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Self-healing epoxy based on cationic chain polymerization

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ABSTRACT

A two-component healing agent consisting of epoxy- and $((C_2H_5)_2O\cdot BF_3)$-loaded microcapsules was synthesized and applied to fabricate self-healing epoxy composites. Curing of epoxy healing agent catalyzed by $(C_2H_5)_2O\cdot BF_3$ belongs to cationic chain polymerization, which is characterized by fast reaction at ambient temperature and low catalyst concentration. The experimental results showed that cracks in the composites containing the above healing system can be quickly re-bonded with satisfied healing efficiency. In the case of 5 wt% epoxy- and 1 wt% $(C_2H_5)_2O\cdot BF_3$-loaded capsules, for example, a ~80% recovery of impact strength was detected within 30 min at 20 °C. Because the healing capsules took effect at low content, mechanical properties of the matrix were largely retained. It is believed that the present healing system provides a possible solution to preparation of self-healing polymeric materials with practical applicability.

1. Introduction

Appearance of microcracks is a fatal problem for polymers and polymer composites utilized as structural components. Development and coalescence of microcracks would cause catastrophic failure. Therefore, imparting self-healing function to the materials is an ideal way for prolonging their lifetimes.

Self-repairing polymers and polymer composites have attracted increasing research interests [1]. Substantial achievements have been made in this field recently, which can be roughly classified into two strategies [2]: (i) intrinsic self-healing – polymers are able to heal cracks by themselves without the aid of any healing agent, and (ii) extrinsic self-healing – healing agent is pre-embedded in the matrix. For the moment, the latter strategy seems to be easier to be commercialized.

To produce an extrinsic self-healing material, healing agent should be stored by fragile containers in advance. Hollow tubes and fibers [3–9], and particles and microcapsules [10–24] are feasible means. Upon cracking they can release healing agent into the damaged areas. As a result of polymerization of the released healant, the cracks are autonomously re-bonded. Therefore, the feature of the chemical reaction of the healing agent and the compatibility between the healant and cracked planes are critical for the degree of restoration of the materials. Moreover, the rate of reaction also determines the rate of rehabilitation. In this context, a fast healing reaction is of particular importance as cracks should be eliminated soon after its appearance to avoid possible propagation.

In our previous works, self-healing epoxy composites were prepared, in which microencapsulated epoxy served as the polymerizable healing agent, while imidazole was used as latent hardener pre-dispersed in the matrix [25–28]. The disadvantage of this system lies in that crack re-mending has to be conducted at elevated temperature due to the catalytic nature of imidazole. To provide the composites with healing ability without the requirement of manual intervention, thiol-loaded microcapsules were used instead [29]. Self-healing was thus allowed to proceed rapidly at or below room temperature offering satisfactory repair effectiveness [30]. However, curing between epoxy and thiol belongs to nucleophilic addition reaction, which needs stoichiometric ratio of the ingredients for obtaining high healing efficiency. This can only be attained by homogeneously mixing both the epoxy- and thiol-loaded capsules in the composites. Additionally, uniform size distribution, identical geometry, density and surface properties of both capsules should be strictly controlled. Evidently, these demands are somewhat difficult to be fulfilled in the case of industrial scale production.

Boron trifluoride diethyl etherate $((C_2H_5)_2O\cdot BF_3)$ has been commercially used as a hardener for low temperature fast cure epoxy adhesives. The curing reaction of epoxy catalyzed by $(C_2H_5)_2O\cdot BF_3$

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proceeds so fast at ambient temperature that tremendous exotherm is produced. Another interesting character of $(C_2H_5)_2O \cdot BF_3$ lies in that the epoxy-BF_3 cure is dominated by cationic chain polymerization mechanism. The aforesaid strict stoichiometric ratio of epoxide/hardener required by addition polymerization is no longer necessary. Therefore, when $(C_2H_5)_2O \cdot BF_3$ is introduced as the partner of epoxy to prepare two-component self-healing agent, it must be superior to epoxy-thiol pair as viewed from the above advantages. Curing of epoxy released from the broken microcapsules would be ignited and spread out quickly so long as the epoxy fluid meets $(C_2H_5)_2O \cdot BF_3$. Furthermore, only a few $(C_2H_5)_2O \cdot BF_3$ (1–5 wt% relative to the quantity of epoxy) is sufficient for initiating the reaction.

Nevertheless, the highly active $(C_2H_5)_2O \cdot BF_3$ is hard to be encapsulated, because it would be easily deactivated during conventional encapsulation process. To solve the problem, the authors developed a novel approach [31]. That is, polymeric hollow microcapsules were firstly produced under UV irradiation, and then $(C_2H_5)_2O \cdot BF_3$ was infiltrated into the spheres. It was found that activity of $(C_2H_5)_2O \cdot BF_3$ was preserved inside the capsules and no bleeding was observed after long term storage.

In this work, self-healing epoxy composites containing epoxy- and $(C_2H_5)_2O \cdot BF_3$- loaded microcapsules were fabricated. Crack healing behavior of the composites was discussed in terms of healing agent content, healing time, and microcapsules size. In the meantime, healing mechanism and influence of addition of the microcapsules on mechanical properties of the composites were presented.

2. Experimental

2.1. Materials

Epoxy resin, diglycidyl ether of bisphenol A (trade name: EPON 828), was purchased from Shell Co., utilizing as both the composite's matrix resin and the polymerizable component of healing agent. The hardener of the composite's matrix, triethylenetetramine (TETA), was supplied by Shanghai Medical Group Reagent Co., China. The catalyst, $(C_2H_5)_2O \cdot BF_3$ acting as the curing agent of the healant, was supplied by Changshu Yangyuan Chemical Engineering Co., China.

Epoxy-loaded microcapsules were prepared via UV irradiation-induced interfacial copolymerization in emulsions [32]. The average sizes of the microcapsules were adjusted from 5 to 45 μm, and the core content (i.e. weight ratio of core to microcapsule) varied from 54 to 79 wt%. The $(C_2H_5)_2O \cdot BF_3$-loaded microcapsules were also made in our laboratory [31]. Their core content and average size were controlled to 20 wt% and 10 μm, respectively. Both the epoxy- and $(C_2H_5)_2O \cdot BF_3$-loaded capsules employed proper substances as the wall-formers to ensure their compatibility with epoxy matrix [31,32]. Fig. 1 shows morphologies and size distribution of these capsules.

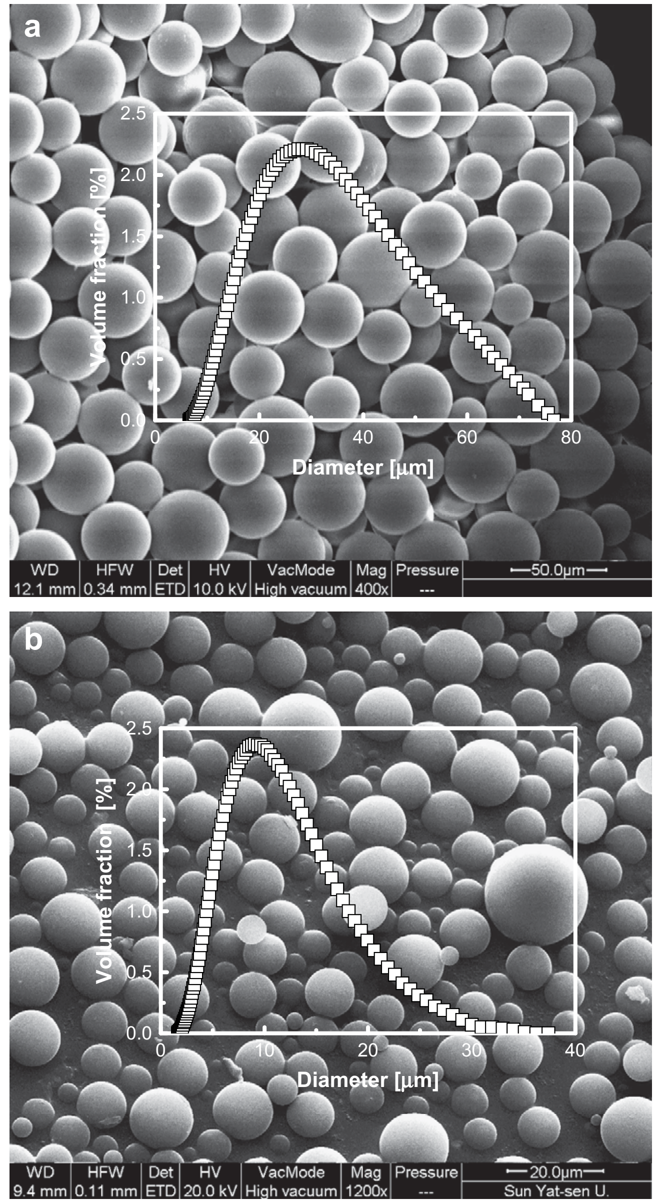

Fig. 1. SEM micrographs and size distributions of (a) epoxy-loaded microcapsules (core content: 70 wt%; average diameter: 30 μm); and (b) $(C_2H_5)_2O \cdot BF_3$-loaded microcapsules (core content: 20 wt%; average diameter: 10 μm).

2.2. Preparation of self-healing epoxy composites

The unfilled epoxy specimens were produced by mixing 100 parts epoxy with 12 parts curing agent TETA. The self-healing epoxy composites were prepared by mixing epoxy-loaded and $(C_2H_5)_2O \cdot BF_3$-loaded microcapsules together with the aforesaid mixture of epoxy and TETA. To obtain cured versions, both the unfilled epoxy and filled compounds were degassed and poured into closed silicone rubber molds and cured for 72 h at room temperature, followed by 48 h at 45 °C. Control specimens containing only one type of the capsules were prepared by the same procedures.

2.3. Characterization

The protocol suggested by Jones et al. was applied to assess healing ability of the composites in terms of impact test [33]. Healing efficiency is defined as the ratio of impact strength of healed and virgin materials. Izod notched tests were conducted at 20 °C according to ASTM D256-04 using a JJ-20 impact tester produced by Changchun Research Institute for Testing Machines Co. Ltd., China. After testing, the specimens that had been broken into two pieces were kept in alignment and intimate contact for healing at 20 °C for different times. To do this, the two halves were carefully aligned between two clean microscope slides using polytetrafluoroethylene (PTFE)-release film and a 250 g weight. The contact pressure at the faces of the two halves was set as 0.2 MPa by a screw. Then, the healed specimens were tested again following the above procedure to check the effect of healing. Each batch included ten specimens to yield averaged value.

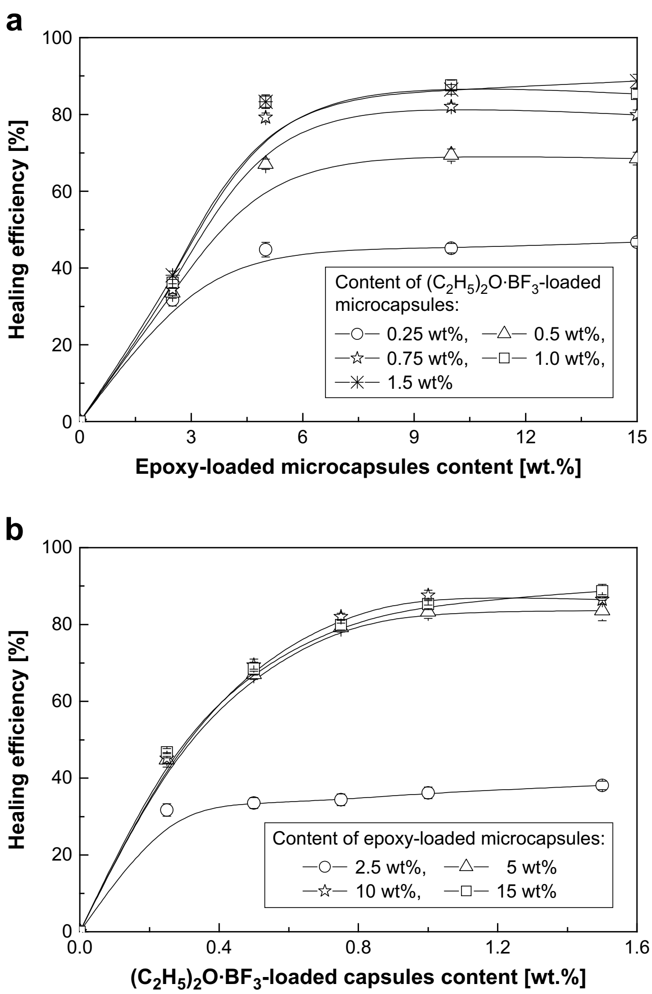

Fig. 2. Dependence of healing efficiency of the self-healing epoxy composites on content of the healing agent. Epoxy-loaded microcapsules: core content = 70 wt%, average diameter = 30 μm. $(C_2H_5)_2O{\cdot}BF_3$-loaded microcapsules: core content = 20 wt%, average diameter = 10 μm. Healing of the fractured specimens was conducted at 20 °C for 2 h.

The reaction feature of epoxy resin catalyzed by $(C_2H_5)_2O{\cdot}BF_3$ was characterized by a Nexus 670 Fourier transform infrared (FTIR) spectroscopy. Epoxy was coated on KBr tablet firstly, and then a drop of $(C_2H_5)_2O{\cdot}BF_3$ is dripped on the surface of the sample. The weight ratio of epoxy/$(C_2H_5)_2O{\cdot}BF_3$ was set at 95/5.

Tensile and flexural properties of the self-healing composites and unfilled epoxy specimens were measured according to ASTM D638 and D790, respectively. 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 samples' surfaces were coated by gold/palladium sputter.

3. Result and discussion

3.1. Composition dependent crack healing behaviors

As mentioned in the Introduction, weight ratios of $(C_2H_5)_2O{\cdot}BF_3$/epoxy ranging from 1 to 5 wt% are sufficient for curing epoxy. However, healing of cracks in composites depends on the curing reaction of the crack-released epoxy with the bled $(C_2H_5)_2O{\cdot}BF_3$. That means, exact proportions of the two types of capsules taking part in the reaction can hardly be predicted for this specific case. The suitable recipe has to be determined from actual tests. For this reason, a series of epoxy composites filled with various contents of epoxy- and $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules at different ratios were prepared and evaluated.

As exhibited in Fig. 2, healing of cracks is available only when both epoxy- and $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules are added to the composites. The system filled with only a single component of the healing agent cannot offer any healing functionality. When the dosage of $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules is fixed, healing efficiency of the epoxy composites increases with the content of epoxy-loaded capsules up to 5 wt%, and then tends to level off (Fig. 2(a)). The maximum healing efficiency is about 88%. At lower content of epoxy-loaded capsules, the released epoxy fluid would be insufficient to cover the broken surface, and hence poor healing effect is detected. This deduction can be evidenced from another angle by the data in Fig. 2(b), in which similarly high healing efficiencies are perceived for all of the epoxy composites containing epoxy-loaded capsules over 5 wt% and $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules over 1 wt%. In contrast, the composite with 2.5 wt% epoxy-loaded capsules only shows healing efficiency of ~30% regardless of content of $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules.

Fig. 2 also illustrates the importance of content of $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules. Healing efficiency of the composites increases with a rise in $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules addition within low content regime, but it becomes nearly independent of the content of $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules at 1 wt% and above.

Supposing that the dual capsules are homogeneously distributed throughout the composites, and all the capsules at the crack surfaces can be fractured, the corresponding $(C_2H_5)_2O{\cdot}BF_3$/epoxy weight ratio of the released healant can be estimated (Table 1). Evidently, for the low content epoxy-loaded capsules (i.e. 2.5 wt%), $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules with contents from 0.25 to 1.5 wt% are sufficient, because the estimated $(C_2H_5)_2O{\cdot}BF_3$/epoxy weight ratios range between 2.9 and 17.1 wt%, agreeing with the standard proportions of 1–5 wt%. Therefore, the aforesaid low healing efficiency of the composites filled with 2.5 wt% epoxy-loaded capsules has to result from the insufficient supply of the released epoxy. On the other hand, 0.25 wt% $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules are too few to induce a complete cure of epoxy healing agent for the composites containing 10–20 wt% epoxy-loaded capsules, since the estimated $(C_2H_5)_2O{\cdot}BF_3$/epoxy weight ratios are only 0.4–0.7 wt%, lower than the lower limit of the recipe (i.e. 1 wt%). The analysis explains the poor healing ability of the composites with low content $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules (Fig. 2).

It is interesting to note that for the composites with 5 wt% epoxy-loaded capsules and 0.25 wt% $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules, the calculated $(C_2H_5)_2O{\cdot}BF_3$/epoxy weight ratio is 1.4%, which exceeds the lower limit of the recipe. Theoretically, the corresponding healing efficiency should also be high. Evidently, it is

Table 1
Estimation of $(C_2H_5)_2O{\cdot}BF_3$/epoxy weight ratio of released healant according to the contents and core contents of epoxy- and $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules.

$(C_2H_5)_2O{\cdot}BF_3$-loaded capsules		Epoxy-loaded capsules		Calculated $(C_2H_5)_2O{\cdot}BF_3$/epoxy weight ratio (wt%)	
Content (wt%)	Core content (wt%)	Content (wt%)	Core content (wt%)	Corresponding to the content range of $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules	Corresponding to 1 wt% $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules
0.25–1.5	20	2.5	70	2.9–17.1	11.4
0.25–1.5	20	5	70	1.4–8.6	5.7
0.25–1.5	20	10	70	0.7–4.3	2.9
0.25–1.5	20	15	70	0.5–2.9	1.9
0.25–1.5	20	20	70	0.4–2.1	1.4

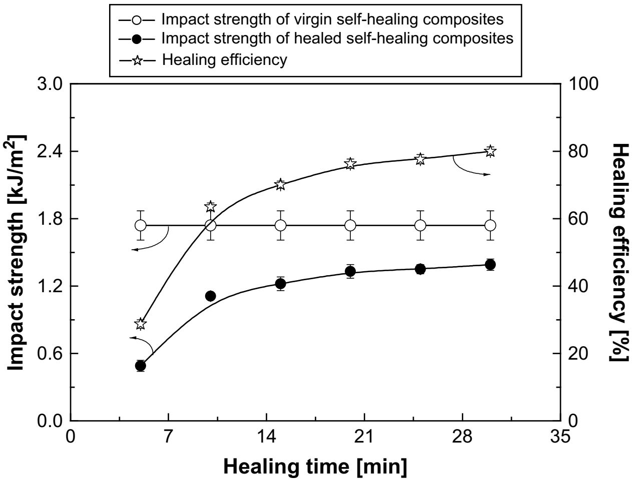

Fig. 3. Dependences of impact strength of healed self-healing epoxy composites and healing efficiency on healing time at 20 °C. Contents of epoxy- and $(C_2H_5)_2O\cdot BF_3$-loaded capsules are 5 and 1 wt%, respectively. Epoxy-loaded microcapsules: core content = 70 wt%, average diameter = 30 μm. $(C_2H_5)_2O\cdot BF_3$-loaded microcapsules: core content = 20 wt%, average diameter = 10 μm.

not the case. The deviation implies that the assumption of the calculation might not always be consistent with the actual case. Heterogeneous distribution of the capsules and their fracture must be responsible for the deviation.

On the whole, the results in Fig. 2 and Table 1 suggest that the $(C_2H_5)_2O\cdot BF_3$/epoxy weight ratios can vary within a relatively wide range. The stoichiometric composition at every inch of repair region required by the healing agent based on epoxy-amine or epoxy-thiol pairs is unnecessary. Actually, so long as the contents of epoxy- and $(C_2H_5)_2O\cdot BF_3$-loaded capsules are respectively higher than 5 and 1 wt%, the repair effect is insensitive to the healant concentration, offering a ∼85% recovery of impact strength. Such low critical fractions of healant must be beneficial to retaining original mechanical properties of the matrix epoxy.

3.2. Rate of healing

To check the rate of crack healing, healing efficiencies of the composites were recorded as a function of healing time (Fig. 3). It is seen that the healing proceeded quite fast at 20 °C, meaning that the curing of epoxy healing agent under catalysis of $(C_2H_5)_2O\cdot BF_3$ must have been completed within short time as expected. The healing efficiency attains 28% after 5 min, exceeds 76% only after 20 min, and reaches the equilibrium at ∼80% after 30 min. It should be emphasized that the healing effect is acquired at very low content of healing agent (5 wt% epoxy-loaded microcapsules and 1.0 wt% $(C_2H_5)_2O\cdot BF_3$-loaded microcapsules) as compared with our previous work (typically 5 wt% epoxy-loaded microcapsules and 5 wt% thiol-loaded microcapsules [30]). Moreover, the rate of healing is much faster than that of thiol catalyzed one, which required 24 h to approach the maximum healing efficiency [30].

Fig. 4 shows FTIR spectra of the curing system recorded at different times. The characteristic peak of epoxide groups at 914 cm^{-1} diminishes with time. When the peak of phenyl ring at 830 cm^{-1} serves as the internal standard, the absorbency of both epoxide groups and phenyl ring can be used to estimate the change of reaction degree, α, with reaction time:

$$\alpha = 1 - (A_t A_{os}/A_o A_{ts})$$

where A_o and A_{os} are the absorbencies of both epoxide groups and phenyl ring at the beginning of the reaction, while A_t and A_{ts} are the absorbencies of these two groups at time of t. It is interesting to find that the development of reaction degree, α, with reaction time is quite similar with the tendency of healing efficiency (c.f. Fig. 3 and inset of Fig. 4). When the reaction carries out for about 30 min, about 87% epoxide groups are consumed (see the inset of Fig. 4), which corresponds to ∼80% recovery of impact strength of the composites. The result demonstrates that the healing agent chosen in this work is suitable for quick repair of cracks in epoxy.

Considering that a complete cure might hardly be attained at 20 °C and the present equilibrium healing efficiency might be further increased after longer rehabilitation period, we tried longer healing time, like 24 h. However, the equilibrium healing efficiency turned out to keep nearly unchanged. It can be understood from the viscosity change of the healing system. According to general law of epoxy curing, viscosity of the reaction system increases with development of the crosslinkages, while contacts between the components are reduced due to diffusion hindrance. Usually, step curing or slowly curing process is applied to maximize the reaction degree. However, in this work, curing of the healing agent proceeds so fast at the test temperature and no measure can be taken to slow

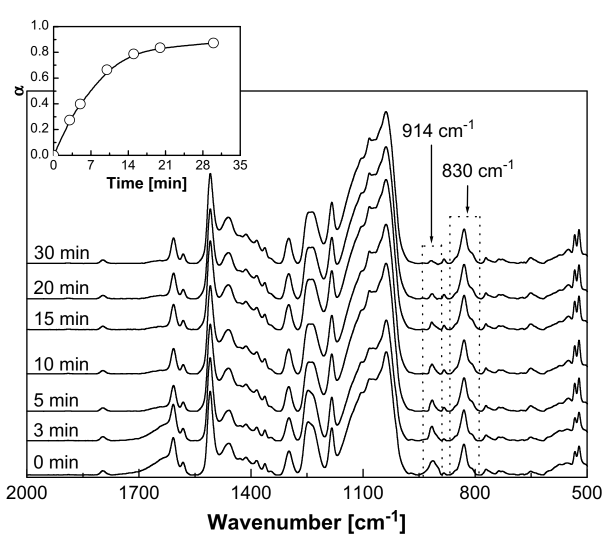

Fig. 4. FTIR spectra showing the reaction between epoxy and $(C_2H_5)_2O\cdot BF_3$ (95/5 by weight) at 20 °C. The inset presents the reaction degree, α, as a function of time.

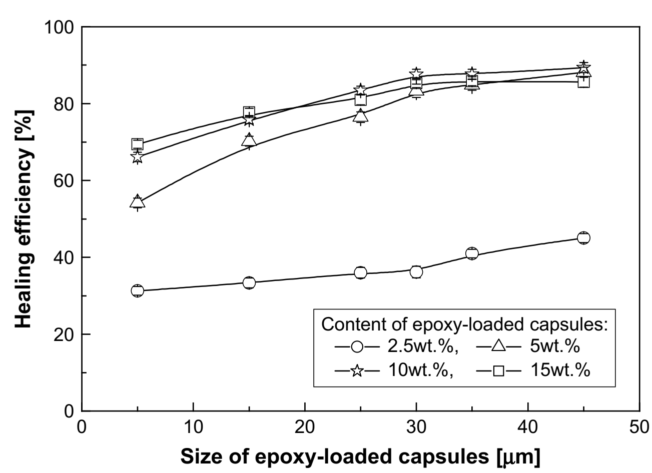

Fig. 5. Dependence of healing efficiency of the self-healing epoxy composites on the average size of epoxy-loaded capsules. Content of $(C_2H_5)_2O\cdot BF_3$-loaded capsules (core content: 20 wt%; average diameter: 10 μm) is 1 wt%. Core contents of epoxy-loaded capsules with average diameters of 5, 15, 25, 30, 35, 45 μm are 54, 60, 68, 70, 75, 79 wt%, respectively. Healing of the fractured specimens was conducted at 20 °C for 2 h.

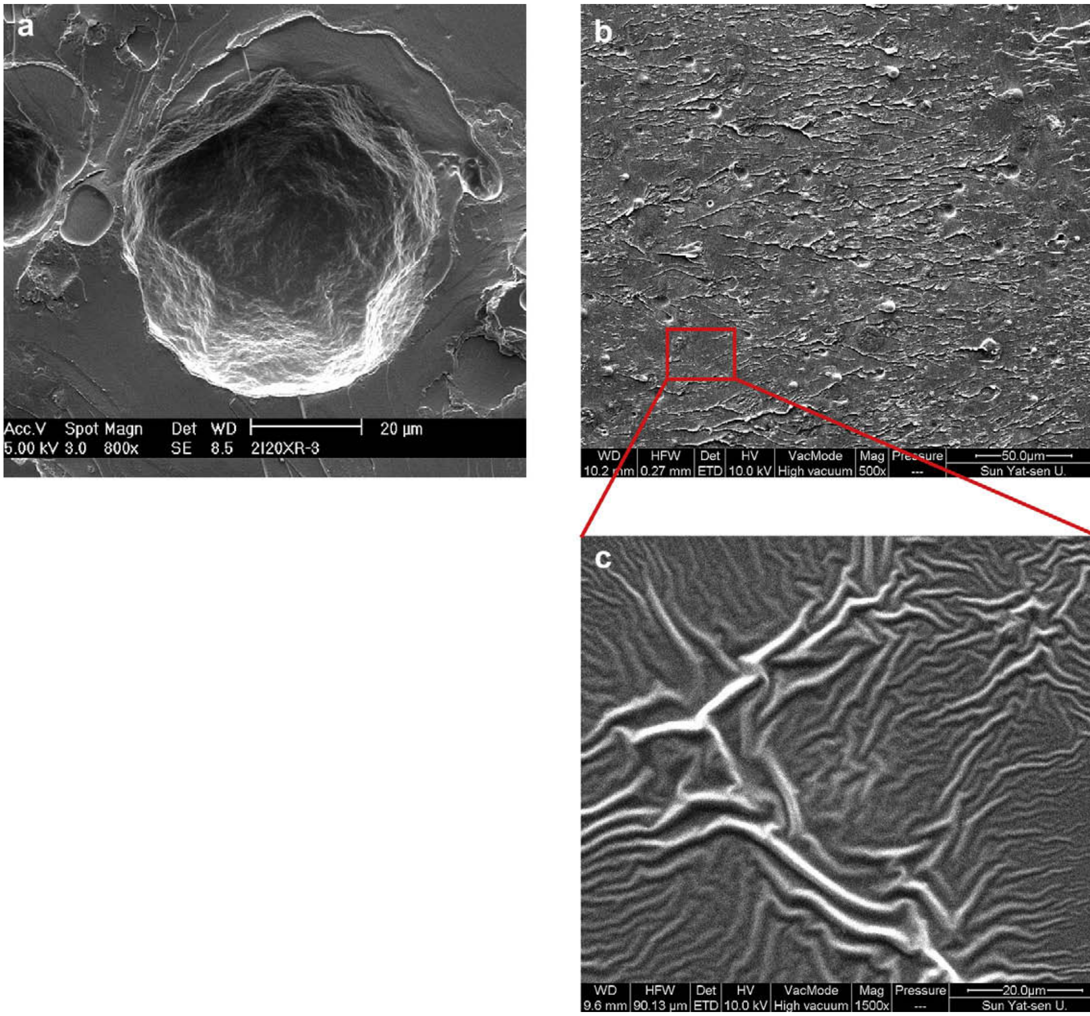

Fig. 6. SEM micrographs of fractured surfaces of (a) virgin self-healing epoxy composite, and (b,c) healed self-healing epoxy composite. Contents of epoxy-loaded microcapsules (30 μm) and $(C_2H_5)_2O \cdot BF_3$-loaded hollow microcapsules (10 μm) are 5 and 1.0 wt%, respectively.

down the reaction. As a result, the equilibrium healing efficiency of ~80% is a trade-off between full recovery and rapid repair.

3.3. Analysis of amount of the delivered healant and healing durability

Besides contents and proportions of the dual capsules, capsules' size, which is closely related to the core content [32], should also be an important factor in determining healing efficiency of the composites. As shown in Fig. 5, for the composites containing 5, 10 and 15 wt% epoxy-loaded capsules, an increase in size of epoxy-loaded capsules tends to improve healing ability of the composites up to 30 μm, while further increase in the capsules' size nearly does not influence the healing efficiency. It should be ascribed to the fact that larger capsules possess higher core content so that the amount of the released epoxy is increased accordingly. When the capsules are large enough to deliver sufficient quantity of epoxy fluid for covering the damaged surfaces, further increase in the capsules' size certainly makes no difference. Considering larger capsules would bring out more negative effect on the mechanical properties of epoxy composites (see Section 3.4), the 30 μm diameter capsules can be considered as the optimum choice. As for the composites containing 2.5 wt% epoxy-loaded microcapsules, a rise in the capsules' size leads to continuous improvement of the healing efficiency. Evidently, the ever shortage of the released epoxy on the fractured plane should account for it.

It is our intention that the present healing system can eventually be applied in self-healing fiber reinforced composites. As the larger size of the microcapsules (with reference to the fiber reinforcements) would hinder them from penetrating into the fiber bundles [27], which is unfavorable to the crack healing of the composites, we are trying to use smaller capsules containing healing fluid with higher flow ability and stronger affinity to the matrix. The results will be discussed in another report of ours.

Fractured surfaces of the specimens before and after healing are illustrated in Fig. 6. It is seen that after failure of the composites, both epoxy- and $(C_2H_5)_2O \cdot BF_3$-loaded microcapsules were fractured but not pull out (Fig. 6(a)), which implies strong bonding between the microcapsules and epoxy matrix. Having been healed, the surface became rough, and some smaller cavities on the virgin surface were covered by the polymerized healing agent (Fig. 6(b)). Under higher magnification, membrane from the crosslinked healing agent can be clearly identified, confirming polymerization of the healing agent (Fig. 6(c)). Furthermore, if the content of epoxy-loaded capsules is high enough (like 15 wt%), only the cured film can be observed on the fracture surface and all the cavities from ruptured capsules are shielded (Fig. 7(c)). EDS mapping analysis of the fractured surface indicates that fluorine is clearly

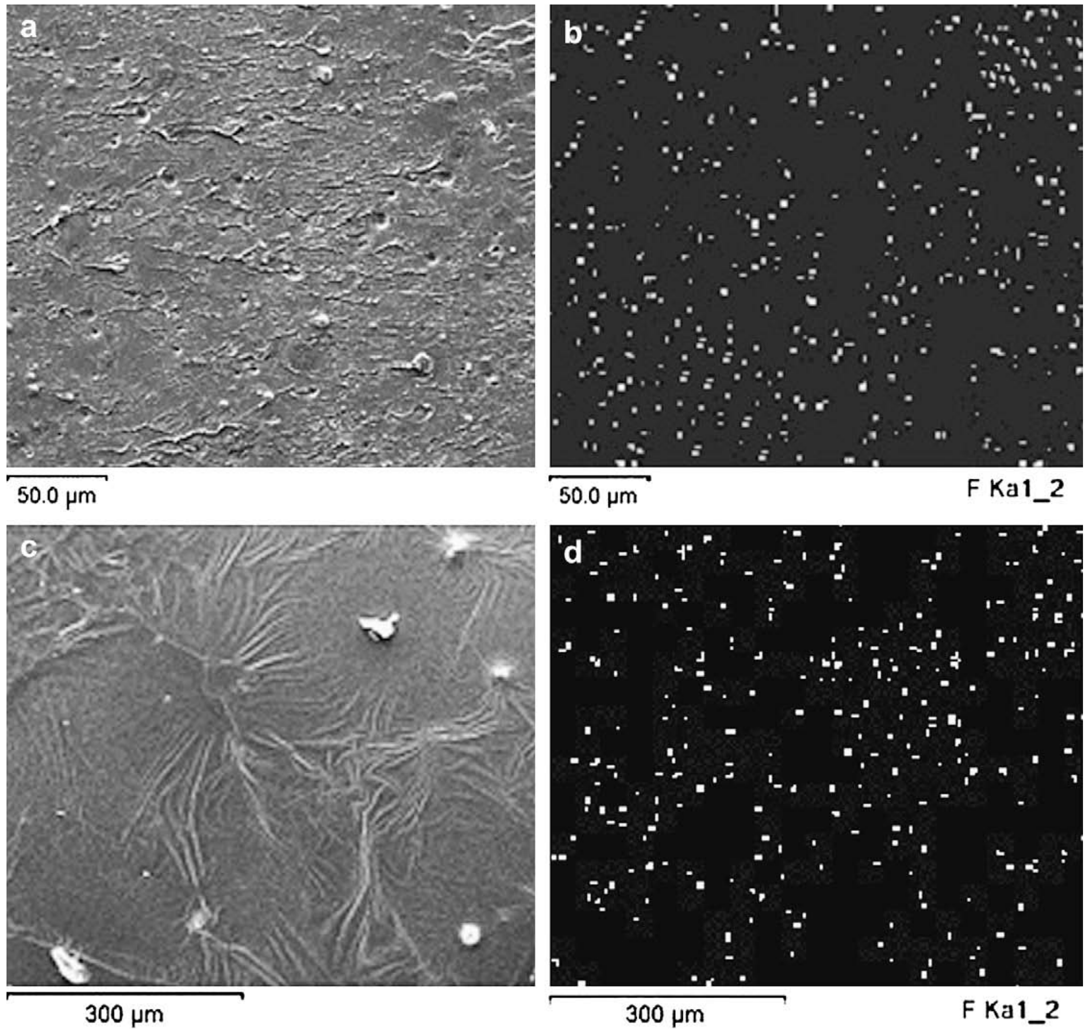

Fig. 7. SEM images in conjunction with EDS analysis (with fluorine as the indicator element) of the fracture surface of a healed self-healing epoxy composite specimen. Contents of epoxy-loaded microcapsules (30 μm) and $(C_2H_5)_2O\cdot BF_3$-loaded microcapsules (10 μm): (a,b) 5.0 wt% and 1.0 wt%, (c,d) 15 wt% and 1.0 wt%, respectively.

visible (Fig. 7(b) and (d)). It coincides with the fact that that the cured film is initiated by $(C_2H_5)_2O\cdot BF_3$. The above results prove that healing of cracks in the epoxy composites should be attributed to the adhesion of polymerized epoxy healing agent coming from the broken microcapsules.

To have a quantitative idea of the amount of the healing agent delivered, average thickness of bled epoxy, $\overline{d}$, is calculated according to the derivation of Rule et al. [22]:

$$\overline{d} = d_c \cdot c \cdot \phi$$

where d_c, c and ϕ stand for the average diameter, core content and weight content of epoxy-loaded capsules, respectively. Here it is assumed that the epoxy-loaded capsules were homogeneously distributed in the composites, and all the capsules at the crack surfaces can be fractured. In addition, the contribution of $(C_2H_5)_2O\cdot BF_3$-loaded microcapsules is neglected because of its low content.

Table 2 lists the calculated values of $\overline{d}$ and the measured healing efficiency in the case of different sizes and contents of epoxy-loaded capsules. It is seen that when $\overline{d}$ approaches 1 μm, the healing efficiency is also close to the highest value (i.e. ~80%). If we set $\overline{d} \approx 1$ μm as the critical value, the requirement is met at least when the content of the epoxy-loaded capsules ≥5 wt%. It agrees with the results given in Figs. 2 and 5. Additionally, Table 2 reveals that although $\overline{d}$ value of the composites containing 2.5 wt% larger size epoxy-loaded capsules ($d_c = 45$ μm) is similar to that of the composites containing 5 wt% smaller size epoxy-loaded capsules ($d_c = 25$ μm), the measured healing efficiencies of the two composites are greatly different. It might result from a geometric effect of the capsules. That is, the 2.5 wt% loading of larger capsules might lead to a localized bleeding of epoxy [34], with not enough or no catalyst being present at this location. The more capsules exist, the higher the probability of a meeting of both constituents and the initiation of the reaction.

Table 2
Estimated average thickness of the bled healing agent delivered to crack planes and the measured healing efficiency (η).[a]

d_c (μm)	c (%)	ϕ (2.5 wt%)		ϕ (5 wt%)		ϕ (10 wt%)		ϕ (15 wt%)	
		$\overline{d}$ (nm)	η (%)	$\overline{d}$ (nm)	η (%)	$\overline{d}$ (nm)	η (%)	$\overline{d}$ (nm)	η (%)
5	54	67	31.3	135	54.2	270	66.1	405	69.4
15	60	225	33.3	450	70.2	900	75.9	1350	77.7
25	68	425	36.0	850	76.5	1700	83.4	2550	81.0
30	70	525	36.2	1050	83.3	2100	87.6	3150	85.4
35	75	656	41.0	1313	84.9	2625	87.7	3938	85.8
45	79	889	45.0	1778	88.2	3555	89.4	5332	85.6

[a] Content of $(C_2H_5)_2O\cdot BF_3$-loaded capsules in the authentic self-healing specimens from which healing efficiency was measured: 1 wt%.

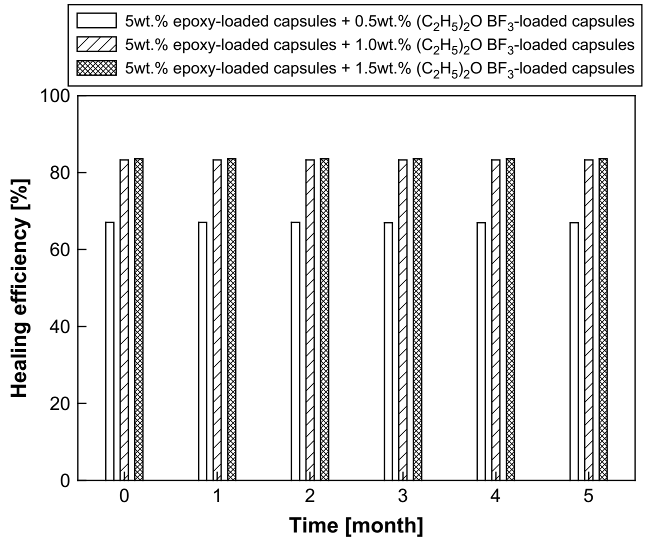

Fig. 8. Healing efficiency of the self-healing epoxy composites as a function of storage time at room temperature.

Stability and durability are important for self-healing materials. During storage at room temperature for 5 months, weight losses of epoxy- and $(C_2H_5)_2O\cdot BF_3$-loaded microcapsules are only around 0.5 and 0.25 wt%, respectively, probably due to evaporation of adsorbed moisture. Since the microcapsules are embedded in composite matrix in practical usage, which would further improve their storage stability. As a result, healing efficiency of the self-healing composite is almost constant within 5 months (Fig. 8). In fact, epoxy-loaded capsules are thermally stable in nature, which show no detectable weight loss at temperature lower than 200 °C [32]. Although boiling point of $(C_2H_5)_2O\cdot BF_3$ is 126–129 °C and its saturated vapor tension at 20 °C is 4.2 mm Hg, meaning that it has certain volatility, our experimental results demonstrate that the catalyst remains active for quite a long time. This should be attributed to the protection of catalyst offered by both the capsules and epoxy matrix.

It is worth noting that the curing temperatures used in the present work are relatively low, but it does not mean that the healing agent is not applicable for moderate or high temperature curable epoxy systems. According to the above thermal stability data, it can be reasonably deduced that the healing agent developed in this work might also be valid in the case of higher curing temperatures. Further experimental work is needed to verify the analysis.

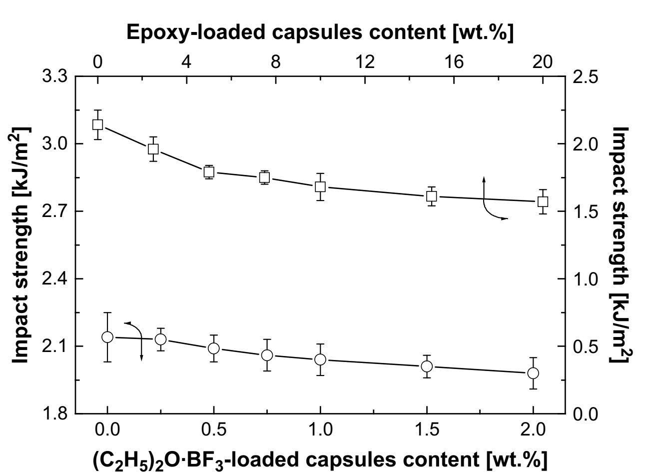

Fig. 9. Effect of contents of epoxy- and $(C_2H_5)_2O\cdot BF_3$-loaded capsules on impact strength of the composite. Epoxy-loaded microcapsules: core content = 70 wt%, average diameter = 30 μm. $(C_2H_5)_2O\cdot BF_3$-loaded microcapsules: core content = 20 wt%, average diameter = 10 μm.

3.4. Effect of healing agent capsules on mechanical properties of the composites

Incorporation of fillers into polymers would change intrinsic mechanical properties of the matrices. It is hoped that the embedded healing agent capsules would not bring about significantly negative influence. The results of mechanical tests demonstrate that addition of either $(C_2H_5)_2O\cdot BF_3$- or epoxy-loaded capsules has nearly no influence on tensile and flexural properties of epoxy composites within the filler content range of interests, except a slight decrease in flexural strength and modulus of the composites with epoxy-loaded capsules. It manifests that the interfacial interaction between the capsules and the matrix resin is quite strong and the microcapsules are able to carry certain load transferred by the interface under static testing condition. On the other hand, impact strength of the composites gradually decreases with a rise in the content of microcapsules, while the decrement is still insignificant (Fig. 9). After all, the capsules are not able to hinder crack propagation in the course of rapid deformation.

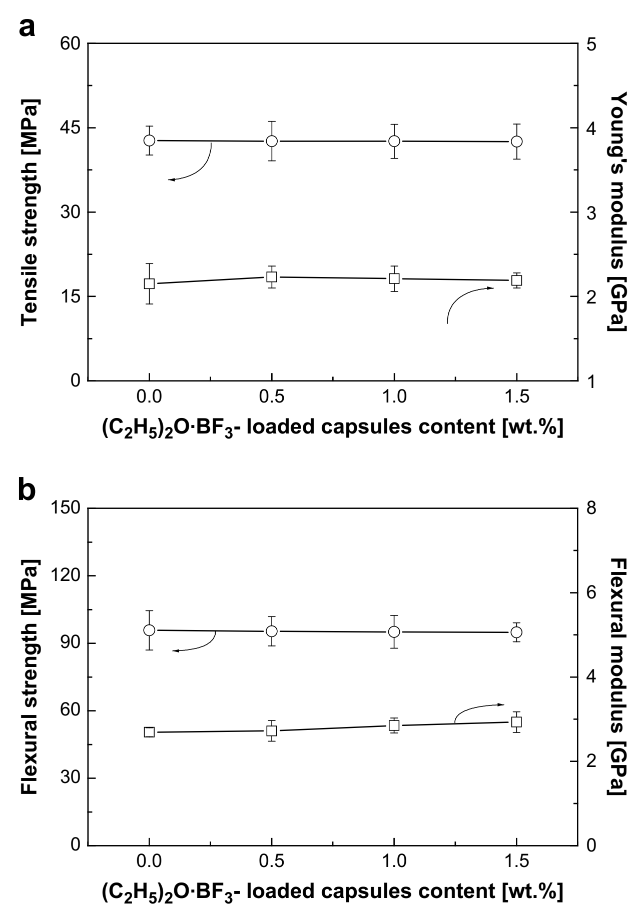

Fig. 10. Influence of content of $(C_2H_5)_2O\cdot BF_3$-loaded capsules on (a) tensile and (b) flexural properties of the self-healing epoxy composites containing 5 wt% epoxy-loaded capsules. Epoxy-loaded microcapsules: core content = 70 wt%, average diameter = 30 μm. $(C_2H_5)_2O\cdot BF_3$-loaded microcapsules: core content = 20 wt%, average diameter = 10 μm.

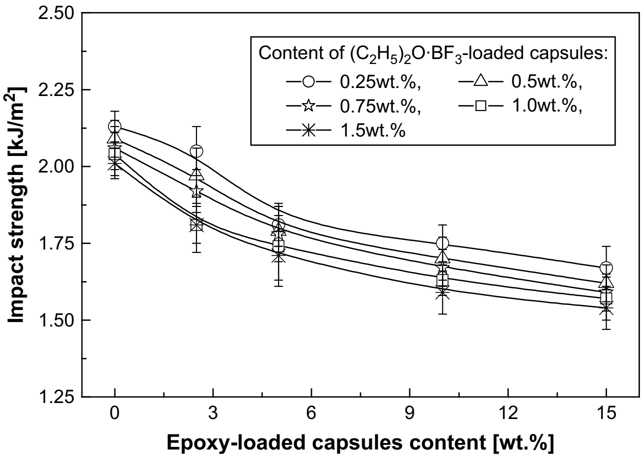

Fig. 11. Dependence of impact strength of the composites on contents of epoxy- and $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules. Epoxy-loaded microcapsules: core content = 70 wt%, average diameter = 30 μm. $(C_2H_5)_2O{\cdot}BF_3$-loaded microcapsules: core content = 20 wt%, average diameter = 10 μm.

To reveal joint action of the two types of microcapsules, mechanical properties of the composites containing both capsules were measured. Fig. 10 shows tensile and flexural properties of the composites with a constant content of epoxy-loaded capsules of 5 wt%, which is chosen because the above healing tests indicate it is the critical value for having high healing efficiency. Similar to the results of addition of individual type of the capsules, incorporation of both types of the capsules still does not lead to remarkable variation in the static mechanical properties (Fig. 10). Nevertheless, addition of the dual capsules can arouse evident decrease in impact strength of the composites (Fig. 11). The trend of embrittlement is more obvious at lower content of epoxy-loaded capsules. For the composite containing 5 wt% epoxy-loaded capsules and 1 wt% $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules, its impact strength is about 81% of that of unfilled epoxy.

Fig. 12 further examines impact performance of the composites as a function of epoxy-loaded capsules' size to understand its effect at constant filling concentrations. Because the capsules cannot arrest the development of cracks, the larger capsules would definitely cause higher stress concentration [35–37] and greater extent of reduction in impact strength. On the whole, the decay in impact strength is not severe, and can be limited to a marginal range so long as the amounts of the embedded capsules are not high.

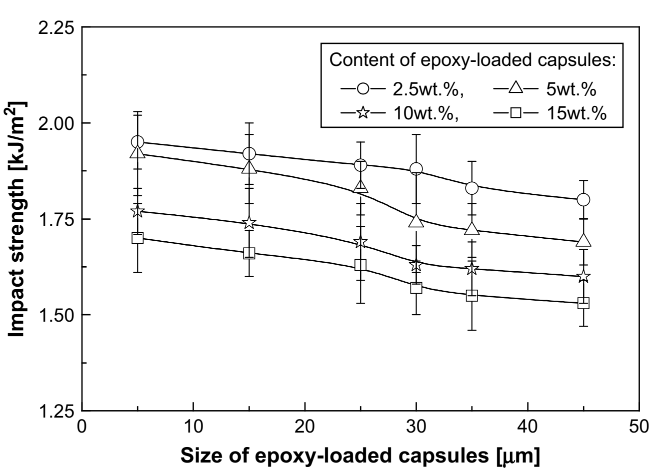

Fig. 12. Effects of size and content of epoxy-loaded capsules on impact strength of the composite containing 1 wt% $(C_2H_5)_2O{\cdot}BF_3$-loaded capsules. Epoxy-loaded microcapsules: core content = 70 wt%, average diameter = 30 μm. $(C_2H_5)_2O{\cdot}BF_3$-loaded microcapsules: core content = 20 wt%, average diameter = 10 μm.

4. Conclusions

The two-component healing agent consisting of epoxy- and $(C_2H_5)_2O{\cdot}BF_3$-loaded microcapsules proved to be effective in bonding cracks in epoxy composites without manual intervention. A very fast repair with satisfied healing efficiency was observed. Compared with the healing chemistry based on addition polymerization (e.g., thiol-epoxy pair [30]), the present one took effect at rather low catalyst content owing to the cationic polymerization character of the reaction. Additionally, stoichiometric ratio between the polymerizable component and its hardener was unnecessary. Long term tests indicated that the self-healing ability remained unchanged within 5 months.

Application of cationic polymerization healing agent also favored retaining original mechanical properties of the matrix owing to the lower content of healing agent capsules. Embedment of the healing agent capsules had nearly no influence on tensile and flexural properties of epoxy composites within the filler content range of interests, while impact strength of the composites slightly decreased with the capsules content. The reduction in impact strength can be limited to a marginal range by controlling the amounts and sizes of the healing capsules.

The high reaction rate of the healing agent resulted in uncompleted curing of epoxy. Increasing flow ability of the epoxy component of the healing agent would help to further improve healing efficiency. The research in this aspect is ongoing in the authors' lab.

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