

# POLYIMIDE/CARBON NANOTUBE COMPOSITE FILMS FOR ELECTROSTATIC CHARGE MITIGATION

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## ABSTRACT

Low color, space environmentally durable polymeric films with sufficient electrical conductivity to mitigate electrostatic charge build-up have been under investigation as part of a materials development activity. In the work described herein, single-walled carbon nanotubes (SWNT) solutions were dispersed in solutions of a novel ionomer in *N,N*-dimethylacetamide resulting in homogenous suspensions or quasi-solutions. The ionomer was used to aid in the dispersal of SWNTs in to a soluble, low color space environmentally durable polyimide. The use of the ionomer as a dispersant enabled the nanotubes to be dispersed at loading levels up to 3 weight % in a polyimide solution without visual agglomeration. The films were further characterized for their electrical and mechanical properties.

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KEY WORDS: Nanocomposites, Electrostatic Charge Mitigation, Carbon Nanotubes

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# 1. INTRODUCTION

Potential applications for single wall carbon nanotube (SWNT) containing materials are numerous. Although there is great potential, the full implementation of the technology will not be realized until issues involving SWNT purity and dispersion are resolved. The dispersion of SWNTs into polymer has been difficult due to many factors including the inability to interface with polymers and the inherent bundling of the tubes due to the strong van der Waal forces present between tube surfaces (1). Even in highly aromatic polymers such as polyimides, the maximum loading level that is attainable while maintaining good dispersion is approximately 0.2 weight % (wt) (2-5). Additionally, the morphology of the tubes aids in the bundling effect as the long rope-like structures intertwine creating vast networks of tightly bound tubes. These networks are not easily separated by mechanical means because of the size domain; however, mechanical methods such as sonication (5) and homogenization (6) have been successfully employed for dispersing SWNTs. Other methods which involve non-mechanical schemes have also been employed to disperse SWNTs. Examples include functionalization of the tubes (7-15) which can alter the electrical and mechanical properties) and the use of surfactants (16).

An alternate approach for the dispersion of SWNTs in polymers is the use of polymers and other molecules that are attracted to the nanotube surfaces and either lie flat along the surface or wrap the tube (17-19). This approach offers a method of dispersing nanotubes in organic solvents without adversely affecting the properties of the nanotubes. The use of these noncovalent modifications to disperse SWNTs usually involves  $\pi$ -conjugated small molecules or polymers (20-28). The use of ionic polymers (29,30) and ionic liquids (31) have also been shown to disperse SWNTs in organic solvents.

In the work described herein, an aromatic, conjugated ionomer (32) with alkyl side chains was used to disperse SWNTs. The ionomer/SWNT dispersions were added to a low color, space durable polyimide in solution. This approach allowed for improved dispersions of SWNTs of higher weight loading in the polyimide than was achievable without the use of the ionomer as a dispersing aid. The overall goal of this work is to prepare transparent, flexible, anti-static, space environmentally durable polymer films for use on future NASA missions.

## 2. EXPERIMENTAL

**2.1 Starting Materials** Bucky Pearl SWNTs were purchased from Carbon Nanotechnologies Incorporated (Houston, TX 77084) and treated as described in section 2.3. 1,3-Bis(3-aminophenoxy) benzene [APB, Mitsui Chemicals America, Inc., mp 107-108.5 °C] was used as received. 4,4'-Hexafluoroisopropylidene diphthalic anhydride (6-FDA, Hoechst Celanese Inc., mp 241-243 °C) was sublimed prior to use. High molecular weight LaRC™ CP2 was purchased from SRS Technologies, Inc. (Huntsville, AL 35806) and used as received. 9,9-Dioctylfluorene was prepared according to a literature procedure (33). All other materials were purchased from commercial sources and used without further purification.

**2.2 Preparation of monomers used in ionomer synthesis** *2,7-Dinitro-9,9-dioctylfluorene* 9,9-Dioctylfluorene (30.53 g, 26.56 mmol) and glacial acetic acid (150 mL) were charged into a three-neck flask to form a biphasic mixture. The mixture was cooled to 0 °C by submersing the flask into an ice bath. Fuming nitric acid (150 mL) was added dropwise through an addition funnel over 45 min. The ice bath was slowly warmed to 55 °C over a period of 2 hrs and then cooled to room temperature. The reaction was allowed to continue at room temperature overnight, during which time a tacky, orange precipitate formed. The contents of the reaction were slowly poured into 1200 mL ice water and stirred for 1 hr. The water was decanted from the solid and the product washed several times with water. The product was dissolved in 400 mL chloroform (CHCl<sub>3</sub>) and washed sequentially with 200 mL each of water, brine, and water. The organic layer was collected and dried over magnesium sulfate and the chloroform was removed by rotary evaporation to afford an orange liquid. This liquid was dissolved in 200 mL hexanes and precipitated by submersing the flask in a dry ice/acetone bath. A yellow solid was collected via filtration and washed with cold hexanes. (mp 69-73 °C). Yield = 27.84 g (74.50%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) \_ 0.5 (m, 4H), 0.8 (t, 6H), 1.0-1.3 (m, 20H), 2.1 (m, 4H), 7.9 (s, 1H), 8.0 (s, 1H), 8.3 (d, 2H), 8.3 (d, 1H), 8.3 (d, 1H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) \_ 14, 23, 24, 29, 29, 29, 30, 32, 40, 57, 119, 122, 124, 145, 149, 154 ppm. Elemental Analysis (EA) calcd. for C<sub>29</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>: %C, 72.47; %H, 8.39; %N, 5.83. Found: %C, 72.12; %H, 8.02; %N, 6.02.

**2.2.1 *2,7-Diamino-9,9-dioctylfluorene (AFDA)***

*2,7-Dinitro-9,9-dioctylfluorene* (27.84 g, 57.93 mmol) was dissolved in absolute ethanol (90 mL) and tetrahydrofuran (THF, 50 mL). Palladium on carbon (5%, 0.5 g) was subsequently added. The mixture was placed on a Parr hydrogenator and shaken under 40 psi of hydrogen for 4 hrs at room temperature. The mixture was filtered through Celite<sup>®</sup> and the solvent removed by rotary evaporation to afford a red-brown liquid. The crude product was dissolved in CHCl<sub>3</sub> and stirred with decolorizing charcoal for 1 hr at room temperature. The solution was filtered and the solvent removed by rotary evaporation to give a red liquid that slowly solidified into needle-like crystals (mp 58-63 °C). Yield = 22.36 g (91.76 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) \_ 0.7 (m, 4H), 0.8 (t, 6H), 1.0-1.3 (m, 20H), 1.9 (m, 4H), 3.6 (s, 4H), 6.6 (m, 4H), 7.3 (d, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) \_ 15, 23, 24, 30, 30, 31, 32, 41, 55, 111, 114, 119, 134, 145, 152 ppm. EA calcd. for C<sub>29</sub>H<sub>46</sub>N<sub>2</sub>: %C, 82.80; %H, 10.54; %N, 6.66. Found: %C, 82.29; %H, 10.06; %N, 6.73.

**2.2.2 *3,3'-(1,4-Phenylene)bis(1,5-di(4-fluorophenyl))-1,5-pentadione***

Terephthalaldehyde (13.40 g, 99.87 mmol) was suspended in 95% ethanol (550 mL). 4-Fluoroacetophenone (77.61 g, 588.9 mmol) was added and the suspension heated until all of the terephthalaldehyde dissolved. A solution of potassium hydroxide (8.42 g, 150 mmol) in water (60 mL) was then added to the mixture over 30 min. A precipitate of the bis-chalcone formed almost immediately and the reaction mixture was heated to reflux for 30 hrs, during which time the solid dissolved. The reaction mixture was cooled to room temperature to afford a yellow precipitate. The solid was collected by vacuum filtration, washed with cold ethanol, and dried in a vacuum oven at 100 °C for 3 hrs (mp 144-157 °C). Yield = 58.27 g (89.7%) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) \_ 3.1-3.5 (m, 8H),

4.1 (m, 2H), 7.1 (t, 8H), 7.2 (s, 4H), 7.9 (t, 8H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) \_ 37, 45, 114, 116, 128, 131, 133, 142, 165, 197 ppm. IR (KBr pellet) 1685, 1232  $\text{cm}^{-1}$ . EA calcd. for  $\text{C}_{40}\text{H}_{30}\text{F}_4\text{O}_4$ : %C, 73.84; %H, 4.65; %F, 11.68. Found: %C, 73.56; %H, 5.03; %F, 11.11.

### 2.2.3 *1,4-Bis(4-(2,6-di(4-fluorophenyl)pyrylium))benzene ditriflate (BPBD)*

Triphenylmethanol (23.73 g, 91.15 mmol) was suspended in acetic anhydride (150 mL). The reaction flask was cooled to 0 °C in an ice bath and 50% trifluoromethylsulfonic acid (34.53 g, 115.0 mmol) was added over 30 min through an addition funnel. One hr after the addition was complete, finely ground 3,3'-(1,4-phenylene)bis(1,5-di(4-fluorophenyl)-1,5-pentadione (24.34 g, 37.41 mmol) was added. The ice bath was removed and the reaction mixture stirred overnight at room temperature. A bright red solid was collected by vacuum filtration, washed with ether, and dried in a vacuum oven for 2 days at 100 °C (dec 355 °C). Yield = 22.67 g (66.54%)  $^1\text{H}$  NMR (300 MHz, dimethyl sulfoxide- $d_6$  (DMSO)) \_ 7.5-7.9 (m, 8H), 7.9-8.3 (m, 4H), 8.3-8.7 (m, 8H), 9.0 (s, 4H) ppm. EA calcd. for  $\text{C}_{42}\text{H}_{25}\text{F}_9\text{O}_8\text{S}_2$ : %C, 55.39, %H, 2.66; %F, 20.86; Found: %C, 53.59; %H, 2.62; %F, 20.47.

**2.3 Preparation of soluble nanotubes (s-tubes) (34)** Into a 250 mL round bottom flask were placed 0.300 g of SWNT and 660 mL 1,2-dichlorobenzene (ODCB). The flask was placed in an ultrasonic bath for 3 hrs. In a separate flask were stirred 0.792 g sodium methoxide (NaOMe) and 240 mL pyridine. The nanotube suspension was subsequently added to the pyridine/NaOMe solution. The mixture was heated to 80 °C while stirring under a nitrogen atmosphere for 16 hrs followed by 3 hrs at reflux (~150 °C). Pyridine was removed by distillation followed by collection of the nanotubes via centrifugation. The nanotubes were obtained as a pellet and washed three times with methanol. The pellet was dried under vacuum for 24 hrs at room temperature resulting in 0.451 g (150 %) of black powder. No changes in the IR, Raman and UV/Vis/NIR spectra of the s-tubes were observed.

**2.4 Preparation of ionomer for use as a dispersant (d-ionomer)** Into a 500 mL three-necked flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed AFDA (5.88 g, 13.97 mmol) and DMSO (90 mL). The mixture was stirred until the diamine completely dissolved. BPBD (12.82 g, 14.08 mmol) was added as a powder followed by additional DMSO (90 mL). While stirring, the flask was slowly heated to 165 °C in an oil bath and held for 5 hr. DMSO (90 mL) was added to the solution upon cooling and the solution was subsequently poured into water (2 L) while rapidly stirring in a Waring blender. The resulting fibers were washed with warm water and then dried in a vacuum oven at 100 °C for 24 hrs. [Inherent viscosity ( $\eta_{\text{inh}}$ )= 1.95 dL/g]

**2.5 Preparation of polyimide-ionomer-nanotube (PIN) nanocomposites via simple mixing** Into a 25 mL round bottom flask equipped with a ground glass stopper were placed s-tubes (8.5 mg) and *N,N*-dimethylacetamide (DMAc, 3.02 g). The flask was placed in a Branson 2510 Branson<sup>®</sup> ultrasonic cleaner bath operating at 42 KHz for 1 hr followed by the addition of d-ionomer (0.2556 g) and DMAc (2.26 g). The suspension was sonicated for an additional hr to give a homogeneous suspension. In a separate 50

mL three-necked flask equipped with nitrogen inlet and a mechanical stirrer were placed LaRC™ CP2 polyimide (0.85 g) and DMAc (1.5422 g). The solution was stirred for 1 hr at room temperature and the ionomer-nanotube solution was added dropwise to the LaRC™ CP2 solution while stirring and sonicating. DMAc (2.2 g) was used to wash in the remaining ionomer-nanotube solution and the entire contents were stirred for 1 hr and subsequently used to cast a film.

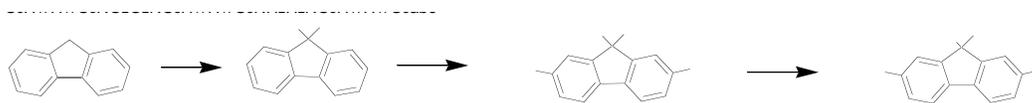
**2.6 Preparation of polyimide-ionomer-nanotube nanocomposites via in-situ polymerization (in-situ PIN)** Into a 100 mL three-necked flask equipped with nitrogen inlet, mechanical stirrer, and drying tube were placed s-tubes (20 mg) and DMAc (11 mL). The tubes were sonicated in a Branson 2510 Bransonic® ultrasonic cleaner bath operating at 42 KHz for 2 hrs followed by the addition of d-ionomer (50 mg). Sonication continued for 1 hr followed by the addition of APB (0.7933 g, 2.71 mmol) as a powder. The reaction mixture was stirred and sonicated for an additional hr. 6-FDA (1.2051 g, 2.71 mmol) was subsequently added as a powder and the reaction stirred under sonication for an additional 1 hr. Sonication was stopped and the polymer solution stirred for 16 hrs at room temperature.

**2.7 Thin Films** Thin films were cast from both control solutions and nanocomposite mixtures from DMAc. The solution or suspension was doctored onto plate glass and dried to a tack-free state under flowing air at room temperature in a low humidity chamber. The films were then placed in a forced air oven and heated for 1 hr each at 100, 150, and 220 °C. The in-situ PIN nanocomposites required an additional hr at 300 °C to induce imidization. Thin-film tensile properties were determined in the direction transverse to the draw direction according to ASTM D882 at room temperature using five specimens from each film.

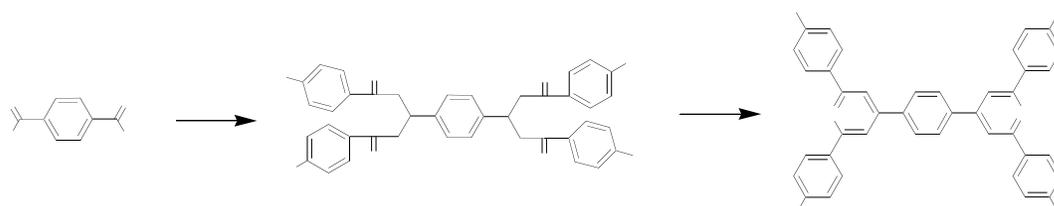
**2.8 Characterization** Elemental analysis was performed by Desert Analytics (Tucson, Arizona). High resolution scanning electron microscopy (HRSEM) images were obtained on a Hitachi S-5200 field emission scanning electron microscopy system operating at or below 5.0 kV. Surface resistivity was determined according to ASTM D-257-99 using a Prostat® PSI-870 Surface Resistance and Resistivity Indicator operating at 9V and reported as an average of three readings. Volume resistivity was determined using a Prostat® PRS-801 Resistance System with a PRF-911 Concentric Ring Fixture operating at 10 – 100 V according to ASTM D-257. Melting point ranges (tangent of onset to melt and the endothermic peak) were determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. Raman spectroscopy was performed using a Thermo Nicolet Almega Dispersive Raman spectrometer equipped with a 785 nm laser. <sup>1</sup>H NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer at 300 MHz with TMS as an internal standard. <sup>13</sup>C NMR spectra were obtained at 75 MHz. Inherent viscosities were obtained on 0.5% (w/v) solutions in DMAc at 25 °C. Fourier Transform Infrared (FTIR) spectra were obtained on a Nicolet Magna-IR™ 750 spectrometer. Ultraviolet/visible/near infrared (UV/Vis/NIR) spectra were obtained on thin films using a Perkin-Elmer Lambda 900.

### 3. RESULTS AND DISCUSSION

**3.1 Preparation of monomers and ionomer** The diamine and the pyrylium salt monomers were prepared as shown in Figures 1 and 2, respectively.

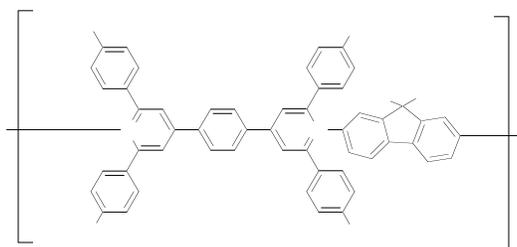


**Figure 1. Synthetic route to AFDA:** (a) THF, n-BuLi, n-octyl bromide, -78 °C (b) acetic acid, fuming nitric acid, 55 °C (c) 5% Pd/C, hydrogen (40 psi), THF/EtOH



**Figure 2. Synthetic route to BPBD:** (a) 95% ethanol, 4-fluoroacetophenone, KOH/H<sub>2</sub>O, reflux (b) acetic anhydride, triphenylmethanol, 50% trifluoromethylsulfonic acid

The monomers were initially reacted in a polar aprotic solvent (DMSO) at 165 °C (35). The ionomer solutions became viscous after ~2 hrs and the reaction stopped after either 3 or 5.5 hrs (longer reaction times resulted in gelation). The ionomer concentration was adjusted to 5% with additional solvent and precipitation into water afforded a fibrous material. The ionomer (Figure 3) was soluble in DMAc and solutions were used to cast amber, fingernail creasable thin films.



**Figure 3. Ionomer structure**

**3.2 Preparation of PIN nanocomposites** Nanocomposites were prepared from polyimides and s-tubes by two different methods. In the first method the s-tubes were dispersed in DMAc followed by the addition of d-ionomer (3:1 to 30:1 ionomer:s-tube) with further sonication. The role of the ionomer in this approach was to serve as a dispersing aid. This homogeneous suspension was subsequently added to a solution of a low-color polyimide (LaRC™ CP2) while sonicating and stirring. The s-tubes initially agglomerated but dispersed upon stirring yielding visually homogenous mixtures. Although PIN films were prepared with as little as 3:1 ionomer:nanotube ratio it was determined that for s-tube loadings  $\geq 1$  wt%, a 30:1 ratio was required to completely

disperse the s-tubes and provide films with no visual agglomeration. The films that had higher relative amounts of ionomer exhibited increasingly better s-tube dispersion. Also, 1% PIN films with lower relative amounts of d-ionomer were darker while those with higher relative amounts of the d-ionomer were less colored. For example the 3:1 ionomer:s-tube film was black with some visual agglomeration while the 30:1 ionomer:s-tube film containing the same amount of s-tubes (1%) was green with no visual agglomeration. Loading levels of up to 3 wt % SWNTs were dispersed in LaRC™ CP2 using this method. In contrast, less than 0.15 wt % s-tubes could be effectively dispersed in LaRC™ CP2 without the d-ionomer (34). Although the use of the d-ionomer as a dispersant for the s-tubes in the polyimide was an effective way to make conductive nanocomposites, it was desirable to use as little d-ionomer as possible so as not to affect the base properties of the LaRC™ CP2, in particular the low color properties.

Another method that was used to prepare PIN nanocomposites involved the in-situ polymerization of LaRC™ CP2 in s-tube/d-ionomer/DMAc suspensions. LaRC™ CP2 monomers (APB and 6FDA, Figure 4) were sequentially added to s-tube/d-ionomer/DMAc suspensions under sonication. It was observed that considerably less d-ionomer was needed to disperse the s-tubes by this method. For example, a 2.5:1 ionomer:s-tube ratio was sufficient to prepare a film with a 1 wt% loading of s-tubes that was visibly transparent.

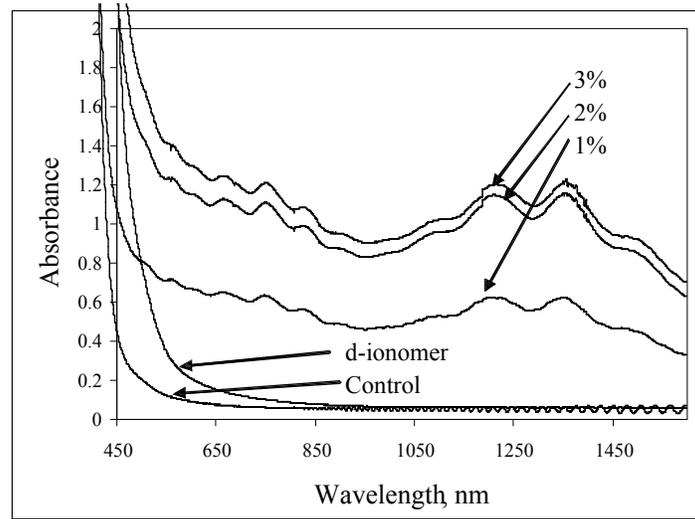


**Figure 4. LaRC™ CP2 monomers**

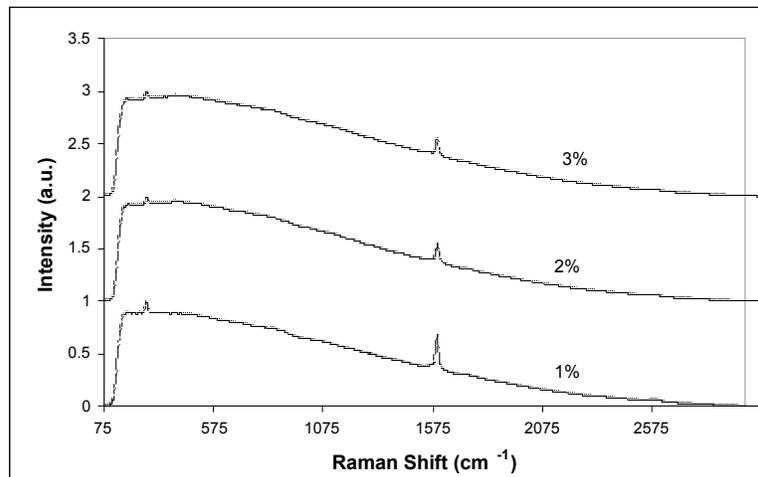
The aromatic ionomer may work well as a dispersing agent because it is attracted to the  $\pi$  character of the tube surface. It is assumed that the aromatic portion of the polymer is in some way associated with the surface of the nanotubes while the alkyl portions are oriented away from the nanotube surface (1). It is not known whether the ionomer is tightly wrapping the s-tubes as suggested for other conjugated polymers (20-28) or if the polymer is only anchored to the surface in local regions (18). Due to the rigid backbone it is not likely that the polymer would tightly wrap the s-tubes. However it is also possible for multiple polymer chains to wrap the same nanotube (22).

**3.3 Characterization of PIN nanocomposites** In preparing the PIN film samples, the d-ionomer/s-tube dispersion was added to the LaRC™ CP2 polyimide in DMAc. The ionomer to s-tube ratio was important in preparing quality films and a 30:1 ionomer:s-tube ratio was found necessary to disperse the tubes at concentrations  $\geq 1$  wt %. A series of PIN films was prepared using this ratio of ionomer:s-tube with loadings of 1, 2, and 3 wt % s-tubes relative to the polyimide (Table 1). Resistivity values of the films (Table 1) are suitable for electrostatic charge dissipation. The UV/Vis/NIR and Raman spectra for these PIN (30:1) are shown in Figures 5 and 6, respectively. The control film is LaRC™ CP2 and contains the same amount of d-ionomer as the 1 wt % PIN film. The light yellow control film starts to absorb at a lower wavelength than the d-ionomer film. The 1 wt % PIN film shows a major absorption at a similar wavelength and although it contains 1 wt % s-tubes it is light green. At higher levels of s-tubes the films are darker in color.

The Raman spectra of the PIN nanocomposites show that the s-tubes were not significantly altered upon nanocomposite preparation.



**Figure 5. UV/Vis/NIR data of PIN films**



**Figure 6. Raman spectra of PIN (30:1) films**

**Table 1. Resistivity of PIN films**

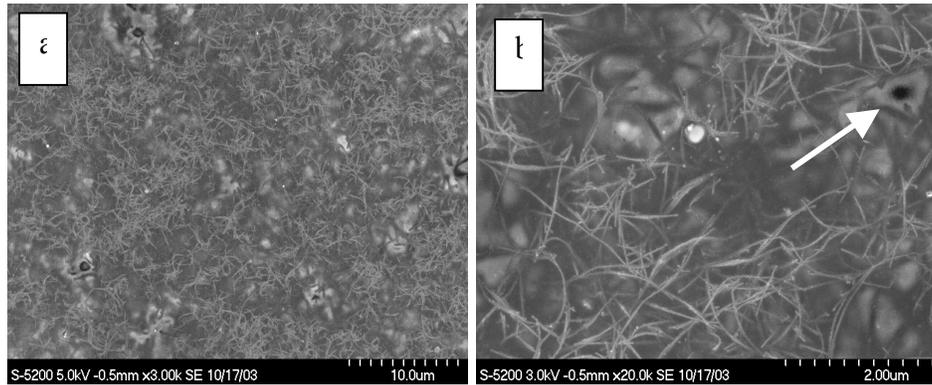
Description (Ionomer:tube ratio)	Ionomer/ 1.0 g CP2, (g)	Tube Loading, (wt %)	Surface Resistivity, ( $\Omega$ /sq)	Volume Resistivity, ( $\Omega$ cm)
PIN (3:1)	0.02	1	$1.6 \times 10^9$	$2.5 \times 10^8$
PIN (5:1)	0.04	1	$6.6 \times 10^8$	$2.2 \times 10^8$
PIN (20:1)	0.20	1	$2.8 \times 10^9$	$2.4 \times 10^8$
PI control	0.30	0	$> 10^{12}$	$> 10^{12}$
PIN (30:1)	0.30	1	$2.8 \times 10^8$	$3.8 \times 10^8$
PIN (30:1)	0.60	2	$4.9 \times 10^7$	$1.2 \times 10^8$
PIN (30:1)	0.90	3	$1.1 \times 10^9$	$3.0 \times 10^8$

The mechanical properties of the films containing a 30:1 ionomer:s-tube ratio as well as the control films were determined with the data presented in Table 2. No significant increase in the tensile properties of the films associated with 1 wt % s-tube loading was observed. The PI control film (0% s-tubes) had the exact same ratio of d-ionomer and polyimide as the PIN 30:1 1 wt % film and the values for modulus, strength, and elongation of these two were similar. The control film also had a lower modulus, strength, and % elongation than neat LaRC™ CP2. This is expected since the d-ionomer film has lower tensile properties than LaRC™ CP2. Since the ionomer lowers the tensile properties of the polymer mixtures, the 2 and 3% PIN films that contain more ionomer may exhibit some tensile property increases associated with the introduction of the s-tubes. However, if any increases in properties exist, the increases are not as large as expected with these high SWNT loadings.

**Table 2. Room temperature thin film tensile properties of PIN films**

Description	Ionomer / 1.0 g CP2, (g)	s-tube loading, (wt %)	Modulus, (MPa)	Strength, (GPa)	Elongation, (%)
LaRC™ CP2	N/A	0	$3.6 \pm 0.2$	$117 \pm 7$	$7 \pm 0.8$
d-Ionomer	N/A	0	$2.9 \pm 0.1$	$55 \pm 13$	$2 \pm 1.0$
PI control	0.30	0	$3.2 \pm 0.1$	$103 \pm 9$	$5 \pm 0.7$
PIN (30:1)*	0.30	1	$3.3 \pm 0.1$	$96 \pm 10$	$5 \pm 1.1$
PIN (30:1)*	0.60	2	$3.4 \pm 0.1$	$89 \pm 2$	$4 \pm 0.2$
PIN (30:1)*	0.90	3	$3.3 \pm 0.1$	$89 \pm 2$	$4 \pm 0.4$

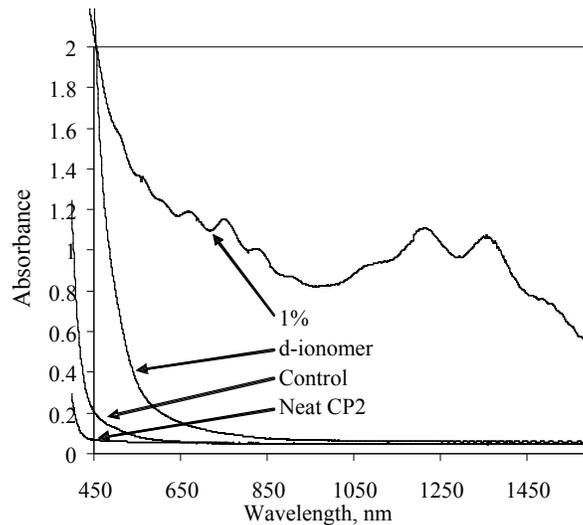
\*Ratio of ionomer:s-tube



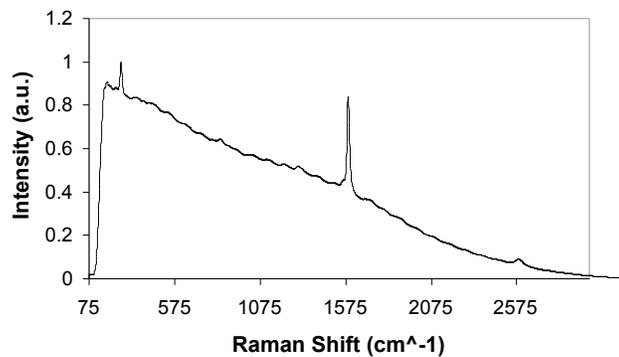
**Figure 7. HRSEM images of 1 wt % PIN films (30:1 ionomer:s-tube)**

HRSEM images of 1 wt % PIN films (30:1 ionomer:s-tube) are shown in Figure 7. In all the images the s-tubes appeared well dispersed and exhibited a random rope-like structure. At high magnifications regions of high polymer content were observed and these regions started to build up charge (as can be seen in the area pointed to in Figure 7b). Even though areas in this 1% PIN film were not included in the percolation network, a robust network of small s-tube bundles throughout the film is clearly seen in Figure 7a.

**3.4 Characterization of in-situ/PIN nanocomposite films** An in-situ PIN nanocomposite film having a 2.5:1 ionomer:s-tube ratio was characterized along with control films. The UV/Vis/NIR and Raman spectra of these films are shown in Figures 8 and 9, respectively. The data in the UV/Vis/NIR associated with the nanotubes is similar to that for the other films; however, the 1 wt % in-situ PIN film was black. The difference in color between the 1 wt % in-situ PIN film (black) and the 1 wt % PIN (green) film can be attributed to the lower amount of d-ionomer used in the in-situ film. The control film had the same amount of d-ionomer as the 1 wt% in-situ PIN film (see Table 3) and was very light yellow. The Raman spectrum of the 1wt% in-situ PIN film showed once again that the s-tubes' chemical structure was unaffected in nanocomposite preparation.



**Figure 8. UV/Vis/NIR of 1 wt% in-situ PIN films**



**Figure 9. Raman of 1 wt % in-situ PIN film**

The resistivity values obtained for this film as well as two control films are shown in Table 3. The surface and volume resistivities of the 1 wt % in-situ PIN film are lower than the resistivity of the 1 wt % PIN film. One explanation for this is that the s-tubes have a more favorable distribution for improved conductivity when prepared via the in-

situ method. A surface resistivity value of  $9.0 \times 10^5 \Omega/\text{sq}$  is suitable for electrostatic charge dissipation.

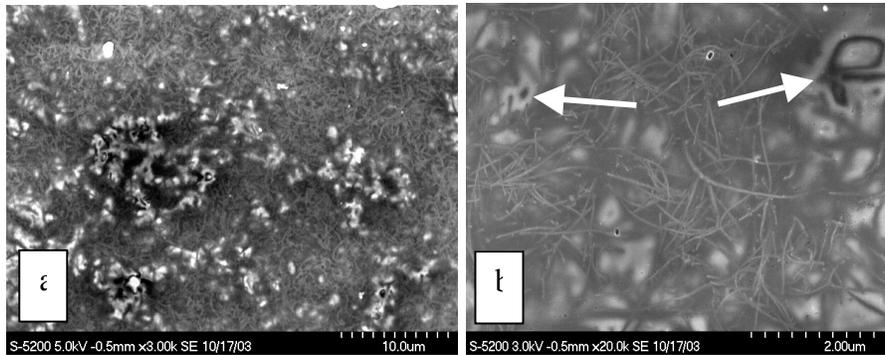
**Table 3. Resistivity of in-situ PIN films**

Film	s-tube loading, (wt %)	Ionomer/ 1.0 g CP2, (g)	Surface Resistivity, ( $\Omega/\text{sq}$ )	Volume Resistivity, ( $\Omega \text{ cm}$ )
LARC™ CP2	0	N/A	$> 10^{12}$	$> 10^{12}$
PI control	0	0.025	$> 10^{12}$	$> 10^{12}$
In-situ PIN	1	0.025	$9.0 \times 10^5$	$3.8 \times 10^6$

The tensile properties (Table 4) of the control film were not significantly affected when compared to neat LaRC™ CP2. As previously observed, the inclusion of 1% s-tubes did not enhance the mechanical properties of the material.

**Table 4. Room temperature thin film tensile properties for in-situ PIN films**

Film	s-tube loading, (wt %)	Ionomer/ 1.0 g CP2, (g)	Modulus, (ksi)	Strength, (ksi)	Elongation, (%)
LARC™ CP2	0	N/A	$2.5 \pm 0.1$	$117 \pm 3$	$6 \pm 1.3$
PI control	0	0.025	$3.4 \pm 0.1$	$110 \pm 6$	$6 \pm 1.1$
In-situ PIN	1	0.025	$3.5 \pm 0.1$	$110 \pm 1$	$5 \pm 0.2$



**Figure 10. HRSEM Images of 1% in-situ PIN film**

The HRSEM image Figure 10a shows that the s-tubes were uniformly dispersed on the surface of the film but the higher magnification images do show areas of high polymer content. These areas started to build up charge (Figure 10b) as was the case of the 1% PIN film (Figure 7). Figure 10b shows that there is an extensive charge-dissipating percolation network of small s-tube bundles throughout the film.

## 4. SUMMARY

Nanocomposites containing SWNTs and an aromatic ionomer were prepared using two different methods and the resulting films characterized for electrical and mechanical properties as well as SWNT dispersion. As much as 3 wt% SWNTs could be incorporated in to a polyimide (LaRC™ CP2) when the ionomer was used to aid in dispersion. The polyimide films were rendered conductive but the mechanical properties were not altered. The best way to prepare polyimide-SWNT nanocomposites is the in-situ preparation of the polyimide in the presence of pre-dispersed SWNTs. A ratio of 2.5:1 ionomer:s-tube was deemed sufficient to disperse up to 1 wt % carbon nanotubes in LaRC™ CP2 using this method. All the nanocomposites contained well dispersed SWNTs with relatively small bundle sizes. This method of nanotube dispersion could be useful in the preparation of other polymer-SWNT nanocomposites.

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