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Micromechanical properties and morphologies of self-healing epoxy nanocomposites with microencapsulated healing agent

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HIGHLIGHTS

- Micromechanical properties of composites were studied before and after healing.
- Nanoindentation test is used on the composites at three different normal loads.
- The surface topographies of the indented regions were monitored via AFM.
- Healing efficiency was evaluated using AFM after nanoscratch test on the composites.
- Microstructures of virgin and healed self-healing composites were determined via SEM.

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ABSTRACT

The effects of microcapsules and carbon nanotubes (CNTs) on the micromechanical properties (elastic modulus, hardness and plasticity index) of self-healing epoxy polymers were investigated via nanoindentation. A standard Berkovich indenter was used to make indentations under three different normal loads. The surface topographies of the indented regions were monitored via AFM to compare the plasticity of the samples. A nanoscratch test was performed on the self-healing composites, and the healing efficiency was evaluated using AFM. The addition of microcapsules reduced the elastic modulus and hardness of the pure polymer matrix; however, the addition of CNTs significantly improved these mechanical properties. We also used nanoindentation tests in the scratched region to study the mechanical properties of the self-healing composite after healing. Furthermore, the microstructures of both the virgin and healed self-healing composites were determined via SEM. This analysis showed that the microcapsules ruptured during scratch propagation and the healing agent release into the cracks.

1. Introduction

Epoxy resins are being increasingly used in composite material matrices for a wide range of automotive, aerospace and shipbuilding applications as well as in electronic devices. These epoxies serve as casting resins, adhesives, and high performance coatings for tribological applications, such as slide bearings and calender roller covers [1,2]. The long-term durability and reliability of these materials are problematic for structural applications [3]. Epoxy resins have highly cross-linked structures that offer poor resistance to the initiation and propagation of cracks. If such damage is not detected and repaired, the matrix can fail prematurely. Many researchers have attempted to improve the toughness of these polymers by reinforcement with soft particles, such as rubber fillers [4]. However, these particles decreases the flexural and elastic moduli [5] while increasing the thermal expansion coefficient. Over the last decade, scientists have design self-healing polymers that mimic living systems in repairing themselves whenever and wherever they are damaged without manual detection or repair. Over the past several years, several self-healing strategies have been developed. One of the most successful and versatile of these strategies utilizes embedded microcapsules that are filled with a liquid healing agent [6,7]. When a crack propagates through the material, it ruptures the microcapsules and releases the healing agent into the damaged area. This healing agent is exposed in the crack plane to a catalyst that has previously been dispersed throughout the material. This catalyst polymerizes the healing agent via a ring-opening metathesis polymerization (ROMP), which

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autonomically repairs the damage. The dicyclopentadiene (DCPD) monomer is the most commonly healing agent in these systems [7,8]. Furthermore, tungsten (VI) chloride (WCl_6) has been identified as the best catalyst for ROMP healing [9]. Atomic force microscopy (AFM), three-point bending and nanoindentation are the most commonly used methods for calculating the micromechanical properties of thin films and nano/microscale materials [10]. Recently, nanoindentation has been used as a powerful, advanced technique for measuring the mechanical properties of polymer nanocomposites, such as the elastic modulus and hardness. For example, Shokrieh et al. [11] used this method to measure the modulus and hardness of epoxy nanocomposites with differing graphene contents. Molazemhosseini et al. [12] used nanoindentation to study the micromechanical properties of poly-ether-ether-ketone (PEEK)-based hybrid composites that were reinforced with short carbon fibers and SiO_2 nanoparticles. Li et al. [13] investigated the micromechanical properties of epoxy nanocomposites containing various weight fractions of single-walled carbon nanotubes (SWCNTs). The authors found that the addition of 1 wt% SWCNTs increased the elastic modulus of the epoxy to approximately 4.5 GPa.

To the best of our knowledge, there are no reports in the literature on the micromechanical properties of self-healing epoxy nanocomposites containing a microencapsulated healing agent before damage and after healing. Therefore, the mechanical behavior of these advanced materials requires studying via advanced methods such as nanoindentation. The objective of this study was to improve the mechanical properties of a self-healing composite by dispersing carbon nanotubes (CNTs) throughout the epoxy matrix. The self-healing composites were cracked using nanoscratching. The micromechanical properties (i.e., elastic modulus, hardness and plasticity index) of the virgin (before damage) and healed (after healing) self-healing epoxy composites containing microcapsules and/or CNTs were investigated via nanoindentation. The surface topographies after both the nanoindentation and nanoscratching of the self-healing composites were monitored by AFM. Scanning electron microscopy (SEM) was also used to observe the morphologies of both the virgin and healed self-healing composites.

2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol A resin (DGEBA or EPON 828) and the curing agent Ancamine diethylenetriamine (DETA) were used as received from Huntsman (UK), and the epoxy samples (EPON 828:DETA) were formed using 12 parts per hundred (pph) of the curing agent in the EPON 828. The tungsten (VI) chloride (WCl_6) catalyst was obtained from Sigma–Aldrich (USA). The SWCNTs were provided by the Research Institute of the Petroleum Industry (Iran). The SWCNTs were prepared via a chemical vapor deposition (CVD) with methane as the carbon source, and both cobalt and molybdenum catalyst systems at 800–1000 °C. The SWCNTs were between 1 and 4 nm in diameter, and their maximum length was less than 10 μm. All of the aforementioned materials were commercial products that were used without further purification. Microcapsules with average diameters of 115 μm and approximately 3 μm thick shell walls were obtained using methods we have described elsewhere [14,15].

2.2. Composite preparation

The unfilled and CNT-filled epoxy specimens (which are denoted by Ep and Ep-CNT, respectively) were produced by mixing 100 parts of DGEBA with 12 parts of the DETA curing agent and/or 1% CNT (by weight). The self-healing epoxy composites were prepared by mixing 15% (by weight) DCPD-loaded microcapsules, 12% (by weight) WCl_6 catalyst, and/or 1% (by weight) CNTs with the aforementioned epoxy and DETA mixture. The mixture was then poured into a silicone rubber mold and degassed in a vacuum oven until no air bubbles were observed on the surface of the mixture. Finally, the mixture was cured for 72 h at room temperature, and then post-cured at 45 °C for 48 h. The compositions of the prepared specimens are listed in Table 1.

2.3. Morphological characterization

The presence of microcapsules and CNTs in the epoxy matrix was investigated via SEM (LEO 1455VP: 15 KV) after sputtering a thin gold layer onto the specimen cross sections. A back-scattered electron (BSE) detector was used to differentiate the WCl_6 catalyst from the composite cross section. Energy dispersive X-ray analyses were also performed using an EDX device coupled to the SEM.

2.4. Micromechanical characterization

The nanoindentation and nanoscratching tests were performed using a Triboindenter system (Hysitron Inc. USA) with a Berkovich indenter under ambient conditions. This system was coupled to the AFM (NanoScope E, Digital Instruments) to investigate the surface topography of the nanoindented and nanoscratched samples. Prior to these experiments, the tip area function was calibrated using methods developed by Oliver and Pharr [16] with a standard fused quartz sample. Three different normal loads, 200, 500 and 700 μN, were applied during the nanoindentation tests at constant rates of 8, 17 and 22 μN/s, respectively. A typical load-hold-unload sequence was used in these indentation experiments. After engaging the sample surface, the tip load increased at a constant rate until the predefined maximum load was achieved. Then, to minimize the time-dependent plastic effect, these maximum loads were held for 10 s. Finally, the tip was withdrawn from the sample surface at the same rate during unloading. For each condition, at least three tests were repeated at random locations on the surface. A schematic of the parameters for the loading and unloading processes is shown in Fig. 1. The indentation depths, h_t, h_e and h_f denote the total depth under a load, P_t, the elastic rebound depth during unloading and the residual impression depth, respectively. h_a was the surface displacement at the perimeter, and h_p was the contact indentation depth. The contact stiffness, S, was defined as the slope at the beginning of the unloading curve and was calculated using by the following equation:

$$S = \frac{dp}{dh} \tag{1}$$

The hardness, H, was calculated from the loading curve and is defined as the maximum normal load, P_{max}, divided by the residual indentation area, A_r:

Table 1
Compositions of samples.

Sample code	Epoxy (wt%)	Microcapsules (wt%)	WCl_6 (wt%)	CNTs (wt%)
Ep	100	–	–	–
Ep-CNT	98	–	–	2
Ep-Caps	73	15	12	–
Ep-CNT-Caps	71	15	12	2