

Trade-off between the Mechanical Strength and Microwave Electrical Properties of Functionalized and Irradiated Carbon Nanotube Sheets

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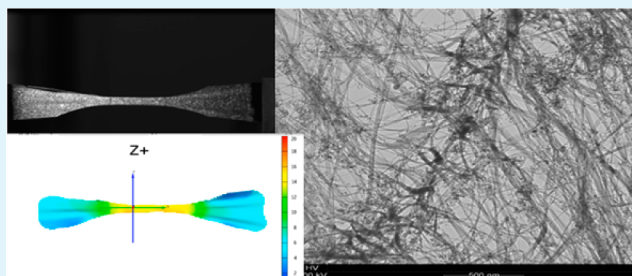
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Supporting Information

ABSTRACT: Carbon nanotube (CNT) sheets represent a novel implementation of CNTs that enable the tailoring of electrical and mechanical properties for applications in the automotive and aerospace industries. Small molecule functionalization and postprocessing techniques, such as irradiation with high-energy particles, are methods that can enhance the mechanical properties of CNTs. However, the effect that these modifications have on the electrical conduction mechanisms has not been extensively explored. By characterizing the mechanical and electrical properties of multiwalled carbon nanotube (MWCNT) sheets with different functional groups and irradiation doses, we can expand our insights into the extent of the trade-off that exists between mechanical strength and electrical conductivity for commercially available CNT sheets. Such insights allow for the optimization of design pathways for engineering applications that require a balance of material property enhancements.

KEYWORDS: multiwalled carbon nanotubes, carbon nanotube sheets, chemical functionalization, tensile strength, electrical conductivity, microwave spectroscopy, electron beam irradiation



■ INTRODUCTION

Multifunctional materials, including structural materials with additional capabilities such as lightning strike protection or structural health monitoring, have been a topic of considerable recent interest due to their potential to save significant weight in aerospace vehicles. Carbon nanotubes are attractive materials for use in these applications due to their high mechanical strength (on the order of 100 GPa for single-walled CNTs)^{1,2} and outstanding electrical and thermal conductivities (10^4 S/cm³ and 3500 W/(m·K),⁴ respectively).

Although a significant amount of research has been devoted to the development of CNT-based multifunctional materials, to date the properties of CNT bulk materials (composites, fibers, fabrics) fall far short of the theoretical properties of individual nanotubes. Various approaches have been investigated to incorporate CNTs into multifunctional materials.⁵ The use of CNTs as additives to polymers and composites has been investigated extensively, and significant improvements have been made in the mechanical, electrical, and thermal properties

of the host polymer or composite.⁵ However, this approach is confounded by the fact that van der Waals forces cause the nanotubes to agglomerate, even for only a few weight percent. Once agglomeration occurs, the properties of the resulting nanocomposite start to degrade. Like most additives, CNTs are effective viscosity modifiers and their addition to a polymer increases its viscosity, which can make processing the resulting nanocomposite difficult.

A more attractive approach that is receiving increased attention is to use CNTs in a fiber or fabric form which could then be used as a “drop-in” replacement for conventional reinforcements. This approach allows for higher loadings of the nanotubes; traditional composites are usually about 50% fiber by volume. Advanced fiber placement techniques currently in use with conventional composites will allow for the fabrication

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of CNT-reinforced composites with well-controlled alignment and placement of the nanotube reinforcement, unlike stochastic dispersions of CNTs into a matrix. Because processing CNT-reinforced composites would require little or no modification to the equipment or techniques currently used in the fabrication of conventional composites, commercialization of these materials should be simpler than that of nanocomposites prepared by CNT dispersions.

Carbon nanotube sheets and yarns have been produced by a number of methods including dry spinning from vertically aligned CNT arrays,⁶ aerogels,⁷ and wet spinning from lyotropic solutions of CNTs in strong acids⁸ or polyelectrolytes.⁹ These processes and the resulting sheets and yarns are in various stages of commercialization. Although considerable progress has been made over the past five years in developing high-strength CNT yarns, the highest reported tensile strength for a CNT yarn is 8.8 GPa,¹⁰ more than an order of magnitude lower than that of a single-wall CNT.¹ The mechanical behavior of CNT sheets and yarns is influenced by two competing factors: van der Waals forces which hold the fibers together and the low friction coefficient on the CNT surface.^{11,12} Under tensile loading, van der Waals forces are not strong enough to counteract the low-friction coefficient, causing the nanotubes to slide past each other,^{12,13} leading to failure in the bulk material prior to failure of individual CNTs.

Improvements in both mechanical and electrical properties of CNT sheets and yarns can be achieved by better aligning the nanotubes within the bulk material.¹⁴ A common method to enhance CNT alignment in these materials involves stretching a sheet or yarn which has been infiltrated with a solvent. Cheng et al. studied the effect of the stretch ratio on the mechanical and electrical properties of MWCNT sheets/bismaleimide composites, and observed that increasing the alignment of the CNT sheets through uniaxial stretching significantly improved both mechanical strength and electrical conductivity.¹⁴ However, simple uniaxial stretching of CNT sheets often results in a nonuniform distribution of CNT alignment, with the best alignment being at the center of the sheets where the tensile forces due to stretching are the highest. In addition, even in highly aligned CNT sheets and yarns, nanotube slippage still occurs and the maximum tensile strengths that have been achieved with stretching and alignment are still significantly lower than that of the individual tubes.

One approach to overcome this is to introduce covalent chemical bonds or cross-links between the CNTs in a sheet or yarn. Simulations by Cornwell and Welch predicted that the formation of covalent bonds in CNT yarns could lead to a tensile strength as high as 60 GPa.¹⁵ Chemical functionalization is one of the most common methods to initiate cross-linking and improve the mechanical strength. On a lab scale, CNT cross-linking can be achieved in a number of ways including cyclo-addition reactions, grafting, photochemistry, and electrochemical approaches.^{16,17} More recent work has utilized irradiation with high-energy particles, such as electron beam (e-beam) irradiation, to introduce cross-links between neighboring CNTs and thereby improve tensile properties.^{18–23} Espinosa and co-workers reported that e-beam irradiation-induced cross-linking of double-wall carbon nanotube bundles in the sample area of a transmission electron microscope (TEM) led to more than an 11-fold improvement in the load-carrying capability of the CNT bundles.¹ Another attractive feature of e-beam irradiation is that it can be used in large-scale processing.²⁴ Cross-linking CNTs in sheets and

yarns is a balancing act between introducing enough covalent bonds to improve tensile strength without significantly changing the bonding within the individual nanotubes and degrading their mechanical properties. In addition, because the hybridization of those carbons involved in the cross-linking changes from sp^2 into sp^3 , the electrical and thermal conductivity can also be adversely affected.

Whereas most work has investigated the effects of functionalization and cross-linking on either the mechanical or electrical properties of CNTs,^{26–29} very few studies have shown how functionalization and cross-linking affects both mechanical and electrical properties simultaneously.^{30,31} The objective of this study is not only to assess the impact of these modifications on CNT sheet mechanical and electrical properties, but also to determine the correlation between mechanical and electrical properties as a function of these modifications. In this study, the surface chemistry of a CNT sheet was modified through small-molecule functionalization in combination with e-beam exposure to promote covalent cross-linking between CNTs. Most other investigations in which e-beam cross-linking was employed have been conducted in the controlled environment of a TEM sample chamber. For this study, we chose to perform our irradiations in a commercial facility and in air to allow for the cross-linking of larger samples and to determine if commercial treatments are effective in enhancing the mechanical properties of CNT sheets. Mechanical properties (strength and modulus) of all CNT sheet samples were characterized by use of tensile testing, while the electrical properties were measured with microwave spectroscopy. We chose the microwave technique because it is noncontact and nondestructive.³² Furthermore, CNT electrical properties at microwave frequencies could be particularly interesting for electromagnetic shielding, and even for lightweight transmission lines.³³

■ EXPERIMENTAL SECTION

Materials. MWCNT sheets were purchased from Nanocomp Technologies Inc.** (lot 5333) in untreated and unwashed forms. The sheet-to-sheet average thickness of the as-received 5333 sheet was approximately $20 \pm 3 \mu\text{m}$, as measured by a dial drop gauge.

Chemical Functionalization. CNT sheets were functionalized with 3-aminopropyl aziridino (APA) and 2-hydroxyethyl aziridino (HEA) groups to introduce $-\text{OH}-$ and $-\text{NH}_2-$ terminated pendant groups that would be reactive with an epoxy resin. The procedures for preparing APA- and HEA-functionalized CNT sheets have been reported previously.²⁷ In brief, APA-functionalized sheet was prepared by adding a mixture of 3-azidopropane-1-amine and *N*-methylpyrrolidone to CNT sheets in a round-bottom flask and heating to approximately 180 °C under a nitrogen atmosphere. Similarly, HEA-functionalized sheets were prepared by adding 2-azidoethanol to the CNT sheets in a round-bottom flask and heating to approximately 180 °C. All CNT sheets were washed through a series of Soxhlet extractions in dimethylformamide, water, and acetone, and dried in a vacuum oven at approximately 45 °C. The yields of HEA (≈ 1.7 mol % functionality) and APA (≈ 3.8 mol % functionality) were determined from the mass increase of the CNT sheets following functionalization.

Electron Beam Irradiation. Electron-beam (e-beam) irradiation experiments of as-received and functionalized CNT sheets were carried out at Mercury Plastics**, a commercial e-beam facility. Sections of CNT sheet were cut from a parent sheet and used for irradiation. All sections were placed on a water-cooled aluminum stage, followed by e-beam irradiation experiments that were conducted in an air environment. CNT sheets were irradiated with a beam energy of 2 MeV and beam current of 36 mA. The materials were irradiated for approximately 20, 40, and 90 min, which corresponded to electron dosages of approximately $4.8 \times 10^{16} \text{ e/cm}^2$, $9.6 \times 10^{16} \text{ e/cm}^2$, and 22.0

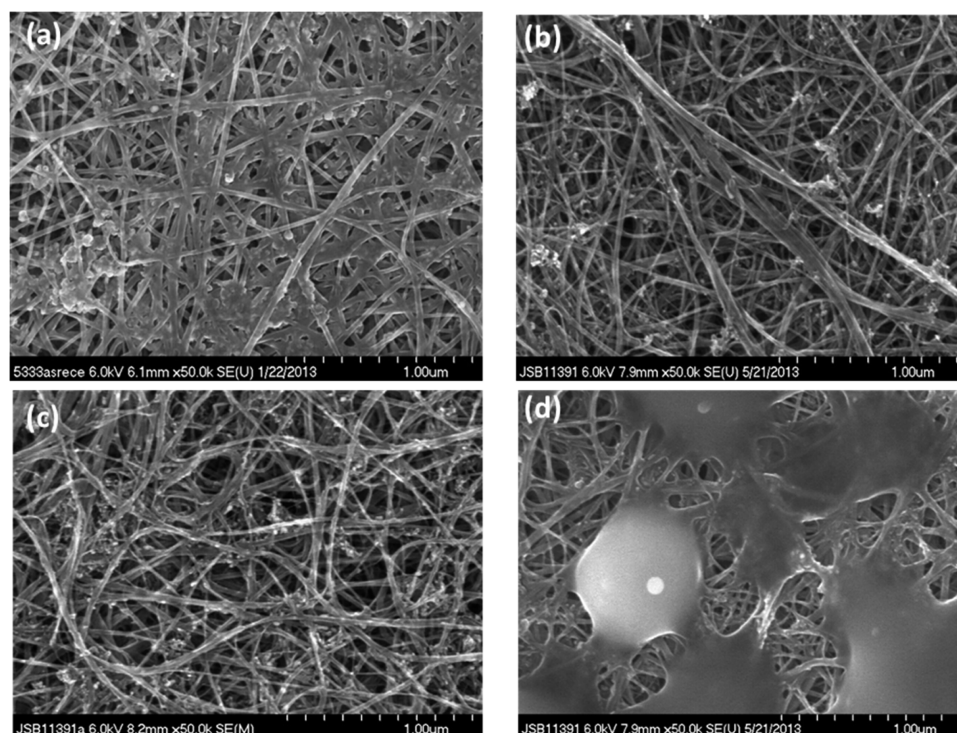


Figure 1. SEM images of (a) as-received carbon nanotube sheets, (b) 2-hydroxyethyl aziridino (HEA)-functionalized sheets, (c) HEA-functionalized sheets at the lowest irradiation dose (4.8×10^{16} e/cm²), and (d) HEA-functionalized sheets after irradiation with the highest dose (22.0×10^{16} e/cm²).

$\times 10^{16}$ e/cm², respectively. Materials designated for a particular irradiation dose were removed after its exposure limit had been reached. All sections requiring longer irradiation exposures were left on the sample stage and irradiation continued through each dose. The CNT sheet sections were then cut into test coupons for characterization.

Spectroscopic Characterization. Raman spectroscopy was performed to observe CNT structural changes as a function of e-beam irradiation dose. Spectra were recorded on a Raman microscope with a 514-nm argon ion laser excitation source. The intensities of the defect-induced D band (I_D) (~ 1300 cm⁻¹) and G band (I_G) (~ 1600 cm⁻¹) were measured with OMNIC software. The reported I_G/I_D ratio of each sample was calculated by measuring the average G/D ratio intensity from 10 different locations on each CNT sheet sample. The locations were randomly determined for each sample.

Mechanical Property Measurements. ASTM Standards D882 and D638 were followed for preparing the tensile specimens and carrying out the testing procedures. Tensile tests were carried out with a benchtop mechanical testing system equipped with a 22 N load cell. The cross-head speed for all measurements was 1.67×10^{-4} m/s (10 mm/min). Tensile specimens (approximately 25.4 mm $\times$ 6.5 mm) were mounted on card stock paper tabs and the tabs were spray-painted for digital imaging correlation. A minimum of five specimens were tested for each sample. The effective gage length was 10 mm for all CNT sheets. Specific strength and modulus data were normalized by each sample's volumetric density (approximately 0.40–0.54 g/cm³). While the CNT bundles in the sheet material exhibited a high degree of anisotropy, the samples were tested in the 0° direction relative to the direction of predominant CNT alignment, which was more than likely induced during processing when the sheets were collected on a drum.

Microwave Spectroscopy. An AC microwave cavity-perturbation technique was used to measure the dielectric constant and electrical conductivity at a microwave frequency of ≈ 7.3 GHz.³² The approach is noncontact, electrode-less, and nondestructive to the sample-under-test. All samples were cut into approximately 12 mm $\times$ 3 mm strips. Samples were mounted onto a polydimethylsiloxane (PDMS)/glass

sample holder and measurements were taken at partial insertions, following the procedure described by Orloff et al.³² For each sample, complex transmission data were measured for a range of insertion percentages from approximately 0.05% to 75% of the total sample length. The natural frequency and damping ratios were extracted from the damped harmonic oscillator³² used to fit the complex transmission as a function of frequency. The natural frequencies and damping ratios were then fit with a linear regression versus effective volume fractions, where the slopes were the real and imaginary parts of the dielectric constant ($\tilde{\epsilon} = \epsilon_r + i\epsilon_i$). The imaginary part of the dielectric constant was then converted into conductivity units ($\sigma = \epsilon_r \epsilon_0 2\pi f$, where ϵ_0 is the permittivity of free space and f is the measurement frequency).

Scanning Electron Microscopy. Scanning electron microscopy (SEM) images were obtained with an accelerating voltage of approximately 6 keV. All carbon nanotube sheet samples were sputter-coated with platinum.

RESULTS AND DISCUSSION

Morphology of CNT sheets. We observed the morphology of the as-received CNT sheets with SEM imaging. Figure 1 shows images of the surfaces of the (a) as-received CNT sheet, (b) HEA-functionalized CNT sheet, (c) HEA-functionalized CNT sheet with lowest e-beam irradiation dose, and (d) the HEA-functionalized CNT sheet with the highest irradiation dose. All sheet materials showed a significant amount of voids between nanotube bundles. In addition, catalysts (areas of agglomerated particles) were observed in the CNT sheets. The average residual catalyst content of the untreated CNT sheet by mass was approximately 13% Fe₂O₃ at ≈ 800 °C in air ($\approx 8\%$ as Fe), as determined by thermogravimetric analysis. Thermogravimetric analysis data can be found in the [Supporting Information](#).

Figure 1a shows amorphous carbon on the surface of the as-received sheets, which was later removed during the washing step of the functionalization process (Figure 1b). The presence

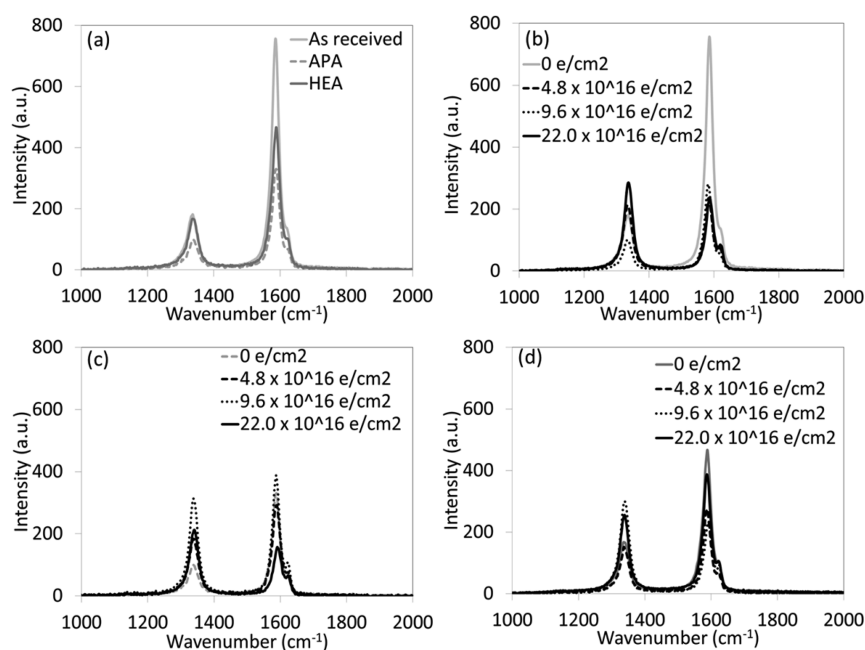


Figure 2. Raman spectra for (a) nonirradiated as-received, APA, and HEA carbon nanotube sheets, (b) irradiated as-received, (c) irradiated 2-aminopropyl aziridino (APA) nanotube sheets, and (d) irradiated 2-hydroxyethyl aziridino (HEA) carbon nanotube sheets.

of amorphous carbon on the surface of the as-received carbon nanotubes was not expected to influence the mechanical strength, but likely played a role in reducing the electrical conductivity of the unfunctionalized CNT sheets. The SEM images do not show a noticeable difference between the HEA-functionalized, nonirradiated sheets (Figure 1b) and HEA-functionalized sheets irradiated at the lowest irradiation dose (Figure 1c). When the HEA-functionalized sheets were treated at the highest irradiation dose (Figure 1d), a coating appeared on the surface. This behavior was only observed in HEA-functionalized samples at the highest irradiation dose. Although all HEA- and APA-functionalized samples underwent a washing step, the presence of a coating may be attributed to excess hydroxyl reactants on the surface of the CNT sheets that flowed and polymerized upon exposure to the highest irradiation dose.

Effect of Small Molecule Functionalization and Electron Beam Irradiation on CNT Structure. Raman spectroscopy (Figure 2) was used to evaluate the effect of chemical functionalization and e-beam irradiation on the chemical structure of the CNTs. Generally, the I_G/I_D ratio provides information about the nature of the chemical bonding within the CNT structure. Table 1 shows that as the irradiation exposure increased, most of the I_G/I_D values for the unfunctionalized and functionalized CNT materials decreased,

which is consistent with a change in hybridization state of some of the carbon atoms from sp^2 to sp^3 .²⁴ The exception was the I_G/I_D for the APA-functionalized sheet at a dosage of approximately $9.6 \times 10^{16} \text{ e/cm}^2$. The reason for this discrepancy may be due to damage to the CNT sheet during the irradiation experiments caused by sample setup error. Data in Table 1 show that significant changes in the I_G/I_D intensities occurred from 0 to $4.8 \times 10^{16} \text{ e/cm}^2$ and from 4.8×10^{16} to $22.0 \times 10^{16} \text{ e/cm}^2$, which was an indication that the largest change in the amount of broken sp^2 bonds caused by the addition of either more chemical functionality or more cross-linking occurred within these time periods.

Effect of Electron Beam Irradiation and Small Molecule Functionalization on the Tensile Properties of CNT Sheets. The effects of e-beam irradiation dosage on the specific tensile strength and modulus of as-received, HEA-, and APA-functionalized CNT sheets are shown in Figures 3a and b.²⁷ The tensile strength of the as-received sheets increased by only approximately 23% after irradiation exposure with the lowest irradiation dose (Figure 3a), which is not as significant as what has been reported by others.²³ As the dose was increased, the tensile strength in the unfunctionalized sheet showed a slight decrease. In prior studies, e-beam irradiations were conducted in a controlled atmosphere and on samples in which CNTs were in close contact with each other.²³ Under these conditions, the free radicals created by e-beam irradiation can react with adjacent nanotubes to produce cross-links.^{11,23} In the present study, the irradiation experiments were conducted in air and on samples where not all nanotubes were in intimate contact. As a result, cross-linking is not as efficient and some carbon-centered free radicals, formed by e-beam irradiation, are quenched by oxygen or other chemical species. This leads to the less-than-expected improvements in the tensile strength and modulus of the as-received sheets.

For HEA- and APA-functionalized sheets, both samples displayed a 48% increase in tensile strength with increasing irradiation dosage. Functionalization leads to enhanced e-beam

Table 1. I_G/I_D Values and Standard Deviation of Unfunctionalized, Functionalized, and Irradiated Carbon Nanotube Sheets²⁷

irradiation dose ($\times 10^{16} \text{ e/cm}^2$)	as-received CNT sheet	HEA-functionalized CNT sheet	APA-functionalized CNT sheet
0	3.0 ± 0.2	3.3 ± 0.5	2.3 ± 0.2
4.8	1.5 ± 0.5	1.5 ± 0.1	1.7 ± 0.1
9.6	1.7 ± 0.7	1.3 ± 0.5	0.7 ± 0.1
22.0	0.9 ± 0.2	0.8 ± 0.1	1.4 ± 0.1

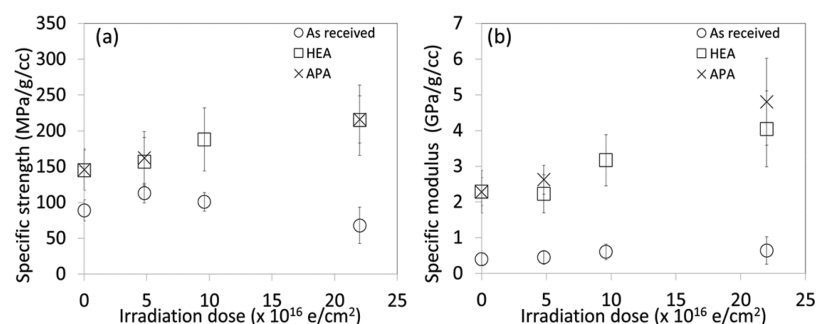


Figure 3. (a) Specific tensile strength and (b) specific tensile modulus comparison of functionalized and irradiated carbon nanotube sheets with increasing irradiation dose. Error bars represent one standard deviation as determined from five specimens.

cross-linking by providing additional sites for free-radical formation and for reaction with radicals that are produced by irradiation. All CNT sheets exhibited ductile failure. The specific yield strength of the as-received irradiated sheets was approximately 115 MPa/g/cm³, while that of the functionalized sheets was approximately 180 MPa/g/cm³. Representative stress–strain curves of the e-beam irradiated CNT sheets can be found in the [Supporting Information](#).

The effect of e-beam irradiation dosage on the specific tensile modulus of as-received, HEA-, and APA-functionalized CNT sheets is illustrated in [Figure 3b](#). The data for the as-received CNT sheets revealed that there is no significant change in tensile modulus with increasing irradiation doses. In the case of the functionalized sheets, the tensile modulus of the HEA-functionalized material increased by approximately 96%, while the APA-functionalized CNT sheets showed about a 125% improvement in tensile modulus after irradiation at the highest dose ([Figure 3b](#)). These modulus improvements are consistent with functionalization-enhanced cross-linking.²⁵

Effect of Electron Beam Irradiation and Chemical Functionalization on the Dielectric Properties of CNT Sheets. The electrical conductivity and dielectric constants of functionalized and irradiated CNT sheets are reported in [Table 2](#). The electrical conductivity of the as-received CNT sheets is approximately 36 S/m. The electrical conductivity of the as-received CNT sheets in this study (Nanocomp Lot 5333**) is lower than electrical conductivity values reported elsewhere in

literature,³⁴ even when electrical conductivity was measured using a similar method.³⁵ The difference in electrical conductivity in the 5333 as-received CNT sheets and previously reported CNT papers or films^{34,35} may be attributed to the methods used to synthesize the individual CNTs and process the bulk CNT formats. Although Nanocomp's** process is proprietary, the CNT sheets are processed in a manufacturing facility where the CNT synthesis takes place in a large furnace through a chemical vapor deposition (CVD) process. The synthesized nanotubes are then collected onto an anchor and deposited onto a belt where multiple layers of the deposited CNTs are compressed and laminated to increase the thickness of the sheet. Variation in the stock CNT material within the sheet would lead to lower electrical properties. In addition, the CNT bundles within sheets exhibit some degree of anisotropy. As a result, the random orientation of individual CNTs within the sheets may have also affected the electrical conductivity by reducing the continuous electron transfer needed for achieving high conductivity.

Functionalizing the as-received CNT sheets with HEA groups was observed to further decrease the conductivity and dielectric constants by approximately 50% and 44%, respectively. In the case of the APA sheets, functionalization led to almost a 75% decrease in electrical conductivity and about a 67% decrease in the dielectric constant. When irradiated, the HEA-functionalized sheets exhibited close to a 49% decrease in conductivity and approximately a 35% decrease in dielectric constant as the irradiation dose increased. On the other hand, a 24% reduction in electrical conductivity and a 9% decrease in the dielectric constant were observed in the APA-functionalized sheets as the irradiation exposure approached the highest dosage. The decrease in the in-plane conductivity is due to the transformation of sp² to sp³ hybridized carbon atoms caused by added chemical functionality or e-beam irradiation.²⁸ Note that catalysts are still present in the sheets following functionalization, but the exact influence of catalysts on the electrical conductivity is unknown. Although there was no clear trend in the dielectric constant data with increasing irradiation exposure, a decrease in dielectric constant was observed after functionalization. The addition of HEA- and APA-functionalization would have resulted in changes to polarization and cross-link density within the CNT sheet, where both of these would influence the dielectric constants.

Relationship between the Electrical and Mechanical Properties of Functionalized and Irradiated CNT Sheets. [Figures 4](#) and [5](#) show the relationship between CNT structural changes and the mechanical and electrical properties of functionalized CNT sheets as a function of irradiation dose.

Table 2. Electrical Properties of Functionalized and Irradiated Carbon Nanotube Sheets

	conductivity (S/m)	uncertainty ^a (S/m)	dielectric constant	uncertainty ^a
as-received sheet	36.1	10.7	2127.8	729.2
0 e/cm ² HEA sheet	17.8	3.5	1179.0	219.7
4.8 × 10 ¹⁶ e/cm ² HEA sheet	15.8	2.9	905.6	146.2
9.6 × 10 ¹⁶ e/cm ² HEA sheet	11.6	1.8	706.8	100.5
22.0 × 10 ¹⁶ e/cm ² HEA sheet	9.11	1.4	770.4	112.5
0 e/cm ² APA sheet	9.2	1.2	710.9	91.0
4.8 × 10 ¹⁶ e/cm ² APA sheet	7.7	1.0	899.9	120.9
22.0 × 10 ¹⁶ e/cm ² APA sheet	6.9	0.9	645.6	77.7

^aUncertainty values were determined by error propagation and a 95% confidence interval.

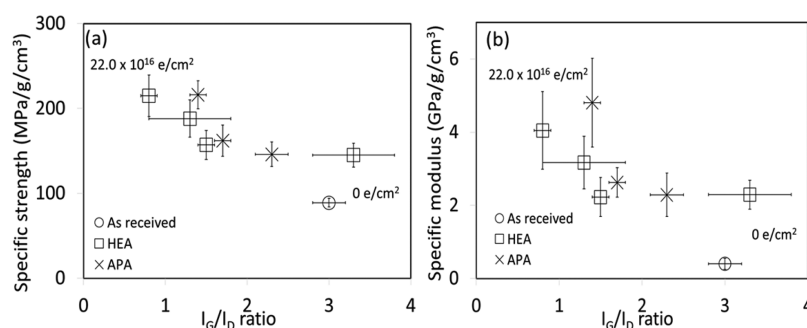


Figure 4. (a) Structure to mechanical strength relationship of functionalized carbon nanotube sheets as a function of irradiation dose. (b) Structure to stiffness relationship of functionalized carbon nanotube sheets as a function of irradiation dose.

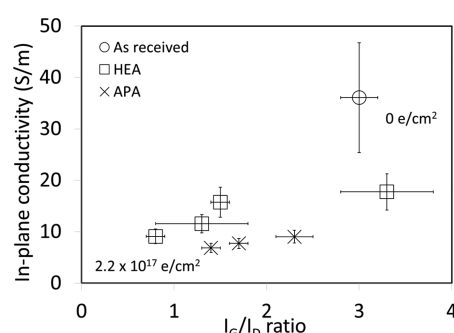


Figure 5. Structure to electrical property relationship of functionalized carbon nanotube sheets as a function of irradiation dose. Uncertainties in in-plane conductivity were computed by error propagation based on a 95% confidence interval.

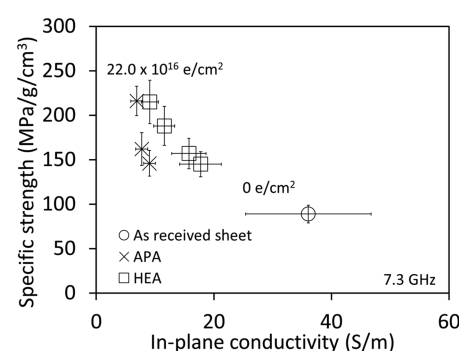


Figure 6. Specific strength and in-plane conductivity relationship of functionalized carbon nanotube sheets as a function of irradiation dose.

In both figures, a correlation was observed between the structural order of the CNT lattice and mechanical strength and the electrical conductivity. Figure 4a and b reveal that the specific tensile strength and modulus increased as the I_G/I_D ratio decreased with higher irradiation doses, while Figure 5 illustrates how the in-plane electrical conductivity and the I_G/I_D ratio decreased with increasing irradiation dose. Table 1 shows that the HEA-functionalized, nonirradiated sheet had a slightly higher I_G/I_D ratio than the as-received, nonirradiated sheet, and a higher electrical conductivity than the as-received sheet would be predicted given the trends in conductivity and the I_G/I_D ratio. However, the increase in the ratio of the order–disorder band for the HEA-functionalized, nonirradiated sheet was not significant. Electrical conductivity of the CNT sheets is affected by both the transformation of sp^2 to sp^3 bonds through CNT covalent cross-linking and cross-linking between functional groups, because both of these parameters will disrupt the continuous path for electron transfer. In this case, only changes in hybridization state resulting from covalent CNT cross-linking were detected by Raman spectroscopy and not covalent cross-linking between functional groups, since the HEA and APA functional groups are not Raman active. This would indicate why the changes in the I_G/I_D ratio were not as significant as the changes in electrical conductivity following the introduction of HEA and APA functional groups.

Figure 6 illustrates the trade-off between the mechanical and electrical properties of functionalized and irradiated CNT sheets. According to Figure 6, the specific strength of the functionalized CNT sheets increased as the electrical conductivity decreased with increasing irradiation doses. The initial electrical conductivity value for the APA-functionalized sheets was half that of the initial electrical conductivity of the

HEA-functionalized sheets, even though the specific strength for both samples approached similar values as the irradiation time progressed. This difference in conductivity between the nonirradiated APA- and HEA-functionalized sheets may be indicative of the larger degree of functionality in the APA sheets compared to the HEA sheets (3.8 mol % vs 1.7 mol %). Another possibility for the differences in conductivity between the APA and HEA nonirradiated sheets could be explained by the possibility of a nonhomogenous distribution of functional groups in the functionalized sheets. If a higher functional group density of APA groups at a particular region of the sample was analyzed, then the conductivity could possibly be lower if the area contained a higher amount of functional groups.

CONCLUSIONS

In summary, an inverse relationship between the mechanical properties and the in-plane electrical conductivity was observed with increasing e-beam dose in APA- and HEA-functionalized CNT sheets. As seen in the Raman spectra, the enhancement in mechanical properties with irradiation came at the price of introducing structural defects in the CNTs, suggesting that defects promote cross-linking and also improve mechanical properties. These cross-linking sites, in turn, reduced the electrical conductivity of the CNT sheets. The application where the CNT reinforcement will be utilized should determine how much covalent cross-linking is needed in order to establish a proper balance between mechanical strength and electrical conductivity. For example, lightning strike resistance for composites in aircraft may need more emphasis on mechanical properties, but if CNT sheets or yarns were to be used in structural health monitoring, the need for

higher conductivity may dominate at the expense of mechanical properties.

The information in this paper is intended to serve as a reference for tailoring the mechanical and electrical properties of bulk CNT formats. Because the mechanical and electrical properties of individual MWCNTs are governed by many factors that influence CNT growth (i.e., catalyst quality, CNT length, chirality, and alignment), these synthesis conditions should first be better controlled and taken into account when selecting methods for covalent cross-linking. Implementing methods to achieve optimal and homogeneous covalent cross-linking in bulk CNT formats are relatively unexplored areas that would provide more understanding into the strategic design of multifunctional CNTs, and if successful, would provide materials with an ideal balance of electrical conductivity and mechanical strength. Additional CNT modification schemes are being investigated to develop other methods that could improve the mechanical properties without significantly reducing the electrical conductivity. Work on functionalization with halogens is being carried out to investigate if both the electrical and mechanical properties can be enhanced through surface modification.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b12303.

Thermogravimetric analysis data and representative stress–strain curves of carbon nanotube sheets (PDF)

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Notes

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The authors declare no competing financial interest.

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