Nanotube Sheet - Graphite Hybrid Nanocomposite for Damage Detection

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Abstract

In this study, we fabricate carbon nanotube (CNT) sheet – graphite powder hybrid nanocomposites and determine their strain dependent electrical resistivity for applications in damage sensing of aerospace composites. CNT sheet – graphite powder nanocomposites are prepared by epoxy resin infiltration under vacuum followed by oven curing. The electrical resistivity of the composites is measured while simultaneously subjecting it to tensile loading. The resistivity of the nanocomposite films without load reduces from about $34.7 \times 10^{-5} \Omega \cdot m$ to $8.1 \times 10^{-5} \Omega \cdot m$ by the addition of varying quantities of graphite powder. Additionally, the change in resistivity with tensile strain shows a significant improvement from $0.85 \times 10^{-5} \Omega \cdot m$ to $8.9 \times 10^{-5} \Omega \cdot m$ when epoxy resin is modified with 5 wt% graphite powder. There is an associated particle size effect. The improvements are observed only when the second phase is graphitic particles (300 -1000 μm) and not for fine graphene flakes (0.5 - 3 μm). We propose the application of these nanocomposites in damage sensing of aerospace carbon-fiber composites.

Introduction

Carbon nanotubes (CNTs), with their remarkable electrical and mechanical properties have attracted research interest since the landmark publication in 1991 by Iijima [1]. Commercial availability of large nanotube sheets (a few square meters in size) in recent times [2] has generated a renewed interest in the use of carbon nanotubes (CNTs) for bulk applications such as in aerospace composites. CNTs have been employed as fillers in a wide range of polymer matrices such as polyethylene [3] polypropylene [4], PEEK [5], PET [6] with the objective of improving mechanical properties and for functional applications based on electrical conductivity.

The discovery of the dramatic and convertible correlation between mechanical deformation and electrical resistance of individual carbon nanotubes [7] has led to the application of CNTs as actuators and strain sensing devices. Several publications discuss utilizing CNTs for strain sensing in the form of nanocomposites [e.g. 8]. Researchers have observed both linear and nonlinear variation of electrical resistance with the application of mechanical load for various matrix materials [8-11]. This piezo-resistive property of CNT composites has been utilized for applications such as gas identification [10] and cardiac and neurophysiological recording [11]. In these studies carbon nanotubes are directly dispersed in the matrix.

Because of the mass production of carbon nanotubes it is now possible to make carbon nanotube sheets in large sizes (few meters square) [2]. These CNT sheets or buckypaper consist of entangled carbon nanotube networks forming into a thin macroscopic membrane with the assistance of van der Waals interactions at the junction of nanotubes [12]. They have been fabricated using single-walled and multi-walled nanotubes both aligned and with random orientations and have been used to make composites with various polymeric matrices [e.g. 13, 14]. Researchers have demonstrated many applications of nanotube sheet composites including actuators [13], sensors [15] and artificial muscles [16].

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Carbon fiber reinforced composites with epoxy matrix are the current materials of choice for the aerospace industry. While the reliability of composite products has increased significantly in the last decade, many manufacturing defects and in-service defects are commonly encountered such as wrinkles and delamination. The piezo-resistive property of CNT sheet composites can be utilized to detect damage in these structures. In this paper, we fabricate epoxy - CNT sheet - graphite powder and epoxy - CNT sheet - graphene composites and test their mechanical behavior and electrical conductivity. The second filler is added in an effort to increase the piezo-resistive response of the composite films. Epoxy matrix is used so that the nanocomposite films can be compatible with aerospace composite structures for damage sensing. The next section describes the experimental procedures followed by results and discussion.

Experimental Procedure

The multiwall carbon nanotube sheet (Buckypaper) consisting of 100% free standing nanotubes was procured form Nano Tech Labs. The product specifications mention area density of 21.7 g/m^2 and surface electrical resistivity of 1.5 Ω/ m^2. The electrical resistivity was independently verified in our experiments. The graphite particles used as the additional filler were prepared by finely chopping low resistance (2.8×10^{-2} Ω/ m^2) graphene sheet supplied by Graphene Supermarket. The suppliers report that this sheet (6 inch x 6 inch) is made out of multiple layers of nanoscale graphene flakes adhesively bonded together. The size of the chopped powder varied between 300 -1000 μm. The fine graphene flakes used in the experiments are carboxyl-Functionalized graphene nanoplatelets, also supplied by Graphene Supermarket. Scanning electron microscope micrographs indicate that these graphene flakes are much smaller than graphite powder and typical size of a flake is in the range of 0.5 - 3 μm. The epoxy resin used in this study is West System # 105 Epoxy Resin combined with West System # 206 Slow Hardener with a 20 minute working time and a resin to hardener ratio of 5:1. Silver-epoxy paste supplied by MG chemicals is used as a conducting adhesive.

The CNT sheet is cut into $6.35 \times 1.27 \times 10^{-2}$ m strip samples using a laser blade. Copper plates gauging 32 with dimension of $1.27 \times 1.27 \times 10^{-2}$ m are attached to both sides of the CNT sheet using by conductive silver- epoxy paste. The copper plates are used for conductivity measurement. These CNT sheets are placed on a peel-ply on a flat aluminum mold. The second filler particles (coarse graphene particles or graphene flakes) are mixed into the epoxy. Several of these epoxy mixtures are prepared with varying quantities of the second filler. Separate mixtures are made with resin and hardener in 1:5 volume ratio with (a) 5 wt% , (b) 10 wt % and (c) 15 wt% coarse graphene powder as well as (d) 5 wt% , (e) 10 wt % and (f)15 wt% graphene flakes. The evenly mixed resin-filler mix is then applied to both surfaces of the samples. It is then covered with another piece of peel-ply and breather film to remove the excess matrix. This setup is sealed under vacuum and a pressure of 88.05 KPa is provided by the vacuum system to assist the breathing film to absorb the extra epoxy. The samples are peeled after curing the resin for 12 hours at room temperature. Copper wires are soldered to the plates on either side to facilitate stable resistance measurement.

The resistance of nanocomposites samples with and without application of mechanical load is obtained by four point probe testing method according to IEEE and ASTM standard test methods [17-19]. This method works by forcing a current and measuring voltage (FCMV) using a four-wire Kelvin-connection scheme. The resistance of the sample is calculated using ohm's law by a passing controlled current (I) of 0.5A and recording a voltage drop (ΔV).

The tensile test for nanocomposite samples is performed using the CS-225 Digital Force Tester. A constant head speed of 0.16 mm/search is applied to the samples and the resistance

change is recorded as the sample is subject to loading is recorded simultaneously. Insulating pads are used between the copper plate and grips to isolate the sample for tensile loading.

Results and Discussion

1. Composite resistivity without load application

The electrical resistivity of the nanocomposite strips is obtained as:

$$\rho = R\ (w \times t)/l \quad (1)$$

Where R is the calculated resistance by ohm's law, w and t are the width and thickness of composite strips. l is the length of the composite strip. The thickness of the samples is obtained using SEM micrographs of cross sections as shown in Figure 1 (a). There is no significant variation in cross-section thickness between samples with different quantities of graphite powder and graphene flake fillers. An average thickness of 100 μm is used in the resistivity calculation. Figure 2 shows the resistivity of the clean buckypaper nanocomposite and buckypaper composite with different quantities of graphene flakes and graphite powder without any application of loading. The values reported are averaged from tests on three identical samples. Table 1 compares the resistivity values for neat buckypaper composite obtained in the current investigation with those from the literature. The resistivity of composites is comparable to similar values in literature, particularly there is a good correlation between values obtained in this study and that by Wang [19] and Chapartegui [20] with Epon862 and benzoxazine matrix materials. The resistivity of the neat CNT sheet without any matrix [19-21] and that with aligned nanotubes [22] is understandably lower than that of the composite in the current study.

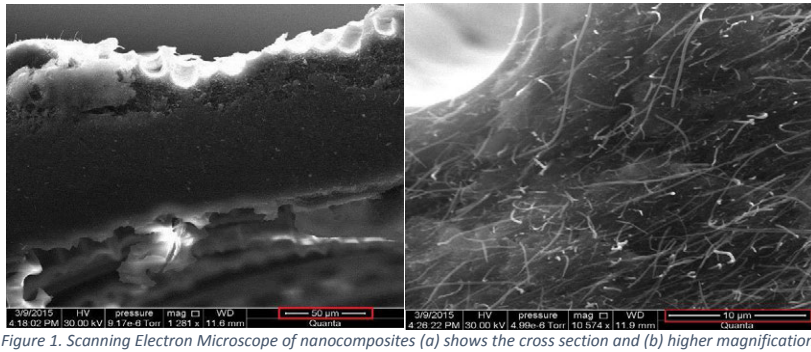

Figure 1. Scanning Electron Microscope of nanocomposites (a) shows the cross section and (b) higher magnifications showing nanotubes.

When the second conductive filler is added to the nanocomposite system the resistivity decreases, but there is a pronounced particle size effect. When the second phase filler is coarse graphite particles there is a significant decrease from 34.7×10^{-5} Ω·m to 13.4×10^{-5} Ω·m using the 5 % graphite powder- epoxy as the matrix. This further decreases as the content of filler is increased to 10 % and 15 %. Though there is a decrease in resistivity using graphene flakes to modify epoxy, the change in resistivity is an order of magnitude lower in comparison.

There are several theoretical models for e.g. by Kirkpatrick [23], McLachlan [24], Mamunya [25] that have been proposed to explain the resistivity (or conductivity) of composites with conductive fillers like carbon nanotubes. Kirkpatrick's model is based on contact between filler particles in a matrix and is given by

$$\sigma_m = \frac{1}{\rho_m} = A(\phi - V_{bc})^b \quad (2)$$

Where σ_m is the conductivity and ρ_m is the resistivity of the composite, A is the conductivity of the fillers, ϕ is volume fraction of the fillers, V_{bc} is the percolation threshold of filler, and b is an experimentally determined constant exponent and depends on the particle shape. This phenomological model has successfully explained conductivity of many particulate and fiber composites including carbon nanotube – polymer composites [26]. There is a significant increase in conductivity when the volume fraction of the filler particles is higher than the percolation threshold (V_{bc}) which represents the minimum quantity of filler to form a continuous network. The percolation threshold as well as the critical exponent have been known to vary depending on particle size [27]. Larger particle typically lowers the percolation threshold as smaller quantities of filler particles can result in a continuous network.

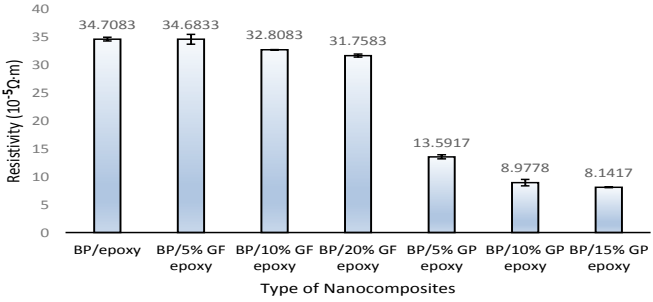

Figure 2. The resistivity of CNT sheet nanocomposites studied

Table 1. The resistivity of buckypaper composites from literature

Reference	Material	Resistivity (10^{-5} Ω·m)
Wang et al [29]	Magnetic aligned MWCNT buckypaper	1.13
Chapartegui et al[30]	Neat buckypaper	22.7
Chang et al [31]	Neat buckypaper	20.8
Wang et al [29]	MWCNT buckypaper/Epon862	39.2
Chapartegui et al[30]	MWCNT buckypaper / Benzoxazine	34.5
Chang et al [31]	MWCNT bucky paper /Parmax	10
Li et al [32]	Aligned MWCNT buckypaper/pCBT [46]	1.9

In the current study, the neat CNT sheet is a connected network therefore has low resistivity. Infiltrating the nonconductive epoxy into the CNT sheet results in reduced connectivity, therefore, increases the resistivity of the composite. Addition, of second conductive filler can reduce the conductivity by (a) increasing the volume fraction of conductive fillers ϕ and (b) reducing the percolation threshold V_{bc} . There is an increase in the content of conductive fillers with both coarse graphite powder and fine graphene flake addition to epoxy resin. In the case of larger graphite powder addition, there is a significant decrease in resistivity, potentially because the percolation threshold for the composite is also reduced. It is known that percolation threshold is lower when the filler particles are larger [27]. The larger size of graphite powder (300 -1000

μm) potentially modifies the percolation threshold in CNT sheet – graphite powder – Epoxy composite while this effect is not present in CNT sheet – graphene flake – Epoxy composite with fine graphene particles (1-3 μm). Results indicate that the coarse graphite powder bridges CNT network more effectively than the graphene flakes.

2. Piezo-resistivity of two-filler composite

Figure 3 shows the stress-strain and resistivity strain response of the graphite powder modified CNT-sheet-epoxy composites. Each dataset corresponds to an average of three samples as shown in Figure 4 for 5% graphite powder reinforced epoxy- buckypaper composite. The neat CNT sheet-epoxy composite shows a linear stress strain response followed by clean fracture at 5% strain. Addition of graphite powder to epoxy and CNT sheet increases the stiffness and strength of the composites. The improvement in stiffness reduces as the graphite powder content is increased. Also the strain at failure is lower (4.1%) when the graphite powder content is increased to 10 and 15 wt %. There is a corresponding increase in tensile strength to 16.12 MPa from 7.28 MPa for neat CNT sheet composite for 15% graphite powder modification. Even with a 5% modification of epoxy matrix the tensile strength increases to 10.28 MPa.

The resistivity of the composites without load application reduces as the quantity of graphite powder in epoxy resin increases. There is a clear increase in resistance with load application in neat CNT-sheet composites from 35.2×10^{-5} Ω·m to 36.03×10^{-5} Ω·m. This effect is increased by an order of magnitude when the epoxy resin is modified by 5 wt% graphite powder addition. The resistivity increases from 18.1×10^{-5} Ω·m to 26.8×10^{-5} Ω·m. There is a similar increase for 10 wt % and 15 wt % graphite powder modified epoxy resin composites, however the change in resistance is highest for 5 wt% graphite powder.

Figure 5 shows the stress-strain and resistivity-strain response of nanotube sheet –epoxy resin composite modified with fine graphene flakes. There is a small increase in stiffness with the addition of graphene flakes, but not as big an increase as that observed with course graphite powder. The strain to failure decreases from 5 % to 4.6 %. Unlike with coarse graphite powder there is no appreciable increase in tensile strength, in fact, tensile strength decreases marginally from 7.28 MPa to 6.59 MPa and 6.404 MPa to 5% and 10% graphene flake modifies resin mixtures.

There is an increase in piezo-resistive response with the graphene flake addition, for example with 5% addition of graphene flakes in resin, the resistivity changes from 32.9×10^{-5} Ω·m to 34.16×10^{-5} Ω·m. The comparable numbers for neat CNT sheet composite are 35.2×10^{-5} Ω·m to 36.03×10^{-5} Ω·m. Though there is a marginal increase, this is not on the same scale as that observed for coarse graphite particles.

There has been a significant research effort over the past decade in using carbon nanotubes as fibers for structural composites. While the carbon nanotubes by themselves have excellent strength, stiffness, the predicted mechanical properties have not yet been realized in nanotube composites. This is because of microstructural problems related to fiber–matrix interfacial strength, dispersion of nanotubes within composite and alignment of the nanotubes in the loading direction. There have been efforts to improve all three aspects, by approaches like functionalization [28], use of surfactants [29] and magnetic or mechanical alignment [19]. Present effort represents another way to improve the mechanical properties by addition of second filler.

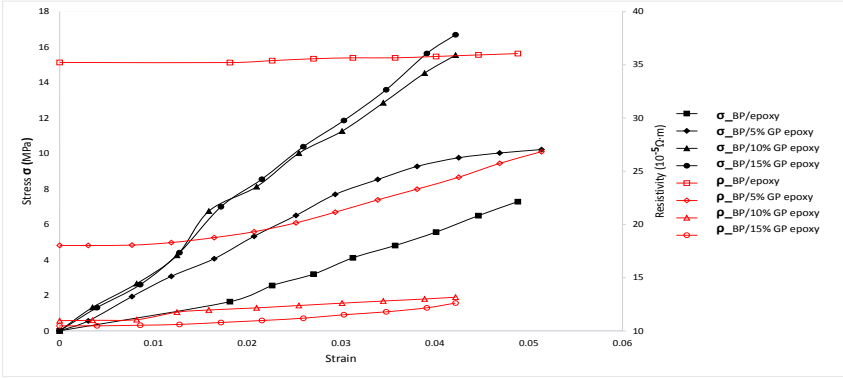

Figure 3. Stress & resistivity for various content of Graphene powder epoxy mixture impregnated Buckypaper

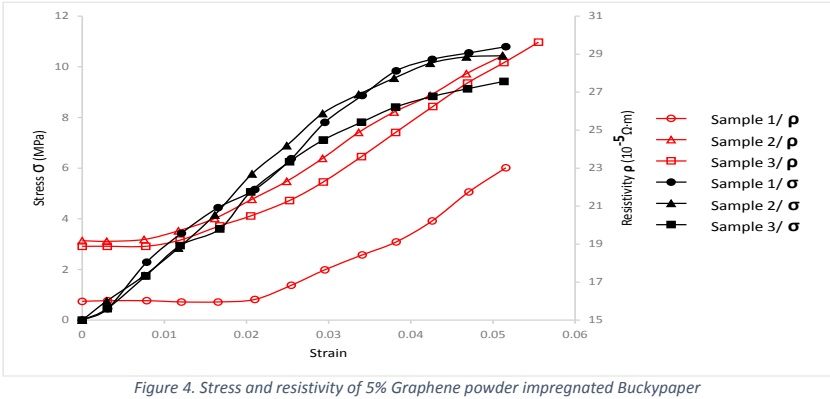

Figure 4. Stress and resistivity of 5% Graphene powder impregnated Buckypaper

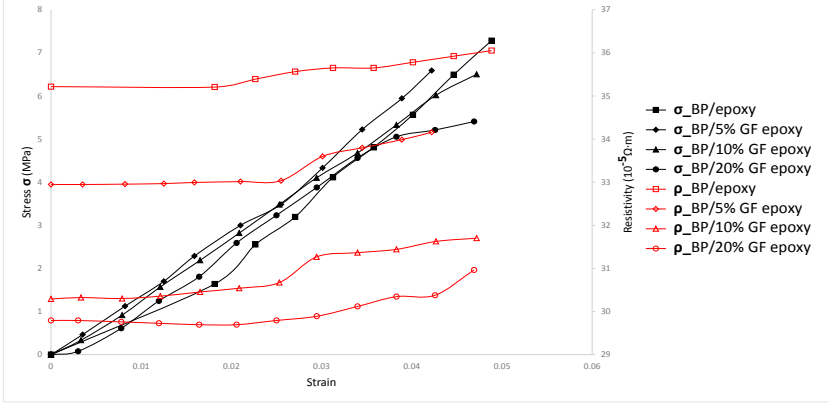

Figure 5. Stress & resistivity for various content of Graphene flakes epoxy compounds prepared Buckypaper

The changes in electrical resistivity with the application of load presents opportunities for many applications in structural health monitoring of aerospace composites. Specifically the order of magnitude increase in resistivity change under tensile loading with the addition of 5 wt% graphene powder to the composite reduces the strain level required to measure resistivity changes for these applications. Though CNTs exhibit intrinsic peizoresistivity [7] researchers have often attributed the change in resistance to modifications of interactions between carbon nanotubes in the network [30]. The addition of second phase particles enhances this effect, therefore an increase in resistivity change is observed for the two fillers considered in this study. There is however much more pronounced change with coarse graphite powder. The breakup of contacts between a large particle and CNT network under loading can affect a larger area of the composite, therefore the piezoresistivity is more pronounced with the addition of coarse particles.

Conclusion

Addition of coarse graphitic particles as a second filler to CNT sheet- epoxy composites results in strength increase and reduction in the resistivity. Further, the change in resistivity with tensile strain shows a significant improvement from 0.85 $x10^{-5}\Omega\cdot m$ to $8.9x10^{-5}\Omega\cdot m$ with 5 wt% graphite powder addition. This has potential applications in composite damage detection.

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