

HYBRIDIZATION OF CARBON NANOTUBE-GLASS FIBER BASED HIERARCHICAL COMPOSITES USING ELECTROPHORETIC DEPOSITION

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ABSTRACT

Hybridization of nanomaterials such as carbon nanotubes with advanced textiles such as glass and carbon fiber enables the creation of hierarchical composites. Traditionally, the hierarchical composites were manufactured using chemical vapor deposition, which is an expensive and energy intensive process and may cause damage to the textiles due to extreme temperatures involved. In this research, we discuss the characterization and applications of hierarchical composites manufactured using a scalable, aqueous dispersion based electrophoretic deposition process. The carbon nanotubes (CNTS) are functionalized with a dendritic polymer polyethylenimine (PEI) which gives the nanotubes a positive charge in the aqueous dispersion. Using electric field, the positively charged PEI functionalized carbon nanotubes are deposited on the cathode. The EPD process is inherently scalable since no harsh chemicals are used and the process can be performed at room temperature.

Along with being a scalable process, the key advantages of this process are its ability to coat conductive and non-conductive substrates and the ability to control the thickness of carbon nanotube coating on the surface of the fibers by varying process parameters such as time of deposition, functionalization of carbon nanotubes, electric field strength and concentration of carbon nanotubes. The mechanism of film formation using EPD is characterized and the influence of processing parameters on the film growth is investigated. A variety of fabrics such as cotton, wool, nylon, polyester and glass fiber are coated.

1. INTRODUCTION

Traditionally, the hierarchical composites were manufactured using chemical vapor deposition, which is an expensive and energy intensive process and may cause damage to the textiles due to extreme temperatures involved. [1] An alternative method to prepare the hierarchical composite materials is electrophoretic deposition (EPD) which is performed at room temperature, without harsh chemicals and low energy consumption. [2-4] The EPD process also offers the opportunity for scale-up using a roll-to-roll approach. Another key advantage of this process is the control over

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the thickness of the carbon nanotube coating by varying the processing parameters such as time of deposition, functionalization of carbon nanotubes, electric field strength and concentration of carbon nanotubes.

Functionalized CNTs were initially deposited on conductive fabric such as carbon fiber. In this case, the carbon fiber is used as one of the electrodes. [2,3] The same technique cannot be used for non-conductive fibers such as glass and aramid. In this case, an additional backing electrode enables deposition. When coating non-conductive fibers, the fabric is placed in direct contact with a stainless steel electrode. The deposition initiates at the electrode surface and the film grows on the fibers in direct contact with the electrode. As the CNT film deposits onto the fibers they become conductive and the electrode effectively extends into the fabric as the conductive nanotube film grows outwards. In this research, the mechanism of film formation of PEI functionalized CNTs on non-conductive fabrics is discussed.

2. EXPERIMENTAL

2.1 Materials

Multi-walled carbon nanotubes (CM-95, Hanwha Nanotech, Korea) were oxidized using ultrasonicated ozonolysis (USO), which is followed by functionalization of polyethyleneimine (PEI, $\text{H}(\text{NHCH}_2\text{CH}_2)_{58}\text{NH}_2$, M_w 25000, Sigma Aldrich, USA). [2] The concentration of the CNT dispersion could be adjusted, but was typically 1 g/L. The pH of the dispersion was adjusted by glacial acetic acid (Sigma-Aldrich) to a pH of 5.8 in order to positively charge the CNTs. Astroquartz III (JPS Composite Materials, USA), a type of glass fiber, woven into 8 harness satin weave fabric was used as a model fabric. To validate the mechanism of CNT film formation on non-conductive fibers, glass fiber epoxy composite plates and rods were also prepared. A 3-D printed fixture was designed to ensure that the glass fabric remained in direct contact with the cathode. The fixture maintained a uniform gap of 3 mm between the cathode and anode. (Figure 1)

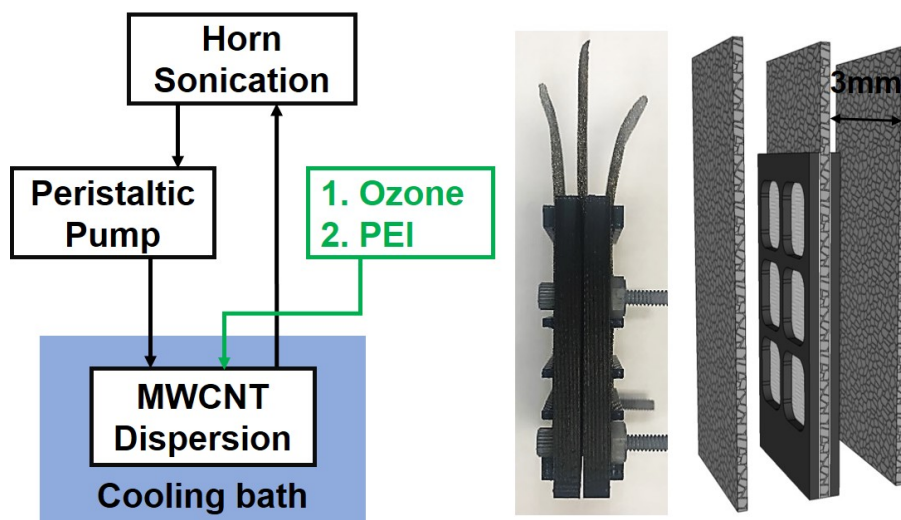


Figure 1 A schematic diagram of MWCNT dispersion preparation and the 3-D printed fixture.

2.2 Composite Manufacturing and Characterization

The glass fabric was dried at 85°C after deposition of the CNTs using EPD which was followed by vacuum assisted infusion with epoxy resin and amine curing agent (EPON 862 and Epi-Kure W, Hexion Specialty Chemicals, USA). To obtain cross-sectional images the composites are polished with silicon carbide polishing paper followed by aluminum oxide colloidal particles. Optical microscopy and scanning electron microscopy were used to examine the CNT films deposited onto the glass fibers.

3. RESULTS AND DISCUSSION

3.1 EPD on Non-Conductive Fabric

EPD enables the CNT deposition onto a variety of non-conductive fabrics such as glass fiber [4], aramid [6] and wool [6], which can be in forms such as woven, non-woven and knitted. Scanning electron micrographs in the Figure 2 show the electrophoretically deposited CNTs on various non-conducting fabrics. They are non-woven random mat of aramid fiber, knitted polyester/nylon fabric and Astroquartz III from the left to the right of the figure. It is observed that functionalized CNTs are uniformly coated on each filament and throughout the fabric regardless of the fabric material and its weaving pattern. It is possible to control the thickness of the CNT films by varying the process parameters such as deposition time, electric field strength, pH of the dispersion, functionality of the CNTs and CNT concentration.

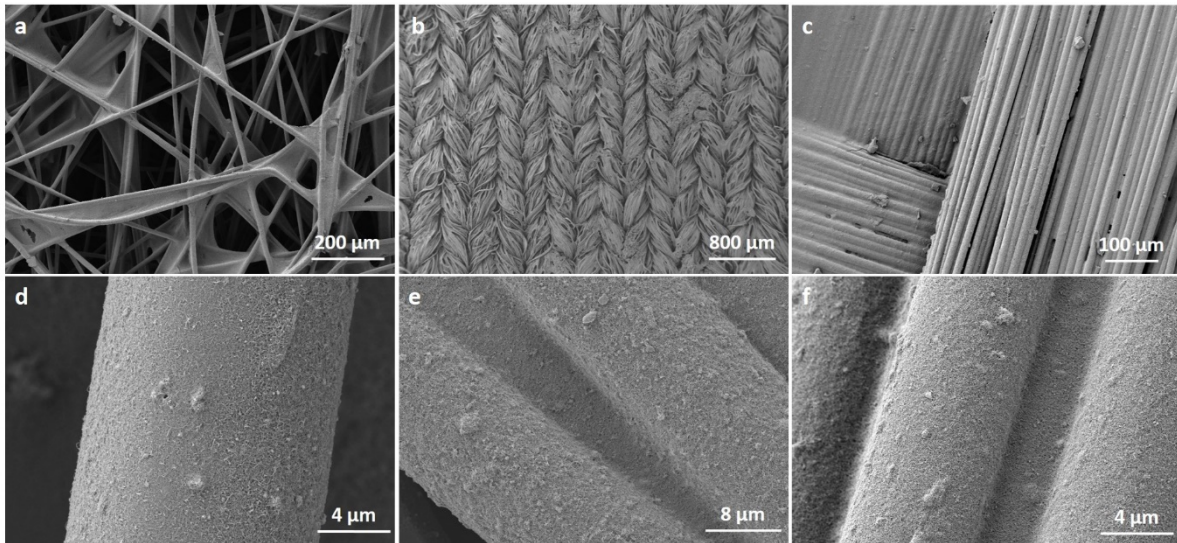


Figure 2 SEM images of electrophoretically deposited non-conductive fabrics. (a, d) Random mat aramid fiber, (b, e) Knitted mix polyester fabric and (c, f) Astroquartz III glass fiber.

The CNT film deposited onto the Astroquartz III fibers was investigated through observing polished samples of the Astroquartz III fiber/CNT/epoxy composite using a scanning gallium ion micrography (SGIM), shown in Figure 3a. Gallium ions can produce a high contrast image between the conductive and insulating materials. The accumulated positive charge of gallium ions can lower the secondary electron emission in the insulating regions. [7] The magnitude of applied electric field and the deposition time were 16.7 V/cm and 10 minutes, respectively. The microstructure shows a thick 2-3 μm film on the outside of the fabric. A bright ring is also observed around individual fibers, indicating a thin coating of CNTs. Figure 3b shows the Astroquartz III

surface in contact with cathode before infusing the epoxy resin showing that the CNT film bridges between the individual filaments.

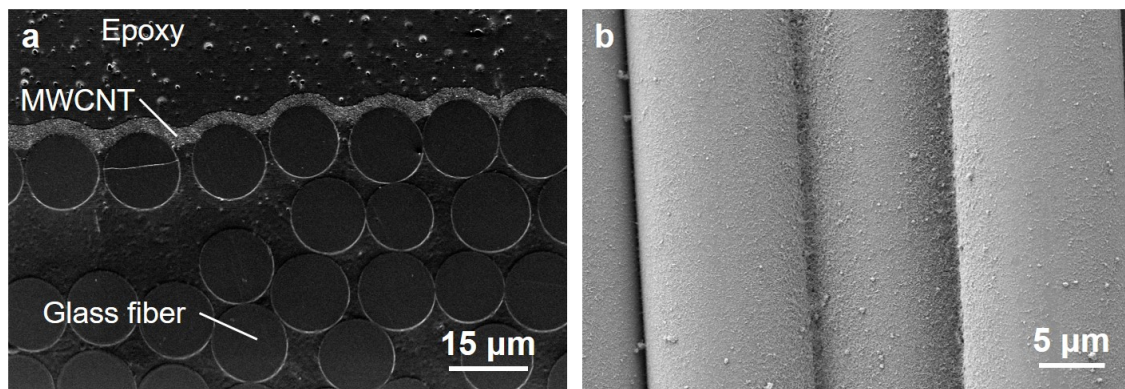


Figure 3 (a) Gallium ion imaging of Astroquartz fiber/MWCNT/epoxy composite cross-section after EPD and (b) SEM image of CNT coated Astroquartz III in contact with the negative electrode.

3.2 CNT Deposition Mechanism

We hypothesize that high-pH gradients at the negative electrode may contribute to the neutralization and precipitation of the positively charged PEI functionalized carbon nanotubes. The PEI-CNT film grows over the fibers in direct contact with the electrode. The conductive film that forms over the fiber behaves like an extension of the electrode, leading to film growth which continues to the other layers, which are not directly in contact with the electrode. After the fibers are coated, the CNT film builds-up on the outer surface of the fabric (Figure 3a).

To validate our hypothesis, a glass fiber epoxy composite was placed on the negative electrode during the process of EPD. The cross section of the composite was examined after each deposition. Figure 4 shows the film formation with increasing time from left to right. At first, a buildup of the PEI-CNT film is seen at the edge in contact with the electrode. With increasing deposition time, the film already deposited acts as an extension of the electrode, enabling additional film growth. A similar experiment was conducted with a glass fiber epoxy composite rod whose diameter is 1.58 mm. The processing parameters are an electric field of 14.5 V/cm, a deposition time of 5 min and the dispersion concentration of 1 gram/liter. Figure 5 shows scanning electron micrographs from the specimen after 5 minutes of deposition. The amount of carbon nanotubes deposited is higher in the region towards the negative electrode.

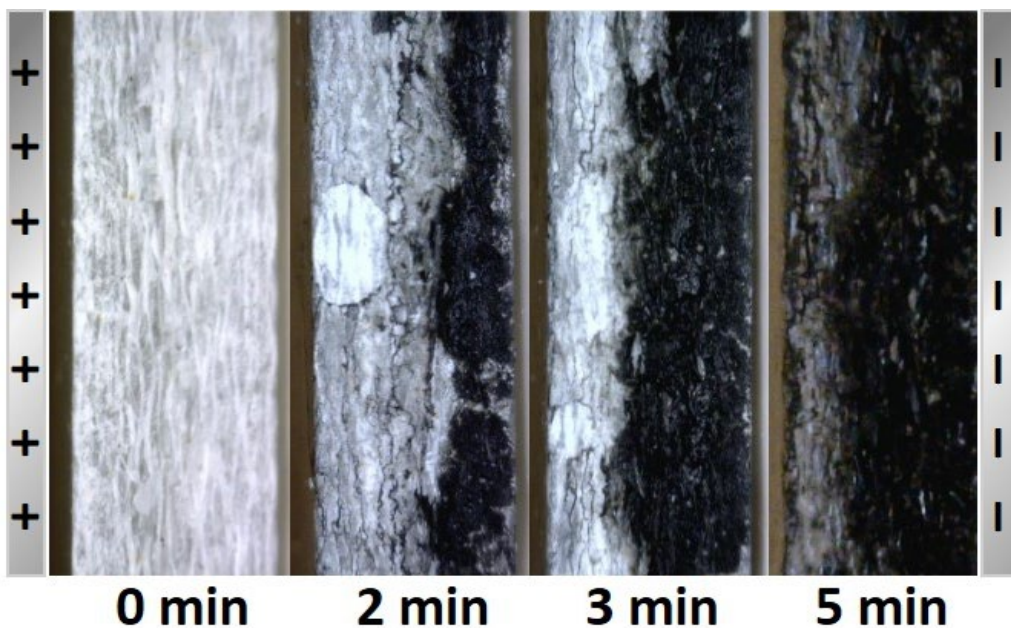


Figure 4 Photographs of the cross-section of the glass fiber epoxy composite at 4 different times, no deposition (0 minutes) on the left followed by 2, 3, 5 minutes of deposition. The film growth initiates from the negative electrode (right) and grows with time. [5]

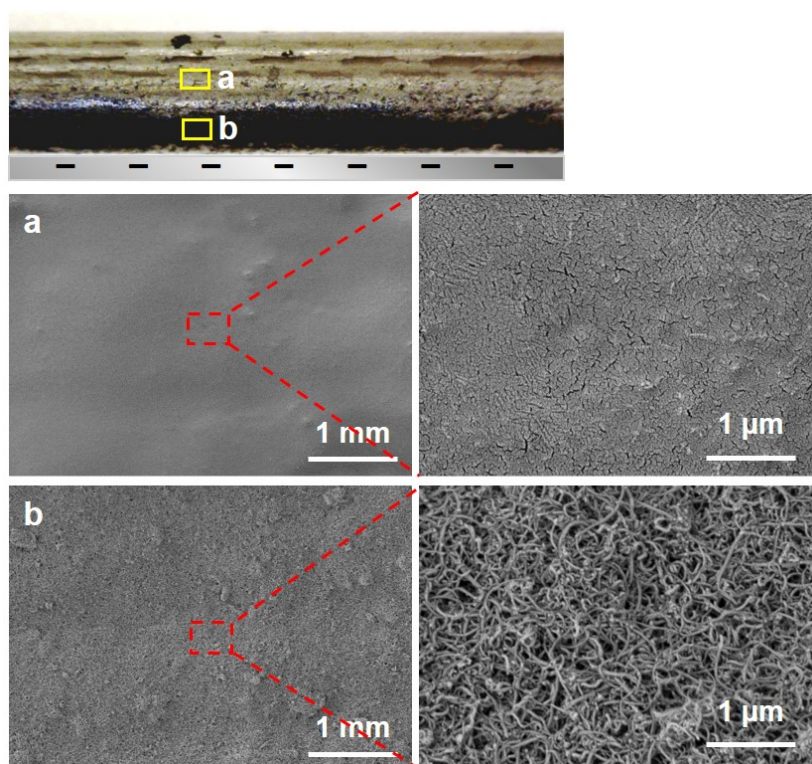


Figure 5 A photograph and SEM images of CNT coated glass rod.

Building on the above results, we conducted EPD experiments on multiple stacks of the glass rods in order to visualize the film growth along the rod surface and the transition of CNT coating from one rod to the next adjacent rod. The first three glass rods were placed on the negative electrode and underwent EPD processing. The second layer of glass rods was then stacked either parallel (Figure 6a) or perpendicular (Figure 6b) to the first layer of rods. When deposition was resumed, the CNT film grew around the second layer of rods in the parallel orientation to the first layer of rods. However, CNTs started to grow mainly at the contact points of the rods in the perpendicular orientation to the first layer of rods. While these experiments were conducted on large diameter glass fiber composite rod, we believe that the coating mechanism would be similar to the process with a conventional glass fabric.

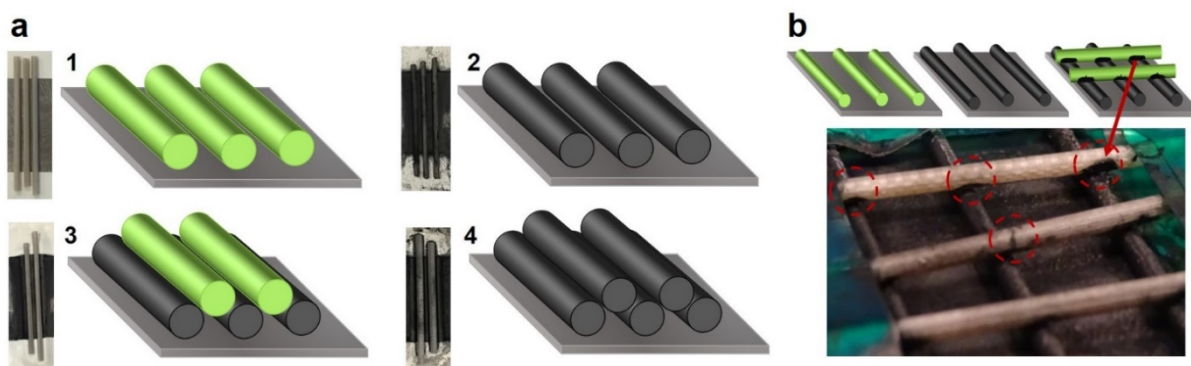


Figure 6 Photographs and schematics showing the EPD processes on multiple layers of glass fiber epoxy composite rods; a. parallel and b. perpendicular stacking sequence.

4. CONCLUSIONS

A well dispersed and stable CNT dispersion was prepared through ultrasonicated ozonolysis and PEI functionalization, followed by pH adjustment. It was observed that the positively charged PEI-CNTs were uniformly deposited onto various non-conductive fibers placed in front of the cathode. In contrast with the electrophoretic deposition mechanism of conductive carbon fibers, we hypothesize that PEI-CNTs may be precipitated at the cathode due to the local pH gradient. The filaments in contact with the cathode are consequently coated with CNT films and become part of the cathode. With ongoing deposition the electrode is effectively extended further into the fabric, eventually leading to through-thickness coating. Several different experiments were conducted with commercially available Astroquartz III glass fiber fabric and glass fiber composite rods to support our hypothesis. We could observe uniform coating over one layer of Astroquartz III glass fiber after an EPD deposition time of less than 1 minute. Once the CNT film builds up the conductive network to the outer fabric surface, PEI-CNTs start to form thick coatings without further infiltration into inter-filament region. Glass fiber macro rods were used to provide an analogue for the individual micro-fibers that comprise the fabrics in the EPD process. CNTs grew around the macro rods in a radial direction from the deposited film and migrated to the adjacent rods at the contact points. More rapid coating of adjacent rods occurred for the parallel orientations due to greater contact areas. Our results indicate that intimate contact between the adjacent fibers in the non-conducting fabric and the electrode is critical for ensuring uniform through-thickness CNT film growth.

5. ACKNOWLEDGMENTS

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