MULTI-SCALE HYBRID COMPOSITES: CARBON NANOTUBE FILM FORMATION ON NON-CONDUCTIVE FIBERS USING ELECTROPHORETIC DEPOSITION

Aris D. Mardirossian¹, Sagar M. Doshi², Andrew N. Rider³ and Erik T. Thostenson⁴

¹ Department of Mechanical Engineering and Center for Composite Materials, University of Delaware, Newark DE 19716 USA, admard@udel.edu

² Department of Mechanical Engineering and Center for Composite Materials, University of Delaware, Newark DE 19716 USA, smdoshi@udel.edu

³ Defence Science and Technology Research Group, Fisherman’s Bend VIC 3207, Australia andrew.rider@dst.defence.gov.au

⁴ Department of Mechanical Engineering, Department of Materials Science & Engineering and Center for Composite Materials, University of Delaware, Newark DE 19716 USA, thosten@udel.edu

Keywords: Carbon Nanotubes, Hybrid Composites, Electrophoretic Deposition

ABSTRACT

The hybridization of micro and nano scales has broad potential developing multifunctional composite materials. Multi-scale hybrid composites composed of carbon nanotubes (CNTs) and traditional advanced fibers have a hierarchical reinforcement structure. This difference in the reinforcement scales enables carbon nanotubes to selectively reinforce the fiber/matrix interface as well as the interlaminar region in between plies. Carbon nanotubes also are electrically conductive and networks of carbon nanotubes can be formed throughout the composite enabling the tailoring of both structural and functional properties. This current research studies electrophoretic deposition (EPD) as a means to deposit CNTs onto the surfaces of non-conductive fibers. Our characterization results show that CNT films deposit initially on the cathode and form coatings on contacting fibers. The film then continues to grow throughout the fiber bundle by bridging between fibers, extending the electrode into the fiber bundle. In order to visualize the growth of the film from the electrode two substrates with rough surfaces were utilized to view the growth of the film starting at the anode.

1 INTRODUCTION

The properties of composites can designed by controlling the microstructure and the phase interactions (reinforcement-matrix interface). The emergence of nanotechnology has enabled the tailoring of properties at smaller length scales. Through hybridization of traditional fiber reinforcements (microns in diameter) with carbon nanotubes the opportunity exists to achieve new properties and functionality by designing nanoscale structures and interactions. Multi-scale hybrid composites composed of carbon nanotubes (CNTs) and traditional advanced fibers have a hierarchical reinforcement structure. This difference in the reinforcement scales enables carbon nanotubes to selectively reinforce the fiber-matrix interface as well as the interlaminar region in between plies. While CNTs possess a number of remarkable mechanical properties, including high Young’s modulus and strength, they are also electrically conductive. The large aspect ratio (length/diameter) of carbon nanotubes enables the formation of electrically conductive networks within the polymer matrix. This hierarchical, electrically conductive structure can be utilized as nerve-like sensors for detection strain and cracks in situ. [1].

Initial approaches at producing these composites focused on growing carbon nanotubes directly on the surfaces of fibers using chemical vapor deposition (CVD) [2-5]. The high temperature chemical growth conditions of the CVD process (600°C – 1000°C) has been shown to degrade the properties of the reinforcing fibers and can alter the surface by removing the fiber sizing. Electrophoretic deposition (EPD) has been recently established as a technique for micro/nano hybridization that exceeds traditional
CVD in numerous performance characteristics. Unlike CVD, EPD does not degrade the properties of the reinforcing fibers. EPD is also an industrially scalable process for future applications.

Initial research on EPD of carbon nanotubes focused on the deposition of nanotubes onto carbon fibers. Because carbon fibers are electrically conductive they act as the electrode for deposition [5-8]. This process has been recently extended to non-conductive fibers by backing the fibers with an electrode [9, 10]. The resulting composites showed a significant increase in composite shear modulus and strength. Model experiments showed that the functionalized carbon nanotubes form chemical bonds with the glass fiber surface which plays a major role in the improvement in strength. The current research work examines the growth of the carbon nanotube film within the fiber bundle during the EPD process.

2 EXPERIMENTAL

Electrophoretic deposition utilizes an electric field to move charged particles in a solution to precipitate onto a substrate. EPD has been widely embraced by industry as an effective coating mechanism for materials of various complexities and geometries. While the practice and application of EPD varies, in its simplest form, an applied voltage potential between two conductive plates submerged in a solution will cause charged particles to approach and precipitate onto an electrode. The charge of the depositing particles determines which electrode (anode or cathode) will be coated. The deposition yield can be represented by Hamaker’s equation [11]:

\[ w = \int_{0}^{t} \mu \cdot E \cdot A \cdot C \cdot dt \]  

where deposition yield \( w \) is correlated to electric field strength \( E \), the electric mobility \( \mu \), the surface area of the electrode \( A \), and the particle mass concentration in the suspension \( C \). Figure 1 shows a schematic of the electrophoretic deposition process for nanoparticles distributed in a fluid.

![Figure 1: The voltage potential applied between the two charged plates creates a magnetic field that moves and precipitates the negatively charged nanoparticles toward the anode.](image)

The current study focuses on depositing onto various substrates located between two stainless steel electrodes (Type 316 Stainless Steel Shim, Trinity Brand Industries, Inc.) to characterize the carbon nanotube film formation. The stainless steel electrodes were attached to a non-conductive glass fiber composite keep the electrodes planar. Prior to deposition, the electrodes are sanded with 400 and 600 grit sandpaper and sonicated in deionized water. The electrode spacing was held constant by inserting 3 mm non-conductive spacers between the electrodes. Figure 2 shows a schematic of the electrode and deposition assembly and photographs of the electrode configuration. For deposition onto different substrates, such as glass fibers, they were attached to the electrode and the entire assembly connected with a binder clip. The depositions were carried out using a DC power supply that provides the desired voltage potential to the electrodes submerged in 40 mL of the functionalized carbon nanotube solution in a 50 mL glass beaker. A field strength of 40 V/cm was used for all depositions in this study.
Functionalization of the carbon nanotubes is essential for the EPD process in that the surface functionality imparts a charge to the nanotubes. This charge stabilizes the dispersion of nanotubes in water and also enables particle mobility and subsequent motion under an applied electric field. A process known as ultrasonic ozonolysis (USO) is used to break-up carbon nanotube agglomerates and oxidize the carbon nanotube surface. A schematic of the USO process is shown in Figure 3. The carbon nanotubes are first mixed in ultra-pure water and the mixture is then pumped through continuous flow sonicator cell (Sonicator 3000, Misonix, USA – 12.7 mm horn diameter at 60 W) while bubbling ozone gas in the mixture (1000BT-12, Taoture International). This dispersion is then sonicated for 16 hrs to produce stable solutions [x]. The carbon nanotubes used in the current work are multi-walled carbon nanotubes (CM-95, Hanwha Nanotech, Korea). Three substrates are deposited onto in the current study. Results are attained and characterized based on results from the deposition onto unidirectional e-glass fibers. Composites for microscopic characterization were then consolidated using vacuum assisted resin transfer molding (VARTM) as described in our previous work [8]. To further visualize the film growth depositions were also conducted onto a planar glass fiber composite surface (Garolite G10 FR4) and a 3-D printed preform with a 45° surface texture.

Figure 3: USO functionalization process for carbon nanotubes [8].
3 RESULTS AND DISCUSSION

As established in our previous research [xx] it is important to have direct contact between the fibers and the backing electrode. Initial experiments revealed that the deposition occurred first on the electrode and then extended to the fiber surfaces. Carbon nanotubes is not simply a physically onto the surface of the fabric but rather the positively charged nanotubes deprotonate due to the electrolysis of water and precipitate locally near the electrode. Figure 4 shows photographs of carbon nanotubes deposited onto glass fibers where the tension of the fabric was reduced, allowing the evolved gas due to electrolysis to lift the fabric off of the cathode. This lack of intimate contact between substrate and electrode caused a non-uniform deposition of carbon nanotubes onto the fabric where the edges that were in contact were coated uniformly. For properly tensioned fabric the nanotubes uniformly coated the fibers, resulting in a highly uniform black coating over the fibers. As shown in Figure 4, the fabric primarily lifted away from the electrode near the center of the fabric and is non-uniformly coated by CNTs. This initial observation of non-uniform coating lead to the hypothesis that the carbon nanotubes deposit first on the backing electrode and that the film then grows over the fibers. Because the deposited carbon nanotubes are conductive, the resulting film becomes an extension of the electrode.

![Figure 4: Photographs showing non-uniform deposition of CNTs on the surface of unidirectional e-glass fibers due to improper pre-tension applied to the fabric prior to deposition.](image)

For fibers with uniform deposition across the surfaces, composites were manufactured using VARTM and were cross-sectioned for microscopic characterization. Figure 5 shows optical micrographs of the cross-sections at varying deposition times. In all micrographs it is evident that there is bridging of the carbon nanotube network between the individual fibers. At longer deposition times there is a larger accumulation of nanotubes on the surface near the anode. Initially the nanotubes appear to deposit on the cathode and then extend onto the fibers. As the film grows throughout the fiber network the electrical percolation of the carbon nanotubes extend the electrode throughout the fiber bundle. At long deposition times, a film on the outer side of the fabric (facing the cathode) starts to build up. We hypothesize that the carbon nanotubes reach electrical percolation throughout the fiber bundle and that the accumulation of nanotubes on the surface results from the fiber bundle, itself, becoming the electrode. Direct observation of the cross-sections of the as-manufactured composite show that a dense film of CNT forms around the cross section of individual fibers and attach themselves to the non-conductive fiber by extending and attaching individual CNTs to the surface of the fiber (Figure 6). Fibers near the anode show a thicker film has accumulated.
Figure 5: Optical micrographs of e-glass fiber substrates following EPD for 15 minutes (left), 20 minutes (right top), and 10 minutes (right bottom). Substrates oriented with bottom surface in intimate contact with anode and top surface facing cathode.

Figure 6: Higher magnification scanning electron micrographs of single fiber cross sections surrounded by CNT film following EPD.

To understand the growth of the carbon nanotube film from the electrode different planar substrates with surface texture were used for deposition. Figure 7 shows the growth of the film over a glass-epoxy surface that was roughly cut using a diamond saw. It is clear that the film extends from the cathode (bottom) and grows towards the anode. It was observed that the film tended to grow around regions that protrude from the planar surface. Carbon nanotubes tended to build-up in the inset regions of the surface while those areas that protrude were not uniformly coated. Additional experiments were conducted on 3-D printed, ABS plastic substrates (Figure 8), where only the lower surface was in intimate contact with the cathode, displayed trends where CNT film would grow within the intersections of diagonal print lines. Despite ABS plastic being inherently hydrophobic, the CNT film would continue its growth toward the anode, extending the conductive network from the cathode.
Figure 7: Growth of a carbon nanotube film over an e-glass composite surface where the film initiates growth from the anode (a) 0 minutes, (b) 2 minutes, (c) 3 minutes and (d) 5 minutes.

Figure 8: Substrate on CNT coated cathode following deposition (left foreground) with non-coated anode behind (left background). Optical micrograph showing the growth pattern of CNT up the substrate (right). CNT film following least resistive path toward anode.

5 CONCLUSIONS

The current study has shown significant insight into the mechanism of carbon nanotube film growth on by electrophoretic deposition. Gathered from the results, it can be understood that CNT film deposits initially begin at the cathode and forms coatings on contacting fibers. The film then continues to grow throughout the fiber bundle by bridging between fibers, extending the conducting pathways throughout the fiber bundle. Additionally, CNT film growth will likely take the least resistive path toward the anode, if significant obstructions are present. Additionally, future work will focus on developing a process which will allow for large scale production of hybridized multifunctional composites using EPD. The
knowledge gained from the current study was critical in providing a foundational understanding of the mechanism of carbon nanotube film growth so that we can move forward with these future ventures.

ACKNOWLEDGEMENTS

The authors from the University of Delaware gratefully acknowledge US National Science Foundation for funding this research (Grant #: 1254540—Dr. Mary Toney, Program Director).

REFERENCES