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Self-healing epoxy composites – Preparation and effect of the healant consisting of microencapsulated epoxy and latent curing agent

Tao Yin [a], Min Zhi Rong [b], Ming Qiu Zhang [b,*], Gui Cheng Yang [a]

[a] *Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, OFCM Institute, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, PR China*
[b] *Materials Science Institute, Zhongshan University, Guangzhou 510275, PR China*

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Abstract

To provide epoxy based composites with self-healing ability, two-component healing system consisting of urea–formaldehyde microcapsules containing epoxy (30–70 μm in diameter) and $CuBr_2(2\text{-MeIm})_4$ (the complex of $CuBr_2$ and 2-methylimidazole) latent hardener was synthesized. When cracks were initiated or propagated in the composites, the neighbor microencapsulated epoxy healing agent would be damaged and released. As the latent hardener is soluble in epoxy, it can be well dispersed in epoxy composites during composites manufacturing, and hence activate the released epoxy wherever it is. As a result, repair of the cracked sites is completed through curing of the released epoxy. The present paper studied the preparation of epoxy microcapsules by amino resins, and the influencing factors as well. On the basis of this work, mechanical properties of the epoxy filled with the healing system were evaluated. It was found that incorporation of the two-component healing system nearly did not change the fracture toughness of the neat epoxy, as indicated by the single-edge notched bending test. In the case of 10 wt% microcapsules and 2 wt% latent hardener, the self-healing epoxy exhibited a 111% recovery of its original fracture toughness. Besides, the preliminary result of double-cantilever beam testing showed that the plain weave glass fabric laminates using the above self-healing epoxy as the matrix received a healing efficiency of 68%.
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1. Introduction

Long-term durability and reliability are critical for polymer–matrix composites used in structural applications [1]. The exposure to harsh environment would lead to the degradations of components made from these materials. Comparatively, microcracking is one of the fatal deteriorations generated in service, which would bring about catastrophic failure of the composites and hence significantly shorten the lifetimes of structures. Considering that the damages inside the composites are difficult to be perceived and to repair in particular, the materials had better to have the ability of self-healing.

So far, the achievements in this aspect fall into two categories: self-healing without and with the aid of healing agent. The works by Chen et al. represent the former school [2,3]. They synthesized highly cross-linked polymeric materials with multi-furan and multi-maleimide via Diels–Alde reaction. At temperatures above 120 °C, the ''intermonomer'' linkages disconnect but then reconnect upon cooling. This process is fully reversible and can be used to restore fractured parts of the polymers. However, the low glass temperatures of these polymers (30–40, 80 °C) [3] obstruct them from replacing epoxy, the thermosetting polymer widely used as the matrix of advanced composites.

For healing agent aided self-mending, the agent should be liquid at least at the healing temperature. It is generally encapsulated and embedded into the composites' matrix.

* Corresponding author. Tel./fax: +86 20 84036576.
E-mail address: ceszmq@zsu.edu.cn (M.Q. Zhang).

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As soon as the cracks destroy the capsules, the healing agent would be released into the crack planes due to capillary effect and heals the cracks. According to the compositions, the healing agents can be classified as single-component and two-component ones. The single-component healants, like cyanoacrylate [4,5] and polyvinyl acetate [6], are able to be cured under the induction of air, and hence not suitable for healing damages deep in the composites. The two-component system consists of polymerizable resin and hardener. When they meet, polymerization is activated so that the cracked parts can be bonded. Usually, encapsulation of the healing agents is conducted using fragile-walled containers. Dry filled the glass pipette tubes with a one-part cyanoacrylate and a two-part epoxy adhesive, respectively [4,5]. Similar approach was adopted by Motuku et al. [7] and Zhao et al. [6]. Because the hollow glass capillaries have diameters (on millimeter scale) much larger than those of the reinforcing fibers in composites, they have to act as initiation for composites failure [8]. Instead, Bleay et al. employed hollow glass fiber (with an external diameter of 15 μm and an internal diameter of 5 μm) to minimize the detrimental effect associated with large diameter fibers [8], but filling of repair species into such fine tubes becomes rather difficult.

White and his co-workers sealed dicyclopentadiene (DCPD) into microcapsules made from urea–formaldehyde resin. Then, the microencapsulated monomer was added into epoxy based composites together with powdered Grubbs' catalyst. In the case of cracking, the released DCPD contacts the catalyst, a ring-opening-metathesis polymerization (ROMP) of DCPD would take place and the cracked faces can thus be repaired [9,10]. The healing at 80 °C yields 80% recovery of virgin interlaminar fracture toughness [11]. Comparatively, this method is superior to the aforesaid ones in practical applicability, despite the fact that it also has some problems as viewed from long-term service. The validity of the healing agent DCPD is limited. Higher temperature or longer resting time might result in polymerization, and of course, invalidation of it. If inhibitor is applied, the rate of healing has to be reduced. Besides, the activity of Grubbs' catalyst would be influenced by the amine curing agent contained in the surrounding epoxy resin.

The present work also used two-component healant, but the recipe is different from those reported previously. Epoxy was microencapsulated as polymerizable healing resin in hopes of guaranteeing miscibility between the healing agent and the epoxy based composites. Besides, the complex of $CuBr_2$ and 2-methylimidazole ($CuBr_2$(2-MeIm)$_4$) was synthesized as the latent hardener of the epoxy healing agent. The complex possesses long-term stability, and would be dissociated into $CuBr_2$ and 2-methylimidazole again at around 130–170 °C [12–14]. Taking advantage of this habit, curing of the released epoxy healing agent catalyzed by 2-methylimidazole (i.e. cracks healing) can be triggered at the dissociation temperature of $CuBr_2$(2-MeIm)$_4$, which is higher than the curing temperature for making the composites. Another advantage of $CuBr_2$(2-MeIm)$_4$ lies in its dissolubility in uncured epoxy. As a result, the latent curing agent can be homogenously pre-dispersed (dissolved) in the composites' matrix on molecular scale. It is believed that this might increase the probability of contact between the epoxy resin from the ruptured microcapsules and the dissociated imidazole. That is, the released epoxy healing agent can be activated wherever it is. In comparison with poly(DCPD), the healing system studied in this work (i.e. $CuBr_2$(2-MeIm)$_4$ cured epoxy) is more compatible with epoxy matrix of composites that usually employs amine curing agent. Consequently, higher adhesion strength and better repair effect can be expected. Fig. 1 shows the concept of the self-healing epoxy based laminates.

The healing method studied here is based on manual intervention (i.e. heating). Its application is related to the development of intelligent structural health monitoring [15] or damage self-sensing techniques [16]. By accurate

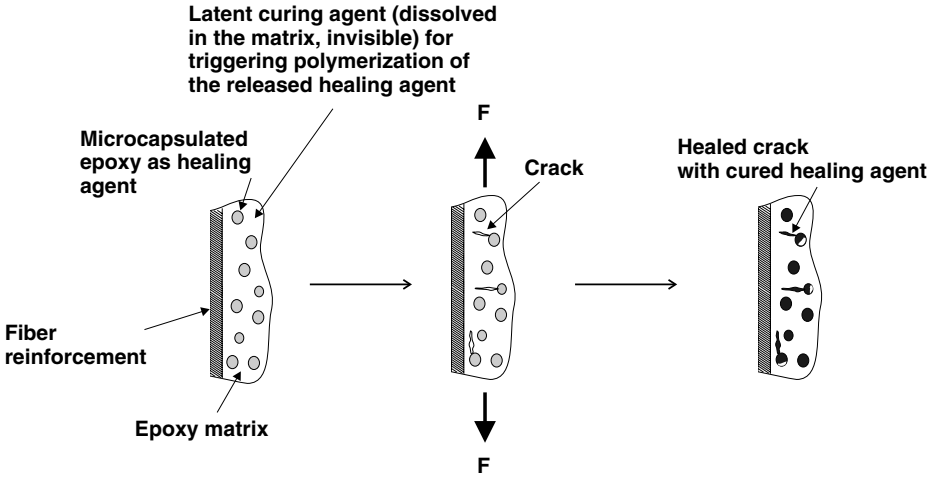

Fig. 1. Schematic drawing of the principle of self-healing epoxy based laminates.

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