ESCA study of poly(vinylidene fluoride), tetrafluoroethylene–ethylene copolymer and polyethylene exposed to atomic oxygen

Morton A. Golub*
Ames Research Center, NASA, Moffett Field, CA 94035, USA

and Robert D. Cormia
Surface Science Laboratories, 1206 Charleston Road, Mountain View, CA 94043, USA
(Received 23 September 1988; revised 1 December 1988; accepted 12 December 1988)

The ESCA (electron spectroscopy for chemical analysis) spectra of films of poly(vinylidene fluoride) (PVDF), tetrafluoroethylene–ethylene copolymer (TFE/ET) and polyethylene (PE) exposed to atomic oxygen ($O(^3P)$), in or out of the glow of a radio-frequency O_2 plasma, were compared. ESCA spectra of PE films exposed to $O(^3P)$ in low Earth orbit (LEO) on the STS-8 Space Shuttle were also examined. Apart from $O(^3P)$-induced surface recession (etching), the various polymer films exhibited surface oxidation, which proceeded towards equilibrium saturation oxygen levels. The maximum surface oxygen uptakes for in-glow or out-of-glow exposures were in the order: PE > TFE/ET > PVDF; for PE itself, the oxygen uptakes were in the order: in glow > out of glow > LEO. Given prior ESCA data on poly(vinyl fluoride) and polytetrafluoroethylene films exposed to $O(^3P)$, the extent of surface oxidation is seen to decrease regularly with increase in fluorine substitution in a family of ethylene-type polymers.

(Keywords: ESCA; poly(vinylidene fluoride); tetrafluoroethylene–ethylene copolymer; polyethylene; atomic oxygen; radio-frequency oxygen plasma; low Earth orbit)

INTRODUCTION

Recently, we reported on an ESCA (electron spectroscopy for chemical analysis) study of the surface oxidation of films of poly(vinyl fluoride) (Tedlar; PVF); tetrafluoroethylene–hexafluoropropylene copolymer (in the form of a Teflon FEP coating on Kapton H, i.e. Kapton F; TFE/HFP) and polytetrafluoroethylene (Teflon TFE; PTFE) when exposed to ground-state atomic oxygen ($O(^3P)$) either in low Earth orbit (LEO) on the STS-8 Space Shuttle or within or downstream from a radio-frequency (r.f.) oxygen plasma[1]. Previously, we presented ESCA data on the surface oxidation of poly(*N*,*N*′-(*p*,*p*′-oxydiphenylene) pyromellitimide) film (Kapton H) when similarly exposed to $O(^3P)$ in LEO or in or out of the glow of an O_2 plasma[2]. Accompanying the surface oxidation is a surface recession (etching) of the films, and a related paper[3] presents a comparative survey of the etch rates for a variety of polymers exposed to $O(^3P)$ in low-pressure, r.f. O_2 discharge apparatus (with O atoms having translational energy of ≈ 0.04 eV) or in LEO (with O atoms having *collisional* energy of ≈ 5 eV, owing to the $8\,\mathrm{km\,s^{-1}}$ velocity of the Space Shuttle).

The availability of still another polymer that was returned from the STS-8 Shuttle flight[4,5], namely polyethylene (PE), as well as two additional fluorocarbon polymer films, namely, poly(vinylidene fluoride) (PVDF) and an alternating tetrafluoroethylene–ethylene copolymer (TFE/ET), made it desirable to follow up our prior ESCA study[1] of PVF, TFE/HFP and PTFE films, subjected to various $O(^3P)$ exposures, with a similar study of PVDF, TFE/ET and PE films. The latter three polymers, combined with the former three, afford data on the effect of fluorine content on $O(^3P)$-induced surface oxidation of ethylene-type polymers. Although ESCA spectra of plasma-etched and plasma-oxidized PE have received much attention[6–9], no ESCA spectra of PE exposed to O atoms downstream from an O_2 plasma have been reported, nor have any ESCA spectra of $O(^3P)$-exposed PVDF or TFE/ET been published. However, some ESCA data on surface oxidation in LEO-exposed PE have appeared recently in the proceedings of a workshop on atomic oxygen effects[10].

EXPERIMENTAL

Disks stamped out of 25 μm thick PVDF, TFE/ET and PE films (the first two, Kynar and Tefzel, from Du Pont; the third, Marlex EHM 6006, from Phillips 66) were individually exposed for various periods of time to $O(^3P)$ either downstream from or within the glow of a low-pressure O_2 plasma, as described previously[1]. Two samples of 25 μm thick, LEO-exposed PE films (one exposed 'day and night' for ≈ 40 h on the STS-8 Space shuttle[4,5] for a fluence, or integrated flux, of $\approx 3.5 \times 10^{20}$ O atoms $\mathrm{cm^{-2}}$, and another exposed 'day only' for an undetermined, but much smaller fluence) were made available for this study. The ESCA analysis of the various polymer films before and/or after $O(^3P)$-induced etching and the determination of the peak binding energies (*BE*) were performed as indicated previously.[1,2]

---

* To whom correspondence should be addressed

0032-3861/89/091576–06$03.00

RESULTS AND DISCUSSION

ESCA spectra of poly(vinylidene fluoride)

Typical C_{1s} ESCA spectra of PVDF before and after exposure to $O(^3P)$ either downstream from or within the glow of an r.f. O_2 plasma are illustrated in *Figure 1*, and the significant ESCA data are summarized in *Table 1*. The exposure times indicated in the caption of *Figure 1* correspond to those required to attain equilibrium saturation levels of surface oxidation for the two types of $O(^3P)$ exposure. (The exposure times indicated in the captions of *Figures 2* and *3* have the same significance.) The F_{1s} spectra of PVDF all presented a single, essentially symmetric peak, while the O_{1s} spectra showed either a very weak, broad peak (unexposed PVDF) or a moderately intense, fairly symmetric peak (exposed PVDF), with binding energies as indicated in *Table 1*; hence, there is no need to show the O_{1s} and F_{1s} spectra corresponding to *Figures 1a–c*. The two strong peaks at 286.0 and 290.4 eV in the C_{1s} spectrum of the unexposed PVDF film, which have approximately the same intensity and remain unshifted in the spectra of the $O(^3P)$-exposed films, are assigned to $-CH_2-$ and $-CF_2-$, respectively, ESCA, however, is not able to distinguish between head-to-tail and head-to-head additions of the $-CH_2CF_2-$ monomer units[11], which are present in PVDF in the molar ratio[12] ≈20:1. An ESCA spectrum similar to *Figure 1a* was presented by Corbin *et al.*[13] for unreacted PVDF, and analysis gave the same F/C ratio (1.0) as that in *Table 1*.

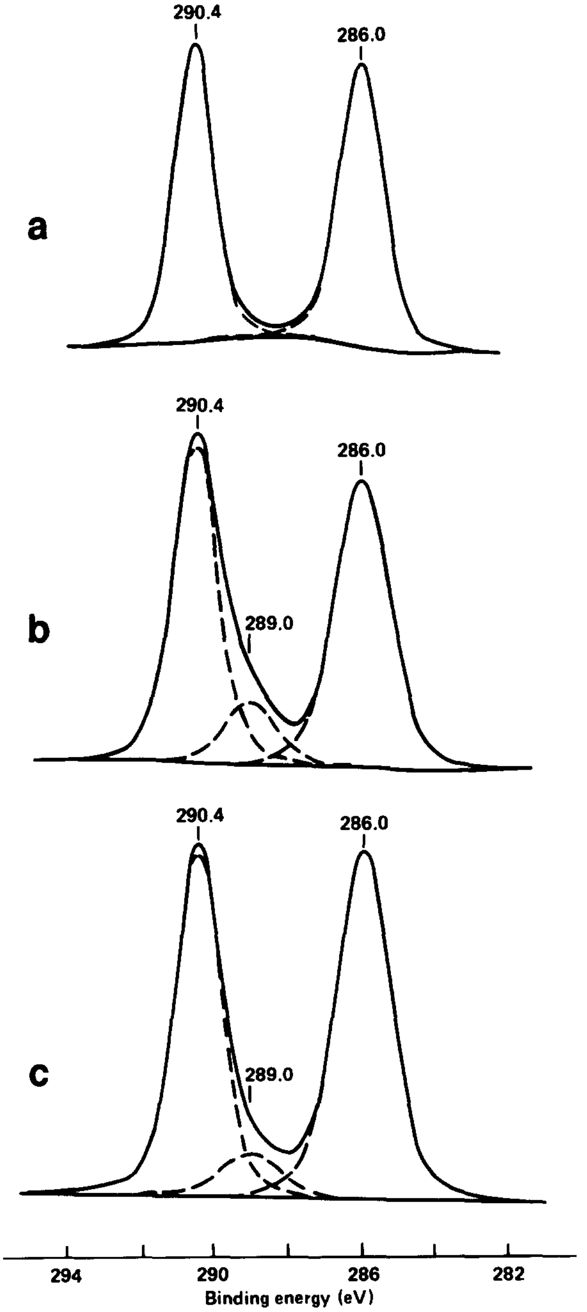

Figure 1 Typical C_{1s} ESCA spectra of PVDF: (a) initial, unexposed film; (b) film after exposure for 8 h to $O(^3P)$ downstream from the r.f. O_2 plasma; (c) film after exposure for 40 min 'in the glow' of an O_2 plasma. The broken curves correspond to deconvolutions of the solid curves

Table 1 ESCA data for PVDF before and after exposure to $O(^3P)$

		Composition (at%)		
Peaks	*BE* (eV)	Unexposed[a]	Out of glow[b]	In glow[c]
C_{1s}	286.0	25.6	24.4	26.2
	289.0	—	4.9	3.2
	290.4	23.7	23.2	21.5
O_{1s}	532.6–533.1	1.5	8.8	4.6
F_{1s}	687.5	49.2	38.7	44.5

[a] F/C ratio = 1.00; theoretical: 1.00 (*Figure 1a*)
[b] F/C ratio = 0.74 (*Figure 1b*)
[c] F/C ratio = 0.87 (*Figure 1c*)

The C_{1s} spectra of PVDF exposed to $O(^3P)$, whether in or out of the glow, show the growth of a new peak at 289.0 eV, which is assigned to a carbon attached to an oxygen, presumably[14] >C=O. Since the single O_{1s} peaks at 532.6–533.1 eV (>C=O; >C–O–)[14] for the $O(^3P)$-exposed PVDF films are each more intense than the corresponding C_{1s} peaks at 289.0 eV (see *Table 1*), the surface oxidation must also involve formation of >C–O– groups. The latter groups, which have C_{1s} peaks at 286.7–287.5 eV[14], would be masked by the dominant $-CH_2-$ peak at 286.0 eV. Accompanying the oxidative etching of PVDF is a loss of fluorine atoms, indicated by a decrease of the F/C ratio from the initial (= theoretical) value of 1.00 to 0.74 and 0.87 for PVDF exposed downstream from or within the glow of an O_2 plasma, respectively. Interestingly, the shapes and *BE* values of the F_{1s} peaks (at 687.5 eV; >CF–) for PVDF before and after $O(^3P)$ exposure are unaffected by surface oxidation. No special significance should be attached to the absolute atomic percentage oxygen values indicated for in-glow *versus* out-of-glow exposure (*Table 1*), since we observed that small changes in operating parameters for both the in-house 'downstream' reactor[3] and the extramural plasma reactor (at Plasma Science) caused variations in the oxidation levels in $O(^3P)$-exposed PVDF.

ESCA spectra of tetrafluoroethylene–ethylene copolymer

Typical C_{1s} spectra of TFE/ET before and after exposure to $O(^3P)$ downstream from or within the glow of an r.f. O_2 plasma are presented in *Figure 2*, and the data are summarized in *Table 2*. Again, there is no need to show the O_{1s} and F_{1s} spectra since they each possessed a single, essentially symmetric peak with the *BE* values given in *Table 2*. Not surprisingly, the C_{1s} spectra in *Figure 2* closely resemble those in *Figure 1*: TFE/ET is a largely alternating tetrafluoroethylene–ethylene

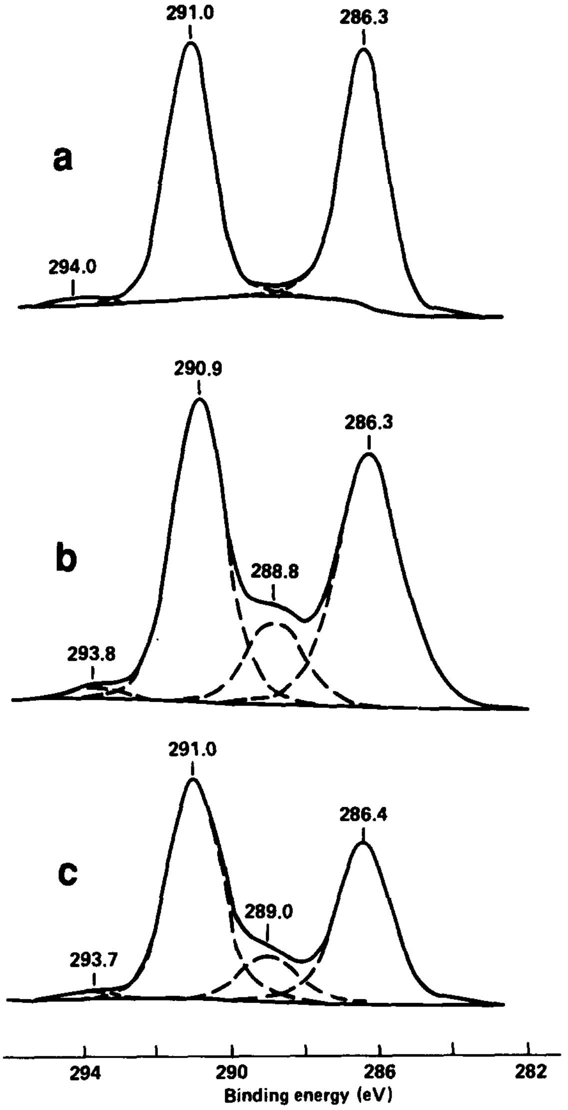

Figure 2 Typical C_{1s} ESCA spectra of TFE/ET: (a) initial, unexposed film; (b) film after exposure for 2 h to $O(^3P)$ downstream from the r.f. O_2 plasma; (c) film after exposure for 30 min 'in the glow' of an O_2 plasma. The broken curves correspond to deconvolutions of the solid curves

Table 2 ESCA data for TFE/ET before and after exposure to $O(^3P)$

		Composition (at%)		
Peaks	*BE* (eV)	Unexposed[a]	Out of glow[b]	In glow[c]
C_{1s}	286.3–286.4	24.9	22.5	17.7
	288.8–289.0	—	6.2	5.3
	290.9–291.0	24.8	21.5	23.0
	293.7–294.0	0.4	0.7	0.5
O_{1s}	533.5–533.8	0.1	12.7	10.4
F_{1s}	688.4	49.8	36.4	43.1

[a] F/C ratio = 0.99; theoretical: 1.00 (*Figure 2a*)
[b] F/C ratio = 0.72 (*Figure 2b*)
[c] F/C ratio = 0.93 (*Figure 2c*)

copolymer (52% TFE)[11], whose structure may be depicted as $-(CH_2CH_2CF_2CF_2)_n-$ or $-(CH_2CF_2CF_2\,CH_2)_n-$, the latter representation being equivalent to an *alternation* of head-to-head and tail-to-tail linkages of the monomer units of PVDF. The C_{1s} spectrum of the unexposed TFE/ET film (*Figure 2a*) thus displays two well resolved peaks of virtually equal intensity at 286.3 and 291.0 eV (corresponding to $-CH_2-$ and $-CF_2-$, respectively) which remain unshifted in the spectra of the $O(^3P)$-exposed films. A spectrum similar to *Figure 2a* was published by Dilks[11] (*BE* separation of 4.6 eV for the two C_{1s} peaks compared with 4.7 eV here), who also presented the F_{1s} spectrum of TFE/ET with its single symmetric peak (at ≈690 eV compared with 688.4 eV here). The very weak signal at 294.0 eV in *Figure 2a*, which persists in *Figures 2b* and *c* (at 293.7–293.8 eV), suggests the presence of $-CF_3$ in trace amounts (≈0.4–0.7 at%; *Table 2*) in TFE/ET both before and after reaction with atomic oxygen.

In common with PVDF, TFE/ET on exposure to $O(^3P)$ shows the development of a new C_{1s} peak at 288.8–289.0 eV and an associated O_{1s} peak at 533.5–533.8 eV; both peaks again signify the formation of $>C{=}O$ and $>C{-}O-$ groups. Although the etch rates of TFE/ET and PVDF downstream from the glow of an O_2 plasma were very similar[3], the former polymer experienced consistently greater surface oxidation than the latter, whether exposed to $O(^3P)$ out of the glow or in the glow, as typified by the data in *Tables 1* and *2*. Thus, the $-CH_2CH_2CF_2CF_2-$ structure, though no more vulnerable to $O(^3P)$-induced etching than $-CH_2CF_2CH_2\,CF_2-$, is apparently more susceptible to surface oxygen uptake. The oxidative etching of TFE/ET, like that of PVDF, is accompanied by a loss of fluorine atoms, indicated by a decrease of the F/C ratio from the initial value of 0.99 (theoretical = 1.00) to 0.72 and 0.93 for TFE/ET exposed downstream from and within the glow of an O_2 plasma, respectively. As before, no significance should be attached to the difference in absolute atomic percentage oxygen values between in-glow and out-of-glow exposures of TFE/ET (*Table 2*).

ESCA spectra of polyethylene

Figure 3 shows the C_{1s} spectra of PE before and after exposure to $O(^3P)$ in LEO ('day only'), or downstream from or within the glow of an r.f. O_2 plasma, and the ESCA data are summarized in *Table 3*. The PE film used in the r.f. exposures was a high density (HD) PE, while that recovered from LEO exposure was of unspecified density but we regard it as a linear low density (LD) PE, based on subtle differences between the transmission infrared spectra of these films[15]. Since Gerenser[9] reported that there were no detectable differences observed between the ESCA spectra of HDPE and LDPE, either before or after O_2 plasma treatment, we shall consider the two PE films to be alike for the purposes of discussing the C_{1s} spectra in *Figure 3*. Again, there is no need to show the O_{1s} spectra of the $O(^3P)$-exposed PE films since they all displayed a single, broad peak in the *BE* range indicated in *Table 3*. Likewise, there is no need to show the N_{1s} spectrum of the LEO-exposed PE film, which revealed a very weak signal (at 400.3 eV) representing some unknown contamination in the recovered PE.

The C_{1s} spectra of PE exposed to $O(^3P)$ downstream from or within the glow of the O_2 plasma (*Figures 3c* and *d*) are very similar, each showing three deconvoluted peaks in the high *BE* tail to the prominent 284.6 eV peak (unreacted $-CH_2-$). The latter peak is, as expected, the sole peak in the C_{1s} spectrum of a clean, unexposed PE film (*Figure 3a*) whose structure is essentially $-(CH_2CH_2)_n-$. Spectra similar to *Figure 3d* have been presented by other workers[6–9], and we may invoke the following assignments[6,7,11] for the high *BE* peaks in both

Figures 3c and *d*: 286.1–286.5 eV (C–O–, as in alcohol, ether, epoxide, hydroperoxide, peroxide, ester); 287.6–287.8 eV (>C=O, as in aldehyde or ketone); and 289.2 eV (–O–C=O, as in carboxylic acid or ester). The C_{1s} spectrum of the LEO-exposed PE film (*Figure 3b*) exhibits an apparently narrower range of oxidative functionalities, the 286.4 eV peak having the aforementioned assignment and the 288.5 eV peak suggesting somewhat more carboxylic acid than aldehyde or ketone. Unfortunately, the C_{1s} spectra do not offer a more definite picture of the functionalities present in the $O(^3P)$-exposed PE films. Nor do the corresponding O_{1s} spectra provide additional insight since they display single, broad peaks at 532.4–532.9 eV due to overlapping contributions from >C=*O* and >C–*O*– groups. What we can say from *Figure 3* and *Table 3* is that there is a quantitative but not qualitative difference between surface oxidations of PE exposed to $O(^3P)$ in or out of the glow, and that there is both a qualitative and a quantitative difference between surface oxidations of PE in LEO and in ground-based, r.f. O_2 discharge apparatus, the oxygen uptakes being in the order: in glow > out of glow > LEO.

The C_{1s} spectrum of another PE film, one exposed 'day and night' in LEO during the STS-8 Shuttle flight, resembled that for the PE film exposed 'day only' (*Figure 3b*) and is therefore omitted; however, the pertinent ESCA data are included in parentheses in *Table 3*. The two PE films exposed together 'day and night' and 'day only' (with surface oxygen contents of 9.1 and 11.8 at% O, respectively), had been thinned[16] in LEO by $\approx$11.5 and 5.4 μm, respectively, erosions presumably related to the fluences encountered. Still another PE film exposed 'night only' in the same STS-8 flight experiment (but not available for ESCA analysis) had been thinned[16] by 5.0 μm. Unfortunately, these limited results leave unresolved the question of a possible synergistic effect of solar ultraviolet radiation on $O(^3P)$-induced surface erosion and oxidation of PE in LEO.

Coulter *et al.*[10] previously reported results of an ESCA analysis of a PE film flown on STS-8 for 40 h and exposed

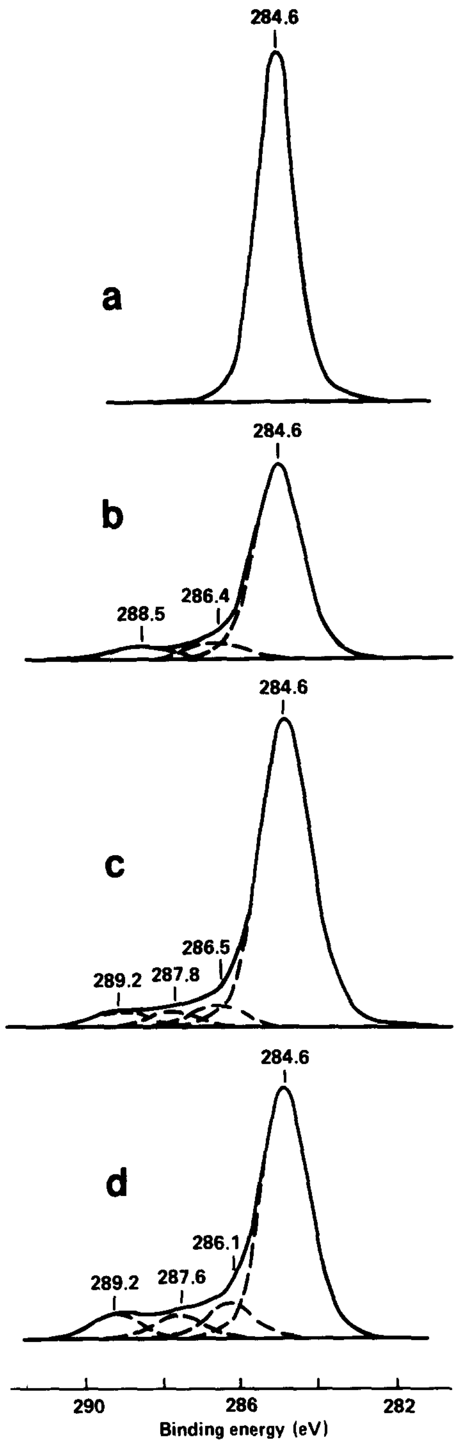

Figure 3 C_{1s} ESCA spectra of PE: (a) typical, initial, unexposed film; (b) film recovered from the STS-8 Space Shuttle flight, involving exposure 'day only' to $O(^3P)$ in LEO; (c) film after exposure for 2 h to $O(^3P)$ downstream from the r.f. plasma; (d) film after exposure for 10 min 'in the glow' of an O_2 plasma. The broken curves correspond to deconvolutions of the solid curves

Table 3 ESCA data for PE before and after various exposures to $O(^3P)$

		Composition (%)			
Peaks	*BE* (eV)	Unexposed[a]	LEO[b]	Out of glow[c]	In glow[d]
C_{1s}	284.6	100.0	76.6 (84.5)	73.7	58.8
	286.1–286.5	—	6.6 (2.9)	4.7	8.1
	287.6–287.8	—	—	2.8	5.7
	288.5	—	4.4 (2.4)	—	—
	289.2	—	—	3.4	6.1
N_{1s}	400.3	—	0.6 (1.1)	—	—
O_{1s}	532.4–532.9	—	11.8 (9.1)	15.4	21.3

[a] *Figure 3a*

[b] Data for 'day only' exposure (*Figure 3b*); data in parentheses are for 'day and night' exposure

[c] *Figure 3c*

[d] *Figure 3d*

to a fluence of $\approx 3\times10^{20}$ O atoms cm^{-2}. Since that PE film was stated to have undergone a weight loss of $\approx$1.3 mg cm^{-2} (equivalent to a thinning of $\approx$14 μm), we may assume that it too was exposed 'day and night' in LEO. Interestingly, the ESCA data obtained by those workers compare favourably with the data indicated in parentheses in *Table 3* for our PE film exposed 'day and night'; thus, they noted three C_{1s} peaks and one O_{1s} peak (but gave no *BE* values) with the following composition (at%): $>C{-}C<$, $>C{=}C<$, 81.5; $>C{=}O$, $>C{-}O{-}C<$, $>C{-}OH$, 4.5; $-COOH$, 3.1; and $>C{=}O$, $>C{-}O{-}$, 9.9. Based on ESCA analysis of the control and exposed PE films that were treated with osmium tetroxide, which adds quantitatively to double bonds, Coulter *et al.* concluded that olefin formation was not an important process in the oxidative erosion of the PE film, the unsaturation having increased from 0.3 to 0.6%. We should note that Chirinos-Padrón *et al.*[17] reported that analysis of a Phillips HDPE (like that used in this work) gave an unsaturation of 0.48 mol%.

Effect of time of exposure to O(^{3}P) on surface oxidation

Various workers[6–9,11] have noted that O(^{3}P)-induced surface oxidation of PE is extremely rapid, reaching a 'saturation' level of $\approx$15–22 at% O after only $\approx$5–30 s of exposure to an r.f. O_2 plasma, and that the oxidation is confined to the outermost layer. The latter point is seen in ESCA measurements at different electron take-off angles and the fact that transmission or ATR infrared spectra of PE before and after O(^{3}P) exposure are practically identical. Our findings for in-glow exposure of PE agree with those observations, and the oxygen uptake was essentially the same whether the exposure was for 10 min (21.3 at% O; *Table 3*) or for 30 s. An almost instantaneous oxygen saturation level was obtained for the out-of-glow exposure of PE, which however yielded a somewhat smaller oxygen uptake (15.4 at% O), while the LEO-exposed PE film exhibited an even smaller oxygen uptake (9.1–11.8 at% O). Unlike the situation with PVDF or TFE/ET, we regard the difference between the oxygen contents of the in-glow and out-of-glow exposures of PE to be qualitatively significant, having reproduced the trend of in glow > out of glow in oxygen uptake despite variations in operating parameters for the respective reactors. To account for the lower oxygen uptake by PE in LEO compared with those in the r.f. O_2 reactors, we again invoke the reaction scheme[2] involving participation of molecular oxygen present in these reactors but absent in LEO; that approach was taken previously for Kapton H polyimide film[2] and PVF[1], two polymers whose surface oxidation – in common with PE – is virtually complete after very short times of exposure to O(^{3}P).

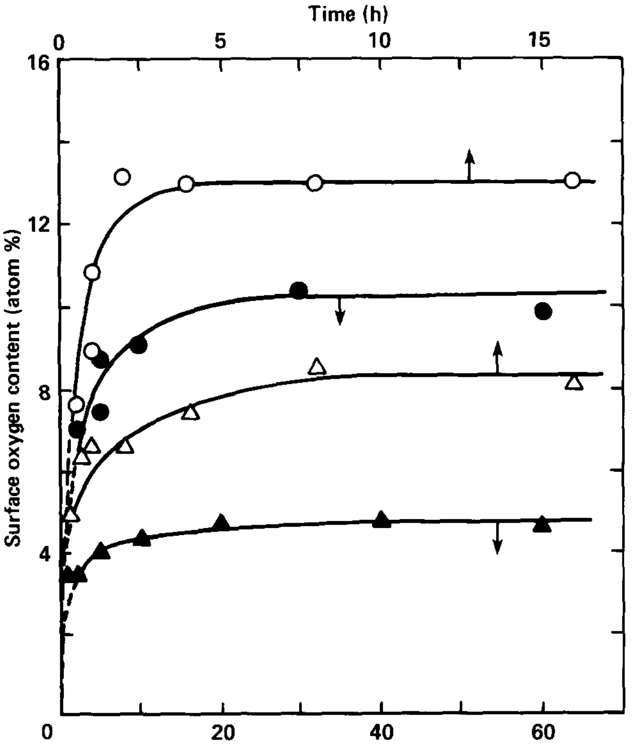

Figure 4 Effect of time of exposure to O(^{3}P) on the surface oxygen uptake of PVDF (△, ▲) and TFE/ET (○, ●); open and filled symbols denote out-of-glow and in-glow exposures, respectively

In contrast to PE, both PVDF and TFE/ET require comparatively long exposure times to reach saturation levels. This is depicted in *Figure 4* for separate series of in-glow and out-of-glow exposures where the operating parameters remained constant: the times to limiting oxygen contents were thus 20–40 min and 2–8 h, respectively. That PVDF and TFE/ET, unlike PE, do not attain maximum oxygen uptakes almost instantaneously may be related to the fact that the etch rate for HDPE, out of the glow of the O_2 plasma[3], was some 70–80 times the corresponding etch rates for PVDF and TFE/ET. We can thus visualize the last two polymers requiring a longer time to reach dynamic equilibrium between surface erosion and oxidation in which the etching front maintains a steady-state elemental composition.

Since the polymer surface is constantly being etched away and renewed during O(^{3}P) attack, the maximum oxygen uptake is effectively independent of any adventitious oxidative functionality initially present at the surface. Thus, the dashed lines in *Figure 4* may be regarded as beginning at the origin, even though PVDF and TFE/ET have initial surface oxygen contents of 1.5 and 0.1 at% O, respectively (see *Tables 1* and *2*).

CONCLUDING REMARKS

Comparing the ESCA data for the three polymers discussed in this paper, we see that for either in-glow or out-of-glow exposures to O(^{3}P), there is a definite trend in maximum surface oxygen uptakes, namely, PE > TFE/ET > PVDF. Recalling prior ESCA data on PVF and PTFE films[1] (with minimum oxygen uptakes of 16.4 and $\approx$0.2–0.5 at% O, respectively), we observe that the extent of surface oxidation decreases regularly with increase in fluorine substitution in a family of ethylene-type polymers, i.e. PE ($-CH_2CH_2-$) > PVF ($-CH_2CHF-$) > TFE/ET ($-CH_2CH_2CF_2CF_2-$) > PVDF ($-CH_2CF_2-$) > PTFE ($-CF_2CF_2-$). This order of maximum surface oxygen uptake does not parallel exactly the corresponding order of etch rates downstream from the glow of an O_2 plasma, however[3]: PVF > HD PE > PVDF ~ TFE/ET > PTFE. Although considerable information regarding etch rates and surface oxidation of various fluoroethylene polymers has been presented in this and in our two previous papers[1,3], much remains to be learnt from analyses of volatiles produced and derivatization studies before detailed mechanism(s) of the reaction of O(^{3}P) with these various polymers can be advanced.

ACKNOWLEDGEMENTS

The authors are indebted to Dr L. J. Leger and Mr J. F. Kuminecz, NASA Johnson Space Center, Houston, Texas, for kindly furnishing FE film samples exposed to atomic oxygen in LEO during the STS-8 shuttle flight. The authors also acknowledge the use of plasma etching apparatus at Plasma Science, Belmont, California, for performing exposures of the three title polymers to atomic oxygen 'in the glow' of an O_2 plasma.

REFERENCES

1 Golub, M. A., Wydeven, T. and Cormia, R. D. *Polymer* 1989, **30**, 1571
2 Golub, M. A., Wydeven, T. and Cormia, R. D. *Polym. Commun.* 1988, **29**, 285
3 Golub, M. A. and Wydeven, T. *Polym. Degrad. Stabil.* 1988, **22**, 325
4 Leger, L. J. and Visentine, J. T. *J. Spacecr. Rockets* 1986, **23**, 505
5 Leger, L., Visentine, J. and Santos-Mason, B. *Int. SAMPE Tech. Conf.* 1986, Vol. 18, p. 1015 and references cited therein
6 Clark, D. T. and Dilks, A. *J. Polym. Sci., Polym. Chem. Edn.* 1979, **17**, 957
7 Clark, D. T. and Wilson, R. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 837 and references cited therein
8 Munro, H. S. and Beer, H. *Polym. Commun.* 1986, **27**, 79
9 Gerenser, L. J. *J. Adhesion Sci. Tech.* 1987, **1**, 303
10 Coulter, D. R., Liang, R. H., Chung, S. Y., Smith, K. O. and Gupta, A. in 'Proceedings of the NASA Workshop on Atomic Oxygen Effects' (Ed. D. E. Brinza), JPL Publication 87-14, 1987, p. 39
11 Dilks, A. in 'Electron Spectroscopy: Theory, Techniques and Applications', Vol. 4 (Eds. C. R. Brundle and A. D. Baker), Academic Press, London, 1981, p. 277
12 Cais, R. E. and Kometani, J. M. *Polymer*, **29**, 168
13 Corbin, G. A., Cohen, R. E. and Baddour, R. F. *Polymer* 1982, **23**, 1546
14 Wydeven, T., Golub, M. A. and Lerner, N. R. *J. Appl. Polym. Sci.* 1989, **37**, 3343
15 Golub, M. A. unpublished results
16 Kuminecz, J. F. NASA-Johnson Space Center, Houston, TX, personal communication
17 Chirinos-Padrón, A. J., Hernández, P H., Chávez, E., Allen, N. S., Vasiliou, C. and DePoortere, M. *Eur. Polym. J.* 1987, **23**, 935