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Effect of Atmosphere on Recovery Dynamics of Polyimide Film Damaged by Electron Radiation

E. Plis[1], D. P. Engelhart[2], R. Cooper[3], S. Humagain [4,6], M. Brunetti[5,6], A. Koch[7], S. Greenbaum[4], D. Ferguson[3], R. Hoffmann[3]

[1] Assurance Technology Corporation, USA
[2] National Research Council at Air Force Research Laboratory, USA
[3] Air Force Research Laboratory, Space Vehicles Directorate, USA, Kirtland AFB, NM, USA
[4] Department of Physics & Astronomy, Hunter College of the City University of New York, USA
[5] Physics Department, New York City College of Technology, The City University of New York, Brooklyn, NY 11201, USA
[6] The Graduate School and University Centre, the City University of New York, New York, NY 10016, USA
[7] Aerospace Engineering Department, Worcester Polytechnic Institute, Worcester, MA 01606, USA
plis@assurtech.com

Abstract. Since electrons are the primary charged particles at the geosynchronous Earth orbit (GEO), understanding of their interactions with spacecraft materials, such as polyimide (PI, Kapton-H®), is important. Understanding of the chemical nature of electron damage and its effect on PI's electrical and optical properties is still limited. Thus, predictive spacecraft models (electrical charging, thermal, etc) are restricted to only pristine material properties. This is a major source of error in spacecraft construction and anomaly resolution, since material properties change after exposure to the space environment. Ground based measurements are critical to understanding the dynamics of spacecraft materials however it will be shown in this work that standard material handling practice and exposure to air are unacceptable for these studies.

1. Introduction

Nowadays, polyimide (PI) films are widely utilized in the spacecraft industry for their insulating properties, mechanical durability, low density, and resistance to radiation and atomic oxygen damage [1]. In particular, Kapton-H ®, a solid organic insulator with a monomeric unit of $C_{22}H_{10}N_2O_5$, is often used as an ultra-lightweight thermal control blanketing, also known as multi-layer insulation or MLI, to provide stable range of operating temperatures for satellite systems [2].

Spacecraft materials are subjected to the harsh effects of space weather, including hard vacuum, atomic oxygen, ultraviolet light, charged particle radiation, etc. causing degradation of their optical and physical properties [3]. It is important to understand the alterations of spacecraft materials properties' induced by the space environment to improve satellite lifetime, system reliability, space situational awareness, and decrease satellite operational costs. Whereas change of PIs' material

properties under simulated space environments, including surface degradation, mechanical properties, conductivity, and absorptivity, has attracted attention of researcher, relation of these radiation-induced changes to the chemical nature of damage still needs to be investigated [4-7].

In general, it has been found that the space environment fundamentally changes spacecraft materials, in particular, their surface becomes very reactive due to the breakage of inter-molecular bonds and formation of free radicals as a result of space environment. Ground based spacecraft material degradation, or aging, typically takes place under ultra-high vacuum conditions, ~ 10^{-9}-10^{-11} Torr, the subsequent material storage and characterization is often performed under uncontrolled laboratory atmosphere. Residual gases, even at low partial pressures, can react with radicals in the modified PIs, changing the properties of aged material in a way that is not properly accounted for. A small number of publications have investigated the effect of humidity on the electrical behavior of undamaged polyimide [8, 9]. However, to the authors' knowledge, little attention has been given to the effects that the storage atmosphere has on the material properties of irradiated PI films.

In the presented study, we first characterized the material properties of electron-irradiated PI as a function of exposure to uncontrolled laboratory atmosphere (air). Second, we evaluated the effects of several major constituents of Earth's atmosphere (Ar, N_2, O_2) on the material properties of electron irradiated PI.

2. Experimental

In terms of total energetic dose experienced by an object in geosynchronous Earth orbit (GEO) over several solar cycles, electrons are the dominant source of energy deposition. In order to simulate an electron dose typical for GEO environment, 76.2 μm thick Kapton-H® films were irradiated with high energy (90 keV) mono-energetic electron radiation gun [10]. Irradiation was performed at an accelerated dose rate of 94.8 Gy/s with vacuum level maintained at lower than 1 x 10^{-6} Torr for the entire duration of the radiation exposure. PI samples in this study were irradiated with doses of 2.3 x 10^7 Gy and 5.5 x 10^7 Gy, equivalent to 9 years and 17 years of GEO electron exposure, respectively**.**

The conductivity of PI samples exposed to air after the irradiation process was measured using the constant voltage method [11]. Conductivity of irradiated PI samples recovered in vacuum under partial pressure of nitrogen, oxygen, or argon gases was derived from a measurement of the surface potential decay [12]. After the PI samples were irradiated with high energy electrons, the radiation-damaged PI film was removed from the aging facility and transferred to the characterization vacuum chamber or portable vacuum container for transfer to the EPR measurement facility. Sample transfer was performed under laboratory atmosphere (air) and was limited to less than 5 min of air exposure. The radical spin population was obtained by comparing the integrated intensity of PI sample spectra with that for a standard sample a known concentration of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO).

3. Results and Discussion

Interaction of PI with highly energetic particles will modify its chemical structure. The extent of this modification is a function of several simultaneous kinetic processes, namely, damage (interaction of material 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 the damaged material which are different from those in the pristine material). Often macroscopic properties are measured, making it difficult to distinguish healing from scarring; hence, we refer to the sum of healing and scarring as recovery. Radiation-induced chemical modifications will induce changes in PI's physical properties, in particular, bulk conductivity [13].

Fig. 1 compares bulk conductivities of Kapton-H® samples irradiated with dose of 5.6 x 10^7 Gy and recovered in air (top panel) and under vacuum (bottom panel). Initial conductivity of damaged PI, measured at time zero, was nearly the same for air-recovered (5 x 10^{-15} $(\Omega \cdot m)^{-1}$) and vacuum-recovered (8 x 10^{-15} $(\Omega \cdot m)^{-1}$) samples, suggesting that our estimation of bulk conductivity of aged PI is reliable. Air exposure of radiation-damaged PI resulted in fast recovery, within 3 hours, of irradiated

material's conductivity from 5 x 10^{-15} $(\Omega \cdot m)^{-1}$ to the one of the pristine Kapton (2 x 10^{-18} $(\Omega \cdot m)^{-1}$), whereas the vacuum recovery of radiation-damaged PI retained the same value, ~ 8 x 10^{-15} $(\Omega \cdot m)^{-1}$, for over three weeks (504 hours) after the damaging process.

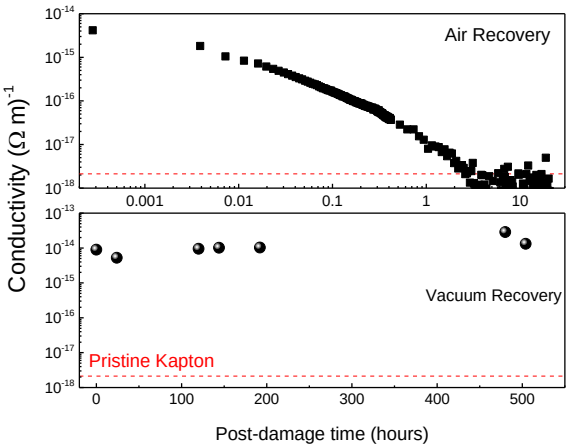

Figure 1. Comparison of air- and vacuum-recovered conductivities of Kapton-H® irradiated with dose equivalent to 2.3 x 10^7 Gy Dashed line indicates the conductivity of pristine Kapton-H®.

To further investigate an effect of damaging radiation on PI, including the concentration and nature of free radicals as well as mechanism of their decay, irradiated PI was sealed in a vacuum EPR tube for EPR measurements. The double integral of the derivative line shape of the EPR spectra was calculated to derive their corresponding radical concentrations. Fig. 2 demonstrates the evolution of radicals concentration in PI film irradiated with dose of 5.5 x 10^7 Gy and recovered in air and under vacuum.

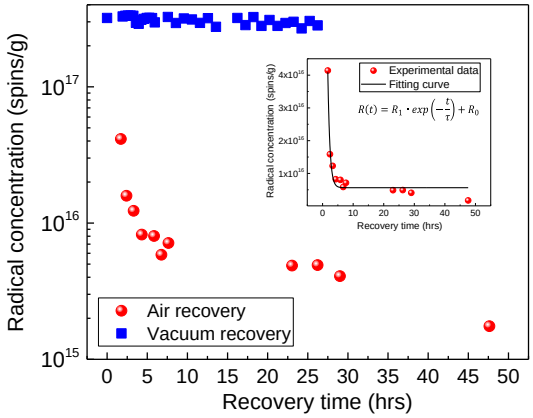

Figure 2. Radical concentration of PI irradiated with dose of 5.5 x 10^7 Gy after air- and vacuum-recovery. Inset shows theoretical fitting to the air-recovery data as well as fitting equation. See text for more details.

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Under vacuum, the concentration of radicals remains constant in the irradiated PI sample, ~ 3 x 10^{17} spins/g, whereas a decay in the radical concentration is observed in air-exposed irradiatied PI material. The first EPR measurement of air-exposed irradiated PI was taken after 1.7 hours of ambient exposure, and radical concentration was lowered by an order of magnitude compared to the radical concentration during the vacuum recovery.

The decay of radicals in the irradiated polymer can proceed via two mechanisms, thermal recombination of the radicals and reaction with the gases in the ambient atmosphere. The time evolution of the radical concentration under air exposure may be fitted using the rate equation shown in the Fig. 2 inset. Here R(t) is the total radical population, spins/g; R_1 and R_0 are constants representing the annealed free-radical population and the surviving radical population under the measurement condition (in ambient at room temperature), respectively; τ is the characteristic time constant which is related to the recovery rate of the annealable radicals. The resulting fit is presented in Fig. 2 inset.

As may be seen from inset to Fig. 2, the rate equation describes well the evolution of the radical population in irradiated PI under air exposure until ~ 8 hours of air exposure, and beyond that it fails to fit the experimental data. This observation is consistent with results reported by Wu *et al* [14]. In [14], authors attributed the fast time decay phase of radical evolution to the thermodinamical recombintation of radicals, whereas the slow decay regime is attributed to the reaction of radicals with the gases in the ambient atmosphere. It should be noted that even the in damaged material that is exposed to air the radical consentration does not return to the prisitine value of zero.

Although the kinetic model of Wu *et al* describes our data well, the results shown in Fig 2 show conclusively that the initial rapid decay of the radical concentration cannot be explained with thermodynamic model. If the rapid decay of the radical signal were thermodynamic, the EPR signal would decay as quickly in vacuum as in air, since in vacuum the PI sample is in thermal equilibrium with the surrounding chamber and sample mount, i.e. 300 K. However, the radical signal measured in vacuum is shown to be stable for > 30 hours. The rapid decay in radical concentration in atmosphere can therefore only be due to the presence of external reactants, such as oxygen or water vapor.

To further evaluate the effects of several major constituents of Earth's atmosphere on the material properties of electron irradiated PI, PI irradiated with dose of 5.5 x 10^7 Gy was stored in a vacuum chamber at a background pressure of 1x10^{-6} Torr and exposed to partial pressures of argon, nitrogen, and oxygen gases. Surface potential decay (SPD) measurements were performed after each individual gas exposure to determine bulk electrical conductivity [31].

Table1. Details and results of the "environmental" experiments.

Environment	Exposure (L)	Resistivity (Ω·m)	Conductivity $(\Omega \cdot m)^{-1}$	Exposure time (hrs)
Vacuum	N/A	5.1 x 10^{15}	1.9 x 10^{-16}	N/A
Argon	35 x 10^{12}	7.8 x 10^{15}	1.3 x 10^{-16}	74.5
Nitrogen	90 x 10^{12}	4.8 x 10^{15}	2.1 x 10^{-16}	125.0
Oxygen	14 x 10^{12}	3.2 x 10^{17}	3.1 x 10^{-18}	92.0

As shown in Table 1, the transport properties of irradiated PI did not change significantly with exposure to an argon or nitrogen environment. However, exposure to an oxygen atmosphere resulted in a degradation of two orders of magnitude in the electrical conductivity compared to that of vacuum-exposed film, from 1.9 x 10^{-16} $(\Omega \cdot m)^{-1}$ to 3.1 x 10^{-18} $(\Omega \cdot m)^{-1}$. This may be attributed to the reaction of radicals in irradiated PI with oxygen molecules. This reaction transforms the radicals into the new

chemical species with no unpaired electrons, thus reducing the number of low-lying trap states in the irradiated material and degrading its conductivity.

4. Summary

Electrical transport properties of radiation-damaged and recovered (both in vacuum and ambient atmosphere) PI films were investigated via EPR and conductivity measurements. We found that even limited exposure to the uncontrolled laboratory atmosphere dramatically affects the properties of interest. In particular, the conductivity of irradiated PI decreased by an order of magnitude, from 5 x 10^{-15} $(\Omega \cdot m)^{-1}$ to 5 x 10^{-16} $(\Omega \cdot m)^{-1}$ after only 2 minutes of air exposure. Concentration of radiation-induced radicals measured by EPR was decreased by an order of magnitude after 1.7 hours of air exposure, from 3 x 10^{17} spins/g (initial value) to 4 x 10^{16} spins/g, respectively. These results are consistent with those we observed earlier [15].

Further, we evaluated the effects of several major constituents of Earth's atmosphere, nitrogen, oxygen, and argon, on the material properties of electron irradiated PI. We found that argon and nitrogen atmosphere do not effect the conductivity of irradiated PI, whereas oxygen exposure results in two orders of magnitude degradation of electrical conductivity of irradiated PI from 1.9 x 10^{-16} $(\Omega \cdot m)^{-1}$ to 3.1 x 10^{-18} $(\Omega \cdot m)^{-1}$.

Thus, we have shown that while PI is an exceptionally stable polymer, damaging radiation makes it sensitive to its surrounding atmosphere. The damaged material's sensitivity to even limited air exposure means that the storage, handling, and characterization protocols of irradiated material must be scrutinized and carefully controlled. Argon or nitrogen atmosphere may be suitable candidates for the assessement of radiation-damaged PI's material properties, resulting in development of reliable models guiding the design of novel technology-enabling materials.

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References

[1] Y. Kimoto, T. Fujita, N. Furuta, A. Kitamura, H. Suzuki. J Spacecr Rockets 1-6 (2016)
[2] H. A. MacEwen, G. G. Fazio, M. Lystrup, N. Batalha, N. Siegler, E. C. Tong. Proc, of SPIE 9904, 990405 (2016)
[3] R. K. Kiefer, W. J. Gabler, M. T. Hovery, S. A. Thiibeault. Rad Phys Chem 80 (2), 126 (2011)
[4] X. Lei, M. Qiao, L. Tian, Y. Chen, Q. Zhang. Corros Sci 98, 560 (2015)
[5] H. Shimamura and T. Nakamura. Polym Degrad Stab 95 (1), 21 (2010)
[6] R. Hanna, T. Paulmier, P. Molinie, M. Belhaj, B. Dirassen, D. Payan, N. Balcon. Appl Phys 115, 033713 (2014)
[7] A.K. Sharma, N. Sridhara. Adv Space Rese 50(10): 1411 (2012)
[8] F. Belluci, I. Khai,s. S. D. Senturia, R. M. Latanision. J Electrochem Soc 137, 1778 (1990)
[9] N. A. Galichin, M. E. Borisova. Russ Electr Eng 78, 129-132 (2007)
[10] R. Cooper and R. Hoffmann, Air Force Report No. AFRL-RV-PS-TP-2015-0012 (2015)
[11] ASTM-D257-14, "Standard Test Methods for DC Resistance or Conductance of Insulating Materials," 2015
[12] J. R. Dennison, J. Brunson, P. Swaminathan, N. W. Green, A. R. Frederickson. IEEE Trans Plasma Sci 34, 2191 (2006).
[13] E. Plis D. P. Engelhart, R. Cooper, and R. Hoffmann. Phys. Stat. Sol B (2017)
[14] Y. Wu, C. Sun, J. Xiao, R. Li, D. Yang, S. He. Polym Degr Stab 95,1219 (2008)
[15] D. P. Engelhart, E. Plis, D. Ferguson, R. Cooper, R. Hoffmann. Presentation at AMOS 2016 conference.