

SCALABLE PROCESSING OF MULTIFUNCTIONAL NANOTUBE/FIBER HYBRID COMPOSITES

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Abstract

The hybridization of micro and nano reinforcement scales offers tremendous opportunity to tailor the mechanical and physical properties of fiber-reinforced composites. Initial research has focused on chemical vapor deposition (CVD) approaches where carbon nanotubes can be grown within fiber bundles in situ. This research focuses on the use of electrophoretic deposition (EPD), where functionalized carbon nanotubes are deposited onto fabric from a water-based solution using an electric field. The EPD approach is readily scalable for future applications and is performed at ambient temperatures. After nanotubes are integrated into the fiber preform composites are then produced using vacuum assisted resin transfer molding. The integration of carbon nanotubes into the fibrous structure drastically decreases the permeability of the fabric, requiring longer infusion times and resulting in voids if layers of varying permeability are infused together. If voids are minimized a significant increase in laminate shear strength can be achieved through the integration of carbon nanotubes.

1. Introduction

As advanced fiber composites are utilized in more primary load-bearing applications it is crucial to improve their durability and damage tolerance. Damage in fiber composites typically initiates in the polymer matrix through the formation of matrix microcracks or delamination at the ply interface. The out-of-plane properties of composites are dominated by the properties of the polymer matrix and, as a consequence, they often have poor interlaminar strength and fracture toughness. Because carbon nanotubes are three orders of magnitude smaller than the scale of the fibers they can penetrate the matrix-rich interlaminar and intra-bundle regions to provide reinforcement. In addition, this hybridization with nanoscale reinforcements offers the opportunity to add new functionality such as *in situ* damage capabilities [1, 2, 3].

Current approaches to integrate nanotubes in traditional composites include dispersion/infusion, direct integration, and spraying in interlaminar regions. For the dispersion/infusion approach, where nanotubes are dispersed into the polymer matrix followed by infusing into the fibers there is a limitation on the achievable fiber volume fraction. The addition of even small quantities of carbon nanotubes, below 1 wt.%, can result in substantial increases in resin viscosity. The spraying approach on either prepreg or fabric

materials results in a concentration of nanoscale reinforcements at the ply interfaces but nanotubes are not distributed throughout the composite. Thostenson *et al.* [1] were among the first to investigate the growth of carbon nanotubes within fiber preforms using chemical vapor deposition (CVD). The CVD approach, where carbon nanotubes are grown from a hydrocarbon gas, is a potentially scalable process. The direct-growth of nanotubes on fibers is a high-energy process that produces a relatively low yield of carbon nanotubes. In addition, there can be catalyst reactions at the fiber surfaces degrade the fiber tensile strength. The high temperature growth conditions, typically above 600°C, also remove sizings that have been applied to fiber surfaces.

As an alternative to CVD we have investigated electrophoretic deposition (EPD) as a method to directly integrate carbon nanotubes within fiber bundles. The process requires first creating an aqueous suspension of functionalized nanotubes. The functionalization process both creates a suspension of nanotubes as well as gives the nanotube a surface charge. This surface charge, known as the zeta-potential, imparts electrophoretic mobility to the carbon nanotube so that under an applied electric field the nanotubes are attracted to the oppositely charged electrode and deposit from solution. Figure 1 shows a general schematic of the electrophoretic deposition process under an applied direct current (DC) field. A key advantage of the EPD process is that the purity and chemical functionality of the nanotubes can be tightly controlled. The chemical functionalization can be utilized to promote adhesion between the nanotubes, the fiber surfaces, and the polymer matrix. In addition, the process is carried-out under ambient conditions and utilizes water as the solvent.

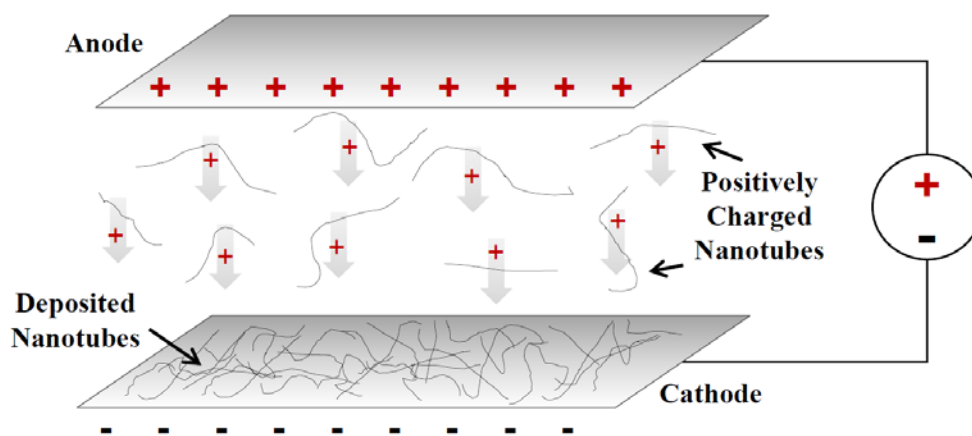


Figure 1. A schematic showing the electrophoretic deposition process where positively charged carbon nanotubes in a direct current field are deposited onto the cathode.

In this research we focus on studying the EPD process in order to integrate carbon nanotubes into carbon fibers and developing the manufacturing approach to produce high-quality composite laminates with integrated carbon nanotubes. Highly stable dispersions of carbon nanotubes were prepared using a combined ozonolysis and ultrasonication approach. The influence of the nanotube chemical functionalization and deposition parameters on the resulting structure is investigated. Composite laminates are then produced for mechanical and microscopic characterization. A particular focus of the research is on producing composite laminates with low void content.

2. Experimental

2.1. Carbon Nanotube Dispersion and Functionalization

Multi-walled carbon nanotubes (CM-95, Hanwha Nanotech, Korea) were dispersed in ultra-pure water using an ultrasonication and ozonolysis approach described in References [2] and [3]. After ozone functionalization some solutions of nanotubes were functionalized with polyethyleneimine (PEI), $(\text{H}(\text{NHCH}_2\text{CH}_2)_{58}\text{NH}_2)$, Mw: 25,000, Sigma-Aldrich, USA). Although PEI has a high-natural pH in solution the addition of acid allows the amine groups to protonate and Sun and Gao [4] demonstrated that a +50mV zeta-potential can be established below a pH of 8. The PEI and ozone-treated nanotube solutions were adjusted to a pH of about 6 using glacial-acetic acid (Sigma-Aldrich). The influence of the PEI alone was also examined by using identical EPD conditions to those for the nanotube coating but without nanotubes present.

For comparison, acid treated nanotubes were prepared by mixing the as-received carbon nanotubes in a concentrated HNO_3 and H_2SO_4 solution (1:3 volume ratio) (Sigma Aldrich, USA) as described in Reference [5, 6]. The acid treated nanotubes were filtered and rinsed with deionized water prior to preparation of aqueous solutions which were ultrasonicated for several hours prior to use.

2.2. Electrophoretic Deposition

The carbon nanotube dispersions were utilized to deposit nanotubes from solution onto carbon fiber and stainless steel substrates. The deposition parameters for the ozone-functionalized nanotubes on carbon fibers was conducted under a direct current (DC) with a field strength of 43 V/cm and the ozone and PEI-functionalized MWCNTs were deposited using a 28 V/cm field strength. The lower field strength for the PEI-MWCNT deposition was used to reduce Joule heating of the higher-conductivity solution. Deposition times up to 40 min were used to coat stainless steel (316 SS McMaster-Carr, USA) and unidirectional carbon-fiber (T700S, Soller Composites, USA) substrates. The stainless steel substrate was used to characterize the as-deposited film morphology. For both substrates electrical connections were made directly to the DC power supply (Figure 2). Although the current deposition work-cell is a batch process, the approach could be easily scaled to a roll-to-roll process.

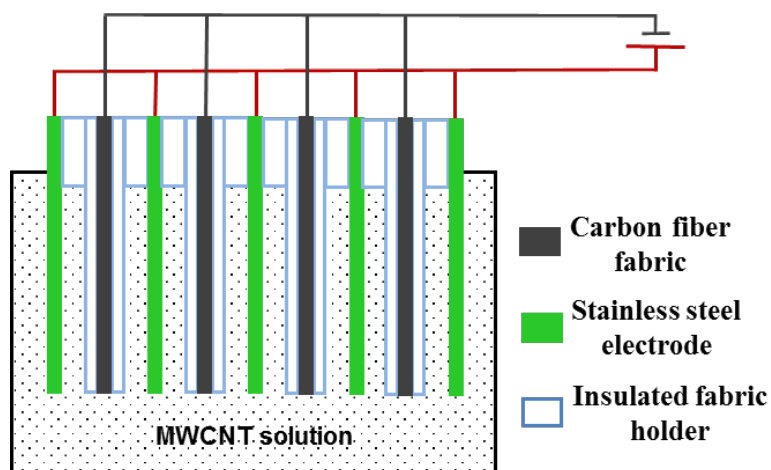


Figure 2. Experimental setup for depositing carbon nanotubes onto unidirectional carbon fabric.

2.3. Composites Manufacturing

After electrophoretic deposition, fabric layers were sealed in a vacuum bag underneath a semi-permeable membrane (Gore Technologies, USA) and dried under vacuum. The compaction pressure of the vacuum kept the fiber layers at a uniform thickness. The nanotube-coated and uncoated carbon fabric layers were infused using a conventional vacuum-assisted resin transfer molding (VARTM) process. The fibers were first sealed in a vacuum bag and resin was infused into the fiber preform using a distribution media layer on the vacuum bag side to speed the infusion process (Figure 3). The epoxy resin used was a bisphenol-F epichlorohydrin epoxy (EPON 862, Momentive Specialty Chemicals) and with an aromatic diamine curing agent (Epi-Kure W, Momentive Specialty Chemicals) mixed at a ratio of 100/26.4. After infusion a second bag with a breather layer was placed over the layup to provide uniform compaction during cure (130°C for 6 hours). Baseline laminates without nanotubes were also produced using the same approach.

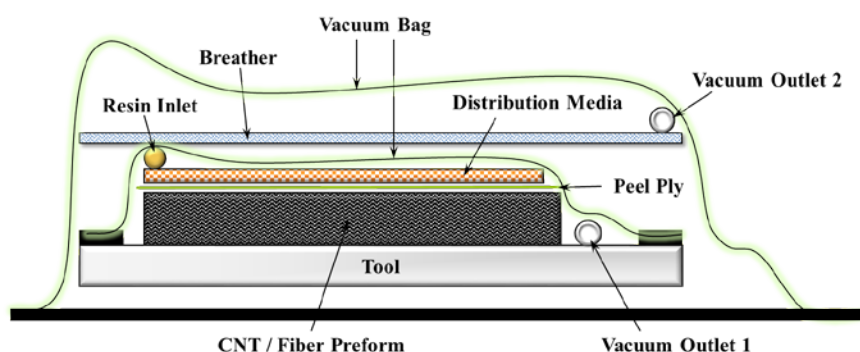


Figure 3. VARTM double-bag setup for manufacturing the nanotube/fiber composites.

2.4. Mechanical and Microscopic Characterization

The morphology of the as-deposited nanotubes and the composite microstructure were examined with optical and scanning electron microscopy. The shear strength of the composite laminates was measured using the double-notch compression (in-plane shear) test based on ASTM D3846-08 [8] and the short beam method based on ASTM D2344 [9]. The composite fiber and nanotube volume fractions were established from density measurements and sulfuric-acid digestion or measurement of optical cross-sections of the laminate after fabrication [10, 11].

3. Results and Discussion

3.1. Carbon Nanotube Morphology

Figure 4 shows the morphology of the as-received carbon nanotubes (Figure 4a) and ultrasonicated PEI-ozone treated carbon nanotubes (Figure 4b) after 16 hours of sonication/ozonolysis time. The as-received carbon nanotubes are highly agglomerated due to their nanoscale entanglement. After dispersion the agglomerates are virtually eliminated. Figure 4c also shows the electrophoretically deposited films of ozone-PEI nanotubes on stainless steel substrates. The films show sub-micron-scale porosity that results from evolved gas produced by water electrolysis. Deposition of the ozone-PEI nanotubes (Figure 4d) onto carbon fibers shows very uniform coverage.

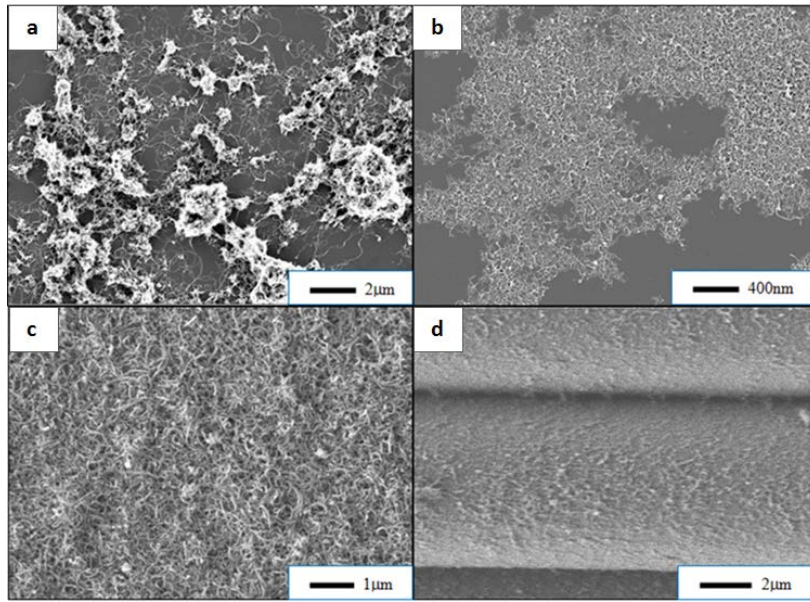


Figure 4. SEM images showing (a) as-received carbon nanotubes, (b) carbon nanotubes after 16 hours of functionalization, (c) electrophoretically deposited nanotubes onto a stainless steel surface and (d) nanotubes deposited onto carbon fibers.

3.2. Mechanical Characterization

Figure 5a shows the short beam strength measured for the untreated carbon fiber-epoxy composites (baseline 1 and 2) compared with the initial composite laminates prepared from the carbon fiber fabric with electrophoretically deposited carbon nanotubes. For both cases the deposition of carbon nanotubes resulted in decreased the short beam strength. In-plane shear strength results for a series of laminates are shown in Figure 5b. The acid treated nanotube laminates show significant reduction in shear strength. For ozone/PEI laminates only one valid test result was obtained, resulting in strength similar to the baseline. The remaining ozone/PEI samples either failed through the notch or away from the central plane.

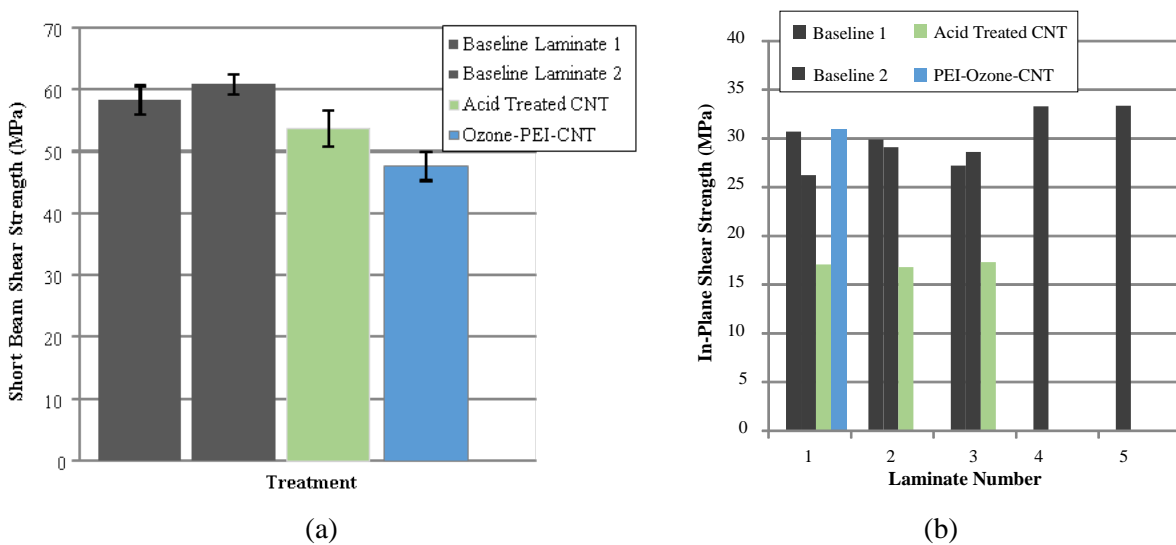


Figure 5. Short beam strength (a) and in-plane shear strength (b) results for unidirectional carbon fiber-epoxy composites with and without electrophoretically-deposited carbon nanotubes produced by infusing all layers together using VARTM.

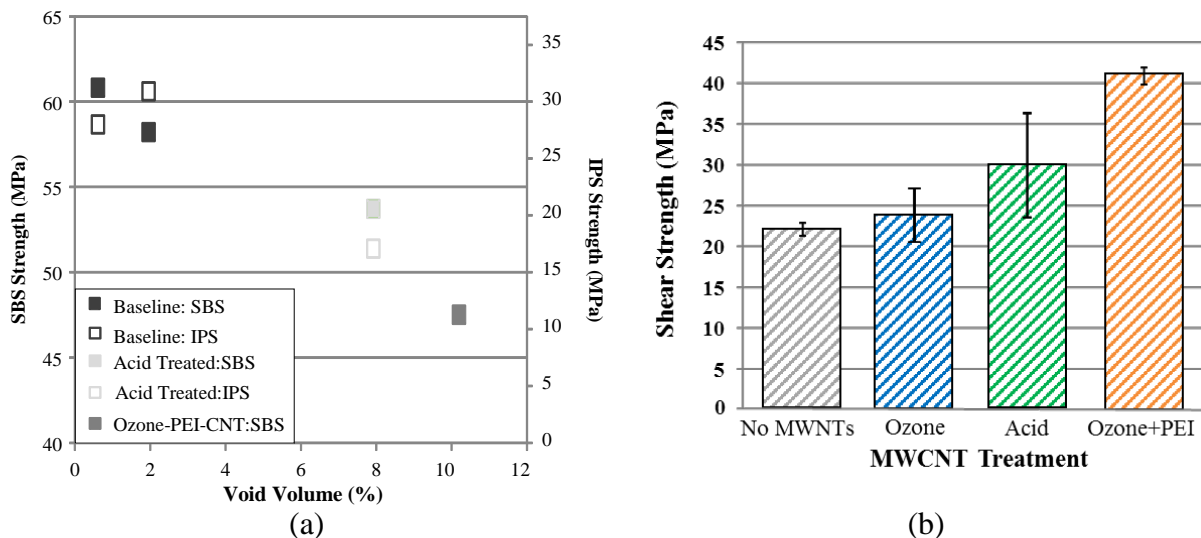


Figure 6. (a) Short beam and in-plane shear strengths as influenced by void fraction for composites where all layers were infused together using VARTM. (b) Shear strength where midplane fabric layers and supporting fabric layers were infused separately and bonded [2].

The decrease in the laminate shear strength with the addition of carbon nanotubes appears to be related to laminate quality. Figure 6(a) shows that there is an inverse correlation between the volume fraction of voids and the short beam and in-plane strengths. The laminates with nanotube layers at the midplane show large amounts of voids. The voids likely result from layers with carbon nanotubes having significantly reduced permeability which impedes the flow front during the VARTM process. In order to overcome these challenges specimens were by infusing four layers of carbon fabric with and without nanotubes separately followed by adhesively bonding laminates without nanotubes to the surface of in order to build-up necessary the thickness for testing. The laminates were bonded to either side of the CNT laminate using an epoxy (EA9309.3 NA, Henkel, USA) followed by room temperature cure and machining of notches to the midplane of the nanotube-treated laminate for in-plane shear strength measurements.

Figure 6(b) shows the in-plane shear strength of the composites where the central layers were infused separately. The ozone-treated nanotubes significantly increase the shear strength but the ozone-PEI treated nanotubes show a 70% increase. The improvement is significantly greater than previously reported improvements in shear properties for carbon/epoxy composites prepared using EPD with PEI-functionalized CNTs [12]. The laminate prepared with the acid-treated nanotubes showed high variability in shear strength. The variability in strength likely results from inhomogeneous-through-thickness distribution of nanotubes.

4. Conclusions

Electrophoretic deposition process for integrating carbon nanotubes into carbon fibers has been established. As compared with *in situ* CVD approaches the electrophoretic deposition approach is a low-energy method that can integrate carbon nanotubes within conventional composite fabric in a controlled manner. The functionalization and dispersion of carbon nanotubes using ultrasonication-ozonolysis and PEI produces highly uniform depositions of nanotubes which can chemically with both the epoxy matrix and fibers in the composite. The addition of carbon nanotubes clearly alters the permeability of the fabric and results in

processing challenges when nanotube composite interlayers are combined with fabric without nanotubes. The introduction of voids results in significantly reduced shear strength. When laminate voids are minimized there are considerable increases in the in-plane shear strength.

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