/995-//7484

# THE SURFACE PROPERTIES OF FLUORINATED POLYIMIDES EXPOSED TO VUV AND ATOMIC OXYGEN

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## ABSTRACT

The effect of atomic oxygen flux and VUV radiation alone and in combination on the surface of fluorinated polyimide films was studied using XPS spectroscopy. Exposure of fluorinated polyimides to VUV radiation alone caused no observable damage to the polymer surface, while an atomic oxygen flux resulted in substantial oxidation of the surface. On the other hand, exposure to VUV radiation and atomic oxygen in combination caused extensive oxidation of the polymer surface after only 2 minutes of exposure. The amount of oxidised carbon on the polymer surface indicated that there is aromatic ring opening oxidation. The changes in the O1s/C1s, N1s/C1s and F1s/C1s ratios suggested that an ablative degradation process is highly favourable. A synergistic effect of VUV radiation in the presence of atomic oxygen is clearly evidenced from the XPS study. The atomic oxygen could be considered as the main factor in the degradation process of fluorinated polyimide films exposed to a low earth orbit environment.

## INTRODUCTION

A need exists for high temperature (200-300°C) stable, flexible polymeric film and coating materials that have high optical transparency in the 300-600 nm region of the solar spectrum for applications in space components, such as insulation blankets, solar cells and thermal control coating systems. Although several classes of polymers are available which are transparent and colourless, such as polyesters or aliphatic polyimides, many of these materials have limited long-term thermal stability. On the other hand, commercially available aromatic polyimides are thermally stable, however they have poor transparency in the visible region of the solar spectrum of interest for space applications. Furthermore, the transparency of these commercial polyimides is reduced dramatically after exposure to the space environment. Several series of linear aromatic polyimide films having maximum optical transparency have been prepared by St. Clair et al. (1). The optical transparency was achieved by using highly purified monomers and the incorporation of meta-linked diamines, bulky electron-withdrawing groups and flexible linkages into the molecular structure, in order to reduce the electronic interactions between polymer chains (2).

Spacecraft in low earth orbit are subjected to significant levels of high energy radiation, including UV and VUV wavelengths. The effects of UV radiation are enhanced over those at the surface of the earth, where the only incident wavelengths are greater than 290 nm. In low earth orbit the incident UV wavelengths extend below 290 nm into the VUV region, where the Lyman $\alpha$ emissions of atomic hydrogen occur at 121 nm. In addition to electromagnetic radiation, in low earth orbit polymer materials may also be subjected to
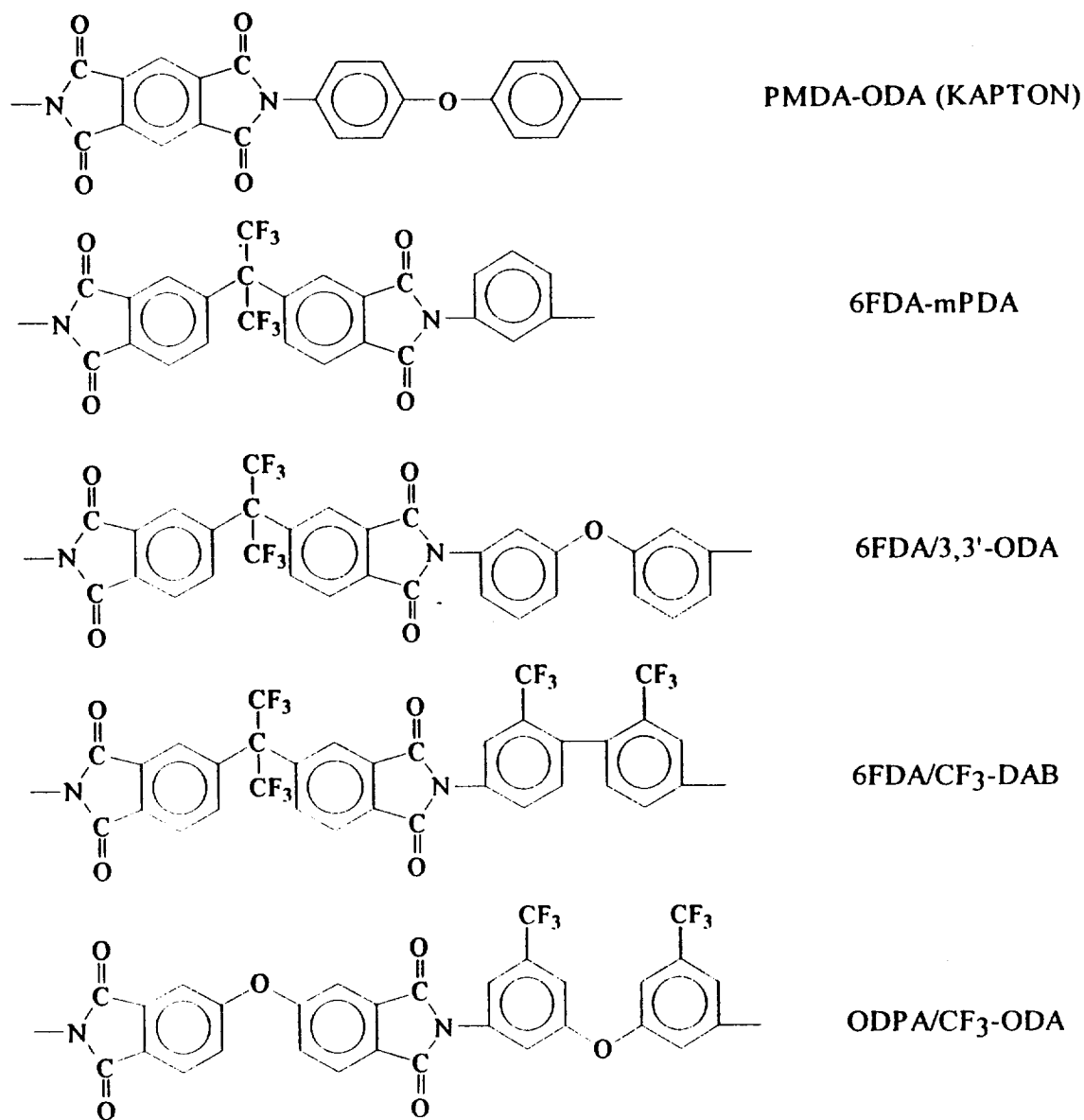
PMDA-ODA (KAPTON)

6FDA-mPDA

6FDA/3,3'-ODA

6FDA/CF₃-DAB

ODPA/CF₃-ODA

**Figure 1**: The chemical structure of fluorinated polyimides and Kapton.

bombardment by atomic oxygen, which will result in direct oxidation of the polymer. Thus polymeric materials for space applications must exhibit a resistance to damage by both VUV radiation and atomic oxygen attack.

As part of a materials evaluation program for space applications, we studied the effects of a simulated low earth orbit environment of VUV and atomic oxygen on a series of fluorinated polyimide films compared to a Kapton reference (see Fig. 1). The major objective of this paper is to assess the effect of atomic oxygen, VUV radiation alone and atomic oxygen and VUV radiation in combination on polyimides surfaces, by using X-ray photoelectron spectroscopy (XPS).

## EXPERIMENTAL

Atomic oxygen and VUV radiation was generated in a specially designed oxygen plasma apparatus, by applying a radio frequency (RF) to oxygen molecules in a flowing system. Pressures of 0.2 torr were used in the apparatus and identical RF power and oxygen flow rates were used in each experiment. Irradiation of the fluorinated polyimide films by VUV in the absence of the atomic oxygen was
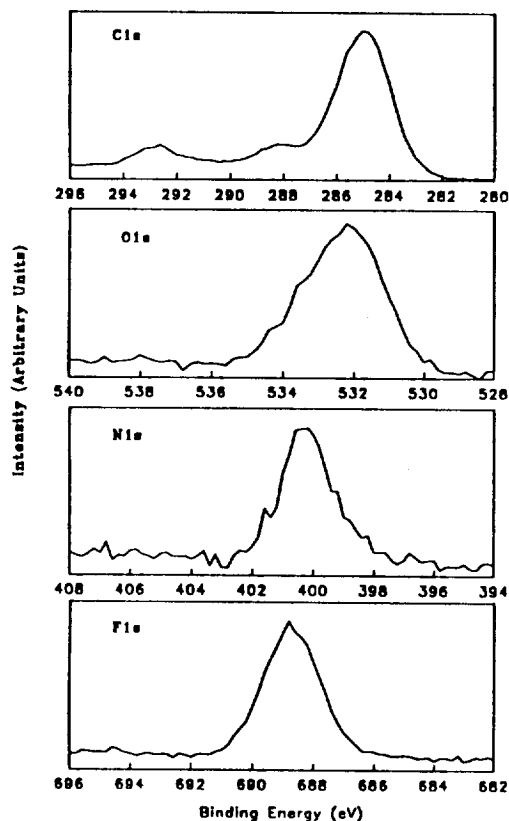


Figure 2: XPS survey spectra of fluorinated polyimide films before and after exposure to VUV and atomic oxygen.



Figure 3: XPS multiplex spectra for C1s, O1s, N1s and F1s regions of unirradiated 6FDA/3,3'-ODA polyimide film.

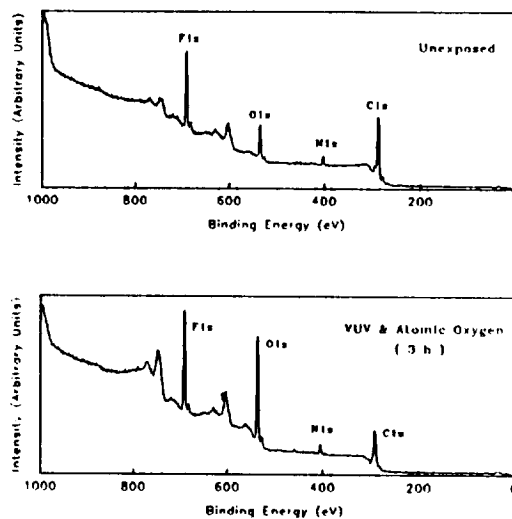achieved by the insertion of a $MgF_2$ window in front of the sample. Exposure of the films to atomic oxygen in the absence of VUV was accomplished by placing the films in a detachable side arm, where only the flow of atomic oxygen was allowed to reach the sample. The XPS spectra were obtained from a Perkin-Elmer PHI Model 560 ESCA/SAM multi-technique analysis system. Un-monochromated Mg $K\alpha_{1,2}$ (1253.6 eV) X-ray radiation source (400 watt, 15 KV) was used.

## RESULTS AND DISCUSSION

Surface analyses of fluorinated polyimide films were conducted using XPS spectroscopy. Typical XPS survey spectra (at 100 eV pass energy) of irradiated and un-irradiated polymer films are shown in Fig 2. It is clearly illustrated from the irradiated polyimide film that the ratio of the O1s/C1s has changed substantially after exposure to VUV and atomic oxygen. The multiplex spectrum (at 25 eV pass energy) of un-irradiated polyimide film for the C1s, O1s, N1s and F1s regions are shown in Fig. 3 for 6FDA 3,3-ODA in comparison to Kapton (Fig 4). The measured ratios of O1s/C1s, N1s/C1s and F1s/C1s were comparable with the theoretical values, which suggests no significant contamination of the polymer surface. The
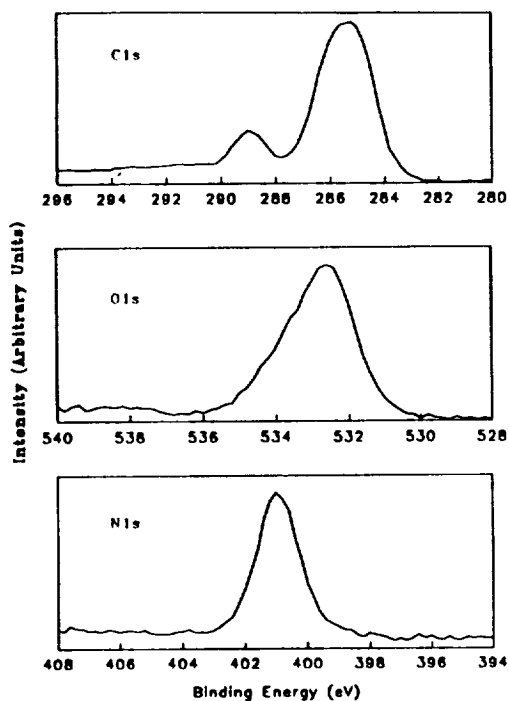
C1s region exhibits three distinct peaks at 285 eV, 288.5 eV and 292.5 eV, which represent the C-C plus C-H, C-O and C-F binding energies respectively. The C-N group, which is less sensitive in the XPS analysis than C-C, occurs at 285.2 eV, and is over shadowed by the stronger C-C peak.

Exposure of fluorinated polyimide films to VUV radiation in the presence of atomic oxygen resulted in extensive oxidation of the polymer surface. Fig 5 shows the changes in the C1s, O1s, N1s and F1s regions due to exposure to VUV and atomic oxygen, while Fig 6 shows the XPS spectra of Kapton exposed to similar conditions. It is clear from Fig. 5 and 6 that the C1s region has changed dramatically after only 2 minutes of exposure. The intensity of the C-O
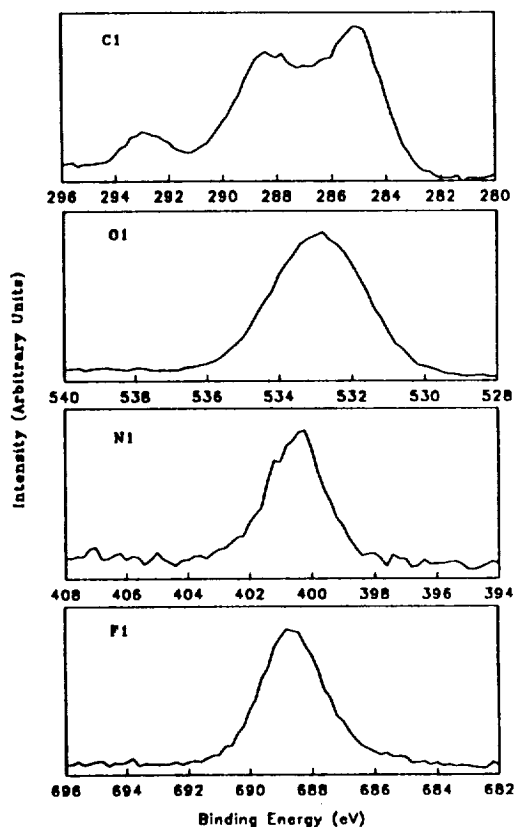
**Figure 4**: XPS multiplex spectra for C1s, O1s, and N1s regions of unirradiated Kapton.

binding energy peak has increased relative to that of C-C, which indicates an increase in surface oxidation. Comparing the O1s region of the exposed polymer film with the same region of the unexposed polymer, shows a broadening of the O1s peak, which suggests the possible presence of different oxidation species on the polymer surface, while the N1s and F1s peaks dose not show any significant change.

Fig. 7 shows a plot of the changes in O1s/C1s ratios with the irradiation time for four different fluorinated polyimide structures in comparison to Kapton. The ratio of O1s/C1s increased sharply after only a few minutes of exposure to VUV and atomic oxygen, and then rapidly reached a plateau for all five polymers after about 10 minutes. The rapid oxidation of the entire surface, and the plateau appearance of the O1s/C1s ratio after short time of exposure to VUV and atomic oxygen could be explained either by



**Figure 5**: XPS multiplex spectra for C1s, O1s, N1s and F1s regions of 6FDA/3,3'-ODA polyimide film exposed to VUV radiation and atomic oxygen.

formation of an oxidised protective layer which is resistant to further oxidation, or by a simultaneous oxidation and ablation processes affecting the polymer surface. The results obtained from the FTIR, ESR and UV absorption spectroscopies suggested that there was a continuous ablation of the polymer surface, which agreed with the latter postulate (3). The initially formed oxidised species on the polymer surface undergo further reaction upon exposure to UV radiation to produce low molecular weight oxidised products, which are removed from the surface by volatilisation. This would result in a continuous renewal of the surface, with a continuous weight loss by erosion.

On the other hand, examination of the changes in the N1s/C1s and the F1s/C1s ratios, revealed a similar rapid increase and levelling off, which could only be related to a reduction in the carbon atom concentration on the polymer surface. This must occur by surface ablation and loss of low molecular weight oxidised species from the polymer surface.
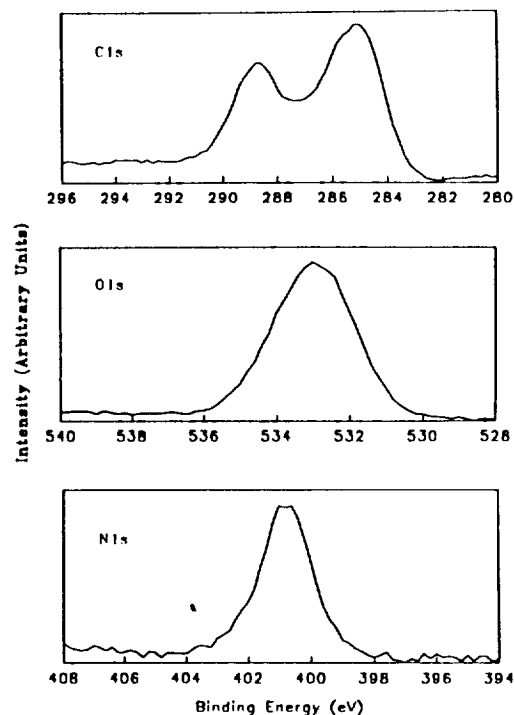


Figure 6: XPS multiplex spectra for C1s, O1s and N1s regions of Kapton exposed to VUV radiation and atomic oxygen.
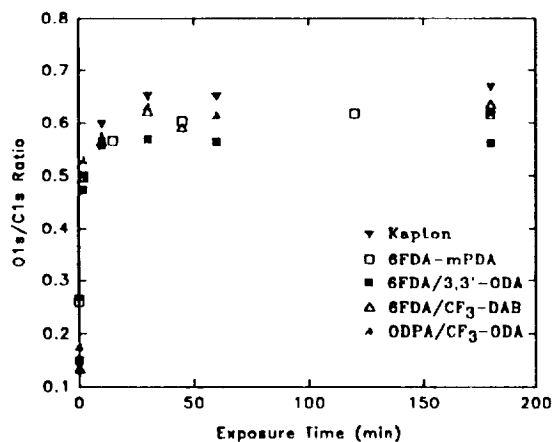


Figure 7: The O1s/C1s ratio of fluorinated polyimide films exposed to VUV radiation and atomic oxygen.

FTIR and weight loss experiments of irradiated polymers later confirmed that an ablative type mechanism is responsible for the degradation of polyimides exposed to a VUV and atomic oxygen environment. Furthermore, it has been reported in the literature that Kapton exposed to UV radiation in air for 10 minutes and then soaked for 1 h in water, showed a decrease in the O1s/C1s ratio to essentially the value for the un-irradiated Kapton, indicating that the highly photooxidised species are effectively removed by washing (4,5). These results reinforce our speculation that surface oxidation and ablation must be the main degradation process for polyimides. Interestingly, it was observ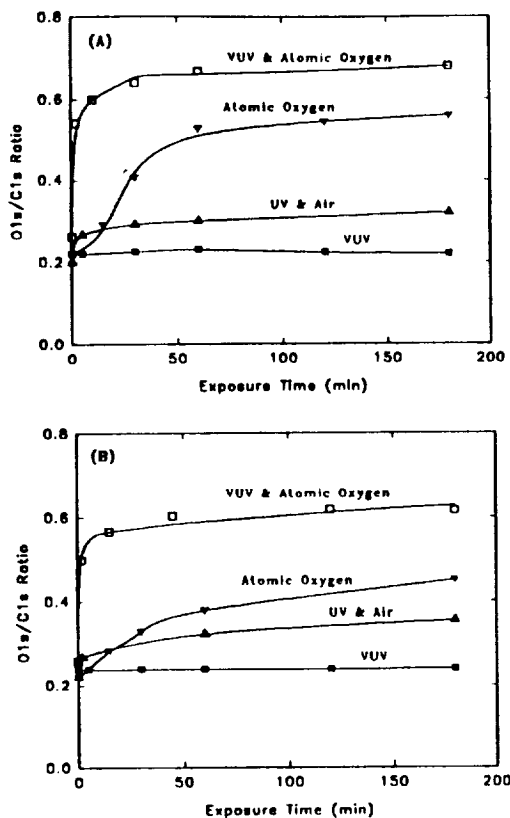ed that the oxidised carbon concentration present on the polymer surface at equilibrium was greater than that for any other carbon functional group. This level of oxidation strongly suggested a ring opening mechanism for the aromatic groups in the polyimides exposed to VUV and atomic oxygen.

Kapton film specimens which flew on the space end of the LDEF and received 5.8 years of

exposure to LEO environment, with the atomic oxygen flux perpendicular to the edge of the film and parallel to its surface, showed a significant decrease in light transmission which was attributed to surface roughening and a diffuse appearance (6). The XPS spectra of LDEF exposed polyimide film showed a drastic increase in oxygen and also the appearance of a distinct silicon peak. Silicon was believed to be associated with the surface contamination of the spacecraft. Whiteside and coworkers (7) related the increase in the oxygen peaks with the silicon contamination. Young suggested that polyimides which received exposure on the LDEF showed surface erosion, however, the presence of silicon on the polymer surface could lead to the formation of silicate upon exposure to atomic oxygen. Silicate is known to be an effective barrier to atomic oxygen (8,9,10), and
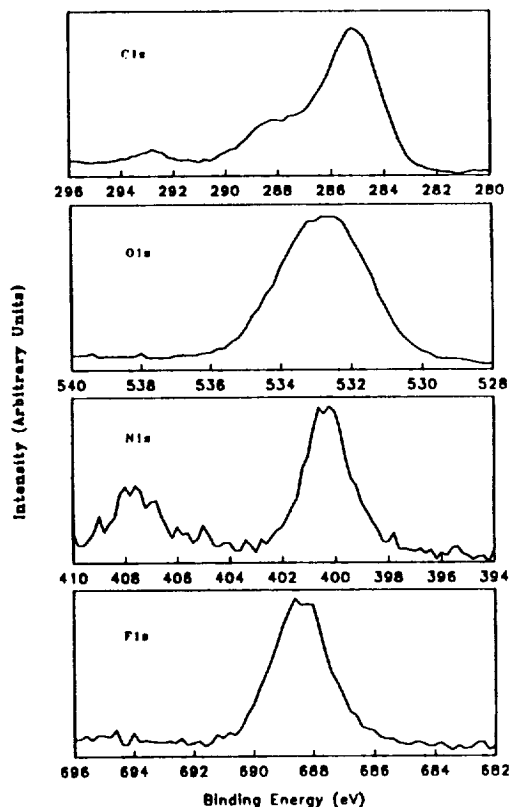
**Figure 8**: The change in the O1s/C1s ratio with exposure time of Kapton (A) and 6FDA-mPDA polyimide film (B).

could act as protective layer against further degradation of polyimide films exposed on the LDEF (11).

Exposure of polyimides films to UV or VUV radiation alone caused minimal or no damage to the polymer surface (see Fig 8), while atomic oxygen causes extensive damage to the polymer surface. The XPS analysis of the fluorinated polyimide films showed that the atomic oxygen flux produces a significant amount of surface oxidation. This was evidenced by an increase in the C=O peak at 288.1 eV and the C-O peak at 285.6 eV. Generally, the XPS spectra in the C1s region showed clearly that polymers exposed to VUV and atomic oxygen were characterised by different oxidised species from the polymers exposed to atomic oxygen alone (see Figs 9



**Figure 9**: XPS multiplex spectra for C1s, O1s, N1s and F1s regions of 6FDA,3,3'-ODA polyimide film exposed to atomic oxygen flux.

and 10 for 6FDA/3,3'-ODA and Kapton respectively). Consequently, the O1s region peak in the atomic oxygen exposure experiment is broad and occurs at a slightly higher binding energy than the peak obtained for the combined VUV and atomic oxygen, which confirmed the formation of different oxidation species. The XPS spectrum in the N1s region of polyimides exposed to atomic oxygen alone also showed two distinctive peaks with binding energies of 400.2 and 407.8 eV. The peak at 407.8 disappeared after about 1 h of further exposure to the atomic oxygen flux. From the binding energy, the transient species was identified as -NO$_2$ (12), which suggested that the imide linkage was susceptible to oxidation. The susceptibility of the imide group in Kapton to atomic
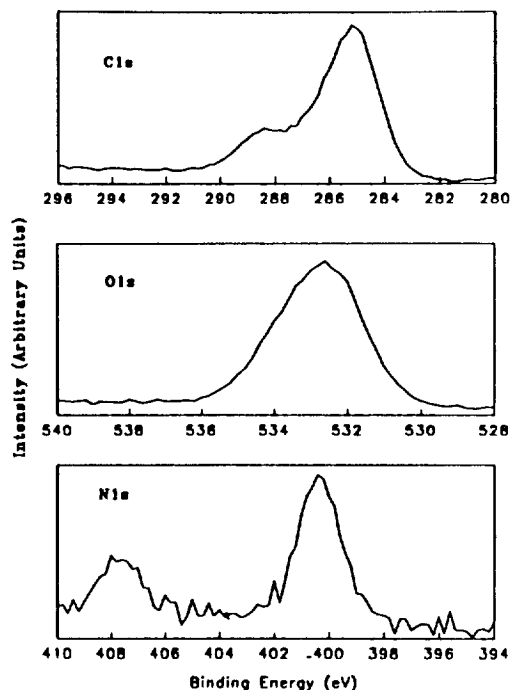


Figure 10: XPS multiplex spectra for C1s, O1s and N1s regions of Kapton exposed to atomic oxygen flux.
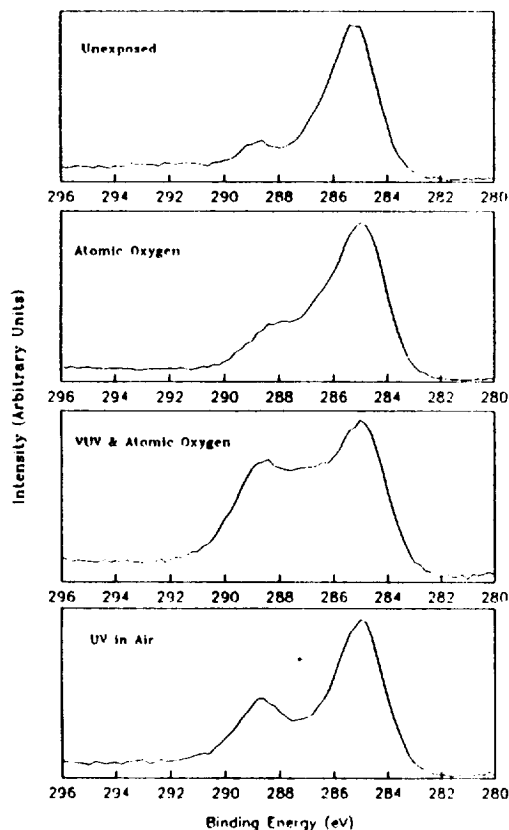


Figure 11: XPS multiplex spectra for C1s regions of ODPA/3,3'-ODA polyimide films exposed to different conditions.

oxygen attack has been suggested by others (13) and recently demonstrated by Minton et al. (14).

The above results suggest that atomic oxygen could be considered to be the main factor in the degradation process of polyimides films exposed to a low earth orbit environment. However, there is evidence for a synergistic effect of VUV radiation in the presence of atomic oxygen, which increases the damage to the polymer surface by photodegradation of oxidised species. Fig 8 clearly illustrates the effect of different exposure conditions on the O1s/C1s ratios of the fluorinated polyimide films in comparison to Kapton. The synergistic effect of VUV and atomic oxygen is obvious, while there is minimal or no observable damage of the polymer surface as result of exposure to either UV or VUV radiation alone. Consequently, atomic oxygen alone causes significant damage to the polymer surface, however the nature of the oxidation species are different from those which appear from the exposure to VUV and atomic oxygen in combination (Figs 11 & 12).

The effect of UV irradiation in air on the O1s/C1s is also presented in Fig 8 for comparison (3). The XPS spectra of the C1s and the O1s regions of polymer films exposed to UV in air suggested that the formation of the C=O group is more favourable, while polymers exposed to atomic oxygen alone or VUV and atomic oxygen in combination showed a more intense peak in the region of C-O, see Figs 11 & 12.

## CONCLUSIONS

The effect of an atomic oxygen flux and VUV radiation alone and in combination on the surface of fluorinated polyimide films was studied using XPS spectroscopy. Exposure of fluorinated polyimide films to VUV radiation in the presence of an atomic oxygen flux resulted in extensive oxidation of the polymer surface after only 2 minutes exposure. The amount of oxidised carbon on the polymer surface indicated that there is aromatic ring opening during oxidation. The ratio of O1s/C1s reached a plateau after a few minutes of exposure, which suggested that an ablative degradation process is highly favourable. The variation in the N1s/C1s and F1s/C1s ratios confirmed this postulate.



Exposure of fluorinated polyimide films to VUV radiation alone caused no damage to the surface, while an atomic oxygen flux resulted in substantial oxidation of the surface. Atomic oxygen exposure produces oxidation species different from those observed for VUV and atomic oxygen in combination, as evidenced from the broadening and the shift to higher binding energy of the O1s peak. Polyimides exposed to UV in air seem to favour the formation of C=O, while VUV and atomic oxygen exposure favour the formation of C-O groups. Furthermore, a new peak at 407.8 eV developed in the N1s region as a result of exposure to atomic oxygen, and was identified as $-NO_2$. This peak diminished after 1 h of further exposure to the atomic oxygen flux. The formation of $-NO_2$ suggested that the imide linkage could be sensitive to oxidation by atomic oxygen. The atomic oxygen could be considered as the main factor in the degradation

**Figure 12**: XPS multiplex spectra for O1s regions of ODPA/3,3'-ODA polyimide films exposed to different conditions.

process of polyimide films exposed to a low earth orbit environment. Obvious evidence of a synergistic effect of VUV radiation in the presence of atomic oxygen, which increases the damage to the polyimide surface, could also be drawn from the XPS study.
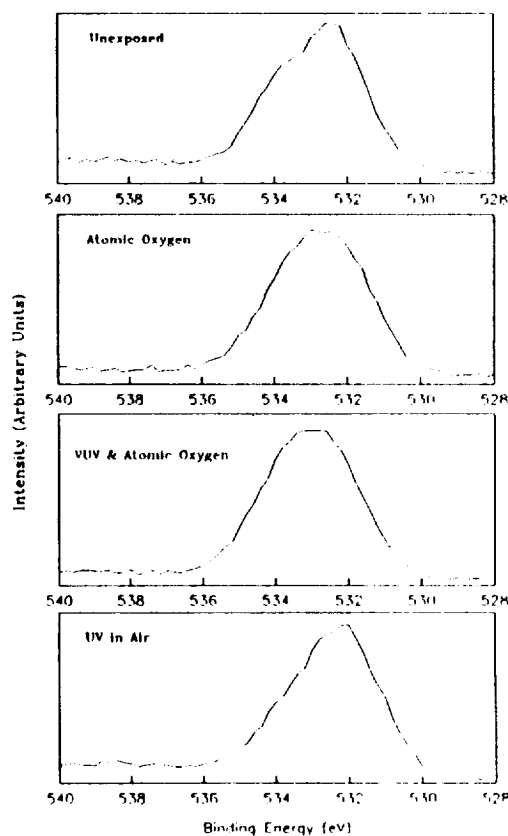
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