Harnessing the Resistive-Elastic Behavior of Novel CNT-Graphene Hybrid Foams for Practical Sensing Applications

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ABSTRACT

We fabricated CNT/graphene hybrid foams with well-controlled morphologies. The foam is lightweight, highly elastic, and conductive. It also exhibits unique and repeatable mechanical and electrical responses to the deformation of the foam. CNT/graphene hybrid foams are expected to have great potential for use as a pressure sensor in practical applications.

Keywords: carbon nanotubes, graphene, CNT foams, pressure sensors, strain sensors, engineered porosity and microstructure, porous materials

1 INTRODUCTION

In recent years, researchers have invested a significant amount of their effort into the field of strain sensors, because of the huge growth in demand for high tech products which rely on various sensors. Carbon nanotube (CNT) foams and aerogels hold promise in the area of strain sensors because of their resistive-elastic behavior under compressive strain. To date one of the largest obstacles in the area of CNT foams and aerogels has been the lack of control over the porosity and microstructure [1,2]. Using a novel foam fabrication method, we are able to create a hybrid CNT-graphene foam with engineered micro-scale pores [3]. By varying the fabrication parameters and ratio of materials, we were able to control the size and shape of the pores, and thereby the porosity and rigidity of our foam. These factors can be altered in order to fabricate samples with a wide range of resistive behavior. Additionally, samples can be tuned in order to exhibit almost uniform distribution of near perfectly spherical pores.

By using a polyacrylonitrile (PAN) precursor, we were able to create the hybrid CNT/graphene material (Fig.1a). Carbonization of this precursor creates graphene features in CNT foam, in the form of crosslinks between the CNT porous networks. These graphene features are able to dramatically improve the robustness and conductivity of the foam. These properties are highly desirable because of the fragility of practical sensors made purely from CNTs.

Most importantly, in response to cyclical compression strain, our material exhibits viscoelastic mechanical behavior, but linear cyclical resistive behavior electrically. Therefore, the mechanical and electrical properties of our novel material lends itself perfectly for use as a pressure sensor for practical applications.

In this article, we demonstrate the sensing behavior of our CNT-graphene hybrid foam. In particular, we focus on the repeatability, reliability, and response time of our foam during cyclical deformation as a proof of concept.

2 EXPERIMENTAL DETAILS

Samples made from our unique material were fabricated by utilizing two different polymers: a thermoplastic (which served as a template to create the designed shape, volume, and distribution), and polyacrylonitrile (which is carbonized to form the crosslinks between CNT networks). Once the CNTs and thermoplastic have been thorougly dispersed, the mixture is subjected to a heat treatment which pyrolyzes the thermoplastic.

Further steps require the addition of the PAN precursor, which upon a strong controlled heat treatment leads to carbonization. This carbonization process causes the formation of graphene crosslinks between the long and interconnected CNT networks (which form the cell walls of the porous foam).

Once the synthesis process is complete, the mechanical and electrical behavior of the samples are tested under cyclical compression strain. Strain is applied to the samples via a microstep stage controller, which has two stages that compress the sample (Fig. 1). A sourcemeter is used to apply voltage to the two stages of the microstep controller, effectively creating two electrodes for a standard two-probe test. Labview software was used to program the experimental setup, such that data acquisition of the time, strain, current, and resistance was measured and collected in sync. All measurements were performed at ambient conditions.

In addition, dynamic mechanical analysis (DMA) was performed to measure the amount of compressive stress which could be applied to the samples. Elasticity testing was also performed in order to determine the effective strain range which could be applied, while still preserving the mechanical behavior of the material.

3 RESULTS AND DISCUSSION

3.1 Material Structure

Scanning Electron Microscope (SEM) images were taken of as-prepared samples in order to verify the shape and distribution of the micro-scale pores.

As seen in Fig. 2, the fabricated foams demonstrate well-controlled 3D morpology. The overall structure of our foam consists of several pores which were formed by pyrolysis of the thermoplastic. This process removed all of the spherical plastic shapes in the sample, leaving us with micro-scale voids in their place (10-30 µm). At the micro-scale (Fig. 2), it is possible to see that the pores consist of long interconnected CNT networks (crosslinked by graphene features), which form the walls enclosing the voids. Also, at the nano-scale we can see that the cell walls contain nano-scale pores between the interwoven CNT networks.

Microscale pore diameters varied between 10-30 µm, depending on the diameter of the thermoplastic used during the fabrication steps. The surface area of the foam was measured to be >350 m^2/g, with a density of 10-20 mg/cm^3.

3.2 Mechanical Behavior

DMA testing was performed from 0% strain to four unique strain ranges: 20%, 40%, 60%, and 80%. The foam demonstrated visco-elastic behavior for all four strain ranges, and demonstrated great robustness due to graphene crosslinks which support the CNT networks.

In Fig. 3, mechanical testing revealed that the foam was able to deform at strain levels up to 80%, while still reverting to its original shape upon springback. Springback occurs almost instantaneously upon release of compressive stress, and samples were still able to retain their visco-elastic mechanical behavior.

The foam demonstrates super-elastic behavior, as evidenced by complete recovery from compression up to 80% strain. Remarkably, the foams can also recover from deformation in the wet state, and their structures do not collapse under strong capillary force. Similar elastic and repeatable deformation was also observed in liquid nitrogen (-197 °C) and at 900 °C in Argon. More importantly, the foam displays a near zero Poisson's ratio.

Pore deformation occurs as a result of the compressive stress being applied to the foam. The deformation mechanism entails a shrinking in the volume of the pores, which increases the amount of contact between the CNT-based cell walls. Increased contact between the cell walls reduced the sample's resistance, because of the increase in electrical contacts across the foam. For this reason, this deformation mechanism lends itself well to the proposed application of a pressure sensor.

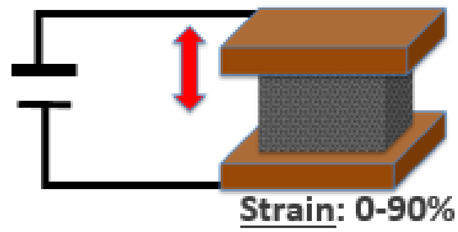

Fig. 1 – Experiment setup used to take electrical and strain measurements for sensing behavior testing. Strain was varied from 0% to up to 90% strain, and the corresponding resistance change was measured using a DAQ.

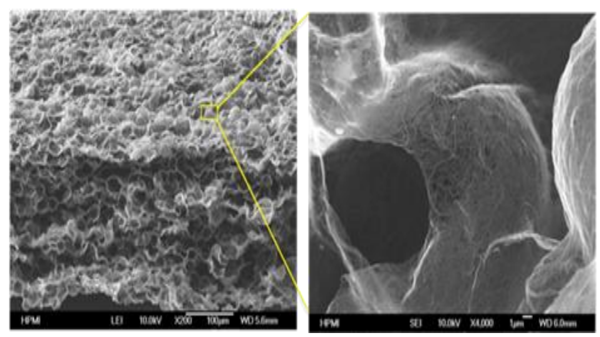

Fig. 2 – SEM images show the overall structure at the microscale, as well as nano-scaled pores between the interwoven CNT networks.

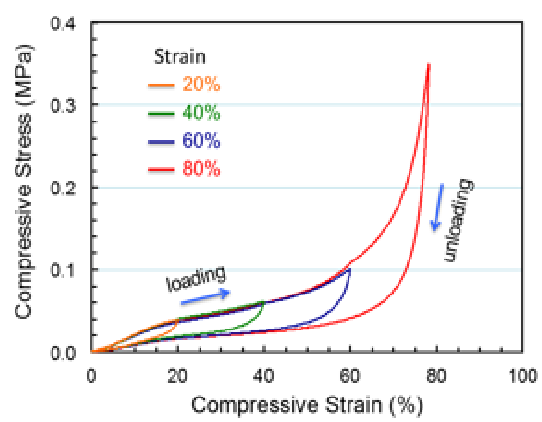

Fig. 3 – DMA testing demonstrates the visco-elastic behavior of the samples under compressive strain.

3.3 Sensing/Electrical Behavior

In order to characterize the electrical behavior of the foam, it was necessary to first perform Impedenace Signature (VI) testing.

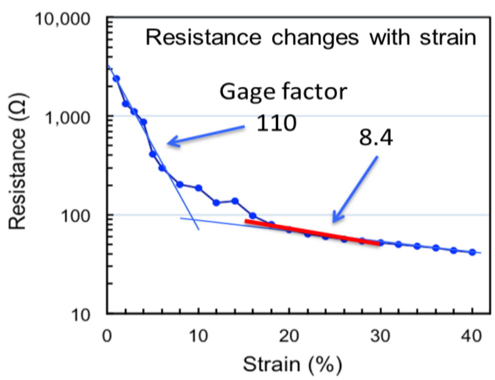

Fig. 4 – VI Testing of a foam sample, which indicates the two unique strain sensing ranges.

The VI testing was performed from -1.0V to 1.0V at intervals of 0.1V. The results indicated two unique linear ranges between 0% to 40% strain. The voltage and current was used to convert to resistance, and the relationship of resistance versus strain applied was plotted (see Fig. 4). A voltage level of 1.0V was selected for further sample testing.

At low levels of strain (<4%) we saw very high resistance which was a combination of contact resistance, surface resistance, and the sample resistance. At these lower levels of strain, contact resistance typically dominated the balance between the three contributing types of resistance. Despite the high level of resistance, the sample demonstrated a linear strain range (log scale) from 0-8% strain, which corresponded to 3000Ω and 250Ω, respectively. The other linear strain range was found between 15-40% strain, with corresponding resistances of approximately 117 Ω to 42Ω, respectively. The first strain range therefore exhibited a gage factor of ~110, while the second strain range exhibited a gage factor of ~8.4. Interestingly, the first strain range demonstrated great sensitivity to a very small strain deformation, with a trade-off of lower stability. The second strain range, however, demonstrated good sensitivity without the trade-off of stability. Therefore, the second strain range of 15-40% strain was selected for further testing.

The first sensing test performed was a combination of the mechanical and electrical behavior, in order to do a side-by-side comparison of the results. The test was performed for a relatively small strain change of 15%, from 15% to 30% strain. The results were quite exciting (Fig. 5), showing the anticipated viscoelastic mechanical behavior, while displaying a linear electricical resistance response to the strain change. Both the mechanical and electrical responses showed very little deviation from the mean behavior, indicating the repeatability property of the foam.

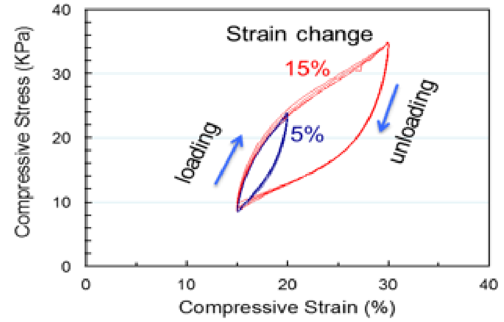

Fig. 5 – Viscoelastic mechanical behavior exhibited over 5% and 15% strain from 15-30% absolute strain.

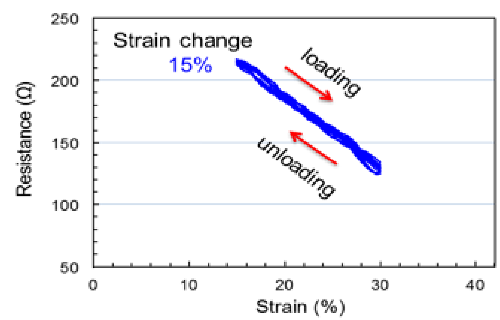

Fig. 6 – Electrical resistance response to the mechanical deformation shown in Fig. 5.

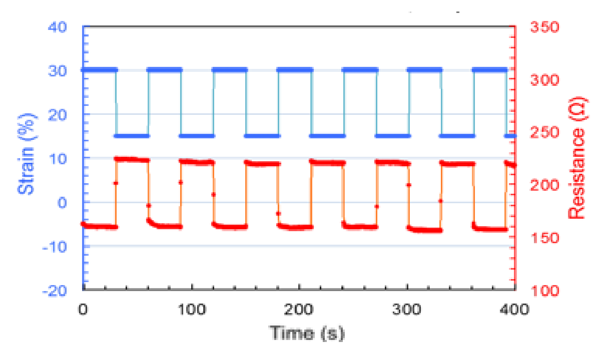

Fig. 7 – Resistance response to instantaneous strain change cycled between 15% and 30% absolute strain.

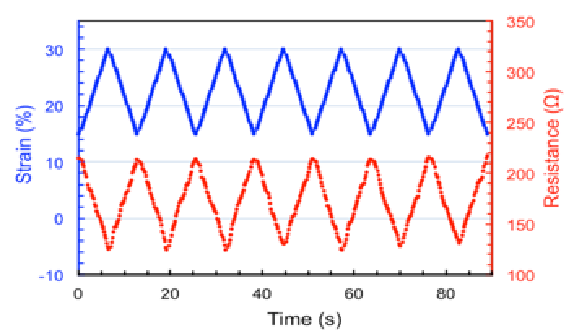

Fig. 8 – Resistance response to continuous strain change cycled between 15% and 30% absolute strain.

The series of experiments performed tested the reliability of the foam by measuring the response rate. Two response rates tests were used: the response to instantaneous strain change (Fig. 7), and the response to continuous strain change (Fig. 8). The instantaneous strain change test demonstrated an almost perfect mirror image between the mechanical and electrical response. For each instantaneous change in the strain, there was 1 or less data points between the upper and lower bound strain for the test; this indicates a very fast response time. Furthermore, the resistance stayed level after the instantaneous strain change, and variance never exceeded 1% of the expected value. The continuous strain change test also indicated an almost exact mirror image between the mechanical and electrical responses. Together, these two tests both indicate very fast response times of <0.1s to a change in strain.

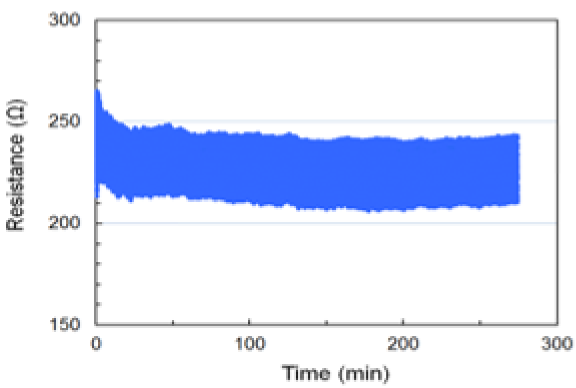

Fig. 9 – Long term reliability testing, indicating the resistive behavior over 5000 cycles.

The final experiment performed was a reliability test, in which the strain was continuously cycled between 15% and 30%. As shown in Fig. 9, the resistance remained stable over the 5000 cycles, thereby demonstrating long term reliability of the material over several thousand continuous deformation cycles.

4 SUMMARY

We fabricated CNT/graphene hybrid foams with well-controlled morphologies. The foam is lightweight, highly elastic, and conductive. The foam exhibits unique mechanical and electrical responses to an applied compressive deformation, which makes it a very desirable material for a pressure sensor. Several experiments were performed to verify its suitability as a sensor. The results show that our material is able to detect small changes in the strain with a very fast response rate, and high reliability and repeatability.

REFERENCES

[1] Ryan R. Kohlmeyer, Maika Lor, Jian Deng, Haiying Liu, Jian Chen. “Preparation of stable carbon nanotube aerogels with high electrical conductivity and porosity,” Carbon 49, 2352-2361, 2011.

[2] Marcus A. Worsley, Sergei O. Kucheyev, Joe H. Satcher, Alex V. Hamza, Theodore F. Bauman. “Mechanically robust and electrically conductive carbon nanotube foams,” Applied Physics Letters 94, 073115, 2009.

[3] Mei Zhang, Yanbin Cui, Shengjuan Li. “Fabrication and characterization of carbon nanotube/graphene hybrid foam,” Proceeding of Nanotech Conference & Expo 2013.