

# **CLEAR, CONDUCTIVE, TRANSPARENT, FLEXIBLE SPACE DURABLE COMPOSITE FILMS FOR ELECTROSTATIC CHARGE MITIGATION**

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## **Abstract**

Space environmentally durable polymeric films with low color and sufficient electrical conductivity to mitigate electrostatic charge (ESC) build-up have been under investigation as part of a materials development activity. These materials have potential applications on advanced spacecraft, particularly on large, deployable, ultra-light weight Gossamer spacecraft. The approach taken to impart sufficient electrical conductivity into the polymer film while maintaining flexibility is to use single wall carbon nanotubes (SWNTs) as conductive additives. Approaches investigated in our lab involved an in-situ polymerization method, addition of SWNTs to a polymer containing reactive end-groups, and spray coating of polymer surfaces. The work described herein is a summary of the current status of this project. Surface conductivities (measured as surface resistance) in the range sufficient for ESC mitigation were achieved with minimal effects on the physical, thermal, mechanical and optical properties of the films. Additionally, the electrical conductivity was not affected by harsh mechanical manipulation of the films. The chemistry and physical properties of these nanocomposites will be discussed.

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## **Introduction**

Large, deployable, ultra-light weight spacecraft require polymeric materials that possess a unique combination of mechanical and optical properties.<sup>1</sup> Specific requirements for the materials are determined by the mission and orbital environment of the spacecraft. A few of the desired properties include atomic oxygen (AO) resistance [for spacecraft in low Earth orbit (LEO)], low solar absorptivity (low color), high thermal emissivity, resistance to ultraviolet (UV) and vacuum UV radiation, good mechanical properties, good processability, tear resistance, the ability to be folded and unfolded, and sufficient electrical conductivity for

mitigation of electrostatic charge (ESC) build-up. The overall goal of this work is to prepare clear, colorless, flexible, anti-static, space environmentally durable polymer films to satisfy material needs for future NASA missions.

Many of the property requirements for these applications are met by using aromatic polyimides due to their exceptional mechanical properties as well as resistance to UV and charged particle radiation. By proper choice of the constituent monomers, low color (low solar absorptivity) and AO resistant polyimides can be prepared.<sup>2-4</sup> However, the incorporation of sufficient electrical conductivity to mitigate ESC build-up without adversely effecting low color and flexibility has been difficult to achieve.

Particles in the Earth's orbital environment include electrons/ions, solar flare protons and cosmic rays.<sup>5-7</sup> Because of the high energies of these particles, they can penetrate spacecraft materials and cause destructive effects including loss of optical and/or mechanical properties. Energetic charged particles, particularly electrons, can also penetrate spacecraft surface layers, depositing a charge onto insulators and other electrically isolated surfaces on a spacecraft. This can result in ESC build-up and development of large electric fields and consequent discharging. Discharge of the built-up charge can cause catastrophic damage to sensitive spacecraft electronics.<sup>8,9</sup> The surface resistivity needed to mitigate ESC build-up on insulators such as polymer films is in the range of  $10^6$  to  $10^8$   $\Omega$ /square.

One approach to imparting surface resistivity into polymer films without severely detracting from the desired optical and thermo-optical properties is through the use of single walled carbon nanotubes (SWNTs). Discovered in the early 1990s,<sup>10,11</sup> SWNTs exhibit great potential for improving the electrical properties of materials. However, achieving good dispersion of SWNTs throughout a polymer matrix has been difficult due to the insolubility of the SWNTs and/or incompatibility with the host resin. SWNTs tend to agglomerate in solvent and the host resin and even if dispersed, typically re-agglomerate soon thereafter due to electrostatic attraction.

Three methods that use SWNTs as conductive additives have been investigated for incorporating surface resistivity into space environmentally durable polymer films. These are 1) an in-situ polymerization approach,<sup>12-14</sup> 2) the addition of SWNTs to amide acid polymers containing reactive alkoxy silane end-groups,<sup>15-17</sup> and 3) the coating of SWNTs onto the surface of polymer films.<sup>13</sup> The first two approaches impart bulk and surface conductivity while the last approach imparts surface conductivity. The best results have been achieved with the last two methods.

This paper discusses two of the aforementioned methods used to prepare clear, conductive space durable materials: 1) end-capping a low color, space environmentally durable polyimide (LaRC™ CP2) with alkoxy silane groups and 2) surface coating polymers with SWNTs. The preparation and physical properties of the materials are described and compared herein.

## Experimental

### Starting materials

Aminophenyltrimethoxysilane (APTS, Gelest Inc., 90% meta, 10% para) and 1,3-bis(3-aminophenoxy)benzene (APB, Mitsui Chemicals America, Inc. mp 107-108.5 °C) were used as-received. 4,4'-Oxydiphthalic dianhydride (ODPA, Imitec, Inc., mp 224-225.5 °C) and 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA, Hoechst Celanese Inc., mp 241-243 °C) were sublimed prior to use. [2,4-Bis(3-aminophenoxy)phenyl]-diphenylphosphine oxide (3-APPO, mp 195-196.5 °C) was prepared as previously reported.<sup>2</sup> HiPco SWNTs (BuckyPearls™) were obtained from Carbon Nanotechnologies Inc. (batch # P0222) and were treated as described below. *m*-Cresol (Fluka) was vacuum distilled prior to use. Isoquinoline, *N,N*-dimethylacetamide (DMAc, anhydrous), *N*-methyl-2-pyrrolidinone (NMP, anhydrous), *N,N*-dimethylformamide (DMF, anhydrous), tetrahydrofuran (THF, anhydrous), 1,2-dichlorobenzene (DCB), sodium methoxide (powder), pyridine, and acetic anhydride were used as-received (Aldrich).

### SWNT treatment

The SWNTs were treated as follows: A 250 mL round-bottom flask was charged with SWNTs (0.100 g) and DCB (220 mL) and the mixture sonicated for 3 hrs at room temperature. In a separate flask, pyridine (80 mL) and sodium methoxide (0.264 g) were stirred under nitrogen at room temperature. The SWNT/DCB mixture was added to the flask containing the pyridine/sodium methoxide mixture and the resulting mixture heated to 80°C. After 16 hrs at 80°C, the temperature of the reaction mixture was increased to reflux. Pyridine was removed by distillation and the reaction mixture was stirred in refluxing DCB for 3 hrs. The mixture was then cooled to room temperature. The SWNTs were isolated via centrifugation, washed numerous times with methanol, and dried in a vacuum oven at 150 °C for 6 hrs. The treated tubes exhibited enhanced solubility properties (stable suspension). The mechanism for the enhanced solubility is currently under investigation. All SWNTs were treated via this process prior to use.

### Polymer synthesis

APB (6.7470 g, 0.0231 mol) and DMAc (30.0 mL) were placed into a 250 mL three neck round-bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube filled with calcium sulfate. Once dissolved, 6FDA (10.3044 g, 0.0232 mole, 0.5% offset) was added with additional DMAc (38.2 mL) to afford a solution with a solids content of 20% (w/w). The solution was stirred overnight at ambient temperature under a nitrogen atmosphere. The polymer was chemically imidized by the addition of 7.1 g of acetic anhydride and 5.5 g of pyridine and stirring at ambient temperature overnight. The polymer was precipitated in a blender containing water, filtered, washed with excess water and dried in a vacuum oven at 110 °C overnight to afford a white, fibrous material. All other polyimides were prepared as reported.<sup>2</sup>

## Synthesis of polymers end capped with alkoxy silanes

The alkoxy silane terminated amide acids (ASTAAs) were prepared by the reaction of 6FDA with APB and end-capped with APTS at a 2.5% molar offset. The calculated number average molecular weight ( $\bar{M}_n$ ) was  $\sim 27,700$  g/mole. The oligomer was prepared by dissolving APB (4.9522 g, 0.0169 mol) and APTS (0.1853 g, 0.0009 mol) in DMAc (7 mL) in a three neck round-bottomed flask equipped with a mechanical stirrer, thermometer and nitrogen gas inlet. The flask was then immersed in a water bath to regulate the temperature. 6FDA (7.7184 g, 0.0174 mol) was added in one portion as a slurry in DMAc (10 mL) and rinsed in with 9 mL of DMAc to afford a solution with a solid content of  $\sim 34.4\%$  (w/w). The reaction was stirred for  $\sim 24$  hrs at ambient temperature under nitrogen. An aliquot was removed to determine inherent viscosity. For film casting, the solution was diluted with an additional 21 mL DMAc to afford a solids content of  $\sim 22.5\%$  (w/w).

## Films

ASTAA-LaRC™ CP2 solutions in DMAc (with and without SWNTs in the bulk) were doctored onto plate glass and dried to tack-free state in a low humidity chamber at ambient temperature. The films were then staged to 300 °C for 1 hr in a forced air oven.

## Spray coating of SWNT

ASTAA-LaRC™ CP2 film solutions in DMAc were doctored onto plate glass and dried to a tack-free state in a low humidity chamber. A SWNT/DMF mixture (1.0 mg SWNT per 5.0 g DMF) was placed in an ultrasonic bath operating at 40 MHz for 6 to 8 hrs. An airbrush (Badger Model 250) was used to apply the SWNT/DMF suspension to the tack-free ASTAA-LaRC™ CP2 films. The films were placed in a low humidity chamber for 16 hrs and then staged to 300°C for 1 hr in a forced air oven.

Polyimide (LaRC™ CP2, TOR-NC<sup>3</sup> and PPO-6FDA, Figure 1) solutions in DMAc (23% wt/wt) were doctored onto plate glass and placed in a low humidity chamber for 15 minutes. A SWNT/THF mixture (1.0 mg SWNT per 5.0 g THF) was placed in an ultrasonic bath operating at 40 MHz for 1 to 2 hrs. An airbrush (Badger Model 250) was used to apply the SWNT/THF suspension to the films. The coated polyimide films were placed in a low humidity chamber for 16 hrs and then staged to 220 °C for 1 hr in a forced air oven.

## Other characterization

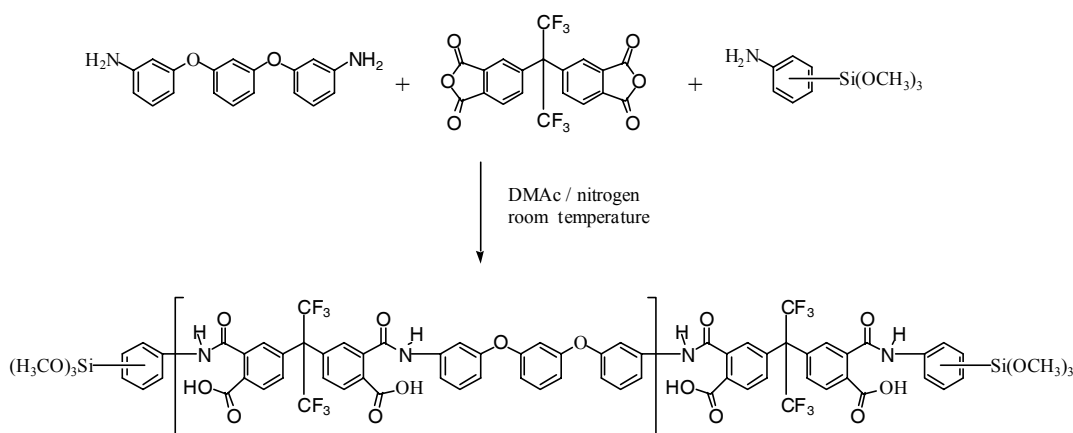
Inherent viscosity was obtained on a 0.5% (w/v) amide acid solution in DMAc at 25 °C. Melting point ranges (tangent of onset to melt and the endothermic peak) were determined by either differential scanning calorimetry (DSC) at a heating rate of 10 °C/min or visually on a Thomas-Hoover capillary melting point apparatus (uncorrected). The % transmission at 500 nm was obtained on thin films using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer. Solar absorptivity ( $\alpha$ ) was measured on an AZ Technology Model LPSR-300 spectrophotometer

with measurements taken between 250 to 2800 nm using a vapor deposited aluminum on Kapton® film (1st surface mirror) as a reflective reference for air mass 0 per ASTM E903. An AZ Technology Temp 2000A infrared reflectometer was used to measure thermal emissivity ( $\epsilon$ ). Surface resistivity was measured using a Prostat® PSI-870 Surface Resistance and Resistivity Indicator per ASTM D-257 and reported as an average of three readings. High-resolution scanning electron microscopy (HRSEM) images were obtained using a Hitachi S-5200 field emission scanning electron microscope (FE-SEM) equipped with a "through-the-lens" secondary electron detector. The FE-SEM was operated in the low voltage mode in order to setup a stable local electric field on the surface of the sample while minimizing beam induced sample damage.

## Results and Discussion

### Alkoxysilane terminated amide acid synthesis

The ASTAA of LaRC™ CP2 was prepared at a 2.5% molar offset corresponding to a calculated  $\bar{M}_n$  of  $\sim 27,700$  g/mol as illustrated in Scheme 1.<sup>14</sup> The diamine and amine-containing end-cap were initially dissolved in DMAc. The dianhydride was then added to the stirred solution. To prevent premature reaction of the alkoxysilane groups due to a temperature increase arising from heat of reaction, the reaction flask was immersed in a water bath at room temperature. The ASTAA mixture was stirred overnight at room temperature under a nitrogen atmosphere. The inherent viscosity of the ASTAA was 0.73 dL/g. This solution was used to cast thin films. For ASTAA samples containing SWNTs, the tubes were sonicated in DMAc for 6 hrs and subsequently added to an aliquot of the ASTAA solution. ASTAA-LaRC™ CP2 samples were prepared with 0, 0.03, 0.05 and 0.08 % (wt/wt) SWNTs.

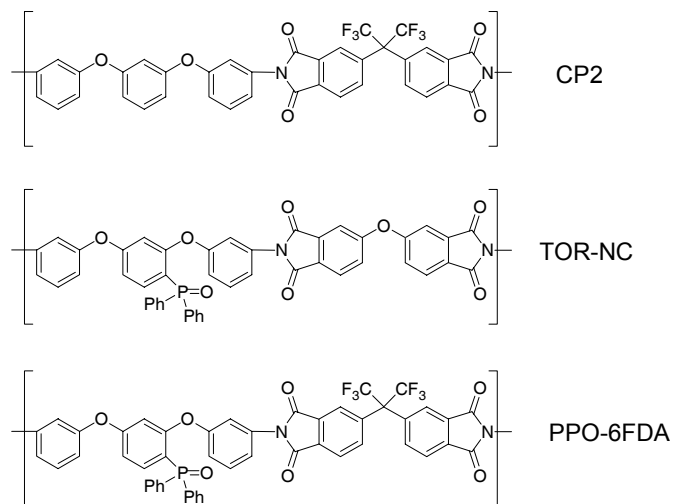


**Scheme 1. Alkoxysilane-Terminated Amide Acid (ASTAA) of LaRC™ CP2 Synthesis**

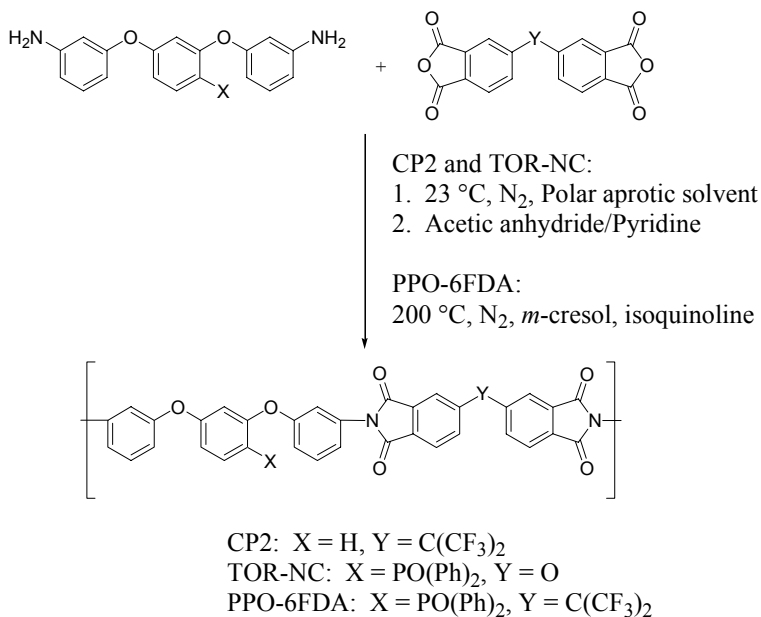
### Polyimide synthesis

Three polyimides (Figure 1) were prepared as shown in Scheme 2. For LaRC™ CP2 and TOR-NC, the polyimides were prepared via the chemical imidization method using pyridine and acetic anhydride as the cyclo-dehydrating agents. PPO-6FDA was prepared in *m*-cresol resulting in the one-step formation of the polyimide. All polyimides were recovered as white fibrous materials.

The three polyimides were chosen for this study because of their low color and space environmental durability. LaRC™ CP2 is resistant to UV radiation and is presently in use on spacecraft in geosynchronous orbit. TOR-NC and PPO-6FDA are low color, UV stable polyimides that are structurally similar to LaRC™ CP2. However, these two polyimides contain pendant phosphine oxide groups that impart AO resistance to the materials, potentially making the polymers suitable for applications on spacecraft in LEO where AO is prevalent.



**Figure 1. Structures of Polyimides**



**Scheme 2. Polyimide Synthesis**

## Spray-coating SWNTs onto polyimide films

To date, sufficient surface resistivity for ESC mitigation has been achieved by dispersing the SWNTs throughout the bulk of the polymer film. By this approach, the loading level needed to attain the percolation threshold has led to visual darkening of the films resulting in changes in the optical and thermo-optical properties of the nanocomposite as compared to the neat material.

Many applications on advanced spacecraft require conductivity on only one surface of the film. One approach to impart sufficient conductivity to one surface for ESC mitigation is by spray-coating the film with SWNTs. Typically a homogeneous solution is used in spray-coating processes; however, homogeneous dispersions of the SWNTs in DMF or THF were found to work well. After several trials, the best results for coating LaRC™ CP2, TOR-NC and PPO-6FDA were obtained using films that were cast from 23% solids in DMAc. These three polyimides (Figure 1) were coated with solutions containing 0.5, 1.0 and 2.0 mg of SWNTs. In addition, a series of alkoxy silane end-capped LaRC™ CP2 films were coated with SWNTs using this spray-coat method.

### Surface resistivity

The conductivity of the films was determined as surface resistivity under ambient conditions with the results presented in Table 1. It was observed that the spray-coated films exhibited surface resistivities that were acceptable for ESC mitigation (range of  $10^6$  to  $10^8$   $\Omega$ /square). For ASTAA LaRC™ CP2, LaRC™ CP2, TOR-NC and PPO-6FDA coated with SWNTs the percent SWNT (wt/wt) for each sample is unknown; instead the amount of SWNT (in milligrams) sprayed is indicated. For LaRC™ CP2, TOR-NC and PPO-6FDA, SWNTs were sprayed in amounts ranging from 0.5 to 2.0 mg of SWNT. One sample of LaRC™ CP2 was sprayed with a solution containing 4.0 mg of SWNT. To maintain consistency, the polyimide films were cast from 23% solutions using 1.0 g of polymer and a doctor blade set at 14 mils. The resulting films had a surface area of approximately 150 cm<sup>2</sup>.

The surface resistivities for the spray-coated films (P2 through P5, P8, P9, P11 through P15) were comparable to those obtained for the films containing the SWNT dispersed throughout the matrix (P18 and P19). The films that were not spray coated (P1, P6, P10) and P16, which did not contain SWNTs, were insulative with surface resistivities of  $10^{12}$   $\Omega$ /square. Film P7 exhibited a surface resistivity of  $7.0 \times 10^{10}$   $\Omega$ /square even though other films spray coated with a comparable quantity of SWNTs (P2, P11) exhibited values of  $10^7$   $\Omega$ /square. As anticipated, the spray-coated films were conductive on only one surface with the opposite surface being insulative ( $>10^{12}$   $\Omega$ /square). Although the SWNTs were dispersed throughout the matrix in P17, the loading level was not sufficient to achieve the percolation threshold needed for conductivity. Previous work with this polymer has indicated that a loading level of 0.04 % (wt/wt) is needed.<sup>17</sup> Film P5 exhibited the lowest surface resistivity of  $2.2 \times 10^5$   $\Omega$ /square. However, a tradeoff in properties occurred as this sample exhibited a higher  $\alpha$  and lower percent transmission at 500 nm as compared to P3 and P4 (discussed in next section). From Table 1 it is shown that there is little difference in the surface resistivities between polymers spray-coated with 0.5, 1.0, and 2.0 mg of SWNTs (P2 through P4, P8 and P9, P11 through P13) with the exception being P7. Film P15

exhibited an order of magnitude decrease in surface resistivity as compared to P14 presumably due to the greater amount of SWNTs sprayed onto the surface.

**Table 1. Surface Resistivity**

ID	Polyimide	% SWNT (wt/wt) <sup>a</sup>	mg of SWNT <sup>b</sup>	Surface Resistivity, $\Omega$ /square
P1	LaRC™ CP2	--	0	$2.5 \times 10^{12}$
P2	LaRC™ CP2	--	0.5	$1.6 \times 10^7$
P3	LaRC™ CP2	--	1.0	$6.1 \times 10^6$
P4	LaRC™ CP2	--	2.0	$2.0 \times 10^7$
P5	LaRC™ CP2	--	4.0	$2.2 \times 10^5$
P6	TOR-NC	--	0	$2.8 \times 10^{12}$
P7	TOR-NC	--	0.5	$7.0 \times 10^{10}$
P8	TOR-NC	--	1.0	$4.5 \times 10^7$
P9	TOR-NC	--	2.0	$7.6 \times 10^7$
P10	PPO-6FDA	--	0	$2.1 \times 10^{12}$
P11	PPO-6FDA	--	0.5	$6.1 \times 10^7$
P12	PPO-6FDA	--	1.0	$3.4 \times 10^7$
P13	PPO-6FDA	--	2.0	$4.5 \times 10^7$
P14	ASTAA LaRC™ CP2	--	0.4	$1 \times 10^8$
P15	ASTAA LaRC™ CP2	--	1.1	$1 \times 10^7$
P16 <sup>c</sup>	ASTAA LaRC™ CP2	0	--	$> 10^{12}$
P17 <sup>c</sup>	ASTAA LaRC™ CP2	0.03	--	$> 10^{11}$
P18 <sup>c</sup>	ASTAA LaRC™ CP2	0.05	--	$1.7 \times 10^7$
P19 <sup>c</sup>	ASTAA LaRC™ CP2	0.08	--	$9.2 \times 10^6$

<sup>a</sup> Weight percent SWNTs in the bulk

<sup>b</sup> Amount of SWNTs in THF sprayed onto 1.0 g of polymer

<sup>c</sup> Reference 14

## Optical properties

The nanocomposite films were measured for optical properties with the results presented in Table 2. The  $\alpha$  pertains to the fraction of incoming solar energy that is absorbed by the film and is typically low ( $\sim 0.1$ ) for a low color film. The thermal emissivity ( $\epsilon$ ) is a measure of the films ability to radiate energy from the film surface.

When SWNTs were distributed throughout the bulk (P17 through P19), the films were observed to be visually darker than the neat polymer (P16). This was quantified by the decrease in % transmittance and increase in  $\alpha$ . The  $\epsilon$  also increased. These films were all of comparable thickness thus allowing for the direct comparison of these properties.

Due to the loss of the deuterium lamp in the instrument, the  $\alpha$  values for P1-P13 were calculated from measurements taken between 420 and 2800 nm and are not valid for air mass 0. Therefore, relative comparisons can only be made between these samples (and not with P14 – P19). Comparisons of P1 through P13 can be made due to essentially comparable film thickness



with the exception being P10. The increase in  $\alpha$  and decrease in %T with increased amount of SWNTs sprayed (P2 through P5, P7 through P9, P11 through P13) is minor as compared to the pristine materials (P1 and P6, respectively), especially considering the increase in surface conductivity. In general, the  $\epsilon$  increased slightly with higher amounts of SWNTs sprayed.

A noticeable increase in  $\alpha$  and decrease in % transmittance was observed for P14 and P15 as compared to the neat polymer (P16). However a direct comparison cannot be made due to a difference in film thickness.

**Table 2. Thermo-Optical and Optical Properties of Films**

ID	Polyimide	% SWNT (wt/wt) <sup>a</sup>	mg of SWNT <sup>b</sup>	Thickness, □m	% Trans. @ 500 nm	$\alpha^c$	$\epsilon$
P1	LaRC™ CP2	--	0	38.1	87	0.02	0.52
P2	LaRC™ CP2	--	0.5	40.6	86	0.03	0.54
P3	LaRC™ CP2	--	1.0	38.1	83	0.03	0.56
P4	LaRC™ CP2	--	2.0	38.1	82	0.06	0.56
P5	LaRC™ CP2	--	4.0	38.1	72	0.21	0.52
P6	TOR-NC	--	0	38.1	86	0.02	0.60
P7	TOR-NC	--	0.5	38.1	84	0.03	0.58
P8	TOR-NC	--	1.0	38.1	81	0.07	0.60
P9	TOR-NC	--	2.0	40.6	78	0.08	0.62
P10	PPO-6FDA	--	0	27.9	88	0.02	0.54
P11	PPO-6FDA	--	0.5	38.1	84	0.04	0.60
P12	PPO-6FDA	--	1.0	40.6	83	0.05	0.60
P13	PPO-6FDA	--	2.0	38.1	81	0.06	0.60
P14	ASTAA LaRC™ CP2	--	0.4	30.5	81	0.12	0.52
P15	ASTAA LaRC™ CP2	--	1.1	32.5	68	0.20	0.56
P16 <sup>d</sup>	ASTAA LaRC™ CP2	0	--	38.1	86	0.07	0.59
P17 <sup>d</sup>	ASTAA LaRC™ CP2	0.03	--	38.1	67	0.21	0.63
P18 <sup>d</sup>	ASTAA LaRC™ CP2	0.05	--	40.6	59	0.30	0.65
P19 <sup>d</sup>	ASTAA LaRC™ CP2	0.08	--	38.1	53	0.35	0.67

<sup>a</sup> Weight percent SWNTs in the bulk

<sup>b</sup> Amount of SWNTs sprayed onto 1.0 g of polymer

<sup>c</sup> The  $\alpha$  for Samples P1 through P13 was calculated from taken between 420 and 2800 nm.

<sup>d</sup> Reference 14

### Charge dissipation

A study to determine charge decay and capacitance loading for ASTAA LaRC™ CP2 polymers with SWNTs dispersed throughout the bulk (P16 – P19) was performed (Table 3). The films were charged to 3000 V for 60 ms. The initial peak voltage for P18 was -145.4 V, and for P19 was -65.50 V. For P16 (neat material), this was -3160 V and -3020 V for P17. According to the data, P18 and P19 (0.05 and 0.08 wt % SWNT, respectively) do not build-up and hold an electrical charge. It is apparent from both the surface resistivity and the charge decay data that P17 (0.03 wt % SWNT) does not contain enough SWNTs to reach the percolation threshold, as

similar values for surface resistivity and charge dissipation were observed for P16 (neat ASTAA). The results indicate that values from the two different methods (surface resistivity and charge decay) of determining charge dissipation are consistent.

**Table 3. Charge Dissipation Data Comparison**

ID	SWNT, %	Initial Voltage Peak, V	Surface Resistivity, $\Omega$ /square
P16	0	-3160	$> 10^{12}$
P17	0.03	-3020	$> 10^{11}$
P18	0.05	-145.5	$1.7 \times 10^7$
P19	0.08	-65.50	$9.2 \times 10^6$

### Film toughness

Transparent, conductive coatings on films commonly used on spacecraft such as indium tin oxide (ITO) are extremely brittle and cannot tolerate folding or bending. In order to assess the robustness of the SWNT spray-coated surface, qualitative handling tests were performed. These tests included creasing, folding and crumpling (Figure 3) a spray-coated LaRC™ CP2 film, measuring surface resistivity after each manipulation. In separate tests, scotch tape was applied to the spray-coated surface and removed several times. Additionally, the film was also placed in a sonicating bath operating at 40 Hz. This was repeated several times. In all of these qualitative tests, the surface resistivity of  $10^7 \Omega$ /square did not change. A similar result was obtained for P18 (where the SWNTs were distributed throughout the bulk), which was folded several times and crumpled into a ball.<sup>14</sup> Such tests applied to an ITO coated film would have resulted in loss of conductivity due to fracture of the coating. These tests indicate that the application of a SWNT dispersion by spray coating and SWNTs distributed throughout the bulk are viable methods to fabricate transparent, conductive, flexible coatings for films.

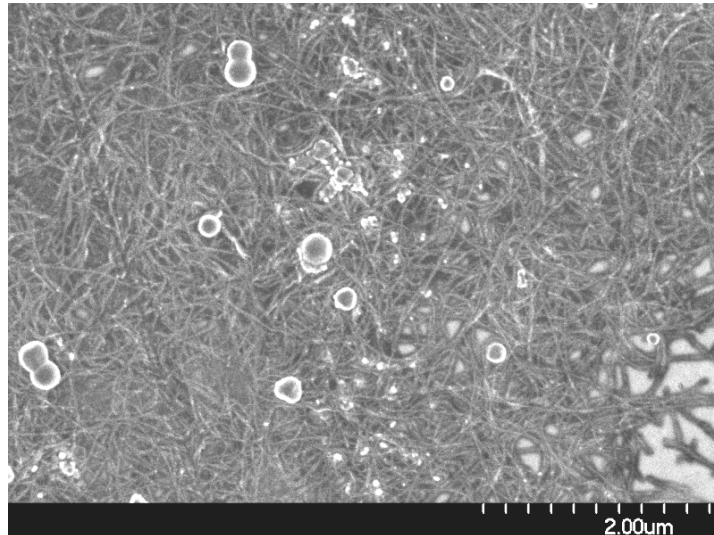


**Figure 3. Mechanical Manipulation of a LaRC™ CP2 film Spray-Coated with SWNT**

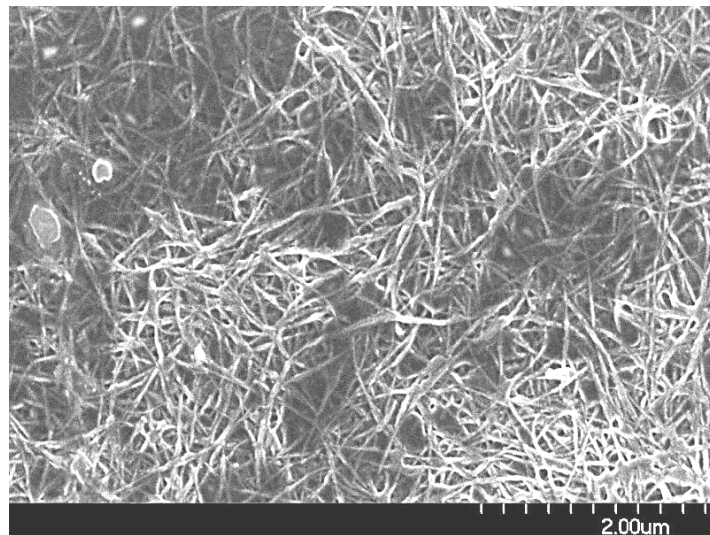
### High resolution scanning electron microscopy

Figures 4 and 5 are HRSEM images of polymer films surface coated with SWNTs at a magnification of 20,000x. The sample in Figure 4 (P2) has a surface resistivity of  $1.6 \times 10^7 \Omega$ /square and the sample in Figure 5 (P5) has a surface resistivity of  $2.2 \times 10^5 \Omega$ /square. From the HRSEM images, P2 shows a layer of SWNTs on the film surface with small regions of

polymer that are uncoated (lower right corner of the image). Sample P5, however, was spray coated with a solution containing eight times the amount of SWNTs as compared to P2. This is evident from the image as what appears to be a thicker layer of SWNT on the film surface. The increased amount of SWNTs on the surface of P5 accounts for both the increased conductivity as well as the changes in optical properties (re: Tables 1 and 2) as compared with P2.



**Figure 4. HRSEM of P2**



**Figure 5. HRSEM of P5**

### **Summary**

Methods to prepare clear, colorless, flexible, space environmentally durable polymers with surface resistivity sufficient for ESC mitigation ( $10^6$  to  $10^8 \Omega/\text{square}$ ) are summarized. One

method involved preparing nanocomposites from alkoxy silane terminated amide acid polymers of LaRC™ CP2 and SWNTs distributed throughout the bulk to afford surface and bulk conductivity. The second method involved spray-coating one surface of the ASTAA films as well as low color polyimides (LaRC™ CP2, TOR-NC and PPO-6FDA) with a suspension of SWNTs in either DMF or THF to afford surface conductivity. Spray coated nanocomposite films exhibited surface resistivities sufficient for ESC mitigation with little degradation in the optical properties (%T and  $\alpha$ ). For nanocomposites containing SWNTs distributed throughout the bulk, noticeable changes in the optical properties as compared to the neat polymer were evident. Additionally, a 0.05 % (wt/wt) SWNT loading was needed to attain surface resistivities sufficient for ESC mitigation. Nanocomposite films prepared by both methods exhibited a high degree of flexibility and robustness as evidenced by retention of surface resistivity after harsh manipulation.

The use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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## References

1. C.H.M. Jenkins, "Gossamer Spacecraft: Membrane and Inflatable Structures Technology for Space Applications", Vol. 191, American Institute of Aeronautics and Astronautics, 2001.
2. K.A. Watson, F. L. Palmieri and J. W. Connell, *Macromolecules*, Vol. 35(13), 4968, 2002.
3. Triton System, Inc. Chelmsford, MA 08124, [www.tritonsys.com](http://www.tritonsys.com).
4. SRS Technologies, Huntsville, AL 35806, [www.srs.com](http://www.srs.com).
5. R. E. Smith and G. S. West, compilers, "Space and Planetary Environment Criteria for Use in Space Vehicle Development", 1982 Revision (Volume 1), NASA TM 82478, 1983.
6. A.S. Jursa, sci. ed., *Handbook of Geophysics and the Space Environment*, Air Force Geophysics Laboratory, Air Force Systems Command USAF, NTIS Document ADA 167000, 1985.
7. *The Radiation Design Handbook*, ESA PSS-01-609, European Space Agency, Paris, 1989.
8. P.A. Robinson, Jr., "Spacecraft Environmental Anomalies Handbook", Geophysics Laboratory, Air Force Systems Command, GL-TR-89-0222, 1989.
9. A.R. Frederickson, L. Levy and C. L. Enloe, "Radiation-induced Electrical Discharges in Complex Structures", *IEEE Transactions on Electrical Insulation*, 27, p. 1166, 1992.
10. S. Iijima and T. Ichihashi, *Nature*, Vol. 363, 603 (1993).
11. D.S. Bethune, C. H. Kiang, M. S. deVries, G. Goreman, R. Savoy, J. Vazquez and R. Beyers, *Nature*, Vol. 363, 605, 1993.
12. K.A. Watson, J.G. Smith Jr. and J. W Connell, *Science for the Advancement of Materials and Process Engineering Technical Conference Series*, Vol. 33, 1551, 2001.
13. C. Park, Z. Ounaies, K. A. Watson, R. E. Crooks, J. G. Smith Jr., S. E. Lowther, J. W. Connell, E. J. Siochi, J. S. Harrison and T. L. St. Clair, *Chemical Physics Letters*, Vol 364, 303, 2002.
14. K.A. Watson, J. G. Smith Jr., and J. W. Connell, "Space Durable Polyimide/Nanocomposite Films For Electrostatic Charge Mitigation", *Science for the Advancement of Materials and Process Engineering Proceedings*, Vol. 48, 1145, 2003.

15. J.G. Smith, Jr., K. A. Watson, C. M. Thompson and J. W. Connell, Science for the Advancement of Materials and Process Engineering Technical Conference Series, Vol. 34, 365, 2002.
16. J.G. Smith, Jr., K. A. Watson, D. M. Delozier and J. W. Connell, "Carbon Nanotube/Conductive Additive/Space Durable Polymer Nanocomposite Films for Electrostatic Charge Dissipation, 35<sup>th</sup> International SAMPE Technical Conference, September 28-October 2, 2003.
17. J.G. Smith, Jr., K. A. Watson, J. W. Connell, D. M. Delozier, P. T. Lillehei, Y. Lin, B. Zhou, and Y.-P. Sun, Polymer, submitted, 2003.