

Electrical Properties of Unidirectional Carbon Fiber Reinforced Epoxy-Graphene Composites

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Abstract. This paper aims at establishing connections between electrical resistivity and stresses in carbon fiber reinforced epoxy-graphene composites. To avoid the interconnection of multiple parameters, we examined composite specimens consisting of a single strand or tow (12,000 carbon fiber filaments) embedded in an epoxy matrix containing up to 1.0 wt% of graphene (TG679) particles. The specimens show resistance increase with the tensile stress. The characteristic of the dependence varies with the content of graphene particles, tending to be linear as the percentage of graphene content increases. We did not observe any significant changes in the ultimate strength of the composite with an increase of the graphene particles concentration.

Keywords: carbon fiber composites, graphene particles, resistivity, stress level, cross-property connections.

1. Introduction. In this paper, we will focus on the electrical resistivity of unidirectional carbon fiber reinforced epoxy-graphene composites, and the dependence of this parameter on the level of tensile stresses. This work builds on the previous results of the present authors on dependence of the electric conductivity on tensile stress in neat carbon tows (Wentzel and Sevostianov, 2013) and epoxy-graphene composites (Wentzel et al., 2017).

Carbon reinforced composites have been used historically in applications where high strength-to-weight ratio is crucial. As the technology of composite materials has advanced, so has the utility

of these materials. Carbon composites are now being used for more than just their mechanical strength: they are also being used for their electrical properties, since carbon fibers and graphite particles are good electrical conductors. Due to that, many results have shown that it is possible to use such composite materials as self-diagnostic materials.

Some of the first research performed was to monitor damage and stress level in continuous carbon fibers (see, for example, Wang and Chung, 1997, 1998). Flandin et al. (1999) first used nanoscopic conductive fillers with different aspect ratios in a thermoplastic matrix to monitor the applied macroscopic mechanical strain and the damage evolution during loading. Nanoscaled carbon black particles (Kupke et al, 2001) as well as microscaled carbon black particles (Muto et al, 2001) have also been used to modify the matrix of glass-fiber reinforced thermosets; this research also showed that external stress as well as apparent mechanical damage can be detected in these multiphase composites via electrical conductivity methods. Böger et al (2008) developed glass fiber reinforced composites with epoxy matrix containing carbon nanotubes (CNTs), and showed that this material has reasonably high electrical conductivity. More recently, graphene, carbon black, and short carbon nanofibers attracted attention of many researchers in this area. It has been shown, for example, that when graphene fills the insulating polymer matrix, a conductive polymer composite results (Kuilla et al, 2010; Belucci, et al, 2011; Galpaya et al, 2012). Such composite materials generally exhibit a non-linear increase of the electrical conductivity as a function of the filler concentration. A theoretical study by Xie et al. (2008) predicted that graphene is more effective for conductivity improvement than competing nanofillers such as CNTs because of their large specific surface area. These findings were subsequently confirmed by experimental measurements of Belucci et al (2011). Ferreira et al (2016) and Khanam et al (2016) provided reviews of the state-of-the-art in the area of conducting polymer matrix composites.

Electrical conductivity of graphene/polymer composites is usually explained by low percolation threshold, when the conductive filler forms a network leading to a sudden rise in the electrical conductivity of the composites. Very often, the conclusions about percolation are made based on electrical conductivity measurements. Stankovich et al (2006), for example, synthesized graphene/polystyrene composites and, based on electrical conductivity measurements, reported a low percolation threshold at 0.1 vol% of graphene. However, they were unable to observe it by microscopy analysis (similarly to Wentzel et al, 2017).

Macias et al (2017) proposed a micromechanical model to explain the conductivity of the polymers containing conducting nanofibers through formation of conducting networks (percolation effect). They assumed that the matrix material is a perfect insulator and did not consider the charge transport across the matrix material. While polymers do have low electrical conductivity, it is not zero. Recently, Kang and Snyder (2016) proposed a model for charge transport phenomena in polymers. It was shown that adding 1.0 wt% of graphene filler increase the conductivity of the epoxy more than two orders of magnitude. This phenomena was quantitatively described using mean-field homogenization models, which accounted for the strongly oblate shape of the graphene particles; that study also observed that the electrical resistivity depends on the strain level. It allows one to use ordinary micromechanical homogenization technique to properly predict overall electrical conductivity in epoxy-graphene composites (Wentzel et al, 2017). This model was then validated by Govorov et. al. (2017) on specimens subjected to compressive stresses: the researchers observed reversible changes in conductivity only at the very beginning of the loading process, followed by a period of minimal resistance changes with increasing compressive loading.

In the present paper, we will focus on electrical conductivity of a composite consisting of uniaxial carbon fibers embedded in an epoxy-graphene matrix (three-phase composites). We will demonstrate that adding 0.5 wt% to 1.0 wt% of graphene filler increases the conductivity of the epoxy-carbon fiber composites while not changing the ultimate tensile strength. This shows potential to allow for electrical change methods to be applied to monitor stresses in the composite material, without affecting that material's strength. We will also propose a simple model to estimate the filament stress at failure and to estimate the number of surviving filaments prior to the failure event.

2. Materials and Methods. Samples were made using TORAY T1000 continuous carbon fiber filament and a two-part epoxy matrix. The nominal filament diameter of T1000 carbon fiber is 5 μm , the electrical resistivity is $1.4 \times 10^{-3} \Omega \cdot \text{cm}$, and the ultimate tensile is 3,040 MPa (Composite) and 6,370 MPa (Filament). The test was designed to study one factor, conductive filler percentage by weight. The levels of conductive filler were; no conductive filler, 0.5 wt% TG679 and 1.0 wt% TG679. Epoxy resin, Epon 862, and 'W' amine curing agent were procured from Hexion. Surface functionalized expanded graphite, TG679, was procured from Adherent Technologies, Albuquerque, NM. All materials were used as received. Nano-particles were dispersed as graphene layers into the matrix material. To control how well dispersed the conductive filler was, the cured graphene/epoxy specimens were examined using scanning electron microscope. We did not observe any clustering or percolation of the graphene flakes (Figure 1).

T1000 material was loaded onto a stand-alone tensioner set at 22.25 N. The tow was fed through a heated resin bath and drawn through a die set to a specific diameter. Once through the die, an additional layer of resin was added to the outside of the strand and fed through a length of

shrink tube. Grips were placed on both sides of the strand, and weight was attached to one grip. Tension was released; then the strand was cut and hung on a rack by one of the grips, with the weight allowed to freely hang on the opposite end. A heat gun was used along of the shrink tube and excess resin was removed. The strand was then hung and cured in an oven. Once cured, the shrink tube was removed from the stand. Fiber volume fraction was controlled between 50%-60%. Test articles are show in Figure 2.

The tensile load was applied to the specimen using a precision electromechanical drive system consisting of the stepper motor, gear reduction, and linear actuator drive assembly. A DC stepper motor with 200 steps per revolution, in conjunction with 10:1 gear reducer driving a precision bearing linear actuator, allowed for the discrete control of the tensile force down to 0.02 N per step. The applied tensile load was recorded with an S-Type load cell with a 0 – 4500 N range. The load frame uses a model SM-1000 load cell manufactured by Interface Inc. A typical load profile is illustrated in Figure 3.

Samples were loaded into a load frame using a grip adapter. The grip adapter's function was to transfer the axial tensile load to the strand coupon while minimizing any lateral load transfer stemming from vertical misalignment between the upper and lower ends of the strand coupon. Load transfer was accomplished using a universal-joint grip adaptor designed to accommodate off-axis misalignment of up to 7°. Load was applied at a constant rate of displacement from a small pre-loaded condition until failure.

Resistance measurements were obtained using a 4-point method with kelvin clip leads. The leads were spaced 10 mm apart and attached to the center region of the gage section (Figure 4).

A calibrated IET Labs Model 1693 RLC Digibridge was used to obtain the resistance measurements. The basic accuracy of the unit has been reported as $\pm 0.02\%$. Prior to testing, the

unit was tested against a known resistance standard to verify calibration, and procedures were followed to zero the unit. This unit was controlled by a custom graphical user interface (GUI) which allowed resistance measurements to be recorded to an Excel spreadsheet. Resistance was measured continuously through the load profile at a sample rate of 5 Hz.

3. Results. The load at failure, baseline resistance, and resistance at failure were all recorded and analyzed for 11 tests (3: unfilled, 4: 0.5 wt% TG, and 3: 1.0 wt% TG). The results are demonstrated in Figure 5.

The average composite stress at failure was 3718 MPa. The mean of unfilled samples was compared with the mean of samples containing graphene particles, to test for a significant difference in the means. The results indicate there was not a significant difference between the sample populations. The baseline resistance was also compared. In comparing the means, there was a significance difference between the sample populations. The addition of graphene particles reduced the mean baseline resistance by as much as factor of two. Likewise analyzing the resistance at failure shows a clear difference between the sample populations.

In addition to load at failure, baseline resistance, and resistance at failure, resistance measurements were taken continuously through the load profile. This data is presented as change in resistance over baseline resistance in Figure 6. This figure presents the averages of three unfilled samples, four 0.5 wt% TG, and three 1.0 wt% TG samples.

Testing indicated both the unfilled and 0.5 wt% TG samples appeared to follow an S-shaped curve in the initial loading period followed by a linear increase to failure. This trend was not evident in the 1.0 wt% TG sample averages, suggesting that, as more conductive filler is added, the primary mechanism leading to changes in resistance switches from broken filaments being the

primary driver, to conductive filler/resin interface dislocations driving the change in resistance. In the 1.0 wt% averages, the trend was almost completely linear up to failure. Other notable feature in the data was the sharp increases and decreases in the resistance ratios: these correspond to a sudden rise or fall in resistance. The sudden rise in resistance at 2000 MPa in the unfilled sample indicates a significant decrease in the number of continuous filaments in the measurement section. The high load decreases in the 0.5 wt% and 1.0 wt% samples are indicative of failure events outside the measurement area that caused a reduction in local cross-section but increased sample length leading to small amount of stress relief just prior to the ultimate failure event.

4. Discussion and Conclusions. One of the goals of this research was to see whether the addition of conductive filler affects the tensile properties of the carbon fiber-epoxy strand. Our research finds that the addition of up to 1.0 wt% graphene particles had no significant measureable effect on the ultimate tensile strength. Our findings are noteworthy because they demonstrate that the electrical properties, specifically conductivity, of composites can be increased (for self-monitoring) without altering the ultimate strength.

The ability to test whether electrical resistance could be used to estimate surviving filaments has been previously investigated for unfilled carbon-fiber epoxy strands by Wentzel and Sevostianov (2013). This method was subsequently shown to be effective for up to 20 filaments by Dandy et al (2015). Figure 7 demonstrates the effectiveness of applying this method to a carbon fiber composite tow consisting of 12,000 filaments. It identifies the estimated resistance based on the number of surviving filaments and the stress as a function of the number of filaments at the average failure load of the unfilled samples.

The average resistance was calculated and identified on the resistance curve. This resistance corresponded to a number of surviving filaments. Based on the average resistance at

failure, the model suggests that approximately 30% of the filaments were still continuous prior to the ultimate failure event. This estimate for surviving filaments was then used to calculate the critical stress in the filaments. The critical stress was calculated to be 5,560 MPa, which is 87% of the ultimate filament strength calculated by the vendor. These findings suggest that this model could be used to predict filament stress in a unidirectional composite sample based on resistance measurements. By further being able to understand the progressive failure nature of carbon fiber composite materials, this technique and model could be used to identify early indicators of failure based on the monitoring of localized areas of a carbon fiber composite materials.

It is still being investigated how the addition of graphene particles into the matrix material adds insight into the unidirectional sample geometry. We observed that the addition of graphene increased sample conductivity, but changed the nature of the stress/resistance dependence, suggesting that, as more conductive filler is added, the primary mechanism leading to changes in resistance changes from broken filaments being the primary driver, to conductive filler/resin interface dislocations driving the change in resistance. Due to this, it is hypothesized that the additional of conductive particles will help understand the material response for composite material with more complex geometries where the mechanical properties are more dependent on the composite bulk properties.

Acknowledgments. The authors would like to thank Dr. Sandi Miller of NASA Glenn Research center for providing the conductive filler material and her involvement in this research effort. The authors would like to thank Chad Hastings of Marshall Space Flight Center and Dr. James Reeder of Langley Research Center for manufacturing the samples.

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Figure captions.

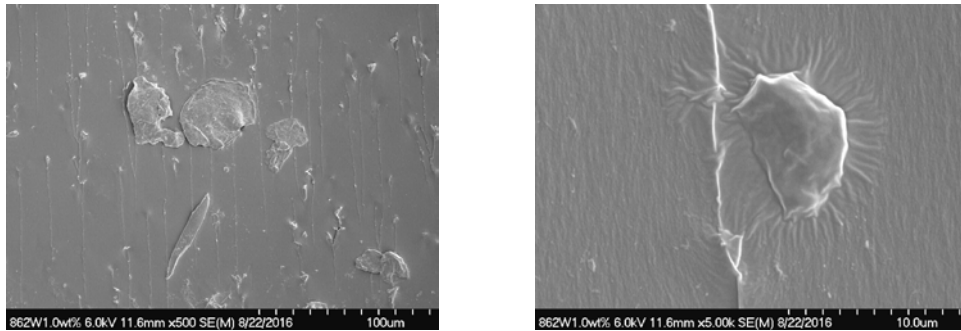


Figure 1. SEM images showing the dispersion of graphene particles.

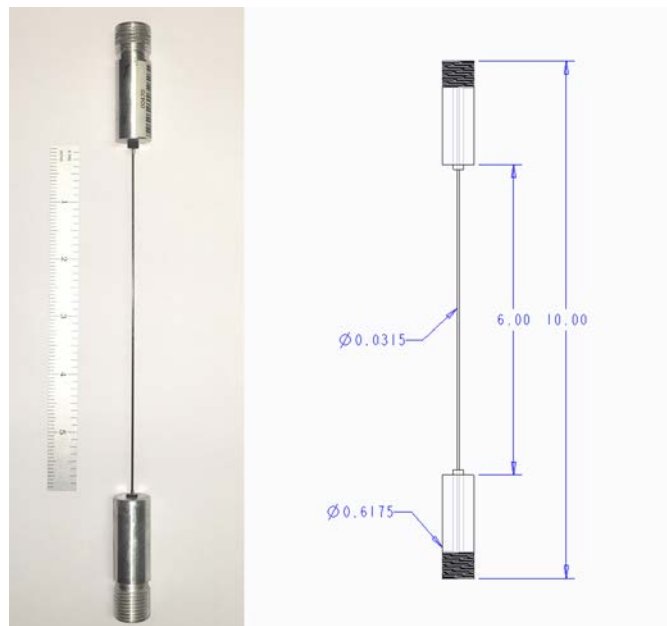


Figure 2. Example of a T1000 carbon fiber strand with dimensions

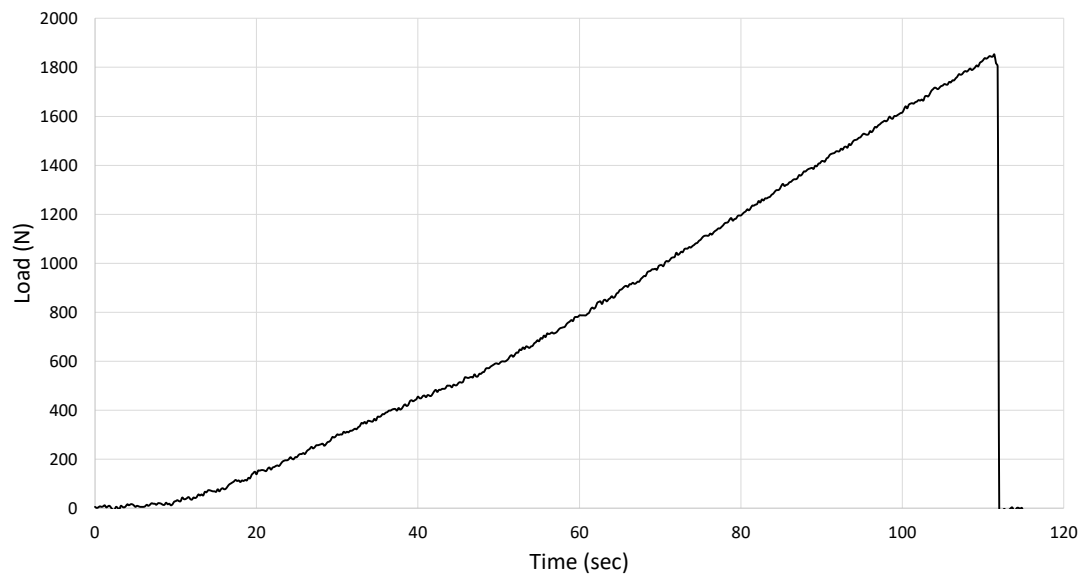


Figure 3. Load profile of a tensile test article

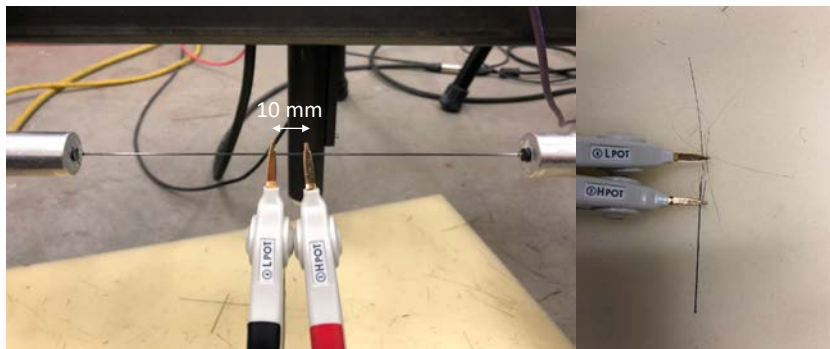


Figure 4. Shows the lead placement on a test article pre- and post-test

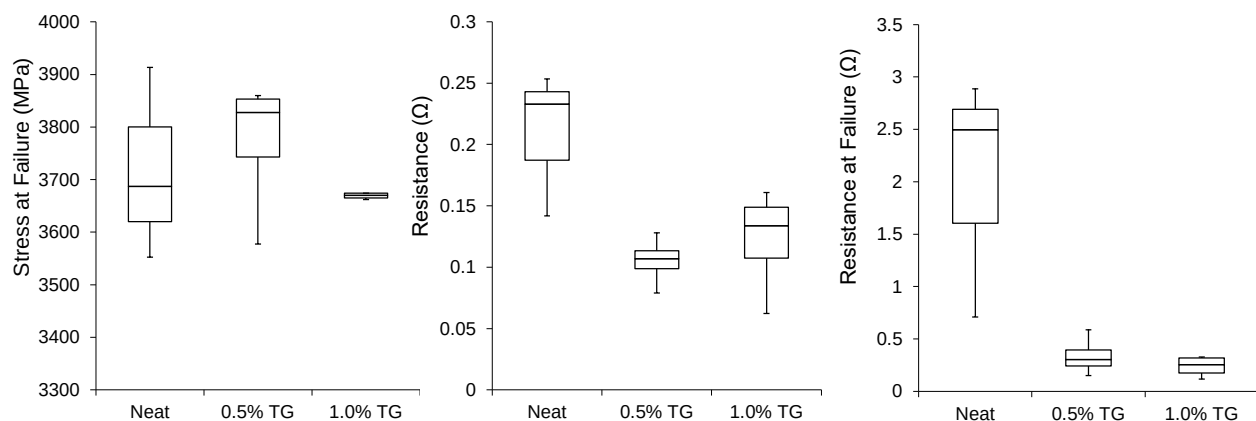


Figure 5. Summary plots of the statistical analysis of ultimate strength, baseline resistance, and resistance at failure.

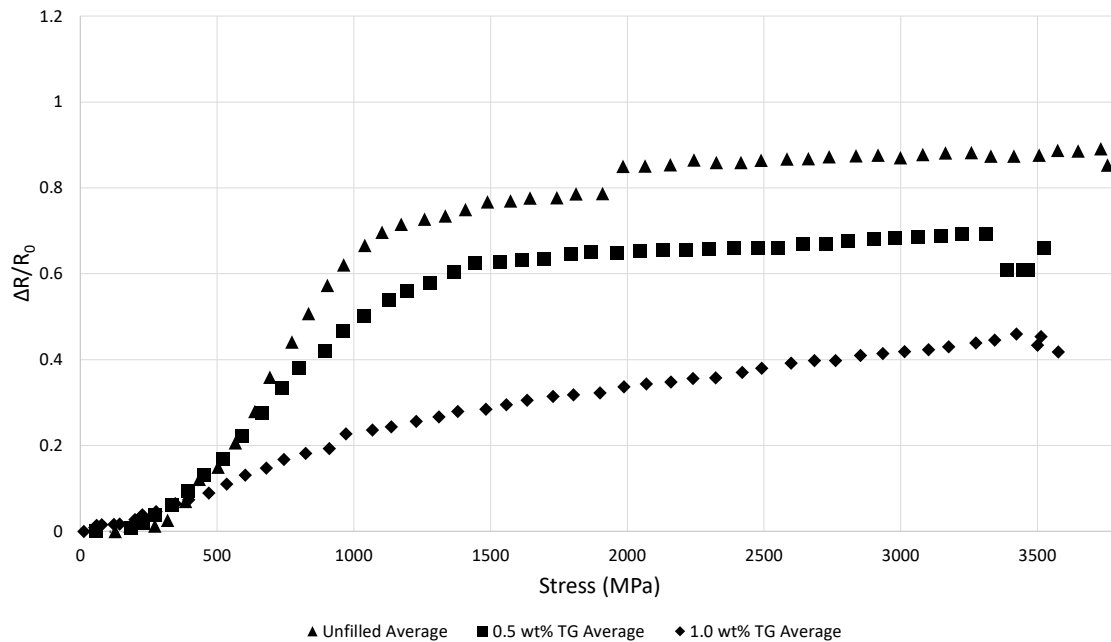


Figure 6. Change in resistance over baseline resistance as a function of stress for 0.0 wt%, 0.5 wt%, and 1.0 wt% samples

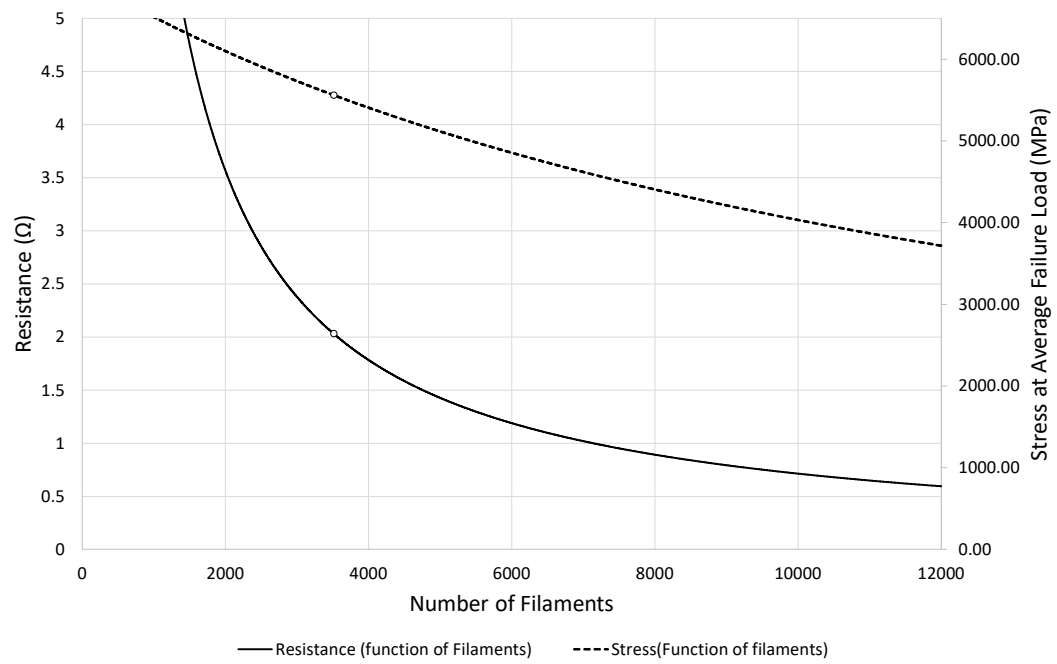


Figure 7. Model predicting critical stress in carbon fiber filament based on resistance measurement.