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1 **Reinforcing epoxy nanocomposites with functionalized carbon**

2 **nanotubes via biotin-streptavidin interactions**

3

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13

Abstract

15 We report on the preparation of nanocomposites consisting of biofunctionalized single-walled

16 carbon nanotubes (BF-SWCNTs) reinforcing an ultraviolet curable epoxy polymer by means of

17 biotin-streptavidin interactions. The as-produced laser ablation SWCNTs are biofunctionalized

18 via acid oxidization based purification process and non-covalent functionalization using

19 surfactant, followed by grafting the resulting nanotubes with biomolecules. The biotin-grafted

20 nanotubes are capable of interacting with epoxy groups in presence of streptavidin molecules by

21 which chemical bridges between BF-SWCNTs and epoxy matrix are formed. The biomolecules

22 grafted to the nanotubes surface not only facilitate the load transfer, but also improve the

23 nanotube dispersion into the epoxy matrix, as observed by optical imaging and scanning

24 electron microscopy. Mechanical characterization on the nanocomposite microfibers

25 demonstrates considerable enhancement in both strength (by 76%) and modulus (by 93%) with

26 the addition of only 1 wt.% of BF-SWCNTs. The electrical measurements reveal a clear change

27 in electrical conductivity of nanocomposite microfibers reinforced with 1 wt.% of BF-SWCNTs

28 in comparison to the microfibers containing solely purified carbon nanotubes. These

29 multifunctional nanocomposite materials could be used to fabricate macro and microstructures

1   for a wide variety of applications such as high strength polymer nanocomposite and potential

2   easily-manipulated biosensors.

3   **Keywords**: A. Carbon nanotube, surface modification, A. Nanocomposite, UV-assisted direct-write

4

5   **1. Introduction**

6   Nanomaterials, such as single-walled carbon nanotubes (SWCNTs), are increasingly used to

7   achieve multifunctional capabilities where they serve as an effective structural reinforcement, as

8   well as large-surface platform for sensing purposes [1,2]. Owing to their high mechanical[3] and

9   electrical [4] properties, SWCNTs show a strong potential for reinforcing polymers for a wide

10   variety of applications such as high-performance structural composites [5,6], electromechanical

11   actuators and sensors[7], non-destructive life prediction technology and shape memory

12   polymers [8]. When compared to other polymer nanocomposites, nanotube-reinforced epoxy

13   systems could exhibit high strength and multifunctional features for aircrafts and electronic

14   products [6,9]. However, several fundamental challenges still have to be addressed in order to

15   take full advantage of the excellent properties of the nanotubes. In particular, the ability to

16   manipulate these entangled structures with their structurally smooth surface is required for their

17   effective use in the development of nanodevices based on an individual nanotube or bulk

18   nanotubes [10,11], as well as nanotube-reinforced nanocomposites [12-16].

19   The chemical treatment of carbon nanotubes surface significantly extends their potential for

20   various applications. The surface functionalization of carbon nanotubes not only leads to their

21   debundling, but also enables the design of an efficient interface to bond them to other active

22   groups, like epoxy groups in nanocomposite materials. In particular, the purification induced

23   covalent grafting of carboxylic groups at the surface of the nanotubes[17] as well as their non-

24   covalent functionalization using surfactants like porphyrins[18] can be used to improve the

25   reinforcing effect when compared to as-produced nanotubes. However, nanotube reinforcement

1   is still far from achieving its theoretical potential and new advances are needed for an efficient

2   load transfer.

3   Functionalized nanotubes have been used for the immobilization of various biomolecules for

4   biosensor applications [10]. Biomolecules bonded to functionalized nanotubes through

5   functional groups are capable of interacting with other active biomolecules via reversible

6   chemical bonding. Among these biomolecules, biotin-streptavidin bonding is known as one of

7   the strongest interactions in nature [19,20]. Therefore, biotin-functionalized nanotubes could be

8   used as a support to immobilize streptavidin molecules in biosensor applications. However,

9   until now, most of the researches undertaken on using nanotubes in microelectronics have been

10 limited to the use of an individual nanotube or bulk nanotubes. Due to the size order of an

11 individual nanotube or their bulk physical state (i.e., powder of entangled structures),

12 manufacturing and manipulation of these materials is quite challenging [10,11]. To address

13 these difficulties, nanotubes have been added to a solution or a polymer matrix, suitable for use

14 in electrospinning [21] and direct-write techniques [22]. Since fibers fabricated by

15 electrospining need additional patterning processes, the ultraviolet (UV)-assisted direct-write

16 assembly [23] could be an alternative to manufacture complex microstructures with desired

17 patterns when an UV-curable epoxy resin is used as a matrix.

18   Here, we report on the use of biotin-streptavidin interactions for further development of a

19 multifunctional nanotube/epoxy composite system. This nanocomposite material was used for

20 the fabrication of nanocomposite microfibers as an example of patterned microstructures for

21 potential micro electromechanical systems (MEMS). Figure 1 shows the schematic of the

22 fabrication process of nanocomposite microfibers suspended between two rectangular pads of

23 nanocomposite by means of UV-assisted direct-write technique. To fabricate the

24 nanocomposites, the SWCNTs were biofunctionalized via acidic treatment and non-covalent

25 functionalization using surfactant, followed by grafting of biomolecules to chemically bridge

1 SWCNTs and epoxy matrix. The different steps of nanotubes functionalization were assessed

2 using various structural characterization techniques. Finally, the effects of SWCNTs

3 biofunctionalization and their dispersion on mechanical and electrical properties of the

4 fabricated epoxy nanocomposite microfibers were studied to understand the nanocomposite

5 structure-property relationship.

6

7 **2. Experimental details**

8 **2.1. SWCNTs synthesis, purification and biofunctionalization**

9 Single-walled carbon nanotubes were synthesized by using UV-laser ablation (248 nm, 20 ns,

10 400 mJ) of a Co/Ni-doped (1.2 at. %) graphite target pellet. The KrF-laser ablation was

11 performed under a controlled argon atmosphere at a temperature of 1150°C through a 45° quartz

12 window (more experimental details on the KrF-laser synthesis and effects of key growth

13 parameters can be found elsewhere [24,25]). The as-produced SWCNTs condensed on a water-

14 cooled collector, located outside of the hot zone of the furnace, onto which they formed a thick

15 rubbery-like film. This SWCNTs mat was peeled off and subjected to subsequent chemical

16 purification treatment. The chemical purification treatment consisted of three main successive

17 steps, each of which is targeted a specific purification. First, the Soxhlet extraction in toluene

18 (for 1h) was conducted on the as-produced SWCNTs to remove residual fullerenes and some

19 disordered carbon nanostructures in the deposit. Second, the SWCNTs were treated by hydrogen

20 peroxide (10%) at room temperature (for 24 h) in order to crack the graphitic shells surrounding

21 the residual catalyst nanoparticles. Finally, HNO_3 (3M) oxidation was conducted to remove

22 metal catalyst particles and covalently functionalize the SWCNTs by the attachment of

23 carboxylic groups at their surface. These chemically P-SWCNTs were collected by vacuum

24 filtration on alumina filters (pore size 20 nm) and after successive rinsing cycles.

1   The desired amounts of P-SWCNTs and 1,3-diaminopropane 99% (D23602, Sigma-Aldrich),

2   with a proportion of 1g P-SWCNTs/5 mL 1,3-diaminopropane 99%, were added to a solution of

3   0.1 mM of zinc protoporphyrin IX (ZnPP, Sigma-Aldrich) in methanol. The suspension was

4   sonicated in an ultrasonic bath (Ultrasonic cleaner 8891, Cole-Parmer) for 1 h. After

5   ultrasonication, the mixture was shaken using a mixer/shaker (Spex CertiPrep 8000M

6   Mixer/Mill) for 12 h at room temperature. The Soxhlet extraction for 2 h with methanol was

7   performed on the aminated P-SWCNTs to remove any unreacted amine. The aminated P-

8   SWCNTs were then added into a solution of 30 mL methanol containing desired amounts of

9   biotin and N,N'-diisopropylcarbodiimide 99% (DIC, D125407, Sigma-Aldrich) with a

10 proportion of 1g biotin/5 mL DIC. Biotinylation of the aminated P-SWCNTs were subsequently

11 performed by shaking the resulting mixture using the mixer/shaker for 12 h at room

12 temperature. Finally, these biotinylated nanotubes were washed with methanol twice, followed

13 by rinsing with distilled water several times to remove any unreacted biotin.

14

15 **2.2. SWCNTs characterization**

16 The KrF-laser synthesized SWCNTs were systematically characterized by various techniques

17 before and after their chemical purification and functionalization. Their Raman spectra were

18 acquired at room temperature in the 100 - 2000 cm^{-1} spectral region under ambient conditions

19 using a back-scattering geometry on a microRaman microscope (Renishaw Imaging Microscope

20 Wire TM) with a 50× objective. A 514.5 nm (2.41 eV) line from an air cooled Ar+ laser was

21 used for excitation radiation. The chemical bonding states of the SWCNTs (before and after

22 chemical purification) were analyzed by means of X-ray photoelectron spectroscopy (XPS)

23 using the Cu K$_\square$ monochromatic radiation (1486.6 eV) of an ESCALAB 200I-XL

24 spectrophotometer. The purified, aminated and biotinylated SWCNTs were characterized by

25 FT-IR (Digilab FTS7000) in order to characterize the chemical components attached to the

1   surface of the nanotubes and assess the biofunctionalization procedure. Finally, the

2   nanostructural characteristics of as-produced, P-SWCNTs and BF-SWCNTs were directly

3   examined by transmission electron microscopy (TEM) using a Jeol JEM-2100F (FEG-TEM,

4   200 kV) microscope.

5

6   **2.3. Nanocomposite preparation**

7   The nanocomposite materials were prepared by mixing an Ultraviolet curable epoxy (UV-

8   epoxy, UVE, UV15DC80, Master Bond Inc.) and either P-SWCNTs or BF-SWCNTs (at two

9   loads of 0.5 wt.% and 1 wt.%). The UV-epoxy used in this study was a special one-component

10   dual cure (ultraviolet/heat curable) epoxy resin which contains a UV photo-initiator having a

11   maximum absorption at 365 nm and a heat-initiator active in the $60 - 80\,^{\circ}\text{C}$ range. Biotin and

12   1,3-diaminopropane 99% (1g biotin/5 mL 1,3-diaminopropane 99%) were stored in 30 mL

13   acetone and ultrasonicated for 30 min. The desired amount of functionalized nanotubes was

14   subsequently added to the solution. Then, the UV-epoxy was slowly mixed with the resulting

15   solution over a magnetic stirring hot plate (Model SP131825, Barnstead international) at $50\,^{\circ}\text{C}$

16   for 4 h. Finally, the streptavidin solution (1 mL 10 μg/mL, S4762, from streptomyces avidinii,

17   Sigma-Aldrich) was slowly added to the nanocomposite mixture and stirred for 1 h. After

18   stirring, the nanocomposite mixture was simultaneously sonicated and heated in the

19   ultrasonication bath at $50\,^{\circ}\text{C}$ for 2 h. The residual trace of solvent was evaporated by heating the

20   nanocomposite mixture at $30\,^{\circ}\text{C}$ for 12 h and at $50\,^{\circ}\text{C}$ for 24 h in a vacuumed-oven (RK-52402,

21   Cole Parmer). The biotin-streptavidin interaction is not affected by the temperature during the

22   solvent evaporation process, since very specific and harsh conditions are required to break the

23   strong biotin-streptavidin bond [19,20].

24   After evaporation of the solvent, the nanocomposites were passed through a very small gap in

25   a three-roll mill mixer (Exakt 80E, Exakt Technologies) for final high shear mixing [26]. The

1 gaps between the rolls varied in three batch-wise progressing steps (10 passes each) with three

2 different gaps at 25 µm, 10 µm and 5 µm, respectively. The speed of the apron roll was adjusted

3 to 250 RPM. The final mixture was then degassed under vacuum for 12 h. For comparison

4 purposes, the nanocomposites with P-SWCNTs were also prepared using the same mixing

5 procedure.

6

7 **2.4. Nanocomposite morphological characterization**

8 For optical imaging purposes, ~20 µm-thick films of the nanocomposites were fabricated by

9 direct deposition on a glass substrate by means of a computer-controlled robot (I & J2200-4, I &

10 J Fisnar) that moves a dispensing apparatus (HP-7X, EFD) along the x, y and z axes [22,27]. The

11 quality of the mixing was observed for the cured nanocomposite films using an optical

12 microscope (BX-61, Olympus) and image analysis software (Image-Pro Plus V5, Media

13 Cybernetics). Microtomed surface of the bulk nanocomposite samples were also observed using

14 field emission scanning electron microscopy (FESEM JEOL, JSM-7600TFE) in order to

15 observe the nanotube dispersion.

16

17 **2.5. Nanocomposite electrical and mechanical characterizations**

18 The ultraviolet-assisted direct-write technique [23] was used to fabricate nanocomposites

19 microfibers in order to assess the reinforcing effects of P-SWCNTs and BF-SWCNTs in the

20 epoxy matrix. Two parallel thick square pads of the nanocomposites with 6 mm gap were first

21 fabricated by extruding the nanocomposites suspensions through a micro-nozzle (5127-0.25-B,

22 Precision Stainless Steel Tips, EFD, internal diameter (ID) = 150 µm) over a glass substrate.

23 Right after, the pads were in situ cured using the optical fibers collected the light from two high-

24 intensity UV light-emitting diodes (LED, NCSU033A, Nichia). Three suspended microfibers

25 were then fabricated between two pads made of the same material. The microfibers were cured

26 using UV exposure while being extruded (Figure 1). The electrical properties of the

7

1 nanocomposite microfibers were characterized using a Keithley 4200 semiconductor parametric

2 analyzer with silver electrodes sputtered on the pads. Mechanical properties (tensile modulus,

3 strength and elongation at break) of the nanocomposites microfibers were measured in a

4 dynamic mechanical analyzer (DMA, DMA2980, TA instruments) using a film tension clamp.

5 The microfibers were tested with a constant loading rate adjusted to reach failure within 20 ± 3 s

6 according to the ASTM D2256 standard. A minimum of five specimens from each

7 nanocomposite sample were tested.

8

9 **3. Results and Discussion**

10 **3.1. Nanotube structural characterization**

11 Figure 2(a) shows typical Raman spectra of the KrF-laser synthesized SWCNTs before and

12 after their chemical purification. The peaks located in the 100-300 cm^{-1} and the 1500-1600 cm^{-1}

13 ranges are typical fingerprints of SWCNTs. The first peak is due to the radial breathing mode

14 (RBM) of the SWCNTs while the second is associated with the tangential vibrations of the C

15 atoms forming the nanotube surface (G band). The RBM peak centred around 182 cm^{-1} arises

16 from SWCNTs with a diameter of 1.26 nm [28]. The D band (1340 cm^{-1}) is generally attributed

17 to the presence of amorphous carbon (a-C) and/or disordered carbon (d-C). The G/D ratio is

18 generally used to qualify the degree of purity of the nanotubes. Here, the G/D ratio is found to

19 decrease for the purified SWCNTs (P-SWCNTs). This is in fact a consequence of the creation of

20 defects on SWCNTs' surface by the nitric acid oxidation step in the purification process. This is

21 further supported by XPS measurements shown in Figure 2(b). The main C 1s core level peak

22 that arises from the C=C bonds is narrow in both samples at 284.5 keV. However, for P-

23 SWCNTs, a shoulder appearing at 288 keV is also present in the spectrum. This component is

24 attributed to the C-O-O carboxylic groups resulting from the covalent functionalization of the

8

1   nanotubes by the nitric acid treatment [29]. Based on the XPS results, it is fair to assume that

2   the purification process led to carboxylic groups grafting onto the SWCNTs surfaces.

3   Figure 2(c) shows a typical TEM micrograph of the as-produced SWCNTs where the

4   nanotubes are found to self assemble, most often into bundles with a diameter in the 5-20 nm

5   range and lengths reaching up to few microns. Other structures, such as carbon-surrounded

6   catalyst nanoparticles and/or graphitic nanostructures (i.e., dark spots in the micrograph) are

7   also present. The various steps of purification are intended to remove residual metal catalyst

8   nanoparticles and most of the undesired carbon forms (e.g., a-C, d-C, fullerenes). Figure 2(d)

9   shows a typical TEM image of the P-SWCNTs. Nevertheless, one can still notice the presence

10   of few dark spots that line the bundles. These are likely some residual catalyst nanoparticles,

11   which were not entirely digested during the nitric acid oxidation treatment. Thermogravimetry

12   analysis (TGA) measurements (not shown here) have demonstrated a substantial decrease (by

13   more than 60%) in the concentration of residual catalyst in the P-SWCNTs samples, when

14   compared to the as-produced SWCNTs.

15   FT-IR spectroscopy was also used to characterize the chemical components attached to the

16   surface of SWCNTs. Figure 3(a) shows the FT-IR spectra of the functionalized SWCNTs at

17   each step of the biofunctionalization process. The FT-IR spectrum of P-SWCNTs shows two

18   specific bands at 1315 cm^{-1} and 1732 cm^{-1}, associated with carboxylic groups [30]. The

19   aminated and biotinylated SWCNTs revealed an appearance of two new strong bands centered

20   at 1450 cm^{-1} and 1479 cm^{-1}, confirming reactions between carboxylic and amino groups [31].

21   The FT-IR spectrum of biofunctionalized carbon nanotubes (i.e., biotinylated SWCNTs) shows

22   appearance of two new broad peaks centered around at 1594 cm^{-1} and 1635 cm^{-1}, which are

23   assigned to 2° amide I and amide II, respectively [31]. The original amide groups of biotin as

24   well as the amide bonds formed between amino groups on the aminated SWCNTs and

25   carboxylic groups on the biotin are believed to be responsible for the two new peaks. The

9

1   appearance of these peaks in the spectrum of biofunctionalized SWCNTs (BF-SWCNTs) proves

2   the grafting of the active biotin groups on the nanotubes surfaces through covalent bonds [31]. A

3   high resolution TEM image (Figure 3(b)) shows individual P-SWCNTs with a very clean

4   surface. This figure permits the direct measurement of the nanotube diameters (1.1-1.3 nm).

5   Finally, Figure 3(c) shows a high-resolution TEM image of a SWCNT covered with a rough-

6   looking material, most likely biomolecules or a mixture of carbonaceous residue and

7   biomolecules, suggesting the effective presence of the grafted biomolecules on the SWCNTs

8   surface [13].

9

10   **3.2. Morphology characterization**

11   Figures 4(a) and 4(b) show optical micrographs of two representative nanocomposites films

12   with 1 wt.% loading of P-SWCNTs and BF-SWCNTs, respectively. The observed dark spots are

13   thought to be nanotubes aggregates or nanotubes entangled around other carbonaceous

14   materials. For the P-SWCNTs (Figure 4(a)), the majority of the nanotube aggregates are in the

15   sub-micron range but some micron-size aggregates with a diameter of up to ~1μm are also

16   present. A drastic change of the size of the aggregates was observed for the nanocomposite film

17   with the BF-SWCNTs (Figure 4(b)). The larger spots observed for the P-SWCNTs-reinforced

18   nanocomposite film became smaller, to 0.7 μm diameter (in average) when the BF-SWCNTs

19   were used. To further support the optical observations, the cross-section of the nanocomposites

20   microfibers was also observed under scanning electron microscopy (SEM). Figures 4(c) and

21   4(d) show typical SEM images of the surface of nanocomposites with 1 wt.% loading of P-

22   SWCNTs and BF-SWCNTs, respectively. In the purified SWCNT-reinforced nanocomposite,

23   the nanotubes formed clusters and large aggregates (i.e., the bright spots). When the

24   biofunctionalized SWCNTs were used, the large aggregates disappeared and it was difficult to

25   spot clusters of SWCNTs. Based on all the above observations, the fairly uniform dispersion of

1   the nanotubes and their associated aggregates for both cases might be attributed to the

2   effectiveness of the nanocomposite mixing procedure combining ultrasonication and three-roll

3   mill mixing methods. Comparing the nanocomposites dispersion suggests that the presence of

4   biomolecules at the nanotube-matrix interface prevented re-aggregation of nanotubes and

5   improved the SWCNTs dispersion.

6

7   **3.3. Mechanical properties**

8   The effect of biofunctionalization of SWCNTs on the mechanical properties was assessed by

9   tensile testing. Figure 5 shows the stress-strain curves along with their resulting histograms of

10   the neat UV-curable epoxy (UV-epoxy) and its associated nanotube-reinforced nanocomposites,

11   prepared either with the P-SWCNTs or BF-SWCNTs. Figure 5(a) shows an optical image of

12   typical microfibers used in the tensile experiments and Figure 5(b) is a representative SEM

13   image of a fiber cross-section after its fracture under tensile loading. The error bars on the

14   histograms were calculated from the 95% confidence intervals on the mean value obtained from

15   the measurements. When the BF-SWCNTs were added to the composite with 0.5 wt.% loading,

16   the average modulus showed an increase of 59% compared to that of the neat resin and an

17   increase of 19% when compared to that of the nanocomposite reinforced with the same

18   nanotube loading of P-SWCNTs. The improvement of modulus for the composites with 1 wt.%

19   BF-SWCNTs loading were found to be 93% and 16% when compared to those of the neat resin

20   and the P-SWCNTs-reinforced composites, respectively. The increased stiffness, from the neat

21   epoxy resin to the nanocomposites, might be attributed to the proper dispersion as well as

22   beneficial orientation of the nanotubes that may occur during the extrusion of the

23   nanocomposite through the micronozzle [32]. For both nanotube loadings, BF-SWCNTs led to

24   nanocomposites ~20% stiffer than that obtained with P-SWCNTs. The contribution of possible

25   orientation in this higher stiffness is unlikely, since all nanocomposite microfibers were

11

1 fabricated under the same extrusion conditions. Therefore, the further improvement of stiffness

2 for the BF-SWCNT-based nanocomposites is most likely attributed to the increased effective

3 aspect ratio of the BF-SWCNTs as a consequence of their better dispersion.

4   The average failure strength of the P-SWCNTs- and BF-SWCNTs-reinforced nanocomposite

5 was also improved with the addition of nanotubes. The incorporation of 0.5 wt.% BF-SWCNTs

6 to the epoxy matrix increased its strength by approximately 50%. The nanocomposite with 1

7 wt.% BF-SWCNTs showed further enhancement (by 75%). For both nanotube loadings, higher

8 failure strength (up to 24%) was achieved for the composites reinforced with BF-SWCNTs

9 when compared to the P-SWCNTs-reinforced composites. More interestingly, the strength of

10 the nanocomposite microfibers containing 0.5 wt.% BF-SWCNTs was found to be very close to

11 that of the 1 wt.% P-SWCNTs-reinforced nanocomposite microfibers. This relatively higher

12 improvement could be attributed to a possible strong nanotube/matrix interfacial interaction and

13 to a good dispersion of nanotubes with the presence of the biomolecules. Considering the

14 quantity of the SWCNTs added, these improvements of both modulus and strength are among

15 the highest improvements for epoxy composites reported so far, as compared in Table 1

16 [9,12,13].

17

18 **3.4. Governing interaction mechanisms**

19   The possible governing interaction mechanisms between nanotubes and epoxy matrix with the

20 presence of biomolecules are schematized in Figure 6. The proposed mechanism can be

21 interpreted in the light of the mechanisms proposed by Wang et al. [31] and Sun et al. [12]. The

22 nanotube biofunctionalization begins with grafting (covalently and non-covalently) carboxylic

23 and amine groups to the surface of SWCNTs (more details on the synthesis procedure are found

24 in experimental section). Grafting biomolecules on the nanotubes surface relies on the

25 carboxylic groups created during the nanotube purification and on the use of Zinc

12

1   protoporphyrin IX (ZnPP) molecules. ZnPP molecules can non-covalently interact with the

2   nanotubes wall through π-π interactions [18,22]. It should be mentioned that the

3   functionalization procedure used in this study is non-destructive to the sidewall by attaching

4   functional groups to the nanotubes. Since the long acidic treatment can destroy the wall integrity

5   and consequently affect the mechanical properties of the resulting nanocomposite, the duration

6   of acidic treatment was effectively controlled in our purification process. The carboxylic groups

7   are capable of interacting with the amine groups and could contribute to further grafting of

8   biomolecules to the surface of nanotubes. Streptavidin molecules offer four active sites which

9   are equally capable of binding with biotin. The streptavidin was added to the BF-SWCNTs

10   mixture in the presence of epoxy resin in order to avoid possible consumption of their four

11   active sites by BF-SWCNTs, since they should be still-active to bridge between BF-SWCNTs

12   and epoxy matrix (Figure 6b). The proposed interaction mechanism between streptavidin, biotin

13   and epoxy resin on the right side of Figure 6b (i.e., epoxy side) was inspired from the work done

14   by Wang et al. [31]. Therefore, a very strong nanotube-epoxy cross-linked network could be

15   obtained by the action of active streptavidin that binds to other biotin molecules, which are

16   attached to either epoxy groups or BF-SWCNTs.

17   The formation of such chemical bonding is believed to be responsible for the reasonable

18   increase of failure strength obtained for the BF-SWCNTs-reinforced nanocomposites. It is worth

19   noting that the average failure strain of 1 wt.% BF-SWCNTs-reinforced nanocomposite

20   microfibers showed a slight increase (by 19%) in comparison to that of neat epoxy microfibers.

21   Considering the flexibility of SWCNTs and their highly elastic behavior, the improvement of

22   failure strain might be another proof of strong interfacial interaction [9]. Another contribution

23   might come from stretching the curved and entangled nanotubes during the mechanical

24   solicitation [9]. These factors could contribute to the increased failure elongation only when the

25   nanotubes are well-bonded to the matrix through strong interfacial interactions. Therefore, the

1   BF-SWCNTs could be used not only as a strong reinforcement but also to slightly improve

2   failure strain and thus to increase toughening properties and impact resistance of intrinsically

3   brittle epoxies as reported in the literature [9,12]. The toughening effect of the nanotubes might

4   be further evolved from the non-linear response of the nanocomposites under strain [32], since

5   the response of the neat epoxy resin is linearly elastic (Figure 5c). It has been reported that

6   carbon nanotubes could promote effective toughening mechanisms such as crack bridging and

7   shear banding, although these reasons were not experimentally verified here. When compared to

8   current toughening methods such as rubber modification of epoxy resins which may decrease

9   their other mechanical properties, well-bonded carbon nanotubes confer an extra benefit without

10   sacrificing other properties. This benefit can be translated to epoxy-based traditional structural

11   composites in order to improve the epoxy matrix toughness of composite laminates in which

12   nanotubes are added to the epoxy matrix. Thus, the toughening affect might be the most

13   important advantage of nanomodification in this new class of composites which are known as

14   multiscale composites.

15

16   **3.5. Electrical conductivity**

17   The effect of biofunctionalization of the nanotubes on electrical conductivity was studied. The

18   electrical conductivity of the P-SWCNTs and BF-SWCNTs-reinforced composite microfibers

19   was characterized upon voltage application between two silver-coated pads. Figure 7 shows the

20   measured current with respect to applied voltage (I-V) curve of the nanocomposite microfibers

21   for two different nanotubes loadings. Linear responses, with different slopes (R), of the currents

22   versus the applied voltage were observed for all nanocomposite microfibers. For the microfibers

23   with nanotube loading of 0.5 wt.%, the BF-SWCNTs were found to lead to slightly lower

24   conductivities (by 19%), but this remains within the uncertainty of the measurements. At

25   nanotube loading of 1 wt.%, the nanocomposite microfibers with BF-SWCNTs showed a

1 decrease of 129% in electrical conductance (i.e., *1/R*) when compared to that of P-SWCNTs-

2 reinforced nanocomposite. The decrease of electrical conductivity might be attributed to the

3 presence of streptavidin molecules that possibly act as a less-conductive layer surrounding the

4 SWCNTs. The measured resistivity was decreased with the addition of more nanotubes (1 wt.%)

5 through which more electrical percolation pathways should be formed. This could be described

6 by the electrical conductivity mechanisms for the nanocomposites which are direct contact of

7 nanotubes in their percolation pathways and/or electron tunneling between neighboring

8 nanotubes at sufficiently close proximity [33]. Depending on nanotube loading, the contribution

9 of these two mechanisms in the measured electrical conductivity varies. At the nanotube

10 loading of 0.5 wt.%, electrons must travel through larger amounts of insulating epoxy matrix

11 between the conductive nanotubes and the contribution of electron tunneling in the electrical

12 conductivity is likely larger when compared to that of nanocomposites with 1 wt.% nanotubes.

13 When more percolation conducting pathways are formed (at higher nanotube loadings),

14 electrons conduct predominantly along the conductive nanotube pathways and thus, the effect of

15 electron tunneling decreases [33]. For bio-functionalized nanotubes, the biomolecules might be

16 placed between conductive nanotubes in their percolation pathways and affect the

17 nanocomposite conductivity. Therefore, it is thought that the presence of biomolecules is more

18 significant at higher nanotube concentrations and responsible for a clear change in the electrical

19 conductivity of the nanocomposite microfibers containing 1 wt.% of SWCNTs. This

20 phenomenon has been used for potential biosensor applications where streptavidin molecules

21 are detected by their attachment to the surface of biotin-functionalized nanotubes [31,34].

22

23 **4. Conclusions**

24   The surface biofunctionalization of SWCNTs and the utilization of an efficient mixing

25 procedure enabled the full integration of nanotubes within an epoxy matrix. Although the

1 nanotube dispersion and mechanical properties of the nanocomposite reinforced with P-

2 SWCNTs were reasonably improved in comparison to the neat epoxy, subsequent grafting of

3 biotin molecules to the P-SWCNTs led to a fairly good dispersion and further enhancement in

4 their reinforcing effect. The failure strength of nanocomposite microfibers reinforced with 1

5 wt.% of BF-SWCNTs showed an increase of 76% when compared to that of pure resin and an

6 increase of 25% when compared to that of the nanocomposite reinforced with P-SWCNTs,

7 indicating the effectiveness of biofunctionalization to facilitate load transfer. The

8 nanocomposite high strength provided by the biomolecules interactions make these

9 multifunctional nanocomposites a good choice for the fabrication of high-performance

10 nanocomposite-based devices in micro electromechanical systems and microelectronics.

11 Considering the ability to change the electrical conductivity of the microfibers under mechanical

12 disturbances and also by capturing biomolecules, the utilization of these multifunctional

13 nanocomposite materials enables the fabrication of easily-manipulated strain sensors and porous

14 microfibers or 3D complex patterns as solid support materials for potential biosensor

15 applications.

16

24

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34
35

36 **Figures and Tables captions**

37 **Figure 1**. Schematic representation of the UV-assisted direct-writing of nanocomposite

38 microfibers: (a) nanocomposite extrusion through a capillary micronozzle by an applied pressure;

39 fibers are partially cured shortly after extrusion under UV illumination, (b) close-up view of the

40 microfibers, and (c) interfacial bonding between SWCNTs and epoxy matrix through biotin-

41 streptavidin interactions.

42

1 **Figure 2**. (a) Raman spectra, (b) X-ray photoelectron spectra of as-produced (bottom) and purified

2 (top) SWCNTs, (c) typical TEM image of as-produced SWCNTs, and (d) TEM image of P-

3 SWCNTs.

4 **Figure 3**. (a) FT-IR spectra of (i) P-SWCNTs (bottom), (ii) aminated SWCNTs (middle), and (iii)

5 biotinylated SWCNTs (BF-SWCNTs) (top), (b) high-resolution TEM image of a P-SWCNTs, and

6 (c) high-resolution TEM image of a BF-SWCNTs.

7

8 **Figure 4.** Optical microscope images of a 20-μm thick film of the nanocomposite containing (a) 1

9 wt% P-SWCNTs and (b) 1 wt% BF-SWCNTs, (c) and (d) typical SEM images of the cross-section

10 surface of the bulk nanocomposites containing 1 wt% P-SWCNTs and 1 wt% BF-SWCNTs,

11 respectively.

12

13 **Figure 5.** Mechanical characterization of the nanocomposite materials: (a) optical image of a

14 typical fabricated specimen consisting of three suspended fibers between two rectangular pads, (b)

15 SEM image of fracture surface of a nanocomposite fiber, (c) typical stress–strain curves and (d)

16 histograms of modulus, strength and failure strain of the pure UV-epoxy and its associated

17 nanocomposites.

18

19 **Figure 6.** Schematics of (a) synthesis procedure of the BF-SWCNTs and (b) proposed interaction

20 mechanisms governing the interaction of the BF-SWCNTs and the epoxy matrix by bridge formation

21 through biotin-streptavidin interactions.

22

23 **Figure 7.** Measured current upon voltage application for the nanocomposite microfibers.

24

25

26

1   **Table 1.** Comparison of the mechanical properties improvements in our work with those reported in

2   literature.

3

4   **Table 1**

SWCNTs type	SWCNTs wt.%	Processing method	Modulus (% increase)	Strength (% increase)	Ref.
NH$_2$-modified	1.0	Solution mixing	31	25	[9]
Amine-modified	1.0	Simple mixing	26	16	[12]
Epoxide-modified	1.0	Solution mixing	60	40	[13]
Carboxyl-modified	1.0	Shear mixing	24	-	[?]
NH$_2$-modified	0.1	Simple mixing	56	12	[?]
Fluorinated	1.0	Solution mixing	30	18	[?]
Purified	5.0	Solution mixing	0	7	[?]
Bio-functionalized	1.0	Solution & shear mixing	93	75	Present work

5

6

Figure 1

Figure 2

(a)

RBM 185

D-band 1350

G-band 1600

- - - As-produced SWCNTs
— Purified SWCNTs

Raman intensity

Raman shift (cm⁻¹)

(b)

sp²

C - O
C = O
C - O - O

- - - As-produced SWCNTs
— Purified SWCNTs

Intensity

Energy (keV)

(c) 50nm

(d) 50nm

Figure 3

(a)

- - - Purified-SWCNTs
— — Aminated-SWCNTs
— Biotinylated-SWCNTs

1479
1450
1635 1594
(iii)
(ii)
(i)
1732
1315

Absorbance

Wavenumber (cm⁻¹)

(b) 2nm

(c) 2nm

Figure 4

Figure 5

(a)

1 mm

(b)

50 μm

(c)

Legend:
- ○ Neat epoxy
- △ 0.5wt%-purified
- ▲ 0.5wt%-biofunctionalized
- □ 1wt%-purified
- ■ 1wt%-biofunctionalized

Axes: Stress (MPa) vs Strain (%)

(d)

Modulus (GPa), Strength (MPa), Failure strain (%)

Legend:
- Neat epoxy
- 0.5wt%-purified
- 0.5wt%-biofunctionalized
- 1wt%-purified
- 1wt%-biofunctionalized

Figure 6

a)

SWCNTs Purification & Non-covalent Functionalization   SWCNTs Amination   SWCNTs Biotinylation

b)

Biofunctionalized SWCNTs   Interphase   Epoxy matrix

Figure 7

Legend:
- 0.5wt%-biofunctionalized
- 0.5wt%-purified
- 1wt%-biofunctionalized
- 1wt%-purified

X-axis: Applied voltage (V)
Y-axis: Current (nA)