

# Erosion properties of polyimide as a monitoring material of atomic oxygen environment in space (3): Synergistic effect of atomic oxygen and ultraviolet

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Erosion property of polyimide was studied through the ground-based synergistic studies. Hyperthermal atomic oxygen and 172nm VUV exposed to polyimide and polyethylene in various conditions. *In-situ* mass loss measurement of polymers during the atomic oxygen and/or VUV exposures was achieved with a quartz crystal microbalance. The effect of simultaneous ultraviolet exposure on the atomic oxygen-induced erosion was observed at the ultraviolet intensity of 0.5-2.6 x 10<sup>-15</sup> mJ/atom for polyethylene. In contrast, the similar effect was observed in polyimide at the relative ultraviolet intensities one order greater than that of polyethylene. It was also found that the effect of 172 nm ultraviolet was different in polyimide and polyethylene; i.e., photo-induced erosion was observed only for polyethylene. It was concluded that polyimide is less sensitive to the simultaneous ultraviolet exposure during atomic oxygen bombardment, and thus evaluated as a better material for measuring atomic oxygen fluence in space.

## 1. Introduction

There exist many environmental factors in low Earth orbit (LEO) such as microgravity, thermal cycling, plasma, ultraviolet, radiation, neutral gas and space debris. In particular, one of the most important factors that gives serious damages to many polymeric materials used at the exterior surfaces of spacecraft is atomic oxygen, which is a dominant neutral species in LEO. Due to the difficulty to simulate atomic oxygen environment in laboratory, details of the erosion properties are still not understood deeply. Many polymeric materials are exposed to real space environment as well as simulated atomic oxygen environment to study their survivability. Since the absolute fluence of atomic oxygen in material exposure test is difficult to determine, Kapton equivalent fluence is widely accepted as a method to measure atomic oxygen fluence. In this method, the material erosion of a targeted polymer is compared with that of Kapton-H whose erosion rate is assumed to be 3.0 x 10<sup>-24</sup> cm<sup>3</sup>/atom. However, it is natural to consider that the material response with hyperthermal atomic oxygen collision depends on a material. It is thus emphasized that the erosion properties of Kapton-H (PMDA-ODA polyimide) in various exposure conditions have to be well-understood as a reference material for material erosion tests. Not only PMDA-ODA polyimide, but also polyethylene and fluorinated polymer should be studied in the same manner since ASTM-E2089, which describes standard method of atomic oxygen testing, requires the measurement of the erosion rate of these polymers as standard materials [1]. One of the key points on erosion properties is the synergistic effect of atomic oxygen and ultraviolet. Among three standard

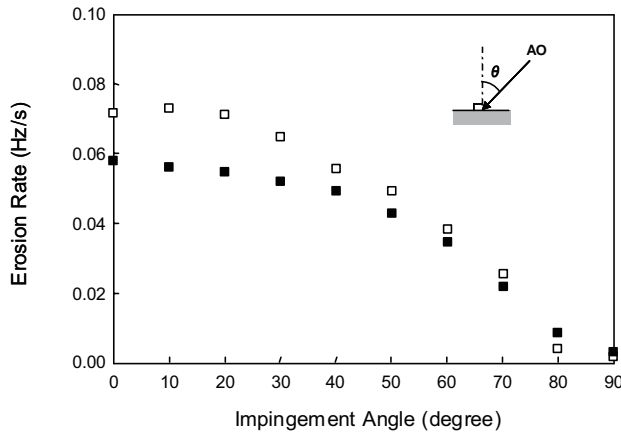
materials, it is recognized that fluorinated polymer is sensitive to ultraviolet. For atomic oxygen measurement, a material insensitive to ultraviolet should be selected.

In this paper, polyethylene and polyimide were compared as an atomic oxygen fluence monitoring material under the bombardment of hyperthermal atomic oxygen and 172 nm ultraviolet radiation. The effect of simultaneous ultraviolet exposure on the atomic oxygen-induced erosion of polyethylene and polyimide was discussed based on the ground-based experimental results.

## 2. Experimental details

The samples used in this experiment were low-density polyethylene (LDPE) and pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide films. Both of the films were spin-coated on QCM sensor crystals. The polyethylene solution containing 0.3 g of LDPE (average molecular weight: 6500) in 40 ml xylene was prepared for polyethylene film. Precursor of PMDA-ODA polyimide was spin-coated on a QCM sensor crystal and then annealed at 150 °C 1h and at 300 °C 1h.

A space environment simulation facility at Kobe University was used in this study. This facility equipped a laser detonation atomic oxygen beam source, which was originally designed by Physical Sciences Inc., as a hyperthermal atomic oxygen source. An excimer light source with a wavelength of 172 nm was used as an ultraviolet source in this study. Axes of the atomic oxygen beam and the ultraviolet crossed 90° and the sample was rotatable with the axis perpendicular both to atomic oxygen and ultraviolet. In this configuration, the effective atomic oxygen and



**Figure 1** Erosion rates of the polyethylene and the polyimide during atomic oxygen exposures measured from the resonant frequency of the QCM. ■: polyethylene (AO Flux:  $6.0 \times 10^{14}$  atoms/cm<sup>2</sup>/s), □: polyimide ( $6.8 \times 10^{14}$  atoms/cm<sup>2</sup>/s).

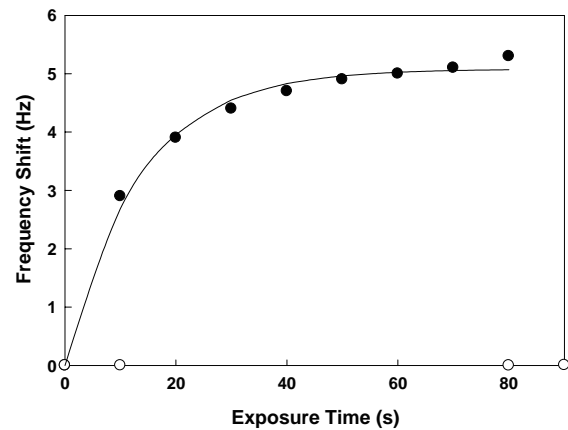
ultraviolet fluxes can be changed by rotating the sample [2]. The maximum atomic oxygen flux and ultraviolet flux at the sample position were  $6.0 - 14.0 \times 10^{14}$  atoms/cm<sup>2</sup>/s and  $0.55 \text{ mW/cm}^2$ , respectively. The erosion rate of polymer film was calculated from the resonant frequency of QCM during the atomic oxygen beam and/or ultraviolet exposures. The sample temperature was kept at 311 K during the experiment by the temperature-controlled circulating water system.

### 3. Results and discussion

#### 3.1 Atomic oxygen-induced polymer erosion

In the experiment reported herein, the relative intensity of atomic oxygen and ultraviolet was adjusted by rotating the QCM sample along with the axis, which is perpendicular to the axes both to atomic oxygen and ultraviolet. However, in this experimental configuration, the incident angle of atomic oxygen at polymer surface is changed when relative atomic oxygen/ultraviolet intensity is adjusted. Therefore, it is necessary to investigate the effect of incident angle of atomic oxygen and ultraviolet on the polymer erosion prior to the quantitative analysis of synergistic effect of atomic oxygen and ultraviolet.

From the previous result regarding the incident angle dependence of atomic oxygen on the erosion of polyimide-coated QCM, it was observed that the erosion rate is linear with time in every incident angle and the erosion rate decreased with increasing incident angle with following a cosine distribution [3]. The experimental result on the incident angle dependence of atomic oxygen-induced erosion of polyethylene showed a similar tendency with those reported on



**Figure 2** Frequency shift of the polyimide-QCM during ultraviolet exposures ( $4.5 \text{ mW/cm}^2$  at normal incidence). ●: pre-exposed to atomic oxygen ( $2.3 \times 10^{18}$  atoms/cm<sup>2</sup>), ○: without pre-exposure to atomic oxygen. Note that atomic oxygen was not exposed during the measurements. Solid line is the best-fit curve using equation 1.

polyimide film as shown in Figure 1 [4]. However, it is not a simple cosine distribution ( $\cos^{0.87} \theta$ ) compared with polyimide ( $\cos^{1.0} \theta$ ). The fact that the incident angle dependence of the erosion rate follows closely to a cosine law indicates that the erosion rates of polyethylene and polyimide are both basically proportional to the effective flux of atomic oxygen. It was thus concluded that the reaction yield of atomic oxygen with these polymers is identical to the incident angle.

It was observed from atomic force microscopy that the surfaces of polymers were roughened by atomic oxygen exposure. Therefore, an actual incident angle of oxygen atom to a surface moiety is not directly related to macroscopic incident angle because surface is not atomically flat due to the presence of microscale roughness. Thus, the macroscopic erosion rate of polymer is simply reflected the effective fluence of atomic oxygen which follows cosine law with the macroscopic incident angle.

#### 3.2 Ultraviolet-induced polymer erosion

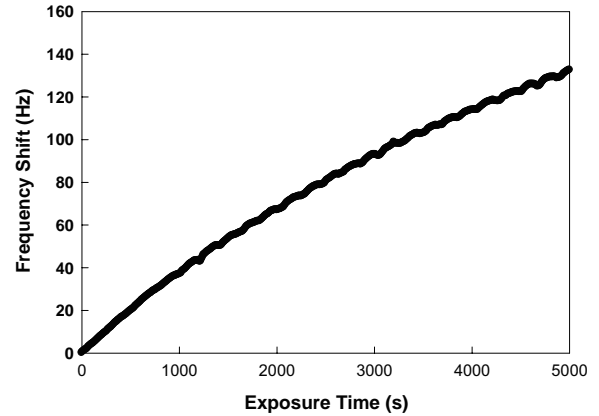
Effect of incident angle of ultraviolet radiation on polyethylene and polyimide erosion was also studied [2]. Figure 2 shows the frequency shift of the polyimide-coated QCM after ultraviolet exposures at normal incidence (solid circle). The flux of 172 nm ultraviolet radiation was  $4.5 \text{ mW/cm}^2$  at normal incidence. Note that the sample surface was exposed to atomic oxygen ( $2.3 \times 10^{18}$  atoms/cm<sup>2</sup>) prior to ultraviolet irradiation in order to avoid the non-linear phenomena. As shown in Figure 2, resonant frequency of the QCM was increased when ultraviolet

starts irradiating due to desorption of the adsorbed gaseous molecules. However, the slope of the curve gradually decreases with time. It has been analyzed that the curve can be fit in the form of

$$\Delta f = A[1 - \exp(-ct)] \quad (1),$$

where  $\Delta f$  is the frequency shift of QCM,  $A$  and  $c$  are the constant, and  $t$  is the exposure time of ultraviolet radiation. The fact that the experimental data was fit by the equation (1) suggests that the surface oxidizing species (CO or CO<sub>2</sub>) are desorbed by ultraviolet exposure (photo-induced desorption). This is confirmed by the fact that the no mass loss was detected by the ultraviolet exposure without pre-oxidation process (open circle in Figure 2). The incident angle dependence of ultraviolet radiation was also examined. By increasing the incident angle of ultraviolet radiation, desorption rate of the oxidized species is decreased. This is explained by the decrease in effective photon flux of ultraviolet radiation.

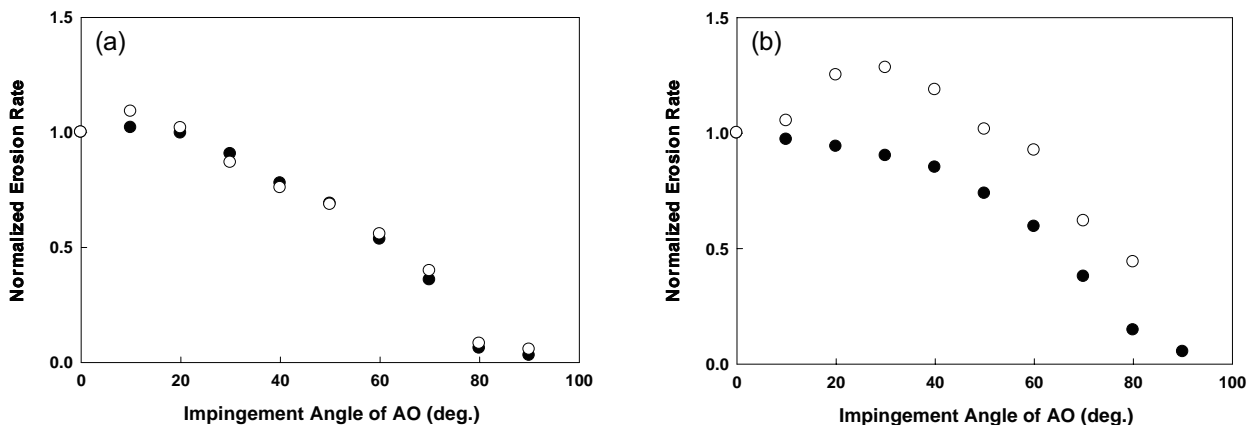
In contrast, polyethylene showed a different tendency of mass change with ultraviolet exposure. Figure 3 showed a typical mass change of polyethylene under 172 nm ultraviolet exposure (4.5 mW/cm<sup>2</sup>). Mass of the polyethylene shows a decrease with exposure time. Unlike polyimide, the saturation of mass loss is not obvious in polyethylene. The absolute mass lost by the ultraviolet exposure was much greater than that of polyimide. This mass loss property suggests that not only the adsorbed gaseous molecules, but also the polyethylene structure is decomposed by the 172 nm ultraviolet exposure.



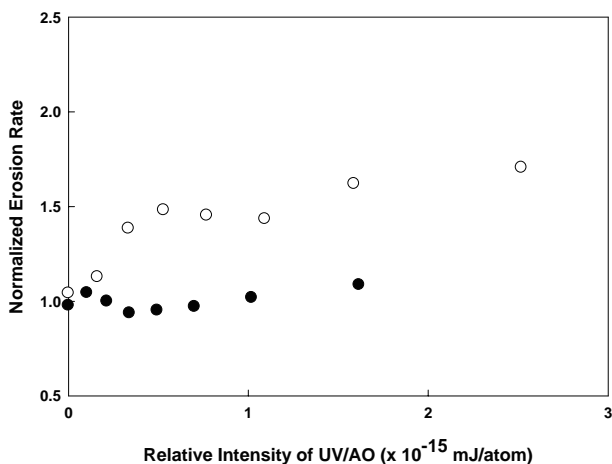
**Figure 3** Frequency shift of the polyethylene- QCM during ultraviolet exposures. Ultraviolet intensity: 4.5 mW/cm<sup>2</sup>. The sample surface was oxidized by atomic oxygen prior to the ultraviolet exposure ( $5.9 \times 10^{17}$  atoms/cm<sup>2</sup>).

### 3.3 Synergistic effect of atomic oxygen and ultraviolet

Atomic oxygen and ultraviolet beams irradiated polymer-coated QCM simultaneously and the erosion rate was recorded by the resonant frequency of QCM. The maximum atomic oxygen flux and ultraviolet flux at the sample position were  $6.8 \times 10^{14}$  atoms/cm<sup>2</sup>/s and 0.55 mW/cm<sup>2</sup>, respectively. Figure 4 (a) and (b) show the erosion rates of polyimide and polyethylene under simultaneous atomic oxygen and ultraviolet exposure condition as a function of incident angle of atomic oxygen. The abscissa is the incident angle of



**Figure 4** Normalized erosion rates of polyimide and polyethylene during atomic oxygen exposure (●) and simultaneous atomic oxygen and ultraviolet exposure (○). (a): polyimide, atomic oxygen flux:  $6.8 \times 10^{14}$  atoms/cm<sup>2</sup>/s, ultraviolet flux: 0.40 mW/cm<sup>2</sup>, (b): polyethylene, atomic oxygen flux:  $6.0 \times 10^{14}$  atoms/cm<sup>2</sup>/s, ultraviolet flux: 0.55 mW/cm<sup>2</sup>.



**Figure 5** The relationship between the relative intensity of UV/AO and the normalized erosion rate. (○): polyethylene, (●): polyimide.

atomic oxygen; i.e., the incident angle of  $0^\circ$  means 100 % atomic oxygen and 0 % ultraviolet, and the incident angle of  $90^\circ$  means 0 % atomic oxygen and 100 % ultraviolet. The longitude is the normalized erosion rate. If no ultraviolet effect was observed, the data points with ultraviolet exposure (open circle) should follow the cosine function. This is the case for polyimide (Figure 4 (a)). In contrast, the erosion rates with ultraviolet exposure (open circle) do not follow cosine function and are 30 to 100 % greater than those without ultraviolet exposures (solid circle) in the case of polyethylene (Figure 4 (b)). It was clear that simultaneous ultraviolet exposure affects the atomic oxygen-induced erosion of polyethylene. The relationship between the relative intensities of ultraviolet per atomic oxygen (UV/AO ratio) and the normalized erosion rate was replotted in Figure 5. The erosion rate of atomic oxygen-induced polyethylene was enhanced 30-80 % at the relatively low UV intensities at UV/AO ratio of  $0.5\text{-}2.6 \times 10^{-15}$  mJ/atom, where polyimide does not show any enhancement of mass loss with ultraviolet exposure. As reported elsewhere [2], the synergistic effect of atomic oxygen and 172 nm ultraviolet on polyimide was obvious when ultraviolet intensity is higher than  $1 \times 10^{-14}$  mJ/atom. However, it was not obvious in the UV/AO ratio lower than  $10^{-15}$  mJ/atom, as demonstrated in Figure 5. In contrast, polyethylene shows a clear synergistic effect of ultraviolet irradiation even in the UV/AO ratio lower than  $10^{-15}$  mJ/atom.

#### 4. Conclusion

Synergistic effects on atomic oxygen-induced erosion of polyimide and polyethylene with 172 nm ultraviolet

were investigated using QCM. In order to change the relative intensity of atomic oxygen and ultraviolet, the polymer sample on QCM was rotated with an axis perpendicular both to the axes of atomic oxygen and ultraviolet. It was found that no ultraviolet-induced erosion was observed for polyimide without atomic oxygen exposure. In contrast, a clear mass loss was obvious when polyethylene was exposed to 172 nm ultraviolet even without atomic oxygen. It was observed that the atomic oxygen-induced erosion of polyethylene increased 30-80 % by a simultaneous ultraviolet exposure in the UV/AO ratio of  $10^{-15}$  mJ/atom. The increase in mass-loss was considered due to the photo-induced decomposition of carboxyl group and C-C backbone of polyethylene. Since the synergistic effect for polyethylene was obvious at the ultraviolet intensities one order lower than that for polyimide, it was concluded that polyimide is a better material as a witness sample for measuring atomic oxygen fluence in LEO from the viewpoint of the synergistic effect with vacuum ultraviolet [5].

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