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Technical Notes

Graphite Nanoplatelets Interlayered Carbon/Epoxy Composites

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I. Introduction

PROPERTY enhancement of a polymer by incorporating nanoparticles such as carbon nanotubes, nanoclays, and graphite nanoplatelets into the polymer is an active research area. Among these nanoparticles, nanoclays and graphite nanoplatelets are layered materials with platelike shapes. Graphite nanoplatelets (GNPs) have high modulus, high strength, and good electrical conductivity of graphite at much lower material cost than carbon nanotubes. This makes GNP an attractive nanoreinforcement material. Several studies have shown that the incorporation of GNPs into a polymer can improve both mechanical and electrical properties [1–5].

The mechanical property improvement of nanocomposites critically depends on the degree of dispersion and the interfacial adhesion. Well-dispersed platelets in the polymer matrix can significantly improve the load transfer efficiency in nanocomposites [6]. Stress concentration can be reduced by a high degree of exfoliation [7]. A good interfacial adhesion is critical to improving the mechanical properties. Without good interfacial adhesion through a proper surface treatment of graphite nanoplatelets, GNPs are just stress raisers, not load carriers. Surface treatment of graphite facilitates −COOH and/or −OH functional groups on the graphite sheets from chemical oxidation [8,9]. GNPs can deflect cracks only if the interface between GNPs and the matrix is strong [10].

Electrical properties might not be sensitive to the size and exfoliation of GNPs as much as mechanical properties. For example, less exfoliated GNPs yielded better conducting composites than highly exfoliated GNPs [4]. The surface treatment does not appear to have any significant effect on the electrical conductivity [5].

In the case of fiber composites, nanoreinforcements have less visible effect on mechanical property improvement, as their overall structural performance is mostly governed by fibers [11,12]. Needless to say, the nanoreinforcement effect will manifest itself in matrix-controlled properties. The in-plane shear and the compressive strength of carbon fiber/epoxy composites with graphite nanoplatelets were increased by 11 and 16%, respectively [13]. Especially when carbon nanotubes (CNTs) were directly grown on the fibers of a SiC fabric composite, the mode I interlaminar fracture toughness increased about 350% [14].

So far, the most effective way of improving interlaminar properties of fiber composites is to align CNTs along the thickness direction of the laminate [14,15]. However, growing CNTs normally on the reinforcing fibers is not an easy process to implement or a costly method in material and processing. The objective of the present study is to develop a scalable and effective manufacturing method to incorporate GNPs and to improve the mechanical properties and the electrical conductivities of graphite fiber composites. Micrographic studies are also conducted to identify microstructures and reinforcement mechanisms.

This Note consists of two parts. For the first part, laminates with VRM34 epoxy resin were processed to show the effect of different GNP contents (1 and 2 vol%) on tensile and in-plane shear properties and electrical conductivities. Unfortunately, no reference laminate with VRM34 resin was available. For the second part, laminates with Epon862 epoxy resin were processed to show the effect of surface treatment of GNPs on in-plane shear properties and electrical conductivities.

II. Experimental Procedure

A. Materials

AS4 plain-weave graphite fabric was used for the fiber reinforcement. Two different resin systems were used: VRM34 epoxy resin and Epon862 epoxy resin with Epikure W curing agent in a weight ratio of 100/26.5.

Figure 1 shows a scanning electron microscopy (SEM) micrograph of GNPs (Asbury 3775) used in the present study. They are thinner than 100 nm and about 6 μm long in the plane. They have been preexfoliated by rapid heating in a furnace at 600°C after acid intercalation [16]. They were used as received for AS4/VRM34 laminates and after nitric acid treatment to improve the interfacial adhesion to the epoxy resin by introducing carboxylic functional groups for AS4/Epon862 laminates. For the surface treatment, GNPs were immersed in a 67% nitric acid (HNO_3) solution and heated to 100°C for 30 min with a 200:1 volume ratio of nitric acid to graphite [5].

B. Fabrication Process

An obvious method to incorporate nanoparticles in fiber composites is to add the nanoparticles to the matrix resin directly. However, in the present study, GNPs were deposited on graphite fabric surfaces first to avoid screening of GNPs during resin infusion process.

GNPs were deposited on an AS4 fabric using an electrostatic spraying method. The electrostatic spraying method is a quick and efficient way of depositing conducting particles such as GNPs on conducting electrodes such as graphite fabric.

A schematic of the electrostatic spraying process used is shown in Fig. 2. The use of no pressurized air and low spraying speed makes it possible to spray nanoplatelets with more precision. The electrostatic spraying setup consists of four main parts: a spraying chamber, a syringe with a needle, a syringe pump, and a high-voltage generator. A syringe pump was used to push out the solution at a constant flow rate. A high-voltage generator was used to generate 20 kV over a distance of 10 cm.

The detailed process steps are as follows:

1) Measure the weight of GNPs and mix them in isopropyl alcohol. The optimal ratio for smooth spray is 17 ml of isopropyl alcohol per 1 g of GNPs.

2) Use an ultrasonic horn (Vibra Cell from Sonic and Materials) at 100 W for 15 min to disperse GNPs and a shear mixer (T8 ULTRA-TURRAX® form IKA) at 13,500 rpm for 15 min for further

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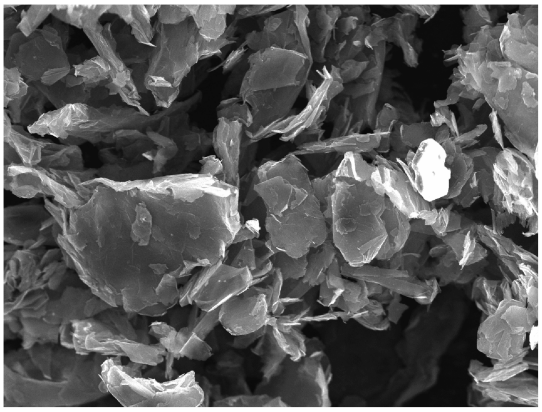

Fig. 1 Graphite nanoplatelets used.

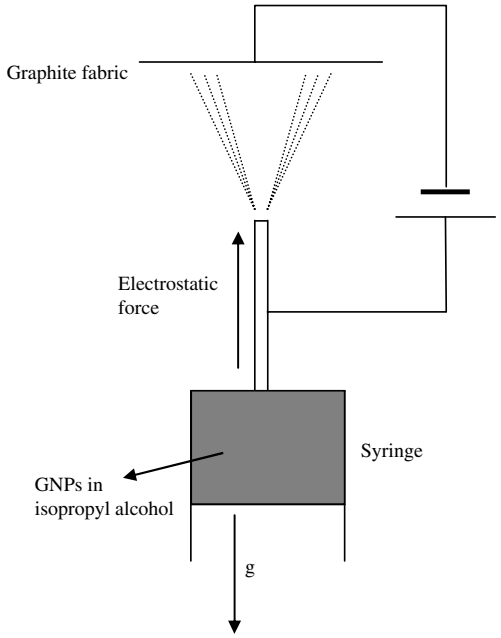

Fig. 2 Schematic of electrostatic spraying setup.

dispersion. While doing so, 1 ml of resin per 1 g of GNPs is added to ensure GNPs' adhesion to the fabric surfaces.

3) Spray the solution on the fabric using the electrostatic spraying setup shown in Fig. 2. The syringe is moved along the path shown in Fig. 3 to cover the entire area of AS4 graphite fabric. Figure 4 is a SEM micrograph that shows GNPs sprayed on the fabric for just a few seconds to observe individual GNPs.

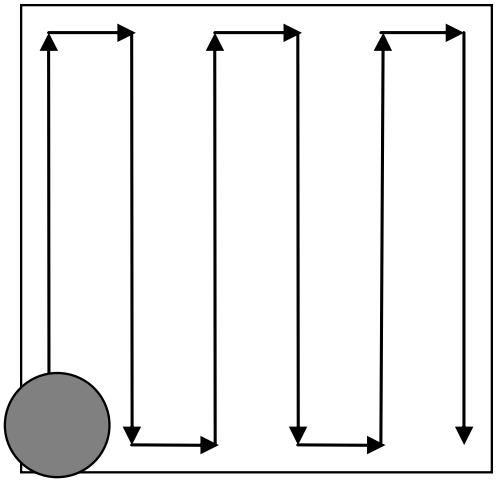

Fig. 3 Syringe path to cover graphite fabric.

4) Dry the fabric with GNPs in the oven at 100°C for 30 min to evaporate isopropyl alcohol.

The GNP-deposited AS4 fabric layers were processed into laminates using a vacuum-assisted resin transfer molding at The Boeing Company and the University of California, Los Angeles, with VRM34 and Epon862 resin, respectively. The fiber volume fraction of composite panels was estimated by using a matrix digestion method in accordance with ASTM D3171 [17] (Table 1).

The loading of GNPs is expressed in a volume ratio to the matrix volume. Volume percent of GNPs in a laminate can be calculated from known densities of GNPs and the matrices, which are 2.3 and 1.2 g/cm^3, respectively. The amount of GNPs sprayed were calculated assuming 55% fiber volume fraction for AS4/VRM34 and 50% for AS4/Epon862. The actual volume percent of GNPs in each laminate is slightly different from the intended loading, due to the difference between the targeted fiber volume fraction and the actual fiber volume fraction of the laminate. Because it is almost impossible to spray only within the fabric sheet, the final loadings of GNPs would be slightly less than the GNP loadings in Table 1.

C. Mechanical and Electrical Testing

The tensile and in-plane shear properties were measured in accordance with ASTM D3039 [18] and ASTM D3518 [19], respectively. All mechanical tests were performed using a mechanical test machine (Instron 4483) under a constant crosshead speed, 1.27 mm/ min. At least three samples were tested for each case.

Both in-plane and out-of-plane electrical conductivities were measured on five specimens for each layup type using an LCR meter (Agilent 4263B). The surfaces of the specimens were polished to expose conducting fibers and then painted silver for better contact

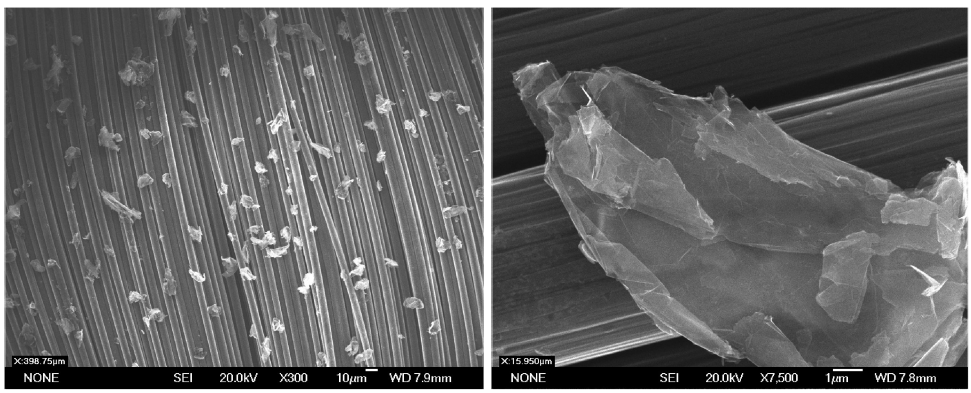

Fig. 4 GNPs sprayed on graphite fabric surface at ×300 (left) and ×7500 (right).

Table 1 Fiber volume fraction of laminates

Materials	AS4/VRM34		AS4/Epon862		
GNP vol%, treatment	1 vol% untreated	2 vol% untreated	0 vol%	1 vol% untreated	1 vol% nitric-acid-treated
Fiber volume fraction (%)	57.5	56.7	47.5	47.0	42.4
Actual GNP loading (vol%)	1.06	2.08	N/A	0.94	0.87

between the surface and electrodes. For the out-of-plane measurement, copper plates were attached on the silver-painted surfaces of a sample and a vise was used for good contact between the copper plates and the sample surfaces. For the in-plane conductivity, the four-point method was used. Figure 5 shows a schematic of the electrical conductivity measurement.

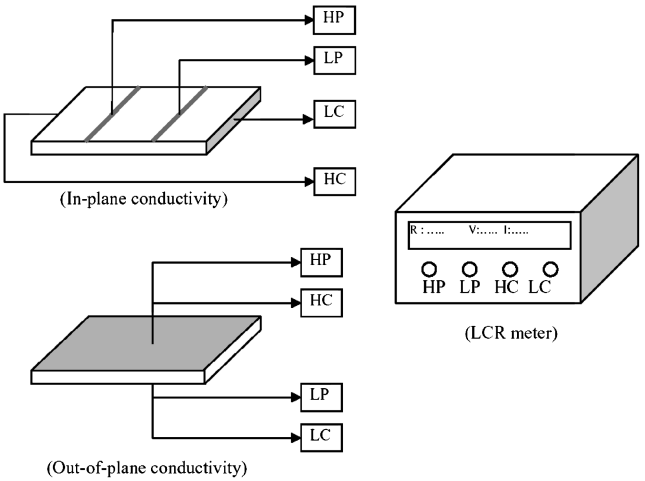

Fig. 5 Schematic of electrical conductivity measurement.

III. Results

A. Microstructure

Even at 1 vol% GNPs, the matrix is covered with GNPs (Fig. 6). Hence, from the planar view, it is not easy to see the difference between 1 and 2 vol% GNPs. However, from the cross-sectional view, more GNPs were observed in 2 vol% than in 1 vol% samples, as expected (Fig. 7). In Fig. 7, GNPs seem to be just gathered rather than agglomerated.

B. Mechanical Properties

The average and standard (in parenthesis) deviations of tensile and shear properties are summarized in Table 2. The results show that 2 vol% GNPs do not result in any improvement in mechanical properties compared with 1 vol% GNPs. On the contrary, specimens with 2 vol% GNPs have slightly lower strength. There could be several probable reasons for this. The key reason may be that interfacial bonding is poor, as GNPs were not surface-treated. Thus, GNPs might act as stress raisers rather than reinforcements. A higher GNP content can also lead to a higher chance of GNP agglomeration, and this can lead to more weak areas in the composite.

In light of the results of the AS4/VRM34 case showing the importance of good interfacial adhesion, AS4/Epon862 case was

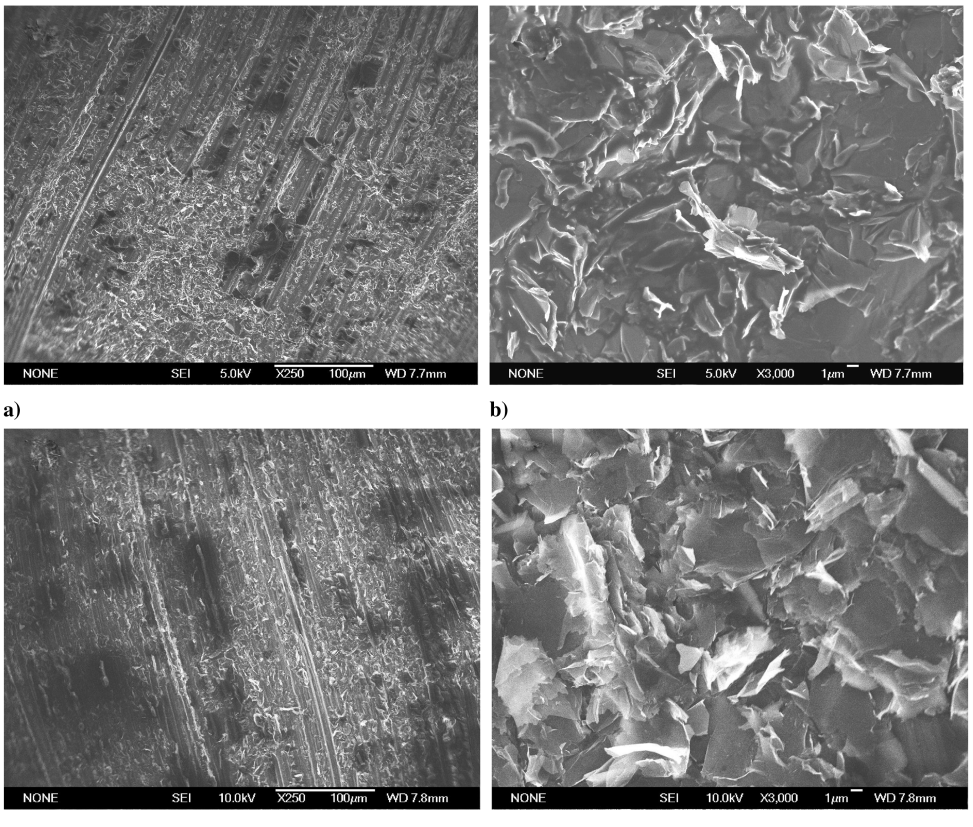

Fig. 6 GNPs on a delaminated layer of 1 vol% GNP sample: a) ×250, b) ×3000, and 2 vol% GNP sample, c) ×250, and d) ×3000 magnification.

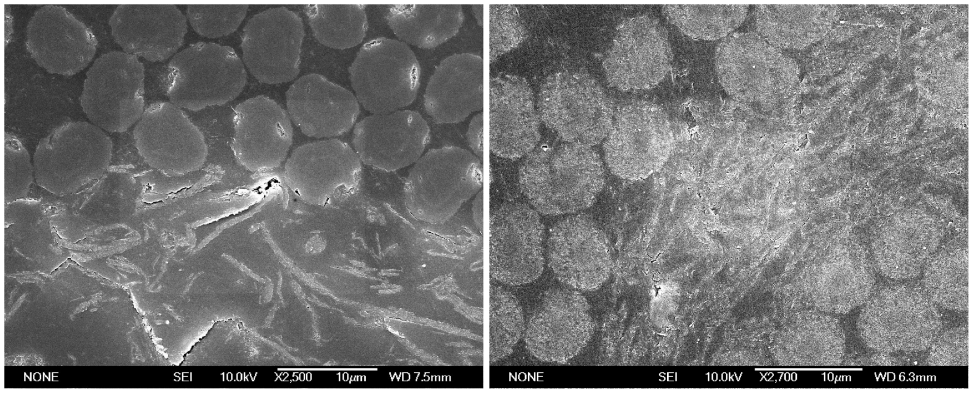

Fig. 7 SEM: Cross-sections of 1 vol% (left) and 2 vol% (right) of GNPs.

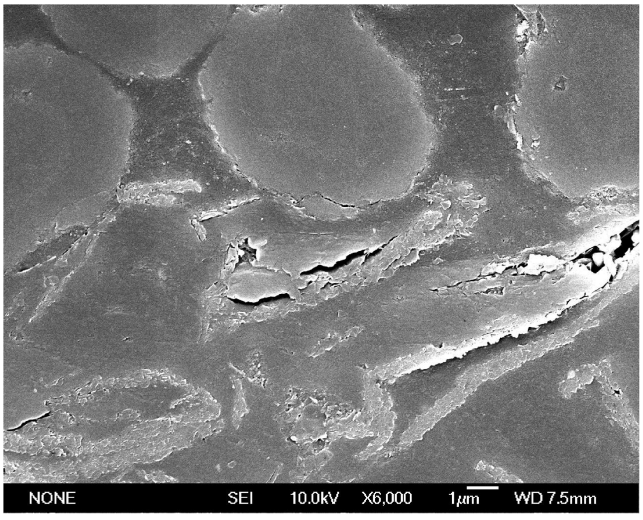

Fig. 8 Untreated GNP-epoxy interface showing poor bonding.

directed toward studying the effect of surface treatment of GNPs on the matrix-dominated in-plane shear properties. Table 2 shows that the shear strength of composites increases significantly after GNPs are acid-treated, although shear modulus increases regardless of the surface treatment. It is noted that untreated GNPs rather reduce the composite strength. This result shows that the matrix-controlled properties such as in-plane shear properties can be improved by a proper surface treatment of GNPs.

Figures 8 and 9 show the interface between the resin and untreated GNPs and nitric-acid-treated GNPs, respectively. Nitric-acid-treated GNPs are expected to have stronger bonding to the epoxy resin system, and Fig. 9 may show this aspect.

C. Electrical Conductivities

The measured electrical conductivities are summarized in Table 3 for (0/90) laminates.

The in-plane electrical conductivity of woven fabric composites (0/90) may be estimated from the assumption of electrical current flowing in 0 deg fibers only. Using 650 S/cm for the conductivity of AS4 fiber and 29 vol% for the percentage of 0 deg fibers, one obtains 195 S/cm for the conductivity of the (0/90) laminate. This rough estimate is quite close to the measured values.

There was no dramatic increase in the electrical conductivities using higher 2 vol% GNP compared with 1 vol% GNP. This may be attributed to the fact that the percolation threshold of GNP dispersion in polymeric matrices is usually less than 1 vol% [4,22–24]. Because the out-of-plane electrical conductivity should show the effect of GNP better than the in-plane electrical conductivity, which must be controlled by highly conductive graphite fibers, only the out-of-plane electrical conductivity was measured for AS4/Epon862 laminates.

The measured out-of-plane electrical conductivities of AS4/Epon862 laminates are summarized in Table 3. The out-of-plane electrical conductivity of the laminate with 1 vol% untreated GNPs is improved by more than 200% compared with that of the laminate without GNPs. The presence of GNPs between composite layers helps electrical current flow better in the out-of-plane direction (Fig. 7). At 1 vol% GNPs, there is a large difference in the out-of-plane electrical conductivity between AS4/VRM34 and AS4/Epon862 laminates. The lower conductivity of AS4/Epon862 laminate is believed to be the result of poor compaction, as evidenced by a lower fiber volume fraction. This conclusion is not surprising in view of a large difference in conductivity between the fibers and matrix. The out-of-plane electrical conductivity of graphite fiber composites depends on the number of contact points between adjacent layers, which is controlled by the distance between the layers (i.e., compaction of laminates [25]). The large increase in the electrical conductivity of GNP sample cannot be attributed to

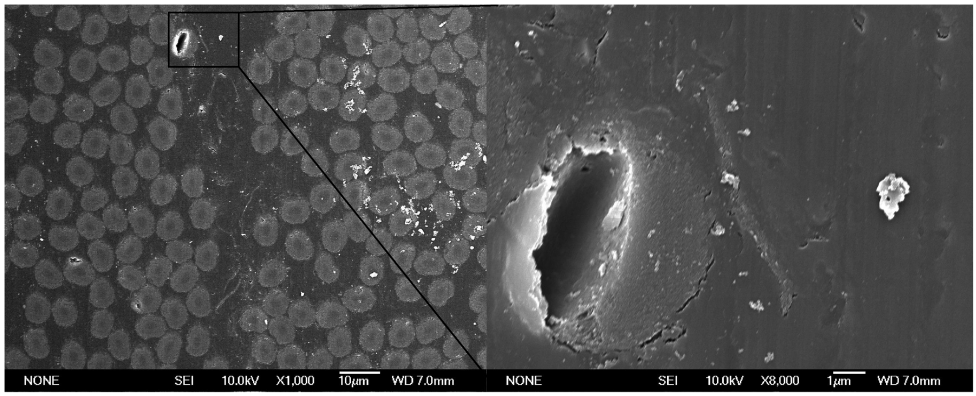

Fig. 9 Nitric-acid-treated GNP-epoxy interface (right) showing good bonding. The cavity is the result of a missing fiber splinter.

Table 2 Tensile and unidirectional shear properties of laminates with GNPs

	Tensile		In-plane shear	
GNP loading, vol%	Modulus, GPa	Strength, MPa	Modulus, GPa	Strength, MPa
		AS4/VRM34		
0	63.4 [a]	807 [a]	4.05 [b]	100 [b]
1	64.2 (0.873)	632 (42.8)	5.41 (0.288)	103 (0.96)
2	65.8 (2.55)	591 (19.2)	5.48 (0.299)	96.2 (1.31)
		AS4/Epon862		
0	——	——	2.88 (0.064)	88.6 (2.67)
1	——	——	3.11 (0.346)	75.7 (2.23)
1, treated	——	——	3.22 (0.090)	98.3 (1.58)

[a]Data for AS4-3501-06 (plain weave) from literature [20,21]
[b]Laminates with VRM34 resin show higher in-plane shear moduli due to higher shear modulus (4.4 GPa) of VRM34 compared with that of Epon862 (1.2 GPa) and higher fiber volume fractions.

Table 3 Electrical conductivities of 0/90 laminates

GNP loading, vol%	Out-of-plane E/C, S/cm	In-plane E/C, S/cm	Fiber volume fraction
	AS4/VRM34		
0	——	——	——
1	0.152 (0.0049)	155 (12.3)	57.5
2	0.155 (0.0098)	156 (17.6)	56.7
	AS4/Epon862		
0	0.0189 (0.00327)	——	47.5
1	0.0574 (0.00305)	——	47.0
1, treated	0.0390 (0.00233)	——	42.4

the fiber volume fraction effect, because the fiber volume fractions of both 0 and 1 vol% samples are very close: 47.5 and 47.0%, respectively.

IV. Conclusions

A manufacturing process was developed to incorporate graphite nanoplatelets (GNPs) into graphite fiber composites. The process consists of the following two sequential steps: deposition of GNPs onto graphite fabric followed by resin transfer molding. Graphite nanoplatelets were deposited on graphite fabric layers using an electrostatic spraying method. These fabric layers were then stacked and impregnated with an epoxy resin using a resin transfer molding process. Two types of GNPs were used: as-received and nitric-acid-treated. As-received GNPs were deleterious to composite properties, whereas acid-treated GNPs were beneficial. With just 1 vol% addition of treated GNPs, the in-plane shear strength increased 11% over the corresponding strength without GNPs. Without surface treatment, GNPs tend to rather degrade these properties. However, electrical conductivity was not increased by the surface treatment: it is sensitive to the fiber volume fraction of laminates at the same GNP content. The out-of-plane electrical conductivity of 1 vol% GNP samples showed more than 200% increase compared with control samples.

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