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Improvement of fatigue resistance of epoxy composite with microencapsulated epoxy-SbF_5 self-healing system

X. J. Ye[1,2], Y. Zhu[2], Y. C. Yuan[3], Y. X. Song[2], G. C. Yang[2], M. Z. Rong[2], M. Q. Zhang[2]*

[1]Guangdong Provincial Public Laboratory of Analysis and Testing Technology, China National Analytical Center, 510070 Guangzhou, P. R. China
[2]Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, GD HPPC Lab, School of Chemistry, Sun Yat-Sen University, 510275 Guangzhou, P. R. China
[3]College of Materials Science and Engineering, South China University of Technology, 510640 Guangzhou, P. R. China

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Abstract. Rapid retardation and arresting of fatigue crack are successfully realized in the epoxy composite containing microencapsulated epoxy and ethanol solution of antimony pentafluoride-ethanol complex ($SbF_5 \cdot HOC_2H_5/HOC_2H_5$). The effects of (i) microcapsules induced-toughening, (ii) hydrodynamic pressure crack tip shielding offered by the released healing agent, and (iii) polymeric wedge and adhesive bonding of cured healing agent account for extension of fatigue life of the material. The two components of the healing agent can quickly react with each other soon after rupture of the microcapsules, and reconnect the crack only 20 seconds as of the test. The applied stress intensity range not only affects the healing efficiency, but also can be used to evaluate the healing speed. The present work offers a very fast healing system, and sets up a framework for characterizing speed of self-healing.

Keywords: *smart polymers, fracture and fatigue, self-healing, epoxy*

1. Introduction

Self-healing has been regarded as an important and smart measure to improve stability and durability of polymeric materials [1–3]. More and more researchers started to study this topic because of its scientific and technical merits. In addition to the degree of properties restoration enabled by self-healing, healing speed has attracted increasing research interests because cracks should be eliminated as soon as they are initiated [4]. It is critical for practice application to prevent catastrophic failure, especially for the products in service. There are two healing strategies available for polymers and polymer composites, i.e. intrinsic and extrinsic self-healing. The former operates through reversible inter- and/or intra-macromolecular interaction (like hydrogen bond [5], π–π stacking [6], ionic interaction [7], host-guest interaction [8], metal-ligand coordination [9], imine bond [10, 11], Diels-Alder bond [12], disulfide bond [13], C–ON bond [14], coumarin derivatives [15], and boronic ester linkages [16]), while the latter relies on the embedded healing agent (mostly fluidic) stored in microcapsules [17, 18] or microtubes [19, 20]. Compared to intrinsic self-healing, extrinsic self-healing is able to burst out fluidic healing agent upon cracking so that it is in a better position to realize high speed rehabilitation [21–26]. On the basis of this consideration, a few fast healing chemistries and the related healing systems were successively explored in our laboratory [27–33]. Cationic chain polymerization of epoxy monomers catalyzed by antimony pentafluoride [29, 30], for example, proved to heal cracks within seconds.

To further examine the fast self-healability of the system in authentic specimen, fatigue performance

*Corresponding author, e-mail: ceszmq@mail.sysu.edu.cn

of epoxy composite containing dual capsules, i.e. epoxy monomer-loaded microcapsules and ethanol solution of antimony pentafluoride-ethanol complex ($SbF_5 \cdot HOC_2H_5/HOC_2H_5$)-loaded microcapsules, is investigated in the present work. It is known that the competition between chemical kinetics of healing agents and mechanical kinetics of crack propagation determines the extent of fatigue life extension [34, 35]. In other words, retardation or arresting of fatigue crack is rather sensitive to the polymerization rate of healing agent. Therefore, the effect of fatigue crack induced liberation of healing agent can be conveniently monitored by mechanical response of the composite, i.e. *in-situ* crack re-binding and growth under cyclic stress. In contrast, other destructive characterization methods, like tensile [15] and impact tests [24, 27], need time for manually recombining the fractured specimens for healing and quite a few fast healing agent would have been cured in advance. The measured dependence of healing efficiency on healing time has to be associated with large error.

So far, fatigue resistance of self-healing polymers and polymer composites has not been extensively studied. Moreover, healing speed is not the main concern of these available works [35–43]. In this context, the present investigation might add to the researches in this area.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (EPON 828, epoxy value: 0.53~0.54 mol/100 g), supplied by Shell Co., served as the composite's matrix and the polymerizable component of healing system. Antimony pentafluoride (SbF_5) was purchased from Tianjin Institute of Physical and Chemical Engineering of Nuclear Industry, China. Borontrifluoride-2,4-dimethylaniline-complex ($BF_3 \cdot DMA$) and methyl hexahydrophthalic anhydride (MHHPA) were bought from Energy Chemical, Shanghai, China. Ethanol, tetraethyl orthosilicate (TEOS), styrene and methyl acrylate were supplied by Alfa Aesar GmbH, Germany. Prior to use, styrene and methyl acrylate were washed with sodium hydroxide aqueous solution (5 wt%), thereafter three times with water, dried over magnesium sulphate, and evaporated to dryness in vacuum. Azobisisobutyronitrile (AIBN) was obtained from Sigma-Aldrich, and purified by recrystallization. Melamine and formaldehyde were supplied by Sinopharm Chemical Reagent Co., Ltd, Shanghai, China.

2.2. Specimens preparation

Epoxy monomer was encapsulated by poly(melamine formaldehyde) (PMF) as described in ref. [44] The average diameter and core content of the resultant spheres are 130 μm and 91 wt%, respectively.

Ethanol solution of antimony pentafluoride·ethanol complex ($SbF_5 \cdot HOC_2H_5/HOC_2H_5$) was prepared by the method mentioned in ref. [45] to reduce the high reactivity of SbF_5 for easy handling. Next, silica walled microcapsules containing $SbF_5 \cdot HOC_2H_5/HOC_2H_5$ were prepared by vacuum aided infiltration [28]. The average diameter and core content of these hardener-loaded microcapsules are 6 μm and about 40 wt%, respectively.

Unfilled tapered double cantilever beam (TDCB) specimens (with groove length of 55 mm [46], Figure 1) were cast from the stoichiometric mixture of accelerant $BF_3 \cdot DMA$ (5 parts), curing agent MHHPA (80 parts) and epoxy EPON 828 (100 parts). Meanwhile, the self-healing TDCB specimens were prepared by uniformly compounding epoxy-loaded microcapsules and $SbF_5 \cdot HOC_2H_5/HOC_2H_5$-loaded microcapsules with the aforesaid mixture of $BF_3 \cdot DMA$, MHHPA and EPON 828. The compounds were degassed, poured into a preheated closed silicone rubber mold, and cured at 50 °C for 60 h and 70 °C for 12 h. Unless otherwise specified, the contents of the epoxy monomer- and hardener-loaded microcapsules were 10 and 0.6 wt%, respectively. The control composite specimen has the same composition as the self-healing one except that the hardener capsules were replaced by ethanol capsules.

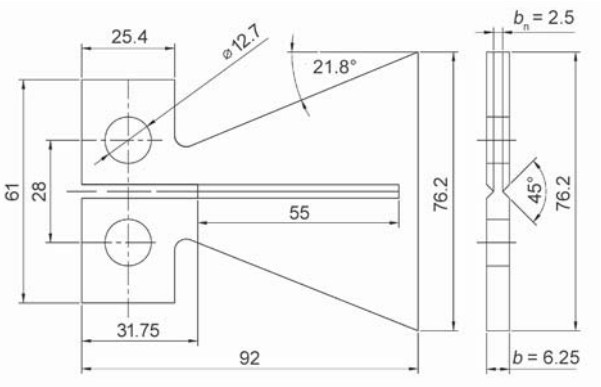

Figure 1. TDCB geometry with 55 mm side groove length. All dimensions are given in mm.

2.3. Characterization

For determination of static fracture toughness, K_{IC}, TDCB specimen was pin loaded and tested with a Hounsfield 10K-S universal testing machine at a crosshead speed of 0.3 mm/min at room temperature (25 °C). Then, the Equation (1) was used for the calculation [46]:

$$K_{IC} = \sqrt{G_{IC}E} = 2P_C\sqrt{\frac{m}{b_n b}} \quad (1)$$

where m (0.60 mm^{-1}) is a constant related to specimen geometry, b denotes specimen thickness, b_n is the crack width, and P_C is the peak force.

Autonomous healing behavior of the TDCB specimens under cyclic stress was evaluated by fatigue test using a Shimadzu air servo fatigue and endurance testing system ADT-AV02K1S5 with 2 kN load cell at 25 °C. The specimens were pre-cracked (~2.5 mm long) by a razor blade, and the pre-crack tip was ensured to be centered in the groove. The specimen was loaded cyclically immediately after the removal of the blade. A triangular waveform of 5 Hz was applied with a stress ratio, R, of 0.1 ($R = K_{min}/K_{max}$, where K_{min} and K_{max} denote the minimum and maximum values of the cyclic stress intensity, respectively). Fatigue cracks were grown within constant mode-I stress intensity factor range, ΔK_I ($\Delta K_I = K_{min} - K_{max}$). Five specimens were tested for each test when measuring static fracture toughness and cycles to failure.

The optically measured crack tip position and specimen compliance were plotted against number of cycles. The linear relationship between optically measured crack length and specimen compliance was used to calculate the crack tip position of the specimens at all times during the experiment [36]. Healing efficiency, λ, was defined by fatigue life extension [37]: $\lambda = (N_{healed} - N_{control})/N_{control}$, where N_{healed} and $N_{control}$ denote the total number of cycles to failure of the healed specimen and that of the control specimen without healing, respectively.

Fracture surfaces were observed by a Hitachi Model S-4800 field emission scanning electron microscope (SEM).

3. Results and discussion

3.1. Effect of the embedded healing capsules on toughness and fatigue life of epoxy composite

Incorporation of fluidic healing agent capsules into epoxy would significantly improve its fatigue performance by increasing the fracture toughness and hence extending the fatigue life [35–38]. Here in this work, the presence of microencapsulated healing agent has also raised the virgin monotonic fracture toughness of epoxy within a wide content range of the capsules. As shown in Figure 2a, when the proportion of epoxy-loaded capsules is less than 6 wt%, K_{IC} of the composite increases with a rise in the capsules concentration. Even when the content of epoxy-loaded capsules exceeds 10 wt%, K_{IC} of the composite starts to decrease but is still higher than that of unfilled epoxy until 14 wt%. The results imply that the microcapsules must be well bonded to the matrix [47], so that different fracture mechanisms than voids or solid particles are induced. Compared with the mirror-like fractured surface of unfilled epoxy (Figure 3a), that represents low resistance to crack propagation, the capsules-filled epoxy composite exhibits

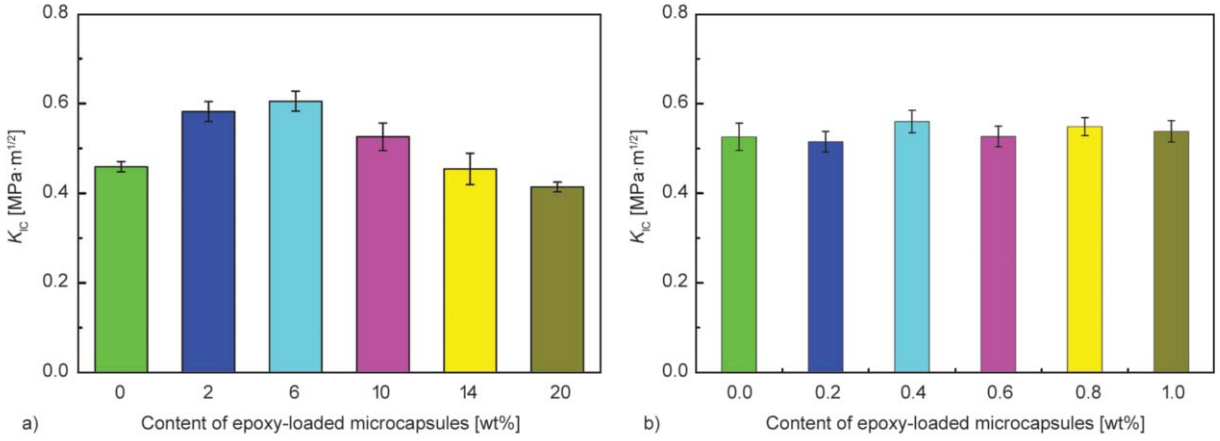

Figure 2. K_{IC} of epoxy composites as a function of (a) content of epoxy-loaded microcapsules and (b) content of hardener-loaded microcapsules. The dosage of hardener-loaded microcapsules is 0 in (a), while that of epoxy-loaded microcapsules is fixed at 10 wt% in (b).

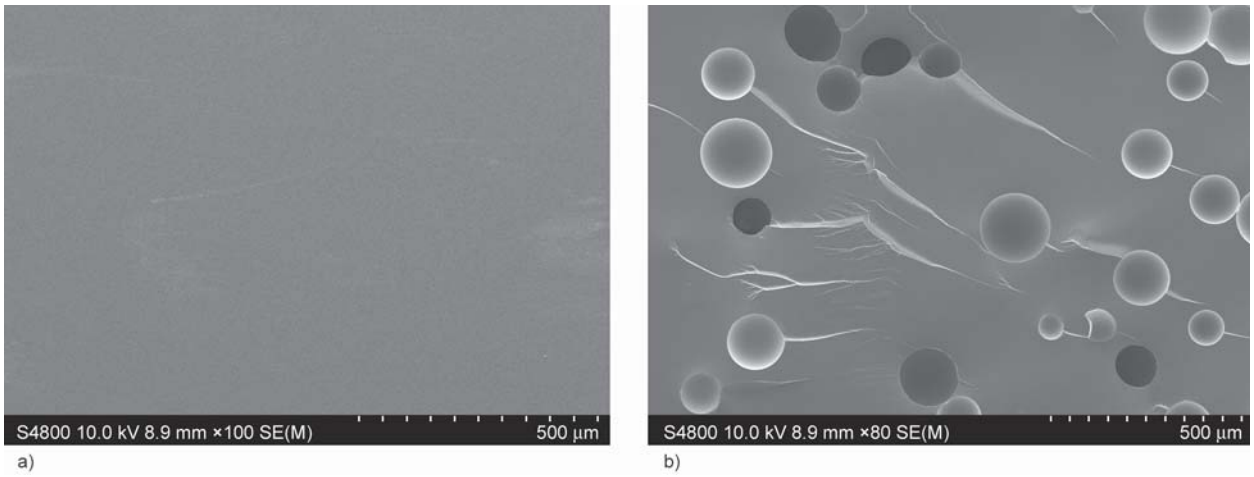

Figure 3. SEM micrographs of fracture surfaces of (a) unfilled epoxy and (b) epoxy composite filled with 10 wt% epoxy-loaded microcapsules. Cracks propagate from left to right in the images.

tails structures resulting from crack pinning and crack deflection [48] (Figure 3b). Such an out-of-plane divergence of cracking consumes more energy and hence offers higher fracture toughness.

Although the increment of fracture toughness is not significant enough, as characterized by the highest increment of 14.6%, the value is comparable to those of other self-healing epoxy composites containing dual capsules (e.g., 20.2% [38], and 35.3% [49]).

It is known that, the content of healing agent microcapsules must be neither too high nor too low [17]. The mechanical properties would be deteriorated when the dosage is too high, while the healing agent (released from the broken capsules) cannot cover the crack plane if the dosage is scarce. According to our study of recovery of impact strength as a function of healing agent concentration of the same self-healing composite, content of the epoxy-loaded microcapsules is fixed at 10 wt% hereinafter, so as to supply enough healing agent to fill the fatigue crack and toughen the epoxy composite as well.

Figure 2b reveals the influence of hardener ($SbF_5 \cdot HOC_2H_5/HOC_2H_5$)-loaded microcapsules on fracture toughness of the composite. Because the curing of epoxy catalyzed by SbF_5 follows the mechanism of cationic chain polymerization [27, 28], only small amount of the hardener is sufficient to ignite the reaction. The stoichiometric ratio of the reaction components required by addition polymerization [44] is no longer necessary so long as the hardener content exceeds a certain critical value, which is an advantage of the present healing system. Accordingly, the loading of the hardener capsules varies below 1.0 wt%. It is clear that K_{IC} of the composite nearly does not change within the range of interests, as the contents of the hardener capsules (≤1.0 wt%) are much lower than that of the epoxy-loaded microcapsules (10 wt%).

Although the hardener-loaded capsules seem to be negligible as a toughening agent when appearing together with epoxy-loaded microcapsules, they play an important role in healing cracks by curing the epoxy monomer released from the broken epoxy-loaded capsules in the crack tip region during fatigue tests [30]. It is seen from Figure 4 that with increasing dosage of the hardener-loaded microcapsules, fatigue life of the self-healing composites increases firstly and then decreases. This is mainly due to the fact that at the beginning the small amount of hardener-loaded microspheres fails to provide enough curing agent for polymerization, leading to incomplete curing of the liberated epoxy. In the case of high

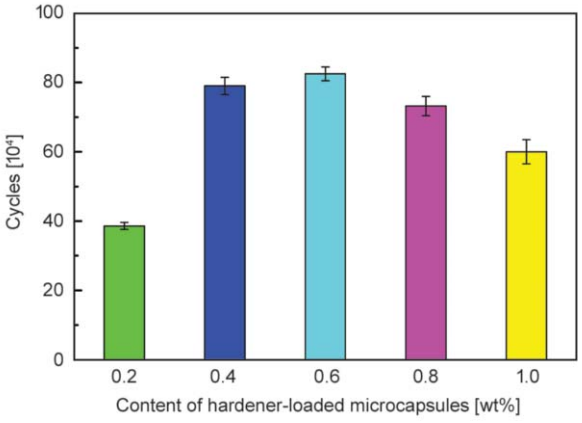

Figure 4. Cycles to failure of self-healing epoxy composites vs. content of hardener-loaded microcapsules. Content of epoxy-loaded microcapsules is fixed at 10 wt%. Testing conditions: $K_{max} = 0.258$ MPa·m$^{1/2}$, $K_{min} = 0.026$·MPa m$^{1/2}$, $\Delta K_I = 0.232$ MPa·m$^{1/2}$, $f =$ 5 Hz, $R = 0.1$.

loading of hardener microspheres, higher amount of ethanol included in the excessive hardener ($SbF_5 \cdot HOC_2H_5/HOC_2H_5$) may produce defects as stress concentration sites in the wedge formed by the cured healing agent. Fatigue life of the composite has to be shortened as a result of the decreased resistance to fatigue crack growth [35]. In this context, the intermediate content of 0.6 wt%, which corresponds to the highest cycle to failure, is chosen as the optimal proportion. Under the circumstances, adequate hardener is guaranteed to quickly and completely cure the released epoxy monomer, without generating remarkable defects in the polymeric wedge.

3.2. Fast self-healing process revealed by fatigue tests

Development of fatigue crack driven by cyclic stress of the related materials is depicted in Figure 5. To rule out the effects of microcapsules toughening and possible hydrodynamic pressure crack-tip shielding of the released healing fluids (an effect of viscous flow within a fatigue crack that decreases the effective range of stress intensity and reduces fatigue crack growth rate [36, 37]), the plot of the control composite containing epoxy- and ethanol-loaded microspheres is also given together with those of unfilled epoxy and self-healing epoxy composite. Relatively speaking, the slope of the dependence of crack length on fatigue cycle of the self-healing specimen (curve 3) is much more gradual, which means that its fatigue life is greatly extended. In the course of fatigue crack growth, the embedded microcapsules in the crack tip are successively ruptured, releasing the healing agent into the crack plane as proved by Figure 6. Accordingly, hydrodynamic pressure crack tip shielding takes effect, as the case of the control specimen (curve 2) where no reaction could occur. Therefore, fatigue life of the control specimen is about 66.7% higher than that of the unfilled epoxy specimen. It is interesting to see when the released healing agent is allowed to be quickly cured to build up a restoration agent membrane at crack tip to provide effects of cured wedge and adhesive bonding, fatigue crack can be more efficiently retarded as a result of significantly reduced effective stress intensity factor range, ΔK_{eff} ($\Delta K_{eff} = \Delta K_I - \Delta K_{toughening} - \Delta K_{liquid} - \Delta K_{bonding} - \Delta K_{wedge}$, where $\Delta K_{toughening}$ is the stress intensity due to microcapsules induced increase of matrix ductility, ΔK_{liquid} the crack-opening and crack-closure stress intensity from viscosity resistance of the liquid, $\Delta K_{bonding}$ the stress intensity due to the combined (tensile) stresses in adhesives across the crack faces, and ΔK_{wedge} the crack-closure stress intensity due to the wedge from adhesives gelling and hardening [38]. The lower ΔK_{eff} implies smaller driving force for the crack growth and hence longer fatigue life). In this case, extension of fatigue crack is further slowed down and fatigue life of the self-healing composite is 282 and 537% longer than those of the control and unfilled epoxy specimens, respectively.

It is worth noting that, the initial slope of curve 3 in Figure 5 is lower than that of the latter part. That is because large amount of healing agent is released and cured when the pre-crack (~2.5 mm long) is made. Comparatively, the quantity of the healing agent subsequently released due to cyclic stress and fatigue crack extension is much smaller. The effects of cured wedge and adhesive bonding of the healing agent in the latter stage are thus less remarkable than those in the initial stage. Nevertheless, the fractographs in Figure 6 demonstrate that the cured membrane generated by the released healing agent

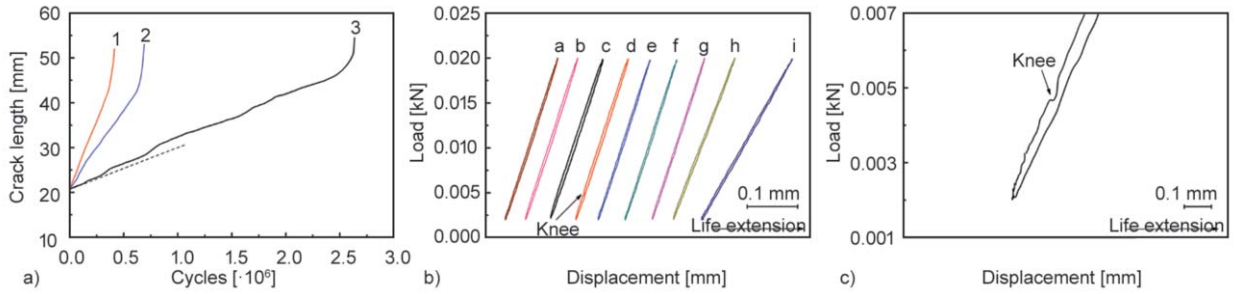

Figure 5. (a) Crack length versus fatigue cycle of (1) unfilled epoxy, (2) control and (3) self-healing epoxy composite. (b) Load-displacement curves of self-healing epoxy composite measured during selected cycles in (a). The times counted from starting of fatigue test are shown on top of the corresponding curves. (c) Enlarged view of the curve at 20 seconds in (b) showing the knee phenomenon. Testing conditions: $K_{max} = 0.224$ MPa·m$^{1/2}$, $K_{min} = 0.022$ MPa·m$^{1/2}$, $\Delta K_I = 0.202$ MPa·m$^{1/2}$, $f = 5$ Hz, $R = 0.1$.

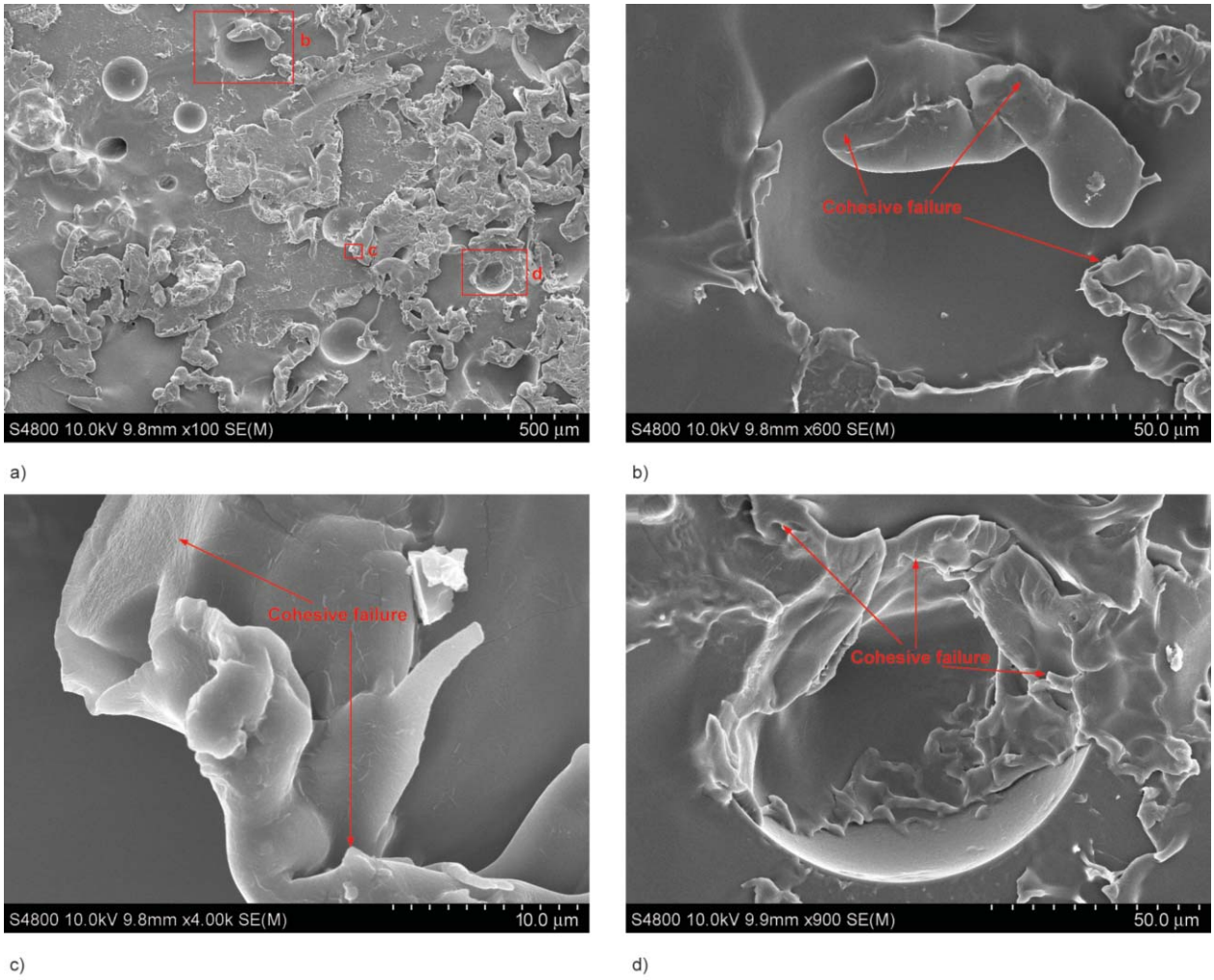

Figure 6. SEM micrographs of fatigue fracture surfaces of the self-healing epoxy composite. Testing conditions: K_{max} = 0.224 MPa· $m^{1/2}$, K_{min} = 0.022 MPa·$m^{1/2}$, ΔK_I = 0.202 MPa·$m^{1/2}$, f = 5 Hz, R = 0.1.

can well cover the crack surfaces. Accompanying cohesive failure of the healing membranes, fatigue crack gradually passes through the polymeric wedge. Moreover, the remains of the broken wedge still adhere to the cracked plane and decrease the effective stress intensity factor range at the crack tip.

Although the variation in the slope of crack length versus fatigue cycle can sensitively reflect the change of the amount of the healing agent and its performance, we still cannot determine when the healing starts. To look into the details of the self-healing process, load versus displacement of the self-healing epoxy composite is analyzed. As shown in Figure 5b and Figure 5c, a knee point or a deflection appears about 20 seconds as the fatigue test begins. Evidently, the healing agent in the crack plane is converted to solid polymeric wedge as of this time. The deduction coincides with the results of the same healing system introduced to the fatigue crack tip of unfilled epoxy specimen in terms of manual infiltration [30]. Therefore, the time at which a knee point is observed on the dependence of load on displacement can be regarded as the onset time of self-healing. Comparatively, the measurable healing of other systems used to be first observed couple of minutes or even longer time after the tests started [24–28, 44, 46, 50]. It means that the present healing agent can offer much faster healing.

3.3. Effect of ΔK_I on self-healing efficiency

Owing to the configuration of fatigue test, the measured self-healing efficiency is closely dependent on the applied stress intensity factor, ΔK_I, in addition to the polymerization rate of embedded healing agent. In the following, fatigue performance of the self-healing epoxy composite measured at three ΔK_I values is discussed.

As shown in Figure 7a and Figure 7b, the repairing efficiencies tested at higher ΔK_I values (0.252 and 0.232 MPa·$m^{1/2}$) are 64.9 and 167%, respectively. In these cases, mechanical kinetics of crack propagation

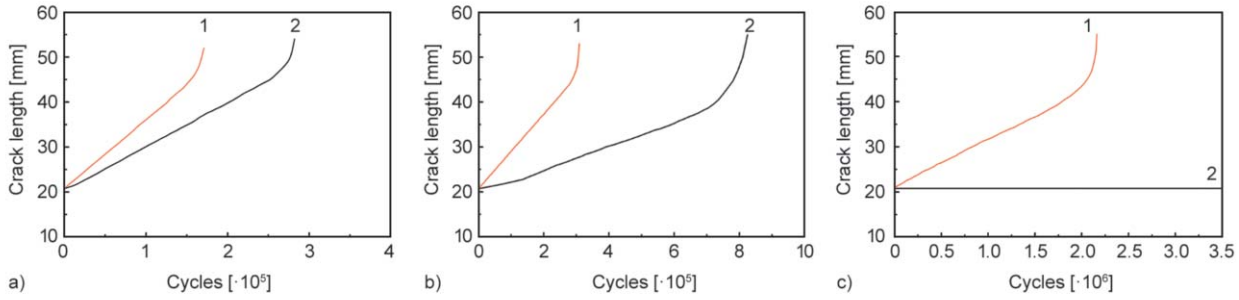

Figure 7. Crack length vs. fatigue cycles of (1) control and (2) self-healing epoxy composite. Testing conditions: (a) K_{max} = 0.280 MPa·m$^{1/2}$, K_{min} = 0.028·MPa m$^{1/2}$, ΔK_I = 0.252 MPa·m$^{1/2}$, f = 5 Hz, R = 0.1; (b) K_{max} = 0.258 MPa·m$^{1/2}$, K_{min} = 0.026 MPa·m$^{1/2}$, ΔK_I = 0.232 MPa·m$^{1/2}$; (c) K_{max} = 0.202 MPa·m$^{1/2}$, K_{min} = 0.020 MPa·m$^{1/2}$, ΔK_I = 0.182 MPa·m$^{1/2}$.

predominates so that fatigue crack grows faster. Moreover, the amount of the released healing agent squeezed out of the crack tip would be higher, implying that the effects of hydrodynamic pressure crack tip shielding and adhesive bonding have to be weakened [36, 37]. In the meantime, the polymeric wedge formed at crack tip is easy to be deformed or even destroyed. All these factors go against fatigue life extension.

When ΔK_I value is reduced to 0.182 MPa·m$^{1/2}$, it is interesting to see from Figure 7c that fatigue crack is arrested as chemical kinetics of healing agent plays the leading role. The crack can hardly advance forward within the entire range of measured cycles, which corresponds to infinite healing efficiency. Under the circumstances, fewer healing agent is squeezed out of crack tip, and bigger polymeric wedge can be produced within short time as a result of the fast curing of the healing system. The experiment clearly highlights the significance of healing speed.

Figure 8 summarizes the healing efficiencies measured at different ranges of applied stress intensity factor. When ΔK_I is decreased, the fatigue crack retardancy is obviously increased as discussed hereinbefore,

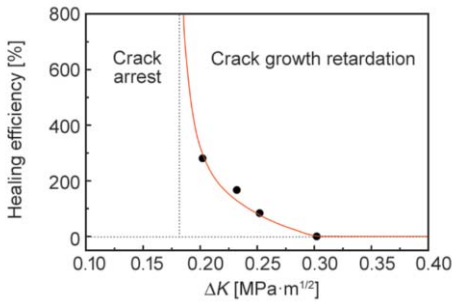

Figure 8. Healing efficiency of self-healing epoxy composite as a function of range of applied stress intensity factor. The data are calculated partly using the results in Figure 5a and Figure 7

leading to longer fatigue life. The critical ΔK_I value lies in 0.182 MPa·m$^{1/2}$. For $\Delta K_I \leq$ 0.182 MPa·m$^{1/2}$, fatigue crack of the self-healing epoxy composite is fully arrested. Based on this finding, it is known that the critical ΔK_I value may act as another measure of healing speed, in addition to the onset healing time estimated from displacement dependence of load (Figure 5). That is, the higher critical ΔK_I value suggests the faster the healing reaction. It reflects the ultimate effect of healing agent, and may be more meaningful than the onset healing time when comparing chemical kinetics of different self-healing agents working for the same polymer (i.e. the polymer to be repaired).

4. Conclusions

Self-healing epoxy composite filled with microencapsulated epoxy monomer and SbF_5 HOC_2H_5/HOC_2H_5 proves to be able to retard or arrest fatigue crack growth. The beneficial effects of the microcapsules are embodied in the form of intact fluid-loaded spheres, released fluidic healing agent, and solidified version of the healing agent. Firstly, the embedded microcapsules toughen the epoxy matrix. Then, the crack induces breakage of the healing capsules, and the liberated fluidic healing agent hinders the advancement of crack via hydrodynamic pressure crack tip shielding. Finally, the released healing agent is polymerized forming polymeric wedge and adhesive bonding, both of which obstruct crack propagation. Because the curing of the healing system proceeds very fast, the healing represented by the generation of solid wedge is detected only 20 seconds after start of the fatigue test. In this context, the healing agent developed in this work possesses the application potential for autonomic fast restoration of polymer products.

Acknowledgements

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