

# Layer-by-Layer Assembled Composites from Multiwall Carbon Nanotubes with Different Morphologies

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## ABSTRACT

We report formation of polyelectrolyte/multiwall carbon nanotube (MWNT) multilayers by the layer-by-layer assembly technique. Both “hollow” and “bamboo” type MWNTs were employed. Scanning electron and atomic force microscopy indicate high structural homogeneity of the prepared composites. Ellipsometry and the absorbance spectroscopy confirm sequential adsorption of oppositely charged nanotubes and the polyelectrolyte resulting in uniform growth of the polyelectrolyte/MWNT films. Measurements of the mechanical properties show that these are strong composite hybrid films with mechanical properties exceeding many carbon nanotube composites made by mixing, or in-situ polymerization. Bamboo-type carbon nanotube composites display ultimate tensile strength of  $150 \pm 35$  MPa and Young modulus of  $4.5 \pm 0.8$  GPa as compared to  $110 \pm 25$  MPa and  $2 \pm 0.5$  GPa in composites made from common hollow MWNTs. This indicates that the morphology of the fibers can substantially improve matrix connectivity on the material mitigating “telescopic effect” in MWNTs. The films made from bamboo-type MWNTs approach in strength recently reported layer-by-layer composite films from single wall carbon nanotubes, while being substantially less expensive. These results confirm the potential of the layering method for the manufacturing of composites with high load of strong filler and importance of uniform distribution and good interconnectivity between carbon nanotubes and the polymer matrix.

**Introduction.** The unique mechanical, electrical, and optical properties<sup>1–4</sup> of multiwall carbon nanotubes (MWNT) make them very attractive for the fabrication of new advanced materials. MWNTs have been found to have exceptional mechanical properties, with an axial Young’s modulus of 300–4000 GPa and bending strength of 14 GPa,<sup>1,5,6</sup> and this makes them useful as reinforcing fillers for high-strength materials. In this context, various polymers have been used as matrix materials, and different preparation techniques employed.<sup>7–16</sup> In general, the tensile modulus and ultimate strengths of the composites are reported to increase, although below the level of expectation.<sup>17–27</sup> Assessment of data accumulated in numerous studies on carbon nanotube composites revealed that effective incorporation of nanotubes into a polymer matrix depends strongly on the homogeneous dispersion of the nanotubes. Good interfacial bonding and interactions between nanotubes and polymers are necessary conditions for improving the mechanical properties of the composites.<sup>13,15,16,28,29</sup> These fairly simple design guide-

lines for carbon nanotube composites permitted substantial advances in their mechanical properties.<sup>30–34</sup> The most common approach to achieve the uniform distribution and tight matrix connectivity is chemical modification of the graphite network of the nanotube walls.<sup>30–37</sup> Here we utilize a different approach based on nanoscale engineering of the composite structure made possible by sequential deposition of thin films. The deposition technique that we took advantage of is called layer-by-layer (LbL) assembly;<sup>38,39</sup> it reduces the phase segregation and makes composites highly homogeneous, with nanocolloids and polymers well dispersed and interpenetrated.<sup>40–42</sup> Alternating adsorption of monolayers of components attracted to each other by electrostatic and van der Waals interactions results in a uniform growth of films containing a high concentration of inorganic filler. Recently, it was demonstrated that it can be very successfully applied to the preparation of single wall nanotube (SWNT) composites.<sup>15,16</sup> Mechanical properties of the composites improve dramatically with an increase of the concentration of nanotubes in the polymer matrix.<sup>8,13</sup> The LbL assembly technique results in a nanotube content in the range  $50\% \pm 5$  wt %, <sup>15</sup> retaining uniform distribution of the filler in the polymer matrix, which is substantially higher than in a typical nanotube composite.<sup>28,29</sup> This is a simple way to produce fundamentally and practically interesting multilayer structures

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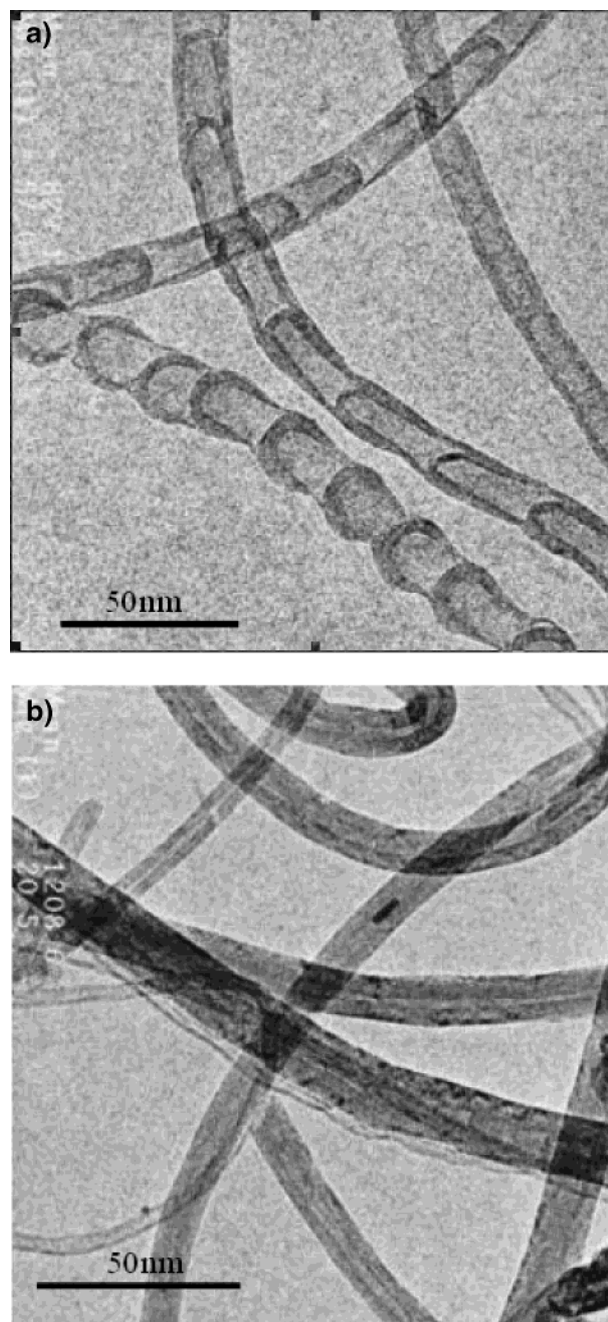
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with unique mechanical properties and precise control over film composition and thickness. More importantly, this technique offers a possibility of multifunctional composites in which the strength will be only one of the factors determining its applications. Additionally, deposition of nanotubes in the form of individual layers opens the way to oriented nanocomposites,<sup>43</sup> taking advantage of the sheer force as in spun fibers<sup>44,45,47</sup> or magnetic fields.<sup>46</sup>

Here we show formation of MWNT/polymer multilayer LbL films based on sequential adsorption of oppositely charged MWNT and polyelectrolytes (PEs). There are two motivations for using MWNTs instead of SWNTs: (1) even extensive surface modification of MWNT does not harm the aromatic bonds inside the multiwall onion structure; (2) MWNTs are substantially less expensive than SWNTs,<sup>46,49</sup> which can accelerate the practical utilization of these composites. On the basis of the investigated structural and mechanical properties of LbL MWNT films, one can see that the tensile strength is much greater than that of nanotube composites made by solution casting, melt-mixing, and the in-situ polymerization of monomers in the presence of nanotubes.<sup>8,10,12,17–27</sup> Additionally, we show that the morphology of the MWNT can also make a big difference in their mechanical performance. The replacement of standard, hollow MWNTs with rather unusual but easily produced bamboo-type MWNT brings about significant improvement in their mechanical performance. The “knots” on the bamboo-like MWNT stem afford tighter matrix connectivity with the polymer, reducing pull-out of the nanotube from the polymer. They also decrease the effect of telescopic extension of MWNT diminishing the Young modulus and ultimate strength.

**Experimental Section. Materials.** MWNTs, both “bamboo” and “hollow” (CVD method, purity > 95%, diameter 10–20 nm, length 5–20  $\mu\text{m}$ ), were obtained from NanoLab (Boston, MA) (Figure 1). Branched polyethyleneimine (PEI-b,  $M_w = 70\,000$ ) and poly(acrylic acid) (PAA,  $M_w = 450\,000$ ) were obtained from Aldrich and used as received. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) for pH adjustment were purchased from Sigma-Aldrich. Nano-disperse AQ specially formulated dispersant obtained from NanoLab was used for creating aqueous dispersions of multiwall carbon nanotubes. Glutaraldehyde (GA) used for cross-linking of LbL multilayer film was obtained from Sigma-Aldrich. Deionized (DI) water (> 18.2  $\text{M}\Omega\text{-cm}$ , Barnstead, E-pure system, pH = 5.6) was used in all solutions and rinsing procedures.

**Preparation of Multilayer Assemblies.** The LbL assembly composites were formed on solid substrates by sequential deposition of oppositely charged polyelectrolytes and MWNTs. Adsorptions were carried out at room temperature in open beakers containing components. After every layer deposition, samples were rinsed with water three times for 2 min and then dried with nitrogen. The samples were manually prepared by cyclic immersion in PEI and MWNT solutions. After every fifth deposition cycle, a layer of MWNTs was replaced with a layer of PAA to introduce carboxyl functionalities for amide cross-linking between polyelectrolytes.



**Figure 1.** SEM pictures of “hollow” (a) and “bamboo” (b) multiwall carbon nanotubes.

The 1% PEI solution was at pH = 8.5; 1%, PAA solution was at pH = 6.5; and MWNT solution was at pH = 6.5. A deposition time of 10 min was used for polyelectrolytes, and 20–40 min for MWNT. All investigations on MWNT/polyelectrolyte multilayer free-standing films were performed on composites with the structure  $[(\text{PEI}/\text{MWNT})_5(\text{PEI}/\text{PAA})_n]$ ; typically in this study we used structures containing  $n = 20$  with a total of 100 PEI/MWNT bilayers (term bilayer does not imply real structural property of produced films).

The layer-by-layer assembly technique is a simple and common method to fabricate thin films of nanoparticles and polyelectrolytes on solid substrates such as glass slides or silicon wafers. In this study we used free-standing LbL films, which were additionally cross linked to force chemical

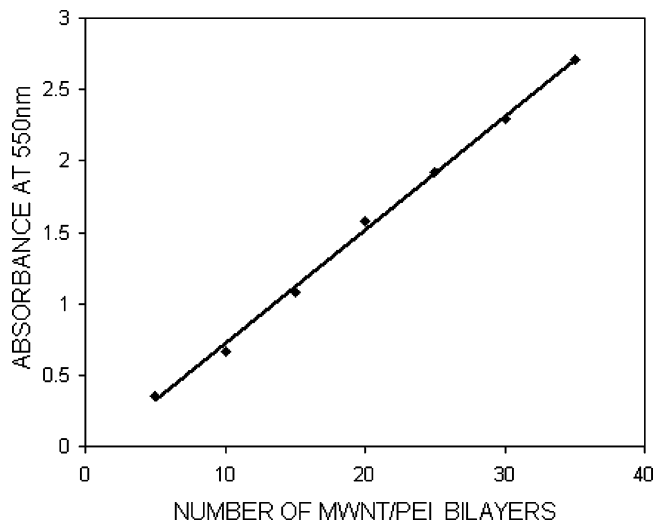
change in the composites, increasing bonds between and within polyelectrolyte chains and carbon nanotubes.<sup>50,51</sup> The film was cross-linked by two methods: heating and chemical reactions using glutaraldehyde (OCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHO), which is the most frequently applied cross-linking agent.<sup>52</sup> After deposition of every five cycles (PEI/MWNT)<sub>5</sub>, the film was heated to 120 °C for 30 min, resulting in amide bonds between PAA and PEI.<sup>50</sup> As well, there are also covalent bonds forming between PEI and MWNT at these temperatures, which further increase matrix connectivity. The film was also cross-linked in 0.5% glutaraldehyde solution for 1.5 h. This treatment bonds together amino groups remaining free after the 120 °C annealing. Subsequently, the film was rinsed three times in deionized water for 15 min to remove unreacted glutaraldehyde. These cross-linking techniques produce a compact network of polyelectrolytes and carbon nanotubes, increasing the stiffness and strength of the composites.

The films were prepared on glass substrates with dimensions of 2.5 cm by 5 cm. After deposition of a given number of layers, the film was peeled from the substrate by chemical delamination.<sup>53</sup> To separate the multilayer composite from glass, samples were immersed into 1% aqueous hydrofluoric acid for 1–2 min and then washed in acetone and deionized water, respectively. Dry films remain strong, flexible, and uniformly colored (deep black); they may be cut to desired size or shape. Silicon wafers and glass slides were used as substrates for LbL assembly. The substrates were cleaned by treatment with 30 wt % solution of nitric acid (HNO<sub>3</sub>) for 30 min, followed by extensive rinsing with DI water and then sonicated for 30 min. Nanodisperse AQ was used to disperse MWNTs in DI water (0.01 g MWNTs, 0.02 g NaAQ, and 20 mL DI water), supplemented with sonication (Ultrasonic Processor Cole-Palmer Inst. Co, 150 W) for 30 min to disperse MWNTs, and centrifugation (5000 rpm, 1 h) to eliminate nondispersed agglomeration of MWNTs. This treatment results in the presence of negative charge on the caps and sides of the walls of multiwall carbon nanotubes and makes suspension stable for months.

The LbL preparation of MWNTs films was also done using a dipping coater, making this technique simple and reasonably fast. We are working on new approach to produce LbL MWNT thick films to make the process faster for industrial applications of strong composites. By automation of immersion and rinsing steps it is possible to produce composites of the desired thickness and size, determined by time of production and shape of substrate. It opens up broad possibilities for technological large-scale fabrication of such strong composites based on MWNTs.

SEM images of the films were taken on a JXM 6400 (JEOL, Peabody, Massachusetts) with an Oxford exL X-ray system and a cryostage operating at an accelerating voltage of 15 kV and a field depth of 8. TEM images were taken on a JEM 100 CX II (JEOL, as before) with a Noran X-ray system operating at 100 kV.

AFM measurements were performed in air by using a Nanoscope IIIa system (Veeco/Digital Instruments, Santa Barbara, California), operating in the tapping mode. UV–



**Figure 2.** Light absorption of LbL films (“bamboo” MWNT) at 550 nm wavelength versus the bilayer number.

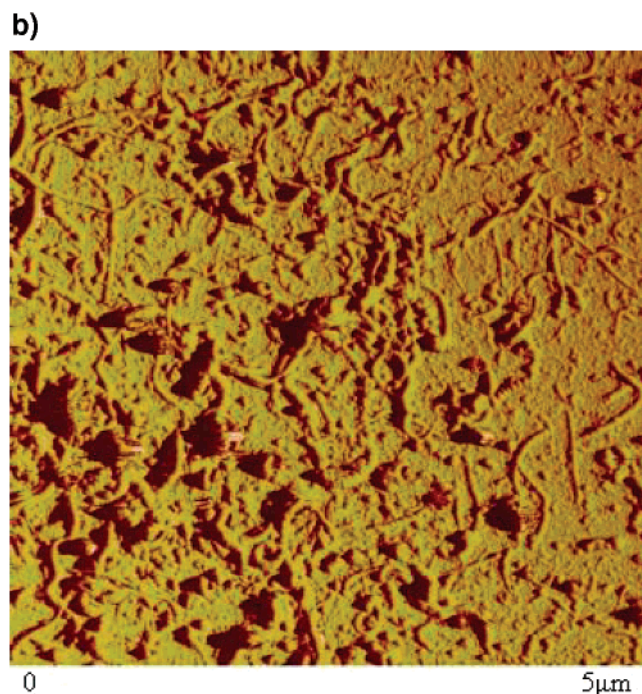
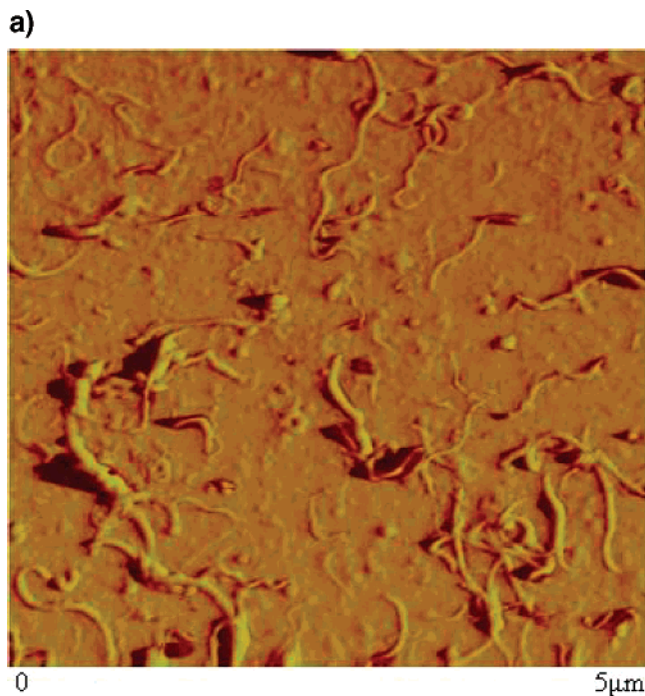
vis optical absorption spectra were obtained on a Hewlett-Packard 8453 diode array spectrophotometer.

Ellipsometry measurements were taken using an M-44 ellipsometer (J. A. Woollam Co, Lincoln, NE).

The mechanical properties of the MWNT composites were measured using a testing device 100R (TestResources, Shakopee, MN). Before experiments, the instrument was calibrated by measuring the mechanical strength of standard films such as cellulose acetate and polyamide–nylon 6.

**Results and Discussion.** The growth of MWNT/PEI multilayer film was examined using UV–vis absorption spectroscopy. Spectra of the composites are largely featureless in this spectral region, with a monotonic increase of absorption with decreasing wavelength. Figure 2 shows dependence of the absorption (at wavelength of 550 nm) on the number of LbL cycles for a composite containing “bamboo” MWNT. The linear increase confirms a reproducible growth of MWNT layers from cycle to cycle, as every dipping cycle results in the deposition of essentially the same amount of nanotubes in the composite. This trend is also confirmed by ellipsometric measurements of multilayer films prepared on silicon wafers. The results again show a linear growth of [(PEI/MWNT)<sub>5</sub>(PEI/PAA)]<sub>n</sub> composites, with essentially the same thickness of every MWNT/PEI bilayer,  $d \sim 13$  nm. Specifically, for films made of “bamboo” MWNTs,  $d = 11–13$  nm for films with  $n = 1$ , and  $d = 12–15$  nm for  $n = 4$ . For films made of “hollow” MWNT,  $d = 12–14$  nm for  $n = 1$ , and  $d = 12–15$  nm for  $n = 4$ .

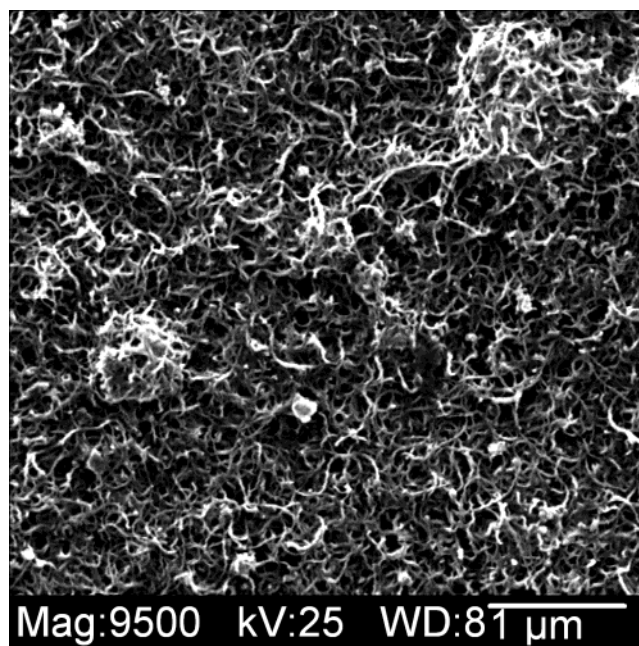
AFM study of LbL films obtained on a silicon wafer substrate that was first treated with PEI and then with MWNTs reveals presence of well-dispersed MWNTs. The image (Figure 3b) shows randomly orientated carbon nanotubes uniformly covering the entire surface of the sample. The density of MWNTs in the first layer is rather small, but the individual carbon nanotubes are interweaved and homogeneously integrated with polyelectrolyte, without any sign of phase segregation. On occasion, MWNTs formed bundles with the average length in the range of 1–5  $\mu\text{m}$  and diameter of 10–19 nm. AFM pictures revealed that adsorption of



**Figure 3.** AFM images of (a) single MWNT on PEI layer, (b) three bilayers of the composite.

carbon nanotubes initially increases with the number of LbL layers (Figure 3a,b). Subsequent PEI/MWNT layers make the film rougher, with carbon nanotube bundles covered with PEI. Further treatment of this film with MWNT solution leads to interweaving of nanotubes with the polyelectrolyte chains, creating a homogeneous composite. After three deposition cycles, images demonstrate an increase in the amount of nanotubes that densely cover the entire film (Figure 3b).

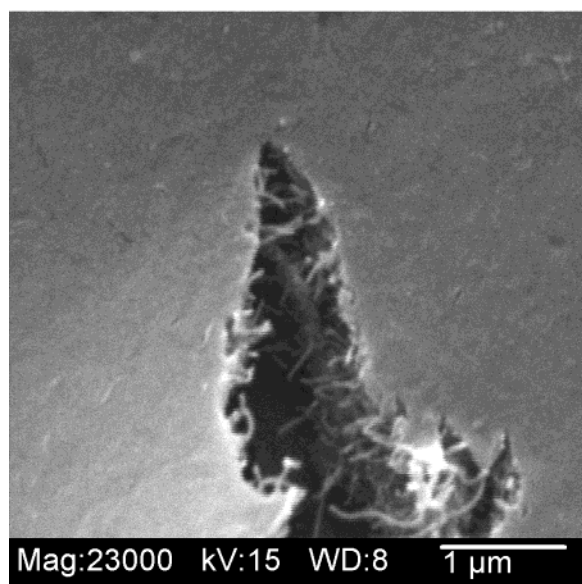
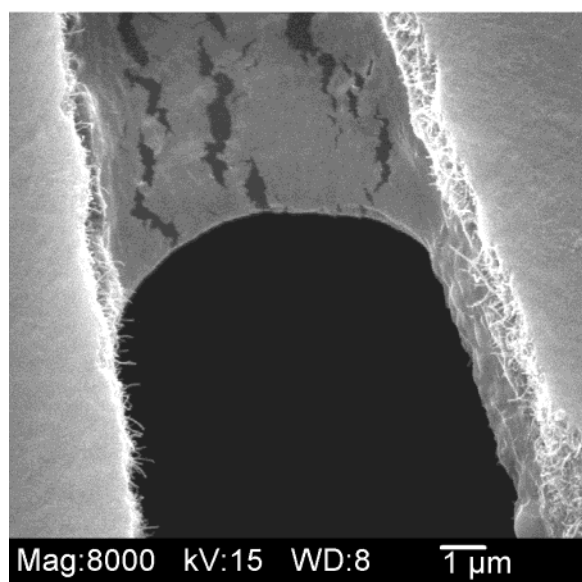
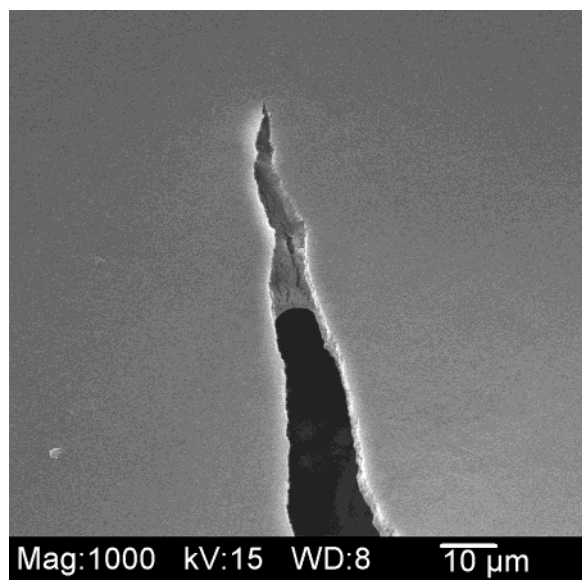
SEM study of free-standing PEI/MWNTs films clearly demonstrates high homogeneity of the samples (Figure 4).



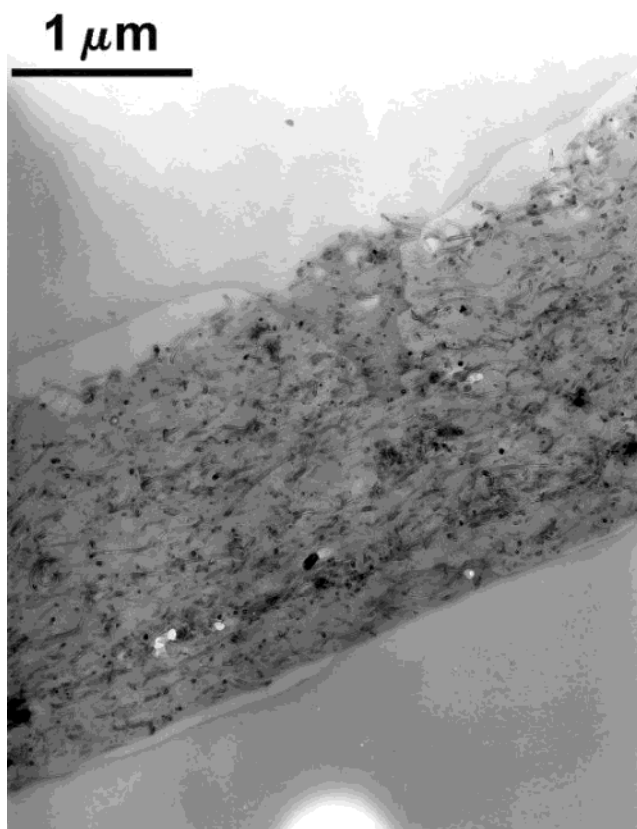
**Figure 4.** SEM image of the surface of a free-standing LbL film.

Nanotubes are uniformly distributed across the matrix, without any preferred orientation. To understand the difference between the mechanisms of the tensile fracture of composites made from SWNTs and MWNTs, we carried out the SEM study of the ruptured areas of the free-standing films. Figure 5 shows an SEM picture of such a rupture region, with nanotube bundles pulled out, or still bridging the break region, mostly aligned perpendicular to the break face. Some nanotubes have been pulled out of the polymer matrix in the area between the break faces (Figure 5). One can recall that this process did not take place for SWNT LbL composites bonded with a similar cross-linking procedure. The pull-out of MWNTs in this case should be attributed to the telescopic effect, when inner tubes slide out of the sleeve made by larger ones.<sup>54</sup>

Recent structural studies of the rupture regions<sup>14,15</sup> showed that numerous carbon nanotubes break under a stretching force and that some defects, for instance due to oxidation, make them drastically weaker. There are many reasons for fractional defects existing on the nanotube walls such as impurity,<sup>8</sup> or chemical oxidation.<sup>55</sup> While single- and multiwall carbon nanotubes with carboxylic groups were used in many studies to form multilayer films based on LbL assembly technique,<sup>15,16</sup> in this study we used a specially formulated agent to disperse MWNTs and to charge the nanotube sides. SEM investigations of rupture areas clearly show that many MWNTs have been pulled out of the matrix, indicating that the used dispersant does not reduce the strength of MWNTs. To compare results, we also used oxidized MWNTs (“hollow”) to produce the LBL film, and carried out investigations of mechanical properties that demonstrated a drastic decrease in tensile strength. Note that the images of pulled-out MWNT strands also suggest a solution to this problem. For this reason, the use of bamboo-type MWNTs can substantially improve the rupture mechanics.



**Figure 5.** SEM images of the rapture region of the MWNT free-standing film after stretching tests.

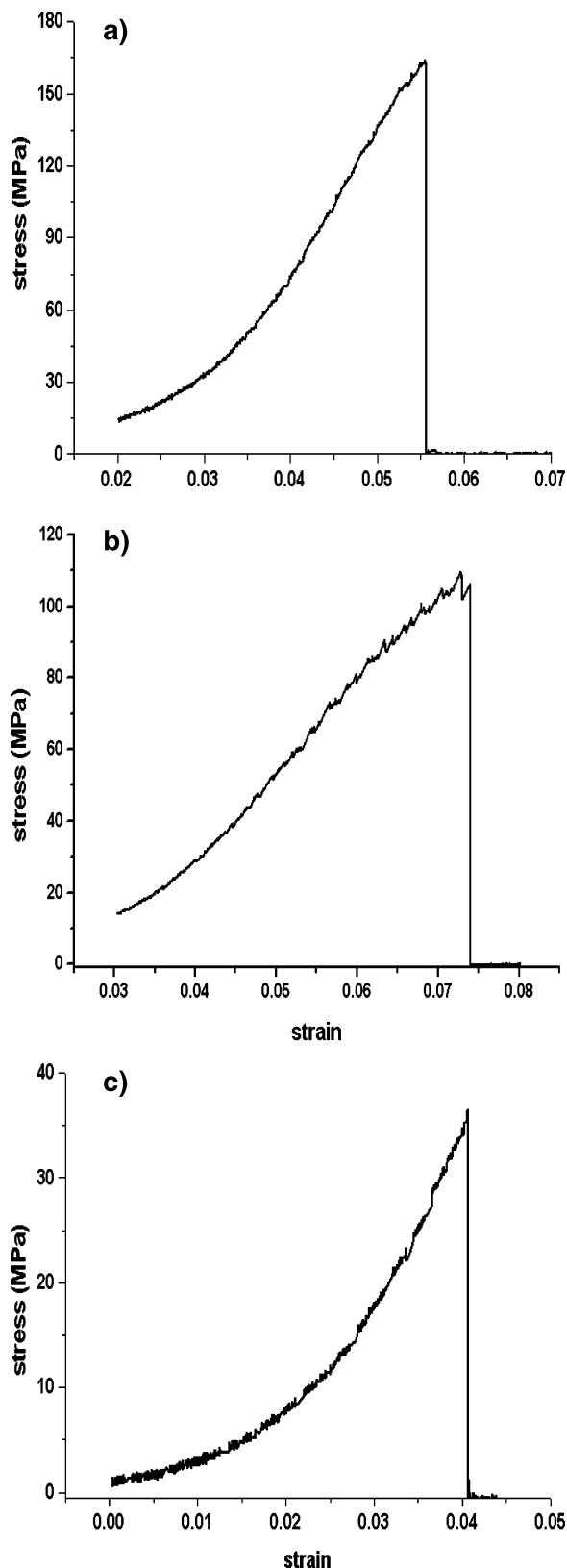


**Figure 6.** TEM image of the cross section of a MWNT free-standing film.

TEM examination also showed that morphology of the multilayer film is fairly homogeneous throughout the whole sample (Figure 6). There are some darker inclusions, which are most likely the small dust and catalyst particles. There were also some air pockets in very small amounts, with the diameter not exceeding a few tens of nm in diameter, which overall, the TEM uniformity of the MWNT LbL multilayer film slice was lower than for SWNT film, although still remaining very high and serving as structural foundation of good mechanical properties of these composites. The lower degree of TEM uniformity can also be related to larger gaps between the MWNT strands in the composite (Figure 4), which are more difficult to fill with the polyelectrolytes than in SWNT LbL films.

The sides of the free-standing film are different in roughness (Figure 4). As expected, the one that was attached to the substrate is smoother. We used the TEM images to estimate the thickness of the free-standing films with  $n = 20$  for both “bamboo” and “hollow” nanotubes. The average thickness of the composites was estimated to be  $1.5 \pm 0.2 \mu\text{m}$ , for each case.

The stress–strain curves of the prepared films from different MWNTs are given in Figure 7. Stretching curves display a linear stress–strain dependence, without any plateau area that would indicate a plastic deformation. There is a clear fracture point in the elastic region of the stress–strain curve. The tensile modulus, strength, and elongation up to the breaking point are:  $4.5 \pm 0.8 \text{ GPa}$ ,  $150 \pm 35 \text{ MPa}$ ,  $0.025\text{--}0.05\%$  for the “bamboo”, and  $2 \pm 0.5 \text{ GPa}$ ,  $110 \pm$



**Figure 7.** Stress–strain curves for (a) LbL “bamboo” composite, (b) LbL “hollow” composite, (c) LbL “hollow”–oxidized nanotube composite.

25 MPa, 0.03–0.06%, for the “hollow” nanotubes, respectively. This is greater than the tensile strength of MWNT composites made by mixing, extruding, or polymerization.<sup>7,11,13,14,56</sup> These results indicate remarkable effects of

carbon nanotubes on the tensile properties of the LbL composites. Similar investigations conducted on LbL free-standing films with polyelectrolytes PEI/PAA only<sup>15</sup> showed that the presence of carbon nanotubes is crucial for achieving improved mechanical properties of polymer-based multilayer stacks. The most important factor is the interfacial bonding between MWNTs and polyelectrolytes, mediated by electrostatic attraction, van der Waals adhesion, mechanical interlocking, and chemical bonding. The stretching results indicate that multilayer films based on the “bamboo” MWNT are mechanically substantially stronger than composites based on the “hollow” nanotubes. The bamboo structure of the carbon nanotubes provides structural anchors, which enhance the mechanical bonds between MWNT and polymer. “Hollow” nanotubes have smooth walls, which reduce the friction forces in the matrix; these nanotubes can be pulled out of the matrix more easily, resulting in the reduction of the film strength.

We have finally investigated the mechanical properties of LBL multilayer films with oxidized “hollow” MWNTs. The nanotubes were treated with nitric acid for 12 h, followed by sonication, and then washed in deionized water. This chemical treatment produces the carboxylic groups on the nanotube walls, thereby reducing their structural integrity. The stretching results now show, as expected, a drastic decrease in the strength of the composite (Figure 7c).

**Conclusions.** The fabrication of the high strength, light-weight composites, utilizing the layer-by-layer assembly technique is reported here. The composites consist of subsequent layers of polyelectrolytes and multiwall carbon nanotubes, chemically cross-linked to each other and to the polymer matrix. Our method ensures a high concentration and homogeneous distribution of nanotubes within a polymer matrix and strong adhesion between the structural components of the composite—all the basic factors affecting the mechanical failure of the material. The overall performance of MWNT films in the mechanical tests approached the results obtained for SWNT multilayers,<sup>15,16</sup> leaving however some room for further improvement, especially considering that different polymers may serve the purpose better.<sup>30–34</sup> The fabrication of such materials opens up a broad range of possibilities for biomedical, space, and structural materials, as well as for nanoscale electronic components with high strength requirements.

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