

## Carbonized electrospun polyacrylonitrile nanofibers as highly sensitive sensors in structural health monitoring of composite structures

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**ABSTRACT:** Electrospun polyacrylonitrile (PAN) nanofibers were stabilized at 280°C for 1 h in an ambient condition, and then carbonized at 850°C in inert argon gas for additional 1 h in order to fabricate highly pure carbonous nanofibers for the development of highly sensitive sensors in structural health monitoring (SHM) of composite aircraft and wind turbines. This study manifests the real-time strain response of the carbonized PAN nanofibers under various tensile loadings. The prepared carbon nanofibers were placed on top of the carbon fiber pre-preg composite as a single layer. Using a hand lay-up method, and then co-cured with the pre-preg composites in a vacuum oven following the curing cycle of the composite. The electric wires were connected to the top surface of the composite panels where the cohesively bonded conductive nanofibers were placed prior to the tensile and compression loadings in the grips of the tensile unit. The test results clearly showed that the carbonized electrospun PAN nanofibers on the carbon fiber composites were remarkably performed well. Even the small strain rates (e.g., 0.020% strain) on the composite panels were easily detected through voltage and resistance changes of the panels. The change in voltage can be mainly attributed to the breakage/deformation of the conductive network of the carbonized PAN nanofibers under the loadings. The primary goal of the present study is to develop a cost-effective, lightweight, and flexible strain sensor for the SHM of composite aircraft and wind turbines. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43235.

**KEYWORDS:** composites; conducting polymers; electrospinning; fibers; mechanical properties

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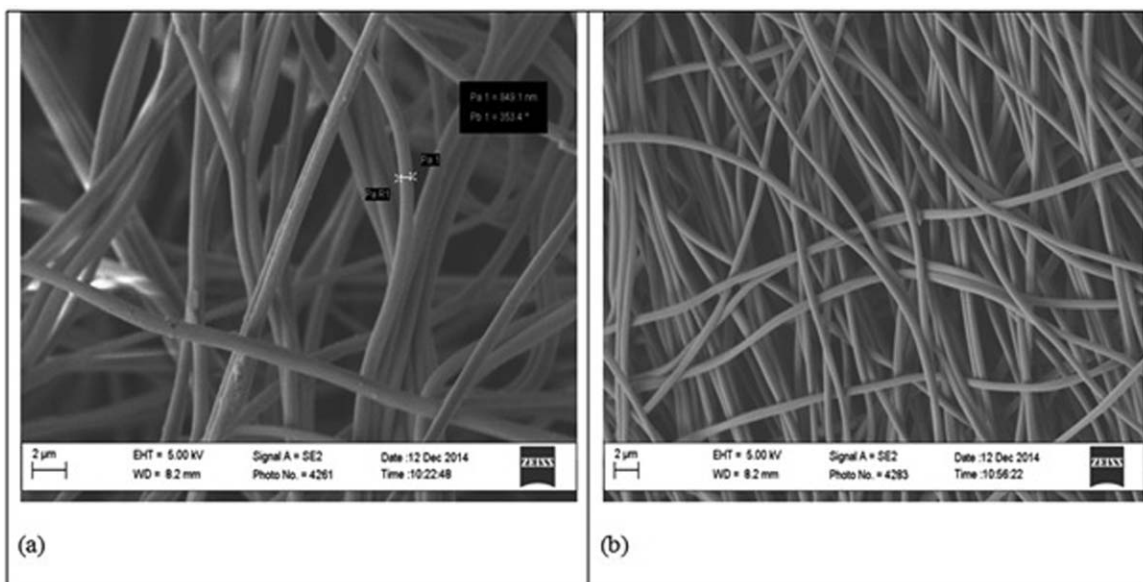
### INTRODUCTION

Structural health monitoring (SHM) is a method of implementing a damage identification strategy for all kinds of infrastructures such as bridges, tunnels, aircrafts, wind turbines, ships, skyscrapers, and towers in order to examine the prevailing health conditions in real-time and provide an approximate estimation of the remaining service life of the structures.<sup>1–3</sup> SHM allows engineers to use the sensing of the structural responses against all types of external and internal loadings during the service in accordance with proper data acquisition and model updating techniques to appraise the condition of a structure. The purpose of SHM is to effectively monitor the damages in infrastructures in real-time by embedding a nondestructive evaluation system (NDE) system into the structure and take preventive measures before a catastrophic failure.<sup>4</sup> A traditional inspection system is costly and time consuming. The SHM system is less time consuming and prevents failure during operation. The prospective advantages of SHM are enormous, since the maintenance procedures for structures can change from schedule-based to condition-based, resulting in cutting down on the period for which structure is out of

service and corresponding cost savings, as well as reduction in labor requirements.

Composite materials present more challenges in inspection due to the presence of voids, anisotropy, resin-rich regions, fiber pull-outs, and delamination. Composite materials generally fail as a result of an interacting damage mode and damages generally occur beneath the top surface of ply. Strain sensors are extensively used in many engineering fields for monitoring and damage detection in infrastructures.<sup>5</sup> Conventional strain gauges are limited by the necessary requirements of the strain gauge to be able to measure strain in a specific direction, and they possess limited sensitivity.<sup>5</sup> The demand for new materials for sensors is on rise, and use of the carbon-based materials for sensors holds the promise of fulfilling the drawbacks that conventional sensors present, owing to their superior mechanical and electrical properties.<sup>6,7</sup> Recently, there has been a major interest in using polymer nanocomposites as strain sensors due to their outstanding properties.<sup>8</sup>

Carbon nanofibers possess excellent thermal and electrical properties; have wide range of applications, such as structural components,



**Figure 1.** The SEM images of electrospun PAN nanofibers (a) before (b) after carbonization process.

wound dressing, and reinforcement in composites, filtration membranes, textiles, electronics, and lithium ions batteries.<sup>9–13</sup> The most promising technique for the synthesis of carbon nanofiber is electrospinning where polyacrylonitrile (PAN) can be used for the main carbon sources of polymeric precursor.<sup>10,11</sup> In this study, PAN-derived carbon fibers were generated through electrospinning process followed by stabilization and carbonization to remove all non-carboneous material and ensure pure carbon material formation in the resulting nanofibers. The main advantage of carbon fibers having diameter in nanosize is the high surface area to volume ratio, which can reach as high as  $10^2$  as compared to microfibers.<sup>14</sup> Electrospun fibers experience large elongation and thinning with a strain rate of around  $1000 \text{ S}^{-1}$  and the drawing ratio is as high as  $10^4$ .<sup>15,16</sup>

The purpose of this study was to use Electrospun Polyacrylonitrile (PAN) nanofibers (PAN-derived carbon fibers) heat-treated them to remove all non-carboneous material and apply them as sensors for composite structures.

## EXPERIMENTAL

### Materials

Polyacrylonitrile (PAN) having molecular weight 150,000 g/mole (CAS no. 25014-41-9) and dimethylformamide (DMF) (CAS no. 68-12-2, 99.8%) were purchased from Sigma-Aldrich and used without any further purification. The pre-preg carbon fibers were purchased from Cytec Engineering Materials (Part No. 5320-1). The pre-preg were cured according to the instructions from manufacturer's manual.

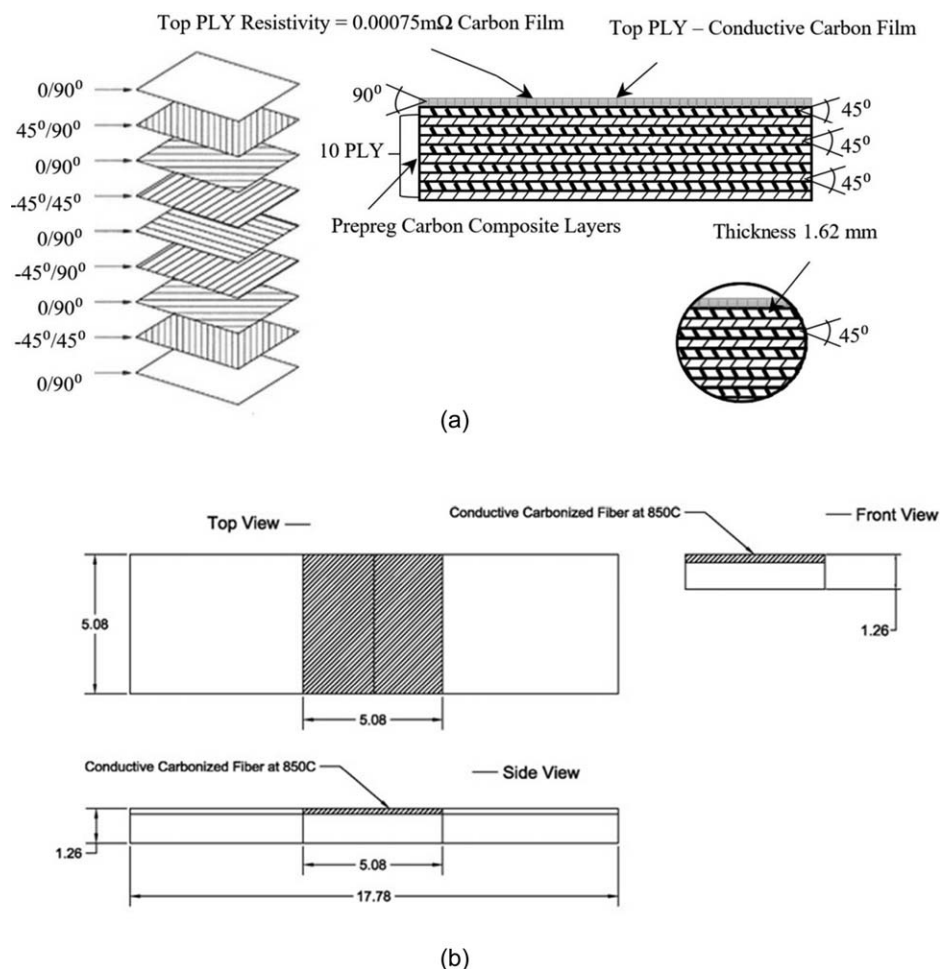
### Method

**Fabrication and Carbonization of PAN Nanofibers.** PAN powder was dissolved in DMF solvent at 90:10% weight ratios and the mixture was subjected to shear mixing at 500 rpm for 1 h on a hot plate. Particular care was taken to ensure a homogeneous blend/dissolution of the mixture (polymeric solution). The polymeric solution was then transformed to a 10 mL syringe with an inside

diameter of 10 mm. Nanofibers were fabricated using an electrospinning process. The electrospinning was carried out at 25 kV DC with 1 mL/h of a feed rate and 25 cm of the distance between the capillary tube and collector screen. The as-produced PAN nanofibers were converted to carbon nanofibers by stabilizing in an ambient environment at 280°C for 1 h, and then subsequently carbonizing at 850°C for another 1 h in an argon atmosphere. During the stabilization, cyclization reaction takes place, in which the nitrile groups in precursor fibers form a ladder-like structure with adjacent groups, thereby strengthening the stability of the polymeric structure. This ladder-like structure can sustain high temperature and improves carbon yields of the PAN fibers.<sup>17</sup> During the carbonization, the carbon chain substances are condensed into carboneous materials, thereby increasing carbon yields and gasses, such as nitrogen, hydrogen, and other compounds are released.

Scanning electron microscopy (SEM) was used to determine the surface morphology and diameters of the PAN nanofibers.

Figure 1 shows the SEM images of electrospun PAN nanofibers before and after the carbonization at 850°C. As is seen in Figure 1(a), the average diameter of the PAN fibers was around  $550 \pm 50 \text{ nm}$  before the carbonization; however, after the carbonization, it was reduced to  $400 \pm 50 \text{ nm}$ , retaining their shape, and morphology. The shrinkage can be divided into the entropic part and chemical part. The entropic shrinkage is caused mainly by the retraction of stretched polymer chains, while the chemical shrinkage is caused primarily by the formations of dense structures after the chemical reactions.<sup>17</sup> Entropic shrinkage constitutes physical changes and is independent of the heating rate; nevertheless, chemical shrinkage can be increased with increasing the heating rate.<sup>17</sup> Microcombustion and pyrolysis of the PAN fibers revealed that the carbonized nanofibers contained around 89.47% carbon, 3.93% nitrogen, 3.08% oxygen, and a minute amount of hydrogen (0.33%).<sup>15</sup> The presence of nitrogen is due to the C–N bonds that are found in PAN when the



**Figure 2.** (a) The schematic views of the test setup for the strain sensing response from the carbon fiber composite incorporated with the carbonized PAN nanofibers. (b) Schematics of specimen used in strain sensing.

annealing process is carried out at a temperature below 2000°C and molecular entrapments during the reactions.<sup>21</sup>

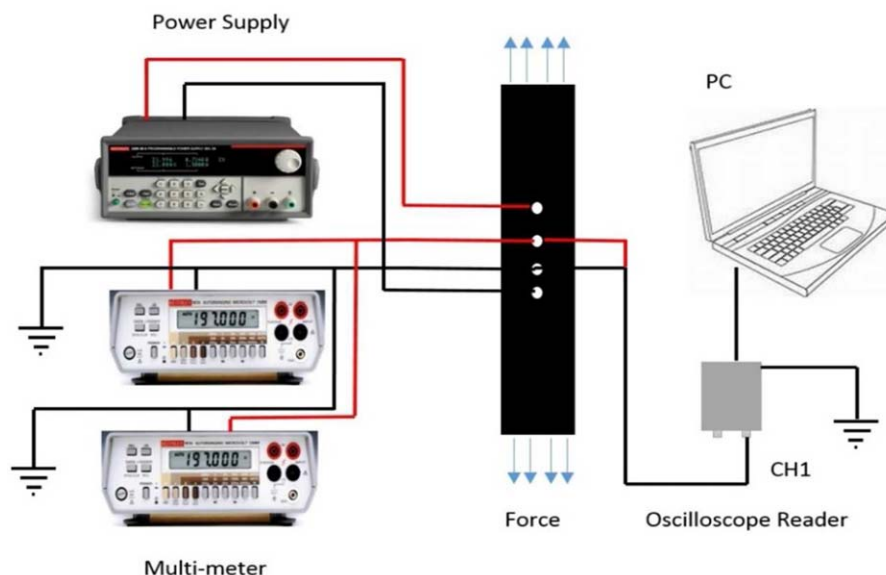
**Conductive PAN Nanofiber Fabrication on Pre-Preg Composites.** Pre-preg technique was employed to fabricate carbon fiber composite panels (5320-1) incorporated with carbonized PAN nanofibers as top layers. The PAN-derived carbon nanofiber (or nanomat) appeared black in color due to the stabilizing and carbonizing processes was used in this study. The nanofiber film thickness was about 0.021 mm. The 10 plies of the epoxy resin pre-preg carbon fibers were laid up at 0, 45, -45, and 90 stacking sequences on flat and smooth Al mold, and then the carbonized PAN nanofiber mat was laid upon the top portion of the pre-preg composites. The resin system was epoxy that included a proper curing agent in a weight proportion of the pre-preg. Figure 2(a) shows the fabrication of the composite scheme incorporated with carbonized PAN nanofiber mats as top layer. The curing cycle followed the four major steps: (1) heating the composite at 50°C for 30 min, (2) heating the composites at 120°C for 60 min, (3) heating the composite at 180°C for 120 min, and (4) reducing health of the composite to 50°C for 30 min. Figure 2(b) shows the schematics of specimen used

in strain sensing tests. Table I gives the properties of the pre-preg composite with PAN nanofiber mat laid up at the top of the pre-preg composite.

**Strain Sensing Tests for SHM.** Figure 3 shows the experimental test setup for the strain sensing study on the prepared composite panel. The composite specimen has a length of 177.8 mm, width of 50.8 mm, and a thickness of 1.62 mm used for tensile tests. A four-circumferential ring probe was employed to measure resistance in the nanocomposite sample. The composite

**Table I.** The Properties of Carbonized Electrospun PAN Nanofibers on Pre-preg Composite

Properties	Values
Thickness	1.62 mm
Resistivity	0.00075 m Ω
Strain	0.085%
Yield stress	350 MPa
Modulus of elasticity	4546.9 MPa
Peak load	2.3882.56 N



**Figure 3.** The experimental view of the test setup for the strain sensing study on the prepared composite coupons. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

specimens were sanded off at locations, where the probes of the electric wires were attached. After sanding off the surface, a silver conductive epoxy adhesive was applied in order to avoid contact resistance. A constant current was applied along the axial direction via outer probes and the corresponding voltage drop between inner probes was measured for various strains along the axial direction as shown in Figure 3.

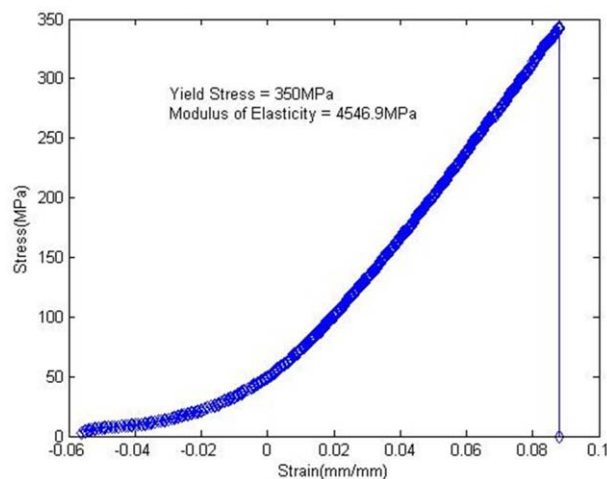
Data was continuously acquired using a Lab VIEW program in the laboratory. The sample was subjected to ramping loads, both tensile and compression. The specimen was loaded at a constant rate of 1 mm/min. The displacement due to the loading was used to calculate the strains under quasi-static loading rates. The specimen was subjected to tension as well as compression cycles in a servo-hydraulic test frame (Figure 3).<sup>30–33</sup> A good contact between specimen and probes was ensured in order to make the voltage across the inner probes stable. The load was applied in increments and held constants for several seconds so that stable readings can be obtained for each test. The input current across the two outer probes was kept constant during the measurement when the voltage reading across the two inner probes and strains from the strain gauge were measured. For each test, at least three readings were taken, and the test results were averaged.

## RESULTS AND DISCUSSION

Figure 4 shows the engineering stress–strain curve of the carbon fiber composites co-bonded with carbonized electrospun PAN nanofibers. It is seen that from 0 strain rate, the composite panel linearly deforms until the fracture failure takes place.<sup>15</sup> The carbon fiber composites usually provide linear behavior because of their brittle structures, so adding carbonized PAN nanofibers can change the overall behavior of the samples.<sup>15</sup> Arshad *et al.* reported that the modulus of elasticity considerably increased with decreasing the fiber diameters.<sup>18</sup> The dependence of fibers strength on diameter has also been studied

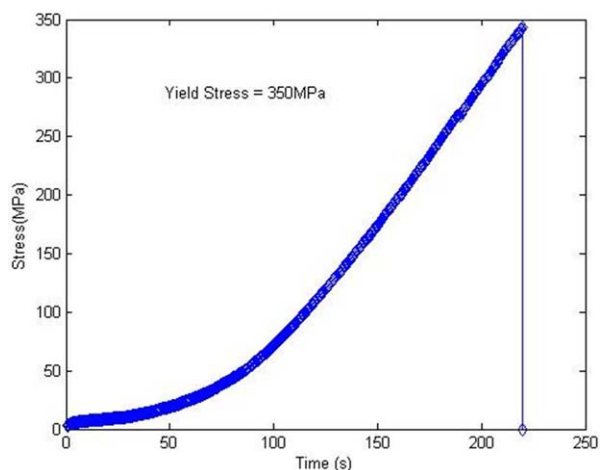
with various fibers, and it has been found that decreasing fiber diameter resulted in lower fiber volume and reduced number of defects and cracks, and thus causing portentous decline in the probability of failure.<sup>19,20</sup> As seen in Figure 4, the percentage elongation at failure is 0.085, which correspond to a stress value of 350 MPa.

Figure 5 shows the monotonic increment of the stress vs. time on the composite specimen co-bonded with the carbonized electrospun PAN nanofibers, while Figure 6 shows the same test with the strain vs. time on the same samples. When the external load was applied the composite specimen, the carbonized PAN nanofibers on the specimen experienced some deformation based on both stress and strain rates. When the nanofibers are electrospun at higher distances (distance between capillary tube and collector screen), they display higher modulus and higher



**Figure 4.** The engineering stress–strain curve for the carbon fiber composites co-bonded with carbonized electrospun PAN nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

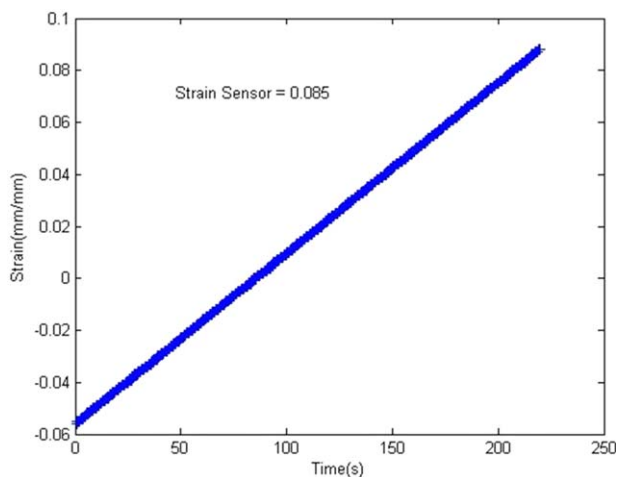




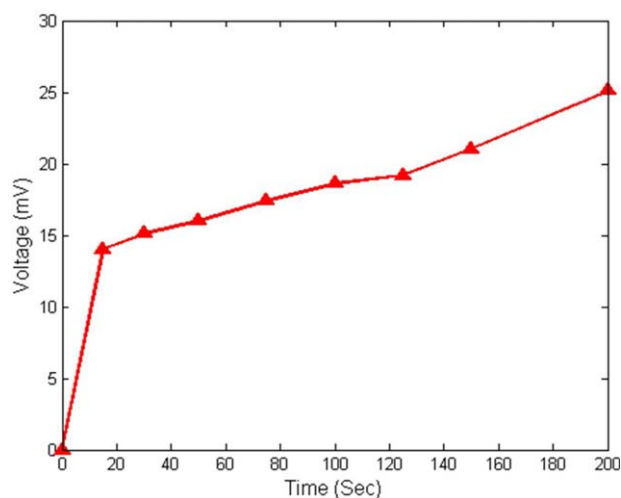
**Figure 5.** The monotonic increment of the stress vs. time on the composite specimen co-bonded with carbonized electrospun PAN nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

tensile strength since they possess better molecular orientation and lesser defects. The recent studies also reported that the PAN nanofibers fabricated at 25 kV, and a 25-cm distance between the target and the collector have the highest tensile strength and modulus; however, the strain failure could be around 200% for those electrospinning conditions.<sup>21</sup> The high modulus of the carbonized PAN nanofibers on the carbon composites might be due to the stabilization at high temperature, which results in a high capacity fraction of a purely ordered phase possibly caused by additional cross-linking reactions and lesser defects.<sup>17</sup>

Figure 7 shows the change in voltage during the loading of the composite specimen co-bonded with carbonized electrospun PAN nanofibers. Figure 6 shows a linear relation between the changes in strain during the loading. The changing in voltage across the two inner probes might be due to the change in dimensions (change in length along the direction of loadings) of the carbon fiber specimen, and can be recognized by the change in resistivity



**Figure 6.** The strain vs. time curve of the composite specimen co-bonded with carbonized electrospun PAN nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** The change in voltage during the loading of the composite specimen co-bonded with carbonized electrospun PAN nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of the specimen.<sup>22</sup> This may be also related to the external tensile loading and the change in the electrical properties of the carbonized PAN nanofibers under tensile testing that greatly changes the voltage. The change in voltage was observed when the specimen experiences a continuous increment in the loading. As soon as the tensile stress/strains increases, the change in voltage increases linearly in the elastic region, as well. Strain sensing using carbonaceous material (carbon nanotubes) was studied by Dharap *et al.*<sup>22</sup> and they found a linear change in voltage across a film subjected to tension and compression.

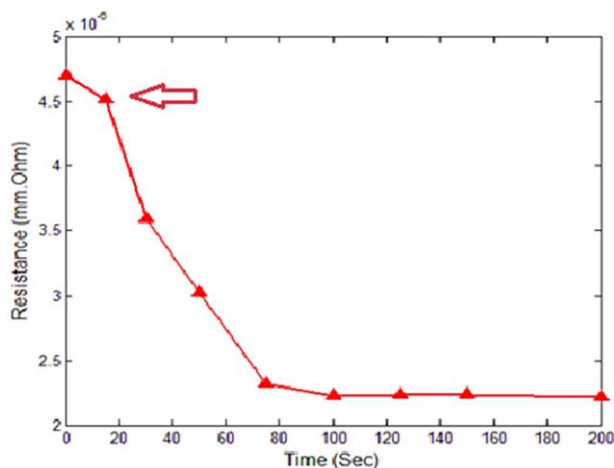
From Figures 5–7, the initial raise in voltage in 20 s is 14.8 mV corresponding to a stress of 10 MPa and a strain rate of 0.03 mm/min. A study was conducted on the functionalized graphene reinforced nanocomposite of polyvinylidene difluoride (PVDF) as strain sensor for an SHM.<sup>23</sup> The PVDF nanocomposite sample containing 2 wt % of the functionalized graphene showed that at 0.02% and 0.85% of strains, voltage changes of about 9 mV and 24 mV were observed in the carbon fiber films, respectively.<sup>8</sup> Our studies as seen in Figures 6 and 7 showed that at 0.02% and 0.85% of strains, voltage changes of about 18 mV and 25 mV were observed in the carbonized PAN nanofibers on the carbon fiber composites. This behavior leads to a nonlinear feature of voltage change when the specimen goes into the inelastic region.<sup>8</sup> The change in voltage can be attributed to tensile loading, internal, and external fractures on the nanofibers, initial defects, and the change in electrical properties of carbonized PAN nanofibers under tensile loadings. The heat treatment can condense/integrate the PAN nanofibers on the composites and develop conducting network since the fibers contain only carbonaceous matter. However, as the compression and tensile loads are applied, this conductive network was disturbed somehow thereby resulting voltage, conductivity, and resistivity changes.

Figure 8 shows the changes in resistance vs. time of the composite specimen co-bonded with the carbonized electrospun PAN nanofibers. As can be seen, the specimen has an initial resistance of 30

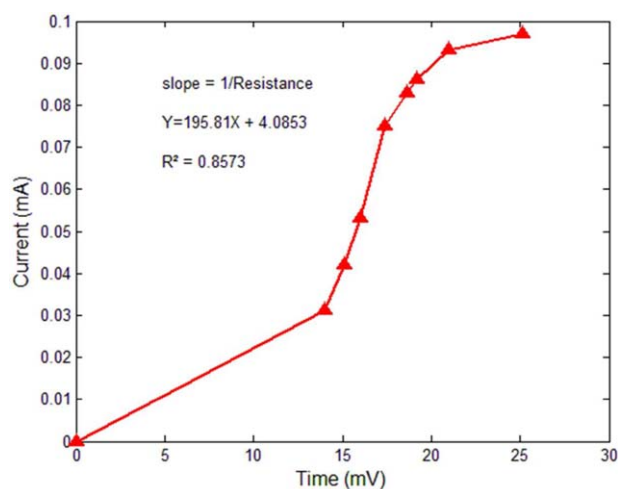
ohms measured via four-point probe. The contact resistance was not taken into account, and the high precision equipment usually allows voltage reading in mV ranges. Recent studies showed that the change in voltage due to the change in dimension was small as compared to change in resistivity of the specimen due to the external loadings.<sup>22</sup> Thus, the change in voltage is mainly attributable to the change in resistivity/conductivity values. The contribution of Poisson's effect also plays a significant role.<sup>22</sup> The resistivity and changes in dimension may have relationships when the material contains cracks, internal defects, and secondary phase formations.<sup>24,25</sup> However, the relationship between dimensional changes and resistivity changes due to loading and unloading requires more research. Park *et al.*<sup>26</sup> investigated the strain-dependent electrical resistance of Multiwalled Carbon Nanotubes/PolyethyleneOxide (MWCNT/PEO) composite film using an experimental set-up to measure the electrical resistance and strain simultaneously, and found repeated relations in resistance versus strain. Li *et al.*<sup>27</sup> conducted an experimental work on MWCNT film as strain sensors and studied the response of MWCNT film to elastic loading and electrical response against dynamic loading.

Figure 9 shows the current (mA) vs. voltage (mV) of the composite specimen co-bonded with the carbonized electrospun PAN nanofibers. The nanofibers may not be homogeneous materials, so the data presented here mainly shows non-ohmic behavior. Even after the heat treatment below 1000°C, the fibers are not entirely composed of carbon, and the other elements still present in carbon fiber structures that can take part substantially in heterogeneity, and thus to the observation of the non-ohmic behavior. When the PAN nanofibers are heat treated between 600 and 800°C temperature ranges, they become more conductors, and, thus, the heterogeneity was evidently most pivotal in determining the properties.<sup>25</sup>

Vilaplana *et al.* stated that the carbon fibers decreased the electrical properties under the applied loads and reported the electrical resistivity value of 0.0000152 m Ω.<sup>25</sup> Luhrs *et al.* studied the oxidation and the carbonization processes in an ambient condition at 300°C, and in an inert atmosphere at 750°C,



**Figure 8.** The changes in resistance vs. time of the composite specimen co-bonded with carbonized electrospun PAN nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9.** The current (mA) vs. voltage (mV) of the composite specimen co-bonded with carbonized electrospun PAN nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

respectively.<sup>28</sup> The strain gauge of the test setup provided a linear relationship between electrical resistances and strain values. The electrical resistance values were drastically decreased as a function of time.<sup>25</sup> The electrical conductivity values of the carbonized electrospun PAN nanofibers can be significantly changed when they are mechanically loaded.<sup>29</sup> These changes are mainly related to the degrees of stress and strain rates, internal and external deformations, time, and other environmental conditions. Highly conductive materials with other superior physical properties can be ideal materials for sensing element and nanopores in the SHM of the composite aircraft and wind turbine structures. The resistivity and conductivity changes on the carbonized PAN nanofibers may indicate the degree of aging process of the composites, level of maneuvering during the flights/operations, impacts of environmental conditions (e.g., storm, tornado, hurricane, heavy rain and snow, hail, etc.), and other internal and external loads.

## CONCLUSIONS

Electrospun PAN nanofibers were stabilized at 280°C for 1 h in an ambient condition, and then carbonized at 850°C in inert argon gas for additional 1 h to produce highly conductive carbon nanofibers for SHM of composite aircraft and wind turbines. The carbonized PAN nanofibers cohesively bonded on the surface of the carbon fiber composite panels were loaded under different tensile and compression loads. A four circumferential probe measurement system was used to determine the electrical response of the composite panels during the uniaxial loadings. The prepared samples detected the very small strain rates formed on the composite panels in the forms of electrical voltage, resistivity, and conductivity changes. This may be because of the extremely high surface area of the carbonized PAN nanofibers. Also, Poisson's effect and internal defects such as pores, cracks, and beads can also play a significant role in electrical signal changes of the composite panels. The share stress tests can be applied to the composite panels to

characterize further the properties of the novel nanomaterials. These nanomaterials and methods may open up new possibilities to develop highly sensitive SHM devices for the composite aircraft and wind turbine, as well as other infrastructures.

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#### REFERENCES

1. Farrar, C. R.; Lieven, N. A. *Philos. Trans. R. Soc. London A Math. Phys. Eng. Sci.* **2007**, *365*, 623.
2. Farrar, C. R.; Worden, K. *Philos. Trans. R. Soc. London A Math. Phys. Eng. Sci.* **2007**, *365*, 303.
3. Farrar, C. R. *Damage Prognosis: Current status and future needs*; Los Alamos National Laboratory, **2003**.
4. Raghavan, A.; Cesnik, C. E. *Shock Vib. Digest* **2007**, *39*, 91.
5. Vemuru, S.; Wahi, R.; Nagarajaiah, S.; Ajayan, P. *J. Strain Anal. Eng. Des.* **2009**, *44*, 555.
6. Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.
7. Mahar, B.; Laslau, C.; Yip, R.; Sun, Y. *IEEE Sens. J.* **2007**, *7*, 266.
8. Eswaraiah, V.; Balasubramaniam, K.; Ramaprabhu, S. *J. Mater. Chem.* **2011**, *21*, 12626.
9. Beese, A. M.; Papkov, D.; Li, S.; Dzenis, Y.; Espinosa, H. D. *Carbon* **2013**, *60*, 246.
10. Nataraj, S.; Yang, K.; Aminabhavi, T. *Prog. Polym. Sci.* **2012**, *37*, 487.
11. Chand, S. *J. Mater. Sci.* **2000**, *35*, 1303.
12. Yun, K. M.; Hogan, C. J.; Matsubayashi, Y.; Kawabe, M.; Iskandar, F.; Okuyama, K. *Chem. Eng. Sci.* **2007**, *62*, 4751.
13. Musale, D. A.; Kumar, A. *J. Appl. Polym. Sci.* **2000**, *77*, 1782.
14. Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. *Compos. Sci. Technol.* **2003**, *63*, 2223.
15. Zussman, E.; Chen, X.; Ding, W.; Calabri, L.; Dikin, D.; Quintana, J.; Ruoff, R. *Carbon* **2005**, *43*, 2175.
16. Reneker, D. H.; Yarin, A. L.; Fong, H.; Koombhongse, S. *J. Appl. Phys.* **2000**, *87*, 4531.
17. Liu, Y. *Stabilization and Carbonization Studies of Polyacrylonitrile/Carbon Nanotube Composite Fibers*, Ph.D. Dissertation, School of Polymer, Textile, and Fiber Engineering, Georgia Institute of Technology, **2010**.
18. Arshad, S. N.; Naraghi, M.; Chasiotis, I. *Carbon* **2011**, *49*, 1710.
19. Griffith, A. A. *SM Trans. Q.* **1968**, *61*, 871.
20. Tagawa, T.; Miyata, T. *Mater. Sci. Eng. A* **1997**, *238*, 336.
21. Arshad, S. N. *High Strength Carbon Nanofibers Derived from Electrospun Polyacrylonitrile*. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, **2010**.
22. Dharap, P.; Li, Z.; Nagarajaiah, S.; Barrera, E. *Nanotechnology* **2004**, *15*, 379.
23. Zhang, W.; Sakalkar, V.; Koratkar, N. *Appl. Phys. Lett.* **2007**, *91*, 133102.
24. Li, Z.; Dharap, P.; Sharma, P.; Nagarajaiah, S.; Jakobson, B. I. *J. Appl. Phys.* **2005**, *97*, 074303.
25. Vilaplana, J. L.; Baeza, F. J.; Galao, O.; Zornoza, E.; Garcés, P. *Materials* **2013**, *6*, 4776.
26. Park, M.; Kim, H.; Youngblood, J. P. *Nanotechnology* **2008**, *19*, 055705.
27. Li, X.; Levy, C.; Elaadil, L. *Nanotechnology* **2008**, *19*, 045501.
28. Luhrs, C. C.; Daskam, C. D.; Gonzalez, E.; Phillips, J. *Materials* **2014**, *7*, 3699.
29. Alexopoulos, N.; Bartholome, C.; Poulin, P.; Marioli-Riga, Z. *Compos. Sci. Technol.* **2010**, *70*, 260.
30. Huang, X. *Materials* **2009**, *2*, 2369.
31. Jayaraman, K.; Kotaki, M.; Zhang, Y.; Mo, X.; Ramakrishna, S. *J. Nanosci. Nanotechnol.* **2004**, *4*, 52.
32. Anton, F. U.S. Pat. 1,975,504 **1934**.
33. Alarifi, I. M.; Alharbi, A.; Khan, W. S.; Asmatulu, R. *SPIE Smart Structures and Materials+ Nondestructive Evaluation and Health Monitoring*, **2015**; p 943032.