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Nanomechanical Properties of Teflon AF-MWCNT Bilayer Films

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ABSTRACT

Teflon AF (TAF) multi-walled carbon nanotube (MWCNT) suspensions have the potential for creating conductive coatings on insulating films for numerous applications. However, there are few studies on polymer MWCNT suspension properties and even fewer that use Teflon. To define mechanical and electrical property relationships, bilayer films of TAF-MWCNT suspensions were created with differing concentrations of functionalized and non-functionalized MWCNTs. Nanoindentation revealed that addition of 8 weight percent MWCNTs to TAF increased the elastic modulus by about 25% and hardness by about 15%. Conducting indentation showed 8 w/o MWCNT films exhibit uniform stable conductance once indentation depth exceeds several hundred nanometers. Films with lower concentrations of CNTs were insulating. The two techniques provide a unique description of structure property relationships in this suspension film system.

INTRODUCTION

Carbon nanotubes have become increasingly useful in the fabrication of conductive nanoparticle filled polymer materials [1] owing to their processability and unique combination of mechanical, electrical, and magnetic properties. Films with insulating and conducting surfaces on opposite sides are particularly interesting for use in applications where variable electrical properties over a short length scale are desired, but properties of the polymer must be maintained. There have been several studies involving polymer MWCNT suspensions [2-4] but very few using Teflon. TAF, an amorphous fluoropolymer, is ideal for electrical applications due to its low dielectric constant and high chemical resistance. A recent patent discusses the use of fluoropolymers as a binder for CNT coatings [5] to increase electrical conductivity, thermal resistance and interfacial adhesion; which suggests TAF would be a useful polymer for the conducting bilayer film. Multi-walled carbon nanotubes are desirable for this application due to their high conductivity (>100 S/cm), high aspect ratios (~1000:1) and relatively low cost compared to single-walled nanotubes. In their pristine form, MWCNTs are not readily soluble in many solvents; however, the surface can be functionalized to improve solubility. Mixtures of functionalized and non-functionalized MWCNTs are combined with TAF to create the conductive films characterized in study.

Nanoindentation is one of the most accepted methods of mechanical characterization for small volumes [6]. Instrumented indentation measures load as a function of displacement, from which hardness and reduced elastic modulus (elastic modulus of both the probe and material combined) are determined [6].

Scanning Probe Microscopy (SPM) is a contact microscopy method conducted by scanning a probe across the surface in a raster pattern. Numerous values can be obtained from the scans, among them the roughness RMS value and peak-to-valley ratio. The roughness of the film can have an effect on the actual contact area of the probe during indentation, thus affecting both mechanical [7] and electrical [8] characterization. In this experiment, the RMS values of polished cross-sections are used to verify the legitimacy of the mechanical and electrical property measurements.

In this study electrical properties of conducting films are determined with electrical contact resistance (ECR). Hysitron's NanoECR® method uses a conducting, boron-doped diamond tip to apply a voltage during indentation, passing current through the sample to a conducting stage. The force, depth, time and current measured throughout loading and unloading; creating a unique description of the mechanical-electrical relationship.

EXPERIMENT

Bilayer film systems were produced such that one side of the film was conductive and the opposite was insulating. The first system (system A) had 8 w/o MWCNT/TAF suspension as the conducting layer and pure TAF as the insulating layer. The second system (system B) had the same the conducting layer but used a 3 w/o suspension as the insulating layer.

The bilayer films were developed by combining MWCNT suspensions with TAF solutions in Fluorinert FC-40 (3M) solvent. The MWCNT suspensions were prepared by dispersing MWCNTs (Cheap Tubes Inc., 8-15 nm O.D., 10-50 µm length, >95% purity) in FC-40 by water bath sonication for 30 min at 50°C, giving a gel-like suspension. The TAF solution was prepared by dissolving Teflon AF 1600 (DuPont) in FC-40. The MWCNT suspension was then added to the TAF solution and sonicated for 30 minutes at 50°C. The films were cast into polyethylene trays followed by drying at 65°C in a forced air oven to remove the solvent. The second layer was cast on top of the first layer and drying again. Figure 1 shows scanning electron microscope (SEM) cross-sectional images of the bilayer films used in this study, System A (left) and System B (right).

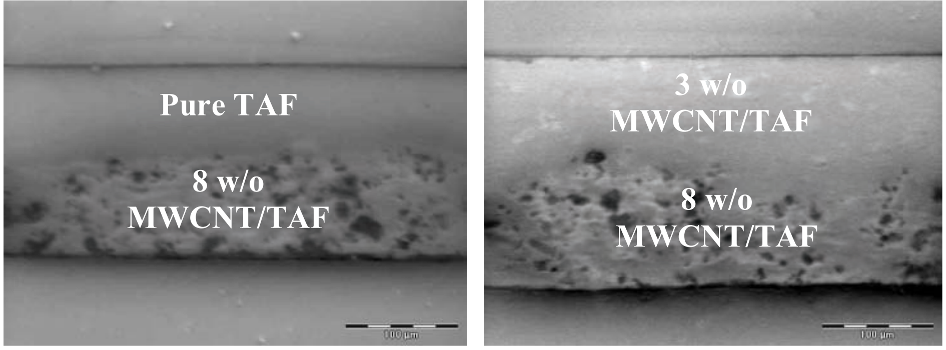

Figure 1. SEM image of the bilayer film systems. System A (left) with 8 w/o MWCNT (bottom half of film) and pure TAF (top half of film) and System B (right) with 8 w/o MWCNT (bottom half of film) and 3 w/o MWCNT (top half of film).

Both bilayer films were mounted in epoxy, cross-sectioned and mechanically polished for topographical, mechanical, and electrical characterization. The films were imaged using *in-situ* scanning probe microscopy with a Hysitron TI 750 Ubi nanoindenter equipped with a 50nm radius Berkovich tip. Each scan consisted of 4 passes at 0.5 Hz with a 10μm scan size. Mechanical properties were determined using the same Hysitron nanoindentation system using a larger radius Berkovich tip. The cross-sections of the films were indented using a load controlled, partial unload technique. The load function comprised ten loading segments with loading/unloading rates of 1000 μN/s and a peak load of 7000μN resulting in measurements at depths of 400 nm to 1500 nm. Indents were spaced 15 μm apart to avoid any interaction between the plastic zones that develop around indents.

Electrical characterization of the conducting film was performed using the NanoECR® feature of a Hysitron TI 900 TriboIndenter. The 8 w/o MWCNT/TAF conducting film of System B was indented at 1 V and peak loads of 6000 μN and 7000 μN. An I-V sweep was also performed from -10V to 10V while indenting to a peak load of 900 μN (corresponding to a depth of about 550 nm). I-V data was obtained at 2, 8, 14, 20, and 26 seconds during loading, and again at 34, 40, 46, 52, and 58 seconds during unloading to determine changes in electrical properties as a function of depth.

DISCUSSION

Cross-section Topographical Characterization

SPM was performed on the pure TAF of System A and both concentrations of System B to determine surface topography. Five different locations were imaged on each film to obtain an accurate topographical representation. Figure 2 shows typical SPM images of the three different concentrations. As the concentration of MWCNT increases, the roughness of the films also increases (1.42±0.31 nm, 2.91±0.45 nm, and 4.49±0.48 nm for pure TAF, 3 w/o and 8 w/o respectively). It should be noted that the RMS standard deviation also increases, indicating more irregularity in higher concentration films, which could be due to an increase in MWCNT agglomerates, or a polishing anomaly resulting from different film hardness.

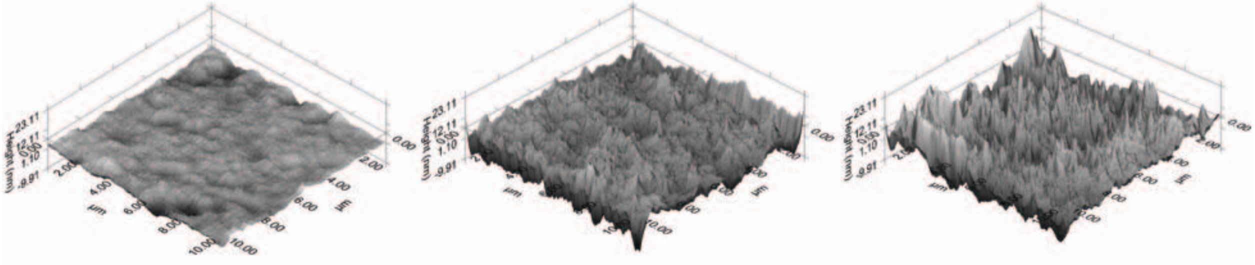

Figure 2. SPM scans of cross-sections of MWCNT-TAF suspension films, Pure TAF (left), 3 w/o (middle) and 8 w/o (right). There is a clear increase in roughness as the weight percent of CNT increases in the film.

Both mechanical and electrical properties are impacted by surface roughness. If the surface of the sample is too rough, the actual contact area, which is used in calculating mechanical properties, would be measured incorrectly leading to inaccurate E_r and hardness values. Since the surface roughness of the films is a few nanometers and mechanical characterization was conducted at several hundred nanometers, the properties reported in this study are representative of the bulk material properties.

Mechanical Properties

The partial unload technique in nanoindentation allows for multiple measurements to be conducted at different depths in a single indent, which increases data throughput and highlights depth dependence. None of the films indicate depth dependence for reduced elastic modulus (E_r) over the range tested; however the hardness increased slightly with depth. Table 1 shows E_r and the hardness of the three different concentrations for both systems.

Table 1. E_r and hardness values of different concentration films in both System A and System B bilayers.

MWCNT concentration (w/o)	E_r (GPa)	Hardness (GPa)
0 (System A)	1.77 ± 0.05	0.094 ± 0.003
8 (System A)	2.20 ± 0.04	0.110 ± 0.004
3 (System B)	1.88 ± 0.07	0.086 ± 0.003
8 (System B)	2.03 ± 0.11	0.096 ± 0.004

Mechanical properties are highly dependent upon processing conditions, specifically the amount of solvent remaining in the films, therefore, only comparisons between concentrations of a single system should be considered. In both systems, when examined individually, E_r and hardness increase as the CNT concentration increases; however, a relationship between all three concentrations cannot be directly determined. There is 22% increase in E_r and 17% increase in hardness between pure TAF and 8 w/o MWCNT in System A, while there is 8% increase in E_r and 12% increase in hardness between 3 and 8 w/o MWCNT in System B.

Both elastic modulus and hardness values are statistically different for the 8 w/o concentrations from System A and B (p value < 0.05 using a Wilcoxon-Whitney-Mann Rank Sum test). The E_r of the 8 w/o MWCNT of System A is 8% higher than System B and the hardness is 15% higher. This difference is most likely due to a higher percentage of retained solvent in System B, which results in greater deformation at a given load (decreasing hardness) and adds a higher percentage of low stiffness material (decreasing E_r).

Mechanical properties of the 8 w/o film from System B were also examined on the left edge (LE), middle (M), and right edge (RE) of a single film (Table 2) to determine uniformity of the bilayer films. Although all values are statistically different, except for LE and RE hardness, they are within 5% of each other, which suggests the MWCNT are evenly distributed across the film. The small variations are most likely due to different sizes of local MWCNT agglomerates.

Table 2. Lateral spatial variation in properties in the 8 w/o MWCNT/TAF of System B.

8 w/o MWCNT (System B)	E_r (GPa)	Hardness (GPa)
Left edge	2.09 ± 0.05	0.099 ± 0.001
Middle	2.04 ± 0.07	0.097 ± 0.004
Right edge	2.13 ± 0.06	0.100 ± 0.005

Electrical Properties

A typical ECR load-current profile is shown in Figure 3 (left). Current flows when at a critical depth, different for each indent, and increases until finally leveling off at the maximum current. The different conduction depths could be a result of polishing damage, different local concentrations of CNTs underneath the tip, or could be indicative of a percolation threshold for the films; whereas, the different maximum currents may be a result of different sizes of CNT agglomerates at the indentation site. Figure 3 (right) shows the relationship between maximum current and conduction depth, with no immediately apparent correlation.

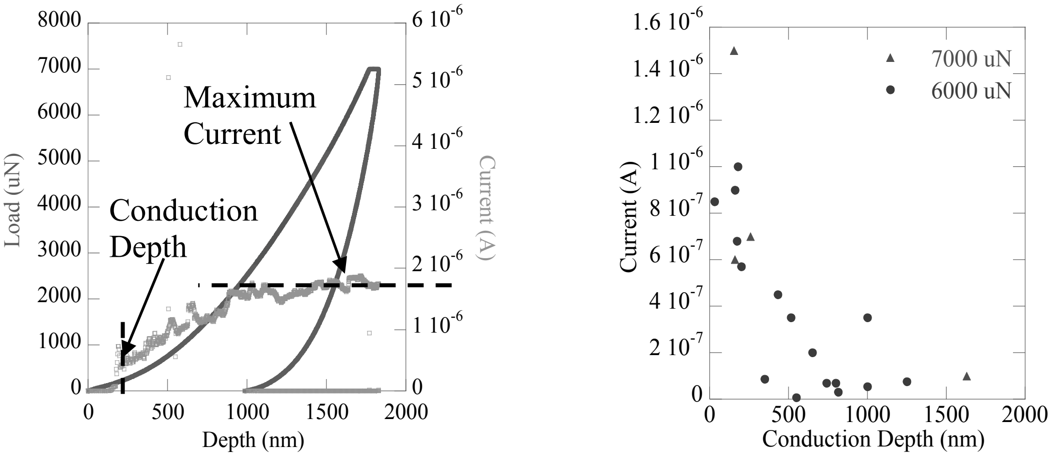

Figure 3. (Left) Typical nanoECR load-current relationship as a function of depth. An example of where the conduction depth and maximum current were determined are labeled. (Right) Maximum current vs. conduction depth for all indents at two different loads.

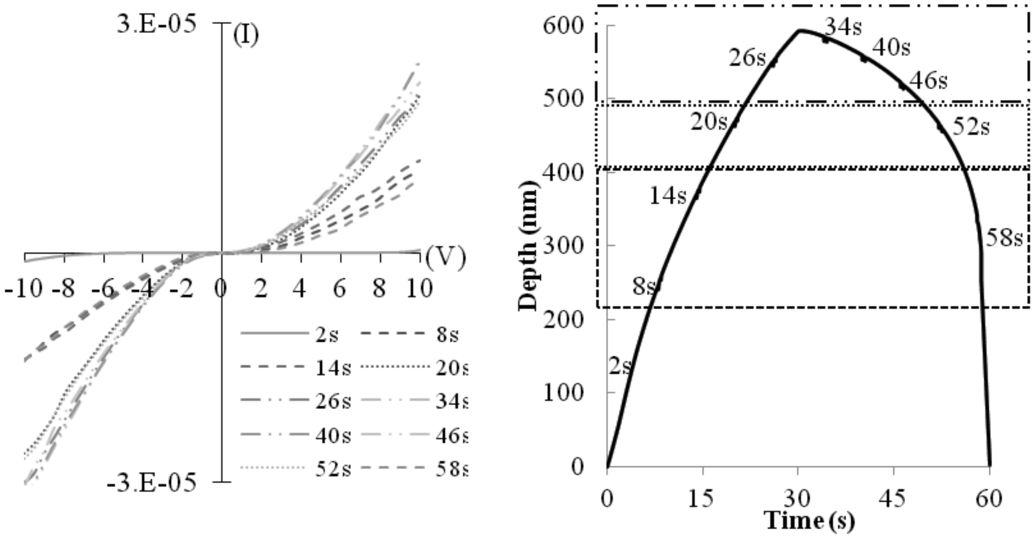

Figure 4. I-V sweep for one particular indent (left) and corresponding depth-time curve (right). Sweeps conducted at different times (analogous to different depths) are outlined in dashed boxes corresponding to the dashed lines in the I-V graph.

Figure 4 (left) shows the result of an I-V sweep for a single indent with the corresponding depth-time curve (right). Sweeps were performed at various times during the indent and correspond to different depths, as shown in the depth-time curve. The I-V curves follow similar trends but maximum current values vary with depth. The three different zones are outlined by the dashed boxes overlaid on the depth-time curve and correspond to similar dashed lines in the I-V graph.

Higher current values correlate to deeper indents, which may indicate a percolation threshold. A greater number of CNTs are forced into contact as more of the film is compressed, resulting in more current passing through the films. Alternatively, higher current values may be a result of increased contact area with the CNTs as the tip penetrates further into the film, allowing more current to pass.

CONCLUSIONS

Mechanical and electrical properties of MWCNT/TAF bilayer films were investigated using nanoindentation and nanoECR. SPM probed surface topography The following conclusions were drawn as a result of the tests:

(1) The elastic modulus and hardness increase as the concentration of CNTs increases.

(2) Processing conditions greatly affect the mechanical properties of the film as indicated by the different hardness and modulus values for 8 w/o from both systems. The lateral spatial variation in the mechanical properties of the films is within 5%. Each indent began conducting at different depths showing no apparent relationship, which could be a result of damage from polishing, an indication of a percolation threshold, or from different local concentrations of CNTs.

(3) I-V sweeps showed higher maximum currents occur at higher indentation depths which may further indicate a percolation threshold.

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