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Study of factors related to performance improvement of self-healing epoxy based on dual encapsulated healant

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ABSTRACT

Our earlier work developed epoxy based self-healing composites with embedded dual microcapsules, which contain unreacted epoxy as the polymerizable component and mercaptan and tertiary amine catalyst as the hardener, respectively. Self-healing was allowed to proceed rapidly, offering attractive repair effectiveness. To give full play to the healing agent, influences of a series of factors on healing chemistry of the composites were studied in this paper. It was found that strong alkality of the catalyst, high activity of mercaptan, and low viscosity of the encapsulated epoxy prepolymer ensured high healing efficiency and rate of healing. In addition, matching of the microcapsules' sizes and fractions was critical for keeping stoichiometric ratio of the components at the damage areas, as required by the mechanism of the healing reaction (i.e. addition polymerization). Homogeneous dispersion of the capsules under proper stirring speed led to timely contacts between the healant fluids flowing out of the fractured capsules. Larger microcapsules favored filling of the cracks in terms of larger amount of the released healing agent, while smaller ones facilitated mixing and interdiffusion of the ingredients. The results provided key data for optimizing the self-healing system.

1. Introduction

Microcracking is a critical problem for polymers and polymer composites during their service in structural applications [1]. Development and coalescence of microcracks would bring about catastrophic failure, deteriorating products' performance and reducing their lifetimes. Therefore, imparting self-healing function to the materials like organisms are ideal for long-term operation [2–4]. So far, the following chemistries: ring-opening metathesis polymerization of dicyclopentadiene (DCPD) [5–10], addition and ionic polymerization of epoxy [11–23], condensation polymerization of polysiloxane [24,25] and organic solvents [26,27], have been successfully employed for automatically repairing cracks in different polymers at room temperature.

To give full play to healing agent, White and co-workers developed the strategy of microencapsulation [5] and extensively investigated the healing performance as a function of a series of parameters including microcapsule size [7], matrix environments [24,25], catalyst [8], external stimuli [8,9] and loading condition [10]. Compared to the case that monomeric healing fluid interacts with solid catalyst particles to initiate healing reaction, activation of two-part liquid healing agent stored in hollow-pipelines [11–16] or microcapsules [17–23] depends on interaction of the two liquid constituents, and hence more complicated factors are involved, like multiple functionality of monomers, viscosity, ability of catalyst, etc. These would certainly affect healing behavior of the composites.

The authors fabricated self-healing epoxy composites with embedded dual encapsulated healant, i.e. two types of microcapsules that respectively include epoxy and mercaptan, which enabled preservation of flowability and reactivity of the core substances [22]. Because of establishment of hydrogen bonds between the capsules and the matrix originating from the polar groups (amine and hydroxyl), timely penetration of cracks through the encapsulated healing agent was ensured [22,28,29]. Upon fracture the unreacted epoxy can be bled into damage sites together with the hardener fluid and then polymerized to repair cracks. The system proved to work as characterized by attractive healing effect and durability. Moreover, addition of the capsules led to toughening of the matrix as a result of crack pinning effect, but slight reduction in modulus and strength. Nevertheless, healant's features, reactants ratios and contacts between the components have not yet been optimized.

In this context, the objective of the present work is to conduct a systematic study on the key issues that are closely related to the chemical reaction of the healant, including species of epoxy,

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Table 1
Properties of epoxy resins.

Code	Chemical name	Epoxide value (mol/100 g)	Epoxy functionality	Viscosity (25 °C, Pa s)
828	Diglycidyl ether of bisphenol A	0.51	2	12.5
731	Diglycidyl phthalate	0.62	2	0.85
711	Diglycidyl tetrahydro-o-phthalate	0.63	2	0.53

mercaptan and catalyst, components proportions, capsules size, etc. It is believed that the refined parameters would favor the healing chemistry and serve as a solid base for future application of the healing system.

2. Experimental

2.1. Materials

Three types of epoxy resin were employed as the polymerizable component of the healing agent (Table 1). They are diglycidyl ether of bisphenol A (EPON 828, Shell Chemicals Inc.), diglycidyl phthalate (trade name: 731, Jindong Chemical Plant, Tianjin, China) and diglycidyl tetrahydro-o-phthalate (trade name: 711, Jindong Chemical Plant, Tianjin, China). Moreover, EPON 828 served as the matrix polymer of the self-healing epoxy composites.

Accordingly, four types of curing agent were used (Table 2). They are diethylenetriamine (DETA) supplied by Shanghai Medical Group Reagent Co. (Shanghai, China) working for the matrix, pentaerythritol tetrakis (3-mercaptopropionate) (PMP, Fluka Chemie AG), trimethylol-propane tri(3-mercaptopropionate) (TMP, Fluka Chemie AG), and tri(bi(2-hydrolpropyl) mercapto) aliphatic ether (trade name: Capcure 3800, Cognis) for the epoxy component of the healing agent. The catalysts, benzyldimethylamine (BDMA), 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) and triphenylphosphine (TPP), were purchased from Shanghai Medical Group Reagent Co. (Shanghai, China).

2.2. Preparation of microcapsules containing epoxy and its hardener [28,29]

Epoxy prepolymer (400.0 g) was added into a 2 wt% aqueous solution of sodium styrene–maleate copolymer (1200 ml). The mixture was vigorously stirred for 5 min and then two drops of 1-octanol were added to eliminate surface bubbles of the epoxy emulsion. The prepolymer of melamine (62.5 g) and 37% formaldehyde (135.5 g) was synthesized at 70 °C for 30 min and pH value of the solution was kept at about 9–10 by adding triethanolamine. Subsequently, the prepolymer solution was added to the above epoxy emulsion at 50 °C with continuous agitation for 1 h while pH value of the system was kept at about 3 by adding citric acid. Eventually, the reaction mixture was cooled down to room temperature and the deposit of microcapsules was separated through a Buchner funnel, rinsed with deionized water and vacuum dried. The core contents and average sizes of the resultant epoxy-loaded microcapsules are listed in Table 3.

Table 2
Properties of mercaptan.

Code	Chemical name	SH content (w/w%)	SH-functionality	Viscosity (25 °C, Pa s)
PMP	Pentaerythritol tetra (3-mercaptopropionate)	26	4	0.45
TMP	Trimethylol-propane tri (3-mercaptopropionate)	24	3	0.12
C38	Tri(bi(2-hydrolpropyl) mercapto) aliphatic ether	11.8	3	1.5

Table 3
Description of the epoxy-loaded microcapsules.

ID	Encapsulated epoxy	Average diameter (μm)	Density (g cm^{-3})	Core content (wt%)
E_L	711	50.7	1.22	87.3
E_S	711	10.6	1.19	78.8
E_{731}	731	11.3	1.25	80.1
E_{828}	828	11.9	1.28	81.4

The microcapsules containing the hardener were prepared in two steps. Firstly, mercaptan was microencapsulated in a similar way as that adopted in making epoxy-loaded microcapsules. Then, the microcapsules were uniformly dispersed into catalyst solution (BDMP or DMP-30) at 40 °C for certain time (0.5–24 h), filtrated, rinsed with ethylether and dried at room temperature. The ultimate contents of the mercaptan and catalyst inside the microcapsules and average sizes of the hardener-loaded microcapsules are listed in Table 4.

2.3. Preparation of self-healing epoxy composites

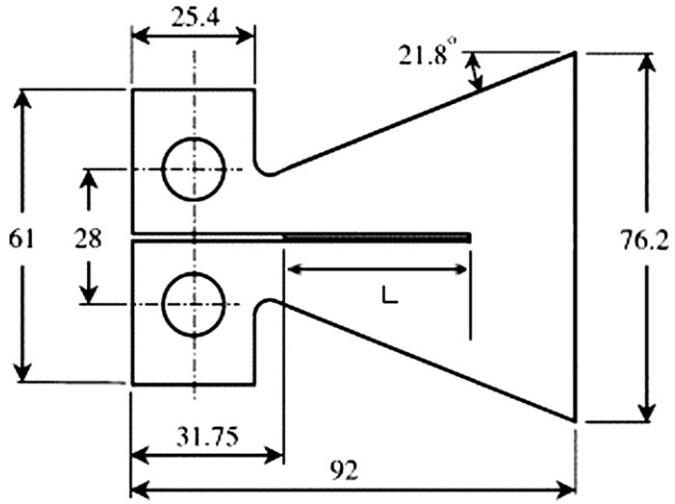
The unfilled epoxy specimens were produced through mixing 100 parts EPON 828 with 12.5 parts curing agent DETA, while the self-healing epoxy composites were prepared by mixing different concentrations and weight ratios of the microcapsules containing epoxy and its hardener with the aforesaid EPON 828/DETA mixture. For the composites containing TPP, the catalyst was dissolved in EPON 828 prior to other steps. Either the unfilled epoxy or the filled version was degassed, poured into a closed silicone rubber mold and cured for 24 h at room temperature, followed by 24 h at 40 °C.

2.4. Characterization

To evaluate self-healing ability of the materials, the protocol proposed by White et al. was used, who carried out fracture tests on tapered double cantilever beam (TDCB) specimens (on which short grooves were made to produce less crack face separation) [5–7]. The groove lengths adopted here were 30, 39, 47 and 55 mm (Scheme 1) for having different crack widths accordingly, while the specimens with groove length of 30 mm were fabricated for the experiments irrelevant to crack width evaluation. The other dimensions of the TDCB specimens were identical to those used in previous self-healing trials. A natural pre-crack was created by inserting a fresh razor blade and gently tapping into the molded notch starter. Subsequently, the specimen was pin loaded and tested with a Hounsfied H10 KS universal testing machine under displacement control using a 0.3 mm min^{-1} displacement rate at 20 ± 0.5 °C and 30 ± 5% humidity. Specimens were fractured only

Table 4
Description of the hardener-loaded microcapsules.

ID	Core content (wt%)		Average diameter (μm)	Density (g cm^{-3})
	Mercaptan	Catalyst		
H_0	87.3 (PMP)	0	52.3	1.28
H_B	87.1 (PMP)	0.7 (BDMA)	52.3	1.27
H_D	86.9 (PMP)	0.6 (DMP-30)	52.6	1.29
H_L	85.3 (PMP)	7.2 (BDMA)	52.4	1.25
H_S	63.8 (PMP)	5.4 (BDMA)	10.2	1.24
H_{TMP}	61.9 (TMP)	5.1 (BDMA)	9.8	1.21
H_{C38}	65.4 (C38)	3.8 (BDMA)	11.1	1.23

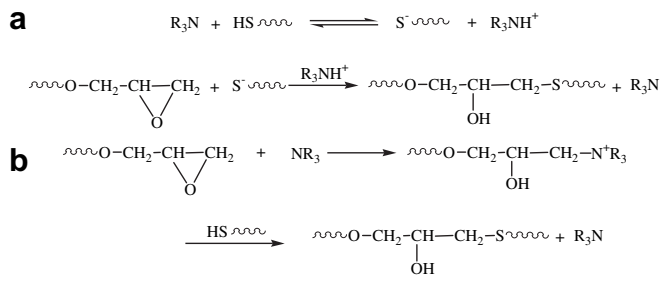


Scheme 1. Modified TDCB geometry (with all dimensions in mm). The side groove lengths, *L*, are 30, 39, 47 and 55 mm, respectively.

to the end of the groove, unloaded and then left to heal for 24 h at 20 ± 0.5 °C. Finally, the healed specimens were tested again following the above procedure. Each batch included ten specimens to yield averaged value. Efficiency of healing is defined as the ratio of fracture toughness, K_{IC}, of healed and virgin materials.

TDCB specimens for simulative healing had full groove frame and contained the same microcapsules formulation as the authentic ones. When the specimen was fractured, the released healing agent on the fracture planes was rapidly eliminated by acetone. After volatilization of acetone, about 0.03 ml of uniformly premixed epoxy and its hardener was injected into the crack planes. Then the two halves of the specimen were clamped in a way that did not exert any force to press the crack faces back together, but only placed them in contact. This procedure resulted in an average crack face separation of about 23 μm near the loading pin holes of the specimen. Healing of the simulative specimens was conducted at 20 ± 0.5 °C for 24 h prior to the second test. Each batch included six specimens to yield averaged value.

Morphological observation and energy dispersive spectroscopy (EDS) analysis were conducted by a Quanta 400 FEG field emission scanning electron microscope (SEM). Prior to the experiment, the sample surface was coated by gold/palladium sputter. The activity of different epoxy–mercaptan pairs was compared in terms of non-isothermal curing behaviors with a TA DSC Q10 calorimeter in N_2. The heating rates for the measurements were 2.5, 5, 7.5 and 10 °C min^{-1}, respectively. Calibration of the calorimeter with regard to temperature and energy was achieved by measuring the temperature and enthalpy of melting of indium as standard material.



Scheme 2. Reactions between epoxide and mercaptan catalyzed by tertiary amine. (a) General base catalysis. (b) Nucleophilic catalysis.

Table 5
Curing kinetics (estimated from non-isothermal DSC studies) and adhesivity (characterized in terms of tensile lap-shear strength) of epoxy-mercaptan pairs at the stoichiometric ratios.[a]

Formulation	Catalyst content (wt%)	$E_{a(kJ/mol)}$	k ($\times 10^3$) at 25 °C	n	ln$A$	Average ΔH (J)	Tensile lap-shear strength (MPa)
711/PMP/BDMA	0	–	–	–	–	–	0
711/PMP/BDMA	1.9	48.29	0.238	0.898	12.23	428.25	2.31
711/PMP/BDMA	3.6	45.57	0.720	0.891	11.14	478.43	4.95
711/PMP/BDMA	7.0	47.19	0.933	0.895	12.06	455.63	2.64
711/PMP/BDMA	10.2	42.55	1.084	0.885	10.34	420.67	1.87
711/PMP/BDMA	13.1	47.17	0.967	0.895	12.09	402.80	1.15
711/PMP/BDMA	18.5	49.94	0.851	0.900	13.08	381.50	0.78
711/PMP/DMP-30	3.6	23.16	1.026	0.807	2.46	461.35	7.46
711/PMP/TPP	3.6	50.45	0.127	0.893	11.38	452.10	4.58

[a] E_a: activation energy; k: reaction rate constant; n: reaction order; A: pre-exponential factor; ΔH: heat of reaction.

To assess adhesivity of the healing systems, tensile lap-shear tests were conducted with a Hounsfied H10 KS universal testing machine under a 5 mm min^{-1} displacement rate at 20 ± 0.5 °C according to ISO 4587-2003.

3. Results and discussion

3.1. Influence of components' features on healing reaction

Healing ability of a self-healing composite is determined by the reaction of healants. The current work utilizes epoxy–mercaptan pair as the healing agent, which comes into action driven by the mechanism of addition polymerization in the presence of catalyst. The reaction is closely related with activity, adhesivity, viscosity and mixing of the reactants. Therefore, reactivity of the healing system should be investigated at the beginning.

Epoxy–mercaptan would hardly react with each other without proper catalysis. The catalysis of epoxide–mercaptan reaction with alkali can be considered as a general base catalysis in which mercaptan first reacts with alkali to give mercaptide ion, and then the ion reacts with epoxide. Alternatively, a nucleophilic catalysis

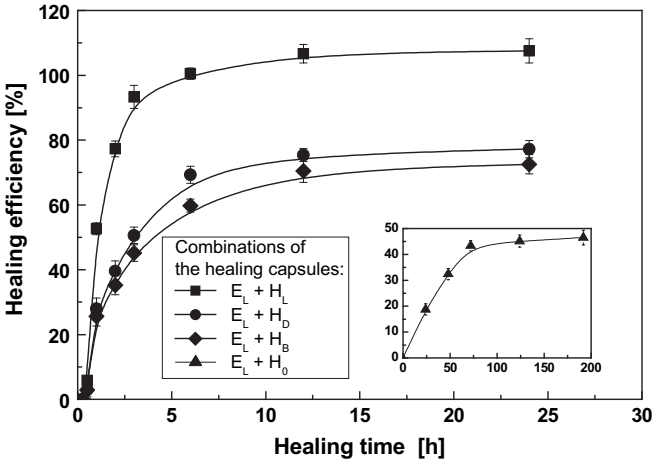


Fig. 1. Influence of species and content of catalyst on healing efficiency of the self-healing composites containing different combinations of the microencapsulated healing agent. Total weight concentration of the embedded microcapsules is 5 wt% for all specimens, while weight ratios of epoxy- to hardener-loaded capsules follow the corresponding optimal values. When $E_L + H_0$ was employed, 5 wt% TPP was directly added into the matrix cooperating with H_0. Healing of the fractured specimens was conducted at 20 °C.

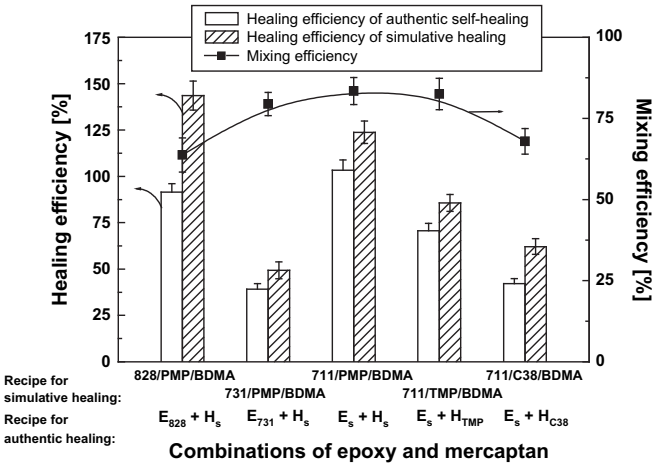


Fig. 2. Influence of combinations of epoxy and mercaptan on healing efficiency. For authentic self-healing, total weight content of the embedded microcapsules is 5 wt%. For simulative self-healing, the recipes of the healing agent are the same as those formulated by the microcapsules in authentic samples. The ratio of epoxy to mercaptan follows the stoichiometric ratio. The catalyst content in the healing agent for simulative healing is equal to that for authentic self-healing (i.e. 3.6 wt%). Healing of the fractured self-healing was conducted at 20 °C for 24 h.

occurs, during which alkali first reacts with epoxide to produce a reactive intermediate and then the intermediate reacts with mercaptan in a nucleophilic displacement (Scheme 2) [30,31].

As reflected by the kinetic parameters of the cure reaction between epoxy prepolymer and mercaptan and the adhesivity as well (Table 5), the catalysts' alkality and content greatly affect rate of the addition polymerization, curing degree and bonding strength. The alkality order of the catalyst is DMP-30 > BDMA > TPP [30], which coincides with the orders of reaction rate and adhesivity revealed in Table 5. That is, a catalyst with stronger alkality would obviously accelerate the reaction and produce better bonding effect.

It is worth noting that, in the case of a fixed formulation of 711/PMP/BDMA, with a rise of BDMA content, the reaction rate reaches the maximum value at 10.2%, while the bonding strength peaks up at 3.6%. Clearly, the rate of healing and healing efficiency (here healing efficiency is supposed to be proportional to the bonding strength in the case of the same ingredients but different contents of the healant) cannot be maximized at identical dosage of the catalyst. The inconsistency should originate from the different dependences of reaction rate and epoxy network development on catalyst concentration. Accordingly, one has to choose between fast rehabilitation and good repair.

On the other hand, the data in Table 5 indicate that a further increase in content of BDMA results in lower rate constant and tensile lap-shear strength. For the former, the tertiary amine at

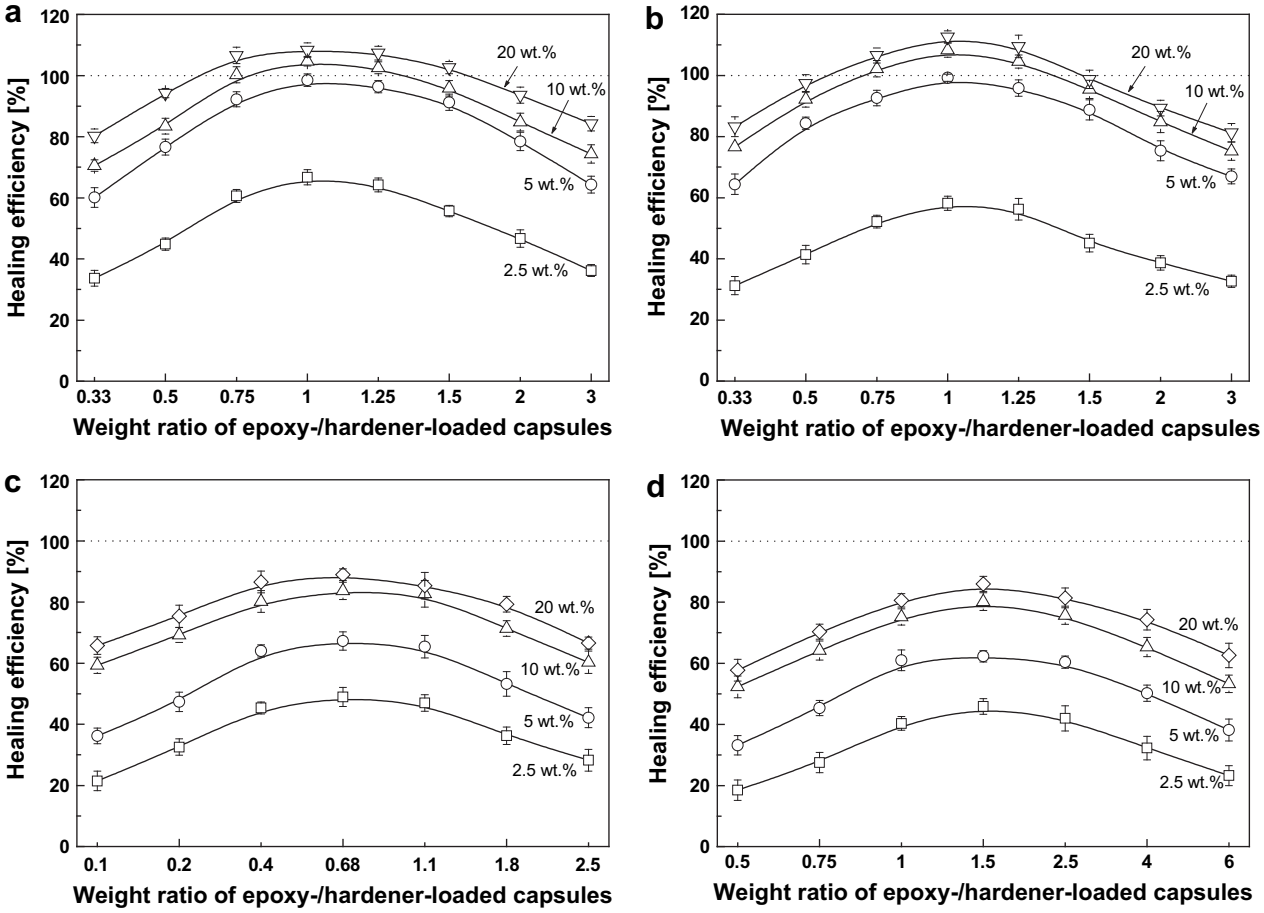


Fig. 3. Influence of weight ratio of embedded epoxy- to hardener-loaded capsules on healing efficiency of the self-healing composites containing different contents of microencapsulated healing agent. Healing of the fractured specimens was conducted at 20 °C for 24 h. Combinations of the healing capsules: (a) $E_L + H_L$; (b) $E_S + H_S$; (c) $E_L + H_S$; and (d) $E_S + H_L$. The weight percentages marked beside the curves represent the total weight concentrations of the dual capsules. The relative weight ratio of epoxy-/hardener-loaded capsules at each total weight concentration of the capsules varies from excessive to insufficient hardener to obtain systematic information.

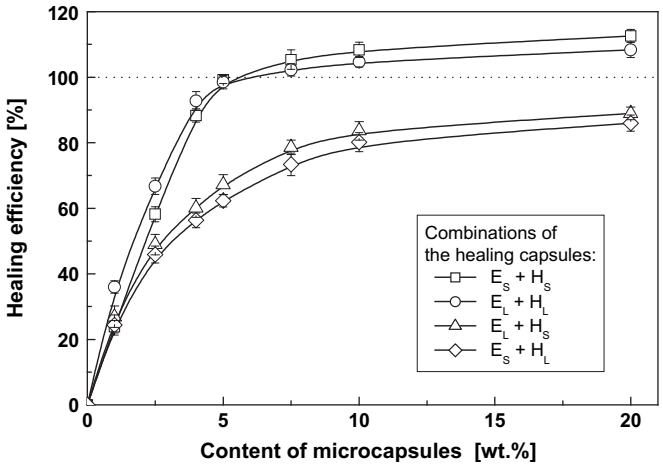


Fig. 4. Influence of content of microencapsulated healing agent on healing efficiency of the self-healing composites. Weight ratios of epoxy- to hardener-loaded capsules for all combinations follow the corresponding optimal values revealed in Fig. 5. Healing of the fractured specimens was conducted at 20 °C for 24 h.

higher loading might be directly involved in the consolidation of epoxy (see Scheme 2(b)) and hence the system viscosity is greatly raised, which in turn decreases the rate of reaction since the cure becomes to be controlled by diffusion. With respect to the latter, the reduction in the adhesivity might be due to plasticization effect of the excessive catalyst.

To evaluate the role of the catalysts in authentic self-healing process, a series of hardener-loaded capsules carrying different catalysts were prepared (Table 4). In terms of infiltration technique, BDMA and DMP-30 were introduced into PMP-loaded microcapsules, respectively. Besides, as TPP cannot be infiltrated into the capsules due to its immiscibility with mercaptan, the catalyst was directly added into the matrix cooperating with PMP-loaded microcapsules (H_0). Fig. 1 shows time dependences of healing efficiency generated by different combinations of the capsules to highlight the influence of the catalysts. With the aid of strong alkaline BDMA or DMP-30, fast repair and high healing efficiency are observed. For weak alkaline TPP, however, slow repair and low healing efficiency are detected. In the case of similar catalyst content, the system with DMP-30 exhibits faster repair rate and higher healing efficiency than that with BDMA as a result of stronger alkality of the former. For a given catalyst (e.g., BDMA) with low content (<3.6%), an increase in its content also leads to higher repair rate and healing efficiency. The results agree with the aforesaid influential order of the three catalysts when epoxide–mercaptan reaction rate is concerned [30,31]. Evidently, the speed of repair and bonding strength of the healing membrane can be controlled by tuning catalyst species and concentration.

On the basis of the above analysis, simulative healing experiments were conducted to understand the highest healing effect that can be offered by the epoxy–mercaptan pairs (Fig. 2). The amount of the manually injected healing agent (0.03 ml) is enough to fill the cracks (crack volume ≈ 0.0035 ml). In general, in the case of authentic healing, viscosity of healing agent would hinder its delivery into cracks and the subsequent mixing, interdiffusion and solidification. Healing efficiency has to be lower than that yielded

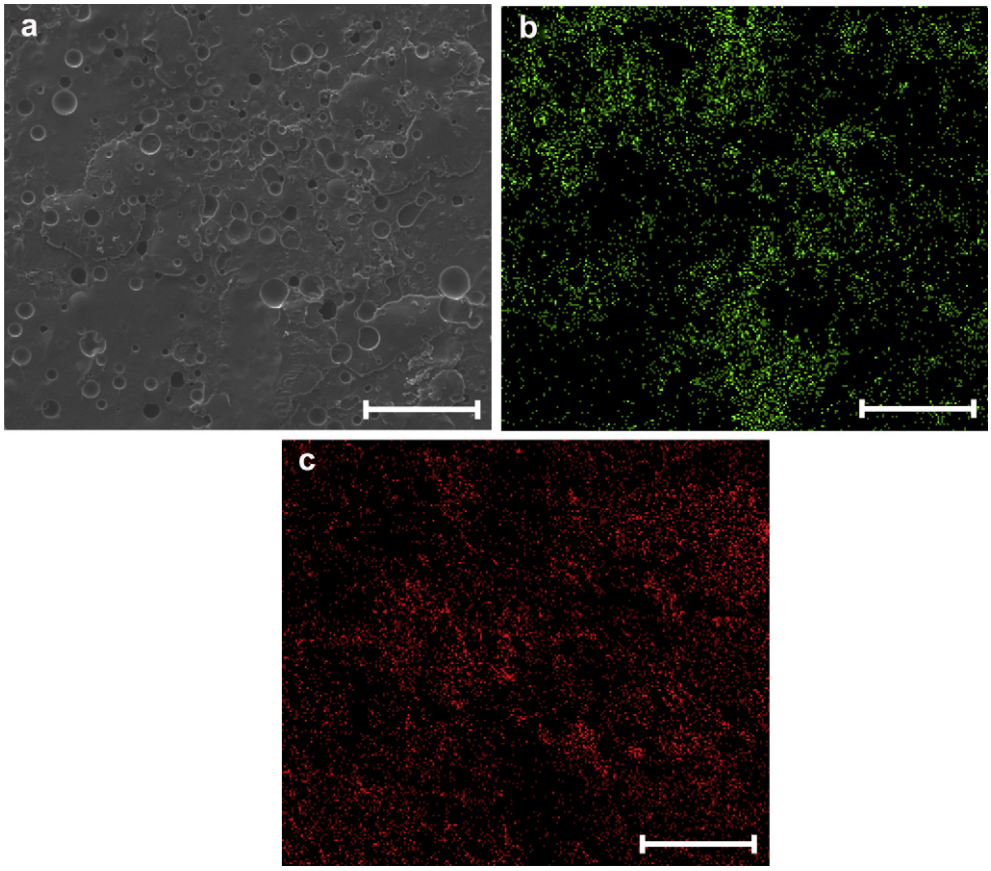


Fig. 5. (a) SEM image and EDS analysis with (b) sulfur and (c) carbon as the indicator elements of the fracture surface of a healed self-healing composite specimen, which contains 10 wt% epoxy-loaded capsules (E_L) and 10 wt% hardener-loaded capsules (H_L). Healing of the fractured specimen was conducted at 20 °C for 24 h. The attached scale bars represent 200 μm in length.

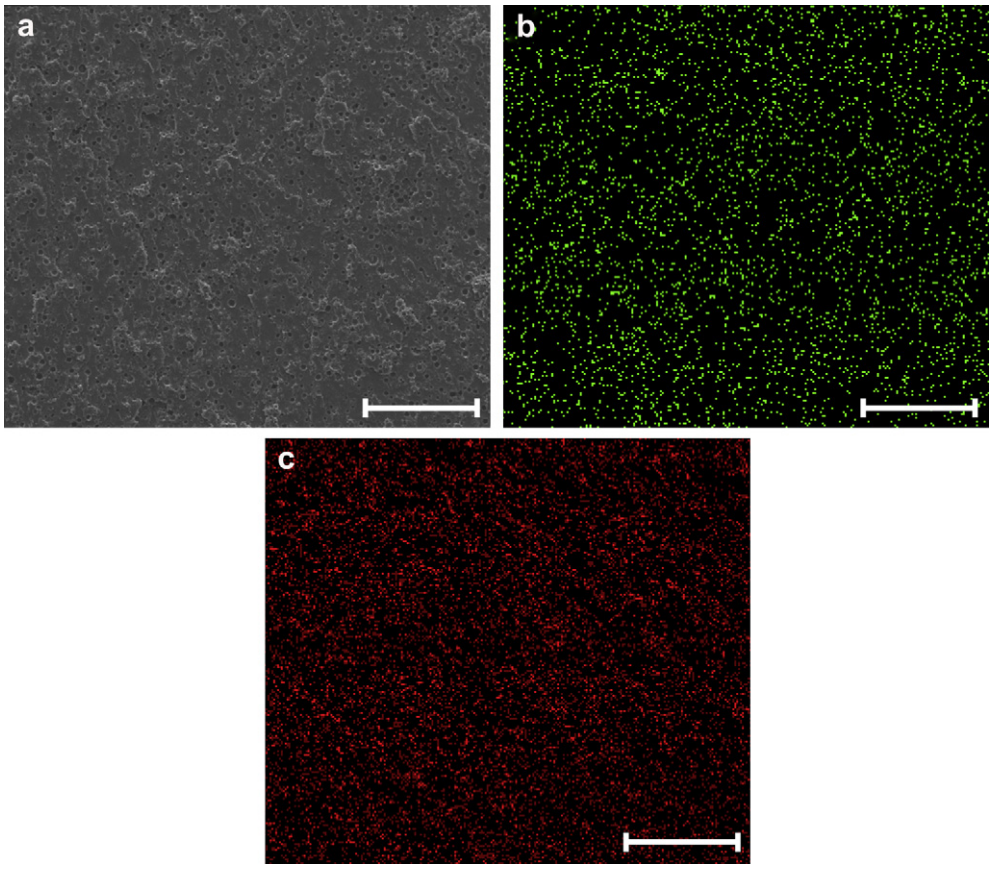


Fig. 6. (a) SEM image and EDS analysis with (b) sulfur and (c) carbon as the indicator elements of the fracture surface of a healed self-healing composite specimen, which contains 10 wt% epoxy-loaded capsules (E_S) and 10 wt% hardener-loaded capsules (H_S). Healing of the fractured specimen was conducted at 20 °C for 24 h. The attached scale bars represent 200 μm in length.

by simulative tests. Here, a mixing efficiency defined as the healing efficiency ratio of authentic healing to that of simulative healing is introduced. It may examine the performance of the healant from a comprehensive angle because the impact of its viscosity, bonding performance and activity is included. As shown in Fig. 2, the low viscosity epoxy 711 (Table 1) achieves the highest mixing efficiency (83.4%), as compared with 731 (79.3%) and 828 (63.7%). For mercaptan, the highest mixing efficiency is perceived in the system with PMP (83.4%), forming a strike contrast to TMP (82.5%) and C38 (67.9%). It implies that content of hydrosulfide group plays the leading role.

In short, chemical features of the healing agent are closely related to healing ability and rate of healing. The above discussion suggests that highly flowable epoxy prepolymer, high activity mercaptan and strong alkality tertiary amine are prerequisites for improving healing ability of the epoxy–mercaptan based healant developed in the authors' lab. In other words, the healing reaction would be favored when the encapsulated epoxy prepolymer has rather low viscosity, mercaptan carries sufficiently large amount of hydrosulfide groups, and the catalyst possesses strong alkality and/or suitable concentration.

3.2. Factors in relation to stoichiometric ratio of reactants

As mentioned above, the healing reaction between epoxy and mercaptan belongs to addition polymerization. Accordingly, stoichiometric ratio of epoxy/mercaptan and uniform mixing at molecule level are critical for a perfect cure [22,31]. Because the capsules size corresponds to the amount of releasable healing agent (i.e. the core content in Tables 3 and 4) and spreading area of healing agent delivered into cracked planes, the embedded epoxy- and hardener-loaded microcapsules with mismatched sizes may lead to localized excess of one ingredient and deviation from the required stoichiometric ratio. Similarly, mismatched fractions of the microcapsules would also bring about the same result. Therefore, a careful study in this aspect should be conducted.

To quantify the aforesaid influence of matching of capsules' sizes and fractions, four combinations of the capsules (i.e., $E_L + H_L$, $E_S + H_S$, $E_L + H_S$ and $E_S + H_L$, see Tables 3 and 4) were incorporated into the epoxy composites and tested, respectively. The data in Fig. 3 indicate that the weight ratio of epoxy-/hardener-loaded capsules corresponding to the highest healing effect for each composite is a function of the combination of the capsules, and hardly varies with the capsules concentration for a given composite (or a given combination of the capsules). These optimal ratios are 1:1, 1:1, 0.68:1 and 1.5:1 for the above four combinations, respectively. According to theoretical estimation [7,30], the stoichiometric weight ratio for the present healant is 1.26, which can be equivalently converted to the weight ratios of epoxy-/hardener-loaded capsules of 1.18:1, 1.02:1, 0.4:1 and 2.33:1 for the four groups. Obviously, the value of the composite with $E_S + H_S$ combination well agrees with the prediction, and that of the composite with $E_L + H_L$ takes the second place, while those of $E_L + H_S$ and $E_S + H_L$ exhibit severe deviation.

Fig. 4 further summarizes the influences of microcapsules' concentration on healing efficiency in the case of the above four combinations of the capsules. The weight ratios of epoxy- and hardener-loaded capsules adopted the optimal ones revealed in

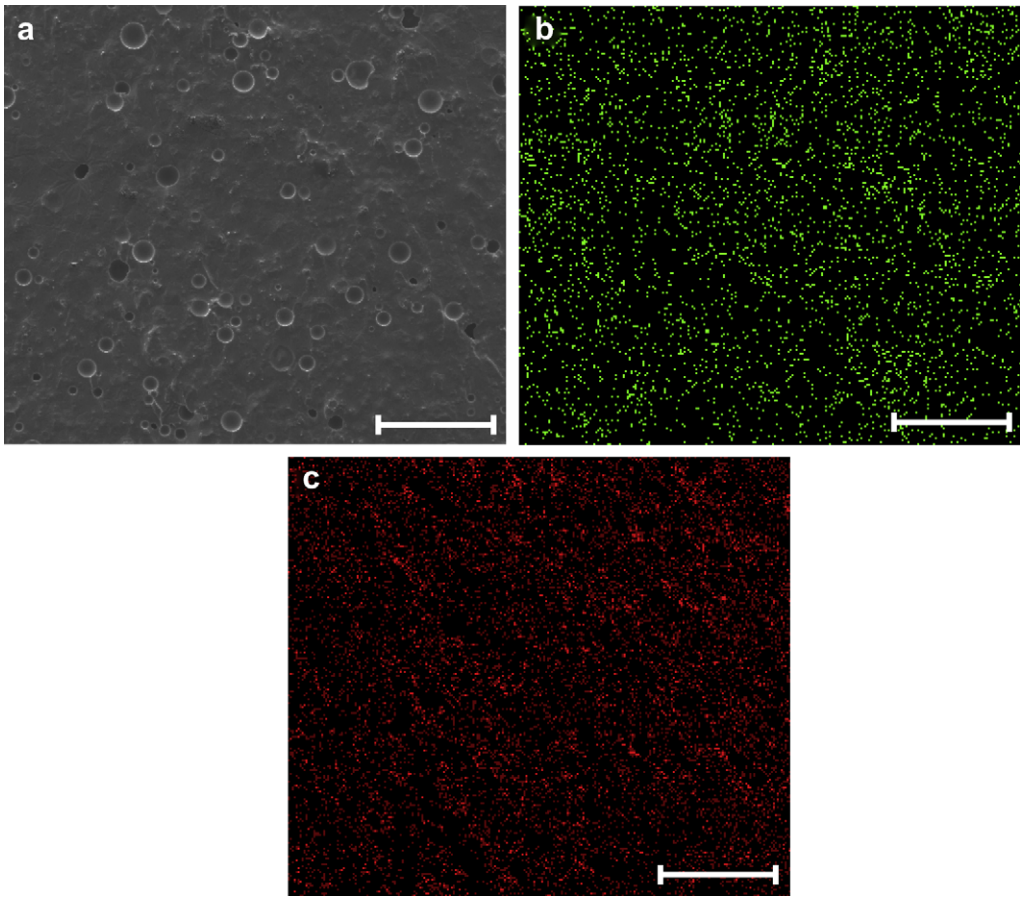


Fig. 7. (a) SEM image and EDS analysis with (b) sulfur and (c) carbon as the indicator elements of the fracture surface of a healed self-healing composite specimen, which contains 10 wt% epoxy-loaded capsules (E_L) and 10 wt% hardener-loaded capsules (H_S). Healing of the fractured specimen was conducted at 20 °C for 24 h. The attached scale bars represent 200 μm in length.

Fig. 3. It is seen that the combinations of $E_L + H_L$ and $E_S + H_S$ offer higher healing efficiency than those of $E_L + H_S$ and $E_S + H_L$ within the entire concentration range of interests. The different healing effects evidence our analysis of the capsules with mismatched sizes at the beginning of this sub-section. Even though the capsules concentration is high enough, the inappropriate combinations of the microcapsules still failed to generate sufficiently high healing efficiency like the proper combinations. The deviation from the required stoichiometric ratio of healants on the fractured surfaces should take the responsibility.

Mapping of sulfur from the released mercaptan on fractured surface of healed composites is related to diameter, core content and distribution of the hardener-loaded capsules in the matrix, mixability and interdiffusion of epoxy and its hardener delivered to the fractured planes, etc. In this context, dispersion status of the released healant from different combinations of the capsules can be visually compared by using SEM images in conjunction of EDS analysis of S and C elements (Figs. 5–8). For the composites with $E_L + H_L$ and $E_S + H_S$ capsules, raised fragments produced by cohesive failure of matrix (because of strong adhesion between cured healing membrane and matrix) appear on the fractured healed planes (Figs. 5(a) and 6(a)), which correspond to slight crack deviation in the course of TDCB tests [22]. Moreover, the raised fragments are characterized by smaller size but larger quantity for the composite with $E_S + H_S$ capsules. It forms a striking contrast to the composite with $E_L + H_L$ capsules possessing only a few big raised fragments. With respect to the distribution of S and C elements (Figs. 5(b) and (c), 6(b) and (c)), more homogeneous patters are observed on the composite with $E_S + H_S$ capsules. It might be due to the fact that the volumes of the core droplets flowing out of smaller capsules are smaller than those from larger capsules, so that contact, intermixing, interdiffusion and addition polymerization reaction between the released epoxy and hardener are favored. As a result, so long as the amount of the healing capsules is adequate for filling cracks (>5 wt% as revealed by Fig. 4), the composites containing smaller capsules possess higher healing efficiency.

As for the composite with $E_L + H_S$ and $E_S + H_L$ capsules, the fractured healed surfaces are relatively smooth (Figs. 7(a) and 8(a)). Accordingly, no crack deviation was discovered during TDCB tests. The distribution of S and C elements is quite uniform on the surface of the composite with $E_L + H_S$ capsules (Fig. 7(b) and (c)). The small hardener-loaded capsules should account for the image in Fig. 7(b). In addition, the localized excessive epoxy 711 (from larger capsules E_L) has similar C content as the matrix, which leads to apparently even distribution of C element in Fig. 7(c). Nevertheless, it does not necessarily represent good mixing of the components of the released healant, because the system offers low healing efficiency (Figs 3(c) and 4). The results suggest that EDS analysis might not always provide correct information. One has to draw reasonable conclusion based on results of other measures. On the other hand, Fig. 8(b) and (c) exhibit that the elements distribution on the fractured planes of healed composite with $E_S + H_L$ capsules is quite uneven. The poor mixing and interdiffusion of epoxy and the hardener should originate from the larger hardener-loaded capsules.

It can thus be concluded that when the embedded epoxy- and hardener-loaded microcapsules are mismatched in their sizes, the

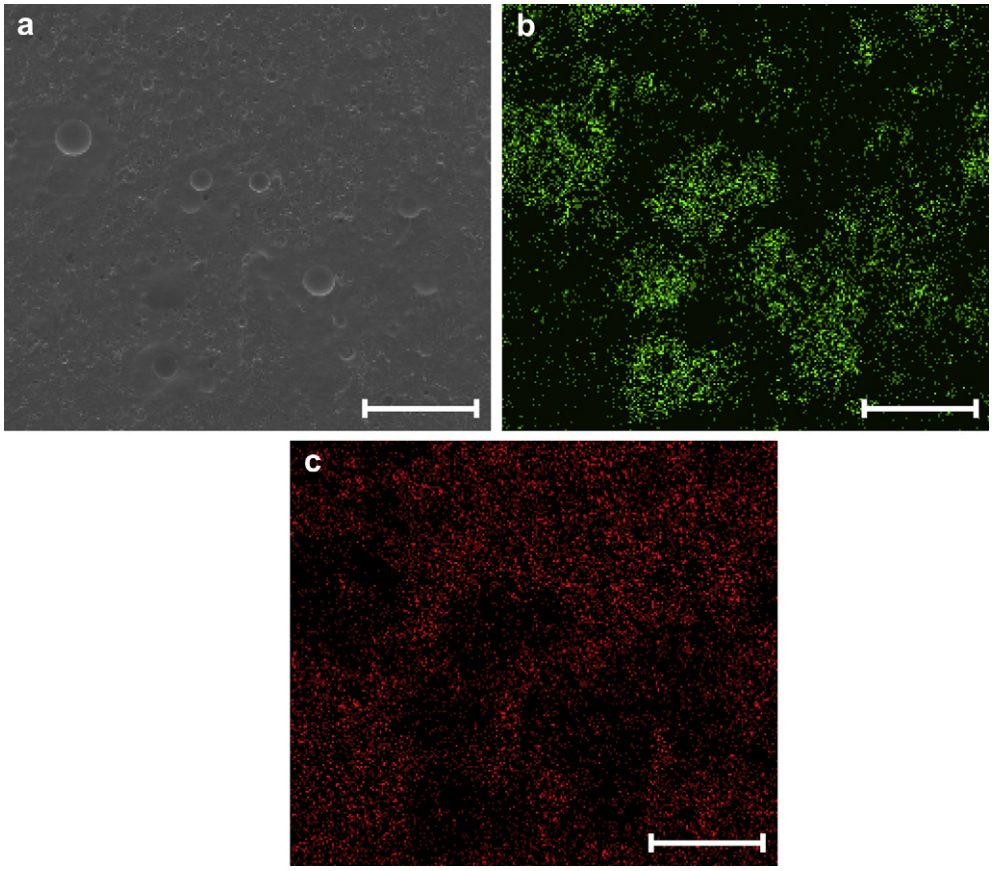


Fig. 8. (a) SEM image and EDS analysis with (b) sulfur and (c) carbon as the indicator elements of the fracture surface of a healed self-healing composite specimen, which contains 10 wt% epoxy-loaded capsules (E_S) and 10 wt% hardener-loaded capsules (H_L). Healing of the fractured specimen was conducted at 20 °C for 24 h. The attached scale bars represent 200 μm in length.

volumes of the core drops given by the broken capsules greatly differ from each other. Even if apparent dosages of the healant meet the stoichiometric ratio by adjusting weight ratio of the capsules, the local composition might still be unbalanced. Consequently, the localized wrong proportion and incomplete mixing and interdiffusion of the healing agent lead to lower curing degree and healing efficiency. Therefore, the dual microcapsules should match each other in both sizes and fractions for raising healing efficiency.

3.3. Processing

The above discussion reveals the importance of stoichiometric ratio of the healing agent as reflected by matching of the healing capsules diameters. It is worth noting that when proper combinations of the capsules with similar sizes are selected (e.g., $E_L + H_L$ or $E_S + H_S$), homogeneous dispersion of the microcapsules should be realized. Otherwise, one could not make the most of the matched capsules.

For preparing the self-healing composites, microcapsules were firstly dispersed in viscous matrix epoxy prepolymer, then curing agent for the matrix was added, and the matrix started to be solidified from gel to stiff material. Spatial distribution of the capsules in composites was fixed basically when the matrix was in the gel state. To homogenize the distribution, the following issues related to the capsules should be satisfied. (i) Both epoxy- and hardener-loaded microcapsules have similar surface feature, physical properties and geometry. (ii) The microcapsules possess mono-dispersivity and do not adhere to each other. (iii) The microcapsules are robust enough to survive handling during composites manufacturing. Our earlier works showed that the microcapsules can be made to meet these criteria by improving encapsulation process [22,28,29]. In addition to these conditions, dispersion rate applied for mixing the microcapsules and matrix resin are also important.

Fig. 9 indicates that healing efficiency of the composites is dependent on the stirring speed. The former reaches the maximum level only at optimal dispersion rate. It is because the shearing force

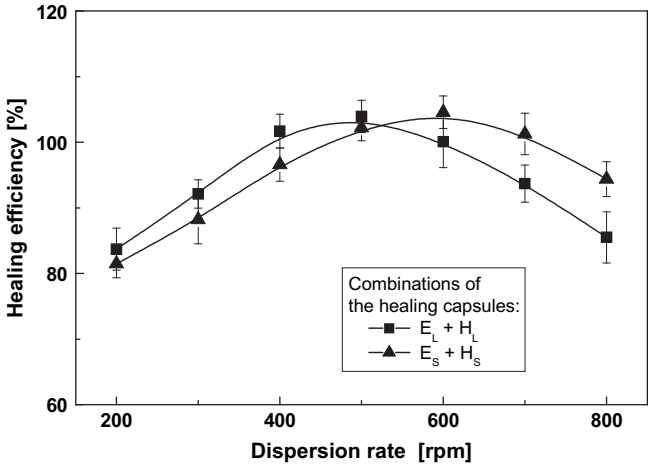


Fig. 9. Influence of mechanical dispersion rate on healing efficiency of the self-healing composites containing 2.5 wt% epoxy-loaded capsules and 2.5 wt% hardener-loaded capsules. Healing of the fractured specimens was conducted at 20 °C for 24 h.

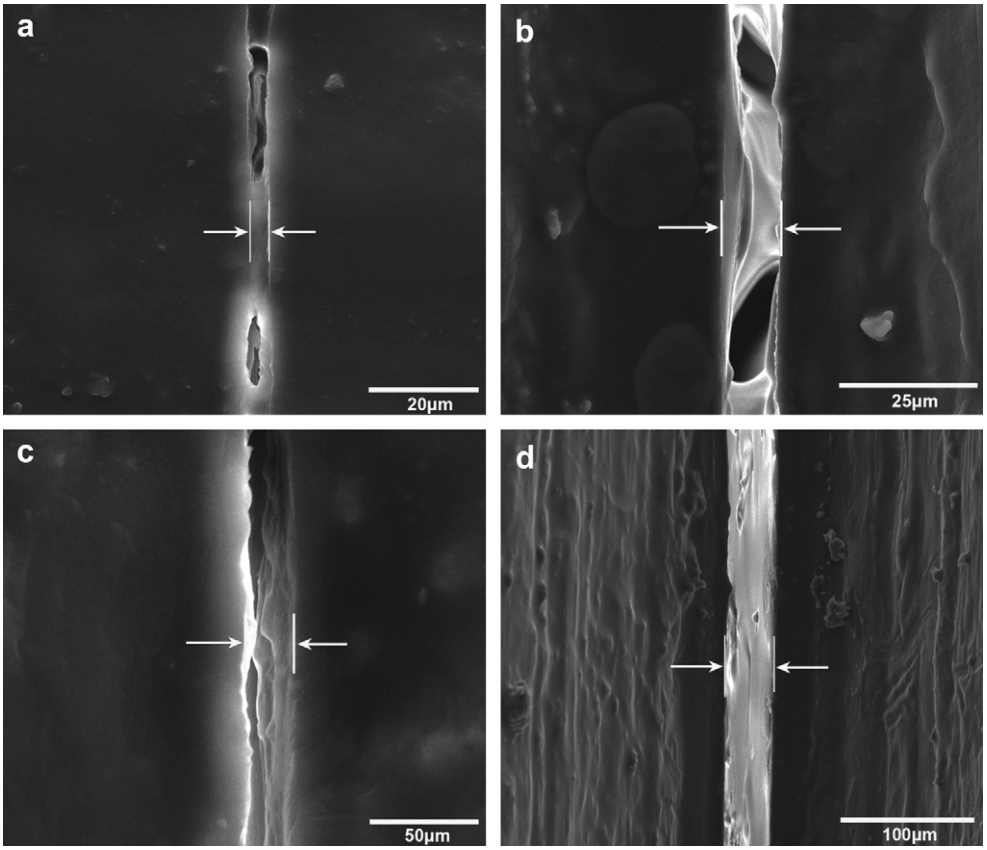


Fig. 10. SEM images of healed cracks near the loading pin holes in the self-healing specimens containing 2.5 wt% epoxy-loaded capsules (E_S) and 2.5 wt% hardener-loaded capsules (H_S). Groove lengths of the TDCB specimens are (a) 30 mm, (b) 39 mm, (c) 47 mm and (d) 55 mm.

at low agitation rate is so weak that the microcapsules could not be well mixed with the matrix epoxy, while that at extremely high dispersion rate would distort or even break the microcapsules. These cases certainly change the actual ratio of the capsules despite it is designed according to the stoichiometric ratio. Moreover, either epoxy or its hardener from the unintentionally fractured microcapsules would participate in curing reaction of the epoxy matrix and change the properties of the composite [30].

Fig. 9 also shows that the optimal dispersion rate for smaller microcapsules is higher than that for larger ones. It should be attributed to the higher specific surface area of the smaller spheres, which leads to higher tendency of agglomeration. As a result, stronger shear has to be used to separate them.

3.4. Crack width

In general, crack healing includes the following stages: surface rearrangement, surface approach, wetting, diffusion, and randomization [2,32]. Comparatively, surface approach is considered the most important. No healing occurs if the surfaces are not brought together or the gap between the fractured planes is not filled with healing fluid. White et al. suggested that healing effect could reach the maximum level only when sufficient healing agent was available to entirely fill the crack [7].

To look into the situation when dual-capsules are included, we adjusted crack widths of the TDCB specimens by changing the groove lengths. The modified TDCB specimens incorporate crack-directing grooves that are reduced from 60.25 mm long to 30, 39, 47 and 55 mm, respectively (Scheme 1). As a result, when the specimen was initially fractured, the virgin crack propagated only until it reached the end of the groove. The sample was then unloaded and set aside allowing occurrence of self-healing. The unfractured portion in front of the crack tip hindered the crack face from complete separation and ensured alignment of the two crack faces. As shown in Fig. 10, the average crack face separations of the specimens near the loading pin holes are about 4.4, 12.5, 23.6 and 34.8 μm, respectively, which gradually decrease towards the crack tip.

Specimen compliance is a measure to distinctly identify the contribution of self-healing in TDCB tests [7]. If there wasn't healing effect as indicated in Fig. 11(a), the second load-displacement curve would exhibit the same compliance established at the end of the virgin fracture test. When self-healing did occur, the healed load-displacement curve would show similar compliance varying tendency of the virgin fracture test (Fig. 11(b)). Therefore, the results in Fig. 11 manifest that for the TDCB specimens with short groove, both the virgin and healed fractures are comparable to those of standard TDCB specimens and the peak loads appear right before crack propagation. That is, our modified TDCB specimens are qualified for evaluating self-healing ability of the composites.

Fig. 12 illustrates the influence of average crack width on healing effect. The maximum capsules content in the composites to be tested was set at 20 wt%. Further increase in capsules concentration would remarkably deteriorate intrinsic mechanical properties of the composites. On the other hand, the greatest healing efficiency is found to be higher than 100%. It is because the healed portions have higher cracking resistance than the matrix [22]. During TDCB tests, crack had to deviate from the original fracture plane.

Clearly, the data in Fig. 12 indicate that healing efficiency is very sensitive to the crack width. For the same formulation, the wider crack, the lower healing effect. In the case of a crack as wide as

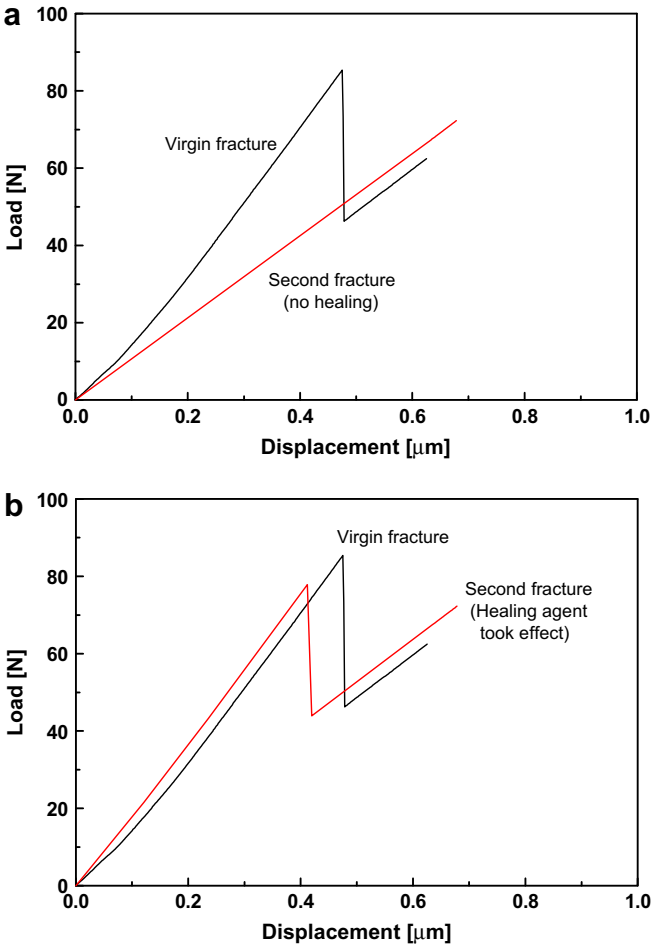


Fig. 11. Typical load-displacement curves recorded during TDCB tests of self-healing composites (groove length of the specimens: 30 mm; healing conditions: 20 °C and 24 h). (a) The specimen contains 2.5 wt% epoxy-loaded capsules (E_L) and 2.5 wt% hardener-loaded capsules (H_0). Because no catalyst is included in the hardener-loaded capsules, the healing reaction cannot proceed and no healing effect is perceived. (b) The specimen contains 2.5 wt% epoxy-loaded capsules (E_L) and 2.5 wt% hardener-loaded capsules (H_L).

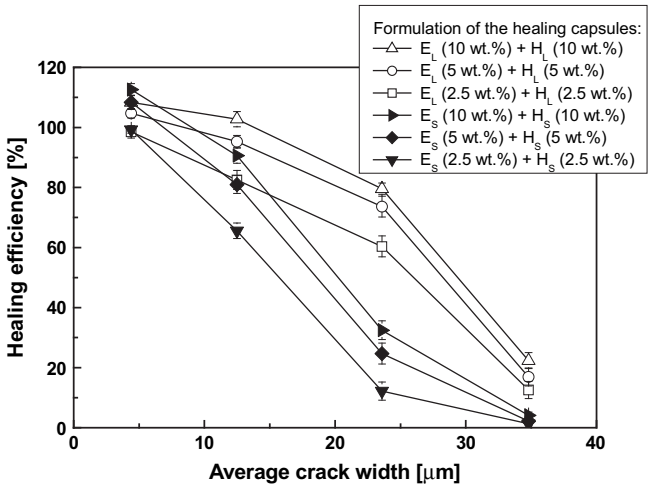


Fig. 12. Influence of crack width near the loading pin holes of the TDCB specimens on healing efficiency of the self-healing composites containing different combinations of the healing capsules. Healing of the fractured specimens was conducted at 20 °C for 24 h.

34.8 μm (Fig. 10(d)), quantity of the released healing agent doesn't meet the need of continuous contact between two fracture planes. Consequently, little bonding effect is perceived. This is true especially when small diameter microcapsules with lower core content are employed. In other words, if the healing fluid only adhered to one surface, little or no healing would occur. It suggests that filling up crack volumes is necessary for crack repair.

On the whole, when the crack widths are greater (i.e. 12.5, 23.6 and 34.8 μm, Fig. 10(b), (c) and (d)), healing effect is proportional to the capsules' size at constant capsules content, because the wider cracks need more healing agent to repair and larger microcapsules meet the requirement. For narrower crack width (e.g., 4.4 μm, Fig. 10(a)), smaller amount of the liberated healing agent is enough to fill the crack, so that self-healing performance easily reaches the highest value. The influence of capsules' size is insignificant accordingly. A careful observation reveals that the smaller microcapsules result in higher healing efficiency than the larger ones. It might be attributed to the fact that the tiny healing agent droplets from the small diameter microcapsules facilitate mixing and interdiffusion of the components of the healing agent.

Therefore, microcapsules with larger size and/or higher concentration are needed by larger cracks, because larger quantity of healing agent would be liberated to damaged portions. On the other hand, microcapsules with smaller size are adapted for healing smaller cracks, as the latter only requires a few amount of healing agent. In this case, mixing and interdiffusion of the healant's components are critical. The above analysis also implies that the two-part healing agent had better to take effect at crack initiation stage. When the cracks are developed into larger ones, healing efficiency has to be rather low or even zero.

4. Conclusions

For self-healing polymer composite with dual microcapsules containing two-part healing agent, its healing performance is controlled by the chemical reaction between the healant's components, which is definitely affected by many interactive factors. Optimization of these factors is necessary for bringing the healant into full play.

Chemical features of the healing agent are correlated with not only healing ability but also rate of healing. The healing reaction of the present recipe is facilitated when the catalyst possesses strong alkality and/or suitable concentration, the encapsulated epoxy prepolymer is highly flowable, and mercaptan has sufficiently large amount of hydrosulfide groups.

The epoxy- and hardener-loaded microcapsules should be matched with each other in their sizes and fractions for offering high healing efficiency. Mismatched capsules result in localized excess of one ingredient and hence deviation from stoichiometric ratio. Bonding strength of the consolidated healing membrane has to be deteriorated accordingly.

Filling up crack volumes is a prerequisite to crack repair. In the case of larger cracks, larger microcapsules and/or higher microcapsules concentration are preferred as larger quantity of healing agent can be delivered to the damaged zones. For smaller cracks, which are easily full of healing agent, smaller microcapsules are favorable because mixing and interdiffusion of the healant's components play the leading role instead.

Acknowledgments

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