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XPS STUDY OF THE EFFECT OF HYDROCARBON CONTAMINATION ON POLYTETRAFLUOROETHYLENE (TEFLON) EXPOSED TO ATOMIC OXYGEN

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ABSTRACT

The presence of hydrocarbon contamination on the surface of polytetrafluoroethylene (PTFE) markedly affects the oxygen uptake, and hence the wettability, of this polymer when exposed to an oxygen plasma. As revealed by XPS (X-ray photoelectron spectroscopy) analysis, the oxygen-to-carbon ratio (O/C) for such a polymer can increase sharply, and correspondingly the fluorine-to-carbon ratio (F/C) can decrease sharply, at very short exposure times; at longer times, however, such changes in the O/C and F/C ratios reverse direction, and these ratios then assume values similar to those of the unexposed PTFE. The greater the extent of hydrocarbon contamination in the PTFE, the larger are the amplitudes of the "spikes" in the O/C- and F/C-exposure time plots. In contrast, a pristine PTFE experiences a very small, *monotonic* increase of surface oxidation or O/C ratio with time of exposure to oxygen atoms, while the F/C ratio is virtually unchanged from that of the unexposed polymer (2.0). Unless the presence of adventitious hydrocarbon is taken into account, anomalous surface properties relating to polymer adhesion may be improperly ascribed to PTFE exposed to an oxygen plasma.

INTRODUCTION

Morra and co-workers (1) recently reported that the surface of the important polymer Teflon, or polytetrafluoroethylene (PTFE), when exposed to an oxygen plasma for very short times exhibited a sharp increase in the oxygen-to-carbon ratio (O/C, increasing from 0.014 to 0.129), and a correspondingly sharp decrease in the fluorine-to-carbon ratio (F/C, decreasing from 1.73 to 1.26), as measured by electron spectroscopy for chemical analysis (ESCA) (or X-ray photoelectron spectroscopy (XPS)). At longer exposure times, however, the changes in the O/C and F/C ratios reversed direction, and these ratios assumed values similar to those of the unexposed PTFE. These ESCA results proved surprising to us since they conflicted with our prior observation (2) that PTFE experienced "a very small [but monotonic] increase of surface oxidation with time of exposure to $O(^3P)$ in an r.f. O_2 discharge [while] the F/C ratios were virtually unchanged from that of the control (2.0)." From a close examination of the ESCA spectra and data presented by Morra and co-workers, we suspected that the spikes observed in their plots of O/C or F/C versus time of exposure to an O_2 plasma were not characteristic of PTFE per se but were instead a result of the hydrocarbon contamination present in their PTFE samples. To be sure, those workers noted that the ESCA spectra of their PTFE, both before and after exposure to an O_2 plasma for 15 min, showed "a weak structure due to hydrocarbon contamination," but they tacitly assumed that this hydrocarbon played no role in the effect of exposure time on the O_2 plasma-induced surface modification of PTFE. We subsequently demonstrated that, on the contrary, the spikes observed in the O/C- and F/C-exposure time plots presented by Morra and co-workers were a direct result of the hydrocarbon contamination present in their PTFE sample (3). Indeed, we pointed out that this contamination was not minor, nor could their untreated polymer be considered to have a *clean* PTFE surface, inasmuch as its F/C ratio (1.73) was well below the theoretical value of 2.0.

DISCUSSION

Figures 1 and 2 present composite plots of O/C and F/C ratios, respectively, as a function of time of exposure to an O₂ plasma for the following sets of data: (a) Data derived from a photo-enlargement of Figure 1 of Morra and co-workers (1) with the aid of a variable scale for accurate interpolations; (b) prior ESCA data from Golub and co-workers (2) for *very clean* PTFE, showing no evidence for hydrocarbon contamination (initial F/C = 2.0), and exposed for 10, 20 and 30 min 'in the glow' of an O₂ plasma, yielding oxygen uptakes of 0.11, 0.15 and 0.21 atom % O, respectively; and (c) new data obtained expressly for the recent article by the latter workers (3), using disks cut from a 25-mm thick PTFE sheet (initial F/C = 1.96, O/C = 0.0098) similar to that used previously (2) and having a small amount of hydrocarbon contamination, but much less than in the PTFE sample used by Morra and co-workers. Figure 3 shows the C_{1s} ESCA spectra of this 'new' PTFE before and after various

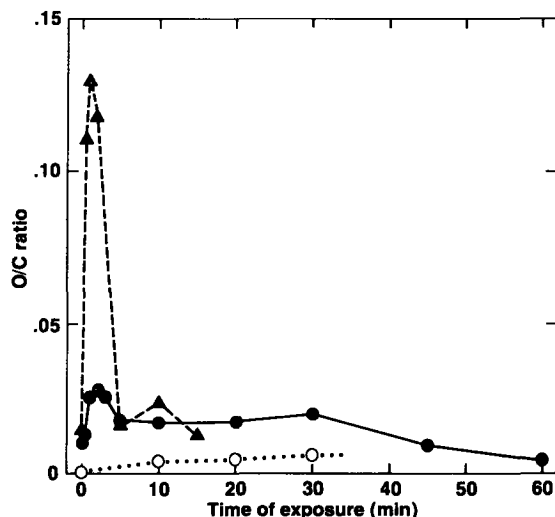


Figure 1. Effect of time of exposure to O₂ plasma on the O/C ratio of PTFE, as determined from ESCA spectra: ●, new data; ○, prior data from Golub and co-workers (2); ▲, data from Morra and co-workers (1).

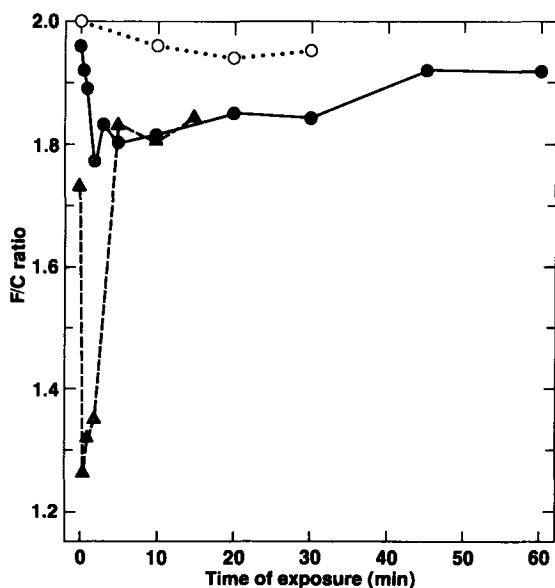


Figure 2. Effect of time of exposure to O₂ plasma on the F/C ratio of PTFE, as determined from ESCA spectra: ●, new data; ○, prior data from Golub and co-workers (2); ▲, data from Morra and co-workers (1).

times of exposure in the same O₂ plasma reactor (and obtained with the same SSX-101 ESCA spectrometer) used to obtain the prior data for the very clean PTFE mentioned under data set (b) above. A crude measure of the hydrocarbon contamination in the 'new' PTFE is given by the ratio of intensities of the peaks at ca. 285 eV (-CH₂- and/or -CH-) and 292 eV (-CF₂-); for the unexposed film, this ratio or II/I is 0.027. In contrast, the corresponding ratio for the unexposed PTFE used by Morra and co-workers is much larger, which we determined as 0.15 by planimetry of the areas under the two peaks in a photoenlargement of their Figure 2.

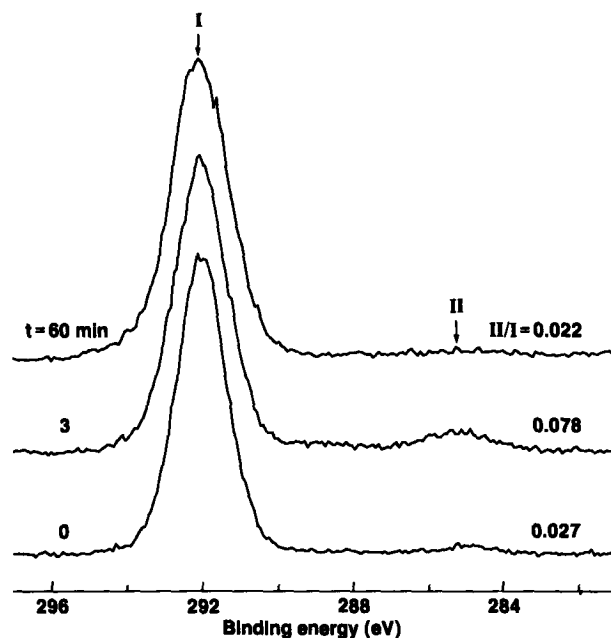


Figure 3. C_{1s} ESCA spectra of 'new' PTFE before and after exposure to O₂ plasma for 3 and 60 min. Peak I centered at ca. 292 eV corresponds to -CF₂- groups, but may overlap contribution from -CF- groups, while peak II at ca. 285 eV corresponds to contributions from hydrocarbon contamination (-CH₂-, -CH-) and oxidized carbon (>C-O-, >C=O).

A better measure of the hydrocarbon content in the unexposed PTFE takes into account the fact that, for small amounts of oxidation, peaks due to >C-O- or >C=O (typically located at 286.0-286.4 eV) will merge with that for -CH₂- / -CH- groups (284.6 eV) into the observed broad 285-eV peak. Also, for the O₂-plasma treated PTFE, where small amounts of -CF- groups may arise from fluorine detachment, the ESCA peak of such groups (at 290.4 eV) will be concealed under the low-eV tail of the broad 292-eV peak, which is due principally to -CF₂- groups (centered at 291.9 eV). (Support for the latter point is seen in the ESCA spectra of Teflon FEP, a tetrafluoroethylene-hexafluoropropylene copolymer (2)) Thus, II/I is a measure of the following ratio of carbon atoms: [-CH₂-, -CH-, >C-O-, >C=O]/[-CF₂-, -CF-]. For simplicity, we will refer to -CH₂- and/or -CH- as CH, >C-O- and/or >C=O as CO, and -CF₂- and -CF- as CF₂ and CF, respectively. Now, noting that F/C = 1.96 and O/C = 0.0098 for the unexposed PTFE in Figure 3, we infer that the initial 'new' PTFE comprises 98 CF₂, 1 CH and 1 CO for every 100 carbon atoms, for an oxygen level of 0.34 atom % O and a calculated ratio for II/I = 0.020; this ratio compares reasonably well with the ESCA-determined ratio of II/I = 0.027. In a similar way, we infer that the unexposed PTFE used by Morra and co-workers (F/C = 1.73; O/C = 0.014) comprises 86.5 CF₂, 12.1 CH and 1.4 CO for every 100 carbon atoms, for an oxygen level of 0.51 atom % O and a calculated ratio for II/I of 0.16, which is virtually the same as the planimeter-derived ratio of 0.15 indicated above.

Returning to the present Figure 1, we observe that Morra's PTFE, with a hydrocarbon content (or CH) ca. 12.1 times that of the 'new' PTFE, exhibits a spike in the O/C-exposure time plot (or Δ(O/C)) whose amplitude is ca. 0.115/0.017, or 6.7, times the amplitude of the spike for the 'new' PTFE. For the *very clean* PTFE (of our prior data (2)), which has no detectable hydrocarbon contamination, there is no spike at all, only a

small, monotonic increase of O/C ratio with time of exposure, tending towards an "equilibrium" oxygen uptake after prolonged exposure as a result of the dynamic competition between oxidation and etching (or surface regeneration). To the extent that there is oxygen uptake by the O₂ plasma-exposed PTFE, the F/C ratio necessarily decreases, whether or not fluorine detachment occurs. This is reflected in Figure 2, which shows changes in the F/C ratios accompanying the changes in the O/C ratios presented in Figure 1. As in the latter figure, we see in Figure 2 that the amplitude of the spike in the F/C-exposure time plot for Morra's PTFE ($\Delta(F/C) = -0.47$) is greater than that (-0.19) for the 'new' PTFE, while the very clean PTFE again shows no such spike. Apropos, it is worth recalling our earlier observation (2) that "apparently there is a correlation between the [oxygen] uptake and the level of hydrocarbon contamination for [PTFE] films exposed to [oxygen atoms in low Earth orbit (LEO)] on the [Space Shuttle] STS-8, and we may speculate that the -CF₂CF₂- structure per se undergoes negligible oxygen uptake on exposure to O(³P) in LEO." Here we wish to stress the need for working with very clean PTFE because the surface properties of this polymer, which has great industrial importance and is easily contaminated by ubiquitous hydrocarbon, are therefore often difficult to reproduce. At any rate, it follows that the changes in surface properties (namely, wetting behavior and contact angle hysteresis) reported at short treatment time by Morra and co-workers cannot be considered representative of pristine PTFE.

That a steady-state surface composition is approached on prolonged exposure to O₂ plasma is seen not only in Figures 1 and 2 but also in Figure 3, where the II/I ratio increases from an initial 0.027 to 0.078 for the 3-min exposure and subsequently drops to 0.022 for the 60-min exposure. Given the II/I ratio and the O/C and F/C ratios (0.026 and 1.83, respectively) for the 'new' PTFE exposed for 3 min, we calculate that its structure comprises 90.0 CF₂, 2.8 CF, 4.6 CH and 2.6 CO for every 100 carbon atoms, for an oxygen level of 0.91 atom % O. Again, given the II/I ratio and the O/C and F/C ratios (0.0038 and 1.92, respectively) for the 'new' PTFE exposed for 60 min, its structure is presumed to comprise 94.0 CF₂, 3.8 CF, 1.8 CH and 0.4 CO for every 100 carbon atoms, for an oxygen level of 0.14 atom % O. The latter value, which is in the range observed earlier for a pristine PTFE exposed to an O₂ plasma for 10-30 min, is less than the initial value (0.34 atom % O) of the unexposed 'new' PTFE.

A similar approach towards a steady-state composition may be deduced from the ESCA results of Morra and co-workers. From Figure 2 of ref 1, the II/I ratio for their PTFE is 0.15 initially and 0.12 after a 15-min exposure to an O₂ plasma. At intermediate exposures, the II/I ratio apparently increases to ca. 0.48 after 1-min exposure, then decreases to ca. 0.070 after 5-min exposure, and remains at ca. 0.087 thereafter. This last statement is seen as follows: Given the O/C and F/C ratios (0.129 and 1.32, respectively) for Morra's PTFE exposed for 1 min, a plausible structure comprises 64.5 CF₂, 3.0 CF, 19.6 CH and 12.9 CO for every 100 carbon atoms. Such a structure yields the ratio II/I = 0.48 just mentioned and, significantly, an oxygen level of 5.3 atom % O -- substantially higher than that encountered in any PTFE exposed to oxygen atoms, including two samples recovered from the STS-8 mission that exhibited some hydrocarbon contamination (2). Again, given the O/C and F/C ratios (0.016 and 0.083, respectively) for Morra's PTFE exposed for 5 min, a plausible structure is 89.0 CF₂, 4.5 CF, 4.9 CH and 1.6 CO, which yields a II/I ratio of 0.070 and an oxygen level of 0.56 atom % O. Lastly, the PTFE exposed for 15 min, given the pertinent O/C and F/C ratios (0.0125 and 1.84, respectively), has a structure (92 CF₂, 6.7 CH, 1.3 CO) which yields a II/I ratio of 0.087, somewhat less than the 0.12 measured planimetrically, and an oxygen level of 0.46 atom % O. To interpret the ESCA results of Morra and co-workers, it is clear that the hydrocarbon present in the PTFE surface is preferentially oxidized in the O₂ plasma, and the oxygen uptake can rapidly reach high levels; for polyethylene exposed to O atoms (4), for example, the "saturation" level is ca. 15-22 atom % O. For Morra's PTFE sample exposed for 1 min, and with a hydrocarbon content (CH/(CF₂ + CF + CH)) of ca. 23%, an oxygen uptake of 0.23 × (15-22) or 3.5-5.1 atom % O may be anticipated; as we saw above, the oxygen level for that sample (5.3 atom % O) is indeed close to this range. Upon prolonged exposure, of course, the hydrocarbon should be fully oxidized away, and this accounts for the fact that Morra's PTFE surface is then comparable to, or even cleaner than, that of the unexposed polymer. On a smaller scale, because of its lower hydrocarbon content, the 'new' PTFE results present the same picture.

There is one additional feature of the foregoing results worth mentioning. Both for Morra's PTFE and the 'new' PTFE, there are definite ESCA indications of an increase in hydrocarbon contamination at short times of exposure, followed by a decrease to the level of the initial polymer, or even below it, upon prolonged exposure. Thus, the CH content in Morra's PTFE increased from ca. 12.1 (per 100 carbon atoms) to ca. 19.6 (at 1-min exposure), decreasing to ca. 4.9 (at 5-min exposure), and ending with ca. 6.7 (at 15-min exposure). Similarly, the CH content in the 'new' PTFE increased from 1.0 (per 100 carbon atoms) to 4.6 (at 3 min-exposure) and decreased

thereafter to 1.8 (at 60-min exposure). This trend of an initial increase, followed by a decrease, in hydrocarbon content with time of exposure is probably not an artifact from handling exposed PTFE samples. Instead, it suggests that as the hydrocarbon content in the surface is oxidized away, additional hydrocarbon "blooms" to the surface of the PTFE (in the manner of blooming of compounding ingredients in vulcanized rubber formulations) from underlying molecular layers until the hydrocarbon in the bulk is eventually removed through the etching process.

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