INVESTIGATION OF EFFECT OF CNT WEIGHT FRACTION ON SMART PAINT FOR STRUCTURAL HEALTH MONITORING OF CARBON FIBER REINFORCED COMPOSITES

Yağmur Ateşcan[1] and Hülya Cebeci[2]

[1]Department of Aeronautics and Astronautics Engineering, Istanbul Technical University, Maslak, Istanbul, 34469, Turkey
Email: atescan@itu.edu.tr, Web Page: http://akademi.itu.edu.tr/atescan/
[2]Department of Aeronautics and Astronautics Engineering, Istanbul Technical University, Maslak, Istanbul, 34469, Turkey
Email: geyikh@itu.edu.tr, Web Page: http://akademi.itu.edu.tr/geyikh/

Keywords: Carbon nanotube, strain sensor, damage sensing, structural health monitoring, smart paint

Abstract

The increased use of composites for load-carrying structures, bring out the critical problem that strain and damage sensing to maintain reliable structures. In this study, carbon nanotube (CNTs) polymer nanocomposites (CNT-PNCs) as a smart paint were used as a strain sensor to follow the mechanical deformations of the structures. First, CNT polymer nanocomposites (CNT-PNCs), with three different CNT weight fractions (0.1, 0.25 and 0.5), were prepared by adding CNTs into the epoxy by shear mixing. Effect of CNT weight fraction on electrical conductivity of CNT-PNCs were investigated by 2-probe electrical conductivity measurement. The results show that even at low concentrations of CNT the electrical conductivity is beyond the percolation threshold. Within these results CNT-PNCs were applied on to the surface of composite structures as a smart paint for in-situ Structural Health Monitoring (SHM). Cyclic loading were applied onto the specimens at a constant voltage of 10 V and the stress and resistivity change data were obtained simultaneously. The test results showed a proper compliance with a damage of the composite structure.

1. Introduction

Fiber reinforced polymer composites are widely used in aerospace, automotive, civil and marine applications, through their excellent mechanical properties like high specific stiffness and strength and low density. However, since the mechanical performance of composite materials may be severely altered when damage occurs, the serious interest in the use of composite materials has led to the necessity of the development of innovative ways to monitor the status of the composite structures in service time **[1-7]**. For this purpose, this study aims to fabricate smart coating based on CNT and epoxy to cover the composite material as a non-invasive method and perform SHM in real time basis.

In-situ SHM of composites for aerospace applications is an ongoing study for many years. Using strain gages, piezoelectric or piezoresistive sensors are the oldest methods for SHM. Also using fiber optic sensors is an ongoing study for SHM, which have not been commercialized as expected yet due to being an invasive method **[8-10]**. From this point of view, nanomaterials such as CNTs may be an alternative solution due to its particular properties like high electrical conductivity, mechanical reinforcing and self-sensing properties without adding weight penalty.

Excerpt from ISBN 978-3-00-053387-7

Overall several approaches on integrating CNTs in composite structure to identify the damage and the mechanism, using them as a paint for strain sensing onto the surface is an easy to apply and measurement technique. When compared as a dispersed state of CNTs at CFRPs, using a CNT paint onto the surface can avoid several critical aspects as agglomeration, non-uniform distribution of CNTs and as well as Joule heating within the composite structure itself.

CNT based polymer nanocomposites are multifunctional materials that, in addition to their basic functions of physical and mechanical properties enhancement, allow the sensing and monitoring of strain or damage by the measurement of the material electrical resistance. The working principle in here is the deformation of CNT based polymer composites or the damage initiation and evolution in the nanocomposites can lead to changes in their electrical resistance. These electrical resistance changes provide the possibility of real-time health monitoring, which improves the safety of structures **[3, 5, 11]**.

Electrical conductivity of composites consisting of conducting fillers and insulating matrices is explained by percolation theory. The critical filler content, where the composite undergoes an insulator to conductor transition, is referred as the percolation threshold. At that point, the measured electrical conductivity of the composite sharply jumps up several orders magnitude due to the formation of continuous electron paths or conducting networks **[12]**. Bauhofer and Kovacs **[13]** carried out a review study to discuss the effect of experimental parameters on the percolation threshold of CNT-polymer nanocomposite. According to results of studies, the important parameters, affect the percolation thresholds are, type, synthesis method and dimensions of CNTs. In addition, polymer type and dispersion methods are also significant to obtain a conductive nanocomposite. According to study of Kovacs et al. **[14]** percolation threshold was achieved with nearly 0.1 wt% filler concentration. Effect of CNT dimensions on the percolation threshold was also studied **[15, 16]**. According to results, the aspect ratio of the CNT affects the percolation threshold in a positive manner and the percolation threshold decrease with increasing aspect ratio. CNT orientation is also a significant parameter for most of applications. In electrical properties, Du et al. **[17]** and Behnam et al. **[18]** showed that, maximum conductivities achieved with slightly aligned, rather than perfectly aligned CNTs. In perfectly aligned CNT systems, each nanotube forms very few junctions with its neighbors, since it lies almost parallel to them. Depending on the decrease in the number of the junctions and the conduction paths, the resistivity increases at the perfectly aligned CNTs. On the other hand, since the randomly aligned CNTs have higher ability to form many junctions, resistivity decreases on the randomly aligned CNTs.

In this study, CNT-PNCs were fabricated with randomly oriented CNTs dispersed in epoxy and CNT PNCs were applied as top cover on CFRP composite as a smart paint to achieve an optimized response on the deformation behavior during testing. The application of CNT smart paint onto the laminated carbon composites like a paint is very much dependent on the effectiveness of dispersion of CNTs inside the epoxy. The resistance change of CNT-PNCs was investigated for its application as a strain sensor on a CFRP composite subjected to cycling loadings.

2. Materials and Methods

The carbon fiber reinforced composites were fabricated using bidirectional carbon fiber fabric and Epikote resin MGS L160/hardener with Epikote curing agent MGS H160. The CNTs for smart paint application was synthesized in house as explained in the next section in details. The epoxy used for polymer nanocomposite manufacturing was Epikote resin MGS L160/hardener with Epikote curing agent MGS H160, as well.

Excerpt from ISBN 978-3-00-053387-7

2.1. Carbon Nanotube Growth with Chemical Vapor Deposition Method

CNTs were synthesized on silicon (Si) wafer substrates by a modified chemical vapor deposition (CVD) method. Si wafers were deposited with 10 nm thick alumina that used as a metal support and a thin layer (~3nm) of Fe was coated onto alumina by electron-beam evaporation. For growth process, a combination of three gases (C_2H_4, H_2, He) was used for growth, nucleation and purging. CNT synthesis was achieved at high temperature (750 ^{0}C) and an optimized protocol was used to grow all CNTs required for this study.

Morphological characterization of CNTs were studied with scanning electron microscopy (SEM) to determine the morphology, orientation and length of the CNTs. According to SEM image growth CNTs were vertically aligned (VA-CNTs). The quality of CNTs were studied with Raman spectroscopy and thermal gravimetric analysis (TGA). From Raman spectroscopy, the G/D ratio is 1.39 (~1.4 at literature for MWCNTs) and according to TGA, ten percentage of thermal degradation (T_d 10%) is found at approximately 600°C.

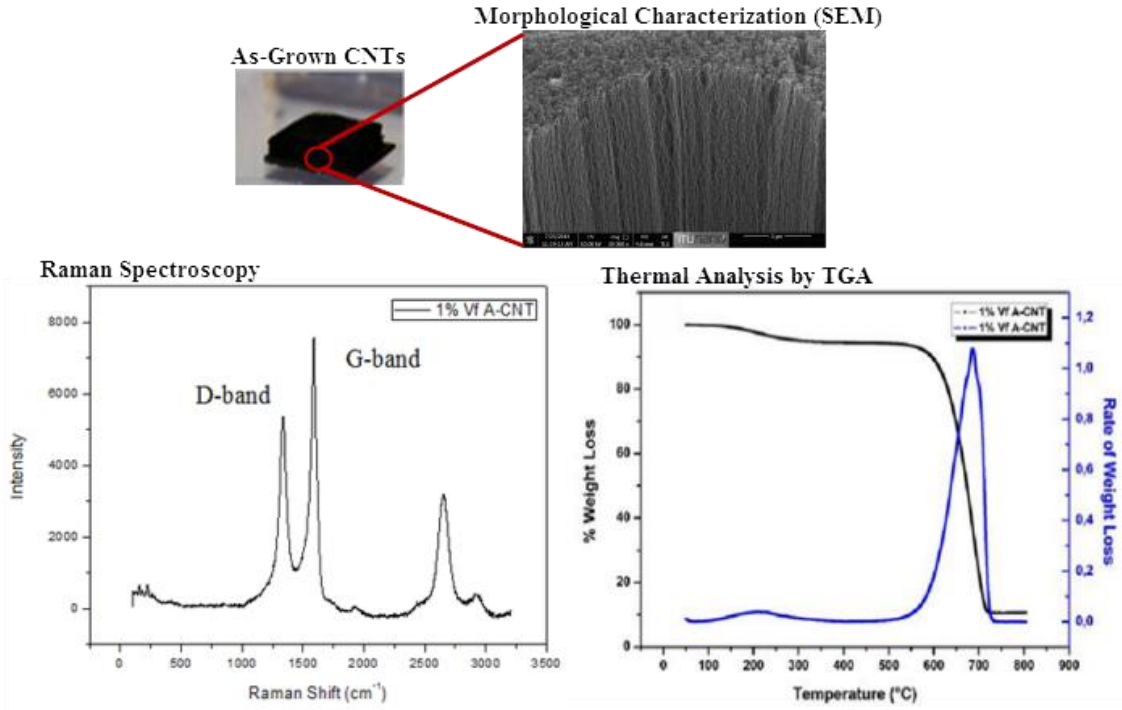

Figure 1. Characterization of VA-CNTs synthesized by CVD method.

2.2. Fabrication and Characterization of CNT Smart Paint

To fabricate CNT-PNCs, as-grown CNTs were directly added into the epoxy system with various weight fractions (0.1, 0.25 and 0.5 wt%). For the dispersion of CNTs shear mixing was applied without any functionalization of nanotubes. Electrical characterization of CNT-PNCs was made with 2-probe electrical conductivity measurements. To prepare conductivity measurement samples, the CNT epoxy mixtures were cured in silicon molds as CNT-PNCs. After curing, surface of CNT-PNCs were sanded and polished to obtain a smooth surface for measurements. Two parallel electrodes were deposited on relevant sample surfaces and voltage (10 Volt) was applied (Figure 2(a)). The current across the sample was measured and resistance of sample was obtained. Conductivity of sample was calculated according to Equation (1), where L (m) is the span between two electrode point, A (m^2) is the cross sectional area of sample and R (Ω) is the resistance.

Excerpt from ISBN 978-3-00-053387-7

$$\sigma = \frac{L}{RA} \quad (1)$$

The measured electrical conductivity of CNT-PNCs was compared with the conductivity of other CNT-PNCs in the literature. As seen from Figure 2 (b), the CNT-PNCs were measured to have better conductivity than most of the other examples and electrical conductivity is beyond the percolation threshold even at low CNTs loading [13].

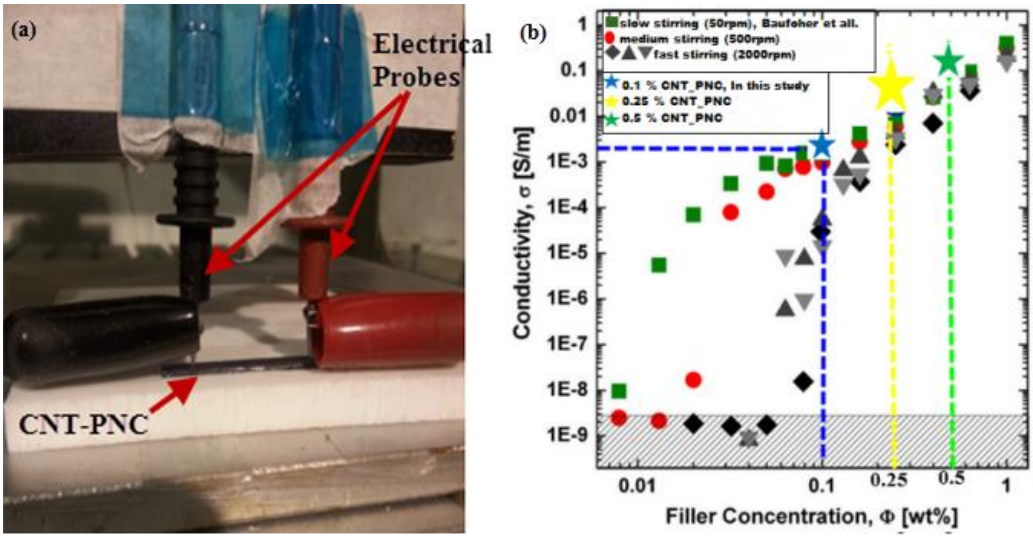

Figure 2. (a) Electrical conductivity measurement setup of CNT-PNCs (b) Comparison of electrical conductivities of CNT-PNCs [13]**.**

Morphological characterizations of CNT-PNCs were performed with a high resolution SEM. The prepared samples were broken from one end and SEM images were taken from this fracture surfaces. As seen from Figure 3, a well CNT dispersion was obtained in polymer system within the shear mixing.

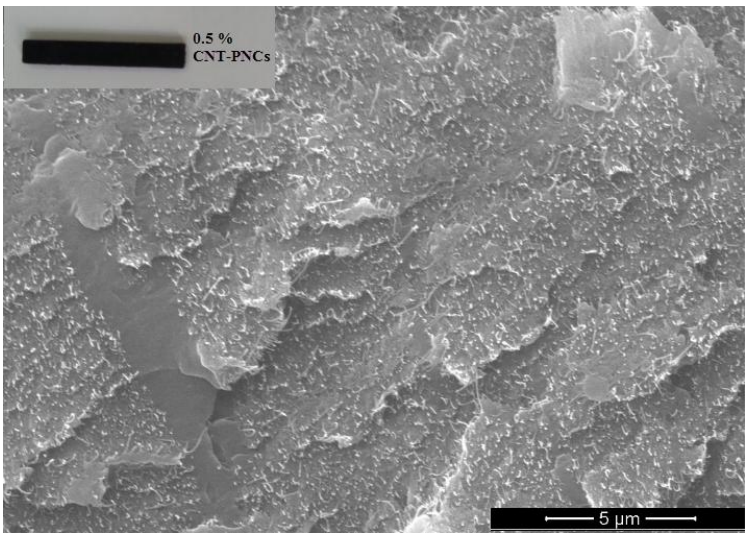

Figure 3. SEM images of 0.5 wt% CNT-PNCs

Excerpt from ISBN 978-3-00-053387-7

2.3. CFRP Composites with CNT Smart Paint

For the fabrication of composite plates, 10 plies bidirectional carbon fiber fabrics were cut at the required dimensions (300 x 300 mm). Each layer was laid on a metal flat plate over and over. Vacuum infusion method was used to fabricate composite plates (Figure 4). Appropriate bagging material was placed, vacuum was applied and the infusion of resin was followed. The plate was cured for 24 h at room temperature. After fabrication of this plate, tension test specimens with specified dimensions, (250 x 25 mm) according to ASTM D3039 Test Method for Tensile Properties of Polymer Matrix Composite Materials Standard [19], were cut from plate.

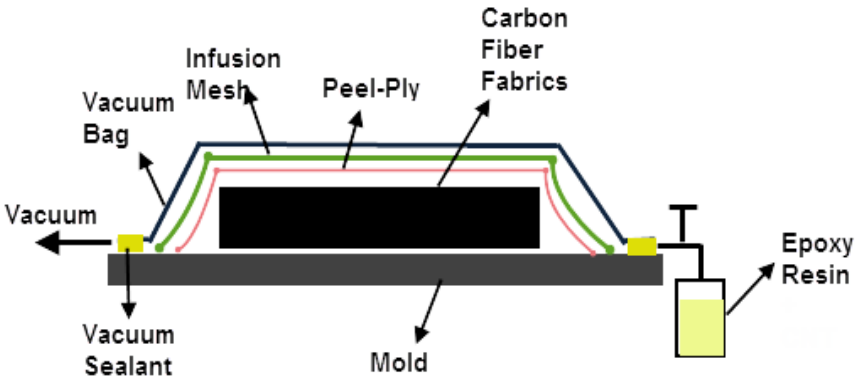

Figure 4. Vacuum Infusion Method for plate fabrication.

CNT-PNC was applied onto the carbon fiber/epoxy composite as a smart paint with specified dimensions (50 x 10 mm). Metal mask with 0.5 mm thickness was used to apply smart paint with specified dimensions (Figure 5 (a)). Before applying smart paint, silver paste was applied onto the specified surface area of composite to avoid an electrical short-circuit. Aluminum electrodes were placed on silver paste and smart paint was applied on them. Finally, specimens were cured for 24 h at room temperature. Figure 5 (b) shows the smart paint coated tension test specimen.

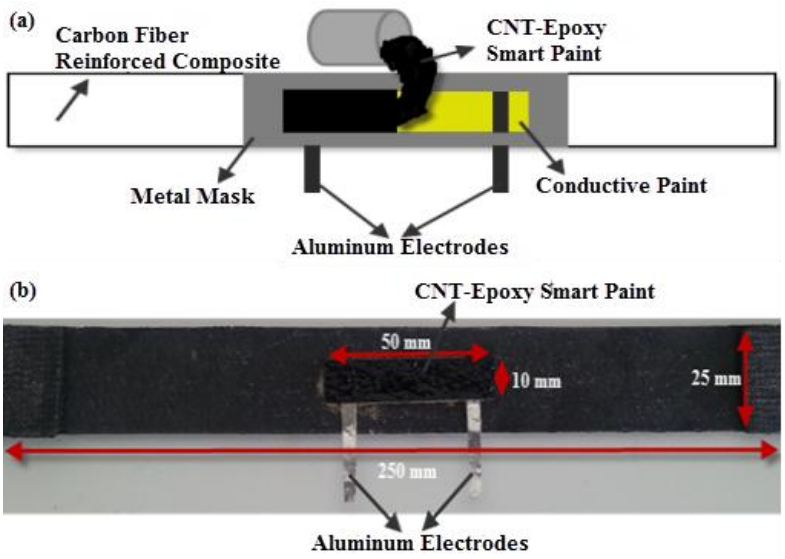

Figure 5. (a) CNT-Epoxy paint application on carbon fiber composite, **(b)** Smart paint coated tension test specimen

Excerpt from ISBN 978-3-00-053387-7

2.2. In-situ Diagnostics at Mechanical Testing

Cycling loading were performed with Shimadzu Universal Testing Machine. Loading speed is 4 kN/min for all cycles. The maximum load for the first cycle is 4 kN and the load increase 4 kN at each cycles. 5 cycles were applied and the maximum load for the last cycle is 20 kN. While mechanical tests were being performed, electrical resistance of the smart paint was recorded simultaneously with a Keithley source meter model 2400. The instrument electrodes were attached to the aluminum conductive strips. A constant voltage of 10 V was applied and current was measured to determine electrical resistance of CNT smart paint. The testing instrument and modified set-up can be seen in Figure 6.

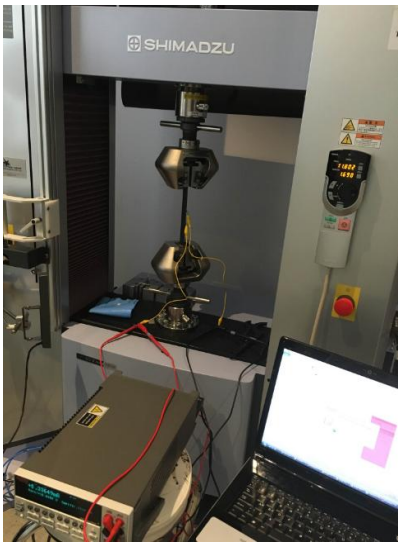

Figure 6. Test system for in situ diagnostics at cycling loading.

In order to develop a strain sensor, it is important to evaluate the relationship between the stress applied to the tested specimens and the piezoresistivity measured by the sensor. The piezoresistivity was calculated according to the definition of Alamusi et al. [20].

$$RC = \frac{R_i - R_0}{R_0} \tag{2}$$

In this equation R_i is the measured resistance during the tests and R_0 is the initial resistance of material. R_0 were measured just before the mechanical loading was started.

3. Results and Discussion

According to electrical conductivity of CNT-PNCs both 0.1, 0.25 and 0.5 wt% CNT-PNCs have better electrical conductivity than most of the other examples. Since electrical conductivity is beyond the percolation threshold even at low CNT loading, 0.1 wt% CNT smart paint was used for first cycling loading applications. As seen from Figure 7, the resistance change increase with the increasing stress conditions. Depending on the rise and fall on stress, the electrical resistance change also shows the rise and fall. The inreases and decreases are more clear at high stresses and electrical resistance change does not show an exact tracking up to 100 MPa.

Excerpt from ISBN 978-3-00-053387-7

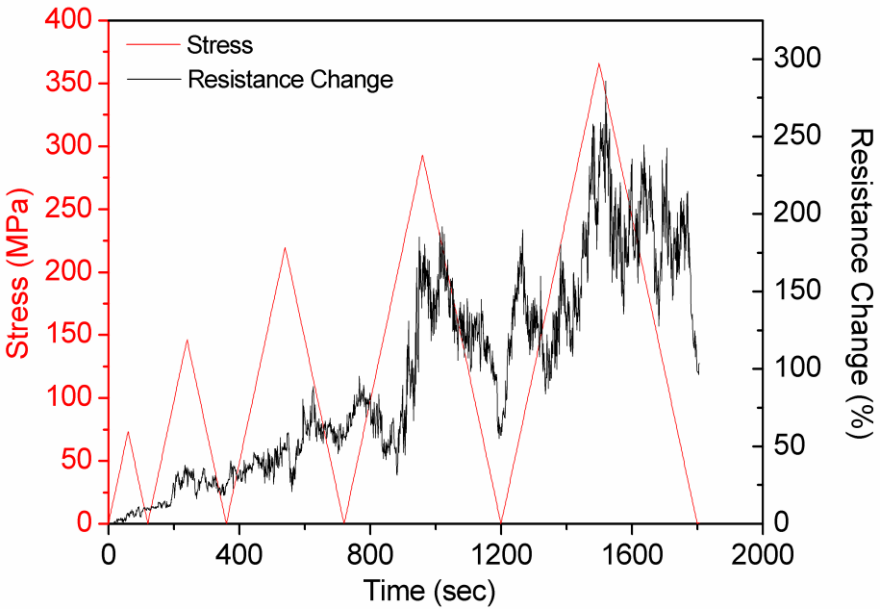

Figure 7. Stress / Resistance Change vs. Time results for 0.1 wt% CNT smart paint

4. Conclusions

The intention of this study is to determine efficiency of CNTs for evaluating in-situ structural health monitoring of mechanically loaded structures. Both electrical conductivity measurements for CNT-PNCs and in-situ electrical resistance change measurements of CNT smart paints were performed in this study. All CNT-PNCs with various CNT loading showed higher electrical conductivity than other examples and all of them were below the percolation threshold. 0.1 wt% CNT smart paint was applied onto the surface of CFRP composites and cycling loading with an increasing triangular load-unload testing protocol was applied to the test specimens. Electrical resistance change of the CNT smart paint was measured simultaneously. Especially for high stress conditions the resistance change showed a critical increase and decrease depending on the rise and fall of stress on the structure. 0.25 and 0.5 wt% CNT smart paints will be also fabricated and tested to determine the their effectiveness on in-situ structural health monitoring as a strain sensor.

References

[1] Alexopoulos ND, Bartholome C, Poulin P, Marioli-Riga Z. Structural health monitoring of glass fiber reinforced composites using embedded carbon nanotube (CNT) fibers. Composites Science and Technology. 2010;70:260-71.
[2] Alexopoulos ND, Poulin P, Bartholome C, Marioli-Riga Z. Real time sensing of structural glass fiber reinforced composites by using embedded PVA - carbon nanotube fibers. Icem 14: 14th International Conference on Experimental Mechanics, Vol 6. 2010;6.
[3] Chiacchiarelli LM, Rallini M, Monti M, Puglia D, Kenny JM, Torre L. The role of irreversible and reversible phenomena in the piezoresistive behavior of graphene epoxy nanocomposites applied to structural health monitoring. Composites Science and Technology. 2013;80:73-9.
[4] Eswaraiah V, Balasubramaniam K, Ramaprabhu S. Functionalized graphene reinforced thermoplastic nanocomposites as strain sensors in structural health monitoring. Journal of Materials Chemistry. 2011;21:12626-8.
[5] Grammatikos SA, Gkikas G, Paipetis A. Monitoring strain and damage in multi phase composite materials using electrical resistance methods. Smart Sensor Phenomena, Technology, Networks, and Systems 2011. 2011;7982.

Excerpt from ISBN 978-3-00-053387-7

[6] Zhao H, Yuan F-G. Carbon nanotube yarn sensors for structural health monitoring of composites. Nondestructive Characterization for Composite Materials, Aerospace Engineering, Civil Infrastructure, and Homeland Security 2011. 2011;7983.
[7] Sebastian J, Schehl N, Bouchard M, Boehle M, Li L, Lagounov A, et al. Health monitoring of structural composites with embedded carbon nanotube coated glass fiber sensors. Carbon. 2014;66:191-200.
[8] Torres Gorriz B, Calderon Garcia P, Paya-Zaforteza IJ, Sales Maicas S. Experimental and numerical analysis of a hybrid FBG long gauge sensor for structural health monitoring. Measurement Science & Technology. 2014;25.
[9] Abry JC, Choi YK, Chateauminois A, Dalloz B, Giraud G, Salvia M. In-situ monitoring of damage in CFRP laminates by means of AC and DC measurements. Composites Science and Technology. 2001;61:855-64.
[10] Lau KT. Structural health monitoring for smart composites using embedded FBG sensor technology. Materials Science and Technology. 2014;30:1642-54.
[11] de Villoria RG, Yamamoto N, Miravete A, Wardle BL. Multi-physics damage sensing in nano-engineered structural composites. Nanotechnology. 2011;22.
[12] Ma P-C, Siddiqui NA, Marom G, Kim J-K. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review. Composites Part a-Applied Science and Manufacturing. 2010;41:1345-67.
[13] Bauhofer W, Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. Composites Science and Technology. 2009;69:1486-98.
[14] Kovacs JZ, Velagala BS, Schulte K, Bauhofer W. Two percolation thresholds in carbon nanotube epoxy composites. Composites Science and Technology. 2007;67:922-8.
[15] Celzard A, McRae E, Deleuze C, Dufort M, Furdin G, Mareche JF. Critical concentration in percolating systems containing a high-aspect-ratio filler. Physical Review B. 1996;53:6209-14.
[16] Bai JB, Allaoui A. Effect of the length and the aggregate size of MWNTs on the improvement efficiency of the mechanical and electrical properties of nanocomposites - experimental investigation. Composites Part a-Applied Science and Manufacturing. 2003;34:689-94.
[17] Du J, Zhao L, Zeng Y, Zhang L, Li F, Liu P, et al. Comparison of electrical properties between multi-walled carbon nanotube and graphene nanosheet/high density polyethylene composites with a segregated network structure. Carbon. 2011;49:1094-100.
[18] Behnam A, Guo J, Ural A. Effects of nanotube alignment and measurement direction on percolation resistivity in single-walled carbon nanotube films. Journal of Applied Physics. 2007;102.
[19] ASTM. D3039 - Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States2008.
[20] Alamusi, Hu N, Fukunaga H, Atobe S, Liu Y, Li J. Piezoresistive Strain Sensors Made from Carbon Nanotubes Based Polymer Nanocomposites. Sensors. 2011;11:10691-723.

Excerpt from ISBN 978-3-00-053387-7