CHEMICAL AND ELECTRICAL DYNAMICS OF POLYIMIDE FILM DAMAGED BY ELECTRON RADIATION

Daniel P. Engelhart [(1)], Elena Plis [(2)], Sunita Humagain [(3)], Steven Greenbaum[(3)], Dale Ferguson[(4)], Russell Cooper[(4)], Ryan Hoffmann[(4)]

[(1)] National Research Council at Air Force Research Laboratory, USA, daniel.engelhart.ctr@us.af.mil
[(2)] Assurance Technology Corporation, USA, plis@assurtech.com
[(3)]Department of Physics & Astronomy, Hunter College of the City University of New York, USA, sgreenba@hunter.cuny.edu
[(4)]Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, NM, USA

ABSTRACT

The processes of electrical charge accumulation and dissipation in dielectric materials are critical to spacecraft construction and operational anomaly resolution. Electrical conductivity, and therefore surface potential, of radiation-damaged materials undergoes unpredicted changes while on orbit. The space environment causes fundamental modifications in the chemical structure of spacecraft materials by breaking inter-molecular bonds and creating free radicals that act as space charge traps. Over time, free radicals react with each other and the material recovers. The rates of free radical formation and loss determine the dynamics of the conductivity of spacecraft materials. Lack of knowledge about dynamic aging is a major impediment to accurate modeling of spacecraft behavior over its mission life.

1. INTRODUCTION

Polyimide (PI, Kapton®) is ubiquitous in the construction of spacecraft. Its long-term thermal and mechanical durability have made it a material of choice for the outer surfaces of spacecraft for decades. High energy electrons (~90 KeV) are one of the most prevalent types of radiation in geosynchronous Earth orbit (GEO)[1], and consequently there are many studies reporting on modification of polyimide's properties under electron irradiation, in particular conductivity [2-9] and absorptivity [10-12]. Changes in absorptivity and reflectivity may have a direct effect on charge accumulation in spacecraft dielectrics, as photoemission changes with reflection. If incident photons are reflected, no photoelectrons are generated; thus, photoelectron charging reduces to zero as a surface approaches a perfect reflector [13]. However, few published studies attempts to understand the space polymers' underlying chemical modifications that give rise to the change in physical properties.

Current models used to predict spacecraft charging characteristics, such as NASCAP[14], rely on laboratory-generated material data to produce accurate models. Currently, these models use material parameters which describe the pristine material. However, exposure of PI to a simulated space environment will change its chemical structure and, therefore, its physical properties. The nature and extent of this change is a function of several simultaneous kinetic processes. We refer to these processes as *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). In order to 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.

2. EXPERIMENT

To understand the chemistry of the healing and scarring processes in PI and their effect on bulk conductivity, PI was exposed to the simulated space environment and subsequently

characterized using complimentary optical spectroscopy and electrical (EPR, constant voltage conductivity) techniques. Damage pathways have been identified immediately after aging; healing and scarring of the damaged PI material were monitored and characterized in different post-damage environments.

The intensity of selected tabulated absorption peak values plotted as a function of exposure time to air is shown in Figure 1. The inset shows a schematic of PI's monomer with chemical constituents highlighted for reference. There is an increase in absorption at the C=O (carbonyl) stretching frequency directly after aging and a decay back to nominal levels after < 200 minutes. We also see an initial loss of absorption in the phenyl ring stretching band that also recovers to near pristine levels on the same time scale as the carbonyl loss. There is also an initial decrease in the absorption at the ether stretching frequency which returns to nearly pristine values on the same time scale.

The transmittance spectra of irradiation damaged PI film measured after 40, 70, 100, and 130 min of air exposure are shown in Figure 2. The transmittance spectrum of reference pristine PI is also presented. A decrease in the optical bandgap was observed for the radiation damaged material which returns to nearly that of the pristine material with increased air exposure.

The volume conductivity of three radiation damaged PI samples was also measured: sample A was stored in air after electron damage; sample B was stored under vacuum and only exposed to air during conductivity measurements; sample C was stored in a separate vacuum chamber between measurements that could be vented and pumped down more quickly than that in which sample B was stored. Sample A demonstrated recovery to a stable conductivity of 1 x 10^{18} 1/Ω-cm within the first ~150 min of air exposure. Samples B and C recovered to the conductivity of 6 x 10^{17} 1/Ω-cm after 250 hrs and 400 hrs, respectively. The conductivity of samples B and C as a function of cumulative air exposure time is plotted in Figure 3.

During the same time period that the conductivity was being measured, EPR measurements were performed on similarly damaged PI and a pristine reference sample to determine the concentration of free radicals in the damaged material. The reference sample showed no EPR signal, indicating that there are no unpaired electrons present in pristine PI, as was expected. However, in the damaged material a strong initial EPR signal was measured that decayed with time. EPR data for the radiation damaged PI material are also plotted in Figure 3.

EPR data show that the decay of the radical signal occurred on the same air-exposure time scale as the decrease in conductivity after initial electron-induced damage. This suggests that these radicals are involved in the transport of electrons through the bulk of the material. Clearly they are reactive; as they react, forming new chemical bonds, the conductivity trends back toward its initial value.

3. CONCLUSION

To model the process of spacecraft charging, it is imperative that the material parameters are accurate throughout the life cycle of the mission. Mission lifetimes and complexity continue to expand, forcing designers and operators to abandon the assumption that spacecraft materials like PI remain stable throughout the mission. In this study, we have shown that the optical and electrical properties of PI are impacted by radiation induced chemistry. The fact that the IR absorption signature and the conductivity both decay on the same time scale as the concentration of radicals suggests that these properties are interconnected. These corresponding time scales are also suggestive that the concentration of radicals plays a critical role in the transport of electrons through the bulk of the material. It is

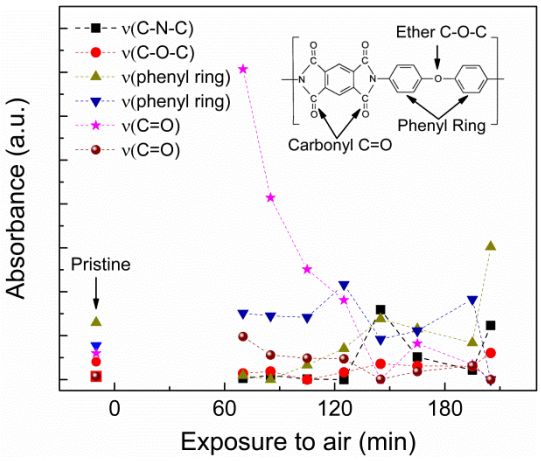

Figure 1. Intensity of selected absorption bands of radiation damaged Kapton film as a function of exposure to air. Inset shows monomer of PI with chemical constituents highlighted for reference.

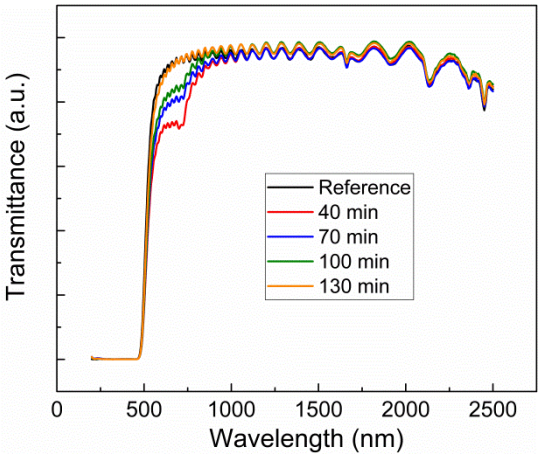

Figure 2. Transmittance spectra of reference PI sample and radiation damaged film measured after 40, 70, 100, and 130 min of air exposure.

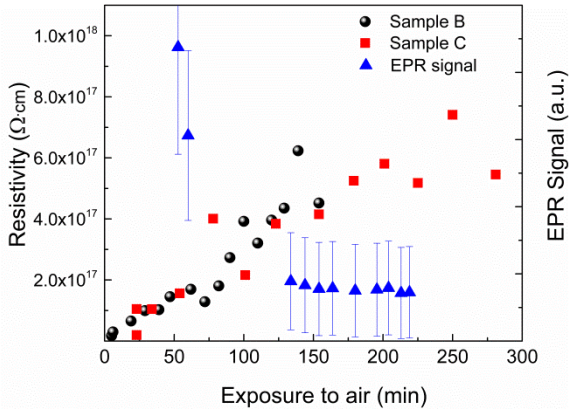

Figure 3. Resistivity (inverse of conductivity) and EPR signal of radiation damaged PI film plotted as a function of cumulative air exposure time.

reasonable to assume that creation and decay of radicals in the material will modify the density and energetic distribution of electron trap states in the bandgap of PI. [11]

It has always been assumed that exposure to air would be deleterious to understanding how materials recover in vacuum. However, since PI is very stable under normal conditions a small amount of air exposure has been accepted as necessary and largely unavoidable. The data plotted in Figure 3 show that air exposure dominates the post damage chemistry of PI and that even limited air exposure (less than 10 min) will cause dramatic and unwanted effects. The results of this study illustrate the necessity of in-vacuum characterization methods as well as a careful examination of material handling techniques when reviewing literature.

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