

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

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Abstract. In this study, PE, PTFE, PS and PMMA were exposed to a He+O₂ APGD and pre and post treatment surface chemistries were 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 and PS, significant surface oxidation showing C-O, C=O, and O-C=O bonding, and a decrease in the surface contact angles was observed. For the PTFE and PMMA, little change in the surface composition was observed. The molecular modeling calculations were performed on single and multiple oligomers and showed regardless of oxidation mechanism, e.g. -OH, =O or a combination thereof, experimentally observed levels of surface oxidation were unlikely to lead to a significant change in the electronic structure of PE and PS, and that the increased hydrophilic properties are the primary reason for the observed changes in its electrostatic behavior. Calculations for PTFE and PMMA argue strongly against significant oxidation of those materials, as confirmed by the XPS results.

1. Introduction

An atmospheric pressure glow discharge (APGD) plasma using He+O₂ was used at Kennedy Space Center on polymeric spaceport materials to enhance the surface charge dissipation and prevent possible electrostatic discharge in spaceport operations [1]. A significant decrease in the charge decay after tribocharging the materials with polytetrafluoroethylene (PTFE) felt was observed. Yanagida *et al.* [2] showed 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 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 [3] 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), polytetrafluoroethylene (PTFE), polystyrene (PS), and polymethylmethacrylate (PMMA) were exposed to a He+O₂ APGD plasma, and the pre and post treatment surface chemistry was analyzed by X-ray photoelectron spectroscopy (XPS) and contact angle measurements. Semi-empirical PM3 Hartree-Fock and *ab-initio* DFT molecular modeling calculations were performed to correlate the experimental results with plausible molecular and electronic structure implications for different arrangements of carbonyl, =O, and hydroxyl, -OH, groups attached to the central carbon chain in both polymers.

2. Experimental

Coupons measuring 25 x 25 x 2 mm thick were cut out of flat sheets of low molecular weight PE, PTFE, PS, and PMMA. 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 to avoid any contamination until used. The He+O₂ plasma (98% He, 2% O₂) 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 at a speed of 15 mm/sec-1 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 [1].

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 K α (h ν = 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 carbon 1s (C1s) peak at 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 peak curve fitting was performed using XPS International SDP v.4.1 data reducing software.

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 μ l drops of de-ionized water (18.2 M Ω) using a motorized syringe assembly, and were taken at 45 +/- 3% RH and at 72 °F. Ten measurements were taken for each sample.

Various models of the plasma-induced oxidation of PE, PTFE, PS, and PMMA were simulated using a variety of molecules (single 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. 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 all polymers. The DFT calculations were run on a 3GHz Pentium-IV Linux workstation.

3. Results and Discussion

The XPS widescan data for the PE before and after APGD treatment are shown in Figures 1 and 2. The high resolution scans of the C1s peak before and after APGD treatment showing peaks at 284.6, 286.5, 288, and 290 eV corresponding to C-C/C-H, C-O, C=O, and O-C=O bonding, respectively, are shown in Figures 3 and 4. Only the XPS scans for PE are shown for brevity. The XPS data is summarized in Tables 1 and 2.

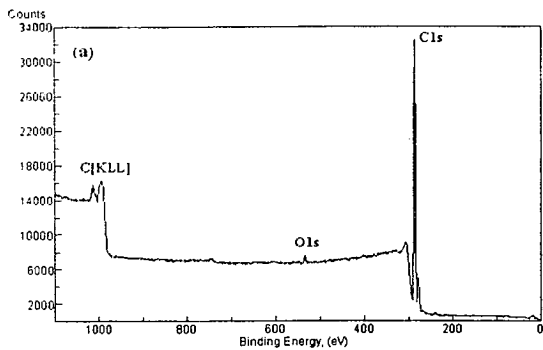


Figure 1. XPS spectrum of PE as-received.

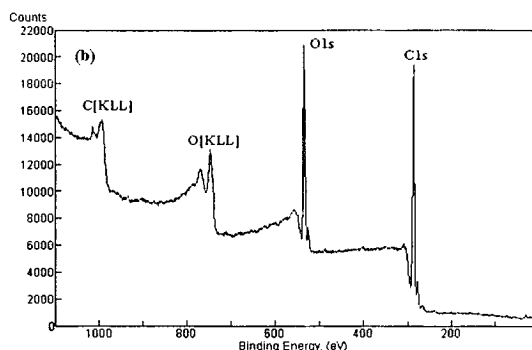


Figure 2. XPS spectrum of PE after APGD.

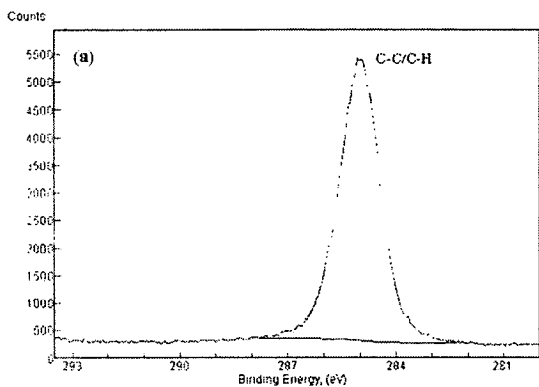


Figure 3. XPS spectrum of PE C1s peak as-received.

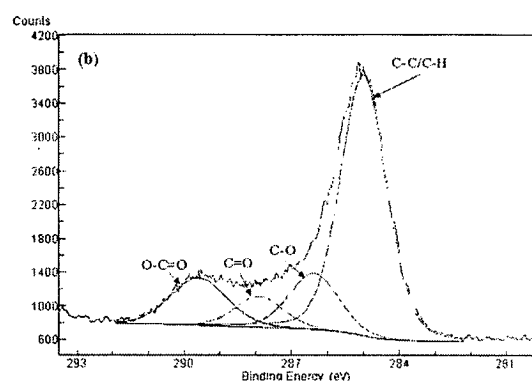


Figure 4. XPS spectrum of PE C1s peak after APGD.

Table 1. Relative atomic concentrations of the polymer surfaces before and after He+O₂ APGD treatment.

	C (at. %)	O (at. %)	F (at. %)	Si (at. %)	N (at. %)
PE	98.7	1.3	-	-	-
PE after APGD	72.3	27.7	-	-	-
PTFE	34.6	0.5	64.9	-	-
PTFE after APGD	32.0	2.1	65.4	0.5	-
PS	89.7	10.3	-	-	-
PS after APGD	73.2	26.3	-	-	0.5
PMMA	68.4	31.6	-	-	-
PMMA after APGD	67.6	32.4	-	-	-

An increase in the oxygen 1s (O1s) peak indicating increased oxidation of the surface is clearly observed for PE and PS. Very little difference was observed in the surface composition of the PTFE and PMMA as a result of the APGD treatment although a slight increase in the oxygen concentration was observed. Minor contaminants were detected on the surface of the PTFE and PS after the treatment. From the C1s peak scans in Table 2, significant oxidation in terms of C-O, C=O, and O-C=O were now observed for the PE, while for the PS, increases in the C=O and formation of O-C=O bonds were observed. However, very little difference was observed in the C1s chemistry for both the PTFE and PMMA before and after APGD treatment.

Table 2. C1s peak functional group atomic concentrations from the XPS data before and after He+O₂ APGD treatment.

	C-C/C-H (at. %)	C-O (at. %)	C=O (at. %)	O-C=O (at. %)	C-F ₂ (at. %)
PE	100.0	-	-	-	-
PE after APGD	64.1	14.4	7.7	13.8	-
PTFE	10.2	1.4	-	-	82.4
PTFE after APGD	7.2	1.4	-	-	86.9
PS	64.4	30.8	4.8	-	-
PS after APGD	55.1	30.7	8.5	5.7	-
PMMA	58.2	21.3	1.3	19.2	-
PMMA after APGD	52.9	22.3	2.9	21.8	-

The contact angle data is presented in Table 3. The mean contact angle for the PE decreased from 98.9° to 61.2° after APGD indicating increased hydrophilicity, but for PS only changed from 80.9° to 77.6°. For the PTFE, no oxidation was detected but the surface contact angle decreased from 122.4° to 108.4° after APGD, although still within the hydrophobic range (> 90°). The PMMA contact angle slightly increased but was similar to as before treatment. For the PE, the significant increase of the oxygen surface is consistent with what has been observed for Ultra-high-weight PE fibers exposed to a He low pressure plasma [4]. For PS, it has been reported that the oxidation of the aromatic rings occurs [5-6], but it was not possible to tell in our data. Wells *et al.* [7] observed that PS experiences a greater oxidation than other polymers that can be attributed to the unsaturated/chromophobic phenyl groups in PS being highly vulnerable towards plasma activation. Oxidation of PTFE by APGD in air has been reported, but only for exposure times of 20 to 120 minutes [8], while long exposure times to an oxygen plasma (> 15 mins.) showed there was some initial oxidation, but the PTFE was chemically similar to the control [9].

Table 3. Contact angle data before and after He+O₂ APGD treatment.

	Mean (degrees)	Standard Deviation
PE	98.89	2.97
PE after APGD	61.22	5.03
PTFE	122.35	7.39
PTFE after APGD	108.43	5.74
PS	80.96	4.76
PS after APGD	77.61	3.93
PMMA	69.07	4.68
PMMA after APGD	72.42	3.59

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. So we are estimating the work function as the energy to remove an electron from the HOMO level ($\phi \approx -\text{EHOMO}$). 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 also, 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 5.) CI

calculations 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 [10] for relative changes or trends, but is not expected to be accurate for absolute ionization energy (see below).

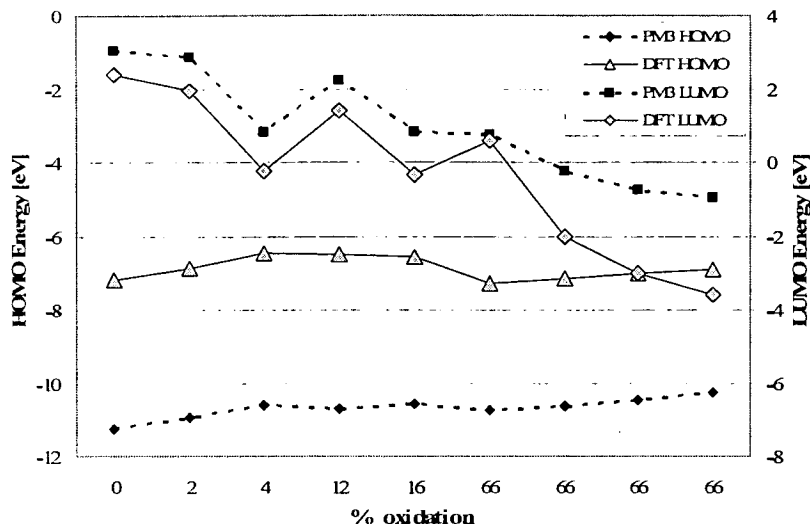


Figure 5. HOMO and LUMO as a function of $-O$ and $=O$ substitutions for PE

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. The HOMO level for PE generally increases (becomes less negative) with increasing oxidation, implying 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) [11].

The results of these calculations show 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. We consider this a key point of the paper.

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 $n=\infty$ behavior was found than with single, longer oligomers and was regarded as an interesting avenue for future model development.

A similar analysis for PTFE was omitted 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.

The chief feature of PS is the presence of the aromatic rings. The carbon 2p states form bonding and anti-bonding π clouds, the bonding being the HOMO orbital and the anti-bonding the LUMO of the aromatic ring. This feature persists in PS, which in an ideal geometry would have many identical rings with identical HOMO and LUMO states. In the actual molecule, and indeed in our theoretical modeling, not all rings are equivalent due to slightly different environments caused by the slightly differing orientations of the rings around the oligomer, the backbone of which may bend slightly. Oxygenating PS introduces C-OH or C=O bonds that are far lower in energy than the electronic states of the aromatic rings, a few eV below the HOMO. So, an oxygen atom added to a ring (in the form of an -OH) simply disrupts the states on that ring, but the other rings are isolated enough to remain unaffected. So, unless all rings are oxygenated, the HOMO, and by analogy the work function, of the molecule, is unaffected. Oxygen bonded to the backbone does even less to change the electronic structure. We also tested many scenarios in which a ring was opened and oxygenated and saw nothing significant in the HOMO/LUMO electronic structure. Our energetic studies indicate that PS readily bonds with oxygen, in agreement with our XPS data.

PMMA does not so readily oxygenate, according to our calculations. There is a slight energetic preference for adding more oxygen to this molecule, but not nearly as much as for PS or PE. This is consistent with our XPS data which shows little additional oxygen upon APGD He+O₂ treatment. As far as the electronic structure is concerned, oxygenation changes almost nothing about the PMMA molecule, which already has C-OH and C=O bonds in abundance.

4. Conclusions

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. Although increased oxidation was observed for the PS, there was no significant increase in the hydrophilicity. However, at this power level, PTFE and PMMA resisted oxidation by the APGD plasma, resulting only in minor changes to the surface characteristics.

The modeling calculations showed relatively minor changes 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. As with PE, we can conclude that any change in the triboelectric properties of PS or PMMA upon APGD treatment is due to changing hydrophilicity and not due to any fundamental change in the electronic structure that might make the material more readily charged by electron transfer.

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

5. References

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