid self-healing agent. Therefore, the complete recovery of mechanical property in PU/WG materials required a relatively larger content of microcapsules ($\sim 20 \text{ wt}\%$) in comparison with the case of self-healing epoxy materials which achieved full recovery of toughness at $\sim 15 \text{ wt}\%$ of capsules.

The load–displacement curves of the original and healed specimens are given in Fig. 10. The compliance of the healed specimen was the same as that of the virgin specimen at the initial stage which implied the recovery of cracks (see Fig. 10a, b). It could be seen from Fig. 10a that when the epoxy materials contained 15 wt% of microcapsules, the self-healing efficiency of the material achieved 105%. As the load increased, the crack propagated and the specimen compliance was slightly increased as the healed crack reopened, which was mainly due to the higher toughness of the cured IPDI than epoxy matrix. Moreover, in the case of PU/WG material with 20 wt% of microcapsules, self-healing efficiency of the material was 101% (see Fig. 10b). The specimen compliance decreased slightly as the healed crack reopened which was mainly aroused by the fill of cured IPDI, whose toughness was lower than that of the PU/WG matrix.

Self-healing mechanism of microcapsules–polymer systems

Scheme 1 illustrated the self-healing mechanism of epoxy and PU/WG materials embedding microcapsules containing self-healing agent IPDI. Epoxy and PU/WG composites were unavoidably subjected to unforeseen cracks during their service life (see

Figure 9 SEM micrographs of self-healing epoxy composites with different contents of microcapsules: **a** non-healed cross section, **b** 5 wt%, **c** 15 wt%, and **d** 25 wt%, and self-healing PU/WG composites with different contents of capsules: **e** without capsules, **f** 5 wt%, **g** 15 wt%, and **h** 25 wt%.



Scheme 1a, d). As the crack propagated, the embedded microcapsules ruptured and then released the healing agent into the crack plane (see Scheme 1b, f). The released IPDI was driven rapidly along the crack channel through capillary action. When the capillary action reached equilibrium, there might be still some marginal areas and cavities not covered with self-healing agent (see Scheme 1b, f). Then, IPDI with low viscosity could continue to diffuse via the carbon dioxide-driven secondary filling effect, which was

produced from the reaction between isocyanates and water or moisture. Thus, the cracks were completely filled by the healing agent from the ruptured microcapsules (see Scheme 1c, g). A large number of minor cavities were distributed on the fracture plane of PU/WG composites (see Scheme 1e and red arrows in Scheme 1f g) which explained why more self-healing agents for PU/WG composites were needed than epoxy materials. Polymerization of the healing agent was triggered through isocyanate–hydroxyl

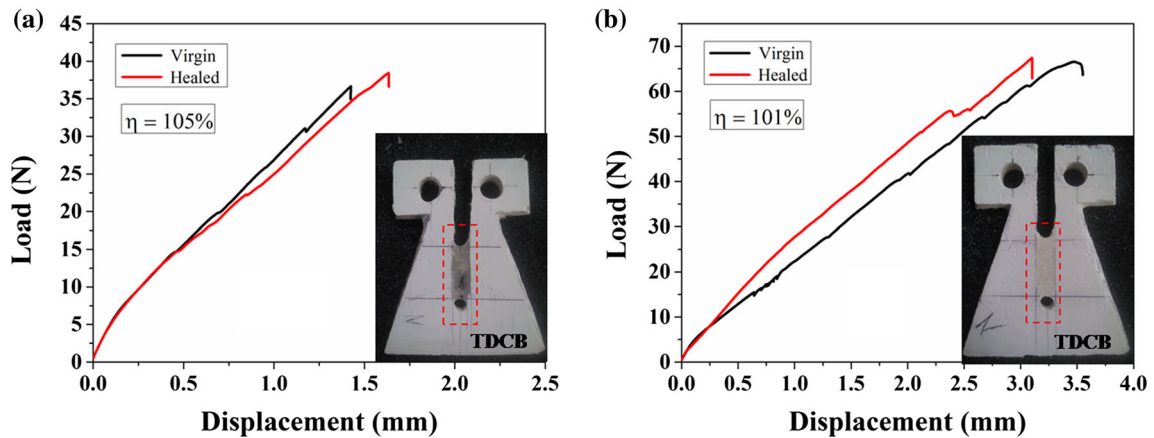
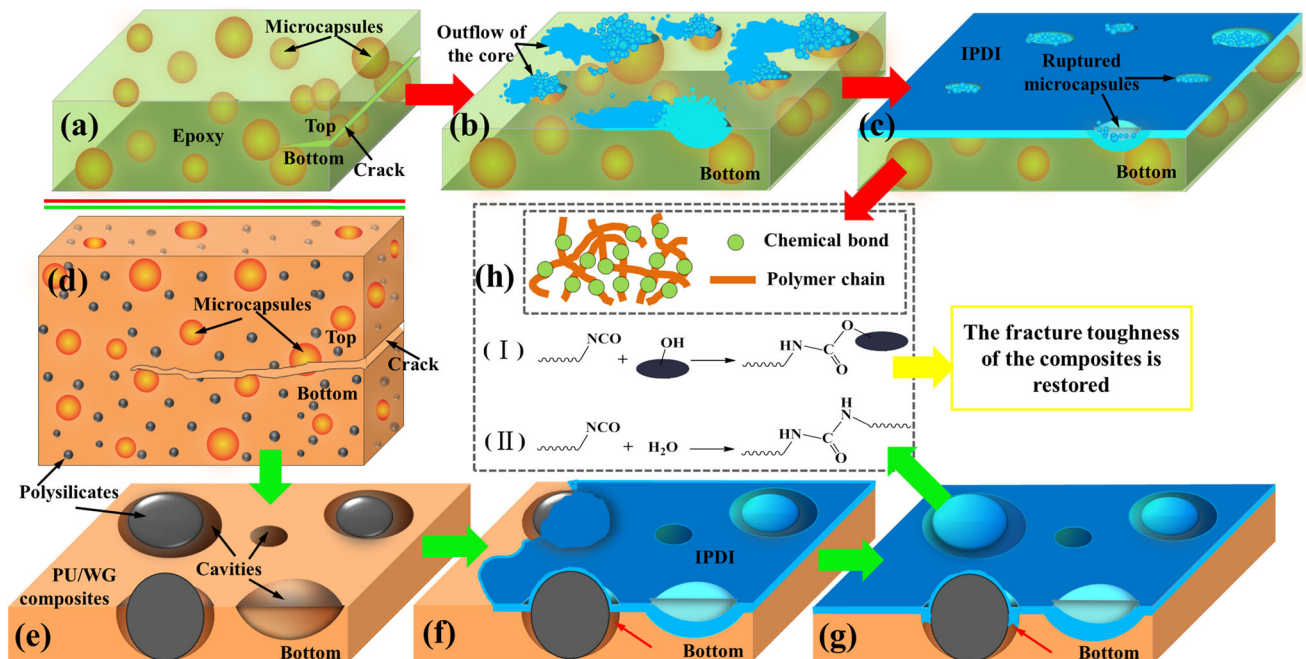


Figure 10 The fracture load–displacement curves of **a** self-healing epoxy materials containing 15 wt% of microcapsules, **b** self-healing PU/WG materials containing 20 wt% of

microcapsules; inset: the corresponding self-healing TDCB specimens (η is the self-healing efficiency of the test specimen).



Scheme 1 Schematic diagram of self-healing process for epoxy: **a** the generation of crack, **b** the fracture plane during the release of self-healing agent and **c** the fracture plane after the release of self-healing agent; and self-healing process for PU/WG composites: **d** the generation of crack, **e** the fracture plane before the release of

self-healing agent, **f** the fracture plane during the release of self-healing agent, **g** the fracture plane after the release of self-healing agent; **h** the isocyanate–hydroxyl chemistry during the self-healing process.

chemistry (see Scheme 1h), bonding the crack surfaces and forming a robust cured phase between the crack planes. Therefore, the cracks in the epoxy and PU/WG composites could be healed automatically, and the fracture toughness of the composites was restored.

Conclusions

Core–shell microcapsules containing liquid self-healing agent IPDI were synthesized with controllable size. The obtained microcapsules exhibited excellent compatibility with polymer resins, e.g., one-component epoxy and multi-component PU/WG

structural materials. The highly cross-linked composite capsule walls effectively protected the reactive liquid isocyanates from leakage and degradation during the processing of composite self-healing materials. With the increasing size and content of microcapsules, a larger number of self-healing agents could be released to the local cracks which enhanced the self-healing efficiency dramatically. In the case of microcapsules with a diameter of $\sim 96 \mu\text{m}$, self-healing efficiency of epoxy resin containing 15 wt% of the capsules and PU/WG grouting materials containing 20 wt% of the capsules obtained a high healing efficiency of 105 and 101%, respectively. Therefore, the presented microcapsules are beneficial to extend the service life of structural polymeric materials accounting for their good processing properties and high self-healing efficiency.

Acknowledgements

The authors gratefully acknowledge the financial support from the Major Science and Technology Project in Shanxi Province (No. 20111101058) and Shanxi Yubang Science and Technology Co., Ltd.

Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s10853-018-03236-3>) contains supplementary material, which is available to authorized users.

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