Composites Science and Technology 72 (2012) 1387–1395

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Reinforcing epoxy nanocomposites with functionalized carbon nanotubes via biotin–streptavidin interactions

Rouhollah Dermanaki Farahani[a], Hamid Dalir[a], Vincent Le Borgne[b], Loick A. Gautier[b], My Ali El Khakani[b], Martin Lévesque[a], Daniel Therriault[a,*]

[a] Laboratory of Multiscale Mechanics, Center for Applied Research on Polymers (CREPEC), École Polytechnique de Montreal, C.P. 6079, Succ. Centre-Ville, Montreal (QC), Canada H3C 3A7

[b] Institut National de la Recherche Scientifique, INRS-Énergie, Matériaux et Télécommunications, 1650 Blvd. Lionel-Boulet, Varennes (QC), Canada J3X 1S2

ARTICLE INFO

Article history:
Received 16 December 2011
Received in revised form 1 April 2012
Accepted 8 May 2012
Available online 17 May 2012

Keywords:
A. Carbon nanotube
A. Nanocomposites
B. Surface treatments
UV-assisted direct-write

ABSTRACT

We report on the preparation of nanocomposites consisting of biofunctionalized single-walled carbon nanotubes (BF-SWCNTs) reinforcing an ultraviolet curable epoxy polymer by means of biotin–streptavidin interactions. The as-produced laser ablation SWCNTs are biofunctionalized via acid oxidization based purification process and non-covalent functionalization using surfactant, followed by grafting the resulting nanotubes with biomolecules. The biotin-grafted nanotubes are capable of interacting with epoxy groups in presence of streptavidin molecules by which chemical bridges between BF-SWCNTs and epoxy matrix are formed. The biomolecules grafted to the nanotubes surface not only facilitate the load transfer, but also improve the nanotube dispersion into the epoxy matrix, as observed by optical imaging and scanning electron microscopy. Mechanical characterization on the nanocomposite microfibers demonstrates considerable enhancement in both strength (by 76%) and modulus (by 93%) with the addition of only 1 wt.% of BF-SWCNTs. The electrical measurements reveal a clear change in electrical conductivity of nanocomposite microfibers reinforced with 1 wt.% of BF-SWCNTs in comparison to the microfibers containing solely purified carbon nanotubes. These multifunctional nanocomposite materials could be used to fabricate macro and microstructures for a wide variety of applications such as high strength polymer nanocomposite and potential easily-manipulated biosensors.

1. Introduction

Nanomaterials, such as single-walled carbon nanotubes (SWCNTs), are increasingly used to achieve multifunctional capabilities where they serve as an effective structural reinforcement, as well as large-surface platform for sensing purposes [1,2]. Owing to their high mechanical [3] and electrical [4] properties, SWCNTs show a strong potential for reinforcing polymers for a wide variety of applications such as high-performance structural composites [5,6], electromechanical actuators and sensors [7], non-destructive life prediction technology and shape memory polymers [8]. When compared to other polymer nanocomposites, nanotube-reinforced epoxy systems could exhibit high strength and multifunctional features for aircrafts and electronic products [6,9]. However, several fundamental challenges still have to be addressed in order to take full advantage of the excellent properties of the nanotubes. In particular, the ability to manipulate these entangled structures with their structurally smooth surface is required for their effective use in the development of nanodevices based on an individual nanotube or bulk nanotubes [10,11], as well as nanotube-reinforced nanocomposites [12–16].

The chemical treatment of carbon nanotubes surface significantly extends their potential for various applications. The surface functionalization of carbon nanotubes not only leads to their debundling, but also enables the design of an efficient interface to bond them to other active groups, like epoxy groups in nanocomposite materials. In particular, the purification induced covalent grafting of carboxylic groups at the surface of the nanotubes [17] as well as their non-covalent functionalization using surfactants like porphyrins [18] can be used to improve the reinforcing effect when compared to as-produced nanotubes. However, nanotube reinforcement is still far from achieving its theoretical potential and new advances are needed for an efficient load transfer.

Functionalized nanotubes have been used for the immobilization of various biomolecules for biosensor applications [10]. Biomolecules bonded to functionalized nanotubes through functional groups are capable of interacting with other active biomolecules via reversible chemical bonding. Among these biomolecules, biotin–streptavidin bonding is known as one of the strongest interactions in nature [19,20]. Therefore, biotin-functionalized nanotubes

---

* Corresponding author. Tel.: +1 514 340 4711x4419; fax: +1 514 340 4176.
E-mail address: daniel.therriault@polymtl.ca (D. Therriault).

0266-3538/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compscitech.2012.05.010

could be used as a support to immobilize streptavidin molecules in biosensor applications. However, until now, most of the researches undertaken on using nanotubes in microelectronics have been limited to the use of an individual nanotube or bulk nanotubes. Due to the size order of an individual nanotube or their bulk physical state (i.e., powder of entangled structures), manufacturing and manipulation of these materials is quite challenging [10,11]. To address these difficulties, nanotubes have been added to a solution or a polymer matrix, suitable for use in electrospinning [21] and direct-write techniques [22]. Since fibers fabricated by electrospinning need additional patterning processes, the ultraviolet (UV)-assisted direct-write assembly [23] could be an alternative to manufacture complex microstructures with desired patterns when an UV-curable epoxy resin is used as a matrix.

Here, we report on the use of biotin–streptavidin interactions for further development of a multifunctional nanotube/epoxy composite system. This nanocomposite material was used for the fabrication of nanocomposite microfibers as an example of patterned microstructures for potential micro electromechanical systems (MEMS). Fig. 1 shows the schematic of the fabrication process of nanocomposite microfibers suspended between two rectangular pads of nanocomposite by means of UV-assisted direct-write technique. To fabricate the nanocomposites, the SWCNTs were biofunctionalized via acidic treatment and non-covalent functionalization using surfactant, followed by grafting of biomolecules to chemically bridge SWCNTs and epoxy matrix. The different steps of nanotubes functionalization were assessed using various structural characterization techniques. Finally, the effects of SWCNTs biofunctionalization and their dispersion on mechanical and electrical properties of the fabricated epoxy nanocomposite microfibers were studied to understand the nanocomposite structure-property relationship.

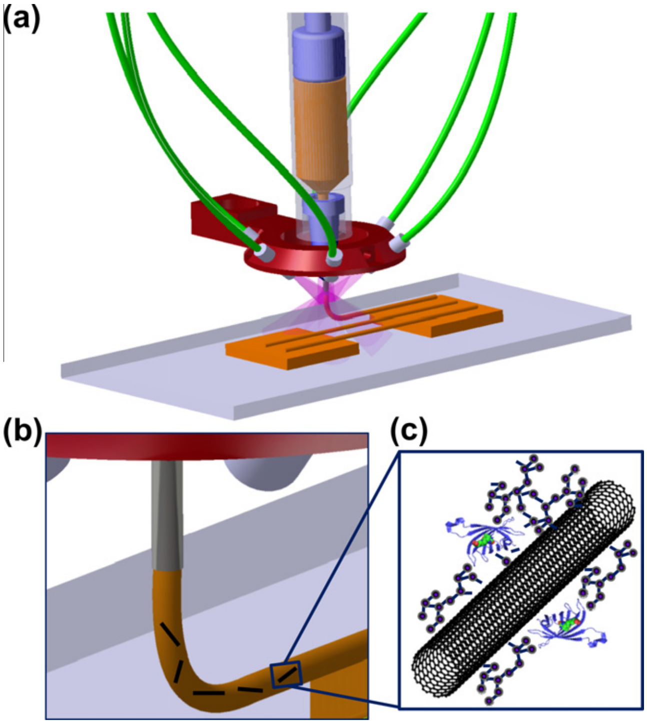

Fig. 1. Schematic representation of the UV-assisted direct-writing of nanocomposite microfibers: (a) nanocomposite extrusion through a capillary micronozzle by an applied pressure; fibers are partially cured shortly after extrusion under UV illumination, (b) close-up view of the microfibers, and (c) interfacial bonding between SWCNTs and epoxy matrix through biotin–streptavidin interactions.

2. Experimental details

2.1. SWCNTs synthesis, purification and biofunctionalization

Single-walled carbon nanotubes were synthesized by using UV-laser ablation (248 nm, 20 ns, 400 mJ) of a Co/Ni-doped (1.2 at.%) graphite target pellet. The KrF-laser ablation was performed under a controlled argon atmosphere at a temperature of 1150 °C through a 45° quartz window (more experimental details on the KrF-laser synthesis and effects of key growth parameters can be found elsewhere [24,25]). The as-produced SWCNTs condensed on a water-cooled collector, located outside of the hot zone of the furnace, onto which they formed a thick rubbery-like film. This SWCNTs mat was peeled off and subjected to subsequent chemical purification treatment. The chemical purification treatment consisted of three main successive steps, each of which is targeted a specific purification. First, the Soxhlet extraction in toluene (for 1 h) was conducted on the as-produced SWCNTs to remove residual fullerenes and some disordered carbon nanostructures in the deposit. Second, the SWCNTs were treated by hydrogen peroxide (10%) at room temperature (for 24 h) in order to crack the graphitic shells surrounding the residual catalyst nanoparticles. Finally, HNO_3 (3 M) oxidation was conducted to remove metal catalyst particles and covalently functionalize the SWCNTs by the attachment of carboxylic groups at their surface. These chemically P-SWCNTs were collected by vacuum filtration on alumina filters (pore size 20 nm) and after successive rinsing cycles.

The desired amounts of P-SWCNTs and 1,3-diaminopropane 99% (D23602, Sigma-Aldrich), with a proportion of 1 g P-SWCNTs/5 mL 1,3-diaminopropane 99%, were added to a solution of 0.1 mM of zinc protoporphyrin IX (ZnPP, Sigma-Aldrich) in methanol. The suspension was sonicated in an ultrasonic bath (Ultrasonic cleaner 8891, Cole-Parmer) for 1 h. After ultrasonication, the mixture was shaken using a mixer/shaker (Spex CertiPrep 8000 M Mixer/Mill) for 12 h at room temperature. The Soxhlet extraction for 2 h with methanol was performed on the aminated P-SWCNTs to remove any unreacted amine. The aminated P-SWCNTs were then added into a solution of 30 mL methanol containing desired amounts of biotin and N,N'-diisopropylcarbodiimide 99% (DIC, D125407, Sigma-Aldrich) with a proportion of 1 g biotin/5 mL DIC. Biotinylation of the aminated P-SWCNTs were subsequently performed by shaking the resulting mixture using the mixer/shaker for 12 h at room temperature. Finally, these biotinylated nanotubes were washed with methanol twice, followed by rinsing with distilled water several times to remove any unreacted biotin.

2.2. SWCNTs characterization

The KrF-laser synthesized SWCNTs were systematically characterized by various techniques before and after their chemical purification and functionalization. Their Raman spectra were acquired at room temperature in the 100–2000 cm^{-1} spectral region under ambient conditions using a back-scattering geometry on a microRaman microscope (Renishaw Imaging Microscope Wire TM) with a 50× objective. A 514.5 nm (2.41 eV) line from an air cooled Ar+ laser was used for excitation radiation. The chemical bonding states of the SWCNTs (before and after chemical purification) were analyzed by means of X-ray photoelectron spectroscopy (XPS) using the Cu Kα monochromatic radiation (1486.6 eV) of an ESCALAB 200I-XL spectrophotometer. The purified, aminated and biotinylated SWCNTs were characterized by FT-IR (Digilab FTS7000) in order to characterize the chemical components attached to the surface of the nanotubes and assess the biofunctionalization procedure. Finally, the nanostructural characteristics