Carbon Fiber / Graphite Nano Platelet Hybrid Composites

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SUMMARY

Continuous carbon fibers were coated with graphite nanoplatelets. Carbon fiber/Epoxy composites made from these modified carbon fibers were produced by a hand layup process. The composite made with the nanographite coated fibers showed significant improvement over control samples in inter laminar shear strength (ILSS) and flexural strength.

Keywords: Nanocomposite, Nanographite, Hybrid composite, Carbon fiber, Epoxy

1. INTRODUCTION

Continuous carbon fiber reinforced plastics (CFRP) have been widely used in many applications such as aerospace, sporting goods, and automotive parts. This is primarily due to its excellent mechanical properties in the fiber direction. However, it is often reported that the matrix dominated properties, such as interlaminar shear strength and longitudinal compressive strength, are the weak points that limit the material.

Since the late 80's, many nanomaterials have been developed and have attracted much attention. These materials include nanoclays, fullerenes, carbon nanotubes, and graphene sheets. Many reports have shown that polymer composites based on these nanomaterials (nanocomposite) can improve the mechanical properties at very low loading levels.

Recently, reports have been made of efforts to combine nanomaterials with conventional continuous-fiber based composites to improve their properties. For example, nanoclays **[1,2]**, carbon nanofibers **[3,4]**, and carbon nanotubes **[5-7]** were incorporated into carbon fiber or glass fiber based composites. Also nanographite platelets were mixed into matrix system to make CFRP. **[8]** The infusion of a nanoparticle modified matrix resin into a fiber prefrom is difficult because of the high viscosity resulting from even a small concentration of nanoparticles as well as the 'filtering' effect caused by trying to impregnate the nanoparticle modified resin through fibers that are in close proximity to each other. To date, however, the integration of nanoparticle and in particular graphite nanoplatelets applied as a fiber coating has not been reported.

The objectives of this research were to investigate the effect of graphite nanoplatelets on the properties of conventional carbon fiber based composites and also to control the placement of these nanoparticles between the carbon fibers through their application as a fiber coating or sizing.

2. EXPERIMENT

2.1 Materials

The continuous carbon fibers (CF) used in this study was HexTow AS4 (12,000 filaments tow, Hexcel Co.) The average diameter of AS4 was determined as 7.2 um by microscope observation. The epoxy resin and curing agent used in this study were Epon 862 (Bisphenol-F based di-functional epoxy, Hexion Special Chemical) and Epikure W (Miller-Stepheneson Chemical Co. Inc.) The exfoliated graphite nanoplatetelets (xGnP® **[9]**) sample used in the study was the xGnP®-1 (Diameter: 1um, Thickness: 10nm, Surface Area: 100m^2/g by BET measurement)[13]. XPS analysis showed that xGnP®-1 has 5.97 atomic % of oxygen and 94.03% of carbons. A non-linear least square curve fitting routine was used to interpret the carbon and oxygen peaks into functional groups, which showed that the surface oxygen groups consisted of 2.3% ether groups, 2.9% hydroxyl groups, and 0.8% carboxyl groups. Z-potential measurements in 0.1 mM KCl water system revealed that the Z-potential of xGnP®-1 was +8.35±0.69 mV. **Figure 1** shows the size distribution curve of the xGnP®-1 particles used in these experiments.

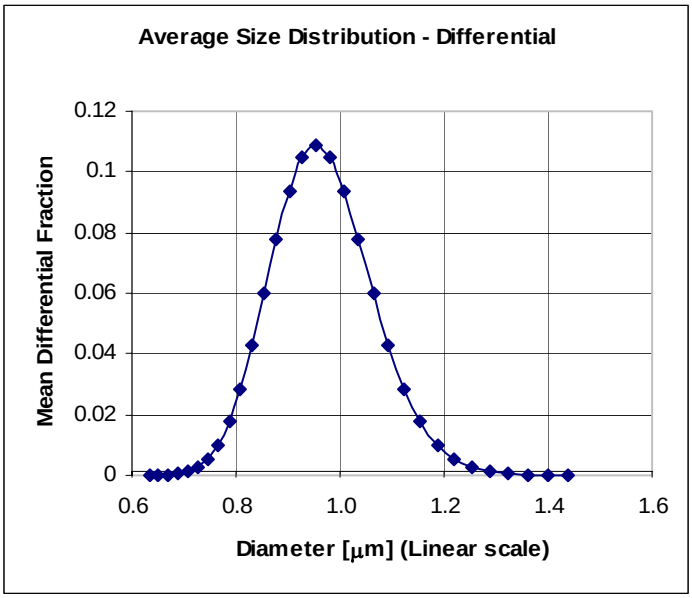

Figure 1. Particle Size Distribution of xGnP®-1

2.2 Carbon Fiber Sizing

Figure 2 shows the sizing tower set up for the CF coating. The sizing solution for CF was prepared as follows. First, 1 wt% of xGnP®-1 was dispersed in a 2-propanol solvent along with 0.5 wt% of Epon 862/Epicure W mixture. The mixing ratio of Epon 862 and Epikure W was 100 to 26.4 by weight. The sizing solution was mixed by an ultrasonic processor at 100W for 2hr. After mixing, the sizing solution was transferred to a sizing bath and was continually stirred by an ultrasonic processor at 20W during the fiber sizing process. The speed of the coating process was constant at 150 cm/min. The temperature of the drying towers were set at 190 ºC. The epoxy system was partially cured during the drying condition so that it was easier to spread the tow during subsequent prepregging. A control sizing solution, which was consist of 0.5 wt% of

Epon 862/Epicure W system in 2-propanol but without nanoparticles, was also prepared. CF was coated with this epoxy sizing solution under the same conditions and served as the control sample.

After the sizing process, CF samples were analyzed and the weight change before and after the sizing was determined. In the case of the control sizing, 0.64 wt% of sizing was left on CF samples. In the case of xGnP®-1/epoxy sizing solution, 1.72 wt% of the nanoparticle modified sizing was left on the CF samples. Based on these results, it was assumed that 0.64 wt % of epoxy and 1.08 wt% of xGnP®-1 was coated on CF. **Figure 3** shows the ESEM images of control and xGnP®-1 coated CF samples.

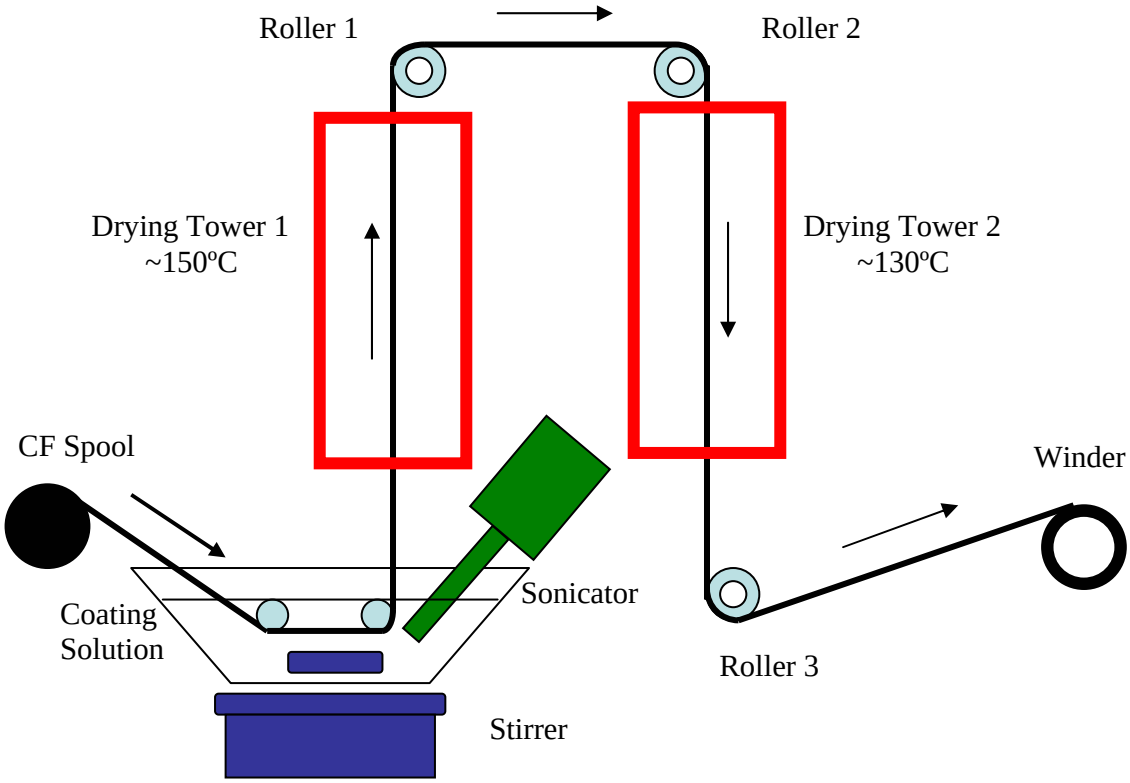

Figure 2. Schematic Diagram of the Sizing Tower

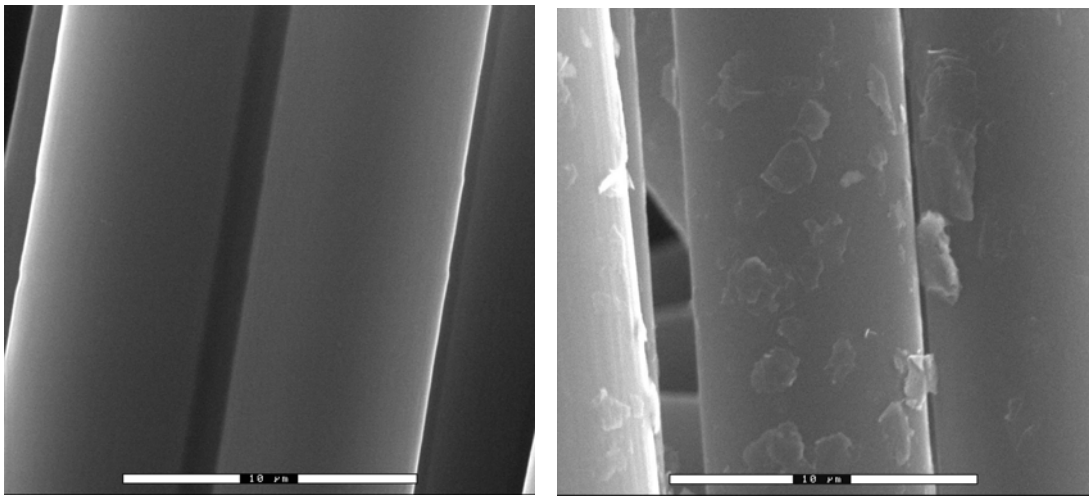

Figure 3. ESEM Images of Control (Left) and xGnP®-1 coated (Right) CF Samples

2.3 Single Fiber Fragmentation Test (SFFT)

Single sized CF fiber samples were selected from the sized CF tow samples. Each single fiber sample was aligned in a standard dog-bone shape silicon mold, then a mixture of Epon 862/Epikure W (100/26.4 by weight) resin was poured into the mold. The epoxy was cured at 75 ºC for 2 hours, and then post cured at 125 ºC for 2 hours. Tensile loading was applied to each SFFT sample under optical microscope observation and the standard single fiber fragmentation test protocol was followed. The number of fragments was measured to calculate the average fragmentation length, and then the critical fiber length was calculated. The tensile strength of AS4 was assumed as 4400 MPa and the average diameter of the fiber was determined as 7.21 um for the control samples and 7.15 um for the xGnP®-1 coated sample. The interfacial shear strength (IFSS) was determined based on Kelly-Tyson model. **[10-13]**

2.4 Prepreg Fabrication

A Research Tool Corporation prepregger was used to make prepreg samples. Resin system (Epon 862 / Epikure W, 100 / 26.4 by weight) was mixed by ultrasonic processor at 50W for 3min, then the system was pre-heated at 50 ºC. The temperature of the resin pot, guide roller, and flattening pins was set at 50 ºC. The speed of drum rotation and drum carriage movement were adjusted so that the spread tow did not overlap and a uniform, gap-free 25 cm x 180 cm unidirectional prepreg tape was made, cut into 5 cm x 15 cm pieces, covered by Teflon sheets, and then stored in a refrigerator.

2.5 Hand Lay-up Composite Fabrication

Nine layers of 5 cm x 15 cm prepreg sheets were laid up in the same direction to make a unidirectional fiber reinforced composite panel. The sample was placed in a stainless steel mold with silicone sheets. Some shims were put in the mold so that the thickness of the final composite panel could be controlled. The mold was put in a Tetrahedron heat press, then 172 kPa of pressure was applied on the mold. The sample was cured at 175 ºC for 60 min under the pressure. After the composite panel was removed from the mold, it was post cured at 175 ºC for another 90 min to ensure complete curing. ESEM observation revealed that a void-free sample was produced by this procedure. Then the cured panel was cut into pieces for short beam shear strength, and flexural tests in both 0 degree and 90 degree directions. The average CF volume fraction of the control samples was 60.1 Vol% while that of xGnP®-1 coated samples was 59.8 Vol%. The measured data were normalized to a CF content of 60 vol%. In the composite samples based on xGnP®-1 coated CF, the fraction of xGnP®-1 in the composite was calculated as 0.53 vol% (0.74 wt%) based on the amount of coating on CF sample.

2.6 Short Beam Strength Measurement (ASTM D2344)

The short beam strength of the composite samples was measured according to ASTM D2344 standard. The loading span was set to four times of the specimen thickness. Before starting the test, 1 lb (454 g) of pre-load was applied to each specimen. The speed of the test was set at 1.27 mm /min (0.05 inches / min). It is

considered that many failure modes can be involved in this experiment. However, failures of unidirectionally aligned fiber reinforced composite are usually dominated by resin and/or interlaminar properties.

2.7 Flexural Test (ASTM D790)

The flexural test was performed on a UTS testing machine [United Calibration Corp.] at room temperature by following ASTM D790 standard test method. The samples were made in a standard bar shape. Before the measurement, the thickness of the samples was checked to be constant through out the samples. The test was performed at flexural rate of 1.27 mm /min (0.05 inches / min).

2.8 Resistivity Test

The resistivity of composite samples was measured by Impedance Spectroscopy by applying a two-probe method at room temperature. Before a measurement, gold coating with about 20nm thickness was applied on each sample. During the process, sidewalls of each sample were masked so that no conductive connections between the top and bottom planes were formed during gold coatings. Then, copper tape was attached to the top and bottom surfaces of the sample and connected to the instrument. The resistance of sample was measured in frequency range of 0.1 to 100,000Hz. Then the data was recalculated to resistivity by incorporating the sample dimensions. The resistivity at 0.1Hz was considered as the DC resistivity since the difference is very small.

2.9 Stress Concentration Analysis by Finite Element Method (FEM)

To investigate the stress concentration in these composite systems, a Finite Element Method was conducted using ANSYS 57. In the simulation, quadrilateral plane elements were used so that each element was defined by eight nodes and each node has two degrees of freedom in the x- and y- directions. All the simulations were performed under plane stress condition.

3. RESULTS AND DISCUSSIONS

3.1 Interfacial Shear Strength (IFSS)

Figure 4 shows the results of IFSS. The xGnP®-1 coated CF reinforced composite showed about 20% better IFSS than the control sample. This result suggests that the xGnP®-1 coating improved the modulus and strength of the interphase region, enhancing load transfer from the matrix to the CF. A stress analysis based on FEM (Finite Element Method) suggested that when a platelet is confined to the vicinity of the CF surface, the stress accumulation is reduced and the strength of the interphase region could be improved. **(Figure 11)** On the other hand, if a platelet is oriented perpendicular to a substrate, the stress concentration became higher, leading to a reduction in interphase strength. **(Figure 10)** Thus, the final morphology of the graphite nanoplatelets on the CF is considered to be the key factor to improve the properties of the interphase and the overall composite sample.

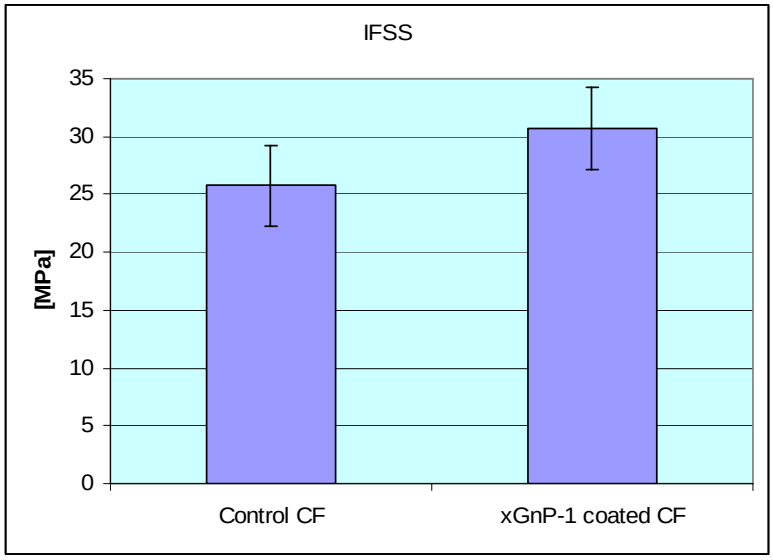

Figure 4. Interfacial Shear Strength of Control and xGnP®-1 Coated CF

3.2 Short Beam Strength

Figure 5 shows the typical Short Beam Strength Stress-Strain curves and short beam strength of the samples. The dominant failure mode for both xGnP®-1 coated CF based composite and control composite is the interlaminar failure followed by inelastic deformation. This interlaminar failure mode was observed by microscope after the experiment and it was consistent with the assumptions required for validity of the test. Based on these results, the xGnP®-1 coated CF based composite showed about a 20% improvement in interlaminar shear strength over the control sample.

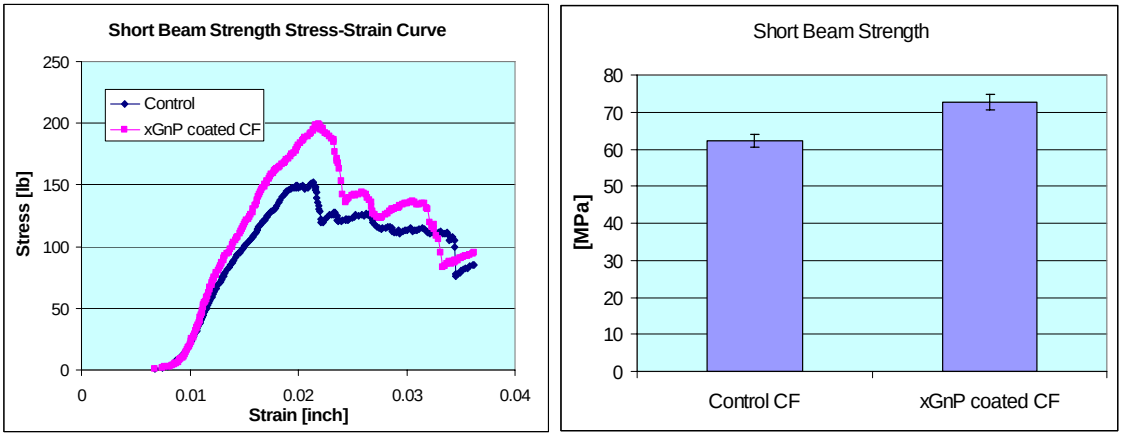

Figure 5. Short Beam Strength Stress-Strain Curve and Short Beam Strength

3.3 Flexural Strength and Modulus

Figure 7 shows the flexural properties of the composite samples in the 90 degree (longitudinal) direction. Compared to the control, the composite made of xGnP®-1 coated CF showed about a 15% improvement in strength and 5% improvement in modulus. **Figure 8** shows the properties in 0 degree (transverse) direction. In this case, the properties are dominated by CF and the differences are considered to be statistically negligible.

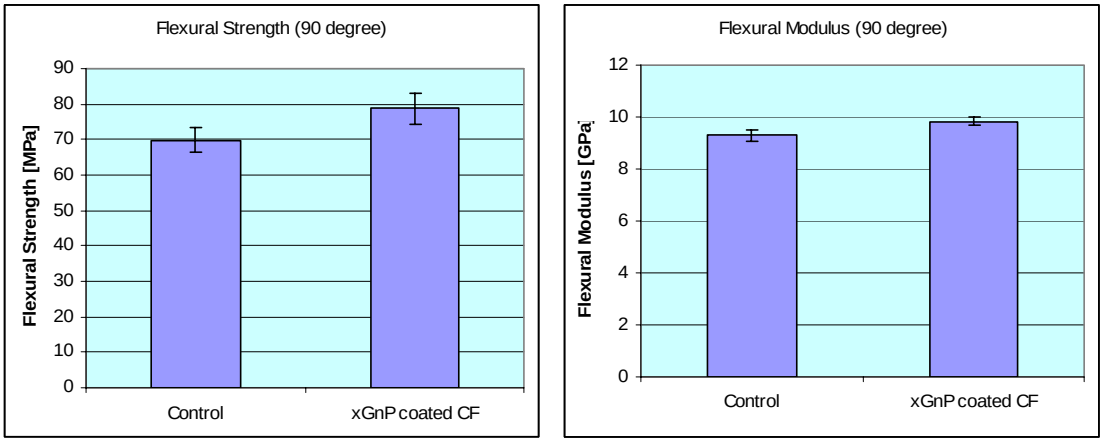

Figure 7 Flexural Properties in 90 degree Direction

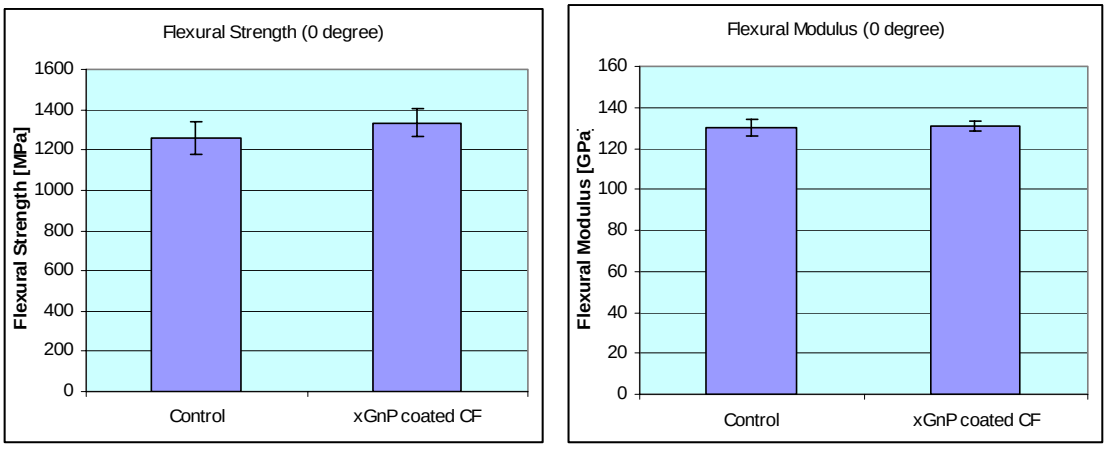

Figure 8. Flexural Properties in 0 degree Direction

3.4 Electrical Conductivity

Figure 9 shows the resistivity data of the samples at 0.1 Hz in the thorough the thickness direction. The resistivity decreased with 0.53 vol% of xGnP®-1 in the system. This implies that adding small amount of conductive nanomaterial into CF based composites could improve the conductivity in through the thickness direction. The resistivity in fiber direction did not show any change as expected since the resistivity would be dominated by the highly conductive CF.

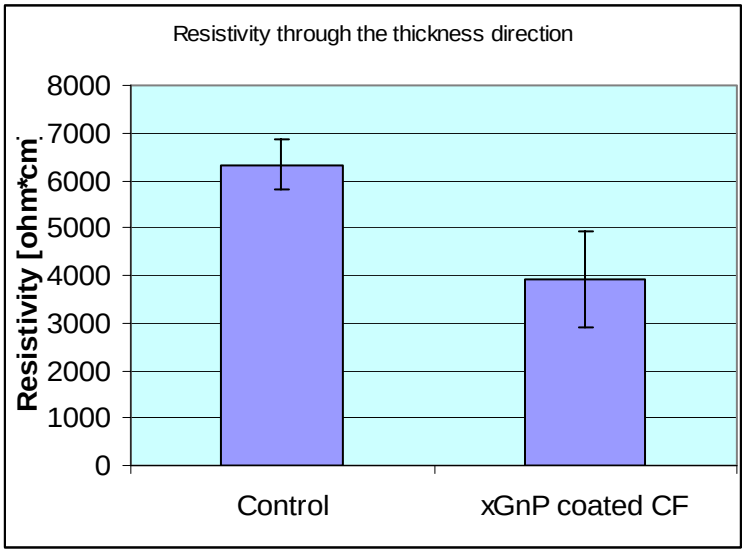

Figure 9. Resistivity in Through The Thickness Direction of Composite Samples

3.5 Finite Element Method

To evaluate the local stress fields, two models of composite systems were used. In the first model, a filler was located perpendicular to the substrate (Model 1). In the other model, a filler was located parallel to the substrate (Model 2). **Figure 10** shows the effective stress in the model 1 composite. In this case, the stress concentration increased with increasing load in both the X and Y directions. This means that the presence of the filler could initiate cracking or plastic failure leadingto a decreased strength of the system. This result implies that if a platelet shaped filler was oreinted perpendicular to the CF, the stress concentration increases and the strength of both the interphase and the whole composite system would decrease. On the other hand, the effective stress in the model 2 composite decreased. **(Figure 11)** This implies that the presence of the filler could improve the strength of the interphase and the whole system by reducing the stress concentration of the system. These results suggest that the morphology of the xGnP®-1 is a very important factor.

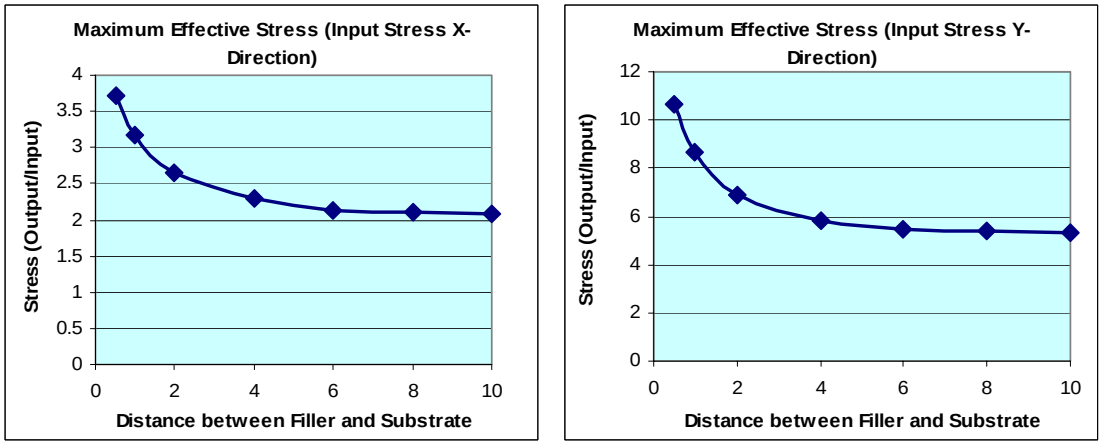

Figure 10. Effective Stress: Filler Perpendicular to Substrate

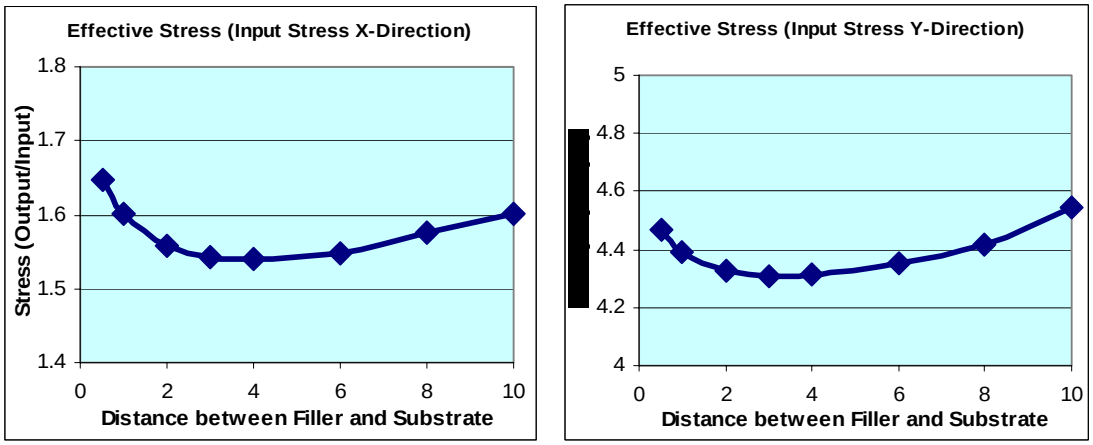

Figure 11. Effective Stress: Filler Parallel to Substrate

4. Conclusion

A continuous process was used to coat (size) carbon fibers with exfoliated graphite nanoplatelets (xGnP®-1, average diameter = 1um, average thickness = 10nm). The resulting CF were coated with a high concentration of xGnP®-1 graphite nanoplatelets on their surface parallel oriented parallel to the CF surface. The coating improved the interfacial shear strength due to improved mechanical properties of the interphase region. The unidirectionally aligned xGnP®-1 coated CF/epoxy composite showed improved short beam strength and flexural properties in 90 degree (transverse direction). A FEM analysis implied that coating CF with platelet shaped fillers can reduce the stress concentration if these platelets are located in the interphase parallel to the CF surface. This can be the mechanism of the property improvement in this system. The xGnP®-1 graphite nanoplatelets provided a percolated path for electrical conductivity perpendicular to the CF direction resulting in increases in electrical conductivity through the thickness direction.

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