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Electrostatic Properties of PE and PTFE Subjected to Atmospheric Pressure Plasma Treatment; Correlation of Experimental Results with Atomistic Modeling

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Abstract—The use of an atmospheric pressure glow discharge (APGD) plasma was used at KSC to increase the hydrophilicity of spaceport materials to enhance their surface charge dissipation and prevent possible ESD in spaceport operations. Significant decreases in charge decay times were observed after tribocharging the materials using the standard KSC tribocharging test. The polarity and amount of charge transferred was dependant upon the effective work function differences between the respective materials. In this study, PE and PTFE were exposed to a $He+O_2$ APGD. The pre and post treatment surface chemistry was analyzed by X-ray photoelectron spectroscopy and contact angle measurements. Semi-empirical and ab initio calculations were performed to correlate the experimental results with some plausible molecular and electronic structure features of the oxidation process. For the PE, significant surface oxidation was observed, as indicated by XPS showing C-O, C=O, and O-C=O bonding, and a decrease in the surface

contact angle from 98.9 ° to 61.2 °. For the PTFE, no C-O bonding appeared and the surface contact angle increased indicating the APGD only succeeded in cleaning the PTFE surface without affecting the surface structure.

The calculations using the PM3 and DFT methods were performed on single and multiple oligomers to simulate a wide variety of oxidation scenarios. Calculated work function results suggest that regardless of oxidation mechanism, e.g. -OH, =O or a combination thereof, the experimentally observed levels of surface oxidation are unlikely to lead to a significant change in the electronic structure of PE and that its increased hydrophilic properties are the primary reason for the observed changes in its electrostatic behavior. The calculations for PTFE argue strongly against significant oxidation of that material, as confirmed by the XPS results.

I. INTRODUCTION

Plasmas are used to treat polymer materials to produce special functional groups at the surface, increase the surface energy, increase or decrease hydrophilicity, improve chemical inertness, introduce cross-linking, remove weak boundary layers and contamination, and increase the surface morphology [1]. The advantage of an atmospheric pressure glow discharge (APGD) plasma is that it can be used in atmosphere eliminating the need for an expensive vacuum chamber, and also operates at low temperatures, minimizing heat damage to the polymer surface. Oxygen-containing plasmas are the most commonly used. An APGD using O_2 creates free radicals and excited species forming active products that chemically react with the surface improving the wettability. APGDs using He+O_2 have been successfully used in several applications [2-6] where He is used as the carrier gas to initiate the plasma to which the treatment gas (O_2) is introduced. The depth of surface modification depends upon the power level and time of treatment. For polymer samples, it is typically several hundred angstroms. An APGD plasma using He+O_2 was used at Kennedy Space Center to increase the hydrophilicity of spaceport materials for the Space Shuttle and International Space Station to enhance their surface charge dissipation and prevent possible electrostatic discharge (ESD) in spaceport operations [7]. The charge decay of the spaceport materials was considerably reduced. When followed by a chemical treatment (Hydrolast©, AST Products Inc) applied after the plasma treatment that "locks" in the surface modification, no hydrophobic recovery was observed by X-ray Photoelectron Spectroscopy (XPS) and contact angle measurements for several weeks. The XPS data showed increases in the surface oxidation of the materials, as monitored by the measured C:O ratio, and was a function of the time and power of the APGD treatment. These materials now passed the KSC standard triboelectric charging test [8]. It is generally accepted in tribocharging that the amount and polarity of charge exchanged between two materials is a function of the difference in the work function of the two contacting materials. For insulators, there is still considerable debate as to the exact mechanism, and although numerous tables of triboelectric series have

been published, the order is not absolute and many variations of it involving insulators may be found [9]. There is some uniformity for some polymers such as nylon and PTFE, which are consistently found on opposing ends of the series, and similarly polyethylene and polystyrene are usually found in consistent positions among different series. Charge exchange between insulators can be predicted from the knowledge of the charge acquired by contact with metals, and so insulator-insulator charging can be partly explained by the same basic mechanism as metal-insulator charging [10]. Hays [11] reported that some of the variability reported in the literature on metal-polymer contact charging can be due to differences in the degree of oxidation, for both the metal and the polymer. It was also shown by Yanagida *et al* [12] that the threshold for photoemission and ionization potentials of certain polymers is related to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, and in substituted polymers, it was found that the triboelectric charging efficiency could be related to the properties of the substitution groups. Their results indicated that electronic states are responsible for contact electrification, and interpreted their results in terms the Duke and Fabish model [10] in that charge transfer could only occur into a narrow window of bulk and surface states close to the Fermi energy within an insulator, and that these states were due to molecular ion side groups. Gibson and Bailey [13] showed tribocharging is linearly correlated with substituent constants for polyethylene and polypropylene.

In this study, in order to understand the oxidation process involved in APGD applications to polymers and how it affects electrostatic properties, coupons of polyethylene (PE) and polytetrafluoroethylene (PTFE) were exposed to a He+O_2 APGD plasma, and the pre and post treatment surface chemistry was analyzed by XPS and contact angle measurements. Semi-empirical and ab initio molecular modeling calculations were performed to correlate the experimental results with plausible molecular and electronic structure features of the oxidation process.

II. EXPERIMENTAL

A. APGD plasma treatment

Coupons measuring 25 x 25 x 2 mm thick were cut out of flat sheets of low molecular weight PE and PTFE. The coupons of each material were ultrasonically cleaned for 10 minutes successively in acetone, methanol, and iso-propanol, and finally rinsed in DI water. The coupons were allowed to air dry in a positive pressure sterile hood until used. The He+O_2 plasma (98% He, 2% O_2) was applied to each coupon at a power of 150 W. The coupons were exposed to the plasma via a 150 x 3 mm slit in the plasma head at a distance of 4 mm. The head was scanned across the coupons so that total exposure time was 5 minutes. Previous experimentation had shown that this was the optimum exposure time as monitored by the O:C ratio measured by XPS [7]. The plasma head set-up is shown in Figure 1.
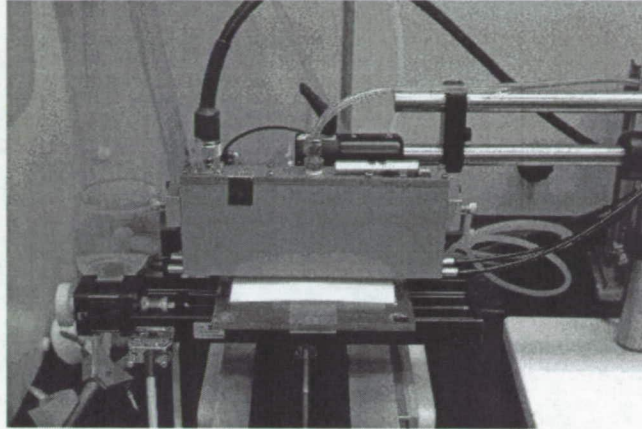
Fig.1. He+O$_2$ plasma head shown treating PTFE sheet

Figure 2 shows the emission spectrum of the APGD plasma. Although the feed gas was predominantly helium, the spectrum shows the oxygen peaks associated with the oxygen atom and ion. The reactions can be written;
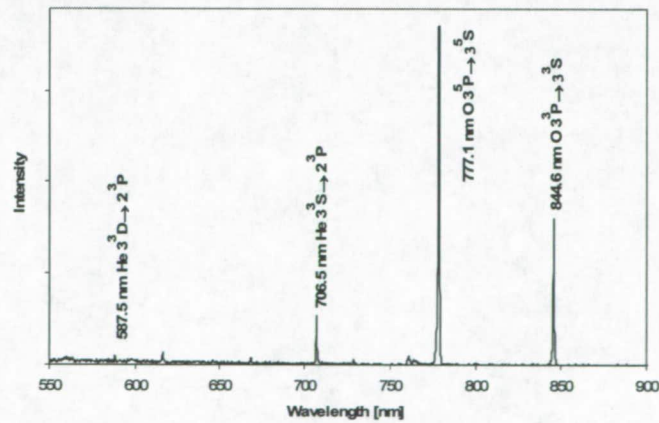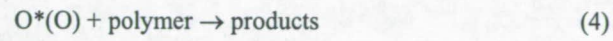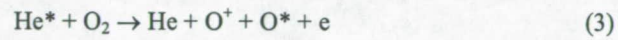
$$He + e \rightarrow He*(2^3P) + e \qquad (1)$$

$$O_2 + e \rightarrow 2O + e \qquad (2)$$

$$He* + O_2 \rightarrow He + O^+ + O* + e \qquad (3)$$

$$O*(O) + polymer \rightarrow products \qquad (4)$$

Fig. 2. Optical emission spectrum of the APGD discharge composed of 98% He+2% O$_2$.

B. XPS analysis

XPS analysis of the pre and post APGD treated coupons were conducted on a Kratos XSAM 800 Spectrometer at a background pressure of 1 x 10^{-9} torr, using a Mg Kα (hv = 1253.6 eV) x-ray source. The x-ray beam used was 150W, 4 - 6 mm in diameter. The collected data were referenced to the C1s peak to 284.6 +/- 0.5 eV. Wide survey scans were collected from 0 - 1100 eV at a pass energy of 80 eV in 1 eV steps with a 50 ms dwell time to determine overall elemental composition. Narrow scans of the C1s peak were collected at a pass energy of 20 eV in 0.1 eV steps with a 300 ms dwell time to determine the carbon bonding. The relative atomic concentrations of the detected elements were calculated and normalized to 100% using sensitivity factors supplied by the instrument manufacturer from known certified standards. The individual element spectra were converted to VAMAS ASCII format and imported to a computer where the peak curve fitting was performed using XPS International SDP v.4.1 data reducing software.

C. Contact angle measurements

Contact angle measurements were performed on a VCA Optima XE contact angle instrument (AST Products Inc.) enclosed in an environmental chamber. The measurements of the advancing angle were performed by depositing 5 μl drops of de-ionized water (18.2 Mohms) using an a motorized syringe assembly, and were taken at 45 +/- 3% RH and at 72 °F. Ten measurements were taken for each sample.

D. Theoretical modeling

Various models of the plasma-induced oxidation of PE and PTFE were simulated using a variety of molecules (singles chains up to 40 carbons in length and even coupled chains) and theoretical methods (semi-empirical PM3 Hartree-Fock, followed up by more rigorous *ab-initio* DFT calculations). The calculations were performed using Spartan 02 for Linux/Unix and Spartan 04 for Windows [14]. The primary purpose of the calculations was to determine the energetic and electronic structure implications for different arrangements of carbonyl, =O, and hydroxyl, -OH, groups attached to the central carbon chain in both polymers. The DFT calculations were time-consuming but practical, running from a minimum of several hours to a couple days, on a typical 3GHz Pentium-IV Linux workstation.

III. RESULTS AND DISCUSSION

A. XPS and contact angle analysis

Figures 3 and 4 show the XPS data for PE before and after APGD treatment. The increase in the O1s peak is clearly observed. The high resolution scan of the C1s peak (Figs. 5) show C-O, C=O, and O-C=O bonding after APGD. The XPS spectra for the PTFE before and after APGD treatment are shown in Figures 7 and 8. The high resolution spectra of the C1s peak are shown in

Figure 9 and 10. Very little difference was observed in the surface composition of the PTFE as a result of the APGD treatment. Closer examination showed a slight increase in the oxygen concentration, but this may be associated with a minor amount of silicon was detected on the surface after APGD. This may be deposited residue from the APGD. The C1s peak showed a slight decrease in the C-C/C-H bonding compared to the C-F$_2$ peak. The XPS data is summarized in Table 1.

The contact angle data is presented in Table 2. The mean contact angle for the PE decreased from 98.9° to 61.2°after APGD indicating increased hydrophilicity. For the PTFE, no C-O bonding was detected and the surface contact angle increased from 101° to 125° after APGD indicating that the APGD treatment for PTFE only succeeded in cleaning the surface of contaminants without affecting the surface structure.

For the PE, the oxygen surface concentration increased significantly (1.3 – 27.7 at. %), with the appearance of C-O, C=O, and O-C=O bonding., and is consistent with what has been observed for Ultra-high-weight PE fibers exposed to an He low pressure plasma [3]. The PTFE showed to be rather resistant to the APGD. Significant oxidation of PTFE by APGD in air has been reported, but only for exposure times of 20 to 120 minutes [15], while long exposure times to an oxygen plasma (> 15 mins.) showed after some initial oxidation, the PTFE was chemically similar to the control [16].

B. Molecular modeling analysis

The difference between the work functions of two materials is a rough guide to the level and sign of charge transfer during triboelectrification. To estimate the work function, φ, of the polymers, it was decided to simply use the highest occupied molecular orbital, HOMO, instead of relying upon any information from unoccupied states, e.g. the lowest unoccupied molecular orbital, LUMO, i.e., using $\varphi \approx -E_{HOMO}$, rather than $\varphi \approx -(E_{HOMO} - \frac{1}{2} E_{gap})$. The reason for this was twofold: first, for large band-gap insulators such as these, the participation of excited states is not likely to be important as these states will not be occupied at room temperature and second, the LUMO levels are unreliable unless sophisticated configuration interaction (CI) calculations are performed. (The LUMO varies wildly for different oxidation scenarios, which can lead to misleading variations in a band gap calculated simply by taking the difference between it and the HOMO. See Figure 11.) CI calculations are prohibitively expensive for even small molecules and were not possible with large chains such as the ones used in this study. For the DFT method used (B3LYP with a 6-31G* basis set), the HOMO is known to be reliable [17] for relative changes or trends, but is not expected to be accurate for absolute ionization energy (see below).
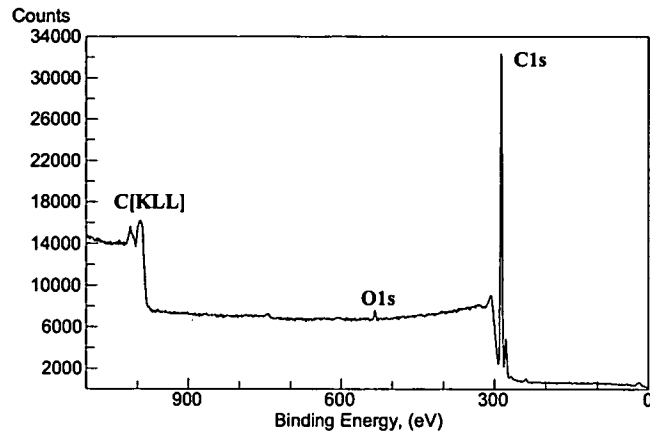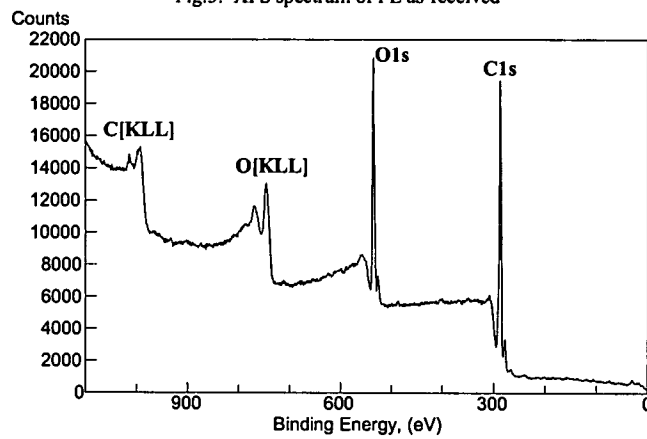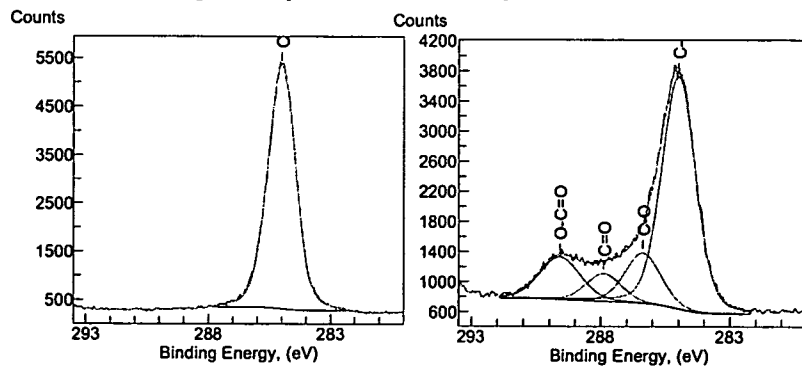
Fig.3. XPS spectrum of PE as-received

Fig.4. XPS spectrum of PE after He+O_2 treatment

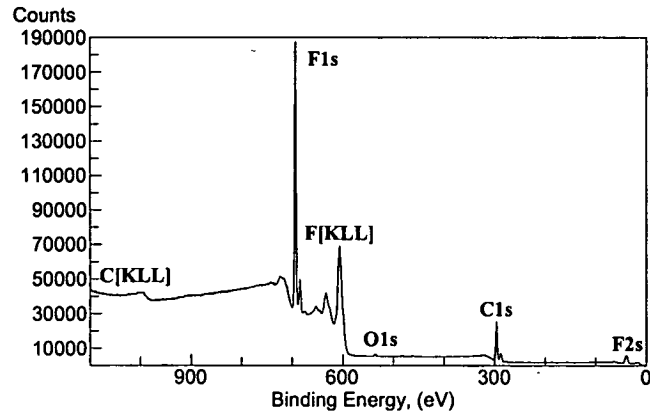Fig.5. XPS spectrum of PE C1s peak (a) before and (b) after He+O_2 APGD
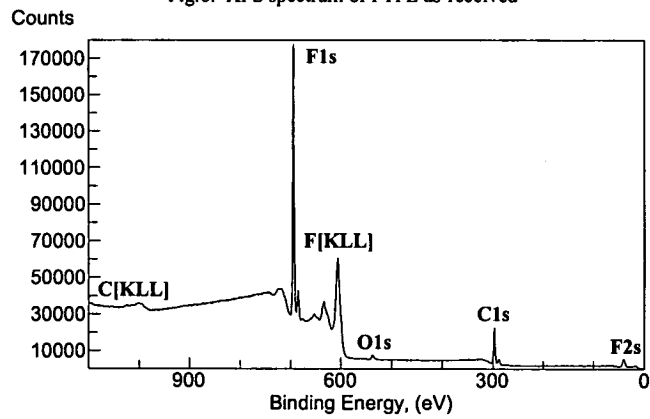
Fig.6. XPS spectrum of PTFE as-received

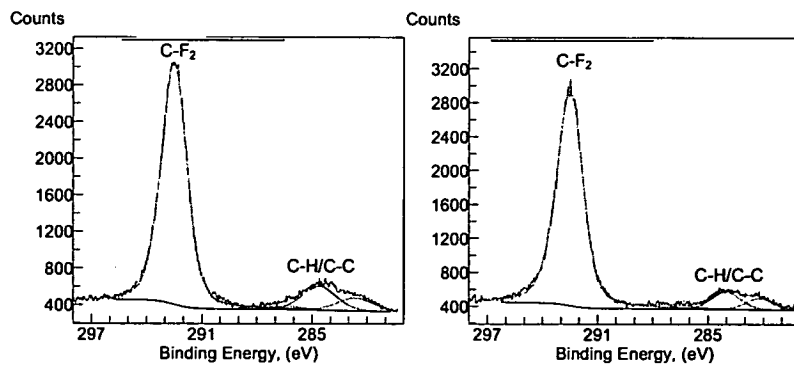Fig.7. XPS spectrum of PTFE after He+O_2 APGD

Fig.8. XPS spectrum of PTFE (a) before and (b) after He+O_2 APGD

TABLE 1: RELATIVE ATOMIC CONCENTRATIONS OF PE AND PTFE FROM THE XPS DATA BEFORE AND AFTER HE+O_2 APGD TREATMENT [%]

	C	O	F	Si
PE	98.7	1.3	-	-
PE post APGD	72.3	27.7	-	-
PTFE	34.6	0.5	64.9	-
PTFE post APGD	32.0	2.1	65.4	0.5

TABLE 2: CONTACT ANGLE DATA FOR PE AND PTFE BEFORE AND AFTER HE+O_2 APGD TREATMENT [DEGREES]

	Mean	SD
PE	98.89	2.97
PE post APGD	61.22	5.03
PTFE	101.4	0.84
PTFE post APGD	124.9	5.47

Using a 24-carbon PE model, more than 30 different oxidation patterns were simulated with the simpler PM3 calculations. Several of these were followed up with DFT calculations, which showed the same trends and which we report here. The HOMO level for PE generally increases (becomes less negative) with increasing oxidation. This implies a decrease in the work function with oxidation. This change is not universal in that for some oxidation patterns the HOMO slightly decreases. However, neither is it dramatic. The energy level changes from the pure PE molecule a maximum of + 0.75 eV (12% oxidation with –OH groups) to a minimum of – 0.1 eV (66% oxidized with a mixture of –OH and =O groups). A few models of other oxidation scenarios, e.g. ester and ether formation, yield very similar results. This behavior is consistent with previously known data on PE (work function = 4.90 eV) and PE oxide (work function = 3.95 - 4.50 eV) [9].

The results of these calculations are summarized in Figure 11 which shows the relatively minor variation in the HOMO level as oxidation is increased dramatically, even well beyond levels seen in the experiments. This suggests, therefore, that the major factor contributing to the decrease in the triboelectric behavior of PE upon plasma treatment is its increased hydrophilic behavior and not a dramatic change in its intrinsic electronic structure.
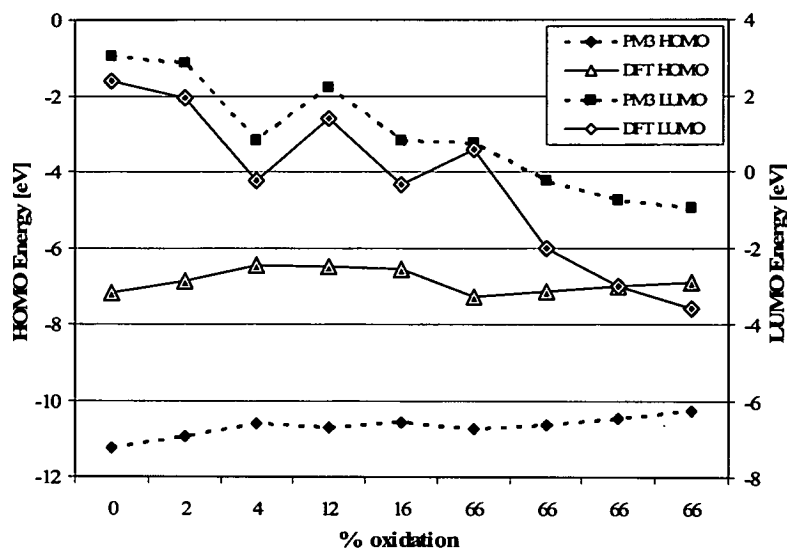
Fig. 11. Variation in the theoretically calculated HOMO and LUMO levels for a 24-carbon PE oligomer in various stages of oxidation. Note the different vertical axes used for HOMO and LUMO energies. The % oxidation for each model is shown on the horizontal axis. Most are mixtures of –OH and =O substitutions. The 0%, 2% and 4% data points refer to the pure material, a single –OH substitution and a single =O substitution, respectively

It is emphasized here that the *change* in the work function is modeled well by the calculations, though clearly the absolute values differ from experimental values. Better modeling of excited states or ionized species (once an electron is removed) or more sophisticated modeling of PE, using actual slabs rather than isolated oligomers, may improve absolute agreement. Simulation of some pairs of smaller PE oligomers (20 carbons) showed the same general behavior upon oxidation, but faster convergence to n=∞ behavior was found than with single, longer oligomers. This was regarded as an interesting avenue for future model development.

It was decided to not do a similar analysis for PTFE due to the fact that no oxidation was observed in the experiments. To correlate this observation with the atomistic simulations, a series of DFT total energy calculations for O_2 combining with a 24-carbon chain of either PE or PTFE were performed. Consistent with this and with chemical intuition, it was found that PE oxidation (either forming C-OH or C=O substitutionals) was favorable, being very exothermic, whereas PTFE oxidation (either forming C-O-F or C=O substitutionals) was endothermic. The numbers from the DFT calculations were generally within 25% of those obtained using standard bond enthalpies from the literature.

IV. CONCLUSION

Atmospheric pressure glow discharge plasma significantly improved the hydrophilicity of PE as determined by the increase in surface oxidation and decrease in the surface contact angle.

PTFE resisted oxidation by the APGD plasma at this power level, resulting only in a cleaning of the surface.

The modeling calculations showed relatively minor change in the HOMO level for increased oxidation of PE, indicating that the observed changes in the electrostatic behavior after APGD were probably due to the increased surface hydrophilicity rather than significant changes in electronic structure.

The calculations for PTFE strongly argued against significant oxidation for the material with APGD, as was observed and confirmed by experiment and the XPS results.

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