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Self-Healing Ag/Epoxy Electrically Conductive Adhesive Using Encapsulated Epoxy-Amine Healing Chemistry

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ABSTRACT: In this study, a dual-microcapsule epoxy-amine self-healing concept is used for electrically conductive adhesives (ECAs). It provides the ECA samples with the ability to recover mechanical and electrical properties automatically. Epoxy and amine microcapsules were prepared and incorporated into silver/epoxy ECAs. The healing efficiency and bulk resistivity of the undamaged, damaged, and healed specimens were measured, respectively. The optimal loading of the epoxy and amine microcapsules is 6 wt % (weight ratio 1.05), and the bulk resistivity of the healed specimens is 3.4×10^{-3} Ω cm. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41483.

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INTRODUCTION

Electronic packaging, the technology of mechanically and electrically interconnecting a multiplicity of components into an integrated system, has been dominated by tin/lead based solders for a long time.[1,2] However, due to the toxicity of lead and its effect on human health, many counties, such as Japan and European Union, have banned the use of lead or are trying to minimize its usage.[3,4] Recently, extensive efforts have been paid to develop environmental friendly alternatives for the Pb-containing solders.

Electrically conductive adhesives (ECAs), which are comprised of polymer binders (provide mechanical strength) and metal fillers (act as channel for charge transport), are considered as one of the most promising replacements of Pb-based solders in electronic assembly applications.[5–8] ECAs possess some potential advantages, such as environmental friendly, finer pitch printing, lower temperature processing and simple processing.[9,10] Since a few decades, they have been used in hybrid, die-attach and display assembly. However, owing to the limitations of ECAs, most of them are related to reliability aspects, for instance, limited impact resistance, unstable contact resistance, low adhesion, and conductivity etc., complete replacement of Pb-based solders by ECAs is yet not possible.[11–13] Besides, during the service life, ECAs undergo changes in mechanical properties leading to formation of microcracks deep in the structure where detection is difficult and repair is almost impossible. These microcracks will subsequently propagate and result in mechanical degradation and electrical failure in microelectronic polymeric components. Although many efforts have been made to improve the electrical,[14,15] mechanical properties,[16]and reliability of ECAs,[17,18] the investigations on the automatic healing method of the microcracks on ECAs are rare.

Self-healing materials have received increasing attention since the concept was proposed in 1980s.[19] This is due to its capability to sense the failure and respond to repair the micro cracks in the polymeric matrixes automatically. Recent studies demonstrated that self-healing polymers show great potential for extending the fatigue life as well as the safety of the materials.[20–22] In general, self-healing polymers could be classified into three categories: (1) using fragile pipelines to storage polymerizable monomers and then compound them with the target matrixes;[23–25] (2) using microencapsulated or phase-separated liquid resins or solvents and then embed them with the materials;[26–28] (3) using inherently reversible bonding in the matrix polymer to affect healing via thermally reversible reactions.[29] Owing to the feasibility of mass production and broadness of application, the microcapsulation strategy is of particular interest.

Several microcapsule-based self-healing systems have been presented, such as dicyclopentadiene/Grubbs' catalyst,[30] epoxy/amine,[31] and polydimethylsiloxane/dimethyldineodecanoate tin

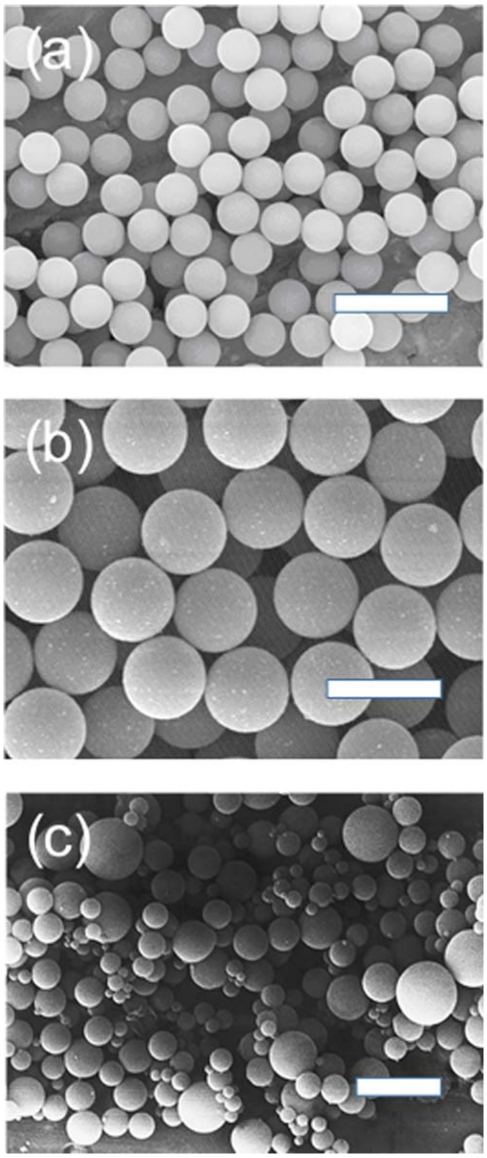

Figure 1. SEM photographs of (a) epoxy-containing microcapsules and (b) amine-containing microcapsules. (c) 1 : 1 mixture of epoxy/amine-containing microcapsules. Inserted scale bar is 50 μm.

catalyst[32] etc. Since epoxy has good adhesion to many materials and is an ideal candidate for versatile healing agent. In addition, epoxy resin is widely used as polymeric binder in ECA formulations because of their outstanding mechanical and thermal properties as well as processability.[33] Herein, we describe the successful application of the self-healing concept to the Ag-epoxy based ECA.

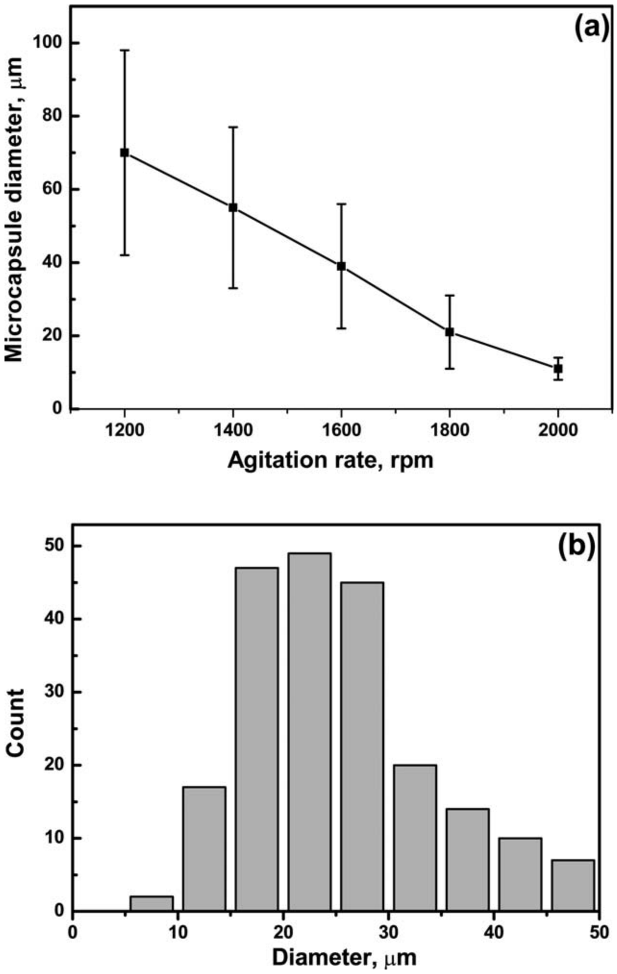

Figure 2. (a) Plot of size distribution of amine-containing microcapsules by agitation rate. (b) Size distribution of amine-containing microcapsules prepared at 1800 RPM.

Diethylenetriamine (DETA) is used as curing agent in ECA formulations. However, the encapsulation of liquid amine (DETA) is very difficult. Since it is an aliphatic amine and possesses extremely high reactivity with epoxy. It can cure the epoxy even at room temperature. Additionally, preparation of ECA samples may rupture microcapsules in some sense. Therefore, a dual-microcapsule epoxy-amine self-healing system was used to provide the EAC samples better storage stability. Epoxy and amine microcapsules were prepared, respectively. Healing performance of the ECAs was measured by tapered double cantilever beam (TDCB). Bulk resistivity of the system was studied as well.

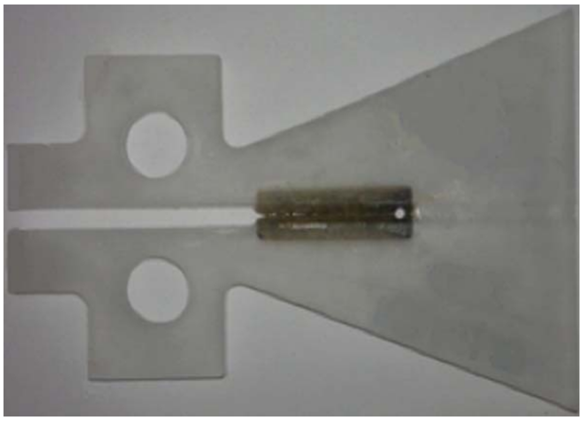

Figure 3. Photograph of TDCB specimen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

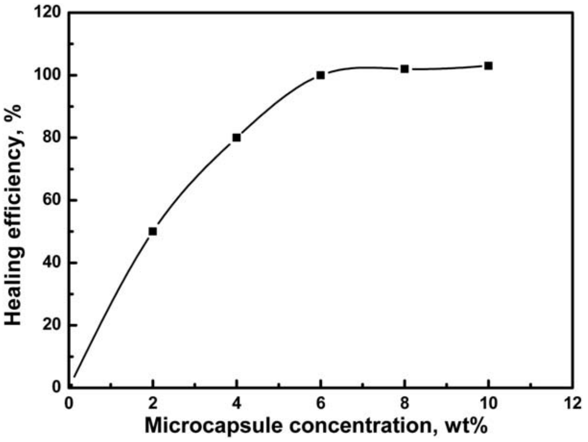

Figure 4. Influence of microcapsule concentration on healing efficiency of the self-healing EACs. Weight ratio of the epoxy/amine-containing microcapsules in all the self-healing specimens is 1 : 1.

EXPERIMENTAL

Preparation of Microcapsules

Epoxy microcapsules with Epon 815C (Shell Chemical) as core material were prepared by *in situ* polymerization of urea-formaldehyde (UF) following the procedure described by Blaiszik et at.[34] Amine microcapsules were prepared by water-in-oil emulsion polymerization. In the beaker, 10 g of 5 pph solution of montmorillonite (Shenzhen Haichen Hi-techo Corp.) in decalin (Sinopharm Chemical Reagent Corp.), 20 g of 20 pph solution of polyisobutylene in decalin and 20 g of 33 pph stock of DETA (Sinopharm Chemical Reagent Corp.) in Jeffamine D-230 (Huntsman Corp.), and 60 g of decalin were added. Subsequently, the mixture was emulsified at 1800 RPM with a three-blade agitator for 10 min. Then 40 mL of 20 pph solution of Diphenylmethane isocyanate (Wanhua Chemical Group) in decalin was added dropwise. The resultant mixture was proceeded at room temperature for additional 2 days to form the desired core-shell structure. The average diameter of the formed microcapsules was 21 ± 10 μm.

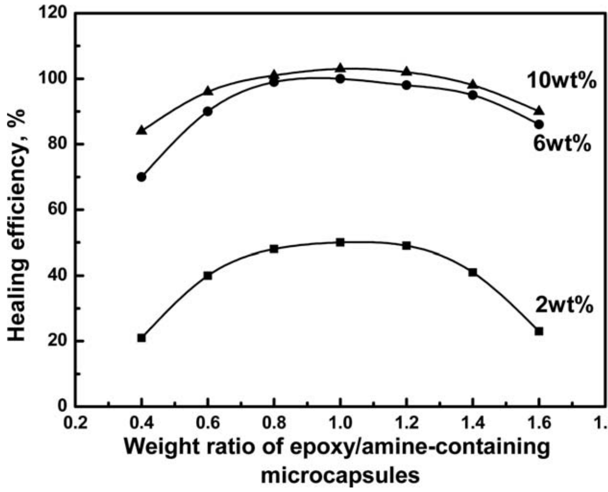

Figure 5. Influence of weight ratio of epoxy/amine-containing microcapsules on healing efficiency of the self-healing EACs containing different contents of microcapsulated healing agents.

Preparation of Samples

Silver powder (Degussa Corp.) and Epon 828 (Shell Chemical) were mixed for 20 min at a speed of 400 RPM at room temperature using the mechanical stirrer. The silver powder loading was 33 vol %. Then the defined ratios of the microcapsules containing epoxy and amine were added to the resultant mixture and stirred for 10 min at 400 RPM. Finally, the curing agent DETA was added to the mixture and stirred for additional 20 min at 400 RPM, followed by a vacuum process for 15 min. The formed mixture was cured at room temperature for 24 h and post-cured at 35°C for 24 h.

Characterization of Microcapsules

Scanning electronic microscope (SEM) images were taken with a Philips XL30 ESEM-FEG instrument using samples that had been sputter coated with gold/palladium. Multiple optical images were taken with a Leica DMR optical interfaced with ImageJ software (version 1.42) and microcapsules size distributions were obtained from these images.

Evaluation of Self-Healing Performance

Fracture test on TDCB proposed by White,[35] was used to evaluate the healing performance of the materials. Efficiency of healing is defined as the ratio of fracture toughness, K_{IC}, of healed and virgin materials. The virgin fracture toughness is determined by propagating the starter crack along the mid-plane of the specimen. Subsequently, the load is removed and the crack is allowed to heal at room temperature for 48 h with no manual intervention. The healed fracture toughness is then measured by retesting the specimen.

Measurements of Bulk Resistivity

The samples with specific dimensions were prepared and used to measure the bulk resistivity. The detailed information regarding the sample dimensions and measurements have been reported by Wong and coworker.[36]

RESULTS AND DISCUSSION

Characterization of Microcapsules

SEM photographs of epoxy and amine microcapsules were given in Figure 1. Electron micrographs showed the microcapsules to be spheroid. Agitation rate can influence the size of microcapsules. Therefore, the size distributions of amine microcapsules were measured for a range of agitation rates (1200–2000 RPM) while holding all other factors constant. It disclosed that increasing agitation rate, the average diameter of the capsules decreases and the size distribution narrows (Figure 2). When the agitator rate is 1800 RPM, the amine microcapsules with the average diameter 21 ± 10 μm were formed and used for further tests.

Evaluation of Self-Healing Performance

Figure 3 shows the photograph of TDCB specimen. Theoretically, the concentration and weight ratio of epoxy and amine microcapsules will show a significant influence on the healing efficiency. Therefore, the specimens with different microcapsule concentrations were prepared and tested. As presented in Figure 4, with the microcapsule concentrations increasing from 0 to 6

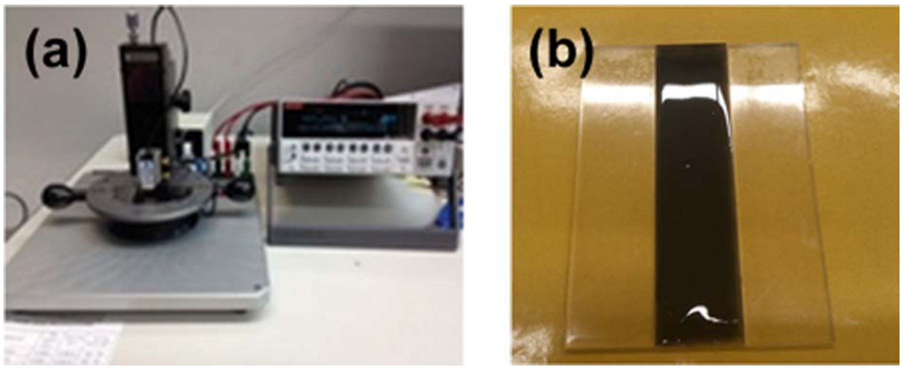

Figure 6. (a) Testing photograph and (b) photograph of the ECA specimen in undamaged condition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wt %, the healing efficiency dramatically increased as well, but further increasing the concentration shows a minor influence. Ideally, when the equivalents of epoxy and amine are equal, the functional groups will fully react and give a highest healing efficiency. Hence, the healing efficiencies with the weight ratios of epoxy/amine microcapsules from 0.3 to 1.8 were measured, as shown in Figure 5. It indicated that the optimal healing efficiency was obtained at the weight ratio of epoxy/amine microcapsules of 1.05.

Relationship Between Healing Efficiency and Conductivity

Figure 6(a) shows the testing photograph of the electrical property of ECA specimen. Figure 6(b) depicts the photo of the ECA specimen. The percolation theory is one of the theories, which are used to explain the electrical properties of conductive epoxy composites. The model predicts that no conduction occurs until one complete conductive path of particles has been created across composites. As for Ag/epoxy conductive adhesive, it means that the distance between Ag fillers shall be close enough to form conductive paths. In other words, the micro cracks, which are difficult to detect and repair, can reduce the electrical conductivity of ECAs.

To define the healing efficiency of the electrical conductivity of the EACs, the Ag/epoxy conductive adhesives with 2, 6, and 10 wt % of epoxy/amine microcapsules (weight ratio is 1.05) were prepared. The bulk resistivity of the specimens was measured on the undamaged, damaged, and healed conditions. Damage was induced by hand scribing using a razor blade. Bulk resistivity of the ECAs was given in Table I. When the specimens were on undamaged condition, with the increased amount of epoxy/amine microcapsules from 2 to 10 wt %, the bulk resistivity was 2.6×10^{-3}, 2.9×10^{-3}, and 4.7×10^{-3} Ω cm, respectively. The reason may be the epoxy/amine microcapsules did not contain Ag fillers, with higher amount of microcapsules loading, with less amount of Ag fillers in the specimens. As can be seen from the table, the bulk resistivity dramatically increased when the specimens were damaged. That may cause by removing small amount of Ag fillers and the contact between the fillers became worse. After healing for 48 h at room temperature, the bulk resistivity reduced. It indicated that the EACs with epoxy/amine microcapsules possess the ability to heal cracks and recover the conductivity automatically, although the bulk resistivity is still higher than undamaged specimen.

Table I. Bulk Resistivity of Undamaged, Damaged, and Healed Specimens

Microcapsule loading (%)	Specimen conditions	Bulk resistivity (Ω·cm)
2	Undamaged	2.6×10^{-3}
2	Damaged	$>10^{5}$
2	Healed	7.2×10^{-3}
6	Undamaged	2.9×10^{-3}
6	Damaged	$>10^{5}$
6	Healed	3.4×10^{-3}
10	Undamaged	4.7×10^{-3}
10	Damaged	$>10^{5}$
10	Healed	5.3×10^{-3}

Mechanism of Self-Healing EACs

An approaching crack will rupture some of the embedded microcapsules, which contain resin and curing agent, and then releasing the repairing agent into the damage zone through capillary action. Subsequently, the released epoxy and amine react and form crosslinked polymers, the cracks are healed. For the reaction mechanism of epoxy with amine, a simplified possibly scenario is proposed. Theoretically, nucleophile may react with oxirane group through two pathays [Figure 7(a)]. In acidic condition, proton (H^+) could open the oxirane ring first and form the secondary carbocation, which possesses better stability than primary carbocation, then nucleophile attack the carbocation and provide the product [Figure 7(a), path a]. However, in basic condition, steric hindrance effect shows a bigger influence on the reaction pathway. In other words, nucleophile will attack the position with less steric hindrance (position 1) and generate the product [Figure 7(a), path b].

Hence, in the ECA formulation, as depicted in Figure 7(b), the primary amino groups attack the less hindrance position of the epoxy firstly; then, the oxirane rings are opened and lead to intermediate **I**. Subsequently, the secondary amino groups react

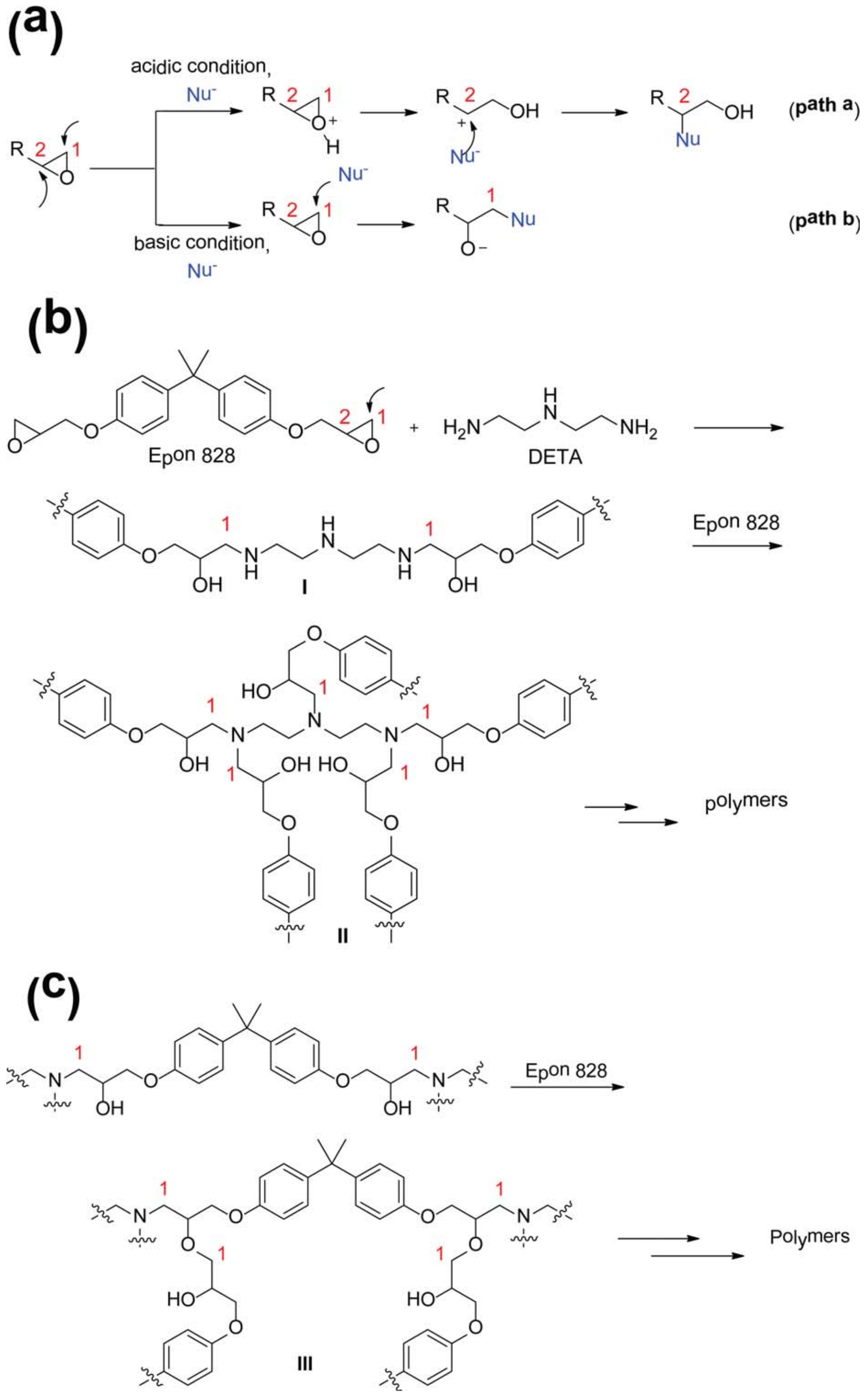

Figure 7. (a) Two pathways for ring-opening of epoxy group. (b,c) Proposed reaction mechanism. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with Epon 828 again and form the crosslinked structure **II** with tertiary amino groups. Additionally, the hydroxyl groups, which are obtained by the reaction of epoxy with amine, can further attack oxirane groups as well, and generate intermediate **III** [Figure 7(c)].

CONCLUSIONS

An Ag/epoxy-based ECA with self-healing ability was reported. Epoxy microcapsules and amine microcapsules were prepared, respectively. The loading of microcapsules is 6 wt % (weight ratio 1.05), which gives the ECAs the optimal healing efficiency.

Additionally, the bulk resistivity of the healed specimen can recover to 3.4×10^{-3} Ω cm. Further investigation on the preparation of microcapsules with nanosilver is ongoing.

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