SELF-HEALING OF CRACKS IN EPOXY VIA FREE RADICAL POLYMERIZATION

M. Q. Zhang, M. Z. Rong and X. B. Jiang

Materials Science Institute, Sun Yat-sen (Zhongshan) University, Guangzhou 510275, P. R. China
Email: ceszmq@mail.sysu.edu.cn

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ABSTRACT

Self-healing polymers and polymer composites have attracted more and more research interests of materials scientists owing to their ability to eliminate internal cracks in an autonomic way. According to the healing mechanisms, these smart materials fall into two categories: intrinsic and extrinsic [1]. The former conducts crack repair without the help of any healing agent, and the macromolecules themselves are able to be reconnected under certain circumstances. In contrast, the latter contains healing agent, which can be delivered to the damaged parts upon cracking of the materials and then rebind the separated faces.

In the case of extrinsic self-healing, the healing agent has to be stored in microcapsules or fine tubes including hollow fibers and micro-channels to preserve its activity. Liberation of the healing agent starts as soon as the fragile reservoirs are broken by the propagating cracks. The subsequent rehabilitation originates from polymerization of the released healing agent (including ring-opening metathesis polymerization of dicyclopentadiene (DCPD) [2], addition and ionic polymerization of epoxy [3-6], and condensation polymerization of polysiloxane [7]) or solvent effect [8].

The authors developed self-healing epoxy with embedded epoxy monomer-loaded microcapsules and hardener (consisting of mercaptan and tertiary amine catalyst)-loaded microcapsules [5]. Considering that healing agent should timely reach the damage sites, high flowability of the chemicals is required. In this context, epoxy monomer has inherent shortcoming because of its higher viscosity.

In this work we propose a healing chemistry based on free radical polymerization of styrene. Compared with epoxy monomer, styrene has much lower viscosity. Accordingly, two types of microcapsules, styrene and accelerant-loaded capsules and benzoyl peroxide (BPO)-loaded capsules, are prepared and embedded in epoxy matrix to fabricate room temperature self-healing epoxy materials. Following the aforesaid extrinsic self-healing mechanism, the product of polymerization of styrene initiated by BPO, i.e. polystyrene (PS), serves as binder to fill up the cracked portions of the matrix epoxy. The authors of this paper discuss manufacturing of the microcapsules, and characterize the resultant self-healing epoxy. It is worth noting that the species of the monomers containing double bonds are far more than those containing epoxide groups. Accordingly, the spectrum of healing agent species would be broadened if the present plan works.

The experimental results show that microencapsulation of styrene and BPO in terms of melamine-formaldehyde resin as the wall material can be successfully conducted via in-situ polymerization in emulsion. By optimizing the reaction conditions, including species of emulsifier, pH value, reaction time, molar ratio of melamine and formaldehyde, etc., qualified microcapsules containing styrene and BPO are produced, respectively. After encapsulation, activity of the highly active BPO proves to be maintained.

When the styrene- and BPO-loaded microcapsules are embedded in epoxy, fracture of the composites proved to be able to induce breakage of the capsules. The core substances (i.e. healing agent) are delivered to the cracked planes and free radical polymerization of styrene initiated by BPO takes place, reconnecting the split composites as characterized by recovery of impact strength to certain extent (Figure 1).

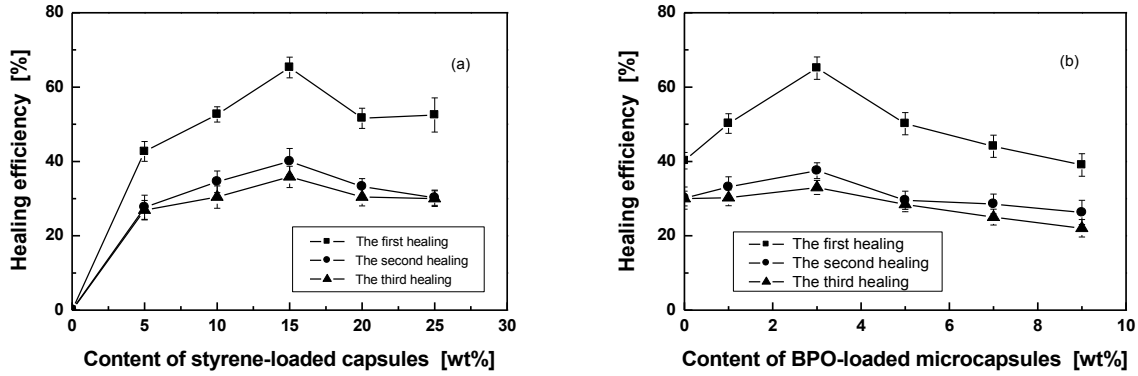

Figure 1: Healing efficiency of self-healing epoxy composites containing styrene- and BPO-loaded microcapsules as a function of (a) content of styrene-loaded capsules at a fixed content of BPO-loaded capsules of 3 wt%, and (b) content of BPO-loaded capsules at a fixed content of styrene-loaded capsules of 15 wt%. Size and core content of the styrene-loaded capsules: 30 μm and 40 wt%. Size and core content of the BPO-loaded capsules: 50 μm and 45 wt%.

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