Preparation and Characterization of Space Durable Polymer Nanocomposite Films from Functionalized Carbon Nanotubes

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Abstract

Low color, flexible, space durable polyimide films with inherent, robust electrical conductivity have been under investigation as part of a continuing materials development activity for future NASA space missions involving Gossamer structures. Electrical conductivity is needed in these films to dissipate electrostatic charge build-up that occurs due to the orbital environment. One method of imparting conductivity is through the use of single walled carbon nanotubes (SWNTs). However, the incompatibility and insolubility of the SWNTs severely hampers their dispersion in polymeric matrices. In an attempt to improve their dispersability, SWNTs were functionalized by the reaction with an alkyl hydrazone. After this functionalization, the SWNTs were soluble in select solvents and dispersed more readily in the polymer matrix. The functionalized SWNTs were characterized by Raman spectroscopy and thermogravimetric analysis (TGA). The functionalized nanotubes were dispersed in the bulk of the films using a solution technique. The functionalized nanotubes were also applied to the surface of polyimide films using a spray coating technique. The resultant polyimide nanocomposite films were evaluated for nanotube dispersion, electrical conductivity, mechanical, and optical properties and compared with previously prepared polyimide-SWNT samples to assess the effects of SWNT functionalization.

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I. Introduction

Current and future NASA space missions involve the use of Gossamer spacecraft that have unique materials requirements. Gossamer spacecraft are large, deployable, lightweight vehicles that can be packaged into small volumes for launch and subsequently deployed in space by inflation, mechanical, or other means. These unique packaging and deployment features require that Gossamer spacecraft be comprised of materials that are compliant, flexible, space durable, conductive, and in some cases have low solar absorptivity. Over the years, NASA-LaRC has developed polyimides with many of these properties, but the incorporation of electrical conductivity into these materials without affecting transparency or flexibility has been elusive.[1]

Electrical conductivity is needed to prevent static charge buildup on the polymeric materials in orbit. Imparting electrical conductivity would also improve the handling characteristics of the films on the ground. A surface resistivity of 10^6 to 10^{10} Ω/square is required to effectively mitigate static charge buildup. It has been shown that SWNTs will increase the conductivity of the polyimides to this level at relatively low loading levels.[2-6] With the incorporation of only small amounts of SWNTs, the desired level of electrical conductivity can be achieved without drastically effecting optical transparency, solar absorptivity, or flexibility.

The use of SWNTs as conductive additives in polymer matrices for space applications is advantageous for a number of reasons. Two major advantages in using these materials over conventional conductive fillers are their small size and high aspect ratio. Due to these features, relatively small amounts can be used to induce conductivity throughout the polymer matrix without significantly altering optical and mechanical properties. Although the SWNTs have some advantageous properties, difficulties encountered in dispersing them have restricted their use. To take advantage of the high aspect ratio of the nanotubes, the SWNTs that usually exist in large bundles need to be separated into smaller bundles and ideally single nanotubes.

There are a number of methods that have been developed to disperse SWNTs in solvents such as the use of surfactants,[7] noncovalent functionalization,[8-10] and chemical functionalization.[11-19] Although these techniques are effective at dispersing SWNTs they have certain limitations and can result in changing properties such as electrical conductivity. For example a surfactant may work well in dispersing the nanotubes in water but when an organic solvent is used in polymer preparation the surfactant may not function well. Even if the surfactant can be used, it will be present in the final product which may not be desirable. Problems with solvent and polymer compatibility also occur with the use of various noncovalent modifications such as wrapping the nanotubes with starch. Chemical functionalization of the nanotube ends and side walls has also been used to increase the dispersion of carbon nanotubes but this can also alter the SWNT properties such as the electrical conductivity or mechanical properties. Chemical functionalization is perhaps the best means to disperse SWNTs in organic solvents, but it is desirable that the functionalization reaction can be controlled to minimize nanotube damage while rendering the tubes soluble.

In the work described herein, the use of tosyl hydrazones was investigated as an approach to achieve solubility while minimizing changes in the SWNT conductivity. It was postulated that the tube ends, due to their curvatures, would exhibit higher reactivity than the side walls because of the higher strain of the carbon carbon bonds. The reaction with tosyl hydrazones is well known for its use in bucky ball functionalization[20] which have carbon carbon bond strains comparable to those of carbon nanotube ends.

Two different tosyl hydrazones were prepared and reacted with the nanotubes using two different synthetic schemes. Modification under certain reaction conditions rendered the SWNTs soluble. These nanotubes were combined with colorless space durable polyimides to prepare nanocomposite films. The nanocomposite films were characterized for nanotube dispersion with high resolution scanning electron microscopy (HRSEM). The electrical conductivity, solar absorptivity (α), and thermal emissivity (ε) of the nanocomposite films are discussed herein.

II. Experimental

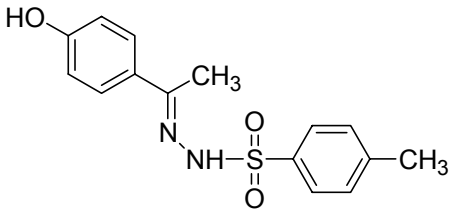
2.1. Starting Materials

SWNTs prepared by the HiPco process were purchased from Carbon Nanotechnologies, Inc and purified by heating at 250 ºC for 16 hrs in a high humidity chamber followed by Soxhlet extraction with hydrochloric acid (~22.2 weight %) for approximately 24 hrs.

1,3-Bis-3-(aminophenoxy) benzene [APB, Mitsui Chemicals America, Inc. melting point (m.p.) 107-108.5 ºC] was used as received and 4,4'-hexafluroisopropylidiene dipthalic anhydride (6-FDA, Hoechst Celanese Inc., m.p. 241-243 ºC) was sublimed prior to use. High molecular weight polyimide powder (CP2) was purchased from SRS Technologies, Inc.

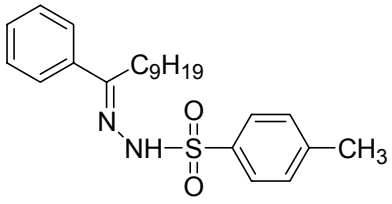
4-Hydroxyacetophenone, *p*-toluenesulfone hydrazide, pyridine, and sodium methoxide (NaOMe) were purchased from Aldrich Chemical Co. and used as-received. Methanol and 1,2-dichlorobenzene (ODCB) were obtained in reagent grade from Aldrich and used as-received. n-Nonaphenone was purchased from Acros Chemical, Inc and used as-received. All other chemicals were purchased from commercial sources and used as received.

2.2. Preparation of tosyl hydrazones



(1)

Into a 200 mL round-bottom flask was placed 4-hydroxy acetophenone (4.5736 g) and methanol (10 mL). Once the powder dissolved, *p*-tolunesulfonehydrazide (6.57 g) was added to the off-white solution along with methanol (30 mL). The reaction was stirred for 6 hrs at reflux yielding a yellow solution. To the cooled, stirred solution, water was added to precipitate the product. The product was collected via filtration and dried at 100 ºC (91% yield, m.p. 160 °C). The H^1 NMR spectrum was consistent with what was expected for this compound.



(2)

Into a 100 mL round-bottom flask was placed n-nonaphenone (8.006 g) and methanol (25 mL). Once the powder dissolved, *p*-tolunesulfonehydrazide (6.766 g) was added to the off-white solution along with methanol (25 mL). The reaction was stirred at reflux for 5 hrs yielding a bright yellow solution. Once cooled, methanol was removed via rotary evaporation yielding a yellow oil. Upon cooling for 48 hrs at 4 ºC the product solidified. The H^1 NMR spectrum was consistent with what was expected for this compound. The yellow product (m.p. 97 ºC) was ground to a fine powder and stored in a dessicator.

2.3. Preparation of functionalized nanotubes (F-tubes) by an in-situ one-step method

Into a 250 mL round-bottom flask was placed SWNTs (0.015 g) and ODCB (15 mL). The mixture was sonicated in a water bath for 3 hrs. Pyridine (60 mL), tosyl hydazone **1** (2.002 g), and sodium methoxide (0.395 g) were stirred for 0.5 hr in a separate 250 mL three-necked round-bottom flask equipped with nitrogen inlet and condenser. The black suspension of SWNTs was added to this slurry along with additional ODCB (30 mL). The reactants were heated to 80 ºC while stirring under a nitrogen atmosphere. Pyridine (40 mL) was added after 3 hrs and the reaction stirred at 80 °C for 16 hrs followed by ramping to reflux for 3 hrs. The product was centrifuged to a pellet and washed three times with methanol. The pellet was then dried under vacuum at room temperature resulting in a black powder.

Similar reactions were performed with tosyl hydrazone **2** but were not used in the preparation of nanocomposites.

2.4. Preparation of functionalionzed tubes from using a two-step procedure

Tosyl hydrazone **2** (4.9977 g) was dissolved in pyridine (50 mL) in a 100 mL three necked flask under a nitrogen atmosphere. The reaction was heated to 63 ºC. After 15 minutes NaOMe (0.7 g) was added and the reaction stirred for 2 hrs at temperature. The yellow solution became pink after 15 min. The red solution generated at the end of the two hours was poured into a pentane/water (100 mL/250 mL) mixture. The product was washed with water four times followed by the removal of the pentane by rotary evaporation to give a red oil (1.1631 g).

The red oil (0.2550 g) was dissolved in ODCB (10 mL). Then 5 mL of this solution was added dropwise to a sonicating mixture of SWNTs (11 mg in 70 mL ODCB). The mixture was then stirred at room temperature for 48 hrs under a nitrogen atmosphere.

2.5. Preparation of soluble nanotubes (s-tubes)

Into a 250 mL round-bottom flask was placed the SWNTs (100 mg) and ODCB (220 mL). The mixture was sonicated in a water bath for 3 hrs. In a separate flask NaOMe (0.264 g) and pyridine (80 mL) were stirred vigorously. The SWNT/ODCB mixture was then added to the pyridine/NaOMe solution dropwise. The reactants were heated at 80 ºC while stirring under a nitrogen atmosphere for 16 hrs followed by heating to reflux for 3 hrs. The pyridine was removed by distillation followed by collection of the nanotubes via centrifugation. The product was centrifuged to a pellet and washed

three times with methanol. The s-tube pellet was then dried under vacuum at 100 ºC resulting in a black powder.

2.6. Preparation of nanotube/CP2 mixtures by simple mixing

Into a 20 mL vial was placed F-tubes (0.002 g) and N,N-dimethylacetamide (DMAc) (9 mL). The vial was submerged in a water bath and sonicated for 2 hrs. This mixture was transferred to a 100 mL three necked flask. While sonicating, solid CP2 polyimide (2 g) was added in two separate additions over a 10 minute period. The sonication was stopped and the mixture was stirred for approximately 1 hr with a mechanical stirrer. The resulting mixture was used to cast a film.

2.7. Preparation of nanotube/CP2 mixtures via in-situ polymerization with sonication

Into a 20-mL vial were placed F-tubes (0.002 g) and DMAc (10 mL). The vial was placed in a water bath and sonicated for 2 hrs. 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 6-FDA (1.8094 g, 8.6 mmol) was subsequently added. Sonication was stopped and the mixture stirred at room temperature for 24 hrs under nitrogen. The resulting black, viscous mixture was used to prepare thin films.

2.8. Preparation of sprayed coated nanotube/CP2 films

Into a 20 mL vial was placed 0.002 g of s-tubes and 10 mL of DMAc. The mixture was placed in a water bath and sonicated for 6 hrs. The mixture was then placed in a sprayer and sprayed on a tacky CP2 film (20 % solids) that had been dried for 4 hrs under flowing nitrogen.

2.9. Thin films

Thin films were cast from both neat polyimide (reference) and polyimide/SWNT mixtures in DMAc. The solution or mixture was doctored onto clean, dry plate glass and dried to a tack-free state under flowing air at room temperature in a low humidity chamber. To effect solvent removal the thermal conditions in flowing air after RT drying were 1 hr each at 100, 150, and 220 °C.

2.10. Characterization

HRSEM images were obtained on Hitachi S-4700 and S-5200 field emission scanning electron microscopy systems operating below 2.0 kV. Solar absorptivity (α) was measured on thin films using an AZ Technology Model LPSR-300 spectroreflectometer with measurements taken between 250 to 2800 nm. Vapor deposited aluminum on Kapton® film (1^{st} surface mirror) was used as the reflective reference for air mass 0 per ASTM E903. An AZ Technology Temp 2000 A infrared reflectometer was used to measure thermal emissivity (ε) of thin films. Surface resistivity was determined according to ASTM D-257-99. The device used was a Prostat® PSI-870 Surface Resistance and Resistivity Indicator operating at 9V and reported as an average of three readings. Thermogravimetric analysis (TGA) was performed on a Seiko SSC/5200 Thermal Analyzer at a heating rate of 5 °C/min in air at

a flow rate of 50 mL/min. Raman spectroscopy was performed using a Thermo Nicolet Almega Dispersive Raman spectrometer equipped with a 785 nm laser.

3. Results and Discussion

3.1. Preparation of functionalized tubes

Two problems to overcome when trying to functionalize SWNTs are agglomeration of the SWNTs and precise control of the reaction. Agglomeration of the SWNTs into bundles minimizes the reactive sites available. This can be overcome to some degree by sonication. Lack of control of the reaction may result in too much of the surface being modified. This can alter the nanotubes electrical and mechanical properties significantly. Thus a reaction that was anticipated to be specific to the tube ends was examined.

The functionalization method chosen for this work involved the use of ODCB as a solvent. The tubes were sonicated in this solvent prior to any chemistry being performed and after sonication the tubes were somewhat dispersed in the solvent. The tosyl hydrazones were converted to the corresponding diazo compound in-situ with pyridine and NaOMe upon heating for a short time in the presence of the tubes. The reaction was allowed to proceed for 16 hrs to allow sufficient time for reaction. Collecting samples via filtration caused the loss of large amounts of materials; thus centrifugation was chosen as the collection method for the F-tubes. After centrifugation a black pellet was obtained as well as a black solution. The liquid was decanted and the pellet was washed several times with methanol to remove any ODCB. The washed tubes were collected via centrifugation followed by drying under vacuum at room temperature. After short periods of sonication in DMAc and THF (~2 mg/20 mL) the F-tubes appeared soluble (~2 mg/20 mL). The reaction scheme is depicted below in Figure 1.

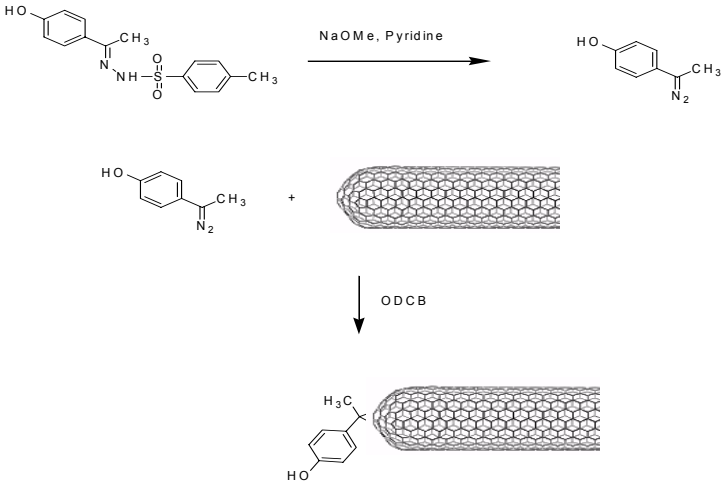


Figure 1. Functionalization of carbon nanotubes

This reaction was performed with tosyl hydrazones **1** and **2** using the one-step synthesis method. Another way to perform the reaction was to generate the diazo in a separate reaction and add it to the SWNTs in an appropriate solvent. This two-step method was attempted with tosyl hydrazone **2.** The two-step method yielded no

improvement in SWNT solubility relative to the neat nanotubes and no further experimentation was performed with these tubes.

The functionalizing of the SWNTs in the one-step method afforded good results as the SWNTs were rendered soluble. Although improvements to solubility were made, there was no conclusive evidence that the reaction had actually occurred. after performing these reactions, characterization of the SWNTs by Raman spectroscopy and TGA was inconclusive. Additional experiments were performed to determine if the SWNTs were indeed being functionalized or if some other phenomenon was causing enhanced solubility. The first step was to remove the tosyl hydrazone reactant while keeping all other reaction conditions the same. After this step, the SWNTs were still soluble indicating that the tosyl hydrazone was not the primary cause of the increased solubility.

3.2. Determination of the efficacy of functionalization

Four separate experiments were followed in order to provide a possible explanation as to how the SWNTs were being solubilized. The neat SWNTs were placed in various solvents and sonicated. They did not disperse well in any solvent but instead would form dispersed aggregates. In a second experiment the SWNTs were placed in a flask in ODCB and sonicated for 3 hrs. These SWNTs were then washed three times in methanol and collected via centrifugation followed by drying in a vacuum oven at 100 ºC for 3 hrs. This provided no improvement in solubility over the neat SWNTs. In another experiment the SWNTs were sonicated for 3 hrs in ODCB and heated to 80 ºC for 16 hrs. Again no improvement in solubility was evident as compared to the neat SWNTs. The final and most successful procedure involved sonicating the SWNTs in ODCB for three hours followed by heating for 16 hrs at 80 ºC with NaOMe and pyridine and then heating to reflux for 3 hrs. These SWNTs were then washed with methanol three times followed by centrifugation. After the SWNTs were washed they were dried in a vacuum oven at 100 ºC for 3 hrs. The tubes from this fourth experiment (s-tubes) were soluble in DMAc, dimethyl formamide (DMF), tetrahydrofuran (THF), and ODCB.

It was speculated at this point that a sonopolymer of ODCB was wrapping the SWNTs, enhancing the solubility of the tubes. To validate this, the reaction was repeated without the addition of ODCB. The SWNTs were sonicated in only pyridine for 3 hrs followed by the addition of NaOMe. The reaction mixture was then heated and worked up in the same manner as the s-tubes. The resulting SWNTs were also soluble in the same solvents as those treated with ODCB. Thus, it appears that the treatment with pyridine and NaOMe were causing the nanotubes to become soluble.

The SWNTs were examined by TGA to determine the effects of the different treatments on the thermal stability (Figure 2). The analysis of the neat SWNTs showed that they decomposed at a temperature near 550 ºC in air (a).

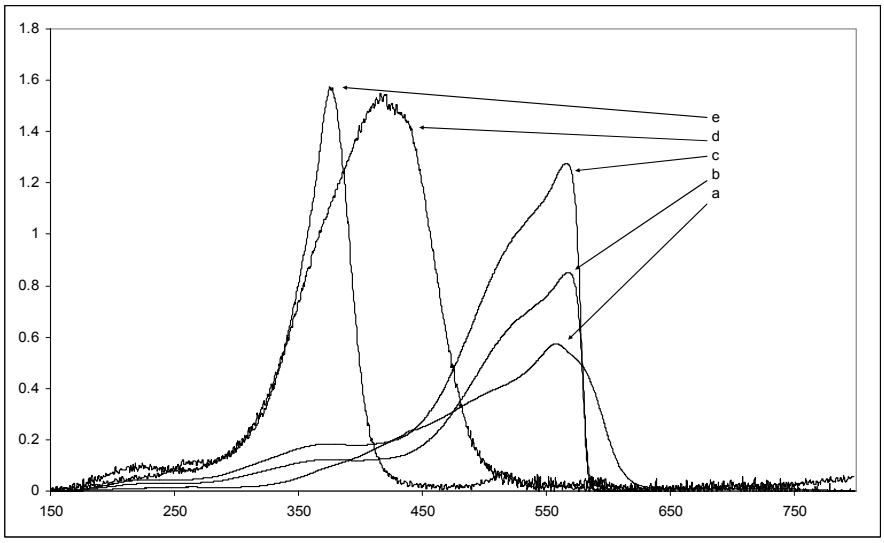


Figure 2. a) Neat SWNTs b) SWNTs sonicated for 3 hrs in ODCB c) SWNTs heated and sonicated d) SWNTs sonicated for 3 hrs in pyridine and heated for 16 hrs in pyridine/ NaOMe e) SWNTs heated and sonicated with pyridine/NaOMe and ODCB

After the SWNTs were sonicated in ODCB for 3 hrs, no significant change was observed in the decomposition temperature of the nanotubes (b). After the SWNTs were subjected to sonication in ODCB and heated there was again no significant change in the decomposition temperature (c). Although the tubes were not affected by the ODCB treatment with heating, the decomposition temperature of the SWNTs after heating in ODCB, pyridine, and NaOMe was altered considerably. This was also the case after the ODCB was removed from the reaction indicating that the SWNTs were solubilized by some interaction involving NaOMe and pyridine.

It was determined that the best method for solubilizing the SWNTs was to use ODCB as a solvent and heat the SWNT/ODCB mixture in the presence of NaOMe and pyridine. This provided SWNTs that were soluble and did not require the use of large amounts of pyridine. The mechanism by which these tubes are solubilized is currently under investigation. These tubes are termed **s-tubes** throughout the rest of the paper.

3.3. Characterization of s-tubes

The neat SWNTs were not soluble in any of the common solvents. The s-tubes (~2 mg/mL) dispersed well in DMAc and would remain in what appeared to be a solution for 5-10 hrs. The s-tubes were more soluble in THF than in DMAc. In THF the tubes would remain suspended for days and even upon centrifugation at 3500 rpm for 30 min the majority of the s-tubes remained suspended. After the centrifuged sample was allowed to stand for 24 hrs a small amount of s-tubes settled out but a significant amount remained in solution. The tubes were also soluble in ODCB and would stay suspended after only short periods of sonication. Figure 3 shows a typical dispersion of the neat nanotubes (left) and the s-tubes after being sonicated in DMAc for 0.5 hr (right).

Figure 3. Nanotube dispersions in DMAc.

The samples were also examined with Raman spectroscopy (Figure 4).

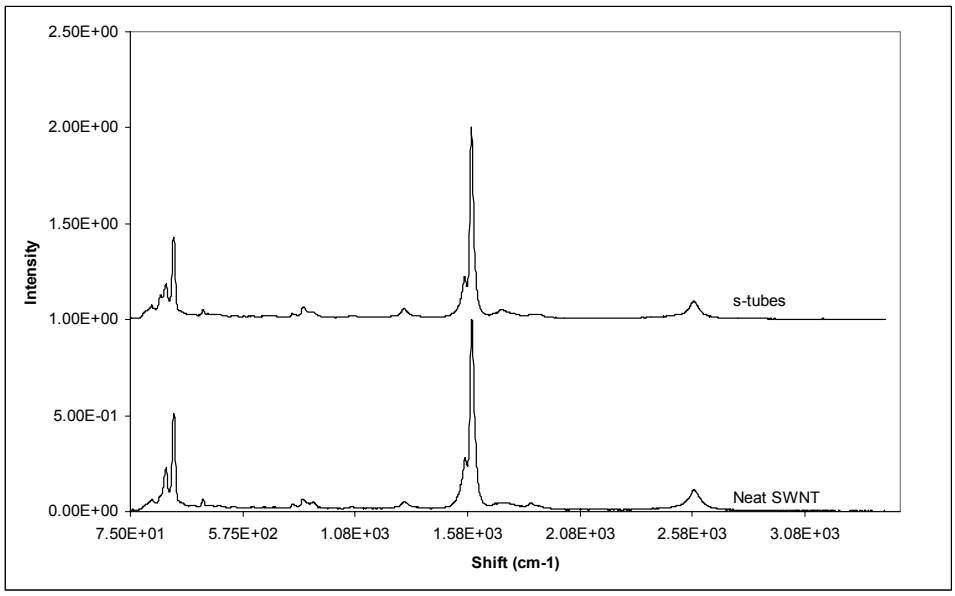


Figure 4. Raman spectra of neat and s-tubes

The Raman spectra indicate that the s-tubes had no fundamental change caused by the treatment in ODCB, NaOMe, and pyridine.

3.4. Preparation of polyimide/SWNT films

The polyimide-nanotube mixtures were prepared in three different ways: simple mixing, in-situ polymerization, and surface coating by a spraying technique. All of the techniques involved the use of CP2 polyimide. The monomers used in the synthesis of this polymer are shown in Figure 5.

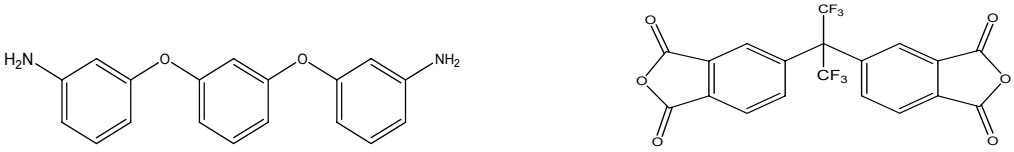


Figure 5. CP2 Monomers

The first technique used to prepare polimide/SWNT films involved simply dissolving the CP2 in F-tube suspensions in DMAc. The polyimide is readily soluble in polar aprotic solvents such as DMAc and without any nanotubes present the solutions of this polymer (20% solids) are viscous, nearly colorless, and transparent. Upon the first addition of the CP2 powder to F-tube mixtures the nanotubes immediately agglomerated but shortly after some of the polymer dissolved the F-tubes became well dispersed yielding a homogeneous black mixture. The mixtures were used in the preparation of thin films that were fingernail creasable and transparent. In contrast to the neat polyimide films the films containing F-tubes were no longer colorless. Little to no agglomeration of the F-tubes was observed at low concentrations of tubes, but at high concentrations of F-tubes (> 0.13% by weight) the films contained some nanotube agglomeration.

The second technique, the in-situ method, involved polymerization in the presence of F-tubes. The monomers, starting with the diamine, were added sequentially to the F-tube mixture as powders while sonicating. The F-tubes appeared to remain dispersed during this process. After the polymer formed, the mixture was removed from sonication and allowed to stir overnight. A film was cast from this mixture; however, the tubes agglomerated somewhat while drying. This film was not further characterized due to the relatively poor dispersion.

The third technique involved the use of SWNT mixtures as an aerosol. The F-tubes were dissolved in DMAc via sonication and then transferred to a bottle connected to an aerosol sprayer. The F-tubes were then sonicated a second time in the bottle prior to spraying onto the surface of a wet CP2 film. The films did not significantly darken using this technique. This technique provided low color, flexible, conductive films.

3.5. Optical and electrical characterization of polyimide/SWNT films

The CP2 films were characterized for surface resistivity, solar absorptivity, thermal emissivity, and % Transmission at 500 nm. The tabulated results are presented below.

Table 1. Optical and electrical properties of nanocomposite samples

Sample	Thickness (mils)	Solar Absoptivity (α)	Thermal Emmissivity (ε)	Transmission @ λ=500 nm	Surface Resistivity (Ω/square)
Neat CP2	1.5	0.08	0.53	84.8	$> 10^{12}$
CP2- 0.1% HiPco tubes	1.5	0.38	0.67	44.6	10^{10}
CP2- 0.06% F-tubes	2.2	0.27	0.66	63.2	$>10^{12}$
CP2- 0.08% F-tubes	2.2	0.34	0.68	59.3	10^{10}
CP2-0.1% F-tubes	2.1	0.38	0.67	55.3	10^{9}
CP2- 0.13% F-tubes	2.1	0.48	0.68	46.6	10^{8}
CP2- 0.18% F-tubes	1.5	0.43	0.64	50.9	10^{8}
CP2- sprayed F-tubes	1.5	0.12	0.55	84.4	10^{7}

The introduction of the F-tubes into the bulk of CP2 yielded conductivity after only 0.08 wt percent were added. The surface resistivity beyond this loading level was sufficient to mitigate static charge buildup. When comparing the film containing 0.1% neat SWNTs and the film containing 0.1% F-tubes it is interesting to note that the conductivity was not adversely affected in the film containing F-tubes indicating that the conductivity of the tubes was not altered upon modification. When the nanotubes were dispersed in the bulk, the solar absorptivity and %T were affected in a manner proportional to the amount of nanotubes added. The thermal emissivities and solar absorptivities of the films increased as nanotube concentration increased.

The introduction of carbon nanotubes as a spray coating on polyimide films yielded the best results in terms of the entire range of properties associated with materials needed for Gossamer spacecraft. The flexibility, color, and %T were not significantly altered while the electrical conductivity was enhanced to allow for static charge mitigation. This approach provided sufficient surface conductivity without significantly detracting from %T, α, or ε. Although an excellent combination of properties was achieved, the surface coating technique provides conductivity only on one side whereas bulk inclusion provides both surface and bulk conductivities.

Pictures of the films are shown below in Figure 6, which indicates the color difference between neat CP2, spray coated CP2, and bulk filled CP2.

Figure 6. Digital photographs of CP2 films

There was little to no difference in the visual appearance of the spray coated film's visual appearance while the bulk loaded film had increased color caused by the addition of 0.1% nanotube.

3.6. HRSEM characterization of spray coated nanocomposite film

HRSEM was used to examine the tubes spray coated onto the polymer surface. The F-tubes in this sample have been spray coated onto the film surface. From Figure 7 it can be seen that the nanotubes were not destroyed during the functionalization. It was also noticed that in general there was uniform covering of the film surface by the nanotubes and in areas where there were holes (right) they were traversed by networks of tubes creating a path of conduction.

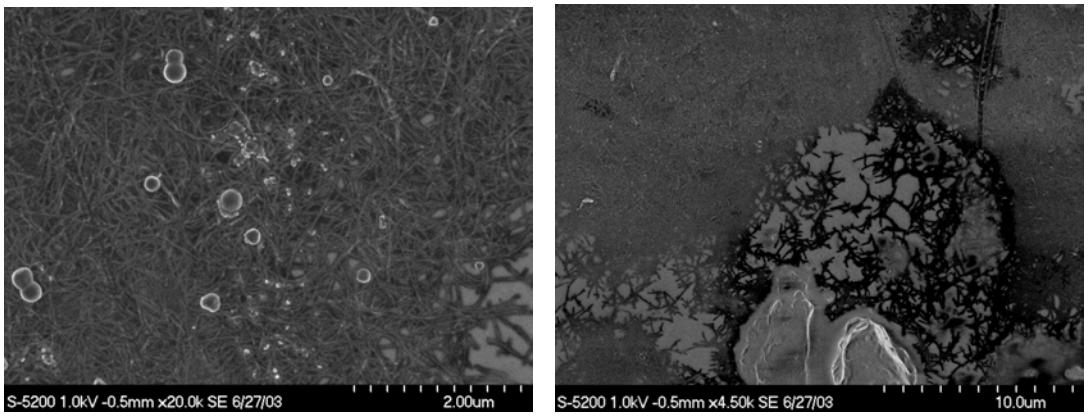


Figure 7. HRSEM pictures of spray coated film

4. Summary

SWNTs were subjected to reaction with tosyl hydrazones as a means of functionalization and consequent solublization. It was determined that the reaction with the tosyl hydrazones was not the primary cause of nanotube solublization. Treatment on the SWNTS with sodium methoxide and pyridine render the SWNTs soluble. The chemistry associated with this solublization is not fully understood and further investigations are ongoing. The soluble SWNTs were incorporated into and spray coated onto space durable polyimide films. Both approaches were successful in achieving the desired level of electrical conductivity without detracting from flexibility. When SWNTs were incorporated into the bulk of the polyimide, the optical and thermo-optical properties of the films were negatively affected. The spray coated films provided an excellent combination of properties and are presently under evaluation for Gossamer spacecraft.

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