JOURNAL OF SPACECRAFT AND ROCKETS
Vol. 39, No. 3, May–June 2002

Effects of Ambient Air Exposure on Atomic Oxygen-Exposed Kapton-H Films

Masahito Tagawa,* Kumiko Yokota,† and Nobuo Ohmae‡
Kobe University, Hyogo 657-8501, Japan
and
Hiroshi Kinoshita§
Osaka University, Osaka 565-0871, Japan

In research reporting on the effect of ambient air exposure on atomic oxygen-exposed Kapton-H film, the surface oxygen concentration of atomic oxygen-exposed Kapton-H increased with increasing atomic oxygen fluence and reached a saturated value even without ambient air exposure. These results are contradictory to the previously reported results by Grossman et al. (Grossman, E., Lifshitz, Y., Wolan, J. T., Mount, C. K., and Hoflund, G. B., "In Situ Erosion Study of Kapton Using Novel Hyperthermal Oxygen Atom Source," *Journal of Spacecraft and Rockets*, Vol. 36, No. 1, 1999, pp. 75–78). From the x-ray photoelectron spectroscopic analysis of the atomic oxygen-exposed Kapton-H with and without ambient air exposures, it was concluded that the atomic oxygen exposure creates a highly oxidized surface and the carbon and oxygen concentrations were affected by the subsequent ambient air exposure. These results clearly indicate that the effect of air exposure should be taken into consideration in the analysis of surface chemistry of materials exposed to low-Earth-orbit space environment.

Nomenclature

E = translational energy
I_{C1s} = relative photoionization cross section for C_{1s} orbit
I_{N1s} = relative photoionization cross section for N_{1s} orbit (relative to C_{1s})
I_{O1s} = relative photoionization cross section for O_{1s} orbit (relative to C_{1s})
$P(E)$ = translational energy distribution

Introduction

A NUMBER of polymeric materials and carbon-based composites are commonly known for susceptible erosion by the hyperthermal atomic oxygen (AO) bombardment in a low-Earth-orbit (LEO) environment. Kapton-H (DuPont) has been selected as one of the reference materials when evaluating the erosion rates of other materials because the erosion yield of 3.00×10^{-24} cm^3/atom for Kapton-H has been well established in LEO environment.[1] Kapton-H has been exposed in many flight experiments flown aboard the space shuttle.[2,3] In the past flight tests Kapton-H has been examined by x-ray photoelectron spectroscopy (XPS) after retrieval. An increase in surface oxygen concentration was detected; however, no drastic change of XPS C1s core level spectrum was observed even when Kapton-H was exposed to an orbital AO environment.[4] The interpretation of this result was that AO reacts with surface carbon atoms and forms volatile products such as CO or CO_2; however, the surface itself was not severely altered by AO bombardment.[5]

However, uncertainty remains on the effect of air exposure to sample surfaces. This uncertainty is because all of the flight samples have been exposed to ambient air prior to the XPS analysis because the pressure of the shuttle cargo bay returns to atmospheric when the orbiter reaches ground level. The effect of air exposure on the surface chemistry of Kapton was reported by Grossman et al.[6] They used an electron stimulated desorption AO source to produce a hyperthermal atomic oxygen beam, and the AO-exposed surface was examined by XPS without air exposure.[7] Their conclusion is that AO exposure leads to a loss of surface oxygen concentration. An increase in oxygen concentration at the AO-exposed surface was not observed after exposure to the air. These results are contradictory to those reported in many other studies showing increase in oxygen concentration by AO exposures. They also indicated particularly from high-resolution XPS spectra that the carbonyl group in the polyimide structure disappeared with AO exposure. However, no explanation was given for these chemical changes of the AO-exposed Kapton-H surface in their reports. Because their results are quite different from those reported previously,[8–11] it is, at least, necessary to show a reasonable explanation for the following points: 1) why the highly reactive O-atom is not chemically, or even physically, adsorbed at the Kapton-H surfaces and 2) why the double bond in the carbonyl group, which has the highest binding energy in the polyimide structure, is predominantly lost with an AO attack. If their results are correct, the knowledge of AO reaction in LEO should be reconstructed because oxidation of materials observed in previous studies is caused by air exposure after retrieval. Therefore, the effect of air exposure should be carefully reexamined by the well-characterized hyperthermal AO beam without air exposure.

In this paper we report the quantitative analytical results of the effect of air exposure on the AO-exposed Kapton-H. The chemical information of the film surface was examined by XPS with and without air exposure. The change in XPS spectra in storage in ambient air is also discussed.

Experiments

Figure 1 represents the top view of the AO beam facility used in this study. Description of this facility has been given elsewhere.[12] The AO source in this facility is a laser-detonation AO source.[13,14] This experimental apparatus includes the time-of-flight (TOF) system, which used a quadrupole mass spectrometer as a detector, in order to characterize the energy and composition of the species included in the beam. The AO flux was calculated by the frequency shift of QCM with a silver surface.[15] The AO flux was measured to be 4.0×10^{13} atoms/cm^2/s at the sample position (135 cm from the nozzle).

Received 10 August 2001; revision received 29 October 2001; accepted for publication 30 October 2001.

*Associate Professor, Department of Mechanical Engineering, Rokko-dai 1-1, Nada, Kobe; tagawa@mech.kobe-u.ac.jp. Member AIAA.

†Research Staff, Department of Mechanical Engineering, Rokko-dai 1-1, Nada, Kobe.

‡Professor, Department of Mechanical Engineering, Rokko-dai 1-1, Nada, Kobe.

§Postdoctoral Fellow, Department of Material and Life Science, Yamada-oka 2-1, Suita.

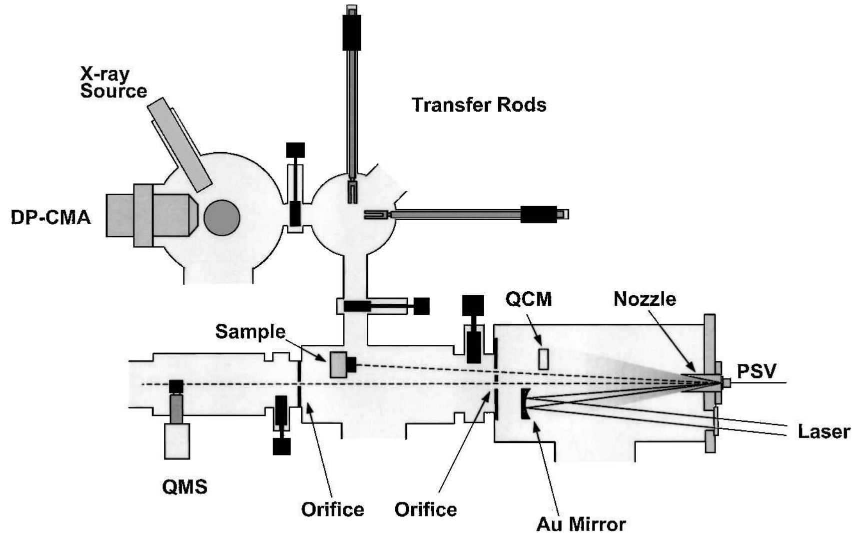
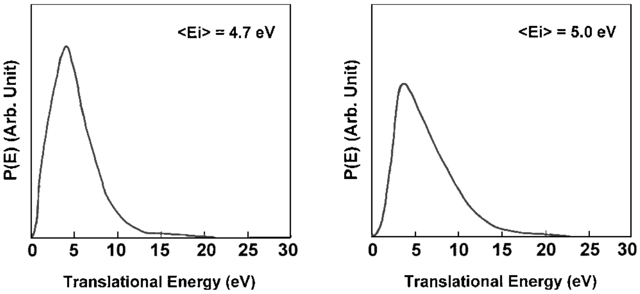


Fig. 1 Top view of the AO beam facility used in this study.



a) $m/e = 16$ b) $m/e = 32$

Fig. 2 Translational energy distributions of a) hyperthermal AO component and b) hyperthermal O_2 component.

Figure 2 shows the typical translational energy distributions $P(E)$ of the hyperthermal AO component and of the hyperthermal O_2 component of the beam. The mean energies of the hyperthermal AO and O_2 components were 4.7 and 5.0 eV, full width at half-maximum (FWHM) being 5.5 and 6.4 eV, respectively. The peak areas of $m/e = 16$ and 32 in the TOF distributions and the relative ionization cross section of AO and O_2 yielded a beam composition of hyperthermal AO 45%, hyperthermal O_2 31%, and thermal O_2 24% (Ref. 16).

The incident angle of the beam was kept at 0 deg in this study (direction of the surface normal). The samples can be transferred from the reaction chamber to the XPS chamber using two vacuum transfer rods without breaking the vacuum (see Fig. 1). The XPS system is a part of this facility, which consists of a 200-W nonmonochromatic, dual-anode x-ray source and a double-pass cylindrical mirror analyzer. The surface composition of the Kapton-H was calculated at the relative peak areas of C1s, O1s, and N1s in XPS spectra using relative photoionization cross sections with MgKα x-ray (I_{C1s}:I_{O1s}:I_{N1s} = 1.00:2.85:1.77).

A commercially available pyromelliticanhydride (PMDA)–oxydianiline (ODA) polyimide (Kapton-H; DuPont) was used as a specimen. Kapton-H films were cleaned by dipping the films into deionized water, ethanol, and ethylether. The cleaning process was repeated three times before the experiment. The XPS measurement of the pristine sample, thus cleaned, provided a surface composition of C:O:N = 74.9%:16.9%:8.2%, which is close to the theoretical value (C:O:N = 75.9%:17.2%:6.9%) and suggesting that any major contamination was removed by the solvent cleaning.

Results and Discussion

Effect of Air Exposure Before the XPS Measurement

Figure 3 shows the change in the surface composition of the AO-exposed Kapton-H as a function of AO fluence. All data points in Fig. 3 were taken from the surfaces that were not subjected to ambient air exposure. It is clearly shown that the oxygen percentage increased and that of carbon decreased with AO fluence, and they reached the saturated values of approximately 30 and 62% at the AO fluences over 4×10^{17} atoms/cm^2, respectively. The amount of N is relatively independent of AO exposure (7–8%). It is clear from Fig. 3 that AO was adsorbed by the Kapton-H surfaces and contributed to the increase of surface oxygen concentration.

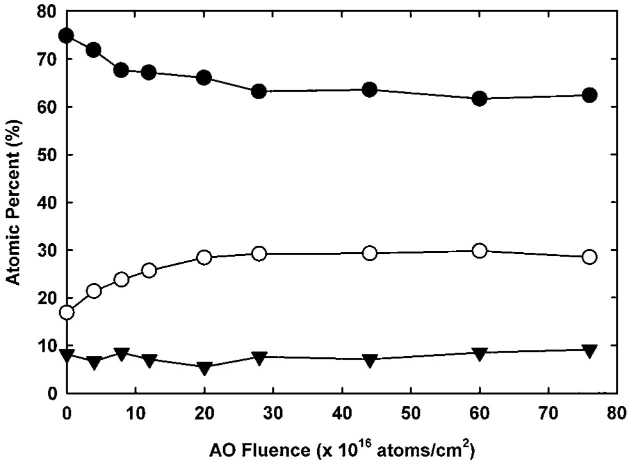


Fig. 3 Surface composition of AO-exposed Kapton-H without air exposure as a function of AO fluence: ●, carbon; ○, oxygen; and ▼, nitrogen.

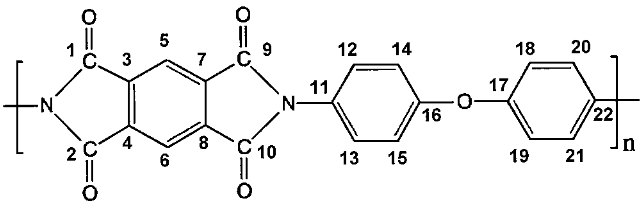


Fig. 4 Repeating unit of Kapton-H.

The adsorption states of oxygen were analyzed by C1s XPS core level spectra. Peak deconvolution protocol was explained in detail in Ref. 9 and will be briefly described in this paper. The protocol is based on the experimental data reported by Beamson and Briggs[17] and on the theoretical results of Silverman et al.[18] Photoelectron signals from eight carbon atoms consisting of ODA (C12, C13, C14, C15, C18, C19, C20, C21 in Fig. 4) appear at 285.0 eV, as do six carbon atoms consisting of PMDA (C3, C4, C5, C6, C7, C8) and two carbon atoms bonded to nitrogen (C11, C22) appear at 286.0 eV; also, carbons in the C-O-C structure (C16, C17) appear at 286.6 eV; and carbon atoms in ketone group bonded with benzene ring and nitrogen (C1, C2, C9, C10) appear at 288.9 eV. Two peaks appeared in the AO-exposed samples at 287.7 eV (carbonyl group bonded to benzene ring and hydrogen) and at 289.6 eV (carbonyl group bonded to benzene ring and OH, namely, carboxyl group). All of the preceding peaks were synthesized by 30% Gaussian–70% Lorentzian distributions with FWHM of 1.6 eV. The background was subtracted using Shirley's method (see Ref. 19).

The C1s peak deconvolution results are indicated in Fig. 5 as a function of AO fluence. From Fig. 5 the formation of carbonyl (287.7 eV; ■) and carboxyl (289.6 eV; □) groups as a result of the AO exposure is obvious. The ketone group (288.9 eV; ∇) also slightly increased with AO exposure. It is clear from Fig. 5 that the oxygen atom reacts to the polymer backbone. From the results shown in Figs. 3 and 5, it is concluded that the AO reacts with Kapton-H and forms surface functional groups (carbonyl and carboxyl). The amount of these surface functional groups are gradually increased with increasing AO fluence until the surface is fully oxidized.

The surface concentration of AO-exposed Kapton-H was also analyzed after ambient air exposure. The results are shown in Fig. 6. The AO-exposed samples were removed from the AO-source chamber and stored in ambient air for one week prior to XPS measurements. Humidity was not controlled during the storage (typically 50–70%). Unlike the results shown in Fig. 3, it is obvious that the oxygen concentration is practically independent of the AO fluence, and it reached the saturated oxygen concentration of approximately 24%, even with AO fluence as low as 4×10^{16} atoms/cm^2. These experimental results indicate that air exposure to the AO-exposed Kapton-H prior to XPS measurements erases the influence of AO fluence, which is clearly observed in Fig. 3. These experimental findings suggest that the XPS analysis of flight samples, which usually does not show remarkable spectral changes compared to control samples, are affected by air exposure and might not reflect actual surface conditions in LEO, that is, the amount of surface oxygen concentration at LEO is expected to be much higher than that analyzed after retrieval.

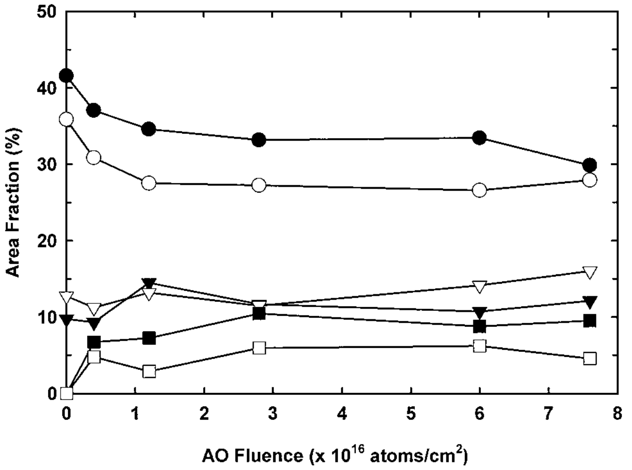


Fig. 5 Synthesized peak intensities of C1s XPS spectra of the AO-exposed Kapton-H without air exposure as a function of AO fluence: ●, 285 eV; ○, 286 eV; ▼, 286.6 eV; ∇, 288.9 eV; ■, 287.7 eV; and □, 289.6 eV.

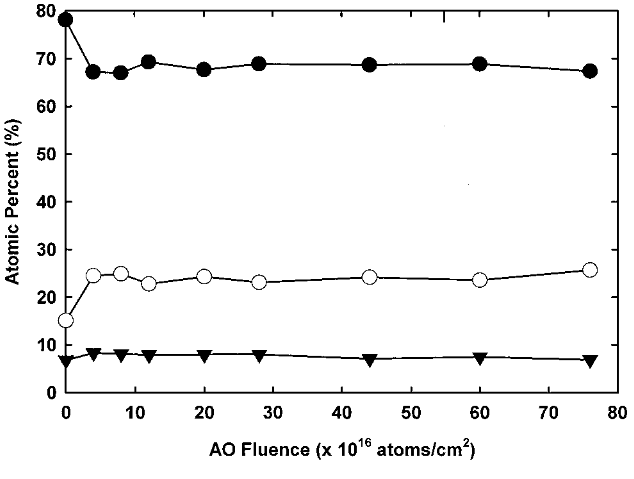


Fig. 6 Surface composition of AO-exposed Kapton-H as a function of AO fluence. All samples were subjected to ambient air exposures prior to XPS measurements: ●, carbon; ○, oxygen; and ▼, nitrogen.

History of Atomic Concentration During Storage

The AO-exposed Kapton-H film with an AO fluence of 7.6×10^{17} atoms/cm^2 was stored in a Teflon® container with a clean air environment of class 10,000, and the XPS spectrum was measured periodically to identify the surface chemistry stability of the AO-exposed Kapton-H. The results are shown in Fig. 7. Time zero in Fig. 7 represents pre-air-exposure data. It was observed that N was relatively stable, whereas the atomic percentage of C increased and that of O decreased with time. Namely, the oxygen and carbon concentrations before air exposure were 29 and 62%, respectively. However, with air exposure of 225 h, the oxygen and carbon concentrations changed to 25 and 69%, that is, saturated. These values are close to the saturated concentration with air exposure shown in Fig. 6 and of the EOIM-3 flight sample (Table 1).

Figure 8 indicates the XPS C1s core level spectra of the AO-exposed Kapton-H films with AO fluence of 7.6×10^{17} atoms/cm^2 without air exposure (Fig. 8a), with air exposure of 220 days (Fig. 8b), and with the flight sample aboard STS-8 (Fig. 8c). Figures 8a and 8b were obtained from the same sample. It is obvious from the comparison of Figs. 8b and 8c that the AO-exposed sample and the flight samples all indicate similar C1s XPS spectra. Both of the samples were analyzed by XPS after ambient air exposure. However, before the ambient air exposure, the AO-exposed surface evidenced the C1s spectrum shown in Fig. 8a, which contains larger amounts of carbonyl (287.7 eV) and ketone (288.9 eV) groups at the surface, that is, a highly oxidized surface. These results indicate that the recoveries of C and O graphed in Fig. 7 were caused by the decrease of carbonyl and ketone groups at the polyimide surface.

Table 1 Comparison of the surface composition of AO-exposed Kapton-H films analyzed by XPS

Samples	Days for air exposure	Atomic percent, %		
		C	O	N
Present results	0	61.7	29.8	8.5
	10	68.7	25.1	6.2
EOIM-3	860	69.2	24.1	6.7

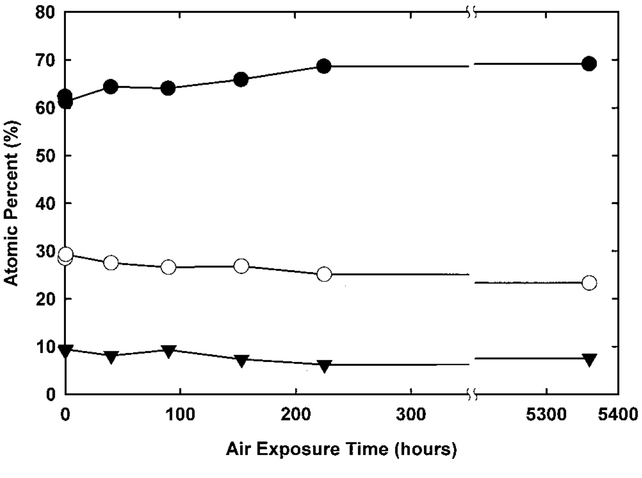
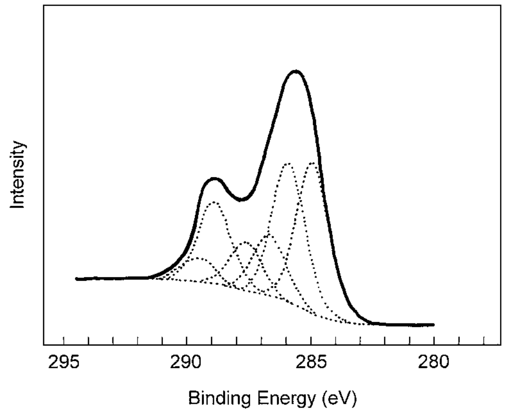
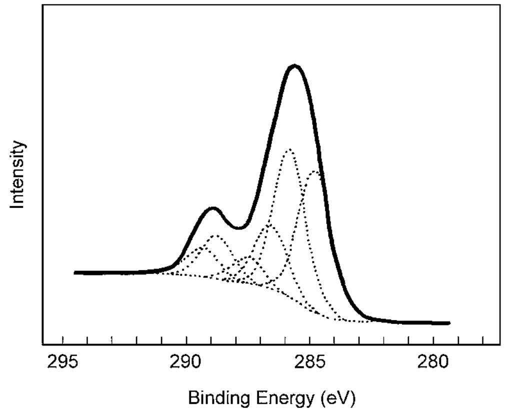


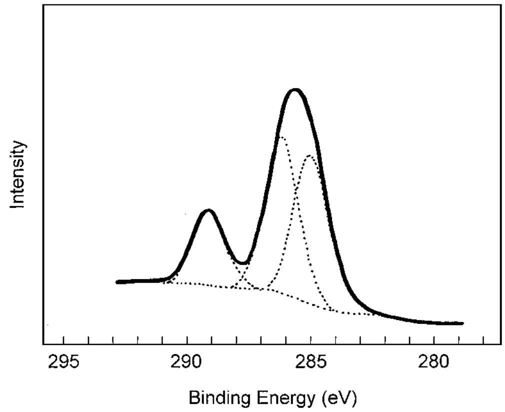
Fig. 7 Effect of storage in the air on surface composition of the AO-exposed Kapton-H film (AO fluence of 7.6×10^{17} atoms/cm^2): ●, carbon; ○, oxygen; and ▼, nitrogen.



a) Before air exposure



b) After air exposure (220 days)



c) Flight sample (STS-8)

Fig. 8 Peak deconvolution results of C1s core level XPS spectra of the AO-exposed Kapton-H films (AO fluence of 7.6 × 10^{17} atoms/cm^2) and flight sample (STS-8).

From the experimental results shown in Fig. 8, it is suggested that the highly oxidized surface, from AO beam exposure, was gradually deoxidized by surface relaxation processes, and the influence of AO exposure was deteriorating lost with time. The deoxidation process would involve both gasification of volatile products (maybe carbon monoxide and/or carbon dioxide) and the decomposition of unsaturated bonds between carbon and oxygen. However, the mechanism of deoxidation is not clear at this time. A similar XPS C1s core level spectrum showing a high content of carbonyl and ketone groups was reported by Golub et al.[20] They used a radio frequency (RF) thermal AO source in order to simulate an AO environment in LEO. They considered the difference in the C1s XPS peak shape of the AO-exposed Kapton-H with the STS-8 flight sample, which is close to that shown in Fig. 8c, to be caused by the large amount of O_2 existing in the afterglow region of RF plasma ($O_2/O \sim 10$ in RF, $O_2/O \sim 0.1$ in LEO). However, a similar XPS C1s core level spectrum was obvious even in the oxidation condition of $O_2/O \sim 1$ with hyperthermal AO in this study. Also, spectral change with time after exposure (Fig. 8b) suggests that such highly oxidized states are commonly formed by AO exposure and are not caused by O_2 content under oxidation conditions.

The experimental results obtained in this study indicate that the postretrieval surface analysis of flight samples, which have been carried out on many space shuttle missions, might not reflect the actual Kapton-H surfaces in LEO environment, meaning that the surface has been altered by ambient air exposure. These results suggest that a method of preserving specimen surfaces needs to be developed for future flight experiments. For ground-based studies the effect of air exposure must be considered when evaluating surfaces after AO exposure.

Comparison with Grossman's Results

Grossman et al.[6] have reported on the effect of air exposure to the AO-exposed Kapton-H film. They reported the decrease in surface oxygen concentration under AO exposure and concluded that the increases in oxygen concentration observed after flight missions and in ground-based studies are caused by ambient air exposure prior to the XPS measurements. Our experimental data reported herein showed a completely opposite behavior: oxygen concentration increased with AO fluence, and it decreased after ambient air exposure. The XPS C1s core level spectra of their specimens showed the almost complete loss of the ketone group, which did not recover even after ambient air exposure. The C1s spectrum of flight samples usually showed an increase of carbonyl and ketone groups and the presence of the carboxyl group (Fig. 8c). Thus, the report of Grossman et al. does not explain the spectral characteristics of the flight samples. In contrast, the XPS data obtained in this study indicate the oxidation of the polymer surface under AO beam exposure along with the formation of additional ketone and carbonyl groups, which may not be stable in routine storage, and also the formation of the stable carboxyl group. The spectral changes of the AO-exposed Kapton-H in this study agree with the analytical results of flight samples[20,21] and ground-based studies,[9–11, 20–22] which indicate the oxidation of polymer surfaces caused by AO bombardment. The reason why their results showed an opposite behavior is not clear. Carbon contamination from their AO source is one of the possibilities. However, this is only speculation. The details of the beam diagnostics and the quality of the vacuum will be needed to clarify the origin of their results.

Conclusions

Herein, further research on the effect of air exposure on AO-exposed Kapton-H has been detailed. Oxygen concentration of the AO-exposed Kapton-H without air exposure increased with AO fluence and then reached a saturated value of approximately 30%. These results deny the results reported by Grossman et al.[6] but explain many of the flight and ground-based results already reported. It is concluded from the XPS C1s core-level spectra that AO exposure creates highly oxidized states even without air exposure. Further ambient air exposure to the AO-exposed Kapton-H reduces carbonyl and ketone groups at the surface and leads to a decrease of surface oxygen concentration. In contrast, air exposure prior to XPS measurement provides a steady-state oxidized surface that is practically independent of AO fluence. These results clearly indicate that the effect of air exposure should be taken into consideration in order to investigate the effects on the surfaces of materials in LEO environment.

Acknowledgments

This study was supported in part by the Grant-in-Aid for Scientific Research and the Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology. Partial support also came from the Japan Space Forum through the Space Utilization Research Promotion. The authors acknowledge S. Y. Chung and T. K. Minton of the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, for supplying the EOIM-3 flight sample and the XPS spectra of the STS-8 flight sample.

References

[1] Minton, T. K., "Protocol for Atomic Oxygen Testing of Materials in Ground-Based Facilities, Version Number 2," Jet Propulsion Lab., Publication 95-17, Pasadena, CA, Sept. 1995.

[2] Visentine, J. T., "Atomic Oxygen Effects Measurements for Shuttle Missions STS-8 and 41G," NASA TM-100459, Sept. 1988.

[3] Chung, S. Y., Brinza, D. E., Minton, T. K., Stiegman, A. E., Kenny, J. T., and Liang, R. H., "Flight- and Ground-Test Correlation Study of BMDO SDS Materials: Phase 1 Report," Jet Propulsion Lab., Publication 93-31, Pasadena, CA, Dec. 1993.

[4] Liang, R. H., Gupta, A., Chung, S. Y., and Oda, K. L., "Mechanistic Studies of Polymeric Samples Exposed Aboard STS-8," Jet Propulsion Lab., Publication 87-25, Pasadena, CA, Oct. 1987.

[5] Minton, T. K., Zhang, J., Garton, D. J., and Seale, J. W., "Collision-Assisted Erosion of Hydrocarbon Polymers in Atomic Oxygen Environment," *High Performance Polymers*, Vol. 12, No. 1, 2000, pp. 27–42.

[6] Grossman, E., Lifshitz, Y., Wolan, J. T., Mount, C. K., and Hoflund, G. B., "In Situ Erosion Study of Kapton Using Novel Hyperthermal Oxygen Atom Source," *Journal of Spacecraft and Rockets*, Vol. 36, No. 1, 1999, pp. 75–78.

[7] Hoflund, G. B., and Weaver, J. F., "Performance Characteristics of a Hyperthermal Oxygen Atom Generator," *Measurement in Science and Technology*, Vol. 53, No. 3, 1994, pp. 201–205.

[8] Whitaker, A. F., and Jang, B. Z., "The Mass Loss Mechanism of Polyimide in a Radio Frequency Induced Atomic Oxygen Environment," *Journal of Applied Polymer Science*, Vol. 48, 1993, pp. 1341–1367.

[9] Golub, M. A., and Wydeven, T., "Reaction of Atomic Oxygen (O(^{3}P)) with Various Polymer Films," *Polymer Degradation and Stability*, Vol. 22, 1998, pp. 325–338.

[10] Kinoshita, H., Tagawa, M., Umeno, M., and Ohmae, N., "Surface Reaction of a Low Flux Atomic Oxygen Beam with a Spin-Coated Polyimide Film: Translational Energy Dependence on the Reaction Efficiency," *Transactions of the Japan Society for Aeronautics and Space Sciences*, Vol. 41, No. 132, 1998, pp. 94–99.

[11] Kinoshita, H., Yokota, K., Tagawa, M., and Ohmae, N., "The Degradation of Polyimide Films due to the Hyperthermal Atomic Oxygen Exposures: In-Situ Mass Loss Measurement and Effect of Air Exposures," *Proceedings of the 8th International Symposium on Materials in a Space Environment and 5th International Space Conference, Protection of Materials and Structures from the LEO Space Environment*, edited by J. Kleiman and E. Werling, Centre National d'Etudes Spatiales, Toulouse, France, 2000, pp. 581–588.

[12] Kinoshita, H., Ikeda, J., Tagawa, M., Umeno, M., and Ohmae, N., "A Fast Atomic Oxygen Beam Facility with In-Situ Testing/Analysis Capabilities," *Review of Scientific Instruments*, Vol. 69, No. 6, 1998, pp. 2273–2277.

[13] Caledonia, G. E., Krech, R. H., and Green, B. D., "A High Flux Source of Energetic Oxygen Atoms for Material Degradation Studies," *AIAA Journal*, Vol. 25, No. 1, 1987, pp. 59–63.

[14] Caledonia, G. E., and Krech, R. H., "Energetic Oxygen Atom Materials Degradation Studies," AIAA Paper 87-0105, Jan. 1987.

[15] Matijasevic, V., Garwin, E. L., and Hammond, R. H., "Atomic Oxygen Detection by Silver-Coated Quartz Deposition Monitor," *Review of Scientific Instruments*, Vol. 61, No. 2, 1990, pp. 1747–1749.

[16] Cazaubon, P. B., and Thomas, B. R., "Utilization of Mass Spectrometry for Characterization of the Interaction of Hyperthermal O-Atom Beams with Materials," *Proceedings of 7th International Symposium on Material in a Space Environment*, edited by A. Paillous, ESA Publications Div., Noordwijk, The Netherlands, 1997, pp. 185–193.

[17] Beamson, G., and Briggs, D., *High Resolution XPS of Organic Polymers, The Scienta ESCA300 Database*, Wiley, New York, 1992, pp. 214, 215.

[18] Silverman, B. D., Bartha, J. W., Clabes, J. G., Ho, P. S., and Rossi, A. R., "Molecular Orbital Analysis of the XPS Spectra of PMDA-ODA Polyimide and Its Polyamic Acid Precursor," *Journal of Polymer Science*, Vol. A24, 1986, pp. 3325–3333.

[19] Briggs, D., and Seah, M. P., *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, Wiley, New York, 1984, pp. 255–258.

[20] Golub, M. A., Wydeven, T., and Cormia, R. D., "ESCA Study of Kapton Exposed to Atomic Oxygen in Low Earth Obit or Downstream from a Radio-Frequency Oxygen Plasma," *Polymer Communications*, Vol. 29, 1988, pp. 285–288.

[21] Kleiman, J. I., Gudimenko, Y. I., Iskanderova, Z. A., Tennyson, R. C., Morison, W. D., McIntyre, M. S., and Davidson, R., "Surface Structure and Properties of Polymers Irradiated with Hyperthermal Atomic Oxygen," *Surface and Interface Analysis*, Vol. 23, 1995, pp. 335–341.

[22] Gotoh, K., Tagawa, M., Ohmae, N., Kinoshita, H., and Tagawa, M., "Surface Characterization of Atomic Oxygen Beam-Exposed Polyimide Films Using Contact Angle Measurements," *Colloid and Polymer Science*, Vol. 279, 2001, pp. 214–220.

I. D. Boyd
Associate Editor