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Electrically conductive self-healing polymer composite coatings

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ABSTRACT

The goal of the research described herein is the fabrication and assessment of electrically conductive partially-cured epoxy coatings which, upon cracking, autonomously restore barrier, mechanical and electrical properties via a microcapsule based healing mechanism. Upon cracking, microcapsules in the crack path release the 'healing' solvent ethyl phenyl acetate (EPA), which locally swells the matrix, promoting crack closure and enabling the diffusion and subsequent reaction of the residual hardener in the vicinity of the crack. Two different self-healing coatings and two controls based on an electrically conductive epoxy resin with approximately 20% carbon nanotubes (CNTs) were fabricated. Electrochemical impedance spectroscopy was employed to evaluate the potential of the CNT and non-CNT containing encapsulated systems to restore relatively large cracks and thus restore the barrier function. An *in situ* electro-tensile test in a microscope revealed that electrical conductivity and mechanical properties were restored to 64% (±23) and 81% (±39) respectively, which correlated to crack closure. Under appropriate testing conditions the system showed successive damage-heal events in terms of electrical conductivity.

1. Introduction

Microelectronic devices are used across all facets of life and industry. The push towards smaller devices with higher reliability provokes the need for failure assessment and subsequent repair of such devices. Inevitably, failure probabilities increase if devices are not consistently maintained and repaired [1–3]. For mass produced miniaturized electronic components, the high cost, difficulty, or even impossibility of repair justify research concerning materials capable of 'self-healing' upon the occurrence of damage [4–7]. Thus, the goal of this research is to fabricate materials commonly used in microelectronics possessing the ability to automatically recover their original functionality much like wound healing within a biological system [3,8–11]. For such systems, the occurrence of local damage in the form of cracks would initiate the transport of new material to the site of failure. Subsequent restoration of the properties (i.e., healing) would occur as a result of the local chemical reaction in and near the crack.

Electrically conductive epoxies (ECAs) are often used as external coatings, 'bulk' packaging materials or as interconnects for electronic devices [12–16]. Thermoset epoxies are commonly chosen due to their relevant properties, such as excellent adhesive strength, good chemical and corrosion resistance, and low cost [6,16–19]. Conductive fillers (e.g. silver, gold, nickel, copper, and carbon) provide the composite with electrical conductivity [6,17]. Carbon nanotubes (CNTs) are ideal as conductive fillers due to their excellent electrical conductivity, nanoscopic size, and high aspect ratio, which facilitate the formation of a network allowing for electron transport along the CNTs. In addition to sufficient electrical conductivity, ECAs based on epoxy and CNTs demonstrate improved adhesion and mechanical properties (including strength) compared to pristine epoxy [20–24]. However, even with the additional reinforcement resulting from CNTs, the epoxy matrix is still prone to cracking which often leads to device failure. In fact, depending on the CNT loading in the epoxy, the incorporation of CNTs can actually increase brittleness and, thus, likelihood of unforeseen cracking.

Many studies have demonstrated the possibility to convert brittle and inert epoxies into self-healing systems via a microcapsule-based mechanism [25–29]. In a microcapsule-based system, the liquid healing agent is confined to small capsules, homogeneously dispersed within the polymer matrix. Upon matrix cracking, the embedded microcapsules near the matrix crack open and release their contents into the damaged site [8,25,30]. White

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et al. 'self-healed' bulk epoxy using microencapsulated dicyclopentadiene (DCPD) monomer and Grubbs' catalyst [25]. This method was later adapted to 'self-healing' of epoxy adhesive films commonly used in the aerospace and automotive industries for bonding metallic and composite substrates [31].

Caruso was first to report a solvent-based microcapsule self-healing system [32] which has since been adapted and utilized in many epoxy matrices [27,33–35]. In such a system, healing only occurs if the epoxy matrix is left under-cured so that some residual hardener remains dormant in the film. In the case of cracking a microcapsule containing the 'healing' solvent ethyl phenyl acetate (EPA), diffusion of EPA in epoxy increases chain mobility and the matrix swells allowing gap closure and enabling the reaction of the residual hardener within the matrix. Thus the crack gap is decreased and cured (i.e., healed) [36]. Of course the limited volume of healing agent in the capsules limits the crack opening distance that can be healed [35], and the EPA healing agent in the capsule has a finite shelf life [34]. However, this system is a good model system that is neither toxic nor costly [27,37,38]. Caruso et al. explained and verified that additional epoxy delivered to the crack plane from the ruptured capsules improves the chance for additional cross-linking and helps bond new thermoset material to the original matrix interface [33]. In addition, Neuser et al. calculated that the additional epoxy should allow for the healing of slightly larger cracks [35]. Recently, microencapsulated suspensions of metal or carbon black were used to restore electrical conductivity in a multilayer microelectronic device and battery electrode respectively [39,40]. However, reported healing in epoxy matrices thus far is limited to crack healing and recovery of mechanical properties without attention paid to electrical conductivity. When considering electrically conductive epoxies, restoration of electrical conductivity is equally, if not more, crucial for device success. Thus, the goal of this research is the inclusion of an electrically conductive epoxy/solvent-based microcapsule 'self-healing' system in an electrically conductive epoxy coating.

To this aim, two different self-healing coatings and two controls based on an electrically conductive epoxy resin with a high concentration (~20%) of CNTs were fabricated. The two self-healing coatings contained microcapsules filled with EPA and either epoxy with CNTs or without CNTs. These model systems allow for the evaluation of solvent-based microcapsule self-healing in electrically conductive coatings. Two methods were developed to assess self-healing of intentionally introduced cracks, with and without 24 h healing periods. The first test method involved electrochemical impedance spectroscopy (EIS) and the second test method is a novel *in situ* electro-tensile test.

EIS is a non-destructive method often used to evaluate functional properties of organic coatings such as barrier, adhesion and active corrosion protection [41–43]. In recent years, the EIS technique has been successfully used to follow healing processes in extrinsic healing coatings using either encapsulation of two agents as in the work by Mehta et al. [44] or a single healing agent as employed by Garcia et al. [45,46]. In the present work, EIS was employed to evaluate the potential of the CNT and non-CNT containing encapsulated systems to bridge and hence restore relatively big cracks. The restoration of the barrier properties in cracked coatings is as important as the restoration of the electrical conductivity.

As EIS does not provide information with respect to the recovery of the electrical conductivity and of the mechanical strength, an *in situ* electro-tensile test was implemented to locally probe the restoration of electrical conductivity and the mechanical integrity at the healed damage. For this, a method was developed to assess self-healing via the controlled introduction of a crack into the coating by pulling it in tension under bright field optical microscopy while simultaneously measuring the change in electrical resistance. This method allows the assessment of electrical conductivity and elastic modulus of the coating.

2. Materials and methods

Fig. 1 shows a sketch of the produced coatings and evaluation tests. The selection and processing of all materials and the characterization methods are described in following sections.

2.1. Materials

The coating is intended for use in microelectronics, thus the material should be electrically conductive, mechanically stable, provide (chemo-) mechanical protection to the underlying component and possess a viscosity allowing for the formation of a thin coating, which cracks during tension without delamination. A bisphenol-A epoxy with a high concentration of CNTs (~20%) that provide electrical conductivity was chosen for the coating (ECNT, Epocyl™ NC E128-02, Nanocyl). At room temperature, this resin has a viscosity of 400 ± 50 Pa.s. An epoxy without CNTs (EPON, Epikote 828 EL, Brenntag) was used as the epoxy matrix of control samples. The hardener, diethylenetriamine (DETA, Sigma–Aldrich) was used to cure both epoxy resins at a concentration of 12.4 wt% as its high reactivity allows for cross-linking at room temperature.

All reagents for shell formulation, urea (Acros), resorcinol (Aldrich) and formaldehyde (Acros), as well as the acidic catalyst ammonium chloride (Fluka) and the ethylene maleic anhydride (EMA, Zeeland) surfactant were used in the as-received state. Hexyl acetate (HA, 99%, Acros Organics) and ethyl phenyl acetate (EPA, 99%, Sigma–Aldrich) were used as solvents. Two different substrate materials were also used, namely a 50 μm thick polyethylene naphthalate foil (PEN, Teonex®, Dupont-Teijin films, an insulating and transparent foil, which provides good bonding to the coating) for the electro-tensile tests and a 1 mm thick aluminum alloy (AA5005, Metallica Sàrl, a magnesium rich alloy exhibiting high mechanical properties and high resistance to corrosion) for the EIS tests.

2.2. Fabrication and processing methods

A total of five different coating compositions, with and without microcapsules were fabricated as reported in Table 1 and detailed as follows.

2.2.1. Microcapsule preparation

In this work, the oil-in-water emulsion technique of Blaiszik et al. was used for microencapsulation [47]. The encapsulated healing agent was a 97.5%:2.5% (by weight) mixture of EPA and either ECNT (composition 1) or EPON (composition 2). The conductive ECNT was incorporated into microcapsules along with the 'healing solvent' EPA to improve not only healing efficiency in terms of mechanical properties, but electrical properties as well. Control samples were fabricated with microcapsules containing the 'non-healing' solvent HA (composition 3), which was found too nonpolar to demonstrate a solvent healing effect in an epoxy matrix [33], and without microcapsules (compositions 4 for ECNT and 5 for EPON).

In detail, 2.5 g of urea, 0.25 g of ammonium chloride and 0.25 g of ground resorcinol were dissolved in a mixture of 100 ml of deionized water (DI) and 25 ml of a 2.5 wt% EMA solution. The pH of the solution was then adjusted from approximately 2.7 to 3.5 using a 20% NaOH solution. The solution was subsequently stirred at a rate of 400 rpm for a few minutes and 60 ml of the core material followed by 6.33 g of formaldehyde were added allowing adequate mixing before each addition. The water bath temperature was then set to 55 °C and the reaction was allowed to proceed for 4 h. Afterwards, the microcapsules were left to cool down overnight and