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Material Behaviour

Towards the development of self-healing carbon/epoxy composites with improved potential provided by efficient encapsulation of healing agents in core-shell nanofibers

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ABSTRACT

A self-healing carbon/epoxy composite was fabricated with the incorporation of healing agent loaded core-shell nanofibers between carbon fiber fabric layers. The healing agents, consisting of two components, a low viscosity epoxy resin and its amine-based curing agent, were encapsulated in Styrene acrylonitrile (SAN) nanofibers via a coaxial electrospinning method. Transmission electron microscope (TEM), Fourier Transform Infrared (FTIR), and thermogravimetric analysis (TGA) results confirmed the successful encapsulation of both epoxy and curing agent in SAN nanofiber shells. TGA and the extraction method confirmed a high encapsulation yield (90% for the epoxy resin and 97% for the curing agent). Mechanical studies of the hybrid composite showed that embedding the fabricated core-shell nanofibers did not lead to a reduction in the mechanical properties of host composite, which was corroborated with statistical analysis. Mechanical evaluations and curing behavior studies both showed that incorporation of the aforementioned nanofibers between carbon layers can imbue the conventional carbon/epoxy composite with a self-healing ability, allowing it to repair itself to restore its mechanical properties for up to three cycles at room temperature in absent of any external driving force.

1. Introduction

Self-healing polymers and polymer composites were proposed for the fabrication of advanced engineering materials with greater durability and reliability [1,2]. One of the most successful strategies to achieve this self-healing ability is through the release of healing agents from ruptured capsules [3–5], hollow fibers [6,7], and vascular networks [8,9], embedded in the material.

Although the research landscape suggests capsule-based systems are the most popular approach to implement autonomous healing performance in a wide range of applications [10], there still remain several critical drawbacks. These include the high effective cost of the encapsulation processes, the poor distribution of capsules, the lack of interaction between the capsules and matrix, and the low availability of healing agents for multiple healing cycles [2,11]. Encapsulating healing agents in hollow fibers and microvasular networks were thus proposed to overcome these challenges. However, research has shown this strategy comes with several drawbacks that make the encapsulation challenging and reduces the eventual performance of the composite. Kousourakis et al. demonstrated embedding such a hollow fiber network in the composite negatively impacts the mechanical properties of the material by introducing local stress concentrations and disrupting the structural organization of the material to accommodate the fibers. Nevertheless, they did note that decreasing the diameters of the embedded fibers tended to mitigate these adverse effects [12].

Since some modes of failure in materials originate at the nanoscale, and are then propagated to the micro and macro levels, nanovessels such as nanocapsules and nanofibers containing healing agents are exciting candidates for the healing of cracks or delamination at their very initial stages of failure [13]. Park et al.,

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proposed coaxial electrospinning to encapsulate healing agents in core-shell nanofibers, successfully prepared a self-healing coating [14]. The successful demonstration of this innovation led to a shift toward shrinking the healing agent encapsulated fibers down to the nanoscale in more recent works [15]. Self-healing carbon-epoxy composites were fabricated via incorporating dicyclopentadiene (DCPD) and isophorone diisocyanate (IPDI), in polyacrylonitrile (PAN) nanofibers [16,17]. Mitchell et al., reported the feasibility of encapsulating a low viscosity epoxy resin in a polyvinyl alcohol (PVA) nanofiber through coaxial electrospinning [18]. Lee et al., reported the successful fabrication self-healing polymers [19,20] and polymer coatings [11,21,22] by incorporating core-shell nanofibers containing siloxane-based healing agents in PAN nanofibers fabricated via emulsion and coaxial electrospinning methods.

In the present work, we aim to produce self-healing conventional carbon/epoxy composites by embedding core-shell nanofibers between the carbon fabric layers. For the first time, a SAN copolymer is used as the shell material, motivated by its extraordinarily high encapsulation yield. In addition, an epoxy resin and its amine based curing agent were selected as the healing agents due to the system's high compatibility with epoxy as the matrix [23], superior mechanical properties, and quicker curing times compared to other healing agent systems [24]. Mechanical tests and curing studies were then employed to evaluate and confirm the self-healing ability of the fabricated hybrid composite.

2. Experimental

2.1. Materials

SAN (M_w = 185 kDa, acrylonitrile 30 wt %) and N, N-dimethylformamide (DMF, 99.8%) were procured from Sigma-Aldrich. Two component epoxy resin (EPIKOTE™ Resin 240) and its amine based curing agent (EPIKURE™ 3370) were purchased from Hexion co., and were used as the healing agent analogous to our previous work [23,25]. Also specified in our previous work, a conventional epoxy resin with its curing agent and unidirectional carbon fiber fabric were employed to fabricate the carbon/epoxy composite [25]. A 25 wt % SAN solution in DMF was used as the shell material to electrospin uniform nanofibers without beading.

2.2. Electrospinning

To prepare the electrospinning solution for the shell, appropriate quantities of SAN powder were added to DMF and stirred with a magnetic stirring for 24 h at room temperature. Subsequently, the prepared uniform solution was fed to outer needle of a core-shell nozzle (gauge 16) while the inner needle (gauge 24) was fed with either the epoxy resin (EPIKOTE™ Resin 240) or the amine based curing agent (EPIKURE™ 3370) separately. Electrospinning process parameters were adjusted as follows in order to provide stable electrospinning yielding nanofibers with the desired core-shell structure: SAN shell solution feed rate of 0.5 ml h^{-1}, epoxy resin core feed rate of 0.09 ml h^{-1}, and amine based curing agent feed rate of 0.10 ml h^{-1}, respectively. In addition, an air gap of 15 cm was maintained between the needle tip and collector for every encapsulation process, and an 18 kV DC voltage was applied to induce the formation of beadles nanofibers from the solution. The optimized core-shell nanofibers were deposited on the surface of carbon fiber fabrics attached to an aluminum drum collector rotating at 50 rpm. The electrospinning duration was calibrated to deposit 1 g m^{-2} of nanofibers on the surface of carbon fiber fabrics in the same proportion for EPIKOTE™ Resin 240 and EPIKURE™ 3370.

2.3. Composite fabrication

Composite panel comprising six layers of carbon fabric and five layers of core-shell nanofibers between them was fabricated via the hand lay-up method followed by the vacuum-assisted resin transfer molding (VARTM) technique as described in our previous work [25].

2.4. Characterization and evaluation

2.4.1. Morphological characterization

To study the morphology of the electrospun core-shell nanofiber mats and the fracture surface of the hybrid composite, a Hitachi S-4300 field emission scanning electron microscope (FE-SEM) was employed.

A JEM 2010F TEM, operating at 200 kV, was then employed in order to investigate the core-shell structure of the fabricated nanofibers and confirm the successful encapsulation of both healing agents (epoxy resin and curing agent) in the SAN shell.

2.4.2. Chemical and physical state of the nanofibers

To investigate the functional groups present in the materials and reveal the successful encapsulation of healing agents without any chemical modification, a FTIR spectroscopy was employed using the KBr pellet method on a Bio-Rad FTS-3500ARX FTIR spectrometer. To prevent the false positive signals from the unencapsulated epoxy and amine curing agent influencing the result, the electrospun nanofibers were washed thoroughly with methanol prior to the FTIR.

To determine the thermal stability and encapsulation content of the core-shell nanofibers, TGA experiments were carried out using a Shimadzu DTG-60H TGA analyzer. Methanol washing was performed to remove the un-encapsulated resin and curing agent from the nanofiber surface. A ramp rate of 10 °C min^{-1} was employed from 25 °C to 700 °C under argon gas at a 50 ml min^{-1} flow rate.

In addition, the core content of the prepared core-shell nanofibers was verified by the extraction method, using methanol as the extracting solvent for both cores. The core-shell nanofibers (approximately 0.1 g) were ground with a pestle on a filter paper and repeatedly washed with methanol five times, before drying in an oven at 80 °C. FTIR tests of the washed SAN shells were conducted to ensure the complete dissolution and removal of the epoxy and amine-based curing agent cores during the methanol washing process. By determining the weight changes from the initial pristine nanofibers (W_i) to that of the residual shell wall (W_s) after grinding, the shell wall content (W_{shell}) and core content (W_{core}) of the core-shell nanofibers can be calculated from the following equations:

$$\%W_{shell} = W_s/W_i \times 100 \quad (1)$$

$$\%W_{core} = (1 - W_s/W_i) \times 100 \quad (2)$$

Furthermore, for both cores, the encapsulation yields (α) were determined based on the amount encapsulated in the nanofibers divided by the amount of material charged to the inner syringes, and were calculated according to equation (3) for both healing agents.

$$\%\alpha = \left(W_{practical}/W_{theoritical}\right) \times 100 \quad (3)$$

Where, $W_{practical}$ is the core content determined from experimental methods (TGA or extraction), and $W_{theoretical}$ is the core content calculated from electrospinning flow rates.