

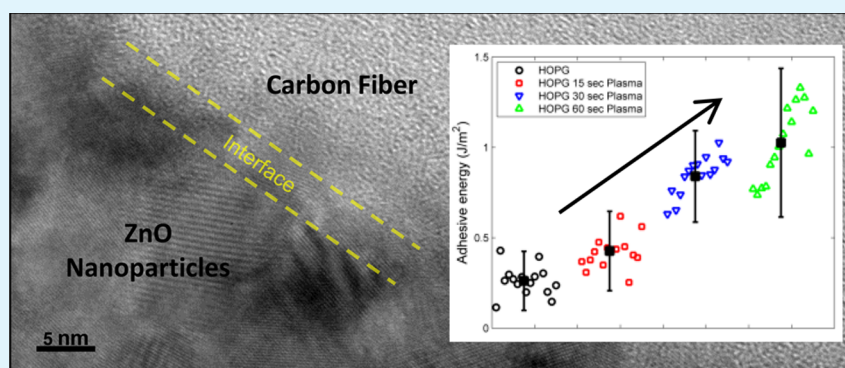
Adhesive Force Measurement between HOPG and Zinc Oxide as an Indicator for Interfacial Bonding of Carbon Fiber Composites

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ABSTRACT: Vertically aligned zinc oxide (ZnO) nanowires have recently been utilized as an interphase to increase the interfacial strength of carbon fiber composites. It was shown that the interaction between the carbon fiber and the ZnO nanowires was a critical parameter in adhesion; however, fiber based testing techniques are dominated by local defects and cannot be used to effectively study the bonding interaction directly. Here, the strength of the interface between ZnO and graphitic carbon is directly measured with atomic force microscopy (AFM) using oxygen plasma treated highly oriented pyrolytic graphite (HOPG) and an AFM tip coated with ZnO nanoparticles. X-ray photoelectron spectroscopy analysis is used to compare the surface chemistry of HOPG and carbon fiber and to quantify the presence of various oxygen functional groups. An indirect measurement of the interfacial strength is then performed through single fiber fragmentation testing (SFF) on functionalized carbon fibers coated with ZnO nanowires to validate the AFM measurements. The SFF and AFM methods showed the same correlation, demonstrating the capacity of the AFM method to study the interfacial properties in composite materials. Additionally, the chemical interactions between oxygen functional groups and the ionic structure of ZnO suggest that intermolecular forces at the interface are responsible for the strong interface.

KEYWORDS: ZnO nanowires, composite interfaces, atomic force microscopy, intermolecular interactions, oxygen functional groups

INTRODUCTION

With current advances in the manipulation of nanoscale structures, it has become possible to create materials that utilize the unique properties observed at nanoscale dimensions and improve the overall bulk properties of a material system. For example, modifying the morphology of nanowires has been used to improve the energy density of high power capacitors^{1,2} and batteries^{3–5} as well as a method to tailor optical and mechanical properties of composites.^{6–10} Recently, zinc oxide (ZnO) nanowires were used in fiber reinforced composites as an interfacial stress gradient between carbon fiber and polymer matrix leading to an interfacial shear strength up to 3.8 times greater than a neat epoxy interface.^{11–14} Upon failure of these composites, it was observed that the ZnO nanowires debonded from the fiber while maintaining their bond with the matrix.¹³ This failure behavior was expected because the morphology of the ZnO nanowires acts as a mechanical interlocking phase and

creates a large contact area between ZnO and epoxy that is more than 2 orders of magnitude greater than the contact area between ZnO and the carbon fiber surface. These observations suggest that a higher adhesive energy exists between ZnO and the carbon fiber surface compared to the adhesive energy between carbon fiber and epoxy.

Further research showed that the strength of the ZnO and carbon fiber interface can be controlled by changing the chemical composition of the fiber's surface. Using single fiber fragmentation testing, it was found that the interfacial shear strength increased with an increase in oxygen surface coverage of the carbon fiber.¹⁵ As the results of the SFF tests suggest, the increasing oxygen functional group coverage on the carbon

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fiber generates stronger intermolecular interactions with the ZnO nanowires, which ultimately leads to a higher interfacial bond strength, adhesive energy, and consequently higher interfacial shear strength.¹⁶ However, because SFF is a composite testing method that is dependent on the material system and can be influenced by several disputed failure modes,^{17–20} additional testing methods are required to measure directly the strength of the interface and determine the effects of oxygen functional groups.

To directly study the behavior of this interface in more detail, the adhesive force between ZnO and oxygen plasma treated highly oriented pyrolytic graphite (HOPG) was measured through atomic force microscopy (AFM). AFM has the sensitivity to measure forces as small as piconewtons and has the lateral resolution capabilities to measure the interactions of individual surface atoms with certain systems.²¹ Previous research has shown that adhesion force measurements can be applied to a myriad of interaction forces, such as chemical and physical bonding, van der Waals, electrostatic, and capillary,^{22–24} but are also very sensitive to surface morphology.^{25,26} With the sensitivity and resolution of the AFM, adhesion force measurements can be utilized to help further distinguish the intermolecular interactions at the ZnO and HOPG interface.

To show correlation between increasing adhesion force of the interface and the interfacial strength of carbon fiber composites, carbon fibers were functionalized by the oxygen plasma, coated with ZnO nanowires, and tested by SFF. Oxygen plasma surface treatments have been extensively used to functionalize carbon fibers and have been shown to increase the fiber surface energy and wettability,²⁷ as well as the interfacial strength of carbon fiber composites.^{28–30} Although an increase in surface energy is advantageous for carbon fiber and epoxy interactions, its effect on the interaction with ZnO is still unknown. Previous work on plasma treated carbon fibers has also shown that functionalization with either oxygen or ozone can create a wide array of oxygen functional groups on the surface.^{31–33} By utilizing this process and its ability to chemically functionalize the fiber surface, the interaction between ZnO and oxygen functional groups may become more evident through subsequent testing.

Here, the combination of two testing methods, adhesion force measurements using AFM and SFF, will be applied to determine the effect of oxygen functional groups at the interface between graphitic carbon and ZnO. Through oxygen plasma surface treatments, both HOPG and carbon fibers surfaces will be oxidized without hindering the mechanical properties. AFM will provide a means to measure sensitive adhesion forces at the interface, whereas SFF will show the applicability of that data to continuous carbon fiber composites with ZnO nanowire interphases. The collective work presented here will thereby help elucidate the strong molecular interactions that occur between graphitic carbon and ZnO and provide a direct means to measure the interfacial bond strength of composites.

RESULTS AND DISCUSSION

AFM adhesion force measurements are useful for the study of intermolecular interactions between dissimilar materials because the ability of the AFM tip to be functionalized. Functionalized tips allow for high resolution interaction measurements at the atomic level between an infinite combination of dissimilar materials.^{24,34,35} In these measurements, the intermolecular forces and adhesive energy can be

calculated by the known stiffness of the AFM's cantilever beam, the contact area of the tip, and the resultant force displacement curve of the test.³⁶

Here, adhesion force measurements were performed between two separately functionalized surfaces. First, HOPG is functionalized with oxygen plasma, and second, the AFM tip is functionalized by a coating of ZnO nanoparticles. This nanoparticle coating is representative of the interface created when ZnO nanowires are grown on carbon fiber surfaces because the same colloidal solution is deposited on the fiber and is used as a nucleation site for subsequent aligned nanowire growth.¹¹ By functionalizing the tip with the ZnO film, the interface created for the measurement of adhesive forces can accurately mimic the interface found in carbon fiber composites with ZnO nanowires. To validate the existence of the ZnO nanoparticle interface, Figure 1 shows a high resolution transmission electron microscopy (HRTEM) image of a carbon fiber surface coated with ZnO nanowires synthesized using a nanoparticle seed layer. As shown in Figure 1, the fiber is in direct contact with the nanoparticles of approximately 10 nm in diameter rather than nanowires that grow out of the nucleated sites.

Although AFM adhesion force measurements may be performed on carbon fibers, the carbon fiber surface often exhibits striations from the spinning and drawing process as well as curvature, both of which would lead to uncertainty in the contact area and the final measurements. Therefore, HOPG (grade ZYH, NT-MDT Co., Moscow, Russia) was used to replicate the carbon fiber surface because of the similar aromatic and graphitic structure, despite their difference in crystallinity. HOPG was then functionalized by oxygen plasma such that a range of oxygen groups (i.e., C—OH, C=O, C—O—C, COOH, etc.) would populate the HOPG surface to better resemble the surface chemistry of carbon fibers.^{37,38} Figure 2a shows the high resolution C 1s spectrum that demonstrates the increasing oxygen content and the change of chemical composition through covalent bonding between carbon and oxygen atoms. Figure 2c shows an incremental increase in oxygen functional group surface coverage as the plasma treatment time is increased. This increase in surface coverage and broadening of the C 1s peak proves that oxygen functional groups are being covalently bonded to the surface, instead of adsorbed oxygen or other radical species.

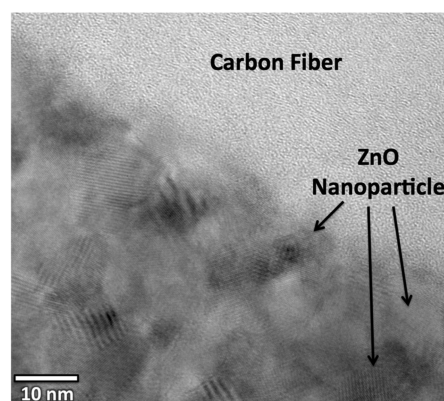


Figure 1. High resolution transmission electron microscopy (HRTEM) image of carbon fiber surface coated with ZnO nanoparticle of approximately 10 nm in diameter.

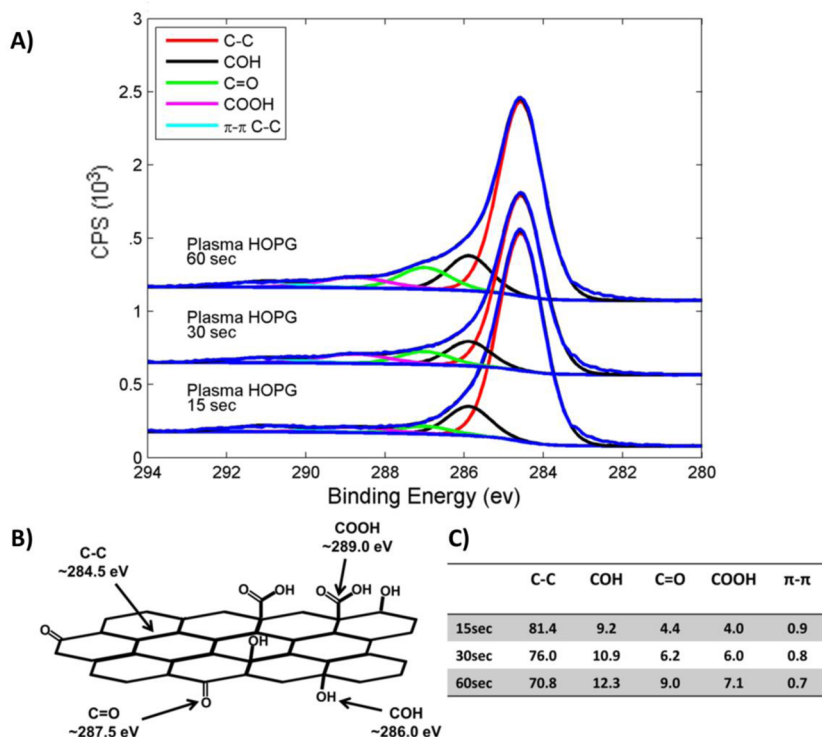


Figure 2. (A) X-ray photoelectric spectroscopy of plasma treated HOPG showing the creation of functional groups. (B) Schematic of the carbon fiber surface covered with functional groups and their respective binding energies. (C) Surface coverage percentages.

After the functionalization procedure, the HOPG samples were tested through AFM adhesion force measurements with the results plotted in Figure 3. Each data point shown represents a single measurement of the adhesive energy with 15 points tested for each case. As observed in Figure 3, when the plasma treatment time increases, the adhesive energy also increases. This trend shows that ZnO has favorable intermolecular interactions with oxygen functional groups, such as hydroxyls, carbonyls, and carboxylic acid. Thus, it can be concluded that the degree of oxygen functional group coverage on the HOPG surface promotes the adhesion of HOPG to ZnO.

To further demonstrate the effect of oxygen functional groups at the interface between ZnO and graphitic carbon,

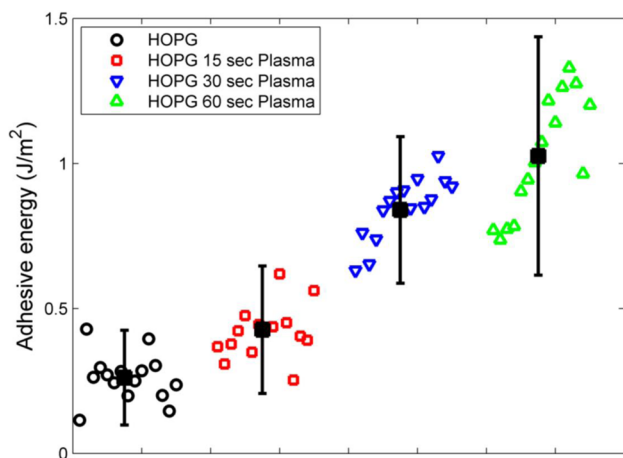


Figure 3. Adhesive energy between functionalized HOPG and ZnO-coated tip measured through AFM adhesion force testing.

carbon fibers were functionalized by oxygen plasma and tested in single fiber composites. X-ray photoelectron spectroscopy (XPS) was first used to characterize the surface chemistry of the functionalized carbon fibers and verify its similarity to functionalized HOPG. Figure 4 shows the C 1s spectrum for untreated IM8 carbon fibers and fibers treated with oxygen plasma for 60 and 120 s. Each C 1s peak was deconvoluted into 5 peaks representative of the different carbon states present. Similarly to the HOPG samples, the data shows an increase in oxygen functional groups as the plasma functionalization duration increases. Additionally, the inset table shows that the

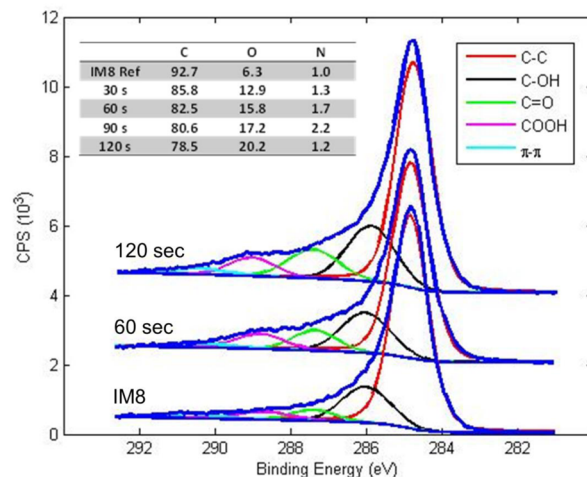


Figure 4. X-ray photoelectric spectroscopy of IM8 carbon fibers treated with oxygen plasma for various durations. Inset table shows an increase in relative oxygen coverage with increasing plasma treatment time.

relative oxygen surface coverage in weight percent incrementally increases when the oxygen plasma surface treatment time is varied from 30 to 120 s. Based on the known surface structures and the resultant XPS data of both HOPG and carbon fiber, the oxygen plasma treatment effectively functionalized the carbon fiber surface creating a similar surface chemistry to HOPG.

After XPS analysis, plasma treated carbon fibers were coated with ZnO nanowires and used to create composite samples for single fiber fragmentation testing and interface characterization. Previous work has demonstrated a clear relationship between the morphology of the nanowires and the interface strength between the matrix and the fiber.¹⁴ Thus, the fibers used in this study retained the same growth conditions throughout in order to maintain a consistent morphology. Each set of functionalized fibers underwent ZnO nanowire synthesis at the same time; therefore, making the relative results not dependent on the morphology of the nanowires but only on the surface treatment of the carbon fibers. After growth, the fibers were inspected by scanning electron microscopy (SEM) to ensure uniform nanowire coverage; a typical image is shown in Figure 5.

Single fiber fragmentation testing was performed on a custom-made fixture under an optical microscope with illumination of both polarized and white light. Having both light sources helped distinguish propagated cracks in the carbon fiber and their resultant birefringence patterns from surface stresses and impurities. In the fragmentation test, strain is applied to the matrix at a constant rate, and load is transferred to the fiber through the interface. Because the fiber has a large surface area and a small cross sectional area, stress will transfer to the fiber and the fiber will fail forming two segments. Upon additional strain, this process continues until the surface area is too small to transfer sufficient load to further fracture the fiber. Once the fiber reaches saturation and no more cracks are formed under increased strain, the interfacial shear strength is calculated with the following equation:

$$\tau = \frac{\sigma_f d}{2l_c} \quad (1)$$

where σ_f is the tensile strength of the fiber at the critical length, d is the diameter of the fiber, and l_c is the critical length of the fiber. The tensile strength at the critical length is found using a Weibull distribution^{39,40} whereas the critical length is estimated through the following equation:

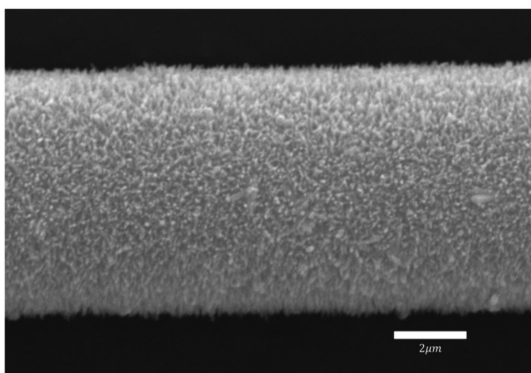


Figure 5. ZnO nanowires grown on IM8 carbon fiber.

$$l_c = \frac{4}{3} \bar{l} \quad (2)$$

where \bar{l} is the average segment length found by dividing the gauge length of the sample by the number of cracks counted at saturation.

The interfacial strength of three ZnO nanowire cases was tested: as-received fibers, 30 s plasma treated fibers, and 60 s plasma treated fibers. The resultant data is shown in Figure 6. The figure clearly shows that the interfacial strength increases with increasing plasma treatment time and follows a trend similar to the AFM measurements. This result shows that oxygen functional groups are a significant contributor to the adhesion of ZnO to the surface of aromatic carbon and that the difference in substrate crystallinity is much less important. Because of the similarity of the results between the two tests, the potential application of the adhesion force measurements for direct composite interface characterization has been discovered.

Following single fiber fragmentation testing of the carbon fibers, tensile tests were performed to quantify the tensile strength and verify that the plasma oxidation process did not affect the fibers' mechanical properties and the subsequent SFF data. ZnO nanowires were not grown on these fibers prior testing because previous research has shown that the growth process alone does not affect the mechanical properties.¹⁴ Figure 7 shows the respective tensile test data and verifies that the functionalization method had negligible effects on the fiber's tensile strength for treatment times of 30, 60, and 90 s compared to untreated fibers. Because the composite interfacial shear strength is dependent on the fiber tensile strength, it can also be concluded that the observed increase was not caused by a decrease in tensile strength, but instead by some induced interaction at the interface.

One of the major advantages of using adhesion force measurements is the capability to directly test and resolve adhesive energies as small as femtojoules at the interface. Because the magnitude of the observed adhesive force, one may suggest that interaction forces that exceed van der Waals, such as electrostatic and induced forces, also exist between the surface functional groups and the ZnO lattice.⁴¹ This speculation would suggest that chelation forms between ZnO and hydroxyl, carbonyl, and carboxylic acid functional groups,

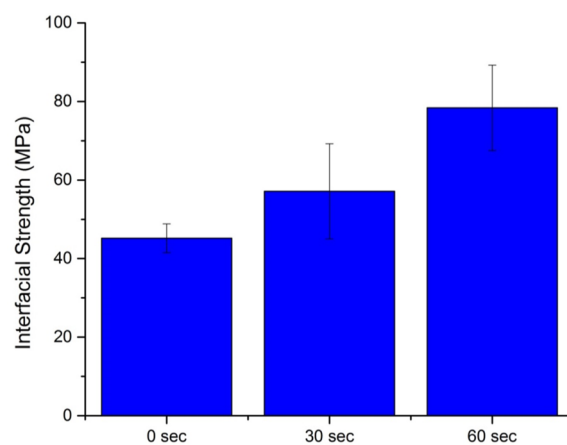


Figure 6. Interfacial strength of carbon fiber composites with ZnO nanowire interphase post oxygen plasma treatment of various durations.

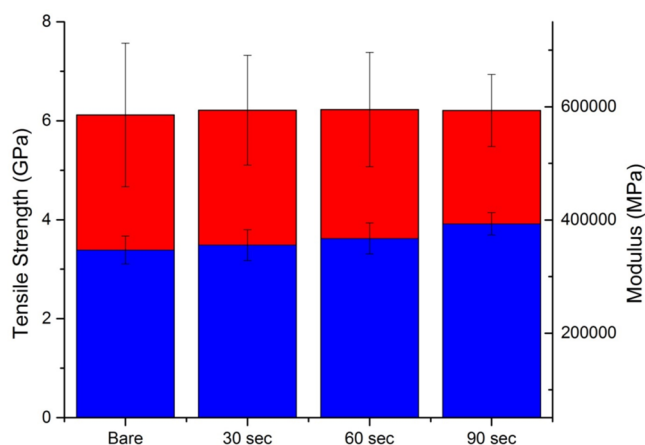


Figure 7. Tensile tests of IM8 carbon fibers treated with oxygen plasma. Red bars indicate tensile strength and blue bars indicate modulus.

causing a major increase in the adhesive force between carbon and ZnO. This chelation to the ZnO lattice could arise as a stabilization mechanism because of the ZnO crystal structure. ZnO is an ionic material with a wurtzite structure, where interatomic bonding is primarily governed by electrostatic interactions between zinc and oxygen ions. The structure of ZnO consists of alternating planes of coordinated O^{2-} and Zn^{2+} ions along the c -axis that produce a dipole moment along the same axis and give rise to two high-energy, unstable polar surfaces: (0001) and (000 $\bar{1}$). Because of these polar surfaces, the wurtzite structure is Tasker type III⁴² and generates an electrostatic field perpendicular to the polar planes. These types of unstable surfaces tend to find some mechanism to lower the high surface energy, whether that is through surface deformation, charge transfer, or molecular adsorption depends on the facet and its surroundings.⁴³ In addition to the (000 $\bar{1}$) plane, the wurtzite structure is also terminated by the nonpolar (10 $\bar{1}0$) plane⁴⁴ that consists of Zn–O dimer rows where the oxygen and zinc ions are tetrahedrally coordinated. The (10 $\bar{1}0$) plane is tilted with oxygen atoms that are raised out of the surface, thus giving the possibility of hydrogen bonding interactions with surrounding molecules.⁴⁵ Here, it is proposed that both the polar and nonpolar surfaces interact with surrounding molecules making them chemically active and are the cause for the strong intermolecular interactions with the functional groups present on the HOPG surface.⁴⁶

Furthermore, the functional groups present on the HOPG surface can also form chemical interactions because of their chemical structure. Hydroxyl groups are known for hydrogen bonding and thus, can form hydrogen bonds with exposed surfaces of the ZnO lattice, such as the (10 $\bar{1}0$) plane.⁴⁵ Carboxylic acid may too bond to exposed ZnO surfaces; however, it has a fixed bond angle of 120° between the carbon and oxygen atoms, thereby making it necessary to match the interaction of the hydrogen and oxygen atoms to a specific planar structure. Previous research has shown that this planar structure may interact with other planar structures and form a network of hydrogen bonds.⁴⁷ However, because ZnO does not contain any planar surfaces, it is possible that carboxylic acid is inactive and does not contribute toward increasing the adhesive energy. Previous research on ZnO carbon fiber composites also showed that the relationship between the surface content of carboxylic acid groups and the interfacial strength with ZnO

had little correlation.¹³ Lastly, it has been reported that the orientation of carbonyls can change depending on local bonds with other molecules.⁴⁸ With the flexibility to change orientation, carbonyls could facilitate van der Waals interactions with exposed ZnO ions and help augment to the high adhesive forces.

Even though there are nonbonded, van der Waals interactions at the interface, the magnitude of the adhesive force results suggest that the intermolecular interaction is caused by long-range forces as well. These long-range forces may arise because of the static charge distribution of the molecules and Columbic interactions, but also by the distortion of a molecule in the presence of neighboring molecules or ions. As other researchers have observed,^{49,50} the magnitude of long-range forces can be significantly bigger than van der Waals forces, which typically have adhesive energies $<0.11 \text{ J/m}^2$.⁵¹ As the results of the adhesion force measurements show, the interaction obtained between ZnO and the functionalized HOPG has an adhesive energy much greater than this. Thus, ZnO has shown the potential capacity to reorient neighboring functional groups and induce long-range interactions as well. Because of these strong interactions, ZnO has been demonstrated to be an effective alternative interface material for fiber composites.

Lastly, this work has shown an experimental method novel to composite interfaces that directly quantifies the speculative intermolecular interactions between ionic ZnO and the functional groups present on graphitic carbon. These results were then demonstrated on carbon fiber composites and confirmed the observations of previous research that oxygen functional groups positively affect the ZnO–graphitic carbon interface.¹⁵ This adaptable testing methodology could be used to help elucidate intermolecular interactions of other type of materials and functional groups in future work and thus, help engineer better composite interfaces.

CONCLUSION

An oxygen plasma treatment was performed on HOPG and IM8 carbon fibers. The direct measurement of the adhesion force and the adhesive energy between ZnO and functionalized HOPG was performed through AFM adhesion force testing. The AFM tests confirmed that the various oxygen functional groups present on the surface of HOPG increase the adhesive energy of the interface. An indirect measurement of interfacial strength was also performed through SFF testing on functionalized carbon fibers and showed a correlated trend despite the acknowledged difference in the substrate's structure. Because of the magnitude of the adhesive energy, specific intermolecular interactions at the ZnO–graphitic carbon interface were speculated. The adhesion force measurements through AFM, along with complementary SFF testing, have shown the direct effect of oxygen functional groups at the ZnO–graphitic carbon interface and the capability to effectively study interfaces for future composites materials.

EXPERIMENTAL SECTION

Materials. Highly oriented pyrolytic graphite (ZYH quality, 3.5–5.0 mosaic spread) was acquired from NT-MDT and used as received. Unsized IM8 carbon fibers were acquired from Hexcel and were washed with ethanol and dried at 80 °C prior to further processing. Zinc nitrate hexahydrate and hexamethylenetetramine were purchase from Sigma-Aldrich, while the reactants for ZnO nanoparticles were from Alfa-Aesar.

Functionalization and Surface Analysis of HOPG and Carbon Fiber. HOPG samples were plasma treated in a SPI Plasma Prep II at 13 Pa of pressure for 15, 30, and 60 s in an oxygen atmosphere (99.6% purity) and at 20 W power. To determine the exact chemical composition of the HOPG surfaces, XPS was performed using a PerkinElmer 5100 XPS system and analyzed with the aid of CASAXPS software. All samples were excited by an Al K α (1486 eV) monochromated X-ray source while a through-the-lens electron flood gun was used to compensate any loss of charge on the sample. Each spectrum was first fit with a Shirley background and then convoluted into peaks representative of each oxidation state. Each XPS dataset was fit with a Gaussian 70% - Lorentzian 30% curve mixture that was constrained in both location and full width at half-maximum (fwhm). All peaks had a fwhm of 1.1–1.7 eV and were constrained to locations of 284.5–285.5, 285.5–287.0, 286.5–288.0, 288.0–290.0, and 291–293 eV for C—C, C—OH, C=O, C—OOH, and π - π C—C bonds, respectively.

IM8 carbon fibers were plasma treated under the same conditions as the HOPG samples, coated with ZnO nanowires, and tested by the SFF test. Prior to surface analysis and nanowire synthesis, IM8 carbon fibers (5.2 μ m diameter) were first rinsed with ethanol, dried for \sim 8 h, and functionalized by oxygen plasma for various durations under the same conditions as HOPG. Some of the fibers were used as substrates for ZnO nanowire growth with subsequent composite fabrication for SFF, whereas other samples were used for chemical surface analysis by XPS and tensile testing. For XPS analysis, fibers were mounted on a stainless steel platform, fastened down by a stainless steel masks, and loaded into a high vacuum exchange chamber ($<2 \times 10^{-8}$ mbar) overnight prior to sample analysis. All data was collected on a PHI 5000 VersaProbe II and processed using the same procedure as the HOPG. Each dataset was fit with curves (a Gaussian 70%–Lorentzian 30% mixture, GL30) that were constrained in location and fwhm to model realistically the chemistry of the fiber.

Adhesion Force Measurements. To make accurate and reproducible adhesion force measurements, the contact area must be measured and be sufficiently large to render a measurable adhesive force. Commercial AFM tips (MikroMasch, San Jose, CA, USA) with a radius of approximately 8 nm are mounted on a cantilever at a downward angle. Thus, the tip was flattened to significantly increase the surface area and create a contact area that is parallel to the substrate. The method described in ref 52 was adopted to flatten the AFM tip by scanning it in contact mode on a diamond lapping film (Model 50-30075 with an average roughness of 11.14 nm). The morphology and diameter of the tip were subsequently quantified through SEM and image analysis software. In addition to the surface area, the stiffness of the cantilever beam must be found to calculate the adhesion energy. Although a calibrated AFM cantilever was used for these experiments, the stiffness value still contains approximately \sim 10% error;⁵³ therefore, the same tip was used throughout all experiments to ensure that the relative change in adhesive energy is accurate even though the absolute value may contain some systematic error.

Adhesion force measurements were then performed on plasma treated HOPG with a functionalized AFM tip. To functionalize the AFM tip, the cantilever was first coated with ZnO nanoparticles. To do so, a colloidal solution of ZnO nanoparticles with a diameter of \sim 5 nm was synthesized according to the method developed by Hu et al.⁵⁴ The AFM tip was then dipped into this solution, dried at 70 °C to evaporate the solvent, and repeated seven times to ensure that a substantial film of ZnO was created on the surface of the tip. Because the size of the nanoparticles is significantly less than the surface area of the flattened AFM tip, a smooth and uniform coating was obtained. Adhesion force measurements were then performed on a Park XE-70 microscope with the assistance of XEI imaging software for data analysis. Using this functionalized tip, 15 adhesion force measurements were taken for each plasma treatment case. After each case, the tip was cleaned in dilute hydrochloric acid, rinsed with deionized water, dried, and recoated with ZnO prior to a change in the substrate. Additional details of this testing method are clearly described in refs 55 and 56.

Single Fiber Fragmentation Testing. Single fiber fragmentation tests were performed on IM8 carbon fibers that were functionalized by oxygen plasma then covered with vertically aligned ZnO nanowires. To synthesize vertically aligned ZnO nanowires, a layer of ZnO nanoparticles must first be deposited on the carbon fibers to act as nucleation sites. This nanoparticle layer was created by dipping the fibers into the same colloidal solution of ZnO nanoparticles that was used to create the ZnO film on the AFM tip. This deposition was followed by an annealing process at 150 °C for 10 min and repeated three times to ensure evaporation of the solvent and a uniform coverage of ZnO nanoparticles on the fiber surface. Once the fibers were coated with nanoparticles, ZnO nanowires were synthesized on the carbon fibers by an aqueous growth method. The growth solution was a zinc nitrate hexahydrate and hexamethylenetetramine solution (1.5 mM for each) prepared in Milli-Q water (500 mL). The solution was stirred and heated until it reached 90 °C, at which point the stirring was stopped, and the fibers were immersed in the solution for 2.5 h. The fibers were then removed from the solutions, washed with deionized water, and thoroughly dried.

Single fiber fragmentation samples were fabricated based on a previously reported method.⁵⁷ To fabricate these composite samples, a single carbon fiber is suspended in a dog bone shaped silicone mold (Dow Corning, 3120 RTV) so that the fiber does not contact any of the inner mold walls. Then, clips (1.1 g) are added to either end of the fiber and hung outside of the mold to ensure that the fiber remains in tension throughout the curing process. Next, an epoxy matrix made from a 16.9:100 weight ratio of Epikure 9553 and Epon 862 is mixed thoroughly, degassed, and cast into the dog bone mold. The samples were then cured at room temperature for at least 5 h, removed from the molds, and cured in a convection oven at 100 and 160 °C, each for one additional hour. Lastly, the samples were polished with a series of SiC grit papers (LECO Corporation) until optically clear and ready to test.

For testing, samples were loaded using a custom-built linear translation stage with a linear variable displacement transducer at a rate of 1 mm/min. Using an optical microscope, both polarized and nonpolarized light was applied so that the formation of fractures in the fiber becomes distinguishable from surface defects and debonding. The number of fiber fractures was counted incrementally until saturation and failure of the matrix.

Tensile Testing of Functionalized Fibers. Tensile tests were performed based on ASTM C1557-03 to determine a single fiber's tensile strength and the effects of the functionalization treatment. For these tests, IM8 carbon fibers were functionalized by the same oxygen plasma process as the HOPG samples for 30, 60, and 90 s. Individual fibers were then fastened with Devcon 5 min epoxy to mounting tabs with a gauge length of 12.7 mm and allowed to cure overnight. Tensile tests were then performed with a 5 N load cell on a 5969 series Instron at an extension rate of 8 μ m/s. Additionally, fibers were imaged by SEM at 20 kV to determine the fiber diameter, which is necessary to compute the fiber tensile strength and the composite interfacial shear strength.

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Notes

The authors declare no competing financial interest.

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