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Verification and Operation of Adaptive Materials in Space

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Verification and Operation of Adaptive Materials in Space

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Abstract

Piezoelectric polymers based on polyvinylidene fluoride (PVDF) are of interest as smart materials for novel space-based telescope applications. Dimensional adjustments of adaptive thin polymer films are achieved via controlled charge deposition. Predicting their long-term performance requires a detailed understanding of the piezoelectric property changes that develop during space environmental exposure. The overall materials performance is governed by a combination of chemical and physical degradation processes occurring in low Earth orbit as established by our past laboratory-based materials performance experiments (see report SAND 2005-6846). Molecular changes are primarily induced via radiative damage, and physical damage from temperature and atomic oxygen exposure is evident as depoling, loss of orientation and surface erosion. The current project extension has allowed us to design and fabricate small experimental units to be exposed to low Earth orbit environments as part of the Materials International Space Station Experiments program. The space exposure of these piezoelectric polymers will verify the observed trends and their degradation pathways, and provide feedback on using piezoelectric polymer films in space. This will be the first time that PVDF-based adaptive polymer films will be operated and exposed to combined atomic oxygen, solar UV and temperature variations in an actual space environment. The experiments are designed to be fully autonomous, involving cyclic application of excitation voltages, sensitive film position sensors and remote data logging. This mission will provide critically needed feedback on the long-term performance and degradation of such materials, and ultimately the feasibility of large adaptive and low weight optical systems utilizing these polymers in space.

Acknowledgements
The authors express their appreciation to Gary Pippin (MISSE coordinator) at Boeing and his various collaborators at other Boeing and NASA groups.

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Nomenclature and Abbreviations

AO = atomic oxygen
CTFE = chlorotrifluoroethylene
d_{33} = piezoelectric strain coefficient in the thickness direction
HFP = hexafluoropropylene
HST = Hubble Space Telescope
ISS = International Space Station
LDEF = Long Duration Exposure Facility
LEO = low Earth orbit
MISSE = Materials International Space Station Experiment
PVDF = poly(vinylidene fluoride)
P_r = remanent polarization
SEM = scanning electron microscopy
TrFE = trifluoroethylene
T_c = Curie transition
T_g = glass transition
T_m = melting temperature
VUV = vacuum ultraviolet

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1. Introduction

1.1 Project purpose

This report summarizes a $30K LDRD project extension of the prior financial year LDRD "Characterization, Performance and Optimization of PVDF as a Piezoelectric Film for Advanced Space Mirror Concepts". The current emphasis was on building and finalizing three experimental units to be deployed on the International Space Station as part of the upcoming MISSE-6 (Materials International Space Station Experiment). This experiment will allow exposing various piezoelectric polymer films to an actual space environment of atomic oxygen, vacuum UV and thermal cycling with synergistic materials degradation to be expected. The materials evaluated are various lightweight, thin piezoelectric polymer films based on polyvinylidene fluoride (PVDF) and its copolymers, which deform in response to the application of electrical fields. The space exposure experiment involving multiple passive and active samples, with remote application of excitation voltage and data logging of the materials responses will provide an avenue to validate the observed degradation and performance of these materials in the laboratory environment (see report SAND2005-6846). The accelerated degradation and performance decrease observed in laboratory experiments has allowed the development of a fundamental understanding of the degradation pathways and a pre-selection of suitable materials. The actual space exposure will verify these trends and provide feedback on synergistic degradation that is difficult to simulate in more limited lab experiements. This combination of experiments will assess the feasibility of using piezoelectric polymer films as the materials for advanced low weight adaptive space mirrors.

1.2 Background

Major steps in space exploration and utilization can only be achieved via far reaching enabling technologies that employ radically new approaches and engineering solutions to complex problems [1]. For many countries space access and utilization is intrinsically linked to national interests and security considerations resulting in the application of leading edge technologies and long-term strategic research directions. The development of more advanced materials is often one of the driving forces behind innovation in this area. An example is the development and potential use of responsive, smart or adaptive materials based on polymers in space applications representing a critical enabling technology for the 21st century.

Large diameter PVDF film-based adaptive optics have been identified as a promising alternative to overcome weight limitations in high-resolution spaced-based telescope systems similar to the James Web Space Telescope. The challenge in designing novel large-aperture adaptive optics systems providing improved sensitivity and ground resolution for future space-based remote sensing systems is to identify suitable high performance thin film polymeric materials. The shape control in adaptive optics utilizes the responsiveness of piezoelectric polymers such as polyvinylidene fluoride (PVDF) to directed charge deposition. Besides developing charge deposition control feedback loops and addressing engineering design issues [2], a detailed understanding of PVDF material changes and performance when exposed to vacuum UV irradiation, thermal cycling, atomic oxygen and other environmental factors in low Earth orbit space environments is absolutely critical. Materials performance depends on primary polymer properties, copolymer type, film processing, molecular orientation, morphology and the applied poling technologies (piezoelectric optimization), as well as relative sensitivities to the various conditions in the space environment. There is no commercial optimized material available for such an application. The MISSE experiment is the final step of a comprehensive evaluation of the important features of various PVDF-based copolymers. It will establish how the accelerated degradation of these polymers and hence piezoelectric performance limitations depend on molecular structure, morphology and synergistic damage accumulation during radiation, temperature and atomic oxygen exposures. Achieving this goal of material qualification and lifetime prediction has been previously addressed by a three-year effort with a multidisciplinary team combining Sandia's expertise in polymer materials characterization and degradation with the satellite group's adaptive optics research experience. The prior LDRD polymer aging and performance research effort as well as the final MISSE experimental requirements were primarily carried out within Dept. 1821.

Piezoelectric polymer films based on PVDF will respond to charge deposition and represent an attractive group of materials for adaptive optics applications. The recent success in wireless shape control methods has demonstrated the feasibility of this technology [2]. Any electron gun control approach for charge deposition requires a detailed understanding of the piezoelectric material responses. Space applications also demand consistent, predictable, and reliable performance. While PVDF (as a generic material class covering various copolymers) so far has been identified as the best material for electrical control purposes, it is also well known that fluorinated polymers are the most sensitive polymers to high-energy radiation. Mechanical properties will suffer with various types of radiation (vacuum UV, γ-, X-ray, charged particles) and extreme temperature fluctuations. Experiments carried out on the low Earth orbit (LEO) long-duration exposure facility (LDEF) in the late 1980's [3-5] and NASA's experience with material selection for both satellite and space station applications, as well as performance feedback from the Hubble space telescope (HST) [6-8] have revealed considerable polymer weaknesses in these environments. While the radiation degradation of polymers is an established field [9] there is little information available on the performance of specialized features such as the piezoelectric and/or similar properties of PVDF with respect to their expected changes upon LEO exposure. Understanding such fundamental issues becomes mandatory for the design and deployment of satellite systems utilizing these materials and technology. Traditional polymer aging studies mostly focus on understanding the chemical and bulk physical property changes with the emphasis on degradation mechanism and their relevance to lifetime prediction methods. Based on existing literature, the precise details of piezoelectric properties are not even fully established in terms of their dependence on morphology, poling, and crystalline features. The need to fully understand the piezoelectric performance of these polymers under complex LEO environments is a challenging task that has not been addressed by industry. We have examined the many problems facing the polymer material scientist when dealing with the identification and optimization of suitable materials for these applications, and have demonstrated important polymer property variations and the key issues that relate to performance considerations.

As for any other materials application in space environments, a comprehensive understanding of the LEO conditions leading to PVDF homo and copolymer performance limitations is required. LEO environmental conditions are highly complex and often synergistic, as well as orbit dependent, so that specific conditions are difficult to predict. Probably the first systematic scientific studies on LEO exposure on polymers and composite materials were conducted as part of the LDEF in the 1980's. They revealed unexpected performance limitations of many materials and demonstrated the complex nature of LEO exposure, synergistic degradation pathways, and associated lifetime prediction [3-5]. The synergistic nature of vacuum UV and atomic oxygen exposure for example was subsequently demonstrated [10,11]. Based on such experimental data, guidance on expected vacuum UV, other energetic radiation and atomic oxygen levels has been provided in a range of NASA publications [12-14]. These discuss actual cumulative environments, as well as experiences with materials performance. Many data have been incorporated and made available in the NASA Materials Selector Expert System database [15]. This database contains information collected on polymer performance and observed damage accumulation originating from many different space missions. The database is intended to provide predictive feedback and allows modeling of expected UV doses, atomic oxygen (AO) and other damage parameters under various orbital conditions. However, there are currently no references or data available on anticipated piezoelectric changes or related degradation for PVDF-based polymers in space environments. For the Hubble space telescope in LEO orbit, significant cracking of the outer layer Teflon fluorinated ethylene propylene (FEP) multi-layer insulation was observed during the second servicing mission after 6.8 years in orbit [6,7]. To better understand the failure mechanism and allow for estimated exposure levels through to the mission end-of-life, a full assessment of environmental conditions and various exposure levels was conducted as part of that study [7]. Environmental exposure was primarily seen as a combination of thermal cycling (from -200 °C in the shadow, up to +200 °C in extreme situations), solar UV and X-ray radiation, trapped electron and proton radiation, and exposure to plasma and atomic oxygen. Often it was concluded that individual exposure components alone could not explain the observed failure, putting the emphasis again on complex synergistic environments. It is interesting to note that in this study there was a distinction between direct solar light and atmospherically reflected light for the solar UV exposures and an assessment of total equivalent sun hours for different positions on the spacecraft [7]. Yet, there was no discussion of specific material sensitivities in certain wavelength regions, estimated UV doses required to induce significant changes, vacuum UV degradation pathways and their exposure time dependencies. In general, there seems to be lack of knowledge in the literature on vacuum UV polymer material absorptivities, degradation mechanisms and failure doses. It would appear that one of the key questions in LEO UV exposure, the correlation of total doses and thus total sun hours with material radiation sensitivities and degradative changes, needs further investigation for meaningful LEO life time predictions. This study incorporates some attempts in this direction and as discussed below, expected vacuum UV exposures and material sensitivities are assessed on the basis of highly energetic radiation doses for correlation with screening studies of accelerated γ-irradiation experiments. This study aims to evaluate the full range of available PVDF copolymer materials, determine their respective properties and provide guidance on a multitude of performance criteria, all relevant to final material selection. The schematic diagram below (Fig. 1) demonstrates this complex task of matching a range of available materials and properties with critical performance requirements.

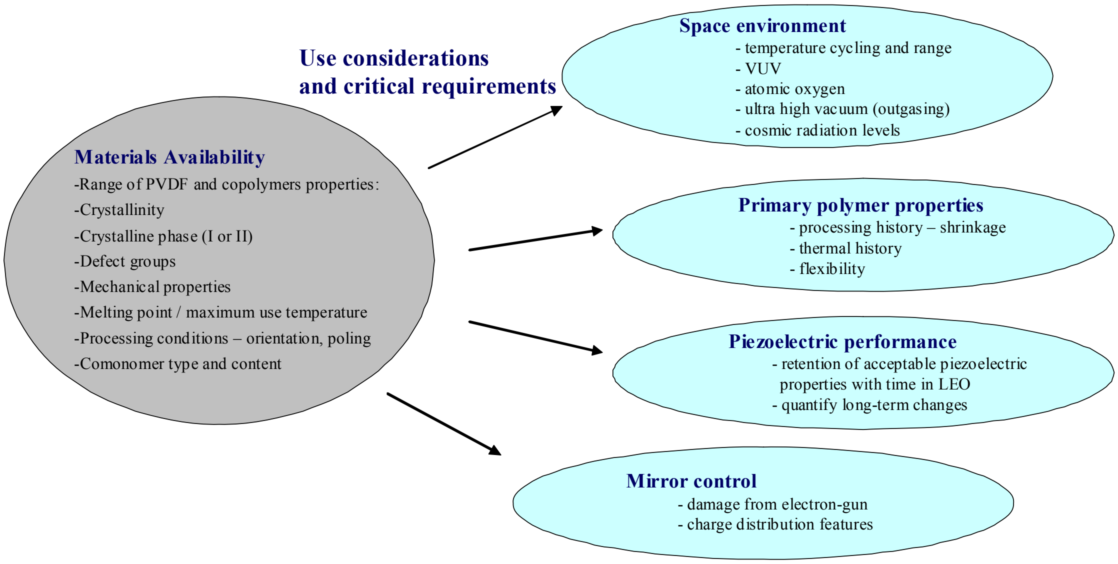
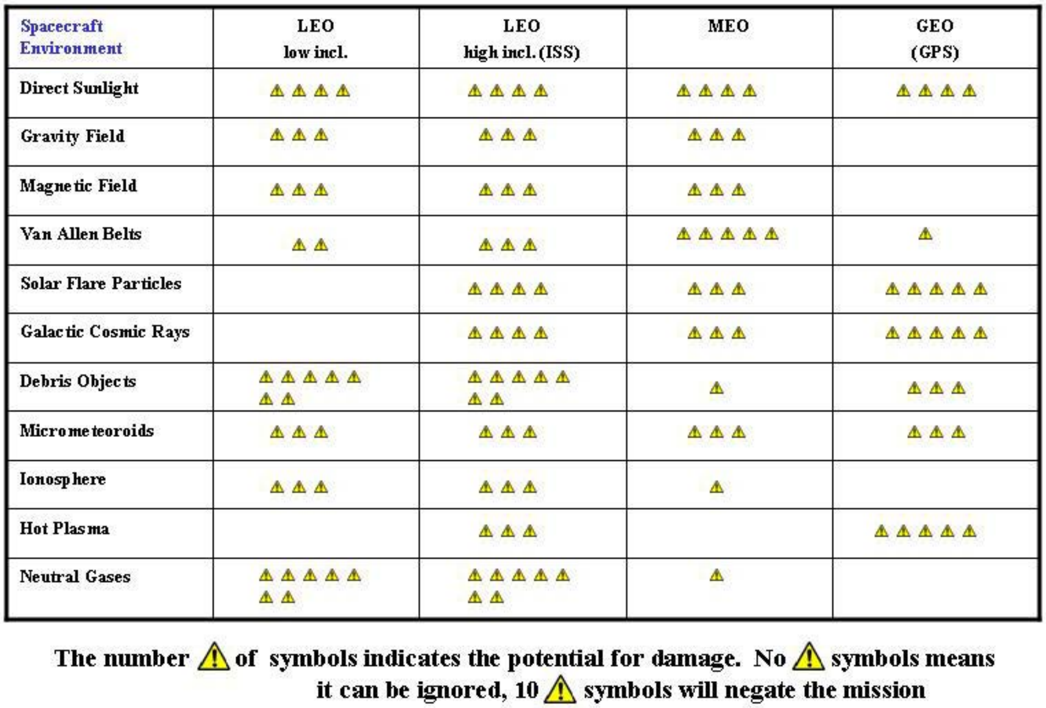


Figure 1. Complex material selection and characterization issues

2. Overview of space environmental conditions

The near-Earth space environment involves a range of highly energetic species, which are potentially damaging to polymeric materials. Many of these species, such as photons from sunlight, particles from solar flares and galactic cosmic rays, originate from the sun and other stars. Others, such as high velocity (relative to the spacecraft) neutral gases, the Van Allen Belts, and the Ionosphere originate from the Earth or interactions between the Earth's upper atmosphere and other energetic species. The concentrations of all of these energetic species vary with altitude and are summarized in terms of importance to the success of a mission in Table 3 for the most common orbits – low Earth orbit (low and high inclination), medium Earth orbit, and geostationary Earth orbit. For the current application we are only concerned with LEO, however, if other orbits are considered in the future then obviously based on the information in Table 1, it will be important to re-evaluate the effects of other particular orbits on the materials. Of the parameters affecting spacecraft in either high or low inclination LEO orbit, the most important to consider are:

Table 1. Environmental effects on spacecraft in LEO, MEO and GEO (adapted from: "Space Environmental Effects on Spacecraft: LEO Materials Selection Guide" E.M. Silverman, NASA Contractor Report 4661 [14])



Spacecraft Environment	LEO low incl.	LEO high incl. (ISS)	MEO	GEO (GPS)
Direct Sunlight	⚠ ⚠ ⚠ ⚠	⚠ ⚠ ⚠ ⚠	⚠ ⚠ ⚠ ⚠	⚠ ⚠ ⚠ ⚠
Gravity Field	⚠ ⚠ ⚠	⚠ ⚠ ⚠	⚠ ⚠ ⚠	
Magnetic Field	⚠ ⚠ ⚠	⚠ ⚠ ⚠	⚠ ⚠ ⚠	
Van Allen Belts	⚠ ⚠	⚠ ⚠ ⚠	⚠ ⚠ ⚠ ⚠ ⚠	⚠
Solar Flare Particles		⚠ ⚠ ⚠ ⚠	⚠ ⚠ ⚠	⚠ ⚠ ⚠ ⚠ ⚠
Galactic Cosmic Rays		⚠ ⚠ ⚠ ⚠	⚠ ⚠ ⚠	⚠ ⚠ ⚠ ⚠ ⚠
Debris Objects	⚠ ⚠ ⚠ ⚠ ⚠ ⚠ ⚠	⚠ ⚠ ⚠ ⚠ ⚠ ⚠ ⚠	⚠	⚠ ⚠ ⚠
Micrometeoroids	⚠ ⚠ ⚠	⚠ ⚠ ⚠	⚠ ⚠ ⚠	⚠ ⚠ ⚠
Ionosphere	⚠ ⚠ ⚠	⚠ ⚠ ⚠	⚠	
Hot Plasma		⚠ ⚠ ⚠		⚠ ⚠ ⚠ ⚠ ⚠
Neutral Gases	⚠ ⚠ ⚠ ⚠ ⚠ ⚠ ⚠	⚠ ⚠ ⚠ ⚠ ⚠ ⚠ ⚠	⚠	

The number ⚠ of symbols indicates the potential for damage. No ⚠ symbols means it can be ignored, 10 ⚠ symbols will negate the mission

Neutral gases. The most abundant and damaging neutral gas in LEO is atomic oxygen formed by photodissociation of the small concentration of molecular oxygen in the upper atmosphere. The flux is approximately 10^{15} atoms/cm^2-s with an orbital speed of 8 km/s, which can cause surface pitting and erosion of polymers. It has repeatedly been shown that exposure of polymers to atomic oxygen causes surface erosion [5,8,11,14,16]. The mechanism, while not fully understood, is believed to be due to oxidation by the highly reactive oxygen atoms followed by volatilization of fragment molecules. When the incident AO is anisotropic (as is the case for orbiting spacecraft) this leads to a highly directional erosion process resulting in patterned surface morphology [17]. Atomic oxygen mainly affects leading edges.

Direct sunlight (vacuum UV). Fluorinated polymers, and particularly PVDF, are excellent materials under terrestrial outdoor exposure conditions. PVDF is in fact the base polymer for many high performance, long-lasting industrial coatings. Terrestrial UV exposure is limited to minimum wavelengths of ~ 285 nm due to protective atmospheric absorption, with the UV-B component (285-325 nm) often regarded as the most damaging for polymer performance. Many fluoropolymers do not absorb above 230-250 nm, which is the reason for their limited environmental UV degradation. Under LEO conditions, however, unprotected polymers are exposed to the full solar spectrum including the highly energetic and damaging vacuum UV components. For example, UV photon energies of 250 nm are equivalent to 478.5 kJ/mol (4.96 eV) and 200 nm to 598.2 kJ/mol (6.2 eV), respectively. Compare this with fluorine-carbon bond energies of 452 kJ/mol (265 nm) for F-CH_3, and 530 kJ/mol (226 nm) for F-C_2F_5. It is obvious that the LEO vacuum UV radiation will be extremely damaging and therefore prediction of degradation levels requires knowledge of UV irradiances. Since the early 1990s there have been two programs to measure solar UV intensities and their dependencies on solar cycles, mostly to provide data for atmospheric modeling. NASA has sponsored the two Solar Ultraviolet Spectral Irradiance Monitor (SUSIM) instruments in these SUSIM programs [18,19] providing data over more than a ten-year period. Fig. 2 shows an example of the direct (90° exposure) solar UV intensities at an average Earth to sun distance of 1.493×10^8 km. Most of the total irradiance below 150 nm is due to the Lyman-α hydrogen line at 121 nm. The integrated irradiance data have been included in Fig. 2 and provide immediate feedback on expected UV energy deposition. Starting from the lowest wavelength up to 200 nm, a total irradiance of 0.1 W/m^2 is expected, up to 227 nm a total flux of 1 W/m^2. Energy deposition in thin polymer films will depend on absorptive and reflective properties and other radiation/material interactions, i.e. energy loss and transfer processes. However, it is well established that polymer films easily absorb UV radiation (UV cut off in absorbance measurements) and that damage is often heterogeneous, i.e. UV exposure often leads to surface cracking and embrittlement due to higher absorbance in the top layers and limited depth penetration as often reported for the weathering of films and coatings.

A simple estimation of the magnitude of UV energy deposition in LEO is accomplished by assuming the ~0.1 W/m^2 (up to 200 nm) irradiance, full energy absorption in a 100 μm thick film, and a one year exposure in a low equatorial orbit. Disregarding orbital latitude or corrections for spacecraft tilt we assume a simplistic orbit of 12 hours shadow and 12 hours of sun illumination where the 12 sun hours equate to the equivalent of ~7.65 hours of vertical sun exposure. Over a one year period the material would thus be exposed to a total of ~1 MJ/m^2 of vacuum UV photons of up to 200 nm. Assuming homogeneous energy absorption within a 1 m^2 of a 100 μm film (density is 1.7 grams/cc for fluorinated PVDF copolymers), which is equivalent to 170 grams of material, equates to 5.9 MJ/kg or 5.9 MGy per year exposure. These are significant radiation dose exposures and of course are dependent on absorption efficiencies. Not knowing real absorbances the expected radiation doses were modeled for different film thicknesses versus % absorbance (see Fig. 3) with even low %-absorbances showing significant radiation doses. These are only guidelines but clearly demonstrate the magnitude of expected radiation exposure. Considering the experimental challenges for using vacuum UV illumination for accelerated degradation experiments it would be beneficial to establish a scientific correlation between highly energetic UV irradiation and γ-irradiation. Both types of radiation are energetic enough to cause indiscriminate chain scission and are expected to display similar polymer radiation chemistry. As discussed below initial experiments to assess the radiation sensitivity of these polymers relied on γ-irradiation.

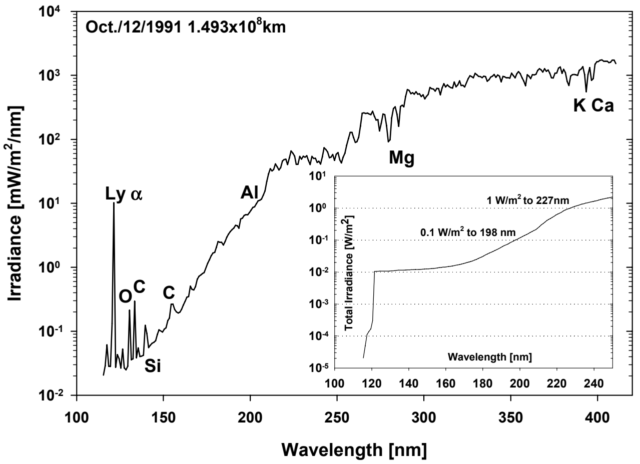


Figure 2. Low Earth orbit SUSIM based UV irradiances [18]

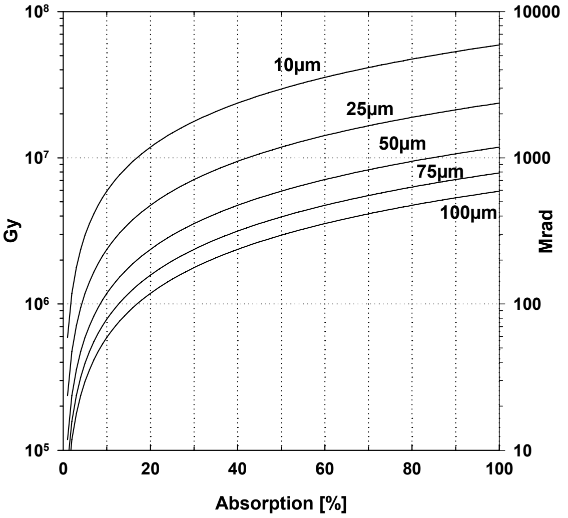


Figure 3. Predicted UV radiation doses for polymer films of different thickness over 1 year LEO exposure at (0.1 W/m^2)

While γ-photons have the potential to result in multiple radiation damage events, energy loss for the UV-photons should be limited to one or two interaction processes due to the much lower UV-photon energy. A better understanding of vacuum UV material degradation sensitivities should be a long-term goal for improved LEO exposure and performance predictions. Likewise, considering the complex LEO radiation environment with various radiation types contributing to material damage, a reasonable approach for material selection would be based on identifying the overall least radiation sensitive material. Screening studies using γ-irradiation for grading of polymer degradation are an excellent avenue for material qualification, since a material found to withstand high doses of γ-irradiation would be expected to also perform well under strong VUV conditions.

Van Allen Belts. The Van Allen Belts consist of trapped protons and electrons of energies in the tens of keV for electrons and MeV for protons. The total doses expected are in the order of only 1 kGy per year on average based on calculations for the FEP on the HST [7]. PVDF and copolymers can easily withstand radiation doses orders of magnitude higher than this so it is not of great concern.

Solar flare particles. Protons and alpha particles from solar flares will largely be shielded by the Earth's magnetic field so that spacecraft in low inclination LEO will be unaffected to any significant degree. In high inclination LEO the dose from protons and alphas particles will be higher due to the 'open' geomagnetic field lines allowing the lower energy protons and ions to impinge on the spacecraft. It is expected that the dose will still be lower than for the protons and electrons in the Van Allen Belts, however if a high inclination mission is planned further investigation would be warranted. X-rays are also linked to solar flares but the doses are less than 1 kGy over 20 years [7].

Galactic cosmic rays (GCR). GCRs consist of alpha particles and electrons and hence have similar behavior to the solar flare particles.

Debris. This is not a materials issue and will not be covered here.

Other issues not included in Table 1, but of concern are temperature and spacecraft charging:

Temperature. The temperature of a surface directly exposed to the conditions of LEO is determined by the incident solar radiation from the sun, reflected solar radiation (albedo) from the Earth, outgoing long wavelength radiation from the Earth and the atmosphere, and a balance of these with the near-absolute zero temperature of space [14]. This balance, in turn, is a function of the ratio of solar absorbance (α_s) to thermal emittance (ε) of the material. Values of α_s and ε will vary immensely depending on the material, surface properties, and its thickness.

Spacecraft charging. Charging is not expected to cause degradation of PVDF, however it may adversely affect the control dynamics of any mirror since it may interfere with the intentional charge deposited from the electrodes. When exposed to the plasma (an electrically neutral ionized gas) present in LEO, a material will become negatively charged due to accumulated electrons stripped from the plasma. If the charge is high enough it may cause unwanted deflection of the bimorph. The extent of the charging and mitigation methods if needed should be taken into consideration during the spacecraft design.

Atomic oxygen exposure: In LEO the high flux of atomic oxygen (AO), (approximately 10^{15} atoms/cm^2-s with an orbital speed of 8 km/s) formed by photo-dissociation of the small concentration of molecular oxygen in the upper atmosphere, causes surface pitting and erosion, with rates of $0.35\text{x}10^{-24}$ cm^3/atom for FEP and $3.0\text{x}10^{-24}$ for Kapton, having been reported [8]. The two commonly used techniques for simulating the atomic oxygen found in LEO are: a) hyperthermal or fast atomic oxygen [20-22], and b) oxygen plasma [11,17]. In our experiments PVDF polymers were exposed to atomic oxygen by an electron cyclotron resonance (ECR) plasma source producing neutral atomic oxygen, as provided by the facility at NASA Glenn [23].

The potential for significant erosion of PVDF polymer films from atomic oxygen was demonstrated in our research paper [23]. There are some methods that have been suggested for reducing the AO erosion yields using coatings or additives. Silica (SiO_2) is extremely resistant to AO erosion. If it is incorporated into a polymer, either as a coating or as part of the bulk material, erosion can be reduced. Coating a polymer with straight SiO_2 as an inorganic glass is not practical since all flexibility would be lost, so instead researchers at NASA Glenn have developed a SiO_x ($1.9 < x < 2.0$) filled PTFE which can be deposited as a film [8]. The method works by using a PTFE and a SiO_2 ion beam target to simultaneously sputter the two components onto the substrate. Compositions up to 16% PTFE by volume have been shown to exhibit high strain-to-failure, high transparency and AO durability. It is possible that such a coating would be suitable for PVDF, however, the thickness and composition of the coating would need to be optimized as to minimize the mechanical clamping effect while maximizing the AO protection. An alternative method for introducing a protective SiO_2 layer can be achieved by the use of nano-sized particles of polyhedral oligomeric silsesquioxanes (POSS) dispersed into PVDF [24-26]. When exposed to AO, the POSS additive will react and form a self passivating, self healing silica layer protecting the underlying polymer. Preliminary experiments in collaboration with Edwards AFB in California have shown that incorporation of POSS into PVDF by blending is possible. Future work would require more detailed investigations on POSS interaction with the polymer and effects on the crystallite structure, Curie temperature, melting point, and piezoelectric properties. It is interesting to note that other workers have incorporated nanoparticles of silica or carbon nanotubes into a PVDF homopolymer and observed formation of the polar β-phase without stretching. If this were also to occur in POSS/PVDF composites it could lead to a novel unstretched version of a piezoelectric PVDF homopolymer with superior properties.

Additional discussion: The space environment can be extremely damaging to polymers. This is no more evident than for the Teflon-FEP used on the Hubble Space Telescope (HST) which is in LEO at an altitude of approximately 600 km. FEP is similar in structure to PVDF; it is a linear polymer containing CF_2 units, however unlike PVDF, it does not contain any hydrogen atoms which make it less radiation resistant than PVDF. FEP makes up the outer layer of the thermal insulation blankets on the HST and is therefore directly exposed to the space environment on both the sun facing and non-sun facing sides.

Servicing missions after 3.6 and 6.8 years found the thermal blankets were cracked due to severe degradation as observed by the servicing astronauts and from retrieval of token samples which were evaluated in ground tests [27,28]. A taskforce was formed to investigate why FEP was degrading in LEO. The work done represents perhaps the most comprehensive body of work on effects of the LEO environment on FEP and much of what was concluded can be applied to PVDF and copolymers [6,7,10,27-30].

The main environmental factors determined to have caused the degradation of FEP were VUV, X-rays from solar flares, electron and proton radiation, and thermal cycling. The dose of X-rays, electrons and protons was in the hundreds of Gy range, which is relatively low. The concentration of atomic oxygen at 600 km altitude is not high enough to cause erosion problems. Unfortunately, after exposing FEP to thermal cycling and synchrotron-generated X-ray and VUV radiation equivalent to the same exposure estimated for the FEP on the HST in ground tests, the amount of damage was far less than that observed in space [6]. In fact, to achieve the same amount of damage in ground tests, it took an X-ray dose equivalent to 30,000 years in space. While exposures to the types of high energy radiation used in ground testing did cause damage to the FEP, clearly the effects are not well understood [6].

Part of the problem with the FEP used on the HST is that it is intrinsically a very vulnerable polymer to use in radiative space environments, in fact it is one of the more radiation sensitive polymers, even under inert conditions [31]. Fortunately PVDF is much less sensitive to radiation and it is expected that X-rays, electrons and protons in the 0.01-0.1 kGy range will have much less impact compared with what was observed for FEP. Rather than trying to account for every type of radiation present in LEO, we have relied on the fact that radiation damage from photons or electrons is indiscriminant of the type of radiation used, so long as the energy is sufficient enough to cause bond breakage. By exposing PVDF and other candidate materials to γ-radiation we can obtain feedback on the general *radiation resistance* in terms of how it affects mechanical and piezoelectric properties. Such an approach is far more practical than considering every type of radiation found in space individually. We believe VUV, atomic oxygen and thermal extremes will play the greatest role in the performance of piezoelectric PVDF in LEO.

3. Materials International Space Station Experiment (MISSE-6)

Until as recently as the 1980s very little was known about LEO environmental effects on polymeric materials. A significant step forward in the understanding of materials-space interactions and materials performance was based on retrieval and testing of materials from the Long Duration Exposure Facility (LDEF) Experiment which spent 69 months orbiting the Earth between 1984 and 1990. The LDEF experiment was a 14-sided passive satellite equipped with almost every type of spacecraft surface or material that was in use in the 1980s, or envisaged for potential use in the foreseeable future [3,5,11]. The LDEF mission demonstrated that all polymeric materials are greatly affected by the LEO environment with sometimes unexpected degradation occurring, that pre-LDEF knowledge of space environmental effects on materials had major flaws, and that synergistic effects of LEO environmental conditions must be considered to predict materials performance [3,5,11].

The LDEF mission spawned a number of subsequent smaller missions testing materials in the space environment aboard the Shuttle orbiter, Russian spacecrafts, and the International Space Station (ISS). Of these, only the Boeing/NASA experiments aboard the ISS (dubbed MISSE for Materials ISS Experiment) had any continuity with MISSE-1 through MISSE-5 having been launched, and MISSE-6 due for launch in late 2007 [32]. The MISSE program is designed to allow participation from government, academia and industry researchers, who require space testing of individual materials but may not have the multimillion-dollar budgets to host a launch. The participants in MISSE-6 are listed in Fig. 4.

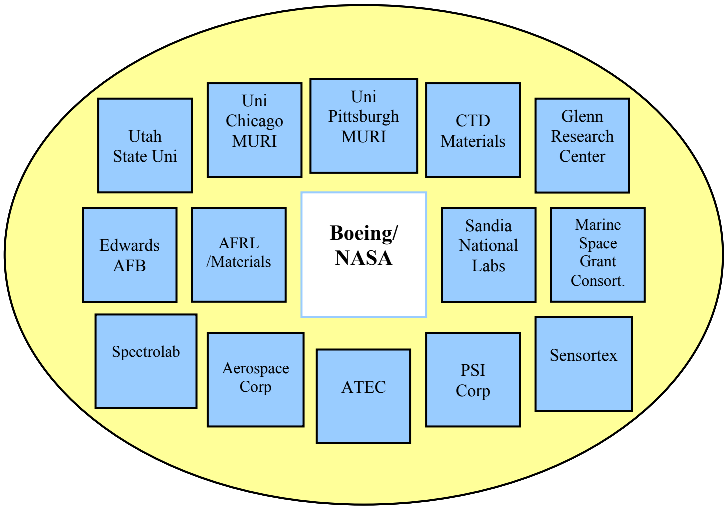


Figure 4. Participants in MISSE-6

Any use of novel responsive polymer components in space applications requires ground testing and ultimately space qualification to accommodate the complex LEO environment and understand materials degradation. SNL has been invited to contribute vinylidene fluoride piezoelectric samples to MISSE-6 offering an excellent opportunity to integrate the first flight experiment of piezoelectric polymers in LEO for space qualification. Since the materials are responsive there is also the opportunity to conduct active experiments, collect real-time data and evaluate the actual performance of these materials. This will be the first time that an active remote experiment has been part of the MISSE project. Both active and passive experiments will be flown allowing for a range of experiments and materials to be tested over the course of the exposure (estimated at 6-8 months, depending on the Shuttle flight program).

The MISSE experiments use a PEC (Passive Experiment Container) which is essentially a simple suitcase which houses the samples. The PEC is launched as a closed container where the samples are located on the inside, and is then attached to the ISS during a spacewalk (Fig. 5) and opened fully inside-out to expose the samples. Depending on which side of the PEC the samples are located, they will either receive primarily vacuum UV (VUV) radiation, or both VUV and atomic oxygen (AO) exposure. SNL has been allocated 6 x 6" on the VUV side and 6 x 4" on the AO/VUV side in which the passive and active experiments need to be located.

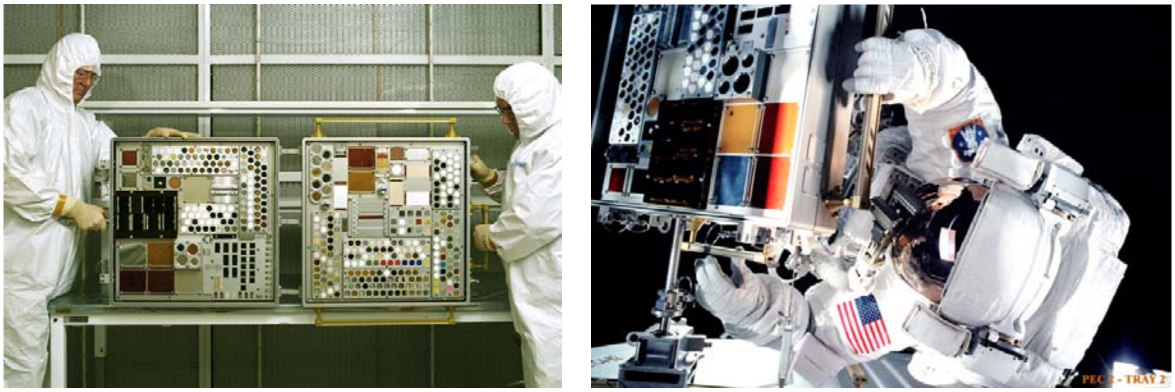


Figure 5. A MISSE PEC partially open **(left)**; installation of a PEC outside the ISS **(right)**

4. MISSE-6 Sample details

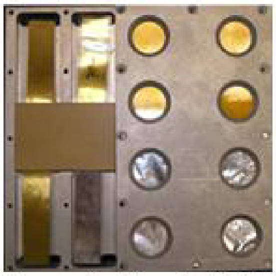
4.1 Overview

Three experimental units each with different experimental focus were designed, fabricated and delivered to NASA Langley. The first unit contains four passive and four active films samples to be exposed to combined atomic oxygen and vacuum UV. The second unit contains 11 passive and 4 active samples to be exposed only to vacuum UV. The third unit has two passive samples with different thicknesses of protective aluminum layers to be exposed to atomic oxygen and vacuum UV. All passive samples will be characterized, both in terms of chemical and physical properties, before and after the mission to determine the effects of the space environmental exposure. Thin foil-type thermocouples will be attached underneath the samples to measure actual temperatures experienced. The active experiments were designed with the aim of obtaining data on the degradation of in-situ piezoelectric operational performance of these materials with exposure time. Such piezoelectric data are required for lifetime and performance predictions of these materials in LEO conditions. The active samples are applied in the form of thin film bimorphs designed to move (flex) up and down with applied voltage at a frequency of once per 48 hrs (24 hours up and 24 hrs down). Underneath the tip of each bimorph (i.e. at the point of maximum deflection) is a photodiode sensor measuring the amount of reflected light from the bimorph (reference beam intensity supplied by the photodiode assembly), which is calibrated to accurately determine the relative bimorph position. The changes in the bimorph position (i.e how much it will flex up or down with applied actuating voltage) over time are used to determine changes in the piezoelectric responsiveness as a function of LEO exposure. Measurements of the bimorph position and temperature (simultaneously logged) will be made every 30 minutes, approximately three times every orbit, so that over time data will be available over the entire temperature cycling range (orbit dependent solar position). Various data loggers are used to measure the output from the photodiodes (proportional to bimorph position) and selective temperature locations. The project and experiment has been described in the Sandia lab news (58(16) August 4 2006, "Sandia experimental package of piezoelectric films to be part of NASA space station experiment") and full details for our package have been provided to the NASA launch hazards assessment team in Sept. 2006.

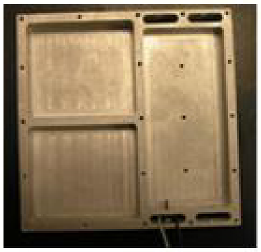
4.2 Detailed description

The passive experiments will use mounting fixtures similar to those used on previous MISSE missions to expose 30 µm and 100 µm films of the PVDF homopolymer and the 80:20 TrFE copolymer to both VUV and combined AO/VUV. Samples will have either no coating, or a gold or aluminum coating to examine the effects of metallization and may be either single films or multilayered bimporphs. Thin contact foil-type thermocouples will be used to measure the temperatures of the films. On return to Earth, the passive samples will be fully characterized to determine the effects of LEO.

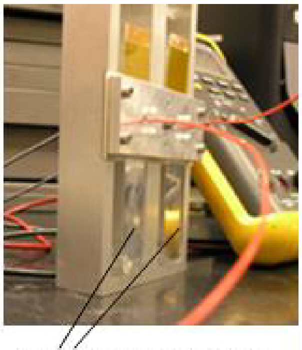
The active experiments were designed so that the performance of bimorphs made from piezoelectric PVDF or a TrFE copolymer mimicking small rectangular sections of a thin-film telescope mirror can be monitored in an actual LEO environment. A design was required that would allow for actuation of the bimorphs with relatively low voltage to produce a deflection large enough for detection with very simple and robust sensors. The chosen design relies on the bimorphs mounted at one end in a counter-lever configuration to give maximum deflection for a low actuation voltage. Under the tip of each bimorph is a LED/photodiode sensor, which can accurately measure a distance to the bimorph based on reflected IR light, with the analog sensor output being recorded using a data logger. The changes in the bimorph position (i.e. how much it will flex up or down with applied actuating voltage) over time will be used to determine relative changes in the piezoelectric responsiveness with LEO exposure. By also recording the temperature from the passive samples it will be possible to correlate the deflection properties with temperature conditions. The advantages of using the LED/photodiodes as opposed to a laser-type position sensor are that they have a larger temperature operating range, and are very robust and lightweight. The data loggers used will be NASA-qualified Veriteq-brand loggers designed for temperature and analog voltage input. The capacity of the data-loggers is limited to 70K 12-bit samples meaning they are not suitable for continuous position logging over the 6-9 months of the experiment. To obtain as much useful data as possible, measurements of the bimorph position and temperature (from the passive samples) will be made simultaneously three times every orbit plus 2 minutes, with the actuation voltage reversed every 24 hours, so that over time data will be available over the entire temperature cycling range (orbit dependent solar position). Four active bimorph experiments will be located on both the VUV and AO/VUV sides (Fig. 6). The materials for testing will be the PVDF homopolymer and the TrFE copolymer in various bimorph configurations as discussed later.



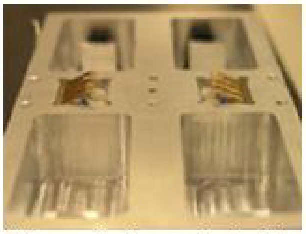
Four active bimorphs (left) and eight passive samples (right) in the fixture



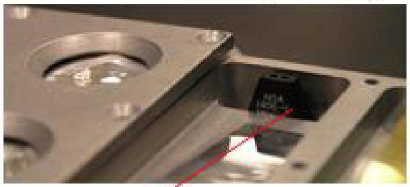
Bottom of the fixture where electronics for actuation control and data logging will be housed



Bimorphs in an aluminum fixture undergoing testing



A fixture showing spring loaded electrodes before bimorph installation



Photodiode position sensor fitted into fixture which will monitor the movement of the piezoelectric films

Figure 6. Photographs of the fixture housing active and passive samples for integration into the MISSE-6 base plate

Other than a power feed from the ISS, the experiments need to be self-sufficient. The sensors are regulated by components that are part of the data acquisition and control printed circuit board that was designed specifically to fit the bimorph mounting case and integrate all electronic features into a single unit. It consists of resistors to provide bias voltages and fuses to protect the sensors and external power supply source. A programmable (non-volatile memory) IC processor PIC 12C671 and 2 driver transistors provide the 24 hour clock pulse that will reverse the 100 volt bimorph excitation voltage via a miniature latching relay. All of these components are very low power consumption and are fuse protected as well. The PC board has a 15 pin D connector that provides the connections to the external 5 volt and 100 volt power supplies and four channels of analog voltage outputs (proportional to bimorph motion) to the external data loggers. The PC board is located inside the bimorph mounting unit where it will be shielded from direct solar irradiation, and to keep the wiring to the optical sensors and bimorph contacts as simple and compact as possible.

The electronics for driving and sensing the bimorphs are expected to receive a deeply penetrating radiation dose on the order of 50 krad (0.5 kGy) in LEO. This dose is far too low to cause any bulk material damage, however, it may cause lattice displacement and other ionization effects, which can temporarily or permanently damage the electronics. The Veriteq data-loggers recently retrieved from MISSE-1 and -2 were found to be fully functional with no evidence of any data corruption, which is encouraging considering that they were not radiation hardened. For qualification purposes an optical sensor was exposed to 1 kGy (twice of what is expected in LEO) of γ-radiation and no negative effects on performance were observed, likewise we anticipate that when the PC board circuitry is exposed to radiation during ground testing it will remain operational.

The sensors work by measuring reflected light from an infrared LED adjacent to the photodiode and as such, are sensitive to stray light. In laboratory tests we found that a 'rolling' baseline was created from the stray light from an infrared lamp switched on and off at regular intervals to simulate passing in and out of the Earth's shadow. By subtracting the baseline it was possible to isolate the output from the sensor relating to the bimorph position. For the MISSE-6 active experiments it is anticipated that some stray light will impinge on the sensor. It should be possible to correct for these variations providing they are not too intense that it causes the sensor to go off-scale. To minimize any stray sunlight effects the sensors are located in the shadow of the bimorph with a window (slightly smaller than the bimorph) covering the sides of the bimorph. This window will reduce the exposure of the bimorph sides to the space environment, but likely will not completely eliminate any complications. In addition to the window, the trough below the bimorphs are anodized resulting in a reduction of reflected light from the fixture onto the sensor.

4.3 Samples on VUV side only (6"x6" unit)

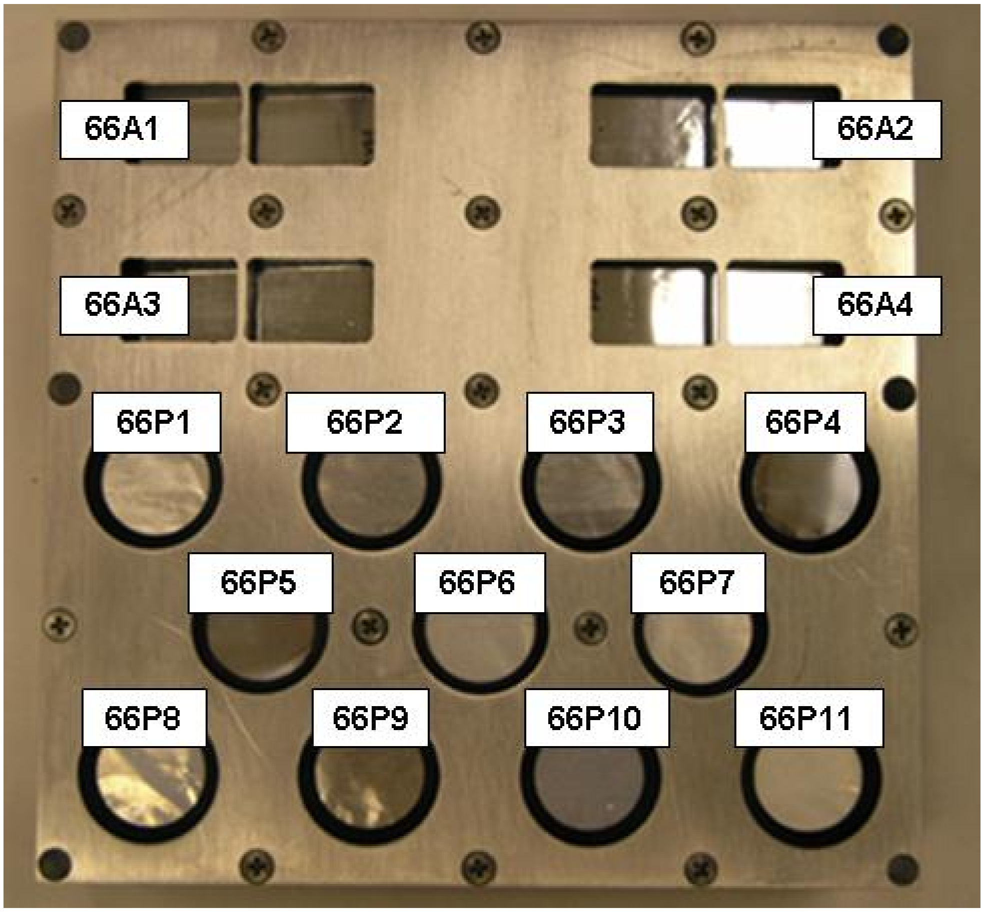


Figure 7. Samples positions on VUV side

Sample details (active and passive):
66A1 = MSI 1-1003352 PVDF bimorph #5 in lab book, 166.426 mg.
66A2 = Ktech TrFE copolymer purchased Nov03 bimorph #9 in lab book 157.450 mg.
66A3 = Ktech TrFE copolymer purchased Feb05 bimorph #? in lab book 140.644 mg.
66A4 = MSI PVDF bimorph #3 in lab book 167.684 mg.
*all electrodes on active samples are aluminum, unless stated otherwise.

66P1 = 80:20 P(VDF-TrFE) film [acetone cast 12/2005], NON-piezoelectric 140.651mg, 85µm.
66P2 = 50:50 VF2-TrFE film [cast in acetone 12/2005] NON-piezoelectric 75.784mg, 63µm.
66P3 = MSI homo 1-1003352, 2 layers: top- 52.462mg, 33µm; bottom- 42.858mg, 32µm.
66P4 = MSI homo 1-1003352 w/600Å Al- 38.291mg, 35µm.
66P5 = MSI homo 1-1003352 with 2600Å Al- 35.278 mg, 33µm.
66P6 = KTECH TrFE 30um purchased Nov03- 28.855mg, 31µm.
66P7 = KTECH TrFE 30um purchased Nov03- 23.844mg, 31µm.
66P8 = KTECH TrFE 30um purchased Feb05, 2 layers: top- 27.751mg, 26µm ;bottom- 21.198mg, 26µm.
66P9 = γ-irradiated MSI homo 1-1003352 [499.4kGy (CaF2)]- 30.307mg, 38µm.
66P10 = KTECH TrFE 30um purchased Feb05- 29.724mg, 26µm.
66P11 = KTECH TrFE 100um purchased Feb05- 79.484mg, 102µm.
*for passive samples, all were placed "shiny side" up when there was a difference in reflectivity between the two sides (unless the sample was metal plated, then the plated side was placed up); an aluminum foil backing was placed under all passive samples, to prevent a possible temperature increase in the sample holder behind translucent samples (black back may absorb transmitted radiation and heat up).

4.4 Samples on VUV plus AO side (4"x6" unit)

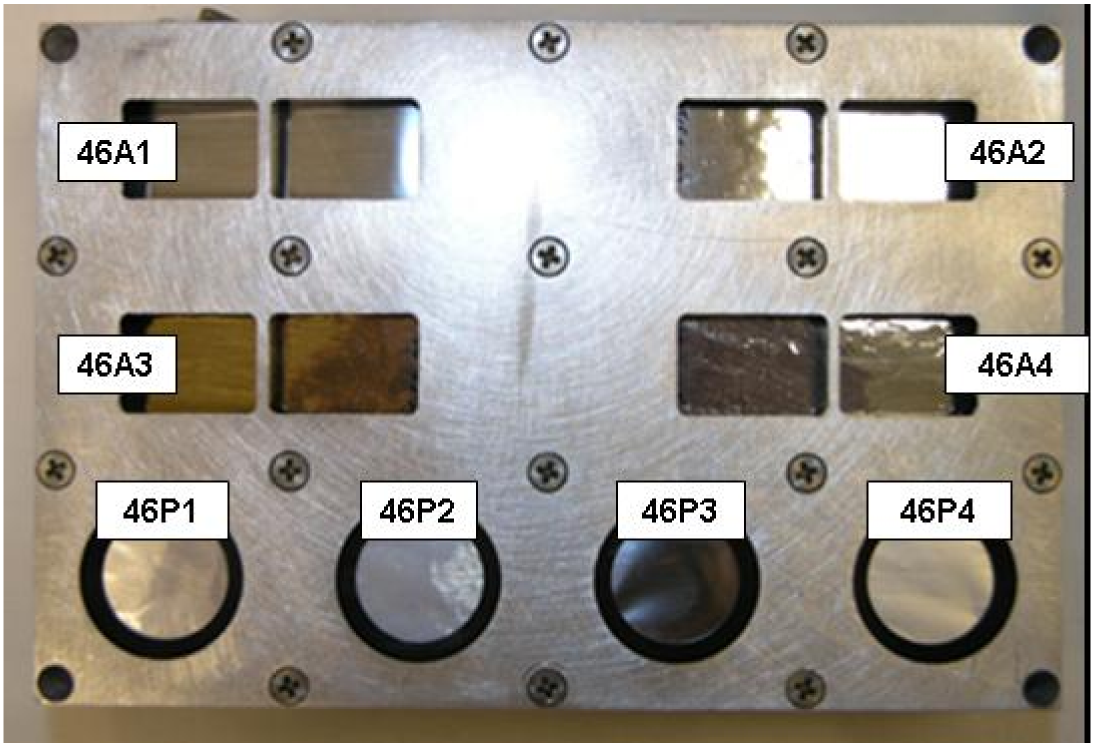


Figure 8. Samples positions on VUV plus AO side

Sample details (active and passive):
46A1 = MSI 1-1003352 PVDF bimorph #4 in lab book- 175.101mg.
46A2 = Ktech TrFE copolymer purchased Nov03 bimorph #8 in lab book- 161.416mg.
46A3 = Ktech TrFE copolymer purchased Nov03 bimorph #12 in lab book, Au electrode- 154.950mg.
46A4 =Ktech TrFE copolymer purchased Feb05 bimorph #13 in lab book- 133.913mg.

46P1 = MSI homo 1-1003352 2 layers; top-52.239mg 32µm, bottom-44.836mg 31µm.
46P2 = KTECH TrFE 30um purchased Feb05, 2 layers: top-34.056mg 22µm, bottom-28.693mg 22µm.
46P3 = MSI homo 1-1003352 w/600Å Al-43.199mg 32µm.
46P4= KTECH TrFE 30um purchased Nov03- 33.302mg 27µm.

4.5 Samples on VUV plus AO side (1 3/4”x3.5” passive unit)

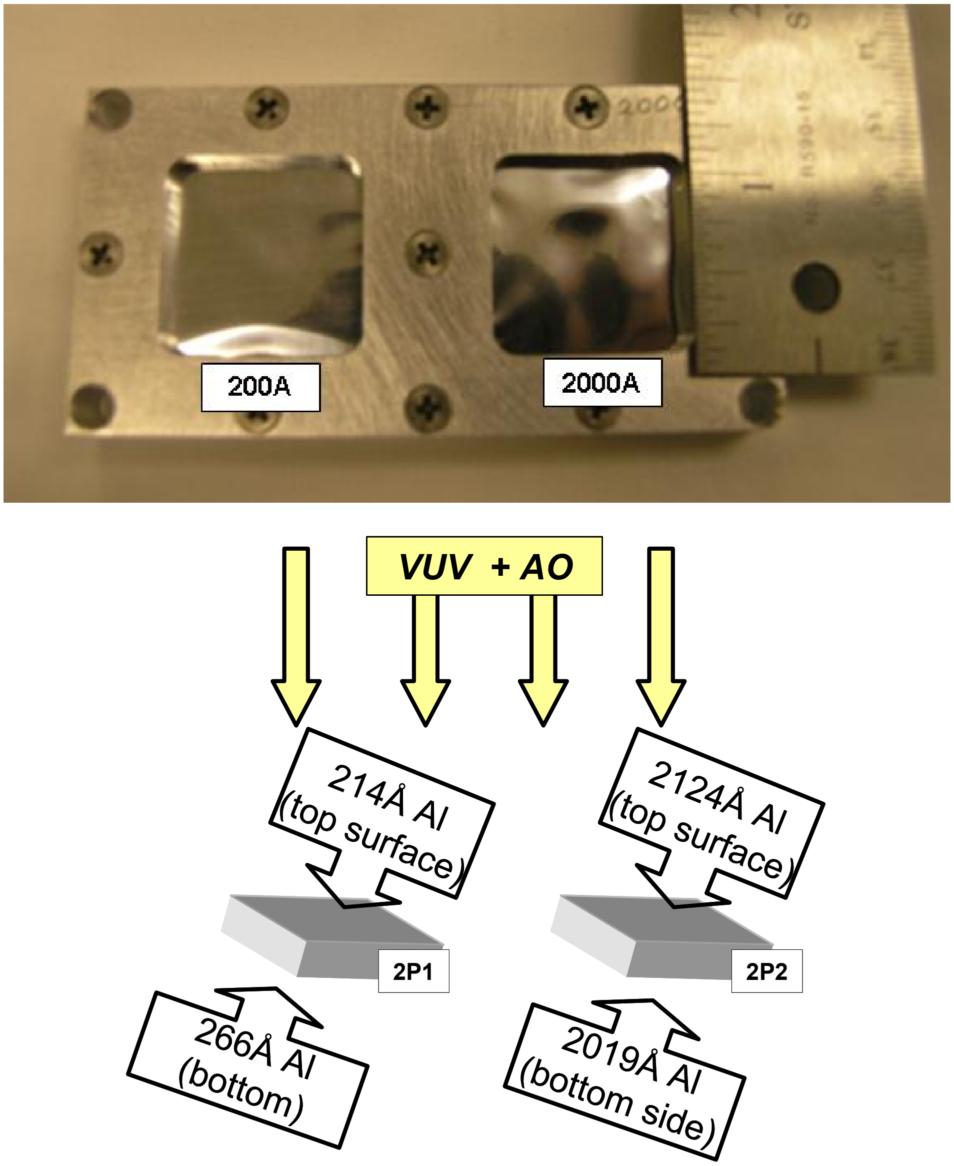


Figure 9. Samples details on small unit VUV plus AO side

Sample details:

Samples are cut from the MSI homopolymer 1-003352.
The aluminum coating on the samples is not exactly 200 or 2000 angstroms; the intent was to expose the side having a value closest to the target value, however a blemish on the 2000 Å film (fingerprint?) forced us to use the other side.
Actual measurements: 200A film- exposure side 214Å Al, bottom side 266 Å Al: 2000 Å film- exposure side 2124 Å Al, bottom side 2019 Å Al.

5. Details of power and data connectors

5.1 VUV side only (6”x6” unit)

Data logger 1, SP4000-411, 4 channel 10VDC

Data:	9 pin male connector; white wires		
Pin # on 9 pin	Sample description	Data logger channel	Via 15 Pin connector: pin #
1	66A1(B1) = MSI 1-1003352 PVDF bimorph #5 in lab book, 166.426 mg	1	1
2	66A3(B2) = Ktech TrFE copolymer purchased Feb05 bimorph #? in lab book 140.644 mg	2	2
3	GROUND	-	10
4	66A4(B3) = MSI PVDF bimorph #3 in lab book 167.684 mg	3	3
5	66A2(B4) = Ktech TrFE copolymer purchased Nov03 bimorph #9 in lab book 157.450 mg	4	4
6	no connection	-	
7	no connection	-	
8	no connection	-	
9	no connection	-	

Power

Power:	9 pin female connector; colored wires	via 15: pin #
Pin # on 9 pin		
1	no connection	
2	+5V	9
3	+5V GROUND	10
4	no connection	
5	no connection	
6	no connection	
7	no connection	
8	+100V	15
9	+100V GROUND	8

5.2 VUV plus AO side (4"x6" unit)

Data logger 2, SP4000-411, 4 channel 10VDC

Data:	**9 pin male connector; white wires**		
Pin # on 9 pin	**Sample description**	**Data logger channel**	**Via 15 Pin connector: pin #**
1	46A1(B1) = MSI 1-1003352 PVDF bimorph #4 in lab book- 175.101mg	1	1
2	46A3(B2) = Ktech TrFE copolymer purchased Nov03 bimorph #12 in lab book, Au electrode-154.950mg	2	2
3	GROUND	-	10
4	46A4(B3) = Ktech TrFE copolymer purchased Feb05 bimorph #13 in lab book- 133.913mg	3	3
5	46A2(B4) = Ktech TrFE copolymer purchased Nov03 bimorph #8 in lab book- 161.416mg	4	4
6	no connection	-	
7	no connection	-	
8	no connection	-	
9	no connection	-	

Power

Power:	**9 pin female connector; colored wires**	**via 15: pin #**
Pin # on 9 pin		
1	no connection	
2	+5V	9
3	+5V GROUND	10
4	no connection	
5	no connection	
6	no connection	
7	no connection	
8	+100V	15
9	+100V GROUND	8

Data and power for each fixture: 15 pin connector wiring per unit; input to 15pin is from 2 9-pin connectors

Pin # on 15pin	Source
1	White pin 1 (66A1/46A1 bimorph data to data logger channel 1)
2	White pin 2 (66A3/46A3 bimorph data to data logger channel 2)
3	White pin 4 (66A4/46A4 bimorph data to data logger channel 3)
4	White pin 5 (66A2/46A2 bimorph data to data logger channel 4)
5	NC
6	NC
7	NC
8	Colored pin 9 (100V) GROUND
9	Colored pin 2 (+5V)
10	White pin 3/Colored pin 3 (5V common) GROUND
11	NC
12	NC
13	NC
14	NC
15	Colored pin 8 (+100V)

6. NASA hazards analysis information

Details of MISSE-6 sample fixtures from Sandia National Laboratories (SNL): Summary for Hazard Analysis provided Sept. 2006.

There are 3 fixtures total: unit 1 being a 6x6" with 4 active and 11 passive samples for the VUV only side, unit 2 being a 4x6" with both 4 active and 4 passive samples for the AO+VUV side, and unit 3 being a 2x3in with 2 passive samples only for the AO+VUV side (no data or T logging required for this unit).

1) Aim of experiments:
Evaluate AO and VUV effects on a range of piezoelectric PVDF based polymers. Passive experiments will simply expose film surfaces. Active experiments will monitor piezoelectric responsiveness of bimorph film samples. Optical displacement sensors monitor deflection (up and down film position at sensor) at 90min intervals as piezoelectric bimorphs are activated via application of +/-100V, switching polarity every 24h.

2) Experiment drawings: See attached slides in the original powerpoint document provided.

3) Materials list: See attached slides in the original powerpoint document provided.

4) Description of any functional tests and assembly verification procedure:
Remove cover plates and connect data loggers, reset sampling memory during launch preparations. Active experiments will self start once 5V and 100V are connected during assembly in space. Make sure temperature is monitored at two locations for each large unit (under active and passive samples) and will activate when data logging commences.

5) Data logger rate (needs 2 loggers SP4000-411, each 4 channel 10VDC):
Logger #1 will be assigned to the 6x6in fixture- logger #2 will be assigned to the 4x6in fixture. Logger memory should be completely empty when loggers are connected to fixtures and needs to be reset as part of the launch preparations (a few days of lost memory is fine). Data sampling needs to be set to intervals of **30 min** and should be set to **STOP after logger is full (do NOT overwrite).** The range of input for channels 1,2,4 and 5 on the loggers is 0 to +5V. Maximum data points per channel is 17600. **Sampling rate = every 30 minutes** = ~365 days capacity on 4 channels (~48 measurements per day) which covers 8-9 month in orbit plus up to two month prior to launch, or limited mission extension reserve. **Important:Temperature needs to be logged simultaneously when reading the data channels**, ie. equal time zero and also 30 min intervals. Each of the large units requires two T sensors (one under active and one under the passive samples).

6) Launch weights:
(weight of fixture in "launch configuration"= fixture plus wires (for 4x6 and 6x6in) minus protective cover)
6x6in: 869.6g **4x6in: 636.1g** **2x3in: 89.89g**

7. Summary and conclusions

Our past laboratory-based materials performance experiments have established the major chemical and physical degradation pathways of PVDF–based polymers. The current project will allow for actual space exposure of these piezoelectric polymers and verify the observed trends. MISSE-6, the Materials International Space Station Experiment is a joint effort between Boeing, NASA and various materials research groups. It represents an excellent and cost-effective opportunity to conduct performance evaluations under space LEO environments for a range of PVDF–based materials. This will be the first time that PVDF-based adaptive polymer films will be remotely operated and exposed to combined atomic oxygen, solar UV and temperature variations in an actual space environment. The experiments are designed to be fully autonomous, involving cyclic application of excitation voltages, sensitive film position sensors and remote data logging. The experiment will provide critical data for the long-term performance and qualification of selected polymers and multi-layer components utilizing these materials, and ultimately the feasibility of advanced low weight adaptive optical systems utilizing piezoelectric polymer films in space. We expect that as long as upper temperatures are limited to less than 110°C and film thicknesses can accommodate some expected losses due to AO erosion, sufficient useful piezoelectric properties should remain and allow for remote actuation of bimorphs manufactured from these materials. MISSE-6 is expected to be launched in late 2007; the exposed materials and associated performance data should be available the following year.

8. Published papers and conference presentations (related to this work)

Further information and details on the experiments conducted as part of this project can be obtained in the open literature. All results and studies were summarized and published as unlimited release information.

8.1 Publications

1) **Sandia experimental package of piezoelectric films to be part of NASA space station experiment,** Sandia Labnews release 58(16) August 4 2006

2) **Characterization, Performance and Optimization of PVDF as a Piezoelectric Film for Advanced Space Mirror Concepts,** Dargaville, T. R., Celina, M. C., Elliott, J. M., Chaplya, P. M., Jones, G. D., Mowery, D. M., Assink, R. A., Clough, R. L., Martin, J. W., SAND report 2005-6846

3) **Piezoelectric PVDF materials performance and operation limits in space environments,** Celina, M. C., Dargaville, T. R., Chaplya, P. M., Clough, R. L., in *Materials for Space Applications,* edited by M. Chipara, D. L. Edwards, R. S. Benson, S. Phillips, *Material Research Society Symposium Proceedings.* **851** (2005) 449-460.

4) **Evaluation of piezoelectric PVDF polymers for use in space environments. Part I: Temperature limitations,** Dargaville, T. R., Celina, M., Chaplya, P. M., *Journal of Polymer Science, Part B Polymer Physics*, **43(11)** (2005) 1310-1320.

5) **Evaluation of piezoelectric PVDF polymers for use in space environments. Part II: Effect of atomic oxygen and vacuum UV,** Dargaville, T. R., Celina, M., Clough, R. L., Banks, B. A., *Journal of Polymer Science, Part B Polymer Physics*, **43(17)** (2005) 2503-2513.

6) **Selection and optimization of piezoelectric polyvinylidene fluoride polymers for adaptive optics in space environments,** Celina, M. C., Dargaville, T. R., Assink, R. A., Martin, J. W., *High Performance Polymers,* 2005, **17** (2005) 575-592.

7) **Evaluation of vinylidene fluoride polymers for use in space environments: Comparison of radiation sensitivities,** Dargaville, T. R., Celina, M., Clough, R. L., *Radiation Physics and Chemistry,* **75** (2006) 432-442.

8) **Evaluation of piezoelectric PVDF polymers for use in space environments. Part III: Comparison of the effects of vacuum UV and γ-radiation**, Dargaville T. R., Elliott J. M., Celina M., J*ournal of Polymer Science, Part B Polymer Physics*, **44** (2006) 3253-3264.

9) **Determining the crystallinity of polyvinylidene fluoride and copolymers**, Dargaville, T. R., Mowery, D. M., Assink, R. A., Tissot, R. G., Celina, M., *in preparation.*

8.2 Contributions to conferences

1) **Characterization, performance and optimization strategies for PVDF thin film piezo-electric materials,** M. Celina, J. Martin, R. Assink, P. Chaplya, S. Winters, R. Clough, *Fluorine in coatings conference V, 1/21-22/03, Orlando, FL.*

2) **Radiation and temperature induced limitations on the long-term piezoelectric properties of PVDF and copolymers,** M. Celina, T. Dargaville, P. Chaplya, J. Martin, R. Assink, R. Clough, *3rd International Symposium on Service Life Prediction, 2/1-2/6/04, Sedona, AZ.*

3) **Optimization of piezo-electric PVDF polymers for adaptive optics in space environments,** M. Celina, T. Dargaville, J. Martin, R. Clough, R. Assink, D. Mowery, *AIAA conference, 4/19-22/2004, Palm Springs, CA.*

4) **Evaluation of piezoelectric polymers for use in space environments,** T. Dargaville, M. Celina, R. Assink, P. Chaplya, *AIAA conference, 4/19-22/2004, Palm Springs, CA.*

5) **Optimization and characterization of piezoelectric PVDF polymers for adaptive optics in space environments,** M. Celina, T. Dargaville, J. Martin, R. Clough, R. Assink, D. Mowery, *National Space & Missile Materials Symposium, 6/21-6/25/2004, Seattle, WA.*

6) **Performance of piezoelectric PVDF copolymers for space applications,** Celina, M. C., Assink, R. A., Dargaville, T. R., Clough, R. L., *Fluoropolymers 2004, 10/7-10/9/2004, Savannah, GA.*

7) **Piezoelectric PVDF materials performance and operation limits in space environments,** M. Celina, T. Dargaville, R. Assink, R. Clough, Invited speaker *MRS Fall Meeting Symposium "Materials for Space Applications", 11/29-12/03/2004, Boston, MA.*

8) **Smart materials for gossamer spacecraft – performance limitations,** T. Dargaville, M. Celina, P. Chaplya, R. Assink, *46th AIAA Structures, Structural Dynamics, and Materials Conference, 4/18-21/2005, Austin, TX.*

9) **Optimization and characterization of piezoelectric PVDF polymers for adaptive optics in space environments,** M. Celina, T. Dargaville, J. Martin, R. Assink, R. Clough, *National Space & Missile Materials Symposium, 6/27-7/01/2005, Las Vegas, NV.*

10) **Piezoelectric vinylidene-fluoride based polymers for use in space environments**, T. R. Dargaville, M. Celina, R. L. Clough, *230th ACS Meeting, 8/28-9/1/2005, Washington, DC.*

11) **Overview of PVDF-based polymer selection and performance criteria for adaptive materials in space applications**, M. Celina, T. R. Dargaville, G. D. Jones, R. L. Clough, *ACS Fluoropolymer 2006, Current Frontiers and Future Trends, October 15-18, 2006, Charleston, SC.*

9. References

[1] Berkey I. Advanced Space System Concepts and Technologies: 2010-2030+. California: The Aerospace Press, 2003.

[2] Martin JW, Redmond JM, Barney PS, Henson TD, Wehlburg JC, Main JA. Distributed Sensing and Shape Control of Piezoelectric Bimorph Mirrors. J Intel Mat Syst Str 2000;11:744.

[3] George PE, Dursch HW. Low Earth orbit effects on organic composites flown on the long duration exposure facility. J Adv Mater 1994;25:10.

[4] Young PR, Slemp WS. Space environmental effects on selected Long Duration Exposure Facility polymeric materials. ACS Symp Ser 1993;527:278.

[5] Young P, Siochi EJ, Slemp WS. Molecular-level response of selected polymeric materials to the low earth orbit environment. ACS Symp Ser 1996;620:264.

[6] Dever JA, de Groh KK, Banks BA, Townsend JA. Effects of radiation and thermal cycling on Teflon FEP. High Perform Polym 1999;11:123.

[7] Dever JA, de Groh KK, Banks BA, Townsend JA, Barth JL, Thomson S, Gregory T, Savage W. Environmental exposure conditions for Teflon fluorinated ethylene propylene on the Hubble space telescope. High Perform Polym 2000;12:125.

[8] Banks BA. In: Scheirs J, ed. Modern Fluoropolymers. Chichester: John Wiley & Sons, 1997. p 103.

[9] Clough RL, Gillen KT. In: Clegg DW, Collyer AA, eds. Irradiation Effects on Polymers. London: Elsevier, 1991. p 79.

[10] Dever JA, Bruckner J, Rodriquez E. Synergistic effects of ultraviolet radiation, thermal cycling, and atomic oxygen on altered and coated Kapton surfaces. NASA Tech Memo 166134 1992:11.

[11] Dursch HW, Pippin HG. In: Srinivasan V, Banks, B., ed. Materials Degradation in Low Earth Orbit (LEO). Warrendale: The Minerals, Metals & Materials Society, 1990. p 207.

[12] Hansen PA, Townsend JA, Yoshikawa Y, Castro JD, Triolo JJ, Peters WC. Degradation of Hubble space telescope metallized teflon FEP thermal control materials. 43rd Int SAMPE Symp,1998:570.

[13] James BF, Norton OW, Alexander MB. NASA Reference Publication 1350, 1994.

[14] Silverman EM. NASA Contractor Report 4661, 1995.

[15] Pippin G. Spacecraft Materials Selector Expert System. http://see.msfc.nasa.gov/see/mp/model_sms.html, cited 16 March 2004.

[16] Stidham CR, Banks BA, Stueber TJ, Dever JA, Rutledgem SK, Bruckner EJ. Low Earth orbital atomic oxygen environmental simulation facility for space materials evaluation. NASA Tech Memo 106128 1993.

[17] Kleiman JI, Iskanderova ZA, Gudimenko YI, Tennyson RC. Potential applications of hyperthermal atomic oxygen for treatment of materials and structures. Surf Interface Anal 1995;23:289.

[18] Navy. SUSIM: An NRL Program to Measure Solar Ultraviolet Irradiance. http://wwwsolar.nrl.navy.mil/susim.html, cited 16 March 2004.

[19] Floyd LE. SUSIM's 11-year observational record of the solar UV irradiance. Adv Space Res 2003;31:2111.

[20] Everett ML, Hoflund GB. Erosion study of poly(ethylene tetrafluoroethylene) (Tefzel) by hyperthermal atomic oxygen. Macromolecules 2004;37:6013.

[21] Gonzalez RI, Phillips SH, Hoflund GB. In Situ atomic oxygen erosion study of fluoropolymer films using X-ray photoelectron spectroscopy. J Appl Polym Sci 2004;92:1977.

[22] Kleiman JI, Gudimenko YI, Iskanderova ZA, Tennyson RC, Morison WD, McIntyre MS, Davidson R. Surface structure and properties of polymers irradiated with hyperthermal atomic oxygen. Surf Interface Anal 1995;23:335.

[23] Dargaville TR, Celina M, Martin JW, Banks BA. Evaluation of piezoelectric PVDF polymers for use in space environments. II. Effects of atomic oxygen and vacuum UV exposure. J Polym Sci Part B: Polym Phys 2005;43:2503.

[24] Gonzalez RI, Tomczak SJ, Minton TK, Brunsvold AL, Hoflund GB. Synthesis and atomic oxygen erosion testing of space-survivable POSS (polyhedral oligomeric silsesquioxane) polyimides. European Space Agency 2003;SP-540:113.

[25] Phillips SH, Haddad TS, Tomczak SJ. Developments in nanoscience: polyhedral oligomeric silsesquioxane (POSS)-polymers. Curr Opin Solid State Mat Sci 2004;8:21.

[26] Tomczak SJ, Marchant D, Svejda S, Minton TK, Brunsvold AL, Gouzman I, Grossman E, Schatz GC, Troya D, Sun L, Gonzalez RI. Properties and improved space survivability of POSS (polyhedral oligomeric silsesquioxane) polyimides. Mat Res Soc Symp Proc 2005;851:395.

[27] Townsend JA, Hansen PA, Dever JA, Triolo JJ. Analysis of retrieved Hubble Space Telescope thermal control material. Sci Adv Mater Process Eng Ser 1998;43:582.

[28] Zuby TM, de Groh KK, Smith DC. Degradation of FEP thermal control materials returned from the Hubble Space Telescope. NASA Tech Memo 104627 1995.

[29] Dever JA, Townsend JA, Gaier JR, Jalics AI. Synchrotron VUV and soft X-ray radiation effects on aluminized teflon FEP. 43rd Int SAMPE Symp, 1998:616.

[30] Townsend JA, Hansen PA, Dever JA, Triolo JJ. Analysis of retrieved Hubble Space Telescope thermal control materials. Int SAMPE Symp Exhib 1998;43:582.

[31] Forsythe JS, Hill DJT. The radiation chemistry of fluoropolymers. Prog Polym Sci 2000;25:101.

[32] Materials International Space Station Experiment. http://misse1.larc.nasa.gov/, cited 7 July 2004.

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