Optical and Chemical Characterization of Polyimide in a GEO-like Environment

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Abstract

Ground- and space-based optical observations of space objects rely on knowledge about how spacecraft materials interact with light. However, this is not a static property. Each material's optical fingerprint changes continuously throughout a spacecraft's orbital lifetime. These changes in optical signature occur because energetic particles break bonds within a material and new bonds subsequently form. The newly formed bonds can be identical to the original bonds or different, resulting in a new material. The chemical bonds comprising the material dictate which wavelengths of light are absorbed. Understanding the processes of material damage and recovery individually will allow development of a predictive model for materials' optical properties as a function of exposure to the space environment. In order to characterize the properties, we have exposed samples of polyimide to high energy electrons comparable to those found in a geostationary earth orbit in order to simulate damage on orbit. The resultant changes in the material's optical fingerprint were then characterized in the wavelength range of 0.2 to 25 microns. The chemical modifications to the material that result in these optical changes have also been identified. After initial electron-induced damage, the rate and mechanism of material recovery have been monitored and found to be extremely sensitive to the exposure of the damaged material to air. The implications of that fact and experimental progress toward complete *in vacuo* characterization will be discussed.

1. INTRODUCTION

Polyimide materials, often referred to by the trade name Kapton®, are used widely in the spacecraft industry. In order to understand the behavior of these materials throughout their mission lifetime, their exposure to ionizing radiation such as protons [1-4], heavy ions [5, 6], oxygen plasma [7, 8], ultraviolet light [9], and their combinations [10-12] has been extensively studied over past two decades. High energy electrons are a primary source of radiation at geosynchronous Earth orbit (GEO), and consequently there are many studies reporting on modification of polyimide's properties under electron irradiation, in particular, conductivity [13-20] and absorptivity [21-23]. Changes in absorptivity or reflectivity may have a direct effect on charge accumulation in spacecraft dielectrics, since photoemission changes with reflection. Few of the published studies attempt to understand the space polymers' underlying chemical modifications that give rise to these physical changes. Most importantly, a careful survey of existing literature shows that the overwhelming majority of studies have neglected the effects of post-irradiation sample handling. [14, 24-27]

It will be shown in this paper that in order to understand and predict the optical changes which occur in a material while on orbit, the material must be not only exposed to a space-like radiation to induce damage, it must be kept in a space-like environment (vacuum) before and during characterization. Exposure of polyimide to a high energy electrons will change its chemical structure and physical properties. The nature and extent of these changes is a function of several simultaneous processes, namely, damage (interaction of PI with highly energetic particles, resulting in broken chemical bonds), healing (formation of bonds identical to those damaged, returning the material to its pristine state), and scarring (formation of new chemical bonds in damaged material which are different from those in the pristine material). When necessary, the processes of healing and scarring will be referred to collectively as material recovery. In order to understand and predict properties of a spacecraft material as a function of time spent in a particular orbit, the processes of damage, healing, and scarring must be understood individually.

In this study, characterization of pristine and damaged polyimide has been undertaken using optical transmission spectroscopy at ultraviolet, visible, and near-infrared spectral regions (UV/Vis), Fourier transform infrared

spectroscopy (FTIR), and conductivity measurements made under ambient and vacuum conditions. It will be shown that the post-irradiation behavior of polyimide is extremely sensitive to the environment in which it was stored. It will be made clear that exposure of the damaged polymer to atmosphere (air) for even the briefest interval can change the results of the characterization dramatically. In order to understand the behavior of polyimides in space, they must be studied under space-like conditions.

2. EXPERIMENTAL

Exposure to space radiation was simulated by bombarding 75 µm thick polyimide coupons with high energy (90 keV) mono-energetic electron radiation from the Kimball Physics EG8105-UD electron flood gun in the Spacecraft Charging and Instrument Calibration Laboratory (SCICL) at Kirtland Air Force Base in New Mexico, USA [28]. The NIST ESTAR database [29] estimates the penetration depth of 90 keV electrons in PI to be 84 µm, which significantly exceeds the thickness of the utilized material samples. Exposure of polyimide material to electrons with a penetration depth greater than the material thickness ensures that energy is deposited uniformly through the bulk of the material and that charge is not deposited. This has been experimentally confirmed by measuring a near-zero surface potential of the polyimide material during the damaging process.

Prior to radiation exposure, a 24 hour vacuum dehydration bake was performed on all samples at 60°C. Samples were then mounted on an aluminum rotating carousel to ensure uniform absorbed dose. Electron energy was deposited at an accelerated dose rate of 94.8 Gy/s, an acceleration factor of approximately 475 over the AE9/AP9 30 day average value of 0.215 Gy/s[30], allowing the equivalent of 1.3 years of GEO exposure in 24 hours. Chamber pressure was maintained at lower than 1×10^{-6} Torr for the entire duration of the radiation exposure.

To characterize the recovery of damaged PI, we employed three material characterization methods: volume conductivity, UV/Vis transmission spectroscopy, and IR absorption/reflection spectroscopy. Depending on the measurement, these tests were carried out to post-irradiation times spanning hours (for air recovery) to weeks (vacuum recovery). In all cases, air exposure time was carefully logged in order to elucidate the role of the sample environment in the recovery processes.

The optical properties of damaged PI during the recovery process were measured with the visual and near infrared (VNIR) absorption/reflection spectroscopy and the directional hemispherical reflectance (DHR) method, performed with Perkin-Elmer Lambda 950 UV/VIS Spectrometer (0.2 – 2.5 µm) and Surface Optics Corporation SOC-400T portable FTIR spectrometer (2 – 25 µm), respectively. Vacuum measurement of conductivity was performed using by monitoring the surface potential of the thin films during bombardment with a ~30 pA/cm2 flux of 5 keV electrons and for some time after the beam was extinguished. These electrons are not fully penetrating. They enter, are deposited, and therefore charge the material. The total electron exposure during this step is <1000 Gy and the electrons do not penetrate deeply into the bulk. We therefore assume aging due to this step is negligible. As with the 90 keV beam, we monitored flux with a Faraday cup mounted next to the samples. We use previously developed models to fit this data and derive pertinent parameters for charge transport such as the bulk conductivity.[31]

3. RESULTS AND DISCUSSION

Simple observation of damaged polyimide samples provided the initial clues about its post-irradiation optical behavior, as shown in Figure 1. The pristine material (left) has a characteristic amber color. Damaged materials which had been freshly removed from the chamber were darkened to brown (lower doses) or blackish (higher doses). During the time required to transport the material to the spectrometer, or mount it in a second chamber to perform conductivity testing, on the order of tens of minutes, the materials lightened noticeably. If, however, the material was left mounted in the aging device under vacuum, observation of the polyimide through a transparent vacuum window showed that the samples underwent no obvious optical change for several hours after the electron beam was extinguished.

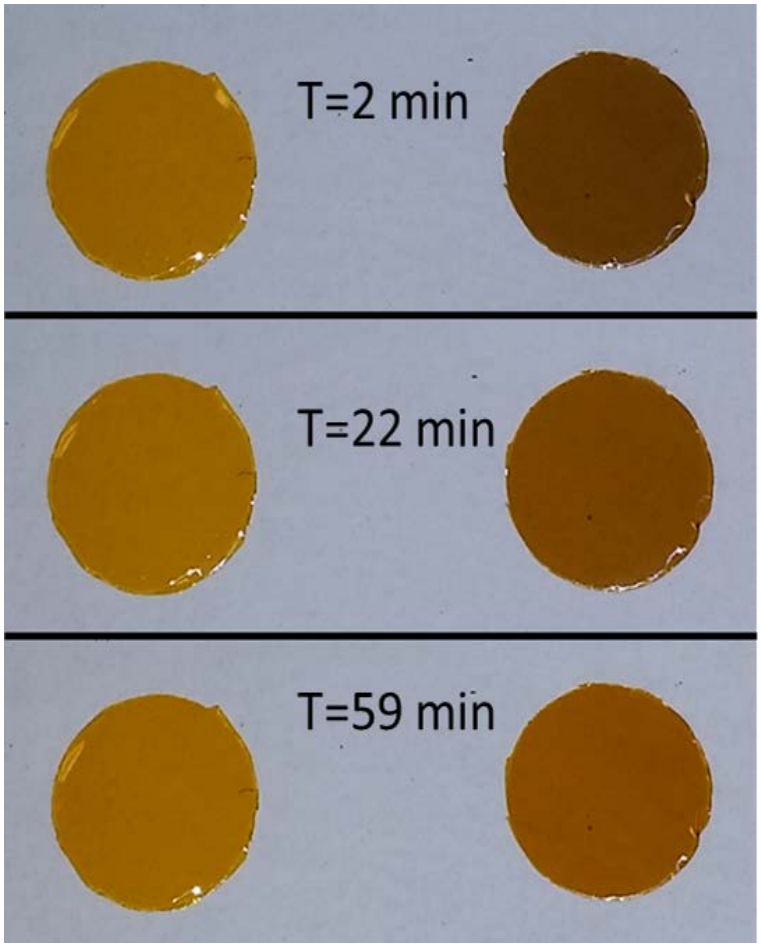

Figure 1 Each row of the figure is a photograph of the same two polyimide samples. The sample on the left is pristine polyimide. The sample on the right is a sample of polyimide which has been aged for the equivalent of 9 years in GEO orbit after 2, 22, and 59 minutes of exposure to air. The change in the material's optical absorption in the visible spectrum with exposure to air is obvious.

In order to characterize the optical fingerprint of electron-damaged polyimide more quantitatively, UV/Vis transmission and IR absorption spectra were measured immediately after irradiation. Due to the setup of the experimental apparatus, the damaged materials were removed from the vacuum chamber and transported to the spectrometers. Exposure to air was carefully logged for both experiments. The change in optical transmission of a PI sample aged to 9 year GEO equivalent is shown in Figure 2. The first spectrum was recorded after 6 minutes of air exposure (red line) and shows several differences from the transmission spectrum of the pristine material (black line). In addition to a small shift in the fundamental band gap, there are two absorption features at 638 and 702 nm and an absorption line at 864 nm. The absorption features at 638 nm and 702 nm are not present in the transmission spectrum of pristine polyimide, while the absorption band at 864 nm is detectable on the transmission spectrum of the pristine material. However, spectra of irradiated polyimide show much stronger absorption at 864 nm. After 60 min of air exposure to the radiation-damaged material, the absorption at 864 nm was indistinguishable from that of the pristine material. With continued air exposure, the decrease in the optical bandgap and the other two absorption features that were observed for the radiation damaged material returned to nearly that of the pristine material.

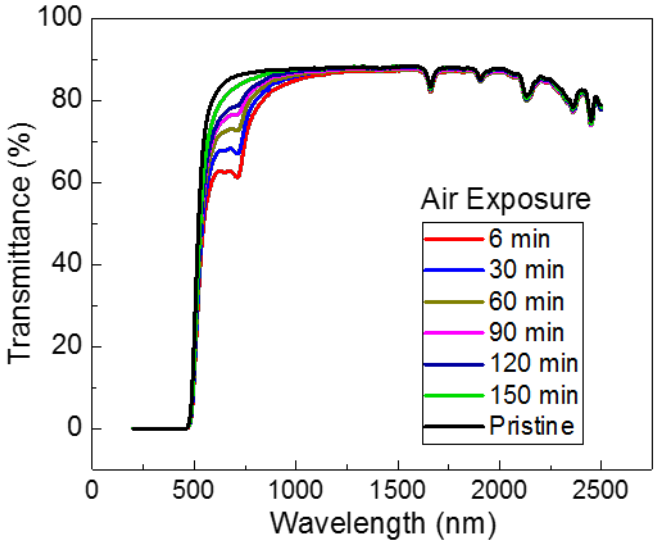

Figure 2 Optical transmission through a 75 µm thick sample of polyimide as a function of exposure to air after being removed from the aging vacuum chamber. It can be seen that the transmission spectrum recorded immediately after the material left vacuum (red line) differs drastically from the transmission spectrum of the pristine material (black line). Additionally, continued exposure to air shows spectra that increasingly resemble that of the pristine sample. See text for more discussion.

Figure 3 shows the relative intensity (damaged/pristine) of selected absorption bands of radiation damaged polyimide as a function of exposure to air. The IR absorption data of damaged and recovered PI shown in Figure 3 yield several tantalizing bits of information. First, it appears that certain moieties of the PI monomer are more susceptible to electron induced damage. After electron bombardment, an increase in carbonyl (C=O) absorption is observed, suggesting that none of the original carbonyls are being lost from the structure. New carbonyl bonds may be only formed by breaking one bond of the ether (C-O-C) group. Accordingly, the absorption at the ether stretching frequency is reduced immediately after damage and recovers to near pristine levels at the same time scale as the carbonyl stretch. Finally, absorption at the frequencies of the phenyl ring after damage shows an initial drop followed by a return to pristine levels on the same time scale. This suggests that electron damage causes scission of the phenyl rings and simultaneous formation of a new carbonyl functional group containing the ether oxygen. Reduction and incomplete recovery of the C-N-C absorption band could be evidence of C-N bond rupture and subsequent crosslinking between polymer chains.

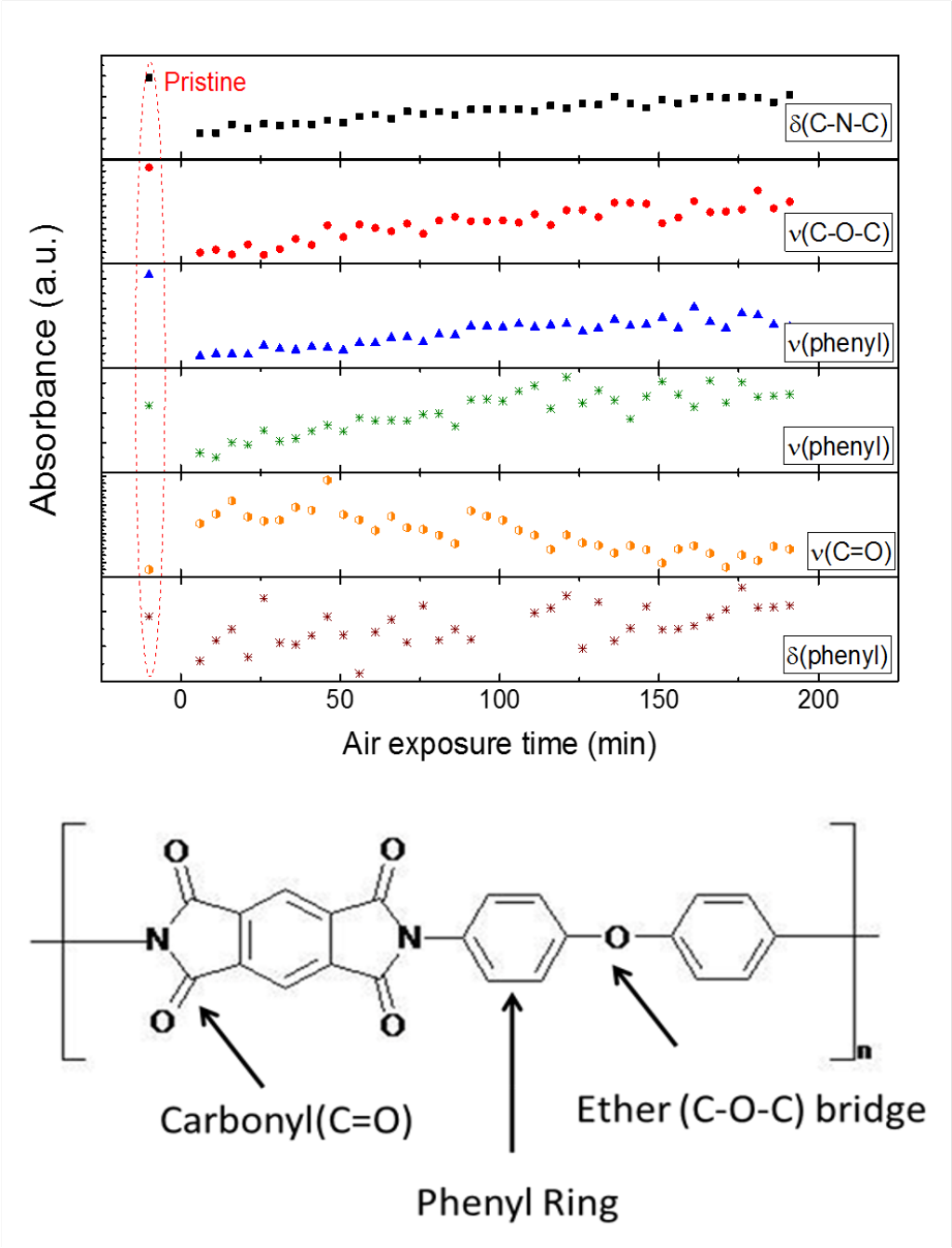

Figure 3 Upper panel: absorption intensity of selected vibrational bands in polyimide. Lower panel: chemical structure of polyimide PMDA-ODA (Kapton®). Electron bombardment leads to an increase in the absorption from carbonyl functional groups (yellow dots) and a reduction in absorption from ether functional groups (red dots). As the ether is the only non-carbonyl oxygen in the structure, the increase in carbonyl absorption must be due to one bond of the ether linkage breaking and the other forming a double bond. Consistent with that interpretation, the intensity of the ether absorption band is shown to decrease immediately after aging. In order for one of the ether bonds to become a carbonyl, an electron must be donated from one of the phenyl rings to the bond. The decrease in the intensity of the phenyl vibration absorption band, coupled with the known scission of phenyl rings under electron bombardment to produce radicals[32], suggests that the formation of a new carbonyl is accompanied by the breaking of at least one phenyl ring. See text for further discussion.

UV/Vis transmission spectra of samples which have undergone different radiation doses are presented in Figure 4. Spectra of polyimide samples aged with 9, 18, and 25 year GEO-equivalent doses show differences in the magnitude, but not the nature of the optical change. The absorption feature at 864 nm is particularly clear for the 25 year aged sample. Investigating the optical recovery of each of these samples showed that for larger doses (18, 25 years), the transmission spectra trend toward pristine values with increased exposure to air, but do not recover completely after several weeks. It can be inferred that increased exposure leads to long-term damage.

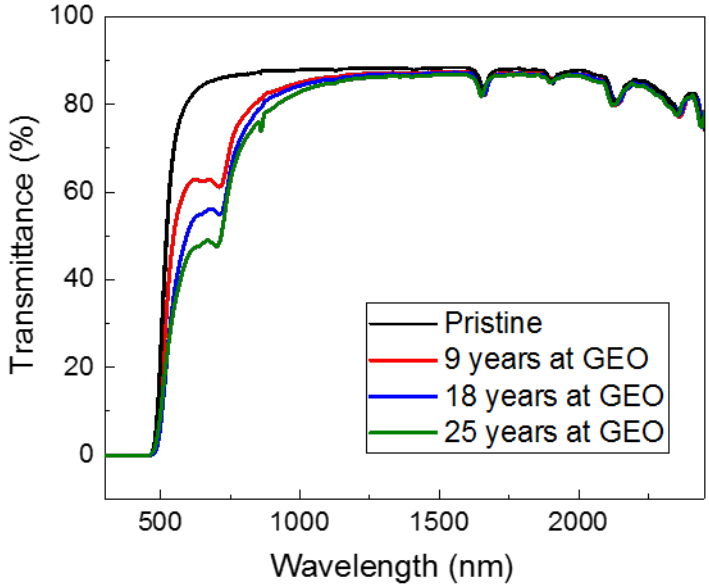

Figure 4 Transmission spectra of polyimide samples exposed to 9, 18, and 25 year GEO-equivalent electron doses. The same features are visible on each spectrum, with the magnitude of the changes increasing with increased electron dose.

Having shown conclusively that the effects of air exposure to electron-aged polyimide samples must be considered in order to accurately model the behavior of these polymers in space, we performed an experiment to investigate the behavior of these materials in vacuum. Due to the limitations of our experiment setup, we could not directly perform optical characterization *in vacuo*. Our studies have shown, however, that the recovery of the material's optical behavior in air proceeds along the same time scale as several more easily measurable physical characteristics. In an earlier publication[33], we demonstrate that the change in a material's volume conductivity and bulk concentration of radicals recover as a function of air exposure on a time scale identical to that of the optical properties. We therefore present the data on material conductivity shown in Figure 5 as an *ersatz* measurement of optical recovery. It can be seen that the recovery of the bulk conductivity of a 9 year GEO equivalent aged sample recovers to near pristine levels within 2 hours of air exposure, exactly as do the material's optical properties. In vacuum, however, no change in the conductivity is detectable for several weeks.

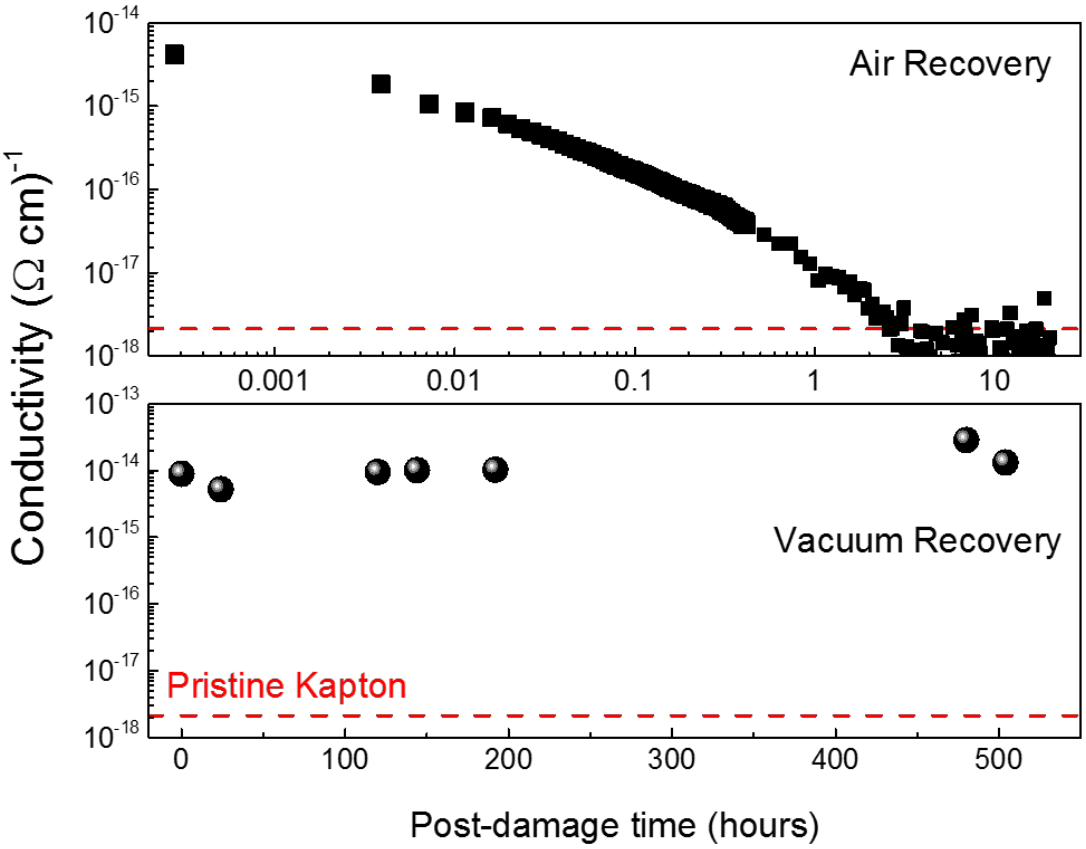

Figure 5 Measurements of bulk conductivity of 9 year GEO-equivalent electron aged polyimide as a function exposure to air (upper panel) and exposure to vacuum (lower panel). It can be seen that the bulk conductivity of electron damaged polyimide which is exposed to air returns to near pristine levels within 2 hours after aging, while no change in the bulk conductivity of electron damaged polyimide is detectable after 500 hours in vacuum. See text for more discussion.

4. CONCLUSION AND OUTLOOK

Polyimide has been exposed to high energy electron radiation in order to simulate the harsh GEO environment. After damaging the material, optical and chemical characterization of the material was undertaken using spectroscopic methods at ultraviolet, visible, and infrared wavelengths. It has been shown that when attempting to simulate the effects of the space environment on the optical and chemical properties of polyimide that even the slightest exposure of the damaged sample to air after the damage process and before characterization can lead to dramatic changes in the measured properties. This can lead to characterization that is not representative of what a material in GEO orbit actually exhibits.

A survey of the existing literature [8, 22, 34-37] (among many others) shows that historically very little attention has been payed to the handling of samples between damage and characterization. In order to develop models which will allow accurate characterization of materials on orbit and the power to predict a material's optical signature as a function of time, accurate characterization must be performed under fully controlled conditions. One small step forward is the development of a "vacuum wallet" which will allow polyimide, or any material of choice, to be aged in vacuum, then sealed in a small vacuum chamber under an IR transparent window in order to transport and store the material and perform characterization all while under vacuum. A prototype of this mini-chamber is shown in Figure 6.

Figure 6 Small "vacuum wallet" for *in vacuo* electron aging and characterization of polymer samples. Initial testing shows that the double o-ring seal maintains vacuum for >2 months. The brass sample mounting surface (center) is spring loaded to ensure good contact between the aged polymer and the CaF_2 window surface in order to minimize multi-surface reflections. Planned upgrades include a small inline pressure gauge in order to characterize the effects of pressure quantitatively.

The experimental procedures developed here to study polyimide can be used to study a host of materials of interest to the satellite detection and characterization community. Optical characterization coupled with chemical analysis will pave the way toward a predictive model of material optical aging in space and provide valuable information to materials scientists when designing new materials.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] Li R, Li C, He S, Di M, Yang D. Radiation effect of keV protons on optical properties of aluminized Kapton film. Radiation Physics and Chemistry 2007;76:1200-4.
[2] Shi J, Gong C, Tian X, Yang S, Chu PK. Optical properties and chemical structures of Kapton-H film after proton irradiation by immersion in a hydrogen plasma. Applied Surface Science 2012;258:3829-34.
[3] Lv M, Zheng F, Wang Q, Wang T, Liang Y. Effect of proton irradiation on the friction and wear properties of polyimide. Wear 2014;316:30-6.
[4] Yue L, Wu Y, Sun C, Shi Y, Zhang Y. Effects of proton pre-irradiation on radiation induced conductivity of polyimide. Radiation Physics and Chemistry 2016;119:130-5.
[5] Sahre K, Eichhorn K-J, Simon F, Pleul D, Janke A, Gerlach G. Characterization of ion-beam modified polyimide layers. Surface and Coatings Technology 2001;139:257-64.
[6] Severin D, Ensinger W, Neumann R, Trautmann C, Walter G, Alig I, et al. Degradation of polyimide under irradiation with swift heavy ions. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2005;236:456-60.
[7] Wohl CJ, Belcher MA, Ghose S, Connell JW. Modification of the surface properties of polyimide films using polyhedral oligomeric silsesquioxane deposition and oxygen plasma exposure. Applied Surface Science 2009;255:8135-44.
[8] Atta A. Modification of the Surface Properties of Polyimide Films Using Oxygen Plasma Exposure. Arab J Nucl Sci Appl 2013;46:115-23.
[9] Wu J, Miyahara A, Khan AR, Iwata M, Toyoda K, Cho M, et al. Effects of ultraviolet irradiation and atomic oxygen erosion on total electron emission yield of polyimide. Plasma Science, IEEE Transactions on 2014;42:191-8.
[10] Tahara H, Kawabata T, Zhang L, Yasui T, Yoshikawa T. Exposure of spacecraft polymers to energetic ions, electrons and ultraviolet light. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 1997;121:446-9.
[11] Russell DA, Connell JW, Fogdall LB. Electron, proton, and ultraviolet radiation effects on thermophysical properties of polymeric films. Journal of spacecraft and rockets 2002;39:833-8.
[12] Shen Z, Mu Y, Ding Y, Liu Y, Zhao C. Study on the mechanical property of polyimide film in space radiation environments. Selected Proceedings of the Chinese Society for Optical Engineering Conferences held November 2015: International Society for Optics and Photonics; 2016. p. 97960U-U-6.
[13] Fukunaga K, Maeno T. Space charge observation of polyimide films under DC electric fields. Solid Dielectrics, 2004 ICSD 2004 Proceedings of the 2004 IEEE International Conference on: IEEE; 2004. p. 178-81.
[14] Zhou L, Wu G, Gao B, Zhou K, Liu J, Cao K, et al. Study on charge transport mechanism and space charge characteristics of polyimide films. Dielectrics and Electrical Insulation, IEEE Transactions on 2009;16:1143-9.
[15] Levy L, Paulmier T, Dirassen B, Inguimbert C, Van Eesbeek M. Aging and Prompt Effects on Space Material Properties. Plasma Science, IEEE Transactions on 2008;36:2228-37.
[16] Hanna R, Paulmier T, Molinie P, Belhaj M, Dirassen B, Payan D, et al. Radiation induced conductivity in space dielectric materials. Journal of Applied Physics 2014;115:033713.
[17] Paulmier T, Dirassen B, Arnaout M, Payan D, Balcon N. Electric properties of space used polymers under high energy electron irradiation. Solid Dielectrics (ICSD), 2013 IEEE International Conference on: IEEE; 2013. p. 788-91.
[18] Yue L, Wu Y, Sun C, Xiao J, Shi Y, Ma G, et al. Investigation on the radiation induced conductivity of space-applied polyimide under cyclic electron irradiation. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2012;291:17-21.

[19] Meng C, Fang W, Jing L, Hai-Bo Z. Charging dynamics of a polymer due to electron irradiation: A simultaneous scattering-transport model and preliminary results. Chinese Physics B 2012;21:127901.
[20] Hanna R, Paulmier T, Molinié P, Belhaj M, Dirassen B, Payan D, et al. Radiation induced conductivity in Teflon FEP irradiated with multienergetic electron beam. Plasma Science, IEEE Transactions on 2013;41:3520-5.
[21] Sharma A, Sridhara N. Degradation of thermal control materials under a simulated radiative space environment. Advances in Space Research 2012;50:1411-24.
[22] Ennis CP, Kaiser RI. Mechanistical studies on the electron-induced degradation of polymethylmethacrylate and Kapton. Physical Chemistry Chemical Physics 2010;12:14902-15.
[23] Lai ST. Importance of surface conditions for spacecraft charging. Journal of Spacecraft and Rockets 2010;47:634-8.
[24] Sun C, Wu Y, Yue L, Shi Y, Xiao J. Investigation on the recombination kinetics of the pyrolytic free-radicals in the irradiated polyimide. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 2012;271:61-4.
[25] Tahara H, Kawabata T, Zhang LL, Yasui T, Yoshikawa T. Exposure of spacecraft polymers to energetic ions, electrons and ultraviolet light. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 1997;121:446-9.
[26] Wu Y, Sun C, Xiao J, Li R, Yang D, He S. A study on the free-radical evolution and its correlation with the optical degradation of 170 keV proton-irradiated polyimide. Polymer Degradation and Stability 2010;95:1219-25.
[27] Mathakari NL, Bhoraskar VN, Dhole SD. 6 MeV pulsed electron beam induced surface and structural changes in polyimide. Materials Science and Engineering: B 2010;168:122-6.
[28] Cooper R, Hoffmann R. JUMBO SPACE ENVIRONMENT SIMULATION AND SPACECRAFT CHARGING CHAMBER CHARACTERIZATION. Air Force Technical Report 2015.
[29] Berger M. ESTAR, PSTAR, and ASTAR: Computer programs for calculating stopping-power and range tables for electrons, protons, and helium ions. Unknown 1992;1.
[30] Ginet G, O'Brien T, Huston S, Johnston W, Guild T, Friedel R, et al. AE9, AP9 and SPM: New models for specifying the trapped energetic particle and space plasma environment. Space science reviews 2013;179:579-615.
[31] Sim A. Unified model of charge transport in insulating polymeric materials. 2013.
[32] Koch T. Introduction to Mass Spectrometry: Fragmentation Mechanisms. Boulder, Colorado: University of Colorado, Boulder; 2003.
[33] Engelhart DP, Plis, Elena; Humagain, Sunita; Greenbaum, Steven; Ferguson, Dale; Cooper, Russell; Hoffmann, Ryan. CHEMICAL AND ELECTRICAL DYNAMICS OF POLYIMIDE FILM DAMAGED BY ELECTRON RADIATION. IEEE Transactions on Plasma Science 2016;Accepted for publication.
[34] George MA, Ramakrishna BL, Glausinger WS. Electron paramagnetic resonance investigation of free radicals in polyimide films. The Journal of Physical Chemistry 1990;94:5159-64.
[35] Hill DJT, Hopewell JL. Effects of 3 MeV proton irradiation on the mechanical properties of polyimide films. Radiation Physics and Chemistry 1996;48:533-7.
[36] Mathakari N, Bhoraskar V, Dhole S. A comparative study on the effects of Co-60 gamma radiation on polypropylene and polyimide. Radiation Effects and Defects in Solids 2014;169:779-90.
[37] Paulmier T, Dirassen B, Payan D, Van Eesbeek M. Material Charging in Space Environment: Experimental Test Simulation and Induced Conductive Mechanisms. Dielectrics and Electrical Insulation, IEEE Transactions on 2009;16:682-8.