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A STUDY OF THE UV AND VUV DEGRADATION OF FEP

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SUMMARY

UV and VUV degradation of fluorinated ethylene propylene (FEP) copolymer was studied using ESR, XPS and SEM. The ESR study revealed the formation of a terminal polymer radical. The stability of this radical has been investigated under different environments. An XPS study of FEP film exposed to VUV and atomic oxygen showed that oxidation takes place on the polymer surface. The study revealed also that the percentage of CF_2 in the polymer surface decreased with exposure time and the percentage of CF, CF_3 and carbon attached to oxygen increased. SEM micrographs of FEP film exposed to VUV and atomic oxygen identified a rough surface with undulations similar to sand dunes.

INTRODUCTION

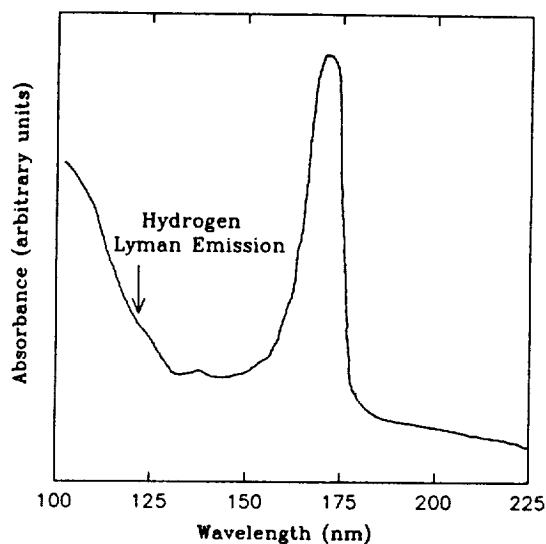
Spacecraft in low orbit are subjected to significant levels of high energy radiation, including UV and VUV wavelengths. The effects of UV radiation are enhanced over those at the surface of the earth, where the only incident wavelengths are greater than 290 nm (1). In low earth orbit the incident UV wavelengths extend below 290 nm into the VUV region, where the Lyman- α emissions of atomic hydrogen occur at 121 nm (2). In addition to electromagnetic radiation, in low earth orbit polymer materials may also be subjected to atomic oxygen particle radiation, which will result in direct oxidation of the polymer (1).

Thus, polymeric materials for space applications must exhibit a resistance to radiation damage of this type. One class of materials which have this characteristic are the fluorinated ethylene-propylene copolymers (FEP).

FEP is produced commercially by the copolymerisation of tetrafluoroethylene and perfluoropropylene in approximately 6:1 mole ratio. The polymer is an insoluble, semi-crystalline thermoplastic (crystallinity 50-60%) with a glass transition temperature (T_g) of approximately $-10^\circ C$ (1).

The extent of photodegradation of a polymer will be determined by the absorption

characteristics of the material. Optically, FEP is transparent in the visible region of the spectrum, but the absorbance begins to rise slowly below 300 nm. A complete absorption spectrum of FEP is not available in the literature, but the absorption spectrum of polytetrafluoroethylene (PTFE) has been reported, (see Fig.1), and that of FEP would be similar. The spectrum of PTFE is characterised by a strong absorption at 161 nm, which has been assigned to a transition from the HOMO levels for the C-C and C-F bonds to a conduction band (3). This peak has a long tail extending into the UV region. Below 130 nm, the absorbance of FEP again increases, due to the onset of the continuous absorption region of the material.



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Figure 1: VUV absorption spectrum of PTFE.

Photoinduced degradation can only occur at wavelengths where there is a significant overlap between the solar spectrum and the absorption of the material (4). In the VUV region there is a significant overlap between the absorption spectrum of FEP and Lyman- α line of atomic hydrogen and the continuous solar emission at wavelengths above 150 nm (2).

Two reports published recently by NASA have dealt with studies of the effect of 5 years and 9 months exposure of FEP thermal blankets to the Low-Earth-Orbit environment (LEO) on the Long Duration Exposure Facility (LDEF)(1 and 5). Stiegman et al.(1) investigated the synergistic effect of VUV and atomic oxygen on the FEP surface. They concluded that samples which received only VUV radiation possessed a hard embrittled surface layer, that was absent in the samples which were exposed to VUV and atomic oxygen, and also in the unexposed control samples. Stiegman suggested that this surface layer resulted from a "synergistic" effect between VUV and atomic oxygen. Young and Slemper (5) concluded from the XPS, FTIR and thermal analyses that there was no significant change at the molecular level for FEP thermal blankets exposed to LEO. However, various microscopic analyses revealed a roughening of the surface due to atomic oxygen erosion, which resulted in some materials changing from specular reflectors to diffuse reflectors (5).

As part of a materials evaluation program for space applications, we have studied the effects of UV-VUV induced degradation processes in FEP virgin polymer (FEP100) and unetched commercial films. The studies involve the photo-generation of radical species in the polymer matrices as the initial steps in the degradation process. It is the aim of this paper to obtain molecular level information for the initial stages of photo-degradation processes by using ESR spectroscopy and also to assess the effect of VUV radiation and atomic oxygen on FEP surfaces using Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS).

EXPERIMENTAL

Samples of FEP commercial films and FEP100 virgin polymer beads were irradiated in vacuum in Spectrosil-A grade quartz ESR tubes (i.d. 3.0 mm), at room temperature using a high power xenon lamp (wavelength > 200 nm). The radical concentrations, $[R^{\cdot}]$, were determined by ESR spectroscopy (Bruker ER-200D), utilising a strong pitch standard reference (3.0×10^{15} spin/cm). Spectra were determined at room temperature using Klystron frequency of 9.25 GHz, microwave power of 27db and magnetic field strength of 0.33 Tesla.

For surface analysis, (XPS and SEM), samples of FEP films were exposed to VUV radiation and atomic oxygen, which are generated using an oxygen plasma source designed specially for this purpose. The plasma tube was equipped with an earthed fine metal grid, which allows the passage of VUV radiation and atomic oxygen only, and prevents the plasma from reaching the polymer. Furthermore, the source was fitted with a removable MgF_2 window so that the polymer films could be separated from the flow of the atomic

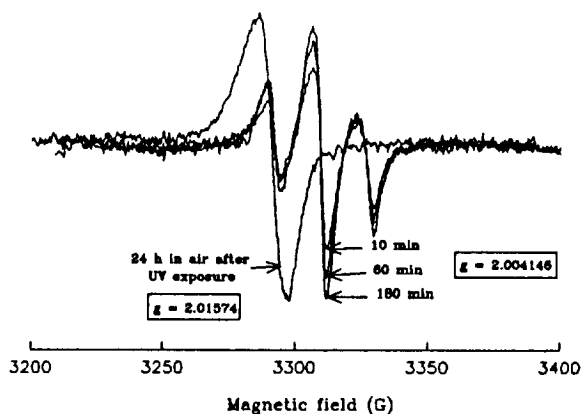


Figure 2: ESR spectra of FEP100 polymer exposed to UV radiation and air.

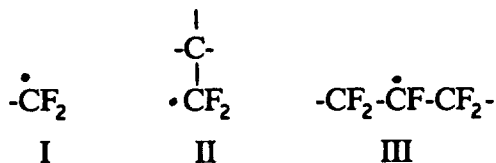
oxygen stream, to allow exposure to VUV radiation only. A Perkin-Elmer model 560 XPS/SAM/SIMS multi-technique surface analysis system and a JEOL model JSM 6400F Scanning Electron Microscope were used to evaluate the effects of VUV radiation and the synergistic effects of VUV and atomic oxygen on the FEP films.

RESULTS AND DISCUSSION

ESR Studies:

Samples of FEP film and virgin polymer beads were irradiated in vacuum by a high power xenon lamp (Intensity = 9.1 mW/cm^2), using quartz tubes at room temperature.

The ESR spectra of the radicals formed on exposure of the virgin FEP polymer beads (FEP100; obtained from DuPont Australia) to UV radiation (10-180 min.) in vacuum at room temperature are shown in Fig.2. The spectra are characterised by a triplet with a splitting of 17-18 G and $g = 2.004$. This triplet is identical to that observed by Kim and Liang (6), who assigned it to the chain scission radical I.



There was no evidence for the formation of radicals of the type II and III, which is also in agreement with Kim and Liang for irradiation with a xenon lamp.

The concentration of the chain scission radical increases with exposure time up to approximately 180 minutes, as shown in Fig.3. For exposure times beyond approximately 200 minutes, the radical concentration started to decline. This decrease in radical concentration could be due to a decrease in the concentration of the species responsible for radical formation.

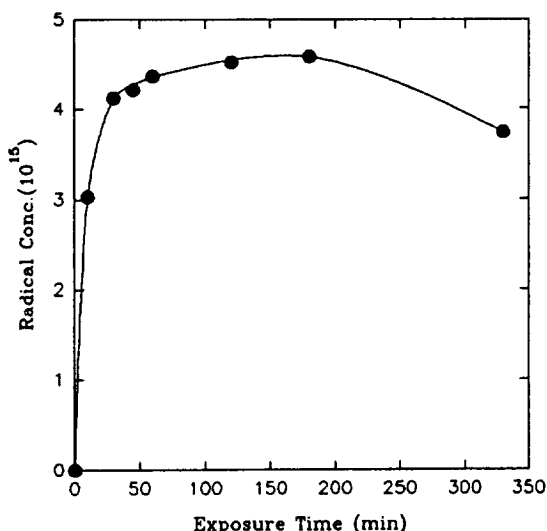
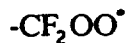


Figure 3: The effect of exposure time on radical concentration for FEP100.

Samples of irradiated virgin polymer (FEP100) stored in the dark under vacuum show a rapid decrease in the radical concentration due to recombination. After 24 h in the dark at room temperature all the chain scission radicals had decayed.

Samples of virgin polymer exposed to UV radiation under vacuum and then exposed to air have an ESR spectrum with a centre field shifted by 19 G to lower field ($g = 2.016$). The original triplet spectrum found for irradiation under vacuum is transformed into a broad singlet with a ΔH_{pp} of 9.3 G.

This spectrum can be assigned to the peroxy radical IV (6). A similar peroxy radical is formed on UV exposure of the virgin polymer in air.



IV

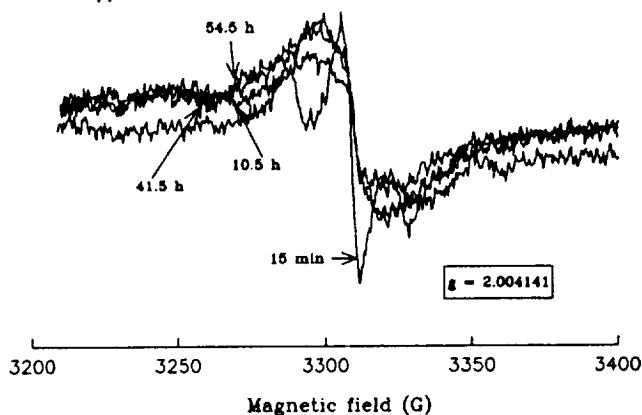


Figure 4: ESR spectra of FEP film exposed to UV radiation.

The ESR spectra of the FEP polymer film shows that samples irradiated for 15 min. produce a radical characterised by a triplet structure with an 18 G splitting (see Fig.4). This triplet is identical to that found for the virgin polymer, and is due to the chain scission radical I. On the other hand, the ESR spectra of the same polymer film irradiated for 1-60 h produces a completely

different spectral shape. The outer peaks of the triplet merge into the central peak. This behaviour could be explained by photodegradation of the FEP to form the chain scission radical, followed by reaction of this radical with an impurity present in the polymer film to form a new and relatively stable carbon centred radical. This impurity in the FEP polymer film could be for example a processing aid used in preparation of the film. The processing aid could be an antioxidant or stabiliser.

Furthermore, it was observed from this experiment that there was a fast build up of radical concentration in the first few minutes (2-15 min) of irradiation and then a sharp drop as the irradiation continued to about 75 min., see Fig.5. This decrease in the radical concentration coincided with the transition from the triplet ESR spectrum to a broad singlet. After approximately 75 minutes, the radical concentration then started to build up to higher values with increasing UV irradiation time (see Fig.5). This behaviour might be related to a time delay between the generation of the first radical species and the activation of the radical scavenger.

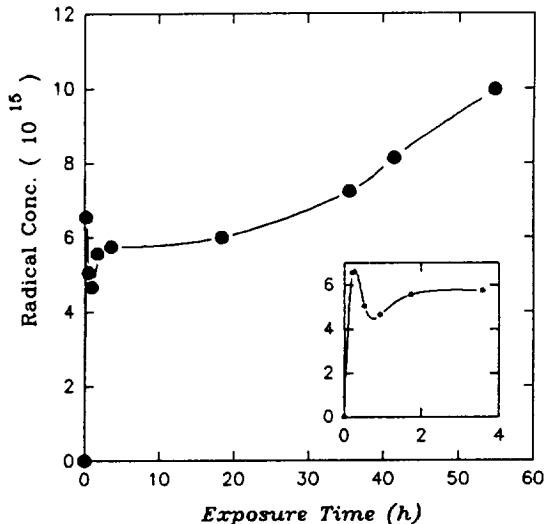


Figure 5: The effect of UV exposure time on radical concentration of FEP film.

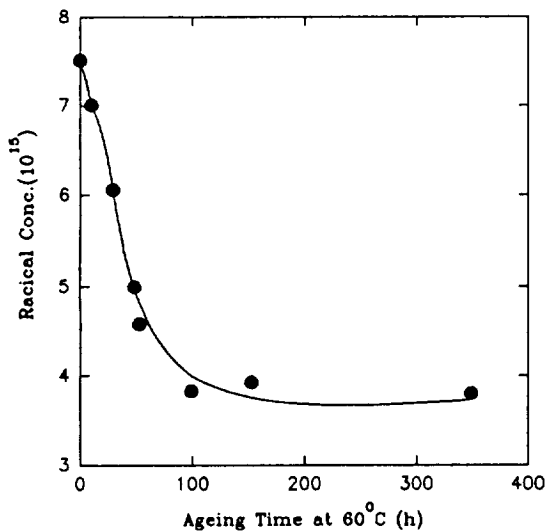


Figure 6: The effect of ageing at 60°C on radical concentration of FEP film exposed to UV radiation.

in the FEP polymer film were stable on exposure to air. Thus, their behaviour contrasts with that observed for the radicals formed by irradiation of virgin polymer, which reacted readily with oxygen to form peroxy radicals ($g = 2.016$).

On ageing, the time dependence of the radical concentration at 60°C exhibited a relatively sharp drop (55%) in the radical concentration up to 100 h (see Fig.6). However, longer ageing to about 400 h produced no significant further change in the radical concentration. A similar trend was observed for the room temperature ageing of the UV irradiated polymer film, however the decay rate in the radical concentration was, as expected, slower than that for 60°C ageing (30% upto 100 h). This behaviour suggests that some of the secondary radicals are restricted from decomposition by their location in the polymer matrix.

The radicals responsible for the broad singlet species ($g = 2.004$) formed

Surface Analysis:

Surface analyses of FEP films were conducted using XPS spectroscopy and SEM.

The XPS multiplex spectrum at 25 eV pass energy of unirradiated FEP film for the C(1s) and F(1s) regions is shown in Fig.7. Using a set of standard sensitivity factors(7) the ratio of C:F was found to be 1:2, as expected for FEP. Thus, there is no significant contamination of the surface layer of the film, but a close examination of the C(1s) peak reveals a small tail in the lower binding energy region, containing approximately 3.6 percent of the total peak area. The reason for this tail is unclear, but possible contributing sources could include crosslinks, end groups, branches and oxidation of the polymer, although there was no evidence of a significant O(1s) peak. Curve fitting of the carbon peak yielded the analysis shown in Table 1. In this simulation, two minor peaks at 286.6 and 288.3 eV were used to account for the tail, but they are unassigned.

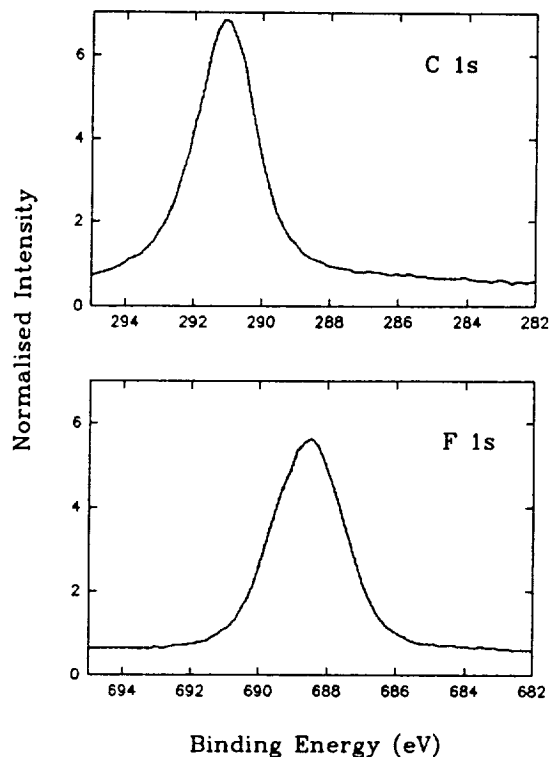


Figure 7: XPS spectrum of unirradiated FEP film.

Table 1: Percent composition of the FEP film from curve fitting of surface analysis data.

Binding Energy(eV)/ Chem.Bond	Unexposed FEP (%)	FEP Exposed to VUV & AO for 15 min. (%)	FEP Exposed to VUV & AO for 75 min. (%)	FEP Exposed to UV rad. then air (%)
285.0/ C-H	-	0.2	0.8	13.8
286.6/ C-C,C-O	1.2	1.2	1.4	5.7
288.3	2.4	2.5	2.7	2.7
289.5/ CF-CF _n	8.5	9.5	9.9	7.1
291.2/ CF ₂	79.5	76.0	73.8	64.0
293.3/ CF ₃	8.4	9.6	9.8	5.7
287.8/ C=O	-	1.0	1.5	1.0

The curve fitting analysis is consistent with a tetrafluoroethylene : perfluoropropylene ratio in the polymer film of 4.2:1. This ratio in the surface is lower than that generally reported for the composition of FEP copolymers, which is 6:1.

Exposure of FEP film to VUV radiation in the presence of atomic oxygen results in the oxidation of the polymer surface. This is revealed in the XPS spectrum, as demonstrated in Fig.8 by the presence of an oxygen peak. Furthermore, it was observed that the oxygen peak is very broad, which suggests the possible presence of various oxygen species. It is also revealed by an increase in the tail of the carbon peak. The curve fitting analysis of the carbon peak is given in Table 1. This increase in the area of the tail has been accounted for by inclusion of an additional peak at 287.8 eV, which has been assigned tentatively to formation of a carbonyl moiety. (The intensities of the unassigned peaks at 286.6 and 288.3 remain constant within experimental error). The important trends observed in Table 1 with increasing irradiation time are: an increase in the percentage of carbon attached to oxygen, a decrease in the percentage of CF_2 and an increase in the percentage of CF and CF_3 . This suggests that oxidation takes place at the fluorinated ethylene units.

The changes in the $F(1s):C(1s)$ and $O(1s):C(1s)$ ratios with increasing irradiation time and atomic oxygen flux are shown in Table 2 and in Figs. 9 and 10, respectively. As the irradiation time increases, the fluorine to carbon ratio decreases and the oxygen to carbon ratio increases. At longer irradiation times, the rate of change in these ratios decreases, and the ratios appear to approach constant values. This observation would be consistent with a

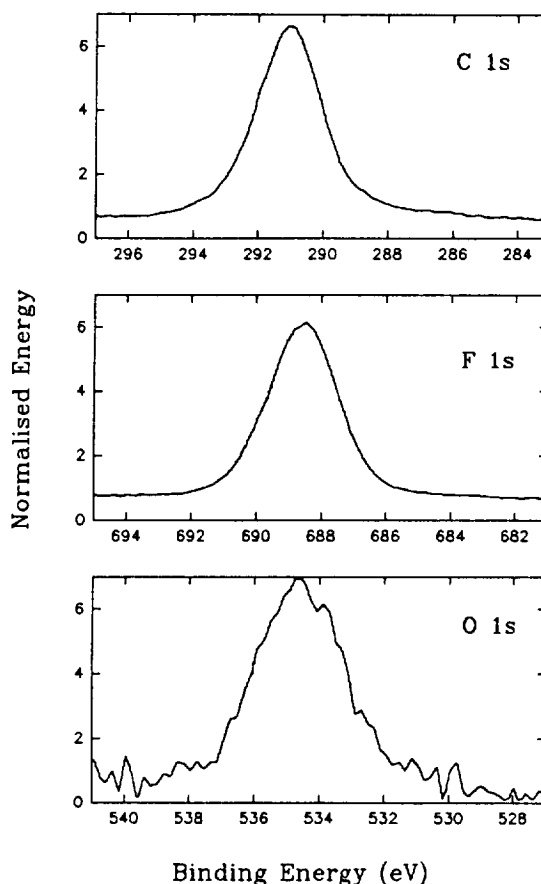


Figure 8: XPS spectrum of FEP film exposed to VUV and atomic oxygen.

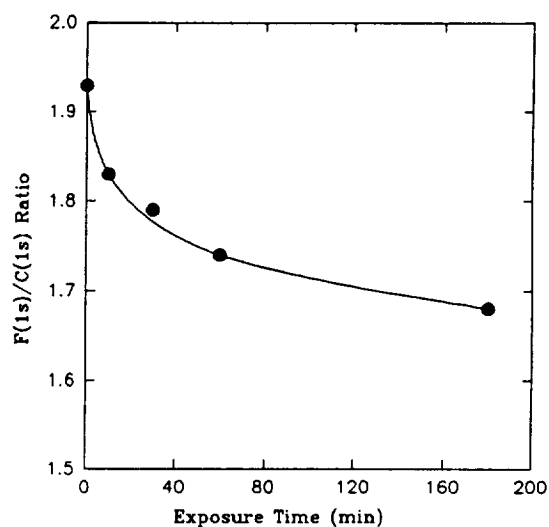


Figure 9: The change of $F(1s)/C(1s)$ ratio in FEP film exposed to VUV and atomic oxygen.

gradual erosion of the polymer surface by the radiation, with a concurrent loss of small molecule products.

The oxygen atom flux was varied by changing the oxygen pressure in the plasma tube and by introduction of a MgF_2 window between the plasma and the polymer film. As shown in Fig. 10, the rate of oxidation of the polymer surface increases with the atomic oxygen flux.

The XPS carbon spectrum (Fig. 11) of FEP polymer film irradiated by UV (xenon lamp) in vacuum and exposed to air immediately after irradiation showed about 1% oxygen atom concentration in the surface. This was attributed to the formation of $C=O$. Furthermore, additional peaks were observed in the C-C (286.6 eV)(8) and C-H (285.0 eV) binding energy regions of the XPS spectrum, which might be assigned to the formation of crosslinks between polymer chains and to the presence of hydrocarbon contamination, which might have resulted from the increased susceptibility of the oxidised polymer surface to laboratory contamination. A similar small hydrocarbon peak was observed in the FEP films exposed to VUV and atomic oxygen (see Table 1).

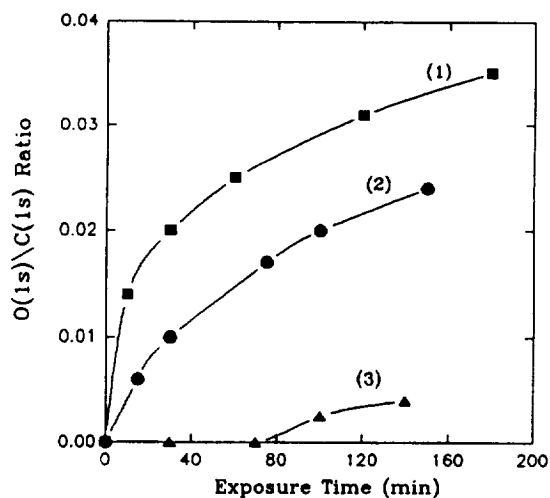


Figure 10: The effect of high(1), medium(2), and zero(3) oxygen atom flux on the surface of FEP film exposed to VUV radiation.

Compared with the films irradiated using VUV, the films irradiated with UV then exposed to air have a lower surface $F(1s)/C(1s)$ ratio and a higher concentration of crosslinks. The $O(1s)$ peak also appears narrower, suggesting a different distribution of oxidation products, which arise via peroxide formation in this case.

Table 2: XPS results for FEP polymer films exposed to simulated and actual space environment.

Peaks	FEP Type A	FEP (VUV & AO)	FEP(UV > 200 nm) and air	Control	A10 Opaque	C8 Opaque
C1s(eV)	291.1	291.1	291.6	290.9	290.9	290.9
AC (%)	34	35.2	40	31.6	28.5	30.4
F1s(eV)	688.6	688.6	688.8	689	688.5	688.8
AC (%)	66	64.1	59	65.6	69.8	66.2
O1s(eV)	-	534.4	532	-	530.9	-
AC (%)	0	0.7	1.0	-	1.3	<0.5

a: Data obtained from NASA technical report no.104096 (5).

AC: Atomic concentration (%).

The surface analysis of the FEP polymer film obtained in the simulated space environment used in the experiments described here are compared in Table 2 with those reported by Young and Slep (5) for FEP polymer films exposed to the space environment in the LDEF experiments.

SEM micrographs of FEP film before and after exposure to VUV and atomic oxygen showed a dramatic change in the polymer surface (see Figs. 12). These micrographs show the extensive loss of polymer material during the VUV and atomic oxygen irradiation of the film. The texture of the surface becomes rough with regular undulations similar to sand dunes. Thus, as the polymer erodes and "new" surfaces are exposed, the chemical composition of the surface would be expected to approach a constant average value; as found by the XPS analysis.

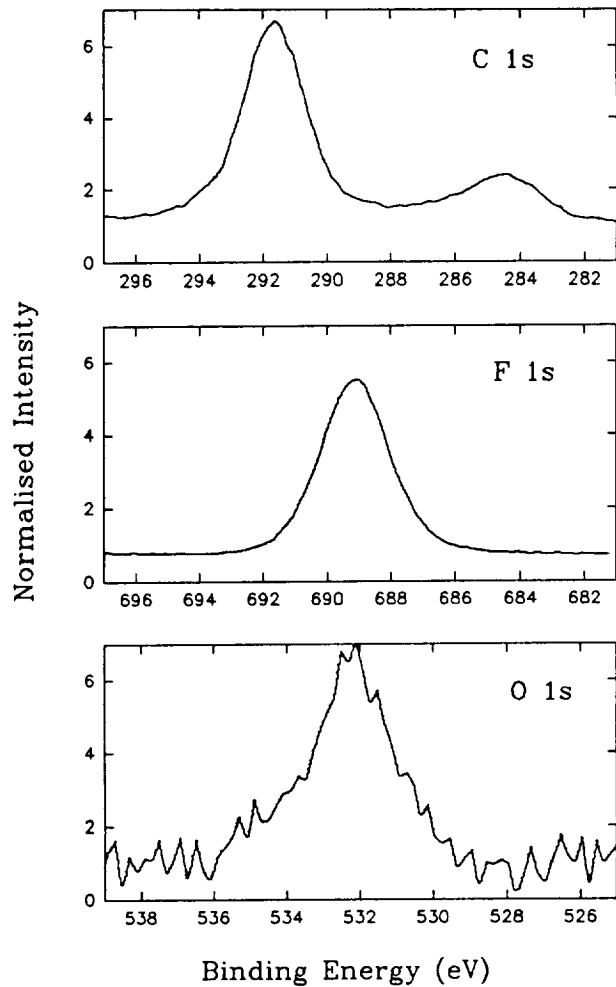


Figure 11: XPS spectrum of FEP film exposed to UV radiation and air.

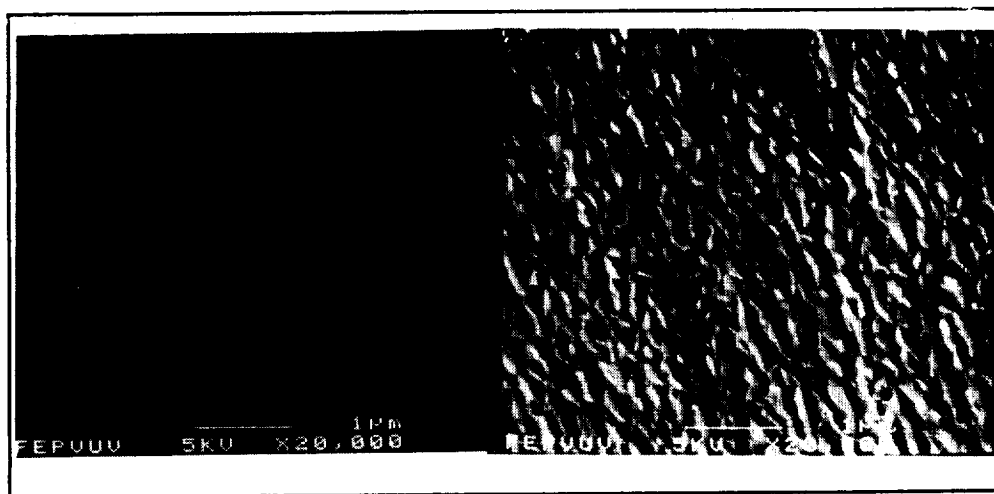


Figure 12: SEM micrograph of FEP film before and after exposure to VUV and atomic oxygen.

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