Polyimide/Carbon Nanotube Composite Films for Electrostatic Charge Mitigation

Joseph G. Smith, Jr., Donavon M. Delozier[‡], and John W. Connell
National Aeronautics and Space Administration
Langley Research Center
Hampton, VA USA 23681-2199

Kent A. Watson
National Institute of Aerospace
144 Research Drive
Hampton, VA 23666

Abstract

Low color, space environmentally durable polymeric films with sufficient electrical conductivity to mitigate electrostatic charge (ESC) build-up have potential applications on large, deployable, ultra-light weight Gossamer spacecraft as thin film membranes on antennas, solar sails, thermal/optical coatings, multi-layer insulation blankets, etc.. The challenge has been to develop a method to impart robust electrical conductivity into these materials without increasing solar absorptivity (α) or decreasing optical transparency or film flexibility. Since these spacecraft will require significant compaction prior to launch, the film portion of the spacecraft will require folding. The state-of-the-art clear, conductive coating (e.g. indium-tin-oxide, ITO) is brittle and cannot tolerate folding. In this report, doping a polymer with single-walled carbon nanotubes (SWNTs) using two different methods afforded materials with good flexibility and surface conductivities in the range sufficient for ESC mitigation. A coating method afforded materials with minimal effects on the mechanical, optical, and thermo-optical properties as compared to dispersal of SWNTs in the matrix. The chemistry and physical properties of these nanocomposites are discussed.

Introduction

Large, deployable, ultra-lightweight vehicles (e.g. Gossamer spacecraft) have been proposed by NASA for several mission concepts.[1] The vehicle would consist of both structural and polymer film components. As proof of concept, solar sails and tori have been constructed by various organizations and tested in ground-based facilities. Examples of on-orbit validation of these concepts were the Russian Znamya-2[2] and the Inflatable Antennae Experiment[3], respectively. Both flight experiments were successful at deploying a Mylar® based film structure in low Earth orbit. Since these were 'proof of concept' experiments, the space durability of the polymer film was not an issue. However, space durability of the film component is a concern for longer-term missions. Depending on the orbital location of the vehicle, different environmental effects will be encountered; therefore, material requirements could include resistance to UV and vacuum UV radiation, electrons and protons, and atomic oxygen (prevalent in low Earth orbit). For some applications high optical transparency, low α, and high thermal emissivity (ε) need to be maintained. The α pertains to the fraction of incoming solar energy that is absorbed by a material and is typically low (~0.1) for a low color film. The ε is a measure of a material's ability to radiate energy from its surface. Low α and high ε values are desirable since the film would effectively absorb little radiation. The film would also need to be folded into a compact volume found on conventional launch vehicles, so compliance is needed. Upon achieving orbit, the folded film would

‡National Research Council research associate located at NASA Langley Research Center

deploy affording structures that are several square meters in size.

Aromatic polyimides possess excellent mechanical and physical properties in addition to radiation resistance to satisfy many of the property requirements for Gossamer applications. Respectable space environmental durability and low color (related to α) have been achieved in polyimides through the proper choice of constituent monomers.[4,5] Like many organic polymers, polyimides are intrinsically insulative and can build-up charge due to the orbital environment. This can result in the material behaving like a capacitor. Considerable damage to surrounding materials and electronics on the vehicle could result when discharge occurs in a single event. To mitigate charge build-up, a surface resistance in the range of 10^6-10^{10} Ω/square is needed. Current methods that meet both the electrical conductance and optical transparency requirement utilize conductive coatings such as ITO to provide surface conductivity. However, these coatings are brittle making handling difficult. If the coating is broken/cracked by either handling or during on-orbit deployment, the conductive pathway is lost.

Electrical conductivity can also be enhanced by the uniform dispersal of a conductive additive in the polymer to provide both surface and bulk conductivity. One additive receiving much attention over the last 5-10 years are SWNTs. Due to their high aspect ratio and electrical properties, SWNTs are excellent candidates for obtaining the electrical conductivity necessary for ESC dissipation at low loading levels. However, achieving good SWNT dispersal has been a challenge due to insolubility and/or incompatibility with the host resin. In general, SWNTs tend to agglomerate as bundles in solution and if dispersed, reagglomerate soon thereafter due to electrostatic attraction. Uniform dispersions of SWNTs have been reported in space durable polymers (e.g. LaRC™ CP2) using an in-situ polymerization approach[6] and by the addition of the SWNTs into polymers terminated with reactive groups.[7] The first approach involved the synthesis of the precursor amide acid polymer in the presence of SWNTs with concurrent ultrasonic treatment followed by thermal cure to afford the polyimide nanocomposite. The latter method involved the addition of SWNTs to a previously prepared amide acid polymer containing reactive end groups and thus negating batch-to-batch variations in the polymer. Both approaches have yielded volume conductivity sufficient for ESC mitigation; however, optical transparency decreased and the color (related to α) increased relative to that of the pristine material.

Many space vehicle applications require only surface conductivity to mitigate ESC build-up. In this case, coating the SWNTs on the surface of space durable polymers was investigated.[8,9] By this method, considerably lower amounts of SWNTs were needed to achieve surface conductivity. Consequently, the optical properties did not deteriorate as much compared to the bulk approach. The preparation and characterization of LaRC™ CP2/SWNT nanocomposites by addition of SWNTs to a polymer containing reactive endgroups (bulk method) and by surface coating are presented herein. The effects upon optical transparency, α, and ε as well as electrical conductivity are discussed.

Experimental

Starting Materials

The synthesis of unendcapped and alkoxysilane endcapped LaRC™ CP2 has been previously reported.[7,8] SWNTs prepared by the HiPco process were obtained from Tubes@Rice and purified by heating at 250°C for ~16 h in a high humidity chamber followed by Soxhlet extraction with hydrochloric acid (22.2 wt%) for ~24 h. All other chemicals were used as received.

SWNT/alkoxysilane terminated amide acid (ASTAA) LaRC™ CP2 Mixture

Nanocomposite solutions were prepared by the addition of a sonicated mixture of SWNTs in N,N-dimethylacetamide (DMAc) to a pre-weighed ASTAA LaRC™ CP2 solution. A representative procedure is described below.

To a 100 mL round-bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube filled with calcium sulfate was charged 11.06 g of an ASTAA solution (~33.5% solids). In a separate vial, SWNTs (0.0011 g) were placed in 3 mL of DMAc and the mixture sonicated for ~2.5 h in a Degussa-Ney ULTRAsonik 57X cleaner operated at ~50% power and degas levels. The initial temperature of the water

bath was ambient and ~40 °C at the conclusion of sonication. The suspended tubes were added to the stirred mixture of ASTAA at room temperature and rinsed in with 4.5 mL of DMAc to afford a solids content of ~20%. The SWNT loading was 0.03 wt%. The mixture was stirred for ~16 h under a nitrogen atmosphere at room temperature prior to film casting.

Films with/without Bulk SWNT Dispersion

DMAc solutions of ASTAA LaRC™ CP2 were doctored onto clean, dry plate glass and dried to tack-free forms in a low humidity chamber at ambient temperature. The films on glass were stage cured in a forced air oven at 100, 200, and 300 °C for 1 h each. The films were subsequently removed from the glass plate and characterized.

Spray Coating of SWNT

1) ASTAA-LaRC™ CP2 film solutions in DMAc were doctored onto clean, dry plate glass and dried to a tack-free state in a low humidity chamber. A SWNT/N,N-dimethylformamide (DMF) mixture (1.0 mg SWNT per 5.0 g DMF) was placed in an ultrasonic bath operating at 40 MHz for 6-8 h. An airbrush (Badger Model 250) was used to apply the SWNT/DMF suspension to the surface of tack-free ASTAA-LARC™ CP2 films. The films were placed in a low humidity chamber for 16 h and then staged to 300 °C for 1 h in a forced air oven. 2) LaRC™ CP2 dissolved in DMAc (23% wt/wt) was doctored onto plate glass and placed in a low humidity chamber for 0.25 h. A SWNT/tetrahydrofuran (THF) mixture (1.0 mg SWNT per 5.0 g THF) was placed in an ultrasonic bath operating at 40 MHz for 1-2 h and then spray coated onto the film surface. The coated films were placed in a low humidity chamber for 16 h and then staged to 220 °C for 1 h in a forced air oven. The films were subsequently removed from the glass plate and characterized.

Characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% (w/v) amide acid solutions in DMAc at 25 °C. Glass transition temperatures (T_gs) were determined by differential scanning calorimetry at a heating rate of 20 °C/min on a Shimadzu DSC-50 thermal analyzer and taken as the inflection point of the ΔH vs. temperature curve. Ultraviolet/visible/near infrared (UV/vis/near-IR) spectra were obtained on thin films using a Perkin-Elmer Lambda 900 spectrometer and reported as % transmission (%T) at 500 nm. The α was obtained on thin films using an AZ Technology Model LPSR-300 spectroreflectometer with measurements taken between 250-2800 nm. Vapor deposited aluminum on Kapton® film (1st surface mirror) was used as the reflective reference for air mass 0 per ASTM E903. An AZ Technology Temp 2000A infrared reflectometer was used to determine ε on thin films. Surface resistivity was determined according to ASTM D-257-99 using a Prostat® PSI-870 operating at 9 V 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.

Results and Discussion

Polymer Synthesis

The space durable polymer chosen for this work was LaRC™ CP2 with and without reactive endgroups (i.e. alkoxysilanes). In Scheme 1, the unendcapped polymer was prepared via the traditional amide acid route. The intermediate amide acid was subsequently converted to the imide by chemical imidization with pyridine and acetic anhydride. The polyimide was isolated as a white fibrous material with an η_{inh} of 0.98 dL/g.

The ASTAA of LaRC™ CP2 was prepared by the same amide acid approach as depicted in Scheme 2. By this approach the dianhydride was added to a stirred mixture of the diamines. To prevent a
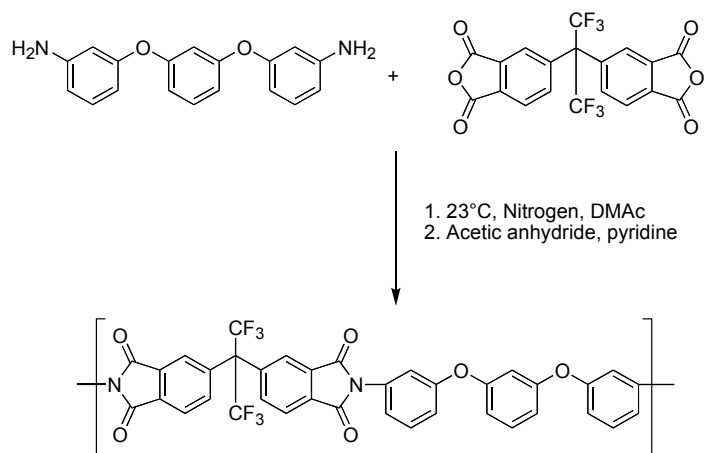
Scheme 1. LaRC™ CP2 Synthesis

temperature increase due to the heat of reaction and mitigate premature reaction of the endgroups, the flask was immersed in a room temperature water bath. The ASTAA solution was stirred overnight at room temperature under a nitrogen atmosphere. The η_{inh} was 0.73 dL/g. This solution was used to cast thin films that were subsequently spray coated with a SWNT dispersion. An ASTAA with an η_{inh} of 0.88 dL/g was used to prepare different wt% SWNT loadings.
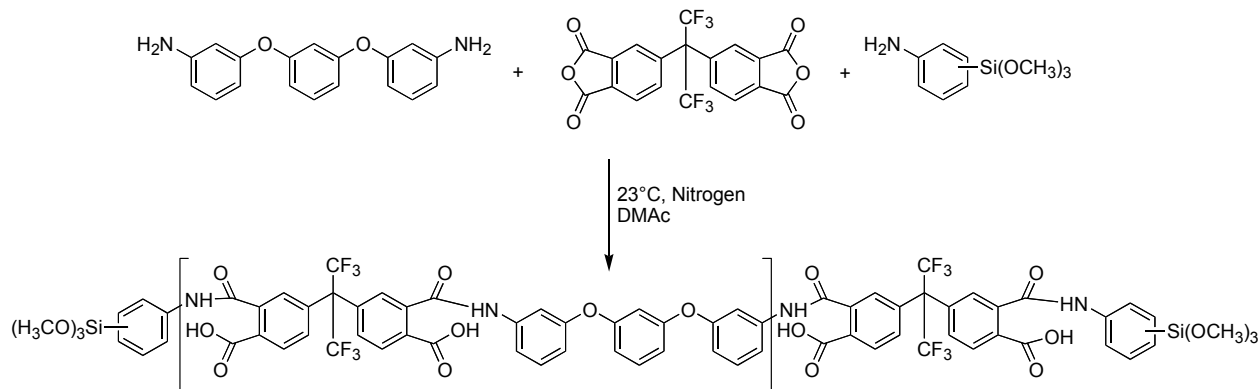
Scheme 2. ASTAA LaRC™ CP2 Synthesis

Nanocomposite Properties per Bulk SWNT Distribution

To achieve both surface and volume conductivities sufficient for ESC mitigation, HiPco SWNTs were distributed throughout the bulk of LaRC™ CP2 prepared from the precursor ASTAA (Scheme 2).[7] Suspended SWNTs were obtained by sonicating the tubes in DMAc. This suspension was then added to the ASTAA and the solution stirred under low shear with a mechanical stirrer at ambient temperature prior to film casting. Tack-free films were stage cured to 300 °C in flowing air to effect imidization and condensation. Due to the acidic nature of the amide acid, no additional acid catalyst was required for the hydrolysis of the alkoxysilane endgroups.[10] The silanol groups generated can condense with another silanol group to form a siloxane chain affording a crosslinked material. Presumably the silanol can also react with carboxylic acid and/or hydroxy functionalities present on purified SWNTs to form a covalent bond and perhaps aid in dispersion.[7]

Table 1. Thermal and Tensile Properties

ID	SWNT, %	T_g, °C	Room Temperature Tensile		Elong. @ Break, %
			Strength, MPa	Modulus, GPa	
P1	HMW*	209	117	2.9	Not reported
P2	0	207	131 ± 4	3.7 ± 0.1	5 ± 1
P3	0.03	205	122 ± 6	3.5 ± 0.2	5 ± 1
P4	0.05	203	139 ± 2	3.7 ± 0.1	6 ± 1
P5	0.08	206	137 ± 6	3.8 ± 0.1	5 ± 1

* High molecular weight, unendcapped LaRC™ CP-2.[5]

The T_g and room temperature tensile properties are shown in Table 1. LaRC™ CP2 properties are shown for comparison.[5] As seen, the T_g of P2 was comparable to that of P1 and was unexpected since crosslinking tends to increase the T_g. However, the mechanical properties increased as expected (P2 vs. P1). Inclusion of SWNTs in the matrix (P3-P5) did not increase the T_g or the mechanical properties compared to P2.

As previously mentioned, low α, high optical transparency, and high ε are important for some Gossamer applications. These properties were determined for P1–P5 and presented in Table 2. The %T at 500 nm is reported since this is where the solar maximum occurs. Optical properties are thickness dependent and thus all attempts were made to obtain films of comparable thickness. Film thickness ranged from 38 to 41 μm allowing comparisons to be made without normalization.

Table 2. Optical, α, and ε Properties

ID	SWNT, wt%	Film Thickness, μm	500 nm		α	ε
			% Transmission	Absorbance*		
P1	0, HMW	38	85	0.0706	0.07	0.53
P2	0	38	86	0.0655	0.07	0.59
P3	0.03	38	67	0.1739	0.21	0.63
P4	0.05	41	59	0.2291	0.30	0.65
P5	0.08	38	53	0.2757	0.35	0.67

*$A = 2 - \log_{10}\%T$

The endcapping agent was found to have a negligible effect on the %T at 500 nm and α for P2 compared to P1. However, ε increased ~10% for P2 compared to P1 and was presumably due to the reaction products from the alkoxysilane endcapping agent. SWNT inclusion in P3-P5 resulted in higher α and ε and lower %T compared to P2. A Beer's law relationship was obtained when absorbance at 500 nm was plotted vs. wt% SWNT (Figure 1). Losses due to scattering and reflectivity were not taken into account. In addition, α vs. wt% SWNT was plotted to afford a Beer's law-like relationship (Figure 1). The α differs from absorbance in the traditional Beer's law equation in that α is obtained over the spectral region of 250-2800 nm instead of a particular wavelength. Linear least-squares fit of the data had correlation coefficients of 0.961 and 0.951, respectively. This data was useful in developing models to predict the absorbance at 500 nm and α for various thicknesses and SWNT loadings.[11] Note that these relationships are dependent upon the polymer and the type, batch, and purity of SWNT used; however, the fundamentals should be applicable for other polymer/SWNT systems.

Electrical conductivity was determined as surface and volume resistivities (Table 3). As seen from the data, the percolation threshold for conductivity was reached at a 0.05 wt% SWNT loading (P4) and was in a range that was acceptable for ESC mitigation (10^6-10^{10} Ω/square). Increasing the SWNT loading to
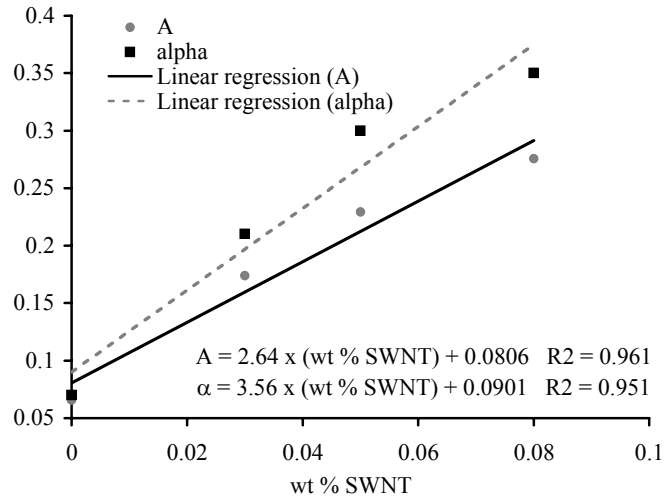
Figure 1: A at 500 nm and α vs. wt% SWNT.

0.08 wt % (P5) resulted in a material exhibiting the same order of magnitude resistivity but decreased %T and increased α compared to P4.

Table 3. Thin Film Electrical Characterization

ID	SWNT, wt%	Surface Resistivity, Ω/square	Volume Resistivity, Ω cm
P2	0	$>10^{12}$	Not Determined
P3	0.03	10^{11}	9.9×10^{14}
P4	0.05	10^{8}	1.7×10^{9}
P5	0.08	10^{8}	1.1×10^{9}

Besides exhibiting good mechanical, optical, and electrical properties, it was desired that the conductive film be compliant (i.e. flexible). Coatings such as ITO are brittle and lose conductivity if the conductive pathway is broken. To determine the robustness of the conductive pathway, P4 was subjected to harsh manipulation (Figure 2). This involved creasing, folding, and finally crumpling the film into a ball with the surface resistivity measured after every manipulation. After all of this harsh teatment, the initial surface resistivity of 10^{8} Ω/square remained unchanged. In addition, the film retained its integrity and did not fracture or tear. As a note these manipulations were harsh and it is unlikely that the materials on a Gossamer spacecraft would have to endure this degree of abuse during packaging and deployment.
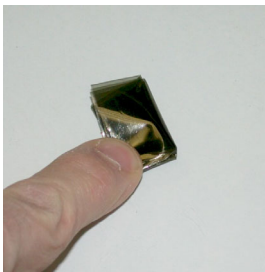
A. Film folded seven times.

B. Film after seven folds and crumpled into a ball.

Figure 2. Mechanical manipulation of P4.

Nanocomposite Properties per Spray Coating SWNT

By the bulk dipersal method, it was observed that the SWNT loading level necessary for ESC mitigation was detrimental to the optical and thermo-optical properties compared to the pristine polymer. However, for many space applications only surface conductivity is needed. Thus, spray coating of SWNTs onto the film surface was investigated.[8,9] Typically a solution is used in spray-coating processes; however, homogeneous dispersions of the SWNTs in DMF and THF were found to work well.

Thin films of unendcapped and alkoxysilane endcapped LaRC™ CP2 were spray coated with various amounts of SWNTs (Table 4). The actual wt% loading was unknown and thus the quantities used in the spraying process are provided.

Film thickness for LaRC™ CP2 (P6-P10) were about the same allowing for direct optical property comparison. A slight decrease in the %T with a slight increase in α and ε were observed for spray coatings up to 2.0 mg SWNT (P7-P9) compared to the uncoated polymer, P6. For P7-P9, the surface resistivities were essentially the same ($\sim 10^7 \Omega$/square) regardless of the increase in the amount of SWNTs sprayed. As expected, the films only exhibited surface resistivity. Film P10 spray coated with 4.0 mg SWNT exhibited a substantial decrease in %T and increase in α than compared to P6-P9; however, ε remained relatively unchanged. The reason for this is unknown. The surface resistivity for P10 was the lowest measured ($10^5 \Omega$/square).

Films of alkoxysilane endcapped LaRC™ CP2 were likewise spray coated with SWNTs. For these samples (P11 and P12) there appeared to be a more substantial decrease in %T and increase in α compared with P2 (Table 2) as was observed for the LaRC™ CP2 samples spray coated with a similar SWNT amount (Table 4, P7 and P8 compared to P6). This may be due to effects of the endcapping agent or variations in spray coating. A comparable surface resistivity to P4 (bulk loading, Table 2) was obtained for P11 with less of an impact on %T, α, and ε by this method. However, P11 exhibited only surface resistivity whereas P4 also possessed comparable volume resistivity. Further comparison of the optical properties of these samples (Table 4, P11 and P12) with samples containing SWNTs distributed throughout the bulk (Table 2, P2-P5) could not be made directly due to thickness differences.

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 spray-coated LaRC™ CP2 film and measuring surface resistivity after each manipulation. In separate tests, scotch tape was applied to the spray-coated surface and removed, and the film also placed in a sonicating bath operating at 40 Hz. This was repeated several times. In all of these qualitative tests, the initial surface resistivity of $10^7 \Omega$/square did not change. Such tests applied to an ITO coated film would have resulted in loss of conductivity due to fracture of the coating.

Table 4. Optical and Electrical Properties

ID	Polymer	SWNT, mg[a]	Film Thickness, μm	% T @ 500 nm	α	ε	Surface Resistivity, Ω/square
P6	LaRC™ CP2	0	38	87	0.06	0.52	2.5×10^{12}
P7	LaRC™ CP2	0.5	41	86	0.07	0.54	1.6×10^{7}
P8	LaRC™ CP2	1.0	38	83	0.09	0.56	6.1×10^{6}
P9	LaRC™ CP2	2.0	38	82	0.09	0.56	2.0×10^{7}
P10	LaRC™ CP2	4.0	38	72	0.21	0.52	2.2×10^{5}
P11	ASTAA LaRC™ CP2	0.4	31	81	0.12	0.52	1×10^{8}
P12	ASTAA LaRC™ CP2	1.1	33	68	0.20	0.56	1×10^{7}

[a] Amount of SWNTs sprayed onto 1.0 g of polymer

Summary

Two methods to prepare clear, colorless, flexible, space environmentally durable polymers with surface resistivity sufficient for ESC mitigation were summarized. One method involved preparing nanocomposites from alkoxysilane terminated amide acid polymers of LaRC™ CP2 and SWNTs distributed throughout the bulk. The second method involved spray-coating the film surface of ASTAA films as well as LaRC™ CP2 with a SWNT suspension. The former method possessed surface and volume resistivities whereas the latter provided conductivity on only one surface. The spray coating method resulted in little change in %T and α   .   .   .   .   . A more substantial effect on these properties was observed with bulk SWNT inclusion. Both methods afforded films that exhibited a high degree of flexibility and robustness as evidenced by retention of surface resistance after harsh manipulation.

The use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by NASA.

References

1. Jenkins CHM. Gossamer Spacecraft: Membrane and Inflatable Structures Technology for Space Applications Vol. 191, American Institute of Aeronautics and Astronautics; 2001.
2. http://www.space.ru/src/inform-e.htm
3. http://www.sti.nasa.gov/tto/spinoff1996/13.html
4. Watson KA and Connell JW. Polym. Mater. Sci. Eng. Proc. 2001; 46:1853.
5. SRS Technologies, Huntsville, AL 35806, http://www.srs.com.
6. Park C, Ounaies Z, Watson KA, Crooks RE, Smith Jr. JG, Lowther SE, Connell JW, Siochi EJ, Harrison JS, and St. Clair TL. Chem. Phys. Lett. 2002; 364:303.
7. Smith Jr. JG, Connell JW, Delozier, DM, Lillehei PT, Watson KA, Lin Y, Zhou B, and Sun Y-P. Polym. 2004; 45:825
8. Watson KA, Smith Jr. JG and Connell JW. Society for the Advancement of Material and Process Engineering Proceedings 2003; 48:1145.
9. Glatkowski P. Society for the Advancement of Material and Process Engineering Proceedings 2003; 48:2146.
10. Tsai MH and Whang WT Polym. 2001; 42:4197.
11. Smith Jr. JG, Connell JW, Watson KA and Danehy, PM. Manuscript in preparation.

Joseph G. Smith, Jr. is a senior polymer scientist in the Advanced Materials and Processing Branch of the Structures and Materials Competency at NASA Langley Research Center (LaRC). He received a B.S. degree from High Point College in 1985 and a Ph.D. from Virginia Commonwealth University (VCU) in 1990. Prior to joining NASA LaRC in September 1994, he held postdoctoral research positions with the University of Akron and VCU. His work at NASA has focused on the development of high performance polymers for aerospace applications.