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Transparent, flexible, conductive carbon nanotube coatings for electrostatic charge mitigation☆

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Abstract

Low color, space environmentally durable polymeric films with sufficient electrical conductivity to mitigate electrostatic charge (ESC) build-up are needed for applications on advanced spacecraft, particularly on large, ultra-light weight space structures. For these applications, the films must exhibit electrical conductivity that can survive the folding and unfolding required for packaging and deployment. The work described herein consists of coating the surface of polymer films with a thin layer of single-walled carbon nanotubes (SWNTs). Surface resistivities in the range sufficient for ESC mitigation were achieved with minimal effects on the optical and thermo-optical properties of the films. Bending, folding or crumpling did not affect the surface resistivity of the coated films. The preparation and characterization of SWNT coated space durable polymer films are discussed.
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Keywords: Low color polyimides; Electrostatic charge mitigation; Space durable polymers

1. Introduction

Large, deployable, ultra-lightweight spacecraft require polymeric materials (e.g. films) that possess a unique combination of mechanical and optical properties [1]. The mission and orbital environment of the spacecraft determine specific performance requirements for the materials. Some 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 without loss of desired properties, and sufficient electrical conductivity for dissipation of electrostatic charge (ESC). The goal of this work was to prepare transparent, flexible, anti-static, space durable polymer films to satisfy material needs for future NASA missions.

Many of the material requirements for space 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 monomers, low color (low solar absorptivity) and AO resistant polyimides have been reported [2,3]. However, the incorporation of sufficient electrical conductivity into polymer films to mitigate ESC build-up without adversely effecting the solar absorptivity (α) and flexibility has been difficult to attain.

Particles prevalent in the Earth's orbital environment include electrons/ions, solar flare protons and galactic cosmic rays [4–6]. The high energies of these particles allow them to penetrate spacecraft surface layers and cause chemical reactions that can ultimately degrade optical and/or mechanical properties of organic polymers. Furthermore, energetic charged particles—particularly electrons—can

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penetrate surface layers, depositing a charge onto insulating materials and other electrically isolated surfaces on a spacecraft. This can result in ESC build-up and development of large electric fields. Consequent discharging can potentially cause catastrophic damage to sensitive spacecraft electronics [7,8]. ESC build-up is also a problem during the manufacturing of polymer films, particularly ultra-thin films. As a result, handling and manipulation of the film during subsequent fabrication processes can be problematic. The surface resistivity (which relates to surface conductivity) required to dissipate ESC build-up on insulators (such as polymer films) is in the range from 10^6 to 10^{10} Ω/square.

One approach to lowering the surface resistivity on 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 [9,10], 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 solvents and the host resin. Even if initially dispersed, they may re-agglomerate soon thereafter depending upon the viscosity of the matrix.

Reasonable dispersions of SWNTs in some space durable polymers have been reported [11–15]. This was achieved by using both an in situ polymerization approach and the addition of SWNTs to amide acid polymers containing reactive end groups [15]. The first method involved the preparation of the amide acid in the presence of the SWNTs with simultaneous ultrasonic treatment followed by thermal conversion to the polyimide. Alternatively, the amide acid/SWNT mixture can be cyclodehydrated chemically in solution provided that the polyimide remains soluble. The second approach involved the dispersion of SWNTs in solutions of alkoxysilane terminated amide acid oligomers. In both of these approaches, the SWNTs were dispersed throughout the polymer matrix and consequently the nanocomposite films exhibited similar surface and volume resistivities. When the SWNT loading level was ≥ 0.05 wt%, surface and volume resistivities sufficient for ESC mitigation were achieved. However, in these films there was notable loss of the optical transparency and an increase in the solar absorptivity compared to the host polymer.

Recently, work on adding a combination of inorganic salts and SWNTs to polymers was reported [16]. Films with surface and volume resistivities sufficient to mitigate ESC build-up were prepared by the incorporation of a low loading level of SWNTs in conjunction with a small amount of inorganic salt. Salt inclusion to a 0.03 wt% SWNT loading afforded materials with comparable resistivity values to that of a 0.04 wt% SWNT loading; however, the optical and thermo-optical properties were not significantly improved.

Many applications for polymers on spacecraft require only surface resistivity to mitigate ESC (volume conductivity is not necessary) [17,18]. The amount of SWNTs necessary to mitigate ESC build-up is greatly reduced when only surface resistivity is required as compared to films containing SWNTs dispersed throughout the bulk. The use of a lower amount of SWNTs would be expected to have negligible effects on the optical and thermo-optical properties of the films. The preparation and characterization of space durable polyimide films surface coated with SWNTs is described herein. Spray-coating techniques were used to apply the SWNTs to three space durable polymers. Films coated with SWNTs were compared with uncoated films as well as those prepared via in situ polymerization.

2. Experimental

2.1. Starting materials

1,3-Bis(3-aminophenoxy)benzene (APB, Mitsui Chemicals America, Inc., mp 107–108.5 °C) was used without further purification. 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 [2]. HiPco SWNTs (BuckyPearls™) were obtained from Carbon Nanotechnologies Inc. (batch # P0222, purified) and treated as described below. *m*-Cresol (Fluka Chemical Co.) was vacuum distilled prior to use. Isoquinoline, *N*,*N*-dimethylacetamide (DMAc, anhydrous), *N*-methyl-2-pyrollidinone (NMP, anhydrous), tetrahydrofuran (THF, anhydrous), 1,2-dichlorobenzene (DCB), sodium methoxide (powder), pyridine, and acetic anhydride were used as received (Aldrich Chemical Co.) without further purification.

2.2. SWNT treatment

SWNTs were treated as follows: a 250 ml round-bottom flask was charged with SWNTs (0.100 g) and DCB (220 ml). The mixture was sonicated for 3 h 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 and sodium methoxide and the resultant mixture heated to 80 °C. After 16 h at 80 °C, the temperature of the reaction mixture was increased to ∼115 °C and the pyridine was removed by distillation. The reaction mixture was then stirred in refluxing DCB for 3 h followed by cooling to room temperature. The SWNTs were isolated via centrifugation, washed several times with methanol, and dried in a vacuum oven at 150 °C for 6 h. The treated SWNTs formed a stable suspension in DMAc, DMF, and THF after sonication for ~1 h. All SWNTs were treated via this process prior to use.

2.3. Polymer synthesis: LaRC™ CP2[3]

APB (13.495 g, 0.0462 mol) and DMAc (60 ml) were added to a 250 ml three neck round-bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and drying tube filled with calcium sulfate. Once all the solids dissolved, 6FDA (20.609 g, 0.0464 mol, 0.5% excess to give a calculated number average molecular weight of ~140,000 g/mol) was added with additional DMAc (76 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. A 0.5% (w/v) solution in DMAc at 25 °C exhibited an inherent viscosity (η_{inh}) of 1.20 dl/g. The polymer was chemically imidized by the addition of 14.2 g of acetic anhydride and 11.0 g of pyridine to the polymer solution and stirred 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.

2.4. Polymer synthesis: TOR-NC[2]

Into a 250 ml three neck round-bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube filled with calcium sulfate were placed 3-APPO (11.8840 g, 0.0241 mol) and NMP (35 ml). Once dissolved, ODPA (7.485 g, 0.0241 mol) was added with additional NMP (45 ml) to give a solution with a solids content of 20% (w/w). The resulting light yellow solution was stirred overnight at room temperature under a nitrogen atmosphere. A 0.5% (w/v) solution in NMP at 25 °C exhibited an η_{inh} of 1.01 dl/g. The remaining polymer was chemically imidized by the addition of 7.45 g of acetic anhydride and 5.75 g of pyridine. The solution was stirred at room temperature overnight. The polymer was precipitated in a blender containing a 50/50 mixture of water/methanol, filtered, washed in hot water three times and dried in a vacuum oven at 110 °C overnight to give a white, fibrous material.

2.5. Polymer synthesis: PPO-6FDA[2]

Into a 250 ml three neck round-bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and condenser were placed 3-APPO (13.144 g, 0.0267 mol) and *m*-cresol (50 ml). The mixture was stirred under nitrogen and warmed to 70 °C until all solids dissolved. 6FDA (11.856 g, 0.0267 mol) was added to the warm solution in one portion followed by additional *m*-cresol (46.7 ml) and isoquinoline (1 ml). The mixture was heated at 200 °C for 5 h and then cooled to 60 °C. Subsequently DMF was added resulting in a ~10% w/w solution. The warm solution was poured into a blender containing methanol. The white fibrous precipitate was macerated in the blender for 15 min, collected by filtration, and washed three times in hot methanol for 30 min each wash. The polymer was then stirred in hot water for 1 h and collected via vacuum filtration. The polymer was dried in a forced air oven for 4 h at 120 °C and then in a vacuum oven for 4 h at 150 °C ($\eta_{\mathrm{inh}} = 1.12$ dl/g).

2.6. Spray-coating films using a SWNT/THF suspension

A representative method for coating the surface of a polyimide film using a SWNT/THF suspension is as follows: SWNTs were added to THF in the ratio of 0.2 mg SWNT per 1.0 g THF. The mixture was placed in an ultrasonic bath (Ultrasonik 57X) operating at room temperature at 40 MHz for 1 h. Polymer solutions were prepared by dissolving 1.0 g of polyimide in 3.35 g of DMAc resulting in a 23% (w/w) solution. Polymer solutions were cast onto plate glass using a doctor blade (330 μm setting) and placed in a dry air box for 15 min. The films (approximately 115 cm^2) were removed from the air box and the SWNT/THF suspension was sprayed onto the film using an airbrush (Badger Model 250) pressurized with dry nitrogen gas. The airbrush was held approximately 15 cm above the plate glass and the SWNT suspension was applied with a sweeping motion to provide for a consistent coating. Films coated with 0.5 mg of SWNT or more per gram of polymer received multiple applications of suspensions containing 0.25 mg SWNT/1.0 g THF. The films were placed in the dry air box for 15 min in between coatings. After the last application, the films were left in the dry air box overnight (tack-free) and then staged to 220 °C for 1 h in a forced air oven. The films were subsequently removed from the plate glass and characterized.

2.7. Spray-coating films using a SWNT/DMAc suspension

A representative method for coating the surface of a polyimide film using a SWNT/DMAc suspension is as follows: SWNTs were added to DMAc in the ratio of 0.2 mg SWNT per 1.0 g DMAc. The mixture was placed in an ultrasonic bath (Ultrasonik 57X) operating at room temperature at 40 MHz for 1 h. Polymer solutions were prepared by dissolving 1.0 g of polyimide in 4.00 g of DMAc resulting in 20% (w/w) solutions. Polymer solutions were cast onto plate glass using a doctor blade (356 μm setting,) and placed in a dry air box for 2 h. The films (approximately 115 cm^2) were removed from the air box and the SWNT/DMAc suspension was sprayed onto the film using an airbrush (Badger Model 250) pressurized with dry nitrogen gas. The airbrush was held approximately 15 cm above the plate glass and the SWNT suspension was applied with a sweeping motion to provide for a consistent coating. Films coated with 0.5 mg of SWNT or more per gram of polymer received multiple applications of suspensions containing 0.25 mg SWNT/1.0 g THF. The films were placed in the dry air box for 2 h in between coatings. After the last application, the films were left in the dry air box overnight (tack-free) and then staged to 220 °C for 1 h in a forced air oven. The films were subsequently removed from the plate glass and characterized.

2.8. Preparation of LaRC™ CP2/SWNT mixtures via in situ polymerization with sonication

Into a 20-ml vial were placed SWNT (0.002 g) and DMAc (10 ml). The vial was placed in a water bath and sonicated at 40 MHz for 2 h. The black mixture was transferred into a 100 ml three neck round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and drying tube containing calcium sulfate. The flask was submerged in a water bath and sonicated while APB (1.1907 g, 8.6 mmol) was added. Sonication continued while the mixture was stirred until the diamine dissolved. Powdered 6FDA (1.8094 g, 8.6 mmol) was subsequently added. Sonication was stopped and the mixture stirred at room temperature for 24 h under nitrogen. The resulting black, viscous mixture was used to prepare thin films.

Films containing SWNT in the bulk were cast from 20% solids in DMAc and doctored onto plate glass. The films were placed in a dry air box for 16 h and then transferred to a forced air oven and staged to 220 °C for 1 h.

2.9. Other characterization

The percent transmission (%*T*) at 500 nm was obtained on films using a Perkin–Elmer Lambda 900 UV/VIS/near-IR spectrometer. Solar absorptivity (α) was measured on an AZ Technology Model LPSR-300 spectroreflectometer with measurements taken from 250 to 2800 nm using a vapor deposited aluminum on Kapton® film as a reflective reference (1st surface mirror) for air mass 0 per ASTM E903. An AZ Technology Temp 2000A infrared reflectometer was used to measure thermal emissivity (ε). Surface resistivity was measured using a Prostat® PRS-801 Resistance System with a PRF-911 Concentric Ring Fixture per ASTM D-257 and reported as an average of three readings. Inherent viscosities were determined in DMAc using 0.5% (wt/wt) polymer solutions at 25 °C. High-resolution SEM 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 set up a stable local electric field on the surface of the sample while minimizing beam induced sample damage. Charge dissipation measurements of the polymer thin films were conducted on a John Chubb Instrumentation JCI-155v4 Charge Decay Test Unit controlled by a computer using DECAY18F software.

3. Results and discussion

3.1. SWNT treatment

SWNTs were treated with sodium methoxide in a solution of DCB and pyridine [19,20]. This treatment allows the SWNTs to form a stable suspension in THF, DMAc, DMF and DCB. Raman spectra of the treated SWNTs indicated that the SWNTs had no fundamental change caused by the sodium methoxide treatment. In addition, the treated SWNTs exhibited negligible changes in surface and volume resistivity measurements as compared to the untreated SWNTs [19,20]. The mechanism for enhanced SWNT dispersal is not known at this time and the phenomenon is currently being investigated.

3.2. Polyimide synthesis

Three polyimides (Fig. 1) were chosen for this study because of their low color and space environmental durability. LaRC™ CP2 is a polyimide that is thermally stable, low in color, and resistant to UV radiation. TOR-NC and PPO-6FDA are low color, UV stable polyimides that are structurally similar to LaRC™ CP2, but contain pendant phosphine oxide groups that impart AO resistance [2].

The three polyimides were prepared as shown in Scheme 1. LaRC™ CP2 and TOR-NC 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. PPO-6FDA was prepared this way because higher molecular weight polymer (as evidenced by higher inherent viscosities) and better quality films were obtained compared to the chemical imidization method. LaRC™ CP2 was prepared at a calculated number average molecular weight of approximately 140,000 g/mol. However, as is the case with condensation polymerizations, it is unlikely that the calculated molecular weight was achieved. TOR-NC

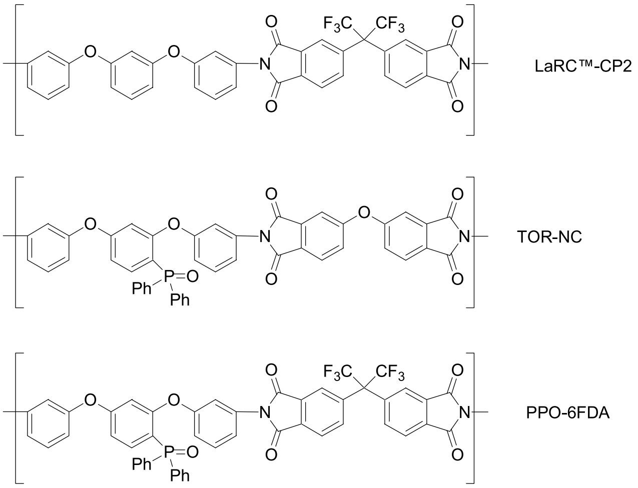
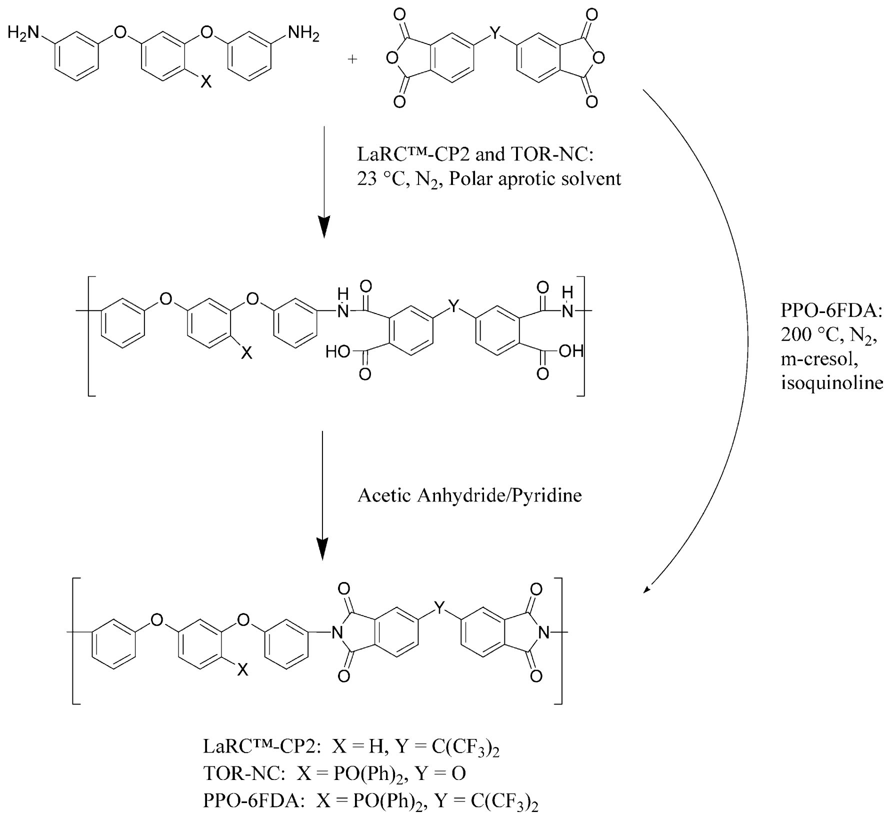


Fig. 1. Structures of polyimides.



Scheme 1. Polyimide synthesis.

and PPO-6FDA were reacted at a 1:1 diamine:dianhydride stoichiometry. No gel permeation chromatography data is available for the polymers to estimate number average molecular weights. The fact that the inherent viscosities for all polymers were >1 and the polymers exhibited good film forming properties indicate medium to high molecular weight polymers were formed.

3.3. Surface-coating SWNTs onto polyimide films: variables

Several variables are associated with applying a coating of SWNTs onto a polymer film. These include type of spray-coater used, concentration and solvent used to prepare SWNT suspensions, area of film to be coated, solvent used to cast film, and the distance of the spray-coater from the film surface.

To minimize some of these variables, a systematic approach was used to spray-coat SWNTs onto polymer films. A Badger Model 250 airbrush was held approximately 15 cm above the film surface and a SWNT/solvent suspension was sprayed onto the film with a sweeping motion by the same operator. For each solvent tested (THF and DMAc), films were cast from polymer solutions of the same volume and concentration and at the same doctor blade setting. This helped to reduce differences in the surface area of the film. Even under the best attempts to minimize variables and achieve consistent results, the largest variable was due to over-spray of the SWNT/solvent suspension. In order to achieve a uniform coating on the film surface, it was necessary to spray beyond the border of the hand-cast films. Because of this, the amount of SWNTs actually applied to the film surface is difficult to determine; however, attempts were made to hand-spray the SWNT/solvent mixtures using the same method for each film. It is envisioned that an optimized system of coating a film could be adopted using a computer controlled automated spray-coat system.

To eliminate variables associated with solvent amounts, an initial study was performed to determine optimal conditions for the spray-coating process. One important variable was the amount of residual solvent left in the film after solution casting. During initial experiments it became clear that to obtain high quality coatings, the amount of residual solvent remaining in the film after casting was important. The SWNTs tended to re-agglomerate back into large bundles due to electrostatic attraction when films containing too much solvent were sprayed. Spraying a SWNT suspension using non-volatile solvents such as DMAc was problematic because the amount of solvent in the solution-cast film was increased after spraying. This led to pooling of the solvent on top of the wet film as well as dilution of the polymer solution. Under these conditions, re-agglomeration of the SWNTs into large bundles readily occurred. Likewise if too little solvent was present in the film, the SWNT/solvent did not adequately wet the film surface.

Table 1 shows surface resistivity data for several LaRC™ CP2 films cast from DMAc solutions at different polymer concentrations with varying film drying times and then sprayed with a SWNT/THF suspension. Casting films from solutions greater than 23% solids was difficult due to the high solution viscosity. To mimic the effect of casting from solutions greater than 23% solids, films were cast at 23% solids and then placed in a dry air box for 2 and 4 h, respectively, (P4 and P5), thus allowing some solvent from the film to evaporate. P6 was dried until tack free (~18 h) before being sprayed with SWNTs and was then dried in a forced air oven. This film crazed and thus no surface resistivity measurements could be taken. The crazing of the film was likely due to incompatibility between the THF and the polymer. The other films did not craze because of the greater amount of DMAc remaining in the film at the time of spraying.

The best results were obtained from samples P3, P4 and P5 with surface resistivities ranging from 8.1×10^6 to 3.7×10^7 Ω/square. For ease of experimentation, all film samples were treated similarly to P3 where the film was cast from 23% solvent and experienced little drying time in the air box. A similar study was repeated with the SWNT/DMAc suspensions. The best results for this non-volatile solvent were obtained by casting films at 20% solids and allowing them sit in a dry nitrogen box with a controlled N_2 flow for 2 h before a SWNT/DMAc suspension was applied.

The THF/DMAc experiments indicated that to achieve a reduction in the surface resistivity, appropriate levels of solvent needed to be present in the film in order to meet three criteria: (1) the SWNTs need to adhere to the surface and not be penetrate beneath the surface, (2) SWNT bundles needed to be in contact with one another to allow for a conductive pathway between the SWNTs, and (3) SWNT suspensions needed to be applied without pooling of the solvent causing re-agglomeration of the SWNTs.

Table 1
Effect of THF content on surface resistivity on LaRC™ CP2 films

ID	Percent solids	Surface resistivity (Ω/square)
P1	17	10^9-10^{12}
P2	20	2.6×10^8
P3	23	8.1×10^6
P4	23[a]	3.7×10^7
P5	23[b]	8.3×10^6
P6[c]	Tack free	ND[d]

Films cast from DMAc, placed in a dry air box for 15 min, and sprayed with 1.0 mg SWNT in 5.0 g THF.

[a] Film placed in a dry air box for 2 h before being sprayed.

[b] Film placed in a dry air box for 4 h before being sprayed.

[c] Film cast from 23% solids, placed in a dry air box until the film was tack free (~18 h).

[d] Not determined due to poor quality film.

3.4. Coatings using SWNT/THF suspensions

Results for films coated with SWNT/THF suspensions are shown in Table 2. Films of LaRC™ CP2, TOR-NC and PPO-6FDA were spray-coated with SWNT amounts ranging from 0.5 mg (0.2 mg for LaRC™ CP2) to 2.0 mg in THF. A LaRC™ CP2 film coated with 0.2 mg of SWNTs (P8) exhibited a high surface resistivity of 4.6×10^9 Ω/square; while P9 (LaRC™ CP2 film coated with 0.5 mg of SWNT) exhibited a surface resistivity of 1.6×10^7 Ω/square. Because of the higher surface resistivity exhibited by P8, the PPO-6FDA and TOR-NC films samples were prepared using a range of 0.5 to 2.0 mg of SWNT in THF. In general it was observed that films coated using SWNT/THF mixtures prepared from 0.5 mg SWNT or greater per gram of polymer exhibited surface resistivities that were acceptable for ESC mitigation. In addition, the percolation threshold appears to be reached with 0.5 mg SWNT or greater per gram of polymer as additional SWNTs does little to decrease the surface resistivity. As expected, the spray-coated films were conductive on only one surface with the opposing surface being insulative (surface resistivity $>10^{12}$ Ω/square).

The effect of SWNT spray-coating on the α and ε was of interest since these properties are important for some applications on Gossamer spacecraft. Solar absorptivity pertains to the fraction of incoming solar energy that is absorbed by the film and is typically below 0.1 for a low color/colorless film. Thermal emissivity is a measure of the films ability to radiate energy from the film surface. Table 2 shows the α and ε data for films coated using SWNT/THF suspensions. Overall, ε values were not greatly affected with increased amounts of SWNTs applied to the film surface. Solar absorptivity values increased somewhat with increased amount of SWNTs, as anticipated. For example, P15 (neat PPO-6FDA) had an α value of 0.05. After application of 1.0 mg of SWNT (P17), the α value increased to 0.09. Similar results were obtained with LaRC™ CP2 and TOR-NC.

Thin films were measured for optical transparency at 500 nm, the solar maximum, with the results presented in Table 2. Overall, the change in optical transparency of the surface coated films was negligible as compared to the neat material. For example, neat LaRC™ CP2 (P7) had a $\%T$ at 500 nm of 87%. Sample P3 (LaRC™ CP2 coated with 1.0 mg of SWNT) had a $\%T$ at 500 nm of 83%, a 95% retention in transmission properties. Similar results were observed for TOR-NC and PPO-6FDA.

3.5. Coatings using SWNT/DMAc suspensions

Results for films coated with SWNT/DMAc suspensions are shown in Table 3. Films of LaRC™ CP2, TOR-NC and PPO-6FDA were spray-coated with SWNTs amounts ranging from 0.2 to 1.0 mg in DMAc. A LaRC™ CP2 film coated with 0.2 mg of SWNTs (P19) exhibited a surface

Table 2
Characterization for films coated with SWNT/THF suspensions

ID	Polyimide	mg of SWNT[a]	Film thickness (μm)	%*T* at 500 nm	α	ε	Surface resistivity (Ω/square)
P7	LaRC™ CP2	0	38	87	0.06	0.52	2.5×10^{12}
P8	LaRC™ CP2	0.2	41	85	0.07	0.52	4.6×10^{9}
P9	LaRC™ CP2	0.5	41	86	0.07	0.54	1.6×10^{7}
P3	LaRC™ CP2	1.0	38	83	0.09	0.56	8.1×10^{6}
P10	LaRC™ CP2	2.0	38	82	0.10	0.56	2.0×10^{7}
P11	TOR-NC	0	38	86	0.05	0.60	2.8×10^{12}
P12	TOR-NC	0.5	38	84	0.06	0.58	4.1×10^{8}
P13	TOR-NC	1.0	38	81	0.09	0.60	4.5×10^{7}
P14	TOR-NC	2.0	36	78	0.12	0.62	5.2×10^{7}
P15	PPO-6FDA	0	38	88	0.05	0.54	2.1×10^{12}
P16	PPO-6FDA	0.5	38	84	0.08	0.60	6.1×10^{7}
P17	PPO-6FDA	1.0	36	83	0.09	0.60	3.4×10^{7}
P18	PPO-6FDA	2.0	38	81	0.10	0.60	4.5×10^{7}

[a] Amount of SWNTs in THF sprayed onto 1.0 g of polymer.

resistivity of 2.1×10^7 Ω/square; P21 (LaRC™ CP2 film coated with 1.0 mg of SWNT) exhibited a surface resistivity of 1.3×10^7 Ω/square. In general, it was observed that films coated using SWNT/DMAc mixtures prepared from 0.2 mg SWNT or greater per gram of polymer exhibited surface resistivities that were acceptable for ESC mitigation (range of 10^6 to 10^{10} Ω/square). The reason a lesser amount of SWNTs is required compared to THF films is discussed in the section on high resolution SEM. In all cases, films sprayed with 1.0 mg SWNT/DMAc exhibited similar increases in surface resistivities as those sprayed with 0.2 mg SWNT; however, the optical properties were adversely affected as shown in Table 3.

Thin films were measured for optical transparency at 500 nm (Table 3). As with the SWNT/THF coatings, the optical transparency of the surface coated films was decreased by a negligible amount due to the presence of SWNTs as compared to the neat material. For example, neat TOR-NC (P11) had a %*T* at 500 nm of 86%. While the same material (Sample P22) coated with 0.2 mg of SWNT had a %*T* at 500 nm of 85%. Similar results were observed for LaRC™ CP2 and PPO-6FDA. The retention of %*T* for P22 is excellent considering a surface resistivity of 3.2×10^7 Ω/square.

The effect of spray-coating the films with SWNT/DMAc suspensions on the α and ε is presented in Table 3. As with the films coated with SWNT/THF suspensions, no significant changes in ε were observed. Solar absorptivity values increased somewhat with increased amount of SWNTs, but as with the SWNT/THF samples, the increases in α values was not significant.

3.6. High resolution SEM

To assess SWNT dispersion on the film surface, P9 sprayed with a SWNT/THF suspension (0.5 mg SWNT) was examined by HR-SEM (Fig. 2). The images show that the SWNTs bundles are poorly dispersed across the surface of the polymer. The left image in Fig. 2 shows large SWNT bundles and the right image shows a more representative SEM image for this particular sample. Fig. 3 is a SEM image of P20, a LaRC™ CP2 sample sprayed with 0.5 mg SWNT in DMAc. The SWNTs appear better dispersed as

Table 3
Characterization for films coated with SWNT/DMAc suspensions

ID	Polyimide	mg of SWNT[a]	Film thickness (μm)	%*T* at 500 nm	α	ε	Surface resistivity (Ω/square)
P7	LaRC™ CP2	0	38	87	0.06	0.52	2.5×10^{12}
P19	LaRC™ CP2	0.2	36	84	0.07	0.53	2.1×10^{7}
P20	LaRC™ CP2	0.5	36	83	0.09	0.52	1.4×10^{7}
P21	LaRC™ CP2	1.0	36	81	0.10	0.53	1.3×10^{7}
P11	TOR-NC	0	38	86	0.05	0.60	2.8×10^{12}
P22	TOR-NC	0.2	33	85	0.07	0.54	3.2×10^{7}
P23	TOR-NC	0.5	38	82	0.08	0.58	1.4×10^{7}
P24	TOR-NC	1.0	36	80	0.10	0.56	1.2×10^{7}
P15	PPO-6FDA	0	38	88	0.05	0.54	2.1×10^{12}
P25	PPO-6FDA	0.2	33	84	0.07	0.56	3.5×10^{7}
P26	PPO-6FDA	0.5	30	83	0.09	0.56	2.0×10^{7}
P27	PPO-6FDA	1.0	33	81	0.10	0.57	1.6×10^{7}

[a] Amount of SWNTs in DMAc sprayed onto 1.0 g of polymer.

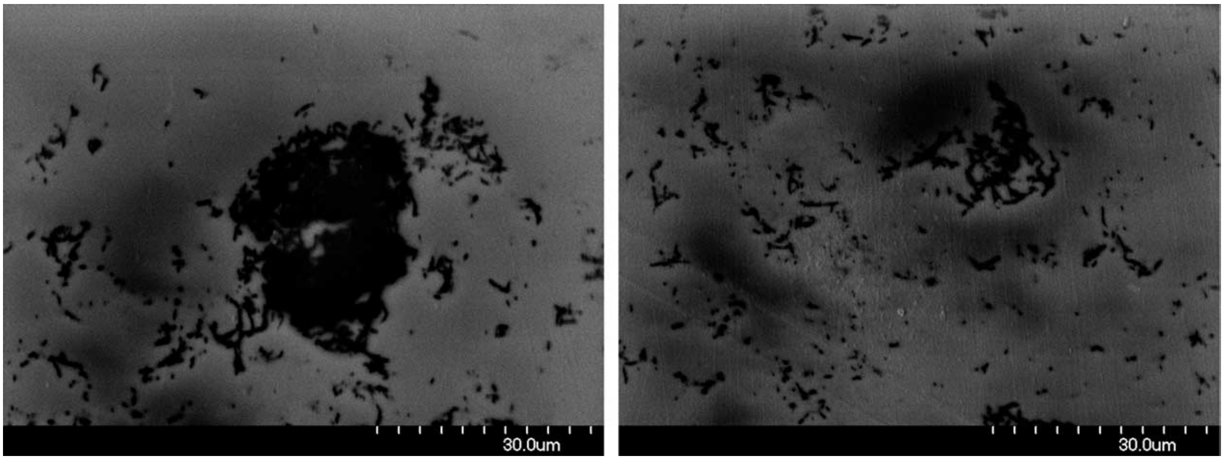


Fig. 2. High resolution SEMs of P9, LaRC™ CP2 film coated with 0.5 mg of SWNT in THF (Magnification = 1500×).

compared with the sample in Fig. 2 when THF was used as the solvent.

The difference in dispersion is possibly due to solvent volatility in the samples described in Figs. 2 and 3. THF has a higher vapor pressure than DMAc, and when sprayed as a fine mist evaporates readily. The majority of the THF evaporates before the SWNT/THF suspension reaches the film surface, and hence the SWNTs have the opportunity to collapse into large bundles in flight. The SEM images in Fig. 2 provide evidence of SWNTs collapsing into large bundles as the THF evaporates. The SEM images in Fig. 4 are of P26 and P23, PPO-6FDA (left) and TOR-NC (right), both sprayed with 0.5 mg of SWNT using DMAc. The images indicate better dispersion of the SWNT bundles using DMAc as a solvent to spray SWNTs compared to using THF. The better dispersion of the SWNTs from DMAc may explain why a lesser amount of SWNTs is necessary to achieve acceptable surface resistivities for ESC compared to using THF.

The SWNTs in Figs. 2–4 appear as dark regions because of the large difference in conductivity between the polymer and the SWNTs. It is the disruption of the electric field caused by the SWNTs that is being imaged and not the SWNT bundles themselves [21–23]. Because of this, the diameter of the SWNT bundles cannot be estimated using HRSEM.

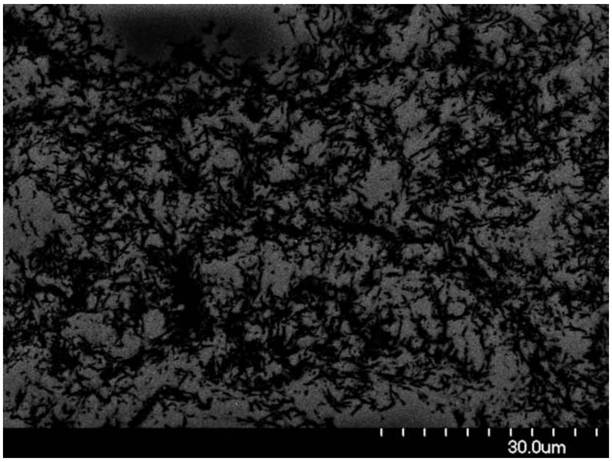


Fig. 3. High resolution SEM of P20, a LaRC™ CP2 film coated with 0.5 mg of SWNT in DMAc (Magnification = 1500×).

3.7. Charge decay

Samples P3, P13 and P17 were tested for their charge decay capabilities with the results shown in Table 4. The instrument was designed to initially charge the film surfaces to ∼3000 V. A neat LaRC™ CP2 film (P28) was charged to 3160 V. For the coated surfaces, the films could only be charged to values ranging from 305 to 370 V. The fact that the films surfaces could not be charged to ∼3000 V indicates that the SWNT coatings provides a mechanism for ESC dissipation. It is also apparent that some type of ESC dissipation mechanism occurs through the bulk of the film because the uncoated sides of the films could only be charged to values ranging from 967 to 1160 V. The trends

Table 4
Charge decay

Sample[a]	Film face[b]	Initial voltage (V)	Decay time (s)
P28 (LaRC™ CP2-neat)	–	3160	2
P3 (LaRC™ CP2)	Top	340	3
P3 (LaRC™ CP2)	Bottom	967	493
P13 (TOR-NC)	Top	305	4
P13 (TOR-NC)	Bottom	1007	1821
P17 (PPO-6FDA)	Top	370	3
P17 (PPO-6FDA)	Bottom	1160	623

[a] 1.0 g of polymer coated with 1.0 mg of SWNT in THF.
[b] Top coated with SWNT, bottom was uncoated surface.

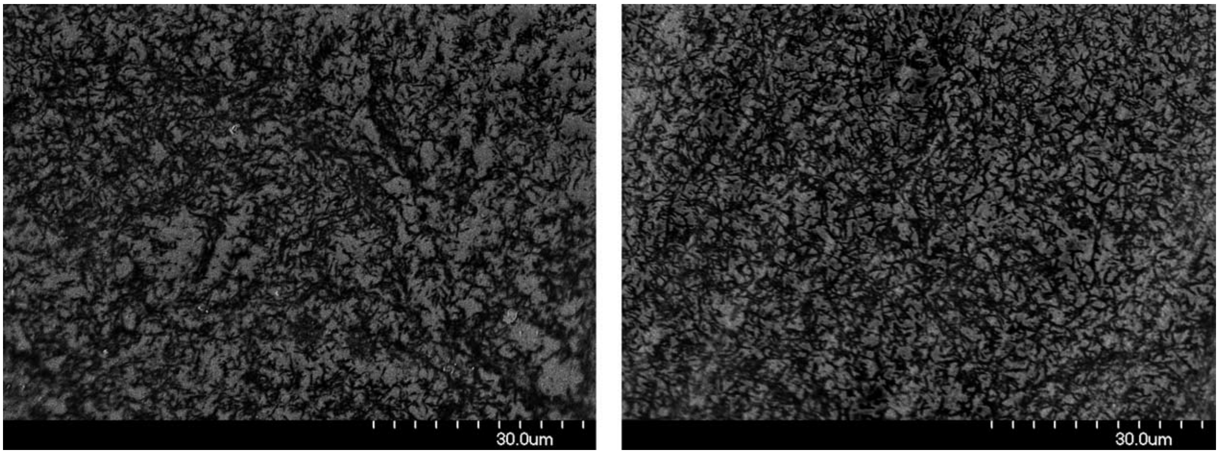


Fig. 4. High resolution SEM of P26 (left, PPO-6FDA) and P23 (right, TOR-NC), both coated with 0.5 mg of SWNT in DMAc (Magnification = 1500×).

associated with initial voltage measurements in Table 4 correlate well with surface resistivity measurements.

3.8. Coating robustness

Indium tin oxide (ITO) is currently used on spacecraft to prepare optically transparent, conductive coatings. ITO coatings, however, are extremely brittle and cannot tolerate folding or bending when applied to flexible surface. In order to assess the robustness of the SWNT spray-coated surface, qualitative handling tests were performed. These tests included creasing, folding and crumpling a LaRC™ CP2 film coated with SWNTs and measuring surface resistivity after each manipulation. Fig. 5 is an image of a LaRC™ CP2 film (P19) coated with SWNT that was folded numerous times and finally crumpled into a ball. The visible lines in the image on the film are creases, not cracks. Table 5 shows the surface resistivity of this film before after folding. The surface resistivity before manipulation was 2.1×10^7 Ω/square and after manipulation remained relatively unchanged at 1.9×10^7 Ω/square. Comparable tests applied to an ITO coated film would have resulted in immediate loss of conductivity due to fracture of the coating upon bending [18]. In a separate test, scotch tape was applied to the spray-coated surface and removed, and this was repeated several times. The surface resistivity was unaffected. These tests indicated that application of a SWNT layer by surface coating is a viable method to fabricate transparent, conductive, flexible/foldable coatings for films.

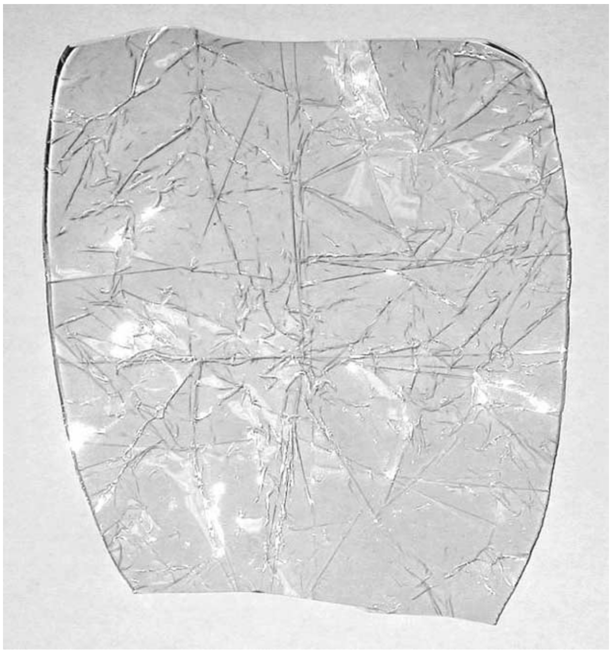


Fig. 5. Photograph of sample P19 after several folds and crumpling into a ball.

3.9. Comparison of coated LaRC™ CP2 films with LaRC™ CP2 films containing SWNT in the bulk

A comparison was made between a spray-coated LaRC™ CP2 film (P19, 0.2 mg SWNTs in DMAc) and LaRC™ CP2 films containing SWNTs mixed throughout the bulk of the film at a loading levels between 0.06 and 0.18 wt% (Table 6). Although films for P30-P33 were thicker than P19, the following trends were observed. It would take more than 0.18 wt% SWNT (P33) to approach the level of surface resistivity that was obtained by coating a 1.0 g sample of LaRC™ CP2 with 0.2 mg of a SWNT/DMAc suspension. Optical comparisons between P19 and P33 can be made

Table 5
SWNT coating durability tests on P19

No. of folds	Surface resistivity (Ω/square)
0	2.1×10^7
1	1.8×10^7
2	2.0×10^7
3	2.0×10^7
4	2.1×10^7
Crumpled[a]	1.9×10^7

[a] See Fig. 5.

Table 6
Comparison between spray-coated LaRC™ CP2 and SWNTs in the bulk

ID	Wt% of SWNT	Film thickness (μm)	%*T* at 500 nm	α	ε	Surface resistivity (Ω/square)
P19	–[a]	36	85	0.07	0.53	2.1×10^{7}
P29	0.06	56	63	0.27	0.66	$>10^{12}$
P30	0.08	56	59	0.34	0.68	1×10^{10}
P31	0.10	53	55	0.38	0.64	1×10^{9}
P32	0.13	53	47	0.48	0.68	1×10^{8}
P33	0.18	38	51	0.43	0.64	1×10^{8}

[a] 1.0 g polymer coated with 0.2 mg of SWNT in DMAc.

because both samples have near equal film thickness (36 and 38 μm, respectively). P33 exhibited a greater decrease and %*T* at 500 nm as compared to P19 (51 %*T* for P33 vs. 85 %*T* for P19), yet P33 has a higher surface resistivity value (less conductive). In addition, P33 showed a detrimental increase in α (0.43) as compared to an α value of 0.07 for P19.

4. Summary

Space environmentally durable polymers with an unprecedented combination of properties were prepared and characterized. Transparent, flexible films with surface resistivities sufficient to mitigate ESC (10^{6} to 10^{8} Ω/square) were prepared by surface coating three different polyimides (LaRC™ CP2, TOR-NC and PPO-6FDA) with a suspension of SWNTs. The surface resistivity and optical properties of the surface coated films were compared to neat films and films containing SWNTs mixed throughout the bulk of the film. Films containing SWNTs throughout the bulk of the film had volume resistivities sufficient for ESC mitigation but the optical properties (α and %*T* at 500 nm) were negatively affected as compared to spray-coated films. In general, it was found that films coated with SWNTs exhibited surface resistivities (1×10^{7} to 1×10^{6} Ω/square), /square), sufficient for ESC mitigation with negligible degradation of the optical properties. Films coated with SWNTs exhibited a high degree of flexibility and robustness as evidenced by retention of surface resistivity after harsh manipulation.

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