

# The Importance of Interfacial Design at the Carbon Nanotube/Polymer Composite Interface

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**ABSTRACT:** This research focuses on the need for interfacial engineering at the carbon nanotube/polymer composite interface in the effort to obtain enhanced mechanical properties. The mechanical properties of multiwall carbon nanotubes (MWNTs)/poly (methyl methacrylate) (PMMA) nanocomposites were studied as a function of both nanotube concentration and surface treatment. One method, plasma enhanced chemical vapor deposition (PECVD), was successfully used to produce a PMMA conformal coating (using methyl methacrylate monomer) on multiwall carbon nanotubes. Excellent suspensions of MWNTs in organic solvents were achieved via the PMMA coating. The coated-MWNTs were dispersed into PMMA via melt mixing and orientation was achieved by melt

drawing. The overall set of mechanical properties indicates that while the conformal polymer coating had a significant effect on the mechanical properties at a 1% concentration of nanotubes as compared to the uncoated nanotube composites, suggesting improved interfacial adhesion between the nanotube and the matrix material. However, the mechanical properties of the 1% coated nanotube composite were not significantly better than those for pure PMMA. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1413–1418, 2006

**Key words:** nanotube dispersion; PMMA; tensile properties; nanocomposite extrusion; melt processing; electron microscopy; plasma enhanced chemical vapor deposition

## INTRODUCTION

Although dispersion of single-wall carbon nanotubes (SWNTs) and higher concentrations of multiwall carbon nanotubes (MWNTs) into a polymer matrix has been a significant challenge,<sup>1</sup> we have recently shown that in addition to a good dispersion, nanotube orientation is necessary to improve the mechanical properties of nanotube reinforced poly(methyl methacrylate) (PMMA).<sup>2</sup> The study showed that while moderate improvements (170% increase) in tensile toughness were observed for 1 wt % MWNTs oriented in PMMA, little improvement in modulus, yield strength, and high rate impact toughness was seen. Even at 10 wt % MWNTs in PMMA, the increase in modulus was marginal. Therefore, based on the mechanical property data, in addition to good dispersion and orientation of the nanotubes, the nanotube/polymer interface needs to be engineered to optimize the nanotube-matrix interface for a combination of adequate stress transfer at low strains and frictional energy dissipation at higher strains.

Research has focused on surface functionalization and modification of carbon nanotubes (CNT) for dispersion in polymer matrices.<sup>3–8</sup> Two recent publications review the state of technology for CNT composites<sup>9,10</sup> and discuss the effects of nanotube functionalization. Current efforts are focused on optimization of the CNT/polymer interface to improve load transfer from matrix to particle.<sup>6</sup> The primary approach for interfacial augmentation has been chemical functionalization of the nanotube, which is reviewed by Andrews and Weisenberger.<sup>9</sup> This paper discusses work that aims to tailor the surface of the MWNTs via plasma enhanced chemical vapor deposition (PECVD) to improve mechanical properties of the composite through improved interfacial bonding at the polymer/nanotube interface.

## EXPERIMENTAL

### Materials

Poly(methyl methacrylate) (Plexiglas<sup>®</sup> V920) was obtained by Atofina Chemicals Inc. (Philadelphia, PA). The number average molecular weight ( $M_n$ ), polydispersity, and density were 45,000 g/mol, 1.9, and 1.19 g/cm<sup>3</sup>, respectively. Multiwall carbon nanotubes were supplied by Nano-Lab (Newton, MA). These nanotubes (with purity > 95 wt % via energy dispersive X-ray analysis) were produced via PECVD using acetylene and ammonia with nickel catalyst particles on the substrate.<sup>11</sup> The diameter of these MWNTs was

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specified by the supplier as 20–50 nm with lengths 5–20  $\mu\text{m}$ . We have confirmed this via both scanning and transmission electron microscopy.

### Experimental techniques

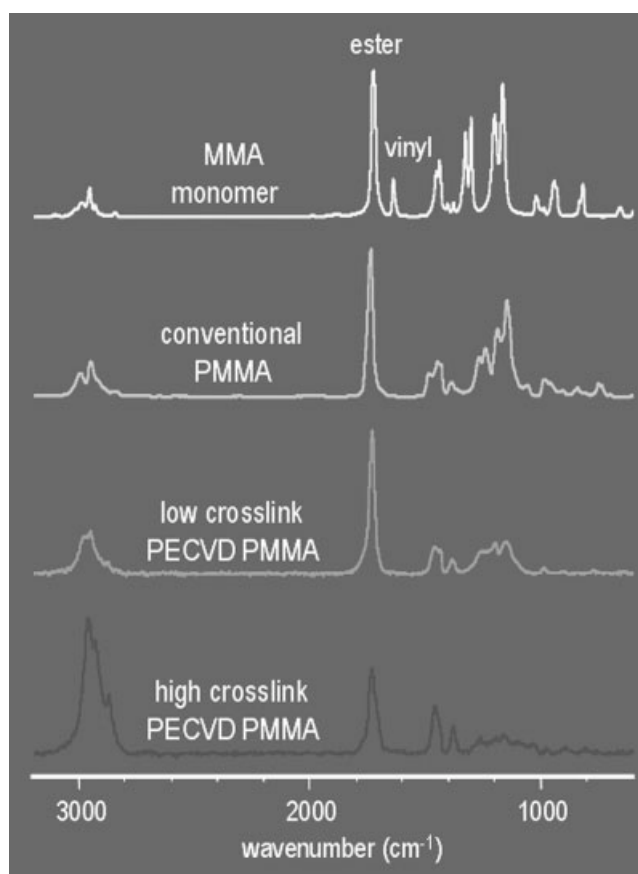
Multiwall carbon nanotubes (MWNT) were coated with PMMA via PECVD. To enhance the ability to achieve a conformal coating around each individual CNT, a fluidized bed PECVD setup was devised to allow continuous agitation of the nanotubes during the plasma coating process. Argon was used as the diluent and fluidizing gas at a flow rate of 55 sccm. Methyl methacrylate monomer (from Aldrich) flow rate was 10 sccm. The process inherently produces crosslinked coatings; the degree of crosslinking was controlled by pulsing the plasma at two different pulse duty cycles or frequencies. The highly crosslinked PMMA was formed at a pulse cycle of 100/50 ms on/off times while the lightly crosslinked PMMA was made at a 10/200 ms on/off pulse cycle (at a peak pulse power of 300 W). A batch size of 0.4 g of nanotubes was coated. Deposition time was 10 min. Fourier transform infrared (FTIR) spectroscopy was used to characterize the PMMA coatings. To facilitate observation, the coatings were made on KBr powder using identical conditions as for the nanotubes described above. FTIR spectra were acquired under transmission with a Thermo Nicolet NEXUS 870 using a DTGS detector at  $4\text{ cm}^{-1}$  resolution. Thermogravimetric analysis (TGA) (Perkin–Elmer Pyris 1) was used to measure the mass fraction of CNTs in the composite. Approximately 20 mg of the composite was heated from  $25^\circ\text{C}$  to  $950^\circ\text{C}$  at a rate of  $20^\circ\text{C}/\text{min}$  in a nitrogen environment.

Nanocomposites were fabricated via melt mixing and extrusion as described in an earlier publication.<sup>2</sup> Tensile measurements were made on drawn and as-extruded strands using a Texture Analyzer TA.XTPlus (Texture Technologies, Scarsdale, NY) with a gauge length of 22 mm and a cross-head speed of 1.2 mm/min. For each sample, 10–20 tensile specimens were tested and each property was averaged. Error bars were calculated using the standard error (standard deviation/(number of specimens tested)<sup>1/2</sup>) for every sample population. Dispersion and orientation of nanotubes was investigated by scanning electron microscopy (SEM) using a JEOL 6320FV (a field-emission high-resolution SEM) and transmission electron microscopy (TEM) using a JEOL 200CX with a tungsten filament. Sample preparation is described in an earlier work.<sup>2</sup>

## RESULTS AND DISCUSSION

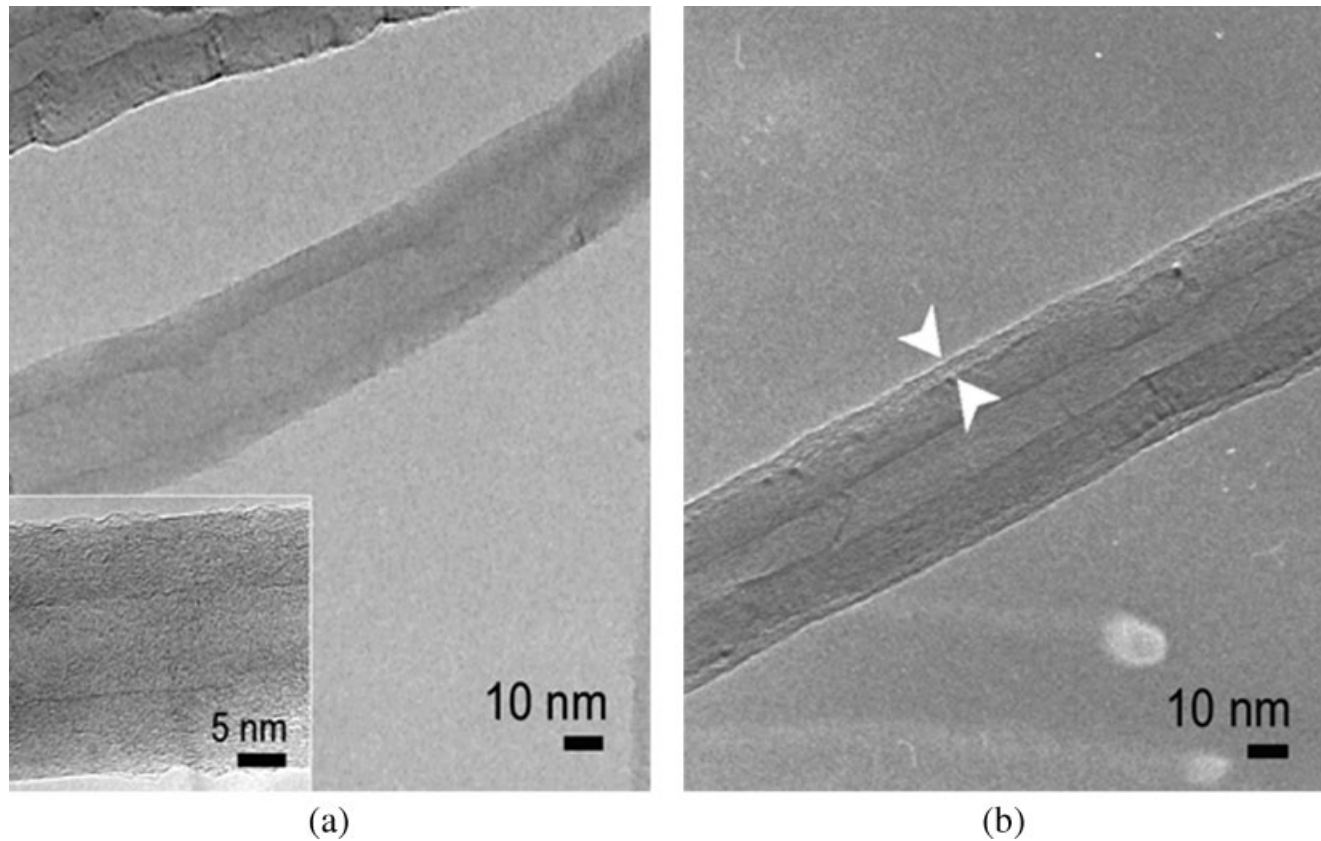
### Analysis of PMMA-coated MWNTs

Figure 1 shows the FTIR spectra of highly crosslinked PMMA and lightly crosslinked PMMA coat-



**Figure 1** Fourier transform infrared spectra of MMA, linear PMMA, low crosslink PECVD PMMA, and high crosslink PECVD PMMA.

ings on KBr, deposited at 100/50 and 10/200 ms on/off plasma pulse cycles, respectively. Both spectra show the presence of the carbonyl stretch at  $1731\text{ cm}^{-1}$ , indicative of the MMA structure. The higher carbonyl peak intensity relative to the  $\text{CH}_x$  stretch in the  $2900\text{--}3000\text{ cm}^{-1}$  region of the 10/200 spectrum confirms the lightly crosslinked structure that preserves more of the MMA unit compared with that of the 100/50 spectrum. The stronger presence of bands at  $1142$ ,  $1193$ ,  $1235$ , and  $1250\text{ cm}^{-1}$  in the 10/200 spectrum, representative of linear PMMA, also supports this view. Figures 2(a) and 2(b) show TEM images of the MWNT before and after PECVD coating, respectively. The polymer coating is measured to be on the order of 10 nm from TEM. Additionally, uniform conformal coatings were achieved via the PECVD process as shown by both TEM and SEM. Figure 3 shows SEM images of uncoated versus PMMA-coated MWNTs. As is seen in the figure, coated nanotubes are considerably thicker. It is conceivable that the PECVD coating could be covalently bonded to the nanotube surface (which could affect load transfer). Currently, the characteristics of the interface between the PECVD coating and the nanotube surface are unknown.

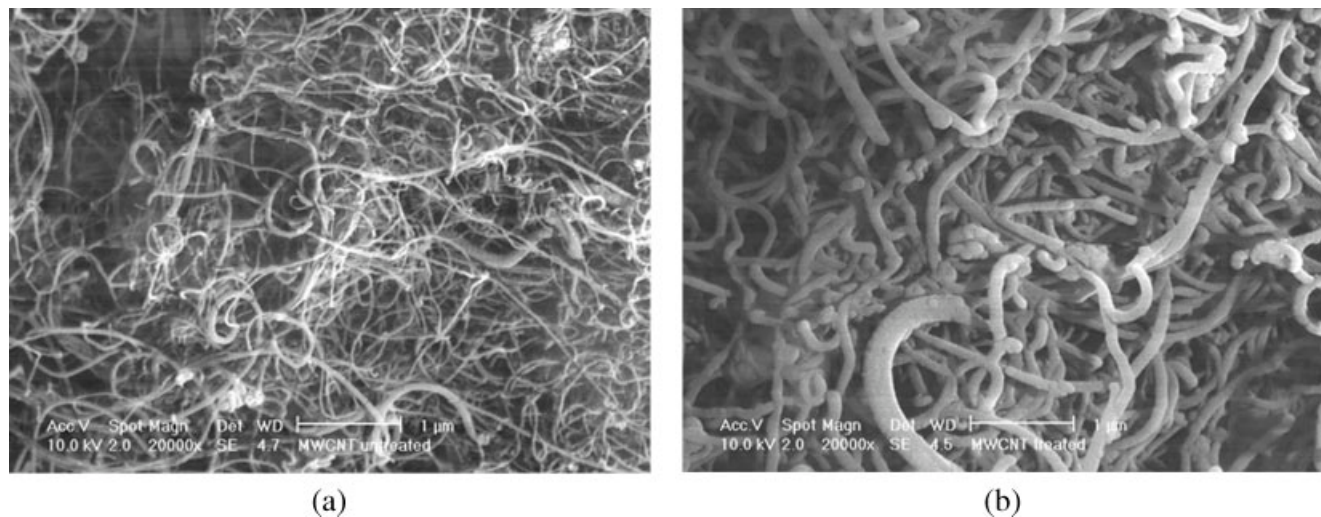


**Figure 2** TEM images of a MWNT (a) before coating and (b) after PECVD coating.

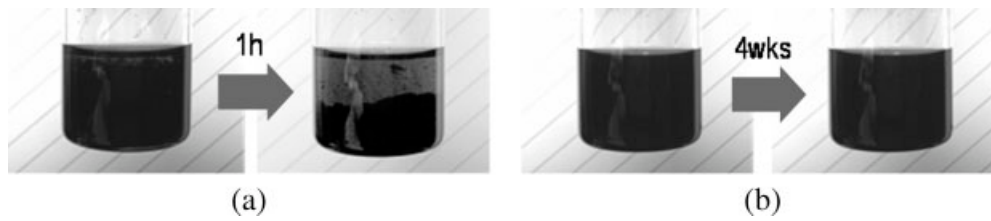
As a first step, the uncoated and PMMA-coated nanotubes were dispersed in a PMMA/toluene solution at concentrations from 0.001/20 w/w to 1/1 w/w. Figure 4 shows the dispersion for the 1/1 w/w ratio. As is seen, the uncoated nanotubes fall out of suspension after only 1 h, whereas the coated nanotubes remain suspended for more than a month.

**Analysis of MWNT/PMMA nanocomposites**

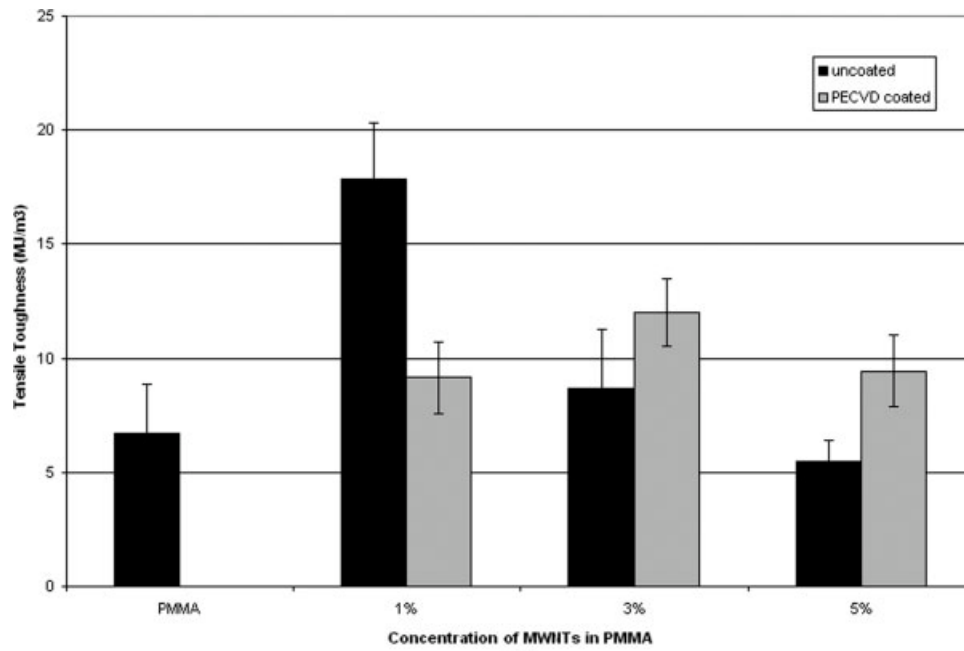
After nanocomposite processing in the melt extruder and subsequent melt drawing, the concentration of MWNTs in the nanocomposite was measured via TGA. The data show that uncoated and PMMA-coated MWNT concentrations were within 10–20% of the nominal loading level. Replicates of samples



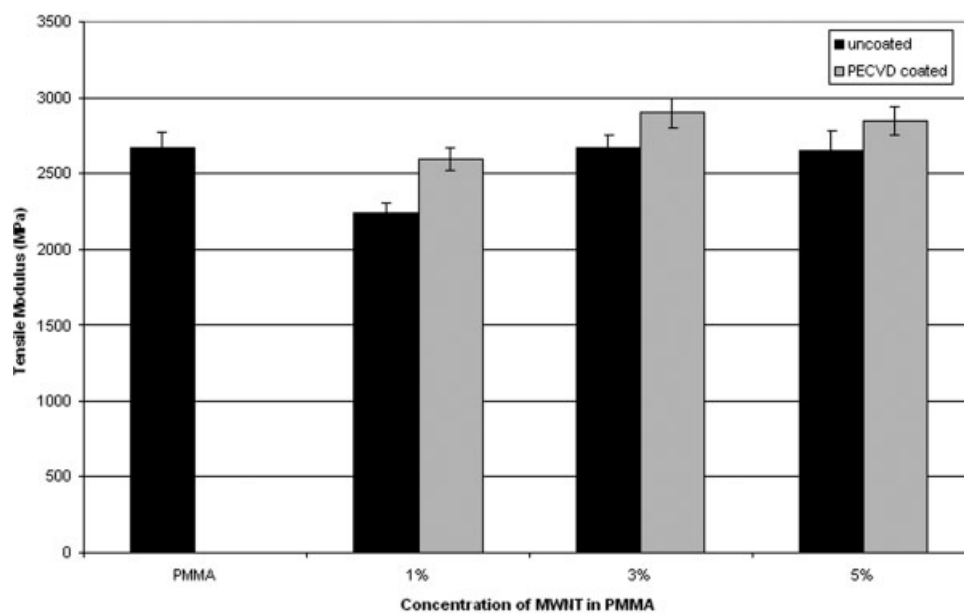
**Figure 3** SEM images of MWNTs (a) before PECVD coating and (b) after the fluidized bed PECVD treatment.



**Figure 4** Photographs of the dispersion of MWNTs in toluene (1/1 w/w ratio) for (a) the uncoated MWNTs and (b) the MWNTs with the PECVD PMMA coating.

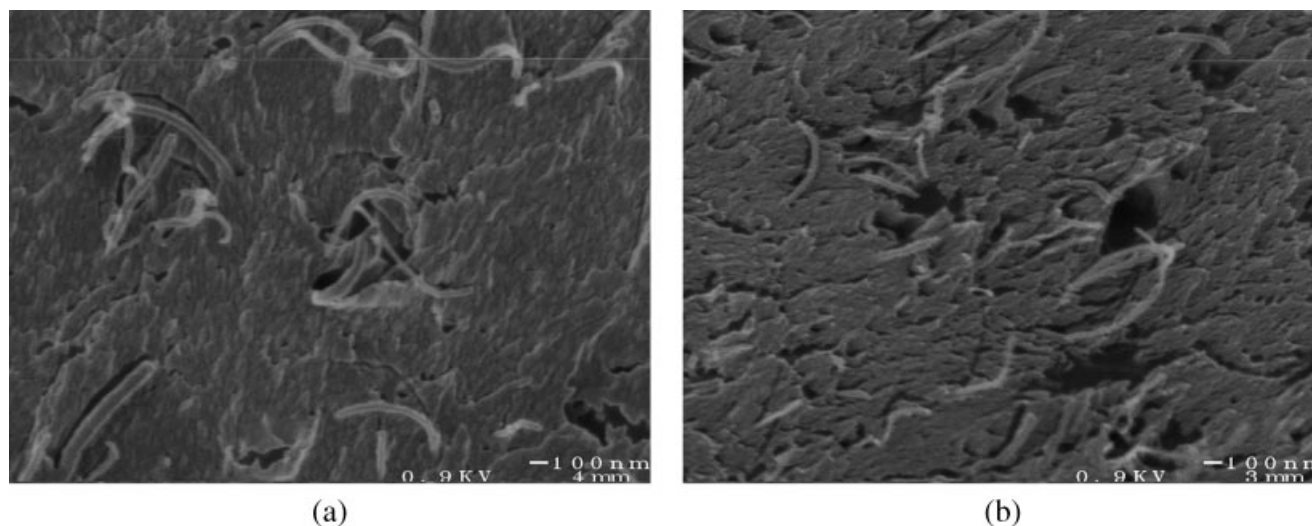


(a)



(b)

**Figure 5** (a) Tensile toughness ( $\text{MJ/m}^3$ ) and (b) modulus (MPa) for drawn (10 : 1) PMMA and 1, 3, and 5 wt % MWNTs uncoated and coated via the PECVD fluidized bed process.



**Figure 6** SEM images of cleaved surfaces (normal to the direction of orientation) for 5 wt % loadings of (a) uncoated and (b) PECVD fluidized bed coated MWNTs in PMMA.

showed the same error range, suggesting that the thickness of the coating had a negligible effect on the final concentration in the nanocomposite. The variability is thought to be a result of local inhomogeneity of nanotubes in the nanocomposite fiber.

The tensile toughness and modulus are extracted from the averaged curve and the statistics were calculated using an analysis of variance. Figure 5 shows the effect of MWNT coating treatment with several different concentrations of MWNTs in PMMA on the tensile toughness and modulus for samples with draw ratios of 10 : 1. (Since there was no statistical difference in mechanical properties for the two coating crosslink densities, only the data for the highly crosslinked coatings are presented. Additionally, the tensile properties for the coated-MWNTs are consistent with the increase in tensile properties as a function of draw ratio, as reported earlier, for the uncoated MWNTs.<sup>2</sup>) The data in Figure 5(a) show that at 1 wt %, the toughness for the coated sample was significantly lower, suggesting that the nanotube crack-bridging toughening mechanism (as reported earlier for the 1 wt % sample)<sup>2</sup> is compromised by the PECVD coating. However, at 5 wt %, the coated sample is statistically tougher than the uncoated sample, but no different from that for pure PMMA. It is also interesting to note that there is no statistical difference in tensile toughness among the nanotube-coated samples as a function of concentration, unlike that for the uncoated samples, which show a maximum at 1 wt % indicating an optimal dispersion as discussed previously.<sup>2</sup> As shown in Figure 5(b), the coating resulted in a slight increase in modulus over the uncoated samples (however only the 1 wt % case was statistically significant). There were no statistical differences in the yield strength (not shown), except

for a slight increase in the 3 wt % coated sample. Overall, the mechanical property data indicate that there is a slight increase in modulus (especially at 1 wt %) for the coated MWNT samples. The increase in modulus (at 1 wt %) is coupled with a decrease in the tensile toughness, consistent with the concept of improved interfacial bonding and reduced frictional energy dissipation. It is important, however, to realize that the modulus for the coated MWNT composites (up to 5 wt %) is not statistically different from that of pure PMMA. Qualitatively, SEM fracture surfaces of the composites show that there is no difference in dispersion and orientation between coated and uncoated MWNTs in the PMMA matrix (as shown in Fig. 6), indicating that the coating had no effect on dispersion or orientation. However, it is well established<sup>2,12</sup> that at increased nanoparticle concentrations, clusters are harder to eliminate, and therefore it is not surprising to expect the nanotube coating to a diminished effect on the mechanical properties at higher nanotube concentrations. Additionally, the increase in nanotube concentration increases the material melt viscosity (as discussed by Winey and coworkers<sup>13</sup>) which could affect the degree of alignment at higher nanotube concentrations. The PECVD coating may also influence the viscosity and therefore the degree of nanotube alignment in the composite. Therefore, the degree of alignment as a function of nanotube concentration and between coated and uncoated nanotubes may not be identical. This is an area for future study. Based on the mechanical property data, the conformal PECVD coating marginally improved the load transfer from matrix to particle as originally anticipated, but the absence of very good nanotube orientation in the specimens masked any major influence

of this altered interfacial interaction on the measured mechanical properties. Also, we note that in the process of creating the conformal nanotube coating, an additional interface is produced. The interface between the PMMA-coating and the PMMA-matrix should be compatible and promote good adhesion at that interface. It is not clear, however, at which interface the breakdown in load transfer occurs, thereby limiting the anticipated stiffness enhancement and improved orientation via incorporation of conformally coated MWNTs.

### CONCLUSIONS

In this work PECVD was used to surface treat MWNTs with a PMMA conformal coating (using MMA monomer). Stable suspensions of MWNTs in organic solvents were achieved via the PMMA coating, whereas uncoated nanotubes precipitated readily. The coated-MWNTs were incorporated into PMMA. Dispersion and orientation were achieved by melt mixing and melt drawing, respectively. The tensile property data indicate that the nanotube coating slightly improved the load transfer from PMMA matrix to particle (over the uncoated MWNTs) as originally anticipated, but it did not significantly influence the dispersion and orientation of the nanotubes using the processing methods employed in the present study, and mechanical properties were not dramatically improved. Next steps may include optimizing the PECVD process to produce a coating that promotes molecular interpenetration at the matrix-coating interface. In addition, tests to determine the

extent of chemical bonding of the PECVD coatings to the nanotube surfaces would help to clarify the absence of significant improvements in mechanical behavior of the composites containing conformally coated nanotubes.

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