Abstract

A novel approach for producing multi-scale hybrid carbon nanotubes (CNT)/fiber composites using an electrophoretic deposition (EPD) technique has been studied as an alternative to in situ chemical vapor deposition growth. After integrating the CNTs within carbon or glass fabric using EPD, epoxy is infused using conventional vacuum-assisted resin transfer molding to produce the hybrid composites. Substantial increases in the matrix-dominated shear strength have been observed and are attributed to selective reinforcement of the CNTs at the fiber/matrix interface. In addition, the EPD treated glass-fiber composite shows a significant increase in electrical conductivity. The CNT/glass fiber laminates also exhibited clear changes in electrical resistance with applied shear-strain and can clearly differentiate the elastic and plastic regions of deformation. This resistance-strain relation offers opportunity for multifunctional in situ self-sensing of strain and damage. Alternating current (AC) electrophoresis is also being studied as an alternative to direct current (DC) electrophoresis for production of high quality, low porosity CNT films.

1 Introduction

Recent advances in the synthesis and characterization of nanostructured composite materials have enabled a broad range of opportunities for engineering the properties of polymer-matrix materials. Carbon nanotubes (CNTs) are known to have exceptional mechanical, electrical and thermal properties. Because of their small size, CNTs can occupy regions between traditional micro-scale reinforcements and create a hierarchical micro/nano structure spanning several orders of magnitude. Since CNTs possess critical reinforcement dimensions below 100 nm, new opportunities exist for tailoring the fiber-matrix interphase regions and ultimately the mechanical and electrical properties of advanced fiber-composites with minimal impact on the fiber-dominated mechanical properties. This growing interest in nanoscale hybridization with conventional fiber reinforcement has highlighted the need to develop new processing techniques for successful CNT integration. Similarly, new modeling techniques which can account for the different reinforcement scales are required [1-3].

Carbon fiber reinforced polymer (CFRP) composites offer good in-plane tensile properties for their equivalent weight in comparison with traditional metallic materials; however, they may exhibit poor interlaminar strength and toughness. In recent years, CNTs grown on fibers have attracted a lot of interest as an additional reinforcing component in conventional fiber reinforced composites to modify the properties of the fiber/matrix interface based on their high strength and stiffness on a sub-micron scale. Good interfacial bonding ensures efficient load transfer from the matrix to the reinforcement, which helps reduce stress concentrations and improve overall mechanical properties. There has been tremendous interest in using chemical vapor deposition (CVD) techniques to modify advanced fiber composites by a direct growth of carbon nanotubes in situ on advanced fibers followed by infusion of the polymer matrix [4-6]. CVD is a high-energy process where the high temperatures and reactions of the catalyst with the fiber surface can degrade the fiber tensile properties. Some recent work suggests that CVD conditions may be optimized to minimize fiber degradation [7]. For
glass fibers, the CVD temperatures are also limited by the softening temperature of glass. Another disadvantage of the CVD approach is that the high processing temperatures burn-off existing sizing that is applied to fibers during their manufacture [8-10].

Electrophoretic deposition (EPD) is a widely used industrial coating process employed in areas ranging from automotive to electronics production [11]. The method has a number of assets which include low energy use and the ability to homogenously coat complex shapes with well adhered films of controlled thickness and density [4,12-14]. EPD involves a two-step process in which the particles in solution move between an applied electric field and then deposit onto the electrode surface, forming a film. Successful EPD of CNTs relies on the functionalization, which enables a surface charge to develop. The surface charge, or zeta-potential, is dependent on the solution pH and helps to aid dispersion and mobility under applied electric fields [15-18]. The EPD process has a distinct advantage over CVD processes in that the deposition is carried out under ambient conditions and allows for control of the nanotube purity and chemical functionality.

This research focuses on studying the EPD process for integration of carbon nanotubes within carbon and glass fiber fabric. A novel system which uses temperature controlled, recirculating, high-energy sonication and an ozone generator has enabled the preparation of large volumes of stable-CNT dispersions suitable for EPD. The nanotubes were also functionalized with polyethyleneimine (PEI) to improve adhesion between the CNTs and the fibers. The influence of deposition parameters and CNT functionalization on the mechanical and electrical properties of as-processed nanotube/fiber composites is characterized in order to understand the processing-structure-property relations.

Current work also explores the use of AC-EPD to further enhance deposition quality. Multiple reasons motivate the exploration of AC deposition techniques. Due to the difference in mobility of the CNTs, based on their different sizes relative to charge, AC deposition may be able to regulate the CNT size-distribution in deposited films. An asymmetric-AC waveform may also reduce water electrolysis and the accompanying changes in electrode surface chemistry during the deposition process that could otherwise affect film formation.

These differences may also lead to different film morphologies between DC and AC deposition.

The success of AC deposition relies on the AC waveform employed. Current theory predicts the velocity of charged particles moving in solution is a nonlinear function of the field strength, i.e.

\[ V_{EPD} = \mu_1 E + \mu_2 E^3 \]  

where \( V_{EPD} \) is the net electrophoretic velocity, \( E \) is the field strength, and \( \mu_1 \) and \( \mu_2 \) are electrophoretic mobilities [19]. Therefore, an asymmetrical waveform, such as Fig.1, can provide net particle migration to the electrode with the highest peak-field strength.

\[ \frac{V_2}{V_1} = \frac{T_1}{T_2} \]

Fig.1. Example asymmetrical waveform for net electrophoretic motion.

\[ \frac{V_2}{V_1} = \frac{T_1}{T_2} \]

2 Experimental

2.1 Nanotube Dispersion and Functionalization

Aqueous dispersions of multi-walled carbon nanotubes (CM-95, Hanwha Nanotech, Korea) were oxidized using ultrasonication-ozonolysis for 16 hours. The setup for ultrasonic ozonolysis is shown in Figure 1. Oxygen was passed through a corona-discharge ozone generator (1000BT-12, Taoture International) at a flow rate of 500 mL/min and bubbled into the MWCNT solution held at an isothermal temperature of 5°C. Ozone levels, determined by iodometric titration [20], reached 20 mg/L after 2 hours. A peristaltic pump (Model MU-D01, Major Science, USA) circulated the MWCNT solution into the sonicator cell (800B Flocell, Qsonica, USA). High-powered sonication (Sonicator 3000, Misonix, USA) used a 12.7mm diameter horn operating at 60W and pulsed with a duty cycle of 15 seconds on and 10 seconds off. The total processing
time during ozonolysis was 16 hours and CNT concentrations for all solutions were 1.0 g/L (Fig. 2).

Fig. 2. Recirculating system used to prepare the CNTs aqueous solutions [21].

An alternative functionalization technique for CNTs involves the use of polyelectrolytes [22]. The ozone-treated MWCNTs were also mixed with polyethyleneimine (H(NHCH₂CH₂)₃₅NH₂, Mw: 25,000 Sigma–Aldrich, USA) at equal concentration to the MWCNTs and sonicated for an additional 4 hours. Although PEI has a high-natural pH in solution the addition of acid allows the amine groups to protonate and Sun and Gao [23] demonstrated that a +50 mV zeta-potential can be established below a pH of 8. The PEI and ozone-treated MWCNT 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 CNT coating but without CNTs present.

2.2 Electrophoretic Deposition (EPD)

2.2.1 Direct current (DC) deposition

The deposition parameters for the ozone-functionalized MWCNTs onto carbon fibers were conducted under a DC field strength of 43 V/cm and the ozone and PEI-functionalized MWCNTs were deposited at 28 V/cm. The lower field-strength for the PEI-MWCNT deposition reduced Joule heating of the higher-conductivity solution. Deposition times of up to 40 min were used to coat stainless steel (316 SS McMaster-Carr, USA) and unidirectional carbonfiber (T700S, Soller Composites, USA) substrates. The stainless steel substrate was used to characterize the as-deposited film morphology. Carbon-fiber deposition used the set-up in Fig. 3.

For glass fibers a different deposition approach was required because the fabric, itself, is non-conductive. EPD of the ozone and PEI functionalized CNTs onto the glass-fiber fabric used a fabric tensioning device, shown in Fig. 4, which enabled intimate contact between the fabric and cathode to facilitate a uniform coating. The fabric tensioning device enabled the anode, cathode and tensioned E-glass unidirectional fabric (Style 7721, 203 g/m², APS sizing, Thayercraft Inc., USA) to be immersed horizontally in the CNT solution. Cathodic deposition used field strengths between 12 and 64 V.cm⁻¹ and deposition times between 10 and 75 minutes. Double-sided coating reversed the fabric surface in contact with the cathode after initial deposition.

2.2.2 Alternative current (AC) deposition

AC deposition onto stainless-steel substrates (Type 316 Stainless Steel Shim, Trinity Brand Industries, Inc.) examined the effects of materials processing and waveform parameters using the arrangement shown in Fig. 5. AC depositions used a function
generator (RIGOL DG1022A) and an AC amplifier (EPX4000 Stereo Power Amplifier) to supply power to the electrode assembly.

![Fig.5. Schematic of electrode and AC deposition setup.](image)

### 2.3 Composites Manufacturing

After electrophoretic deposition the fabrics were sealed in a vacuum bag and dried under vacuum using a semi-permeable membrane (Gore Technologies, USA). The dry, MWCNT coated and uncoated carbon and glass fabric layers were infused using conventional vacuum assisted resin transfer molding (VARTM) with EPON 862 and Epi-Kure W (Hexion Specialty Chemicals) at a ratio of 100/26.4. Infusion of the vacuum-degassed resin occurred under full vacuum (-100 kPa) and 55 °C using a flow media to aid through-thickness resin diffusion followed by curing at 130°C for 6 hours. Baseline laminates without nanotubes were also produced using the same VARTM technique and cure cycle.

### 2.4 Surface Analysis & Thermal Characterization

Surface analysis was conducted using x-ray photoelectron spectroscopy (XPS; Kratos Nova, U.K.) and scanning electron microscopy (SEM). XPS spectra were obtained using a monochromatic Al \(K_{\alpha1}\) source operating at 150 W and an analysis area of 700 x 300 \(\mu m^2\) with an electron flood gun to neutralize charge build-up on the insulating samples. SEM (JEOL JSM-7400F and LEO 1530VP) was used to characterize the CNT-film morphology after functionalization and electrophoresis, as well as the composite fracture-surfaces. An accelerating voltage of 3 kV was used with either a 5 nm Pt/Au or 1.5 nm Ir layer to prevent charging.

A thermogravimetric analyzer (TGA) (Mettler-Toledo, TGA/DSC 1 STARe), was used to analyze the MWCNTs after functionalization. Samples were heated from 30 to 1000 °C at a ramp heating rate of 2 °C min\(^{-1}\) under a nitrogen flow rate of 80 mL min\(^{-1}\). Dynamic mechanical thermal analysis (DMTA) of the composites with the CNT treatments used a Polymer Laboratories DMTA Mk III. Samples were tested in single cantilever bending (0.1% strain, 1 Hz) using a temperature ramp rate of 5 °C/min to measure the glass transition temperature (\(T_g\)) of the matrix from the onset of the decrease in storage modulus over a 60 °C to 250 °C range.

### 2.5 Mechanical and Electrical Characterization

Shear strength test specimens were prepared by adhesively bonding laminates without nanotubes to the surface of the as-produced CNT/fiber composites in order to build-up necessary 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 mid-point of the CNT-treated laminate. Prior to bonding the outer surface of each laminate was lightly sanded, followed by cleaning with distilled water and a final treatment with an Atomflo\textsuperscript{TM} plasma unit (Surfx Technologies, USA).

The in-plane shear strength of the composite laminates was measured using the double-notch compression test based on ASTM D3846-02 [25]. Shear strain was monitored using biaxial-strain gauges and the elastic region was determined from 2000 \(\mu e\) to 6000 \(\mu e\). 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 [26,27].

Electrical conductivity measurements of the nanotube/glass fiber composites were conducted using a Keithley 6430 sub femtoamp remote sourcemeter with a constant source voltage of 20V (ASTM D257-07) [28]. Electrode surfaces were polished and coated with silver paint prior to application of electrodes using conductive silver epoxy resin. In addition, electrical and mechanical measurements were recorded simultaneously using a customized data acquisition system.

### 3 Results and Discussion
3.1 Chemical Characterization

Changes in the surface chemical composition of the electrophoretically deposited CNTs after ozone and PEI functionalization are summarized in Table 1. The major changes are associated with an increase in oxygen and nitrogen due to the ozone and PEI treatments, respectively.

Table 1. Elemental concentrations for EPD films of CNTs functionalized by ozone and PEI [24].

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Atomic Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O 1s</td>
</tr>
<tr>
<td>CNTs</td>
<td>0.55</td>
</tr>
<tr>
<td>OZONE-PEI”</td>
<td>11.39</td>
</tr>
<tr>
<td>OZONE-PEI”a</td>
<td>10.61</td>
</tr>
</tbody>
</table>

a Trace levels of Fe, Mo, Na, Al, F
b Trace levels of Fe, Mo detected

3.2 Thermal Characterization

Fig. 6 shows the TGA results for the MWCNTs after ultrasonic-ozonolysis and PEI-functionalization. The results suggest that the EPD coating contains around 25% PEI, which is within the range estimated from the XPS measurements. The decomposition temperatures are also quite similar to those reported for benzoic acid and PEI-functionalized CNTs [29].

Table 2 shows the $T_g$ values for E-glass/epoxy composites with varying CNT volume-fractions. The results indicate that even with the high CNT volume-fractions of CNTs and PEI in the matrix, the epoxy cross-linking reactions have not been affected [30].

Table 2. Glass transition temperatures ($T_g$) for CNT treated E-glass/epoxy laminates indicating volume fraction of CNTs ($V_{CNTs}$) and PEI ($V_{PEI}$) in the matrix ($V_m$) [24].

<table>
<thead>
<tr>
<th>Base-line</th>
<th>CNT-1</th>
<th>CNT-2</th>
<th>CNT-3</th>
<th>CNT-4</th>
<th>CNT-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{CNTs}$/$V_m$ (%)</td>
<td>0</td>
<td>14</td>
<td>12</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>$V_{CNTs}$/$V_{PEI}$ (%)</td>
<td>0</td>
<td>17</td>
<td>14</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>$T_g$ (°C)</td>
<td>142</td>
<td>141</td>
<td>138</td>
<td>142</td>
<td>141</td>
</tr>
</tbody>
</table>

3.3 Film Growth and Characterization

3.3.1 Nanotube deposition on conductive substrates

Fig. 7 shows the film morphology of the untreated (Fig. 7a) and ultrasonicated PEI-ozone treated MWCNTs (Fig. 7b) at 16 hours treatment time. The images show a clear reduction in the number of agglomerates, with the film produced after 16 hours treatment exhibiting a good homogeneity. Fig. 7 also shows the EPD films deposited on stainless steel produced from the ozone-PEI MWCNTs (Fig. 7c). The film shows sub-micron-scale porosity resulting from evolved gas produced by water electrolysis, but indicates a film free of large-CNT clusters, although some smaller agglomerates below 50nm are present. EPD of the ozone-PEI MWCNTs (Fig. 7d) onto the T700S carbon-fibers for short treatment times shows very uniform coverage and similar porosity to the films deposited on the planar stainless-steel surfaces.
SEM images of the deposited films at 1 minute (Figure 8a) and 20 minutes (Figure 8b) suggest that sub-micron porosity of the film increases with deposition time due to vigorous gas evolution.

Fig. 8. SEM micrographs indicating the change in film morphology with deposition times of ozone-PEI MWCNTs: (a) 1 minute (b) 20 minutes [21].

Preliminary AC deposition of CNTs has shown promising results. Fig.9b shows the AC-EPD of ozone-functionalized carbon nanotubes on a stainless-steel substrate. A comparison with DC ozone-functionalized CNT films (Fig.9a) reveals significantly less agglomerates and a very even film. This might be due to the reduced mobility of the large agglomerates within the solution, relative to DC-EPD, attributable to the nonlinear particle-velocity dependence resulting from the asymmetric-AC waveform employed (Equation [1]).

AC results also showed a strong dependence on waveform shape, frequency, and solution concentration. While necessary to maintain a frequency high enough to avoid electrolysis (<~20Hz), it was observed that too high of a frequency did not allow efficient particle movement. An optimal frequency of approximately 50Hz has been identified, though further optimization is necessary. Furthermore, results were inconsistent with CNT solution concentrations less than 4 g/L. Work continues to modify the waveform shape to achieve optimal deposition rates and quality.

3.3.2 Nanotube deposition on nonconductive substrate

Fig.10 estimated the CNT deposition rate dependence on field strength. The deposition rate is compared to that measured for carbon fibers. The glass deposition rate at the same field strength is about the same as on carbon where the solution concentration was only 0.5 g/L, which suggests that the deposition rate on glass is around half that observed on carbon fibers. The reduced rate may be expected as the film deposition process on nonconductive substrate would differ to a conducting substrate. Once a sufficient quantity of CNTs precipitates onto the glass fibers and reaches the electrical percolation threshold the glass then behaves like a conductive substrate.

Fig. 10. Film deposition rate as a function of field strength for E-glass and carbon-fiber fabric [24].

Fig.11 shows CNTs deposited on the E-glass fiber from the CNT dispersion at 25 V/cm for 15 minutes. The film appears to be compact with the CNTs embedded in the PEI polymer. The outer surface of the fabric (Fig.11a and 11b) shows a uniform film around 2 μm thick. Deeper into the fabric tow (Fig.11c) the film appears to reduce with thicknesses between 50 and 200 nm. This trend in thickness also confirms that once the fiber bundles reach electrical percolation and become conductive the film builds up at a faster rate on the outer fiber surface.
Fig. 11. SEM images of the E-glass fiber after EPD coating with the ozone and PEI-functionalized CNTs indicating (a) the outer fiber surface, (b) a cross-section through the outer coating, (c) coating towards the fiber-tow interior [24].

### 3.4 In-plane Shear Strength

Fig. 12 shows the in-plane shear strength for the carbon/epoxy laminates as a function of deposition time as well as weight percentage of the functionalized CNTs on the fabric. The results indicate that there is a significant increase in shear strength with deposition time. The maximum increase in shear strength is about 70% at 13% CNT volume fractions. The increase in strength at 40 minutes deposition time, where the increase in MWCNT weight is small must be related to changes in the CNT-coating morphology and distribution.

Fig. 13. In-plane shear strength measured for E-glass/epoxy laminates with different CNT volume fractions [24].

### 3.5 Laminate Characterization

Fracture surfaces for carbon/epoxy and E-glass/epoxy composite are shown in Fig. 14 and Fig. 15. Progressively, two changes in the interfacial fiber to matrix fracture can be observed. Firstly, there appears to be an increase in the plasticity of the fracture in the resin-rich interlaminar area, which corresponds to higher MWCNT concentrations in the matrix. Secondly, the baseline fiber surfaces show thin-localized islands of resin where some failure in the resin interphase has occurred. The percentage of failure within a thin, MWCNT-resin-rich layer on the fiber surface appears to increase for the CNT coated laminate compared to the baseline laminate, which indicated that the strength is strongly influenced by the adhesion strength at the fiber-epoxy interface and affected by a thin heterogeneous resin interphase region. Both these changes in fracture appearance would suggest that there is a better coverage of MWCNTs and improved bonding between the MWCNT coating and the as-received sized-fiber is established, which would both be expected to contribute to the improved mechanical strength.
3.6 Electrical Properties

The volume conductivity for the CNT treated E-glass/epoxy laminates is shown in Fig.16 for measurements taken parallel and normal to the fiber direction. A fit to the data used the classical equation from percolation theory,

\[ \sigma = \sigma_0 (p - p_c)^t \]

[2]

where \( \sigma \) is the volume conductivity, \( \sigma_0 \) is a fitted constant indicative of the reinforcement conductivity, \( p \) is the reinforcement concentration, \( p_c \) is the critical reinforcement concentration for percolation and \( t \) is the exponent relating to the matrix microstructure and reinforcement aspect ratio. The best fit values for the conductivity results in Fig.16 estimate the exponent \( t \) at 1.35 and 1.2 and a percolation threshold of 0.1% and 0.7% for the parallel and normal directions, respectively.

4 Conclusions

Electrophoretic deposition can be successfully applied tocoat practical carbon and E-glass fabrics with high concentrations of CNTs, which also offered a low-energy method to modify the multifunctional properties of hierarchical composites in a controlled manner. The functionalization of
CNTs using ultrasonication-ozonolysis and PEI produces highly uniform depositions of CNTs which chemically link with both the epoxy matrix and sized fibers in the composite laminates. Considerable increases in the in-plane shear strength of the hierarchical composite laminates resulted from the EPD treatment with CNTs. CNT-modification led to significant increases in glass/epoxy laminate conductivity that was comparable to polyimide based nanocomposites. The CNT-treated glass/epoxy laminates also exhibited electrical-resistance sensitivity to applied shear-strain, with the rate of change dependent on the extent of plastic deformation.

Preliminary AC work has shown significant promise for reducing the presence of agglomerates in deposited CNT-films and achieving increased film uniformity. Ongoing research seeks to modify the AC waveform to achieve improved deposition rates and quality. Future work will focus on using AC deposition to deposit CNTs onto reinforcing fibers to enable further development of multifunctional composites.

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6 References


