

Effect of Electron Beam Irradiation on the Tensile Properties of Carbon Nanotubes Sheets and Yarns

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ABSTRACT

Carbon nanotube sheets and yarns were irradiated using electron beam (e-beam) energy to determine the effect of irradiation dose on the tensile properties. Results showed that a slight change in tensile strength occurred after irradiating as-received CNT sheets for 20 minutes, and a slight decrease in tensile strength as the irradiation time approached 90 minutes. On the other hand, the addition of small molecules to the CNT sheet surface had a greater effect on the tensile properties of e-beam irradiated CNT sheets. Some functionalized CNT sheets displayed up to a 57% increase in tensile strength following 90 minutes of e-beam exposure. In addition, as-received CNT yarns showed a significant increase in tensile strength as the irradiation time increased.

Keywords: Carbon nanotubes, buckypaper, tensile strength, electron beam irradiation, yarns

1 INTRODUCTION

Carbon nanotubes (CNTs) have been widely investigated in the development of high strength reinforcements to replace conventional fibers in composites with a goal of producing higher strength, lower density materials. The theoretical tensile strength and modulus values for single wall CNTs are reported to be as high as 100 GPa and 1 TPa, respectively [1]. Unfortunately, the theoretical values have not been observed experimentally in carbon nanotube derived reinforcements, such as dry spun nanotube sheets

and yarns due to the CNTs being held together by van der Waals and electrostatic forces, resulting in slippage and detrimentally decreasing the mechanical properties [2]. To improve the properties, various routes for enhancing the strength and stiffness of nanostructured carbon nanotube reinforcements have been explored.

The most common methods designed to increase the bonding strength in these materials have involved the introduction of various functional groups onto the nanotube surfaces. More recent advances have entailed modifying the structure through radiation [3-9]. Electron beam (e-beam) irradiation is believed to offer the most promising results with respect to large scale irradiation which facilitates scale-up processing [4]. Previous reports on e-beam irradiation of CNTs presented evidence of the formation of covalent crosslinks through the generation of vacancies and defects caused by collisions in atoms of the CNT structure upon exposure to electron beam energy [6, 7]. Although these studies have shown the possible formation of covalent crosslinks via e-beam irradiation, there have been only a few reports discussing how the tensile properties of CNT-based materials were affected after such treatment [4-7]. The objective of this study is to explore various approaches to increase the tensile properties of CNT-based yarns and sheets through the use of e-beam irradiation.

2 EXPERIMENTAL

2.1 Materials

Untreated multi-walled carbon nanotube sheets (Lot # 5333) and yarns (Lot # 5279) were received from Nanocomp Inc. (Concord, NH). Additional wires were obtained from General Nano (Cincinnati, OH).

2.2 Methods

E-beam irradiation of carbon nanotube sheets and yarns were carried out at the Northeast Ohio (NEO) Beam Facility (Middlefield, OH). All materials were irradiated at 2 MeV with a beam current of 36 mA. The CNT sheets and yarns were irradiated for approximately 20, 40, and 90 minutes, which corresponded to dosages of 4.8×10^{16} e/cm², 9.6×10^{16} e/cm², and 2.2×10^{17} e/cm², respectively. The samples were cooled on an aluminum water cooled stage during irradiation.

Functionalized carbon nanotube sheets were also irradiated. CNT sheets functionalized with hydroxyl or amine containing groups were irradiated to determine how the presence of e-beam reactive functional groups affected the tensile properties of irradiated sheets.

CNT sheets and yarns were prepped for tensile testing by mounting the sheets and yarns to paper tabs and bonding each sample to the cardstock with epoxy. The tensile properties of carbon nanotube sheets and yarns were tested using a Tytron MicroTester testing system equipped with a 25N load cell. Carbon nanotube sheets were strained at 10 mm/min, while the CNT yarns were strained at a rate of 7 mm/min. Five specimens were tested for each sample set of CNT sheets. At least ten specimens per sample set were tested for CNT yarns. The diameters of the CNT yarns were measured by optical microscopy. The effective gage length was 10 mm for both CNT sheets and yarns.

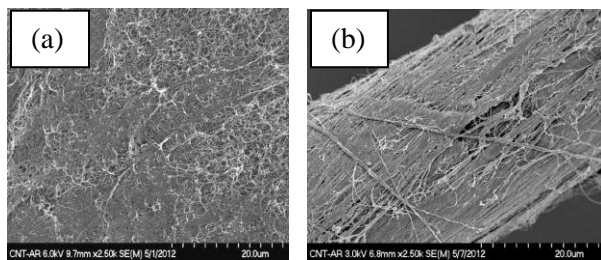


Figure 1. SEM images of (a) As-received CNT sheets (Nanocomp) and (b) CNT yarns (General Nano)

3 RESULTS AND DISCUSSION

Carbon nanotube sheets (Nanocomp) and CNT yarns (General Nano and Nanocomp) were irradiated to determine the effect of irradiation dose on the tensile properties. Figure 1 shows SEM images of the CNT sheet and yarns before irradiation. The CNT sheets have a thickness of approx. 30 μ m, and the CNT yarns have diameters between approx. 55-120 μ m, depending on the manufacturer and/or the processing method.

Table 1 shows the effect of irradiation time on the tensile strength and modulus of as-received CNT sheets. The data shows that little change occurred in the tensile strength after 40 minutes of e- beam irradiation. The tensile strength for the as-received sheets was observed to be the lowest at 90 minutes. At this point, it is not clear if the slightly lower properties after 90 minutes of irradiation were the result of defects being introduced within the individual nanotubes.

Table 1. Effect of irradiation time on the tensile strength of as-received CNT sheets

	0min	20min	40min	90min
Tensile strength (MPa/g/cc)	89.1 \pm 14.9	112.9 \pm 13.5	101.2 \pm 12.9	67.6 \pm 25.4

To promote e-beam crosslinking within the CNT sheets, various functional groups were attached to the nanotube surfaces prior to irradiation. Figure 2 shows the effect of small molecule functionalization on the specific tensile strength of e-beam irradiated CNT sheets. The CNT sheets in Figure 2 were functionalized with either hydroxyl or amine groups. Results showed that although the specific tensile strengths of hydroxyl and amine functionalized CNT sheets were very similar, attaching functional groups significantly increased the tensile strength of CNT sheets compared to as-received CNT sheets prior to e-beam irradiation. While e-beam irradiation of the as-received CNT sheets did not have much of an effect on specific tensile strength, irradiation of both the hydroxyl and amine

functionalized sheets led to significant increases. The specific tensile strength of these functionalized sheets increased with increasing dose, with the sheets irradiated for 90 minutes having a 57% higher specific tensile strength. The specific tensile strength of these sheets was more than twice that of the non-irradiated as-received sheets. Theoretical studies have shown that adding covalent cross-links between nanotubes in CNT fibers can lead to tensile strengths up to 60 GPa [10].

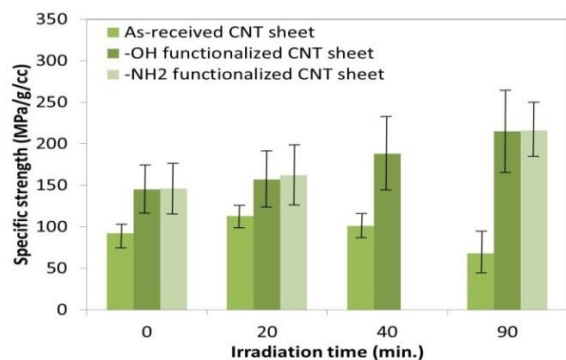


Figure 2. Effect of functionalization on specific strength of irradiated CNT sheets

After the tensile properties of the CNT sheets were obtained, scanning electron microscopy (SEM) was used to determine the effects of irradiation on the fracture surfaces of CNT sheets. SEM images of the largest damaged areas of the unfunctionalized as-received and irradiated sheets are shown in Figures 3(a) and 3(b), respectively. According to the micrographs, Figure 3(b) appeared to show some peeling on the surface, which may give an indication about the decrease in tensile properties observed after irradiating for 90 minutes. Additional characterization methods will be needed to provide more information about the changes in the structure-property behavior of functionalized and unfunctionalized CNT sheets as a function of e-beam irradiation dose.

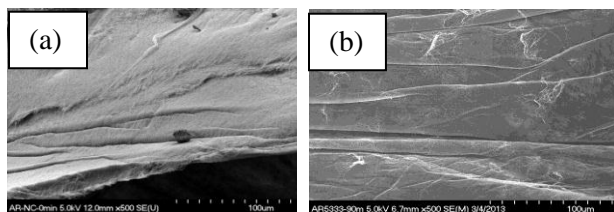


Figure 3. CNT sheets of (a) as-received and (b) irradiated (90 min). following tensile failure

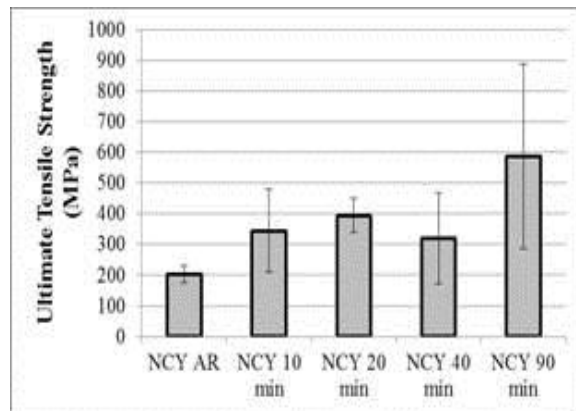


Figure 4. Tensile strength of as-received irradiated CNT yarns (Nanocomp)

The effect of e-beam irradiation on the tensile properties of CNT yarns was also investigated. Unlike unfunctionalized CNT sheets, the tensile properties of unfunctionalized CNT yarns increased significantly with e-beam irradiation (Figure 4). This could be due to the higher density of nanotubes in the yarns and also better alignment of the individual CNTs compared to that of the sheets. We are currently exploring the effects of e-beam irradiation on hydroxyl and amine functionalized yarns.

4 SUMMARY

Carbon nanotube sheets with and without amine and hydroxyl group functionalization and unfunctionalized carbon nanotube yarns were irradiated for up to 90 minutes with 2 MeV electrons. The tensile properties of these materials changed as a function of irradiation time and dose. The largest increases in specific tensile strength of CNT sheets were measured for hydroxyl and amine functionalized materials that were irradiated for 90 minutes. This treatment resulted in a 57% increase over the non-irradiated functionalized sheets and a greater than 200% increase over non-irradiated sheets having no prior functionalization. In comparison, 90 minute irradiation of CNT sheets with no functionalization resulted in a loss of specific tensile strength. This may suggest that functionalization with e-beam active groups facilitates the formation of covalent bonds (cross-links) between the

individual nanotubes within the sheets leading to increased tensile properties. Preliminary studies also demonstrated that e-beam irradiation of unfunctionalized CNT yarns resulted in as much as a 3-fold increase in specific tensile strength. This is likely due to the fact that CNTs in the yarns are more tightly packed and more aligned than those in sheets.

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