Studies of Carbon Nanotubes

Final Report
NASA Faculty Research Program - 2004
Johnson Space Center

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Date Submitted: August, 2004

Contract Number: NAG 9-1526 and NNJ04F93A

ABSTRACT

The fellowship experience for this summer for 2004 pertains to carbon nanotube coatings for various space-related applications. They involve the following projects: (a) EMI protection films from HiPco-polymers, and (b) Thermal protection nanosilica materials.

EMI protection films are targeted to be eventually applied onto casings of laptop computers. These coatings are composites of electrically-conductive SWNTs and compatible polymers. The substrate polymer will be polycarbonate, since computer housings are typically made of carbon composites of this type of polymer. A new experimental copolymer was used last year to generate electrically-conductive and thermal films with HiPco at 50/50 wt/wt composition. This will be one of the possible formulations. Reference films will be base polycarbonate and neat HiPco onto polycarbonate films. Other coating materials that will be tried will be based on HiPco composites with commercial enamels (polyurethane, acrylic, polyester), which could be compatible with the polycarbonate substrate.

Nanosilica fibers are planned for possible use as thermal protection tiles on the shuttle orbiter. Right now, microscale silica is used. Going to the nanoscale will increase the surface-volume-per-unit-area of radiative heat dissipation. Nanoscale carbon fibers/nanotubes can be used as templates for the generation of nanosilica. A sol-gel operation is employed for this purpose.

INTRODUCTION

Carbon nanotubes are of interest within NASA, as lightweight materials with enhanced mechanical, thermal, and electrical properties. For example, single carbon nanotube fibers have been shown to be stronger per weight compared to stainless steel (up to 100 times stronger) and Kevlar (14 times stronger). Also, they can posses electrical and thermal conductivities better than Copper. Within a polymeric matrix, thermal diffusivities can be at least 30 times that of the neat polymer.

EMI protection is normally associated with electrically conductive materials. Figure 1 below shows some of the previous results of comparisons of surface resistivities from various polymeric composites.[1]
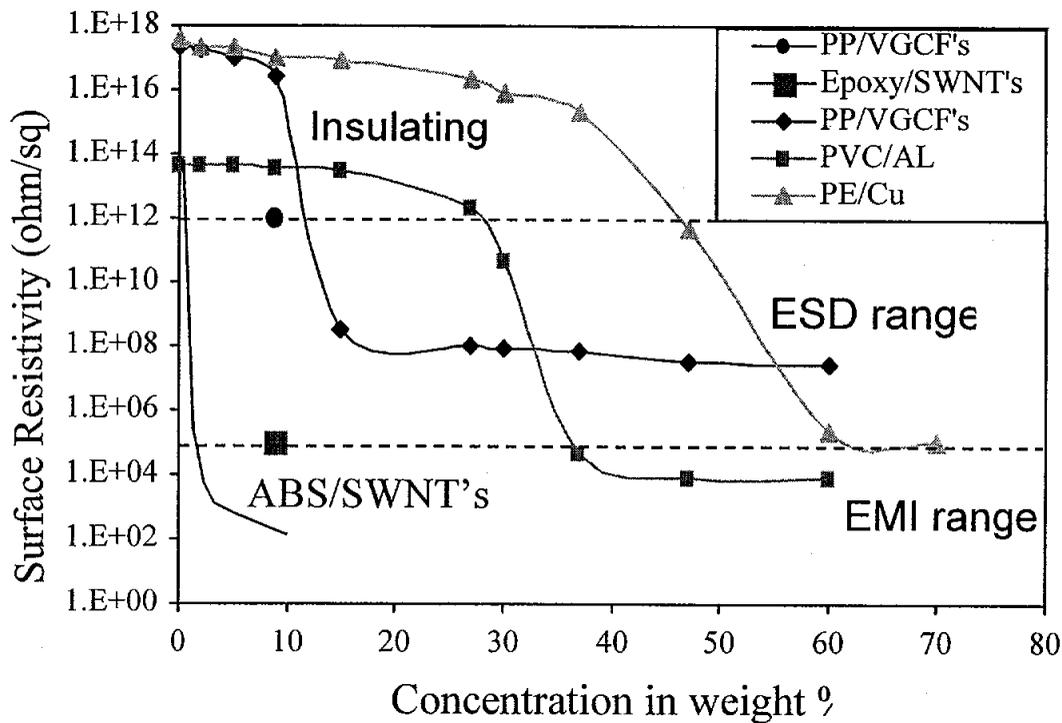
Figure 1: Surface resistivities of various polymeric composites.[1] Various nonconducting polymers are polypropylene (PP), epoxy, poly(vinyl chloride) (PVC), polyethylene (PE), and acrylonitrile-butadiene-styrene terpolymer (ABS). Conducting material fillers are vapor-grown carbon fibers (VGCF), single-walled carbon nanotubes (SWNT), Aluminum (AL), and Copper (Cu).

Based on Figure 1, EMI protection can be obtained if surface resistivities are below 10^5 Ohm/sq. This type of performance is obtained at much lower weight loadings for SWNT than for Copper and Aluminum fillers. This is not surprising, since single

SWNT fibers have similar electrical conductivities as metals at 1/5th the density. A possible stumbling block is that the Avionics has specified surface resistivities <50 mOhms/sq of 2.5-3 μm thick films. This is equivalent to a volume resistivities <0.125-0.15 μOhm-m or electrical conductivities >6.7-8x10^6 (Ohm-m)$^{-1}$. Such electrical conductivity values are just an order of magnitude less than those of metals. For example, Silver, Copper, Gold, and Aluminum have electrical conductivities of 6.8, 6.0, 4.3, and 3.8x10^7 (Ohm-m)$^{-1}$, respectively.[2] Even though a single crystal SWNT fiber could have a calculated electrical conductivity of 10^8 (Ohm-m)$^{-1}$,[3] it will be a challenge to attain the minimum required value of 6.7-8x10^6 (Ohm-m)$^{-1}$. The fellow believes that the required value was based on metallic systems, which are heavier than SWNT-based films. In the end, a balance between performance and weight would have to be determined.

Surface resistance (R_S) and surface resistivity (ρ_S) are obtained from the basic setup in Figure 2 below.[4]
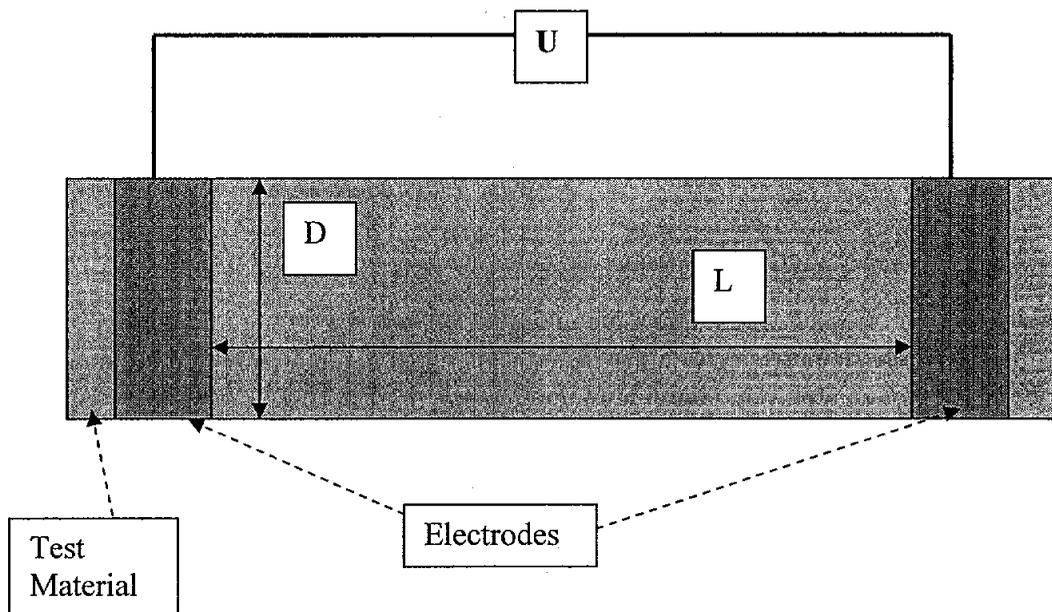
Figure 2: Top view of the basic setup for surface resistance (R_S) and surface resistivity (ρ_S) measurements.

The surface resistance is defined as the DC voltage (U) divided by the current (I_S) flowing between the two electrodes in contact with the surface of the test material (Figure 2).

$$R_S = \frac{U}{I_S} \qquad (1).$$

The surface resistivity, ρ_S, is determined by the ratio of the DC voltage drop (U) per unit length (L) to the surface current (IS) per unit width (D).

$$(2)$$

The surface resistivity is an inherent property of the material, and should remain the same regardless of the method and configuration of the electrodes. The surface resistance is specific to the setup and method of measurement. Based on Eqs. 1-2, both quantities should have dimensions of Ohms. To make the distinction, the surface resistivity is nominaly given the units of Ohms/sq instead.

To convert surface resistivity (ρ_S) to bulk resistivity (ρ)

$$\rho = (\delta_S)(\rho_S) \qquad (3)$$

where δ_S is the depth of the surface layer. Thus, the bulk resistivity would have units of Ohm-cm or Ohm-m. Finally, the conductivity (S) is defined as the reciprocal of the bulk resistivity, or

$$S = \frac{1}{\rho} \qquad (4).$$

The fellow will assist in the development of applications that involve polymeric coatings onto SWNTs. A particular focus area of application pertains to films for lightweight electrostatic and electromagnetic shielding. We will look into various organic polymer coatings that will be compatible with electrically conductive single-walled carbon nanotubes SWCNTs and various substrates within laptop computers used in the International Space Station (ISS). SWCNT/polymer films will be produced that could be applied onto an appropriate computer casing material. Working with engineers in the Avionics Division, electrical conductivity and static discharge properties will be obtained from these films in the future.

Another area of work is the use of carbon nanotubes for the development of thermal protection materials. This involves the application of silica coatings onto multi-walled CNTs. Silica-coated CNTs will be processed to remove the carbon core, in order to produce nanoscale silica tubes that could be used in the next generation of thermal protection tiles. Current thermal tiles are fused microscale silica rods. Since 90% of heat dissipation during the shuttle reentry is by radiative heat transfer, increasing the surface

area per volume of the tile material could be beneficial. Thus, there is interest in the development of silica nanotubes for this purpose.

EXPERIMENTAL

EMI Protection Films:

Since laptop computer cases have been found to comprise of polycarbonate composites, Lexan™ sheets have been envisioned as a good reference material. Base films will be purified HiPco and Laser nanotubes that will be cast onto Lexan™ sheets with DMF. The SWNT will be dispersed with the aid of an ultrasonic bath. Films will be cast using a handheld spray coating apparatus.

Other binders that will be investigated include: an experimental VA-t-AA copolymer with 6 wt % AA content[5] and commercial enamels, such as polyurethane, acrylics, polyester, and even epoxies. Film loading will be determined based on the amount of solid used per spray area. Finally, surface resistivity values will be obtained using the concentric cylinder apparatus at the RITF laboratory as well as a home-made version of Figure 2. Four measurements will be done at the sides of the four samples, and an average will be obtained.

Thermal Protection Nanosilica:

The procedure for the generation of silica nanofibers that can possibly be used as thermal protection materials is shown below.[6,7]

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┌─────────────────────┐                    ┌──────────────────────────────┐
│ PEI-Coated CNTs or  │                    │ 2:1:4 wt/wt/wt TEOS/Water    │
│ VGCFs in Water      │                    │ (pH=6 by HCl)/EtOH Sol for 48│
│                     │                    │ hrs                          │
└─────────────────────┘                    └──────────────────────────────┘
             \                5:1 wt/wt           /
              \                                  /
               \                                /
                \            ⊗                 /
                             │
                             │     Sonicate (80 W, 135 kHz) for 10 h
                             │     Let stand or mix for 100 h
                             │     Wash with EtOH
                             │     Centrifuge to collect solid product
                             │
                          ┌──┴──┐
                          │─────│
                          └──┬──┘
                             │
                             │     Dry @100°C for 6 hrs
                             │     Calcine @450°C for 12 h
                             │     Remove CNTs or  VGCFs by heating @
                             │        700°C for 12 h
                             ▼
                      ┌─────────────┐
                      │ SiOx        │
                      │ Nanotubes   │
                      └─────────────┘
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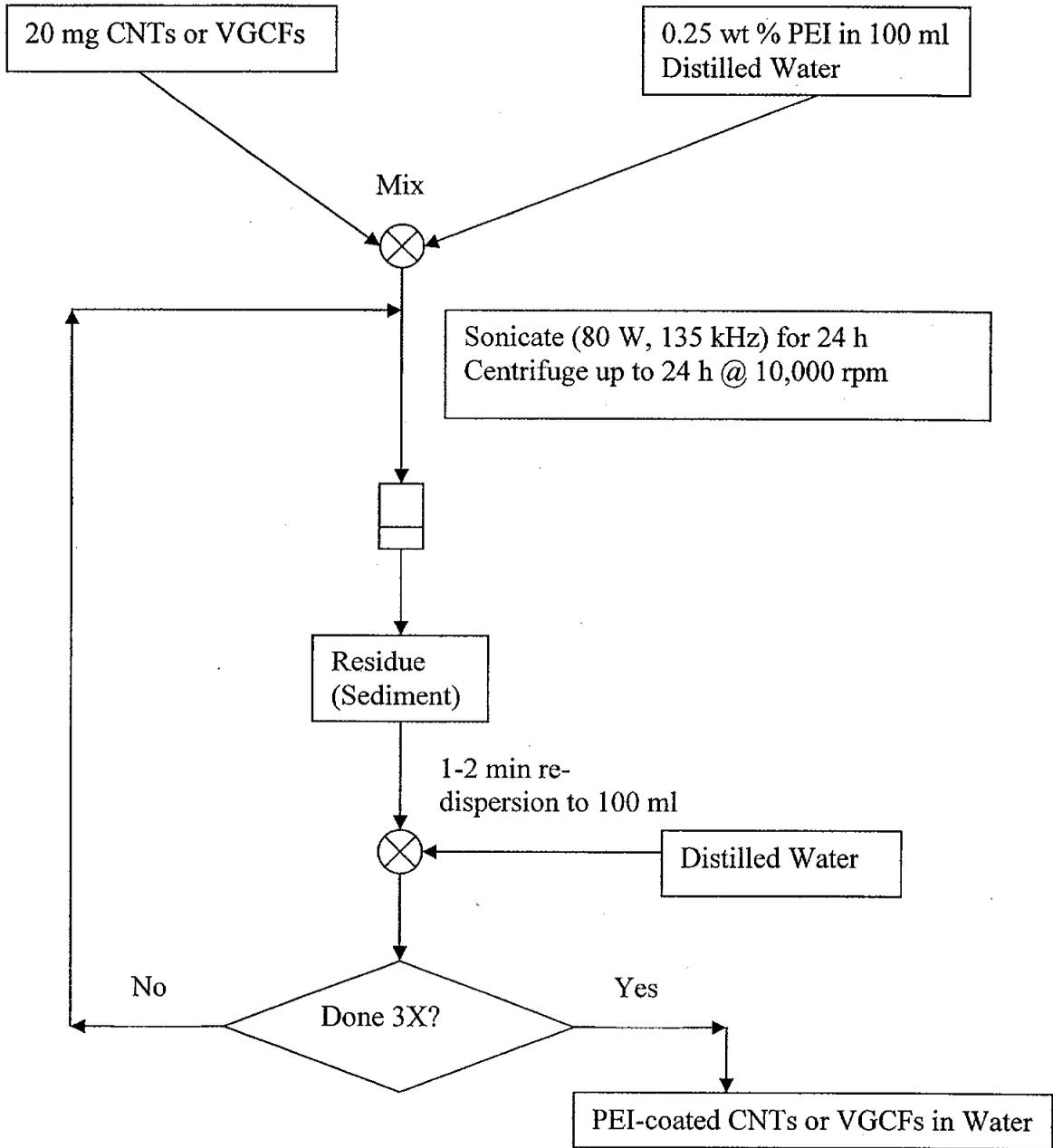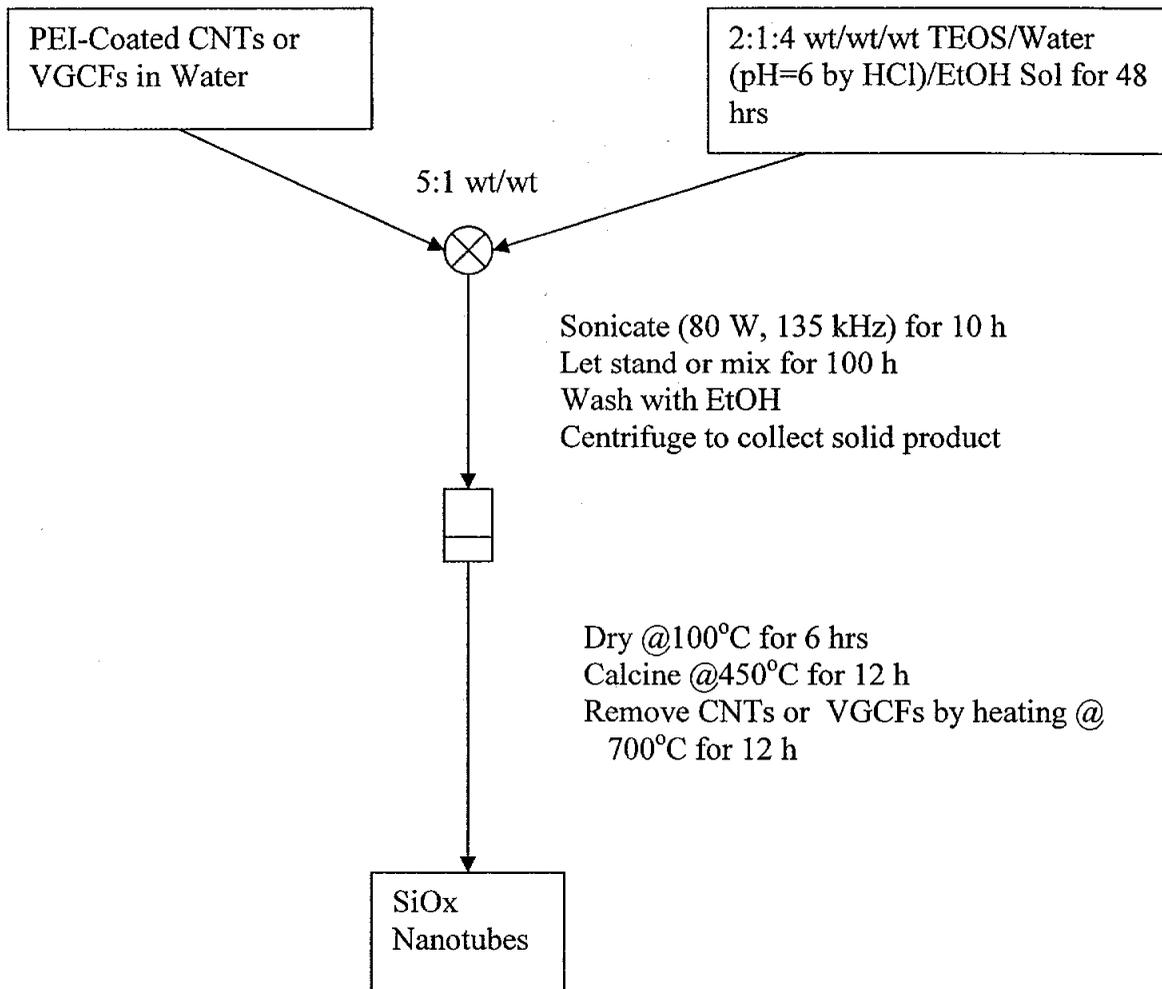
The mechanism of conventional sol-gel silica formation process is shown below. We note that there is a need for basic VGCF or CNT surface to form the silica via nucleation and growth.

◆ Hydrolysis
   $Si(OR)_4 + nH_2O = Si(OR)_m(OH)_n + nROH$
   Tetraethylorthosilicate or TEOS
                                    where n+m=4
Also,
   $Si(OR)_m(OH)_n = Si(OR)_m(OH)_{n-k}O^{k-} + kH^+$
   where m=0 in a basic environment
   $[pK_k] = [9.8 \quad 12.4 \quad 15 \quad 17.6]$

◆ Condensation
   (1) $SiOH + SiOH \dashrightarrow SiOSi + H_2O$
   (2) $SiOH + SiOR \dashrightarrow SiOSi + ROH$
   Condensation Rxn (1) is favored when $\alpha >> 2$
   Condensation Rxn (2) is favored when $\alpha << 2$
   $\alpha = H_2O/Si$ feed (mole/mole)

◆ Thus, a basic substrate will favor silica adsorption when $\alpha >> 2$

RESULTS AND DISCUSSION

EMI Protections Films:

Since DMF is the solvent of choice for the dispersion of CNTs, its compatibility with proposed additives for coatings formation was tested first. This was done by attempting to dissolve a small amount of the additives in DMF. Complete dissolution is needed; otherwise downstream processing will not be successful.

Results indicate that only the VA-t-AA copolymer would dissolve in DMF completely. The polyurethane enamel from Minwax did not dissolve at all. The acrylic material from Rust-Oleum did not completely dissolve either. Lastly, the polyester material formed a jelly fluid structure with DMF even without the presence of the catalyst. It is believed that the amine group in DMF acted as a catalyst. Therefore, these preliminary tests narrowed down our coating systems to SWNT/DMF and SWNT/VA-t-AA/DMF mixtures.

Another test was done on how DMF will dry onto a polycarbonate surface. This was done by applying a couple of drops of DMF onto a Lexan™ sheet and then leaving the DMF to dry in a fume hood. After a day of drying, area on the Lexan™ sheet that used to contain the DMF turned white, but the sheet did not deform. This means that the DMF partially swelled the Lexan™ surface and extracted low molecular weight moeties toward the surface. This might be a good thing, especially for the coating formulation that contains SWNT and DMF only. Here the SWNT would be deposited in the subsurface region of the Lexan™ sheet.

Mixtures containing 0.05-0.1 wt % SWNT (HiPco and Laser SWNT) were dispersed and sonicated; some of them contained various amounts of the VA-t-AA copolymer. The, the dispersed mixtures were sprayed onto the 4.5"x4.5"x0.093" Lexan™ sheets one layer at a time. It took at least one hour to dry a thin layer of the dispersion before the next spray. After drying the last spray, the coated Lexan™ coupon was vacuum dried at 60°C for 2 hrs. In Figure 3 below, SEM pictures of surfaces are shown.
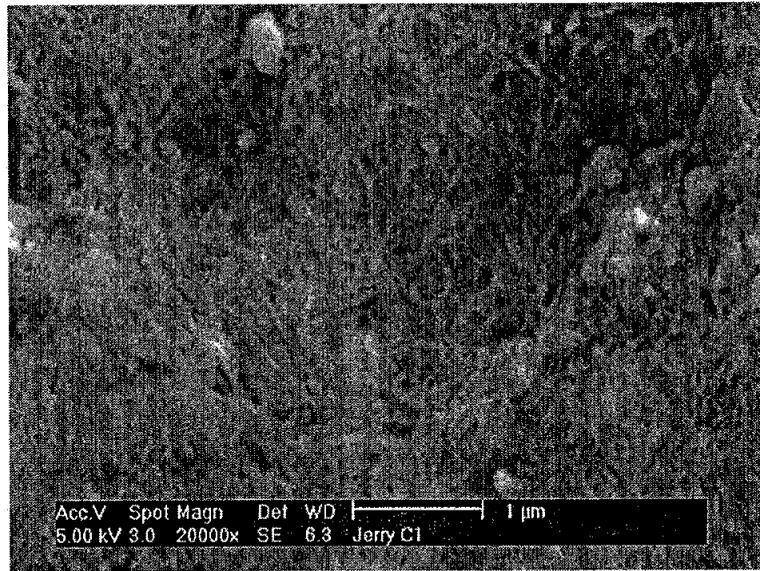
(a)
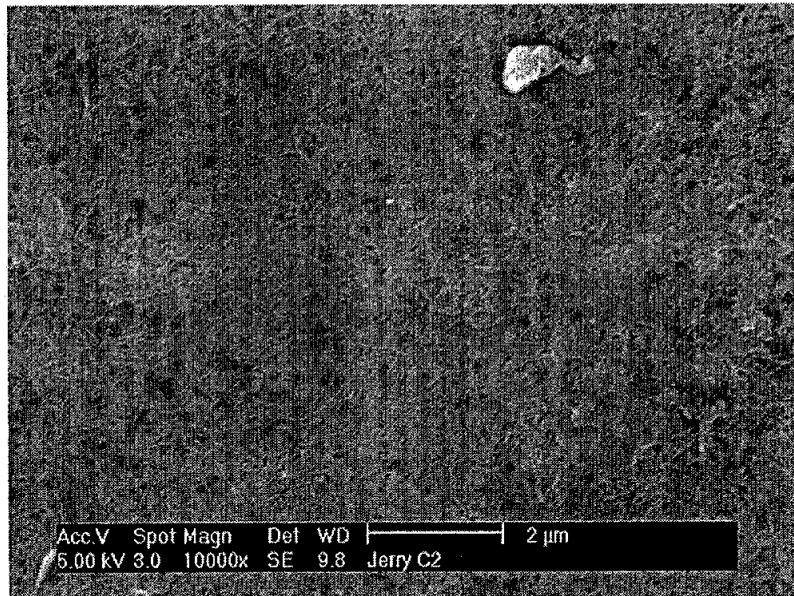
(b)

Figure 3: SEM pictures of surfaces of HiPco onto Lexan™ at HiPco loadings of (a) 0.12 mg/cm^2 and (b) 0.020 mg/cm^2.

Based on Figures 3(a) and 3(b), SWNTs were clearly seen on the Lexan™ surfaces when they were spray-coated from SWNT/DMF dispersions. As the SWNT loading increased,

the more the SWNT bundles are exposed on the surface. It seems that the swelling of the Lexan™ can accommodate only a finite layer of the SWNT. With the addition of a polymeric additive (VA-t-AA Copolymer), the SWNT bundles seem to become more and more embedded in the polymer as the VA-t-AA Copolymer proportion increases relative to the SWNT (Figure 4).
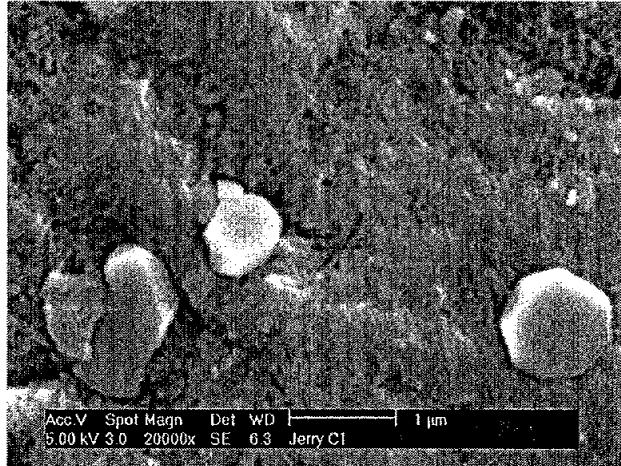
Figure 4: SEM of the surface of 91/9 VA-t-AA/HiPco on Lexan™ at a HiPco loading of 0.18 mg/cm^2.

Surface resistivities of four coated as well as the Lexan™ reference are shown in Table 1 below:

TABLE 1: Surface resistivities of costings onto Lexan™

Sample, Coating	Surface Resistivity based on Method in Figure 2, k-Ohms/sq		Surface Resistivity based on Concentric Circle Method, k-Ohms/sq	
	Readings	Average	Readings	Average
Reference - Lexan™	∞	∞	∞	∞
Pure HiPco @ 0.12 mg HiPco/cm^2	1.7,0.8,0.9,1.1	1.1	2.0,1.8,1.6,2.3	1.9
Pure HiPco @ 0.020 mg HiPco/cm^2	2.0,2.0,1.6,1.9	1.9	5.9,4.3,5.4,6.1	5.4
50/50 VA-t-AA/HiPco @ 0.10 mg HiPco/cm^2	3.3,2.3,1.8,2.8	2.6	3.5,5.6,4.5,2.8	4.1

91/9 VA-t-AA/HiPco @ 0.18 mg HiPco/cm^2	13,10,7,13	11	15,13,11,18	14

Readings based on the apparatus in Figure 2 are lower than those based on the Concentric Circle Method. The former is more reliable than the latter because test coupons are not completely flat. In general, more HiPco loading onto Lexan™ resulted in lower surface resistivities at the conductive range. For the VA-t-AA/HiPco composite onto Lexan™, surface resistivities depend on the HiPco loading and HiPco proportion in the surface composite layer. Even at a higher HiPco loading, surface resistivites can be relatively low at low HiPco proportion in the VA-t-AA/HiPco composite layer.

In order to determine the level of adhesion of the coatings onto the substrate, cross-cuts from a knife are made onto the coating surface in such a way that there are 25 1/8-inch-squares of coating material. Then, a Scotch™ tape is applied onto the cross-cuts with moderate pressure to ensure contact between the tape and the squares cut from the coating. Then, the tape is removed quickly. The equivalent number of squares removed determines the level of adhesion. In the samples indicated in Table 1, the pure HiPco coating @ 0.12 mg/cm^2 showed excellent adhesion at <1 Equivalent Squares removed. This is followed by the 91/9 VA-t-AA/HiPco coating with 16-20 Equivalent Squares removed. The rest of the coatings indicated 21-25 Equivalent Squares removed. Note that these adhesion measurements are done at the best regions of each of the coatings. With better spraying equipment, they would apply to the entire coatings.

Based on the above findings, it is better to use apply pure HiPco material onto Lexan™ using an appropriate solvent, such as DMF. In this case, DMF seems to be a slight swelling agent to Lexan™, which promotes some anchoring of SWNT onto the polymer surface. This work is preliminary, and more exhaustive studies are needed using better spraying equipment. Then the coatings have to be subjected to mechanical vibrational studies, to determine how performance will be affected.

In order to obtain better conductivity of SWNT-based coatings, the SWNT bundles and fibers can be aligned rheologically or by other means while the coating layers are drying. Also, metal nanoparticles can be added to the formulation, presumably to establish better connectivity between ends of SWNT fibers.

Thermal Protection Nanosilica:

The following carbon-containing starting mixtures were prepared for overnight sonication:
Mixture #1 – 20 mg VGCF, 250 mg 1.2 KDaltons PEI, 100 g DI Water
Mixture #2 – 20 mg VGCF, 250 mg 1.2 KDaltons PEI, 100 g DI Water

Mixture #3 – 20 mg MWNT#1, 250 mg 1.2 KDaltons PEI, 100 g DI Water
Mixture #4 – 20 mg MWNT#1, 250 mg 1.2 KDaltons PEI, 100 g DI Water
Mixture #5 – 20 mg VGCF, 250 mg 10 KDaltons PEI, 100 g DI Water
Mixture #6 – 20 mg VGCF, 250 mg 10 KDaltons PEI, 100 g DI Water
Mixture #7 – 20 mg MWNT#1, 250 mg 10 KDaltons PEI, 100 g DI Water
Mixture #8 – 20 mg MWNT#1, 250 mg 10 KDaltons PEI, 100 g DI Water

After overnight sonication, only Mixtures #7 and #8 were reasonably dispersed. The rest settled completely to the bottom of the containers when allowed to stand for at least a day. Dry residues of the bottom layers of Mixtures #7 and #8 are 27 and 22 mg, respectively. Since the residues contain both CNTs and PEI, relative amounts of the residues are 10 and 8 wt %, respectively. Thus, continuation of the above-mentioned procedure was done with Mixtures #7 and #8.

Mixtures #7 and #8 were centrifuged starting at 1,600 RPM but found it to work at 10,000 RPM for 1 hr. Supernatants were removed and their pH values were measured to be equal to 9. Then, 100 ml DI Water was added to each residue, and the mixtures were sonicated again overnight. The, it took 13 hrs of centrifugation at 10,000 RPM to reasonably settle the residue. Even with careful removal of supernatants, only 60-65 ml were removed. This means that the MWNTs were well dispersed. Both supernatants registered a pH of 6. Again, DI Water was added to approximate total volumes to 100 ml. After overnight sonication, Mixture #8 was centrifuged at 10,000 RPM for 16 hrs. Then, 70 ml of the supernatant was decanted off with a pH of 5.3. Finally, DI Water was added to both mixtures to bring them 10 100 ml each, and then sonicated overnight.

The following TEOS-containing mixture was prepared and stirred for 48 hrs: 5 g DI Water with pH adjusted to 5 using HCl, 10 g TEOS, and 20 g ethanol. For 75 g each of Mixtures #7 and #8, 15 g each of the TEOS-containing mixture. These two resulting mixtures were sonicated overnight and stirred for 1000 hrs. Gel formation was evident and the mixtures became a little grayish. Sol-gel reaction was stopped by addition of ethanol to 300 ml in each mixture. Grayish gel residues were obtained after the resulting mixtures were centrifuged at 5,000 RPM for 30 minutes. An attempt was made to disperse these wet gels by adding ethanol and sonicating overnight. In the end, only a small percentage (about 5 wt % at most) was dispersed. Thus, the gels and liquid with small dispersions were dried in air and then in vacuum at 100°C for 8 hrs. Dry materials became black and turned into bits of brittle material. Figure 5 below shows their basic morphologies.

If the objective is to produce silica nanotubes, the pre-cursor material shown in Figure 5 indicates that the silica-formation reaction onto the CNTs was allowed to proceed longer than needed. Structures in Figure 5 can be explained as that of the early stages of coarsening, whereby a slender network structure evolved into a thick-walled open cell structure with rounded nodes.
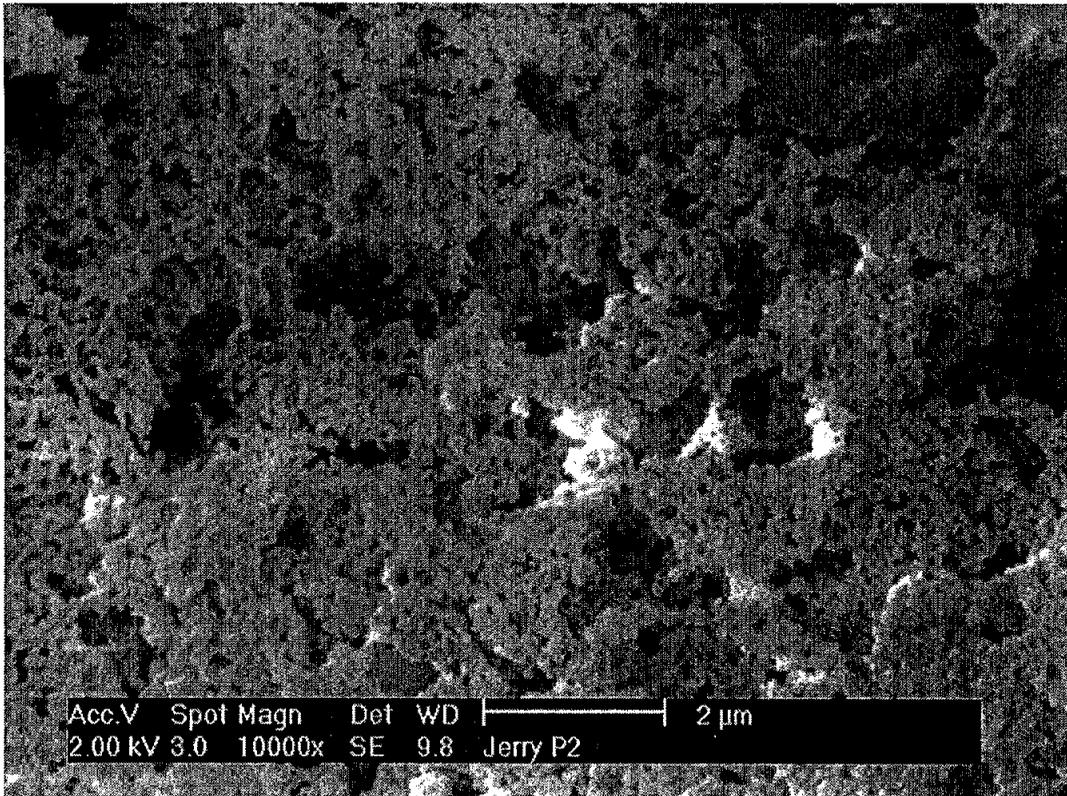
Figure 5: SEM of Silica templated from MWNT #8 before calcinations, showing an open cell network structure.

Calcination was done by heating the dried materials at 450°C for 12 hrs. We found that this resulted in some collapse of the open cell porous structure on Figure 5. After MWNT burn-off at 700°C for 12 hrs, surface area analysis was done with the products. Results still showed

In a new run, we took samples of various times during the MWNT-templated sol-gel process, and used a calcinations temperature of only 300°C for 12 hrs. Then, the MWNTs were burned off at 750°C for another 12 hrs. Resulting solid powdery materials are colored white, and Figure 6 below shows holes in the structure where the MWNTs have been burned off. These burned off regions appear to be look like eye sockets from spheroidal shells.

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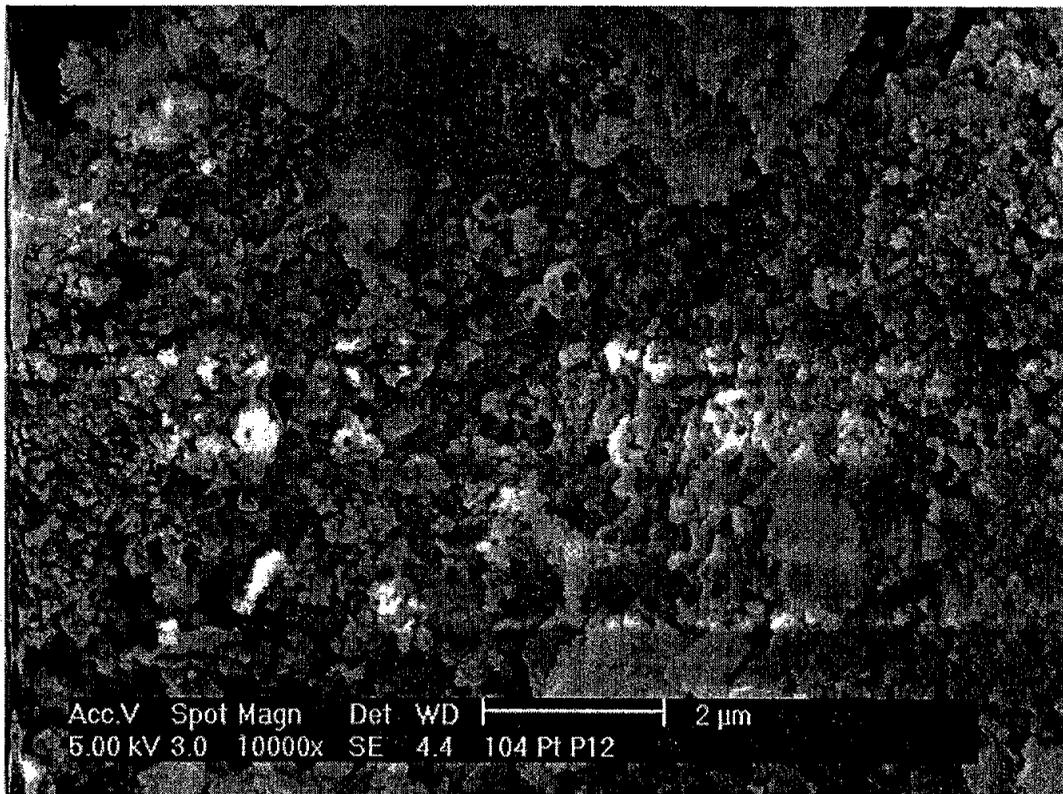
Figure 6: SEM of Silica after MWNT burn-off from MWNT-templated Sol-Gel process at 2 hrs of reaction. Regions where MWNT bundles (50-100 nm) have been burned off are seen in the form of "eye sockets" from spheroidal shells.

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