

Fabrication of Carbonnanotube/Polymer Nanocomposite Sheets and Its Mechanical Performance

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Abstract

Carbon nanocomposites have received a great deal of attention in recent years in view of their special properties such as low density, superior thermal and mechanical properties. However, poor dispersion and poor interfacial bonding limit the full utilization of carbon nanotubes as reinforcing agent in polymer nanocomposites. This paper presents an approach developed for production of polymer matrix nanocomposites with uniformly distributed multi-walled carbon nanotube (MWCNT). This approach involves preparation of a stable MWCNT in Nafion[®] polymer matrix followed by fabrication of MWCNT-Nafion[®] nanocomposite via a novel electrochemical co-deposition process (ECD). The ECD process introduced here follows the similar basic principles of traditional electrophoretic deposition. Morphology and microstructure of fabricated MWCNT-Nafion[®] nanocomposite sheets were evaluated through scanning electron microscopy (SEM). The mechanical performance of the nanocomposite was assessed by tension tests per ASTM D3039. Deposition of the MWCNT-Nafion[®] nanocomposite on an aluminum sheet produced significant gains in the tensile properties of the sheet. This finding confirms that uniform dispersion of MWCNT in a polymer matrix can produce nanocomposites with desired mechanical properties.

Keywords: Carbon nanotubes, Electrochemical Co-deposition, Nanocomposite, Nafion[®]

Introduction

Since their discovery, carbon nanotubes (CNT) have attracted a great deal of interest in composite fabrication because of their exceptional mechanical, electrical, thermal and optical properties [1,2]. For example experimental measurements on individual multi-walled carbon nanotubes (MWCNT) suggest values for Young's modulus around 1000 GPa [3]. This corresponds to one of the stiffest and strongest materials known. Because of their high aspect ratio, high modulus, and strength, nanotubes are promising candidates as reinforcement fillers for polymer nanocomposites. These materials show a great promise for many potential applications: for example, aerospace, nanoelectronics and sporting goods etc. It has also been shown experimentally that the introduction of CNT into polymer matrix improves electrical conductivity as well as mechanical properties of the matrix [4, 5, 6]. However incorporating CNT into a polymer matrix and effectively utilize these unique properties is an ongoing challenge.

The effective utilization of CNT in composite applications depends strongly on the ability to disperse CNT homogeneously throughout the matrix without destroying the integrity of CNT. Furthermore, good interfacial bonding is required to achieve the load transfer

across the CNT-matrix interface, a necessary condition for improving the mechanical properties of polymer composites [7]. Although several studies have focused on producing polymer CNT composites, many practical challenges remain before their potential can be fully realized [4,5,8-11]. Dispersing the nanotubes individually and uniformly into the matrix seems to be fundamental in producing composites with reproducible and optimal properties.

A major barrier for developing CNT-based devices is the problems with dispersion of CNT in solvents [12]. The challenges associated with dispersion of CNT have been addressed through their covalent modification or noncovalent functionalization [13-18]. The low dispersability stems from the tendency of as-prepared CNT tends to assemble into bundles or ropes that contain hundreds of well-aligned CNT arranged in a close-packed triangular lattice, due to van der Waals attraction. The over-micrometer-long ropes further entangle into networks. A recent calculation suggests that the typical intertube attraction is on the order of 36 kT for every nanometer of overlap between adjacent tubes, leading to cohesive energy of few thousands of kT per micrometer-long tubes [19]. Current approaches for dispersing and exfoliating bundled CNT into individual nanotubes include covalent modifications, π - π interactions, surfactant adsorption, and more [20-28]. Most of these methods are designed to reduce the short-range attraction between adjacent nanotubes through introduction of a repulsive interaction

of similar strength. Consequently, these treatments often lead to modification of the structural, electronic and mechanical properties of CNT. The challenge is to disperse CNT's without altering their unique properties.

This paper addresses how to overcome the dispersing challenges of CNT and to achieve uniformly distributed CNT in the polymer matrix via novel electrochemical co-deposition process, and the subsequent characterization studies of polymer CNT nanocomposite sheet. The electrochemical co-deposition process (ECD) introduced here follows the same basic principles as electrophoretic deposition (EPD). Electrochemical deposition techniques have grown beyond conventional electrolytic plating; EPD techniques have found growing applications to broad categories of polymers and ceramics, and are under consideration for applications at nano-scale for processing broad categories of nanocomposites. There are several nanocomposite fabrication processes available some of these are; chemical vapor deposition (CVD), dry-state spinning, and vacuum filtering [29-31]. Out of the different processes available for nanocomposite fabrication we chose EPD process because of the many attractive features [32]. Electrophoresis offers the promise to deposit relatively thick coatings (of several millimeter thicknesses) [33]. This technique is highly versatile, and allows processing of broad categories of nano-scaled ingredients and polymers into nanocomposites under controlled conditions, and provides substantial control over spatial distributions and interfacial interactions at nanoscale. EPD is an attractive technique for fabrication of carbon nanotube polymer composites [34-37].

A suspension for electrophoretic deposition is a complex system in which each component has a substantial effect on deposition efficiency. Important factors to consider when selecting a binder-dispersant-solvent system for EPD are: chemical compatibility of components, solubility of binder and additives, particle charge, viscosity, and electric resistivity of the suspension. It is very important to obtain well-dispersed and stable suspensions. In general, suspensions can be dispersed by electrostatic, steric, or electrosteric stabilization mechanisms. Organic macromolecules could be utilized to induce steric stabilization, where the macromolecules are attached to nanoparticle surfaces, or they could facilitate depletion stabilization where the macromolecules are free in suspension [38]. The steric stabilization is effective in both aqueous and non-aqueous media. Polyelectrolytes are widely used as additives that can impart electrostatic and steric stabilization to achieve uniform dispersion of MWCNT [21, 27, 39-41].

In this study we choose multi-walled carbon nanotubes (MWCNT) instead of single-walled carbon nanotubes (SWCNT) because they are less expensive thus can be easily scale up. We choose the bamboo-like structure rather than hollow structure because the "knots" on the bamboo-like MWCNT allows tighter matrix connectivity with the polymer, reducing pull-out of the MWCNT from the polymer matrix. In particular, "wrapping" of MWCNT in polymeric chains can be useful for improving their dispersability without sacrificing their unique physical attributes. Gentle sonication causes exfoliation of ropes into individual nanotubes. The exfoliated tubes may be stabilized in the liquid medium, with aggregation prevented by introduction of relatively weak repulsion at a large distance between MWCNT, such as osmotic (steric) repulsion among the tails of the tethered polymers in proper solvents, or electrostatic repulsion by the charged ends of tethered polymers.

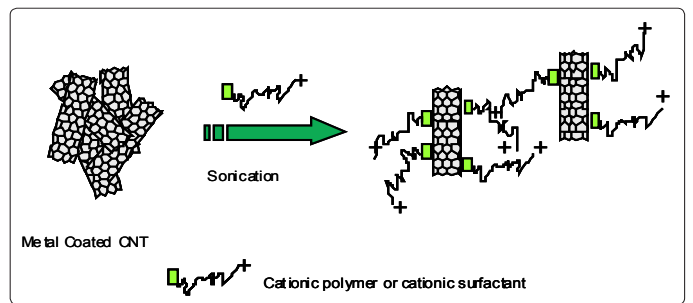


Figure 1: Schematic Representation of Dispersion of MWCNT

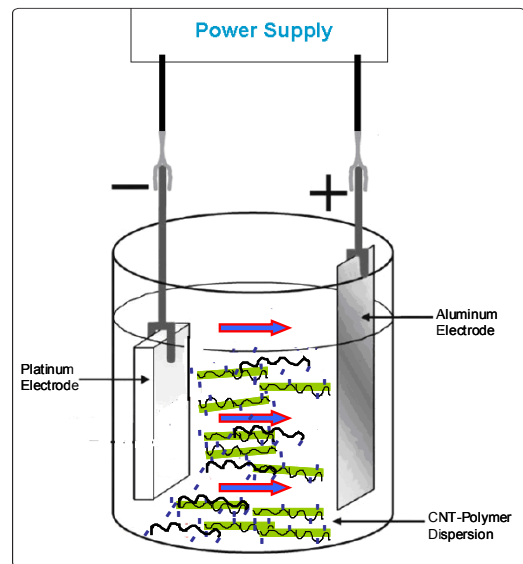


Figure 2: Schematic Representation of Electrochemical Co-Deposition of MWCNT.

Materials and Experimental Programs

Multi-walled carbon nanotubes with "bamboo" structure (MWCNT, chemical vapor deposition (CVD) method, purity >95%, outer diameter 30 ± 10 nm, length 1-5 μm) were purchased from NanoLab (Boston, MA) (Figure 3). For dispersion preparation 5% Nafion® solution in low aliphatic alcohol and tetrahydrofuran (THF, 99+% ACS reagents) were purchased from Aldrich. Aluminum sheets were used as both anode and cathode were purchased from McMaster Carr. Cathode sheet was 0.006" and anode sheet was 0.002" in thickness.

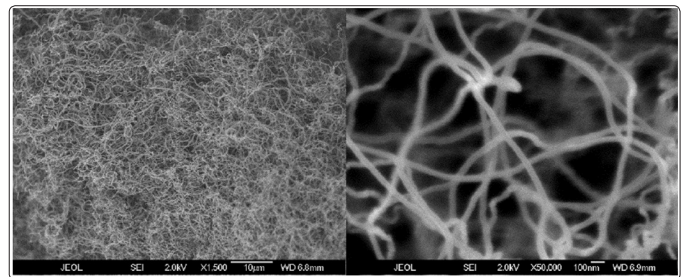


Figure 3: Scanning electron images of carbon nanotube at low and high magnifications.

Preparation of MWCNT Dispersion in THF

MWCNT (0.3 mg/mL or 0.5 mg/mL) was dispersed in Nafion® by sonication to give either 10 wt.% (10 mL) or 20 wt.% (20 mL) Nafion® solutions. Then diluted to 100 mL with THF and sonicated

further until a uniform solution was obtained. Allowed the dispersion to sit for at least 30 minutes to make sure that the dispersion is not separating and a stable dispersion was obtained. These solutions were found to be very stable over several months without any settling of nanotubes.

Electrochemical Co-Deposition of MWCNT on Aluminum Sheet

Aluminum plate (cathode) and thin aluminum sheet, anode were clamped in a polypropylene mold (Figure 4). Clamping will prevent possible shortening during electrophoretic deposition as well as it will limit the deposition to one side. Then the two electrodes are connected to a DC voltage constant voltage power supply and 10 V was applied continuously (in some cases voltage was applied for 10 minute time intervals and after each 10 minute sheet was allowed dry in air at room temperature). This voltage application procedure was continued until desired thickness/ weight gain was achieved.

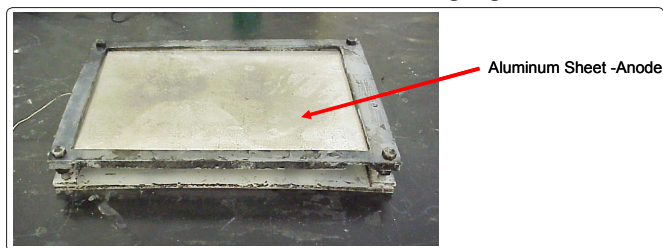


Figure 4: Polypropylene Mold Used for Electrophoretic Deposition

During ECD, the electrodes were placed flat (horizontally), with the anode (where deposition takes place) placed on the top (facing the cathode, which is placed on the bottom of the container). This position will prevent the settling of particles disturbing the ECD process because the potential gradient is opposite to the gravitational force; hence, a more uniform deposit can be obtained.

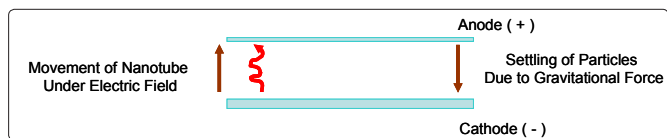


Figure 5: Different Forces Exist During Electrochemical Co-Deposition of MWCNT.

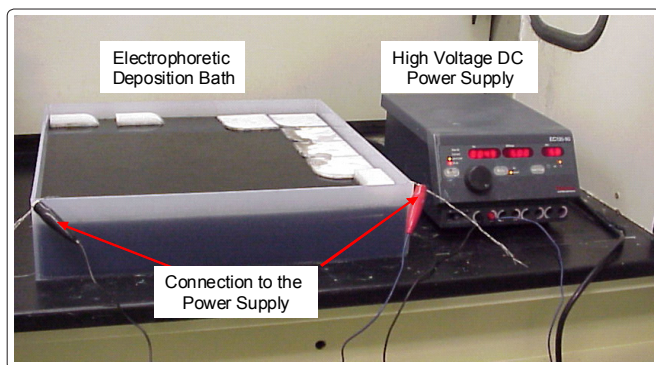


Figure 6: The Electrochemical Co-Deposition Set-Up

Post-Deposition Treatment

After deposition of nanocomposite, samples were heated to 100°C under vacuum. Upon cooling down thin MWCNT/polymer nanocomposite was easily peeled off from the substrate aluminum shim, resulting a flexible free standing MWCNT-polymer nanocomposite film (Figure 7).

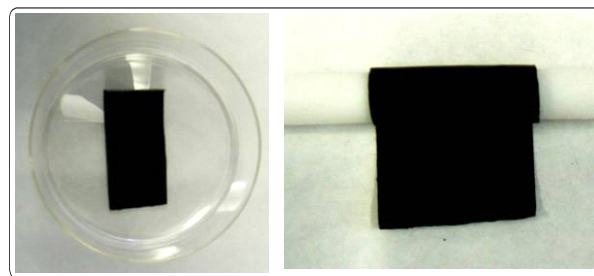


Figure 7: Free standing MWCNT-Nafion® Nanocomposite Sheet

Tension Tests

Tension test specimen was prepared according to ASTM D3039, with specimen dimensions shown in the Figure 8. Tabs (same thickness as aluminum sheets) were glued on to both ends of the rectangular specimen and left overnight for curing. Tension tests were performed for nanocomposite coated sheets as well as uncoated aluminum sheet for comparison.

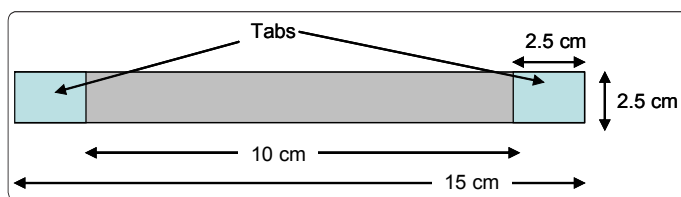


Figure 8: Schematic Presentation of the Tension Test Specimen

The tension test set-up is depicted in Figure 9. Sheets with and without nanocomposite deposits were clamped between the metal grips of the hydraulic test machine. Just before the test, thickness of the specimen was measured. During the test, load and deflection data were recorded by a computer-based data acquisition system.

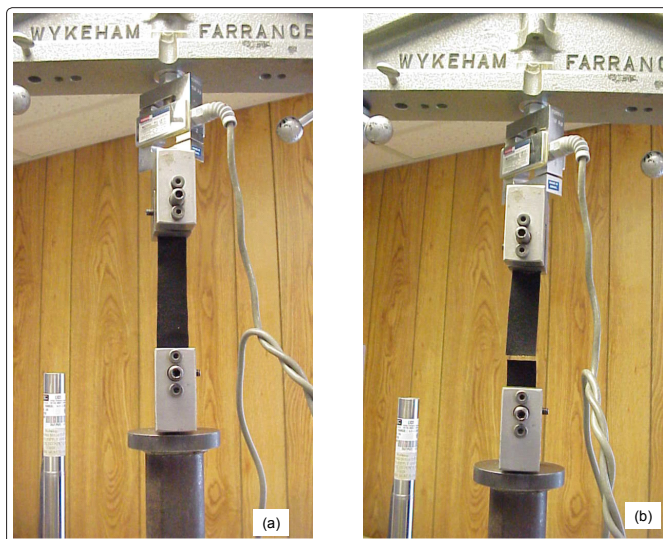


Figure 9: Tension Test Set-Up for Sheet with MWCNT-Nafion® Nanocomposite Deposit: (a) Just Before the Test; and (b) After the Test

Results and Discussions

Dispersion of carbon nanotubes and their interactions with polymer chains determine the reinforcement efficiency in polymer nanocomposites. The relatively small surface charge of carbon nanotubes lowers their interfacial interactions in layer-by-layer

self-assembly where electrostatic attractions are important factors. Increasing the charge density of carbon nanotubes can thus enhance their reinforcement efficiency in polymer nanocomposites processed via layer-by-layer self-assembly. One option to enhance the charge density of carbon nanotubes is to wrap them with chains of a polymer that comprises charged end groups. Nafion® is a polymer that binds well with nanotube walls and also increases the negative charge density of nanotubes; it is thus a strong candidate for use as both a processing aid and the polymer matrix in the nanocomposite. Polymer-wrapped carbon nanotubes are also expected to exhibit enhanced dispersability due to electrostatic effects.

In this study Nafion® was used as the dispersant and Figure 10 shows the chemical structure of Nafion®. Nafion® has high density of fluorine groups, can strongly interact with nanotube walls through formation of hydrophobic bonds (since nanotube walls are also hydrophobic) [42]. As CNTs are naturally not water soluble, modification through chemical functionalization using suitable dispersants and surfactants can enhance solubility and is essential for their controlled dispersion. For example, constituent polar molecules can render CNTs soluble, whereas nonpolar moieties make CNTs immiscible. Fluorine groups will be attached to the nanotube walls and sulfonate end group will be sticking out from the surface. These sulfonate groups make nanotube walls negatively charged. Introduction of charge will allow the formation of good dispersion of nanotubes in organic solvents due to electrostatic stabilization; bulky polymer chains of Nafion® also provide for steric stabilization of nanotubes.

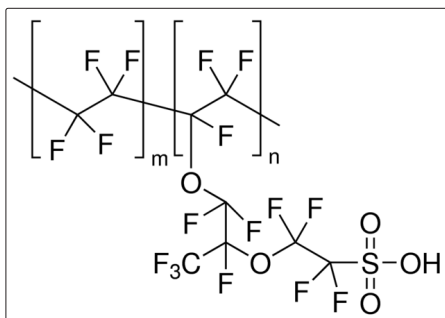


Figure 10: Nafion® Structure.

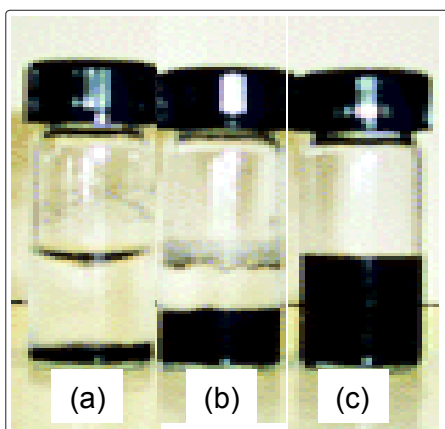


Figure 11: Dispersion and Stabilization of MWCNT in Nafion®.

Overall negative charge on MWCNT allows deposition through ECD. When DC voltage is applied negatively charged particles will migrate to the positively charged anode and deposit at the anode thus giving a MWCNT-Nafion® nanocomposite coating on aluminum scaffolds. Figure 12 shows the visual appearance of the MWCNT-

Nafion® nanocomposite deposit before and after performance of the tension test.

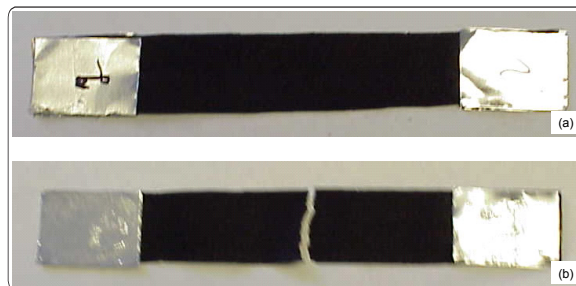


Figure 12: MWCNT- Nafion® Nanocomposite Deposit: (a) Before; and (b) After Tension Test.

Table 1 presents a summary of tension test results for aluminum sheet and nanocomposite deposit on aluminum sheet. The strength/density ratio of nanocomposites was higher by a factor of ~30 when compared with aluminum. Figure 13 shows the comparison of load-deflection curves for aluminum sheets with and without nanocomposite deposit. Nanocomposites are observed to offer balanced gains in strength and ductility.

Table 1: Summary of Tension Test Results for Aluminum Sheet and MWCNT- Nafion® Nanocomposite Deposits

	Peak Load [N]	Strength [MPa]	Strength/Density
Plain Aluminum	53	42.4	15.7
Sample 231-1	198	965	535
Sample 231-2	189	905	505
Sample 231-3	185	880	490
Sample 231-4	194	940	520

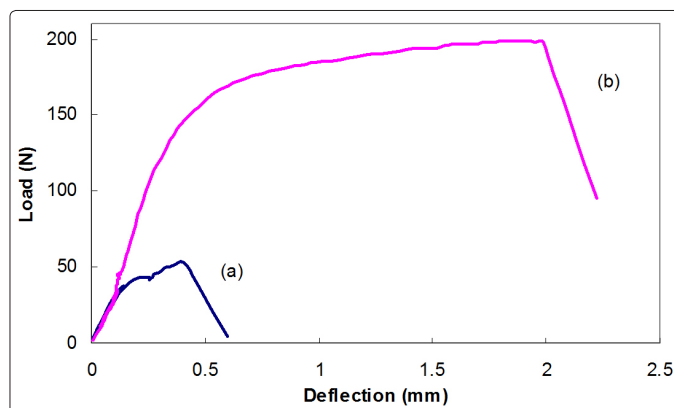


Figure 13: Load-Deflection Curves for Aluminum Sheets: (a) Scaffold Aluminum Sheet; and (b) With MWCNT-Nafion® Nanocomposite Deposit

Microscopic structure of MWCNT-Nafion® nanocomposite coating was studied. Scanning electron microscopy (SEM) techniques were employed to assess the uniformity and thickness of nanocomposite Coatings. Figure 14 SEM images of aluminum sheet (a) without, and (b) with MWCNT-Nafion® nanocomposite deposit.

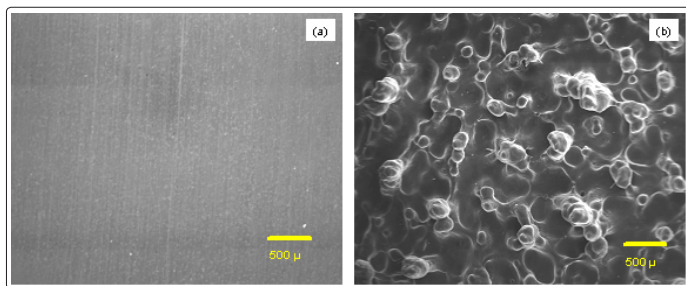


Figure 14: SEM Images of: (a) Scaffold Aluminum Sheet; and (b) MWCNT- Nafion® Nanocomposite Deposit.

Conclusions

Electrophoretic deposition represents a very powerful tool for the ordered deposition of MWCNT- Nafion® nanocomposite on aluminum sheets. Stable multi-walled carbon nanotube dispersion was prepared in a Nafion® matrix. Electrophoretic depositions of MWCNT/Nafion® dispersion on aluminum sheet exhibited enhanced mechanical property such as tensile strength. The ratio of strength/density nanocomposites was higher by a factor of ~30 when compared to that of scaffold aluminum.

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