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Plasma Modification of Poly(ether sulfone)

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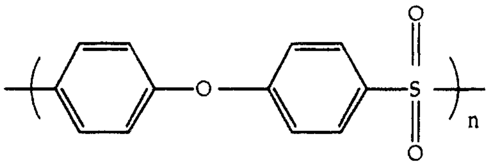
ABSTRACT: Surface treatment of poly(ether sulfone) by O_2, H_2, He, Ne, Ar, and CF_4 nonisothermal glow discharges has been investigated by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The chemical and topographical modification of the surface is found to be strongly influenced by the type of feed gas employed.

Introduction

Poly(ether sulfone) is renowned for good thermal, mechanical, and electrical properties.[1] The sulfur to carbon linkages located at the diaryl sulfone groups along the polymer backbone are stabilized via conjugation, which in turn imparts chemical resistance to this type of polymeric structure.



Polyethersulfone (PES)

Nonisothermal glow discharge treatment of polymer surfaces can give rise to desirable adhesive and wettability characteristics.[2,3] The active plasma medium consists of atomic and molecular species, as well as ions, electrons, and a broad electromagnetic spectrum.[4] This highly reactive and complex mixture can offer a low cost, environmentally friendly means for altering the physicochemical characteristics of a polymer surface at ambient temperatures.[5]

This study examines the chemical and topographical changes encountered at the poly(ether sulfone) surface during exposure to a variety of nonpolymerizable glow discharge treatments.

Experimental Section

Small strips of poly(ether sulfone) (Westlake Plastics Co.) were ultrasonically washed in an isopropyl alcohol/hexane mixture for 30 s and dried in air. High purity oxygen (99.6%), hydrogen (99.99%), helium (99.995%), neon (99.999%), argon (99.999%), and carbon tetrafluoride (99.7%) gases were used for the various types of plasma treatment.

Glow discharge experiments were carried out in a cylindrical glass reactor (4.5 cm diameter, 515 cm^3 volume, base pressure of 1.5×10^{-3} Torr, and with a leak rate better than 2.0×10^{-3} cm^3 min^{-1}) enclosed in a Faraday cage.[6] This was fitted with a gas inlet, a Pirani pressure gauge, and a 27 L min^{-1} two-stage rotary pump attached to a liquid nitrogen cold trap. A matching network was used to inductively couple a copper coil (4 mm diameter, 13 turns, spanning 9–18 cm from the gas inlet) wound around the reactor to a 13.56 MHz radio frequency (RF) source. All joints were grease-free. Gas flow and leak rates were calculated by assuming ideal gas behavior.[7] A typical experimental run comprised initially scrubbing the reactor with detergent, rinsing with isopropyl alcohol, and oven drying; this was followed by a 60 min high power (50 W) air plasma cleaning treatment. Next, the reactor was opened up to atmosphere, a strip of polymer was inserted into the center of the RF coils, and then the system was evacuated back down to its original base pressure. Subsequently, the gas of interest was introduced into the reaction chamber at 2×10^{-1} Torr pressure and a flow rate of approximately 1.9 cm^3 min^{-1} (i.e. at least 99.6% of the reactor contents). After 10 min was allowed for purging, the glow discharge was ignited at 20 W for 5 min. Upon termination of treatment, the RF generator was switched off, and the system was flushed with feed gas for 5 min before venting to atmospheric pressure. Each sample was characterized immediately after electrical discharge treatment by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

A Kratos ES300 electron spectrometer equipped with a Mg $K\alpha$ X-ray source (1253.6 eV) and a hemispherical analyzer was used for XPS surface analysis. Photoemitted core level electrons were collected at a takeoff angle of 30° from the substrate normal, with electron detection in the fixed retarding ratio (FRR, 22:1) mode. XPS spectra were accumulated on an interfaced PC computer. Instrumentally determined sensitivity factors for unit stoichiometry were taken as being C(1s):O(1s):S(2p):N(1s):F(1s) equals 1.00:0.55:0.54:0.74:0.53. XPS was used to check the cleanliness of the poly(ether sulfone) substrate and for the absence of any surface-active inorganic additives. Gross and experimental errors were calculated for each surface modification.

Atomic force microscopy offers structural characterization of surfaces in the 10^{-4}–10^{-10} m range without the prerequisite of special sample preparation (e.g. metallization). A Digital Instruments Nanoscope III atomic force microscope was used to examine the topographical nature of the poly(ether sulfone) surface prior to and after electrical discharge exposure. All of the AFM images were acquired in air using the Tapping mode[8] and are presented as unfiltered data. This technique employs a stiff silicon cantilever oscillating at a large amplitude near its resonance frequency (several hundred kilohertz). The RMS amplitude is detected by an optical beam system. A large RMS amplitude is used to overcome the capillary attraction of the surface layer, while the high oscillation frequency allows the cantilever to strike the surface many times before being displaced laterally by one tip diameter. These features offer the advantage of low contact forces and no shear forces.

Results

Clean Poly(ether sulfone). The C:O:S ratio for untreated PES film obtained from XPS is in good agreement with the theoretically predicted value, Table 1. The slightly higher concentration of sulfur can be attributed to preferential orientation of the sulfone group at the polymer surface.[9,10] C(1s) XPS spectra were fitted with Gaussian peaks of equal full-widths-at-half-maximum (FWHM),[11] using a Marquart minimization computer program. Aromatic carbon atoms attached to hydrogen, sulfone, and ether groups exhibit C(1s) core level binding energies of 285.0, 285.6, and 286.6 eV, respectively.[9,10,12] Low-energy π–π^* shape-up transitions accompanying core level ionization around 291.7 eV were fitted with a Gaussian

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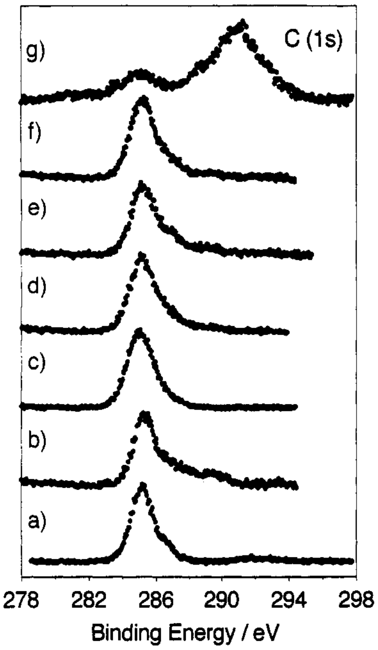


Figure 1. C(1s) XPS spectra of poly(ether sulfone): (a) clean, (b) O_2 plasma treated, (c) H_2 plasma treated, (d) He plasma treated, (e) Ne plasma treated, (f) Ar plasma treated, and (g) CF_4 plasma treated.

Table 1. Summary of Changes in Elemental Composition Following Plasma Modification of Poly(ether sulfone) (20 W, 5 min)

treatment	% C	% S	% O	% N	% F
theoretical	75.0	6.3	18.7		
untreated	76.3 ± 1.5	7.9 ± 0.8	15.9 ± 0.8		
O_2 plasma	55.6 ± 3.2	7.2 ± 0.4	34.4 ± 0.04	2.7 ± 0.2	
H_2 plasma	84.9 ± 1.5	3.2 ± 0.3	10.9 ± 0.2	2.2	
He plasma	64.3 ± 1.1	5.4 ± 0.5	25.5 ± 0.5	3.2 ± 0.6	
Ne plasma	64.0 ± 0.5	6.6 ± 0.3	24.7 ± 0.4	3.9 ± 0.2	
Ar plasma	68.4 ± 3.03	6.7 ± 0.9	26.3 ± 3.1	3.0 ± 0.6	
CF_4 plasma	40.9 ± 0.8	1.2 ± 0.1	10.3 ± 0.1		47.5 ± 1.1

peak of a different FWHM in order to assess the level of aromaticity present before and after glow discharge treatment,[13,14] Figure 1. A doublet structure was noted in the O(1s) region with a 2:1 intensity ratio, which corresponds to twice as many oxygen atoms attached to sulfur in sulfone groups (531.9 eV) as there are oxygen atoms located in ether environments (533.5 eV),[9,12] Figure 2. The $S(2p_{1/2,3/2})$ peak was found to be an unresolved 2:1 doublet at 168.0 eV, this can be taken as being characteristic of a sulfone group, rather than a sulfide (163.6 eV), or sulfate (169.3 eV) environment[10,12,14,15] (Figure 3).

Poly(ether sulfone) is usually found in the amorphous state.[16] A very low level of surface roughness was measured for the clean poly(ether sulfone) substrate by AFM with no evidence for any ordered regions, Table 4 and Figure 4.

Oxygen Plasma Treatment. All of the glow discharge treatments undertaken in this study were found to result in complete disappearance of the C(1s) π–π* shake-up satellite and loss of the resolved O(1s) doublet into a broad single peak. A small amount of nitrogen was detected (approximately 2%) on some treated poly(ether sulfone) samples, the most likely origin for this being reaction between trapped free radical centers at the surface and the atmosphere during transport of the modified substrate from the glow discharge apparatus to the XPS spectrometer.

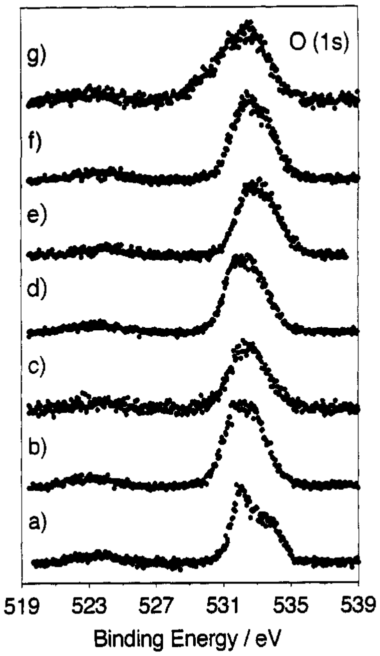


Figure 2. O(1s) XPS spectra of poly(ether sulfone): (a) clean, (b) O_2 plasma treated, (c) H_2 plasma treated, (d) He plasma treated, (e) Ne plasma treated, (f) Ar plasma treated, and (g) CF_4 plasma treated.

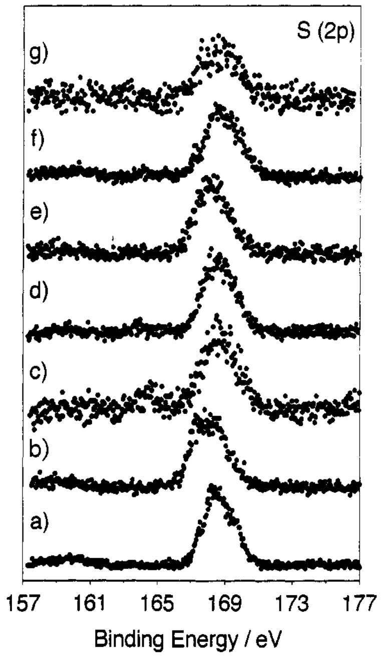
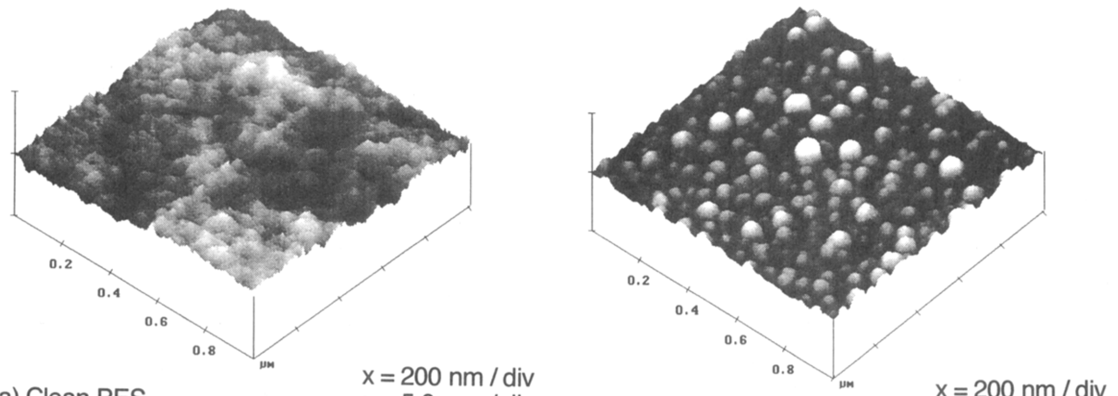


Figure 3. $S(2p_{1/2,3/2})$ XPS spectra of poly(ether sulfone): (a) clean, (b) O_2 plasma treated, (c) H_2 plasma treated, (d) He plasma treated, (e) Ne plasma treated, (f) Ar plasma treated, and (g) CF_4 plasma treated.

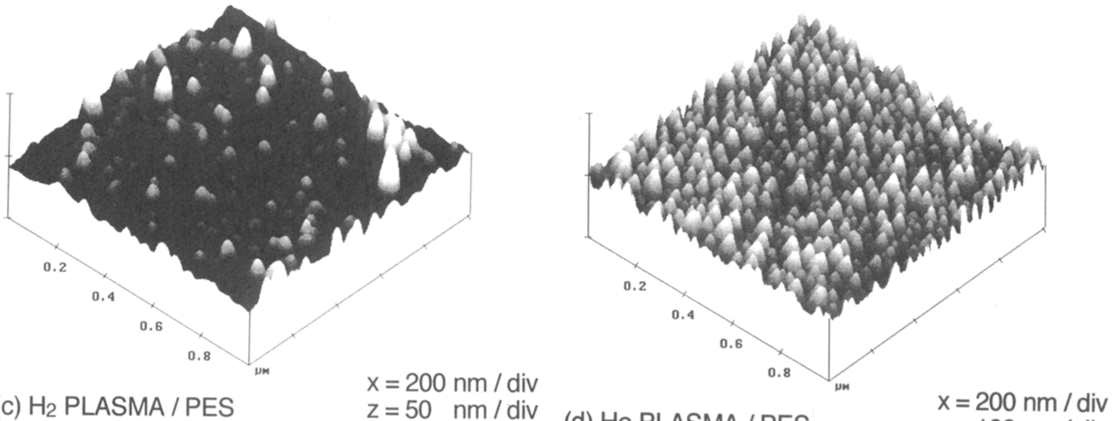
Clearly the greatest degree of oxidation occurs for the oxygen plasma treatment, Table 1. There was virtually no change in the $S(2p_{1/2,3/2})$ binding energy value, or in its FWHM. Sulfate species are absent following oxygen glow discharge treatment of poly(ether sulfone), whereas these groups are generated during the UV photooxidation of poly(ether sulfone).[17] The most likely explanation for this difference in behavior is that a less oxidized surface will form during the course of plasma oxidation, due to there being simultaneous sputtering and UV photoirradiation of the substrate.[18]

Oxygen plasma treatment of poly(ether sulfone) has a severe influence on the surface topography. A very uneven surface is generated which exhibits a globular texture, Figure 4.



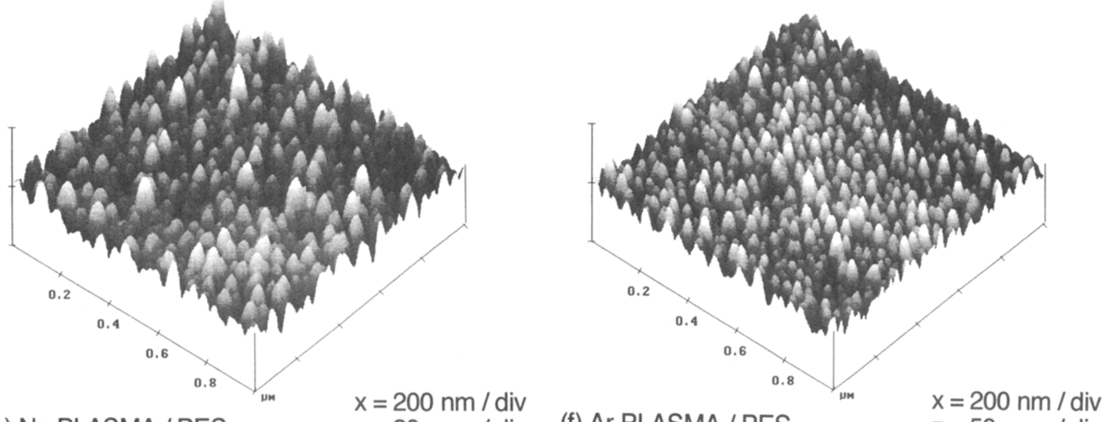
(a) Clean PES

(b) O_2 PLASMA / PES



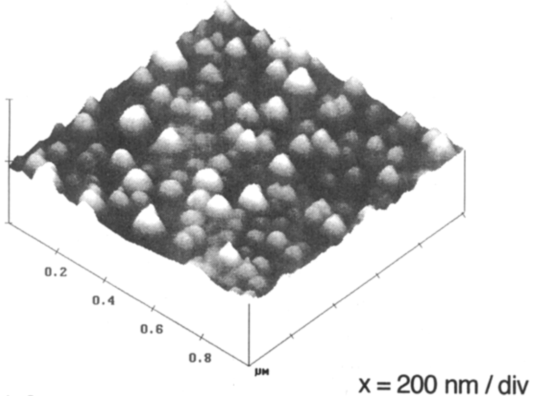
(c) H_2 PLASMA / PES

(d) He PLASMA / PES



(e) Ne PLASMA / PES

(f) Ar PLASMA / PES



(g) CF_4 PLASMA / PES

Figure 4. Atomic force micrographs of poly(ether sulfone): (a) clean, (b) O_2 plasma treated, (c) H_2 plasma treated, (d) He plasma treated, (e) Ne plasma treated, (f) Ar plasma treated, and (g) CF_4 plasma treated.

Hydrogen Plasma Treatment. An increase in the amount of carbon and a drop in oxygen and sulfur content was noted for hydrogen glow discharge treatment. A strong attenuation in the relative proportion of oxygenated carbon centers is discernible in the C(1s) XPS envelope. The $S(2p_{1/2,3/2})$ region displays an extra shoulder toward the

Table 2. Summary of Peak Fits of $S(2p_{1/2,3/2})$ Spectra Following Plasma Modification of Poly(ether sulfone) (20 W, 5 min)

treatment	% —C—*S*—O— 164.3 eV	% O=*S*=O 167.7 eV
theoretical	0.0	100.0
untreated	0.0	100.0
O_2 plasma	0.0	100.0
H_2 plasma	12.8 ± 0.1	87.2 ± 0.1
He plasma	5.6 ± 0.6	94.4 ± 0.6
Ne plasma	3.2 ± 1.1	96.8 ± 1.1
Ar plasma	3.4 ± 0.6	96.7 ± 0.6

Table 3. Comparison of the Theoretical and Experimental Values for Completely Fluorinated Poly(ether sulfone) (20 W, 5 min)

elemental %	theoretical fluorinated PES	exptl PES
C	38.3	40.9 ± 0.8
O	12.8	10.3 ± 0.1
S	8.5	1.2 ± 0.1
F	40.4	47.5 ± 1.1

Table 4. AFM Measurements

gas treatment	RMS roughness/nm	globule height/nm	no. of globules per μm^2
clean	0.4		
O_2	9.8		
H_2	5.1		
He	11.0	31.5 ± 5.4	445
Ne	3.0	6.6 ± 1.7	380
Ar	5.5	15.5 ± 2.0	452
CF_4	2.5		

low binding energy side of the main —*S*O_2 peak at 164.3 eV (this is consistent with a —C—*S*—O— cross-linked environment);[19] the corresponding C(1s) binding energy for this linkage is 285.6 eV.[9,12] From these experiments it can be concluded that hydrogen glow discharge treatment causes surface reduction: the constituent phenyl rings in poly(ether sulfone) probably undergo hydrogenation and cross-linking, whereas the ether and sulfone linkages are eliminated as gaseous H_2O and H_2S, respectively.

AFM of hydrogen plasma treated poly(ether sulfone) shows a significant degree of disruption compared to the clean surface with a strong variation in the surface topography, Figure 4.

Inert Gas Plasma Treatment (Helium, Neon, and Argon). Helium, neon, and argon glow discharge modification of poly(ether sulfone) yield very similar chemical changes at the polymer surface. The carbon and sulfur content decrease during plasma treatment, whereas there is a buildup of oxygenated functionalities. This behavior is similar to that reported previously for the argon glow discharge treatment of a structurally related polysulfone polymer.[14] A slight shoulder toward lower binding energy is evident in the $S(2p_{1/2,3/2})$ spectra, this can be attributed to the occurrence of a small level of sulfone reduction, Table 3. There are a number of plausible explanations for the rise in oxygen content during surface modification by these non-oxygen containing glow discharges: (i) reaction of the activated polymer surface with the atmosphere during sample transfer to the XPS spectrometer; (ii) photochemical main chain scission,[20] which could lead to preferential elimination of sulfone groups attached to chromophoric phenyl species; (iii) subsequent recombination of sputtered oxygen species with different sites at the poly(ether sulfone) surface; or (iv) surface rearrangement. It is surprising that the amount of sulfur retained at the polymer surface varies as argon ~ neon > helium; this is contradictory to what might have been expected in terms of a simple momentum transfer sputtering model.

All three types of inert gas plasma result in the growth of a uniform columnar surface topography, this effect being greatest with helium plasmas, Figure 4. Much larger globular features have been observed previously during corona treatment of polypropylene;[21,22] this was attributed to the agglomeration of low-molecular-weight oxidized material[23] which could be washed off with solvent. This possibility was checked for by comparing the AFM micrographs of noble gas plasma treated poly(ether sulfone) surfaces before and after washing with water, isopropyl alcohol, and hexane. No change in the surface texture was observed following rinsing in these solvents. Hence it can be concluded that the helium glow discharge causes the greatest chemical and physical disruption at the poly(ether sulfone) surface.

CF_4 Plasma Treatment. CF_4 plasma treatment of poly(ether sulfone) results in a substantial amount of fluorination at the surface (approximately 50%). This is accompanied by a dramatic change in the C(1s) XPS spectrum: 13% is *C*F_3 (293.6 eV), 40.9% is *C*F_2 (291.2 eV), and there are also some *C*F—CF_n (289.5 eV) functionalities which overlap in binding energy with oxygenated carbon centers.[12] The 2:1 O(1s) doublet can no longer be resolved, and the $S(2p_{1/2,3/2})$ feature is strongly attenuated.

Contrary to what might have been expected in terms of the highly reactive nature of CF_4 glow discharges, the treated poly(ether sulfone) surface exhibits the smoothest texture among the series of feed gases under investigation, Figure 4. A similar behavior has been previously reported using SEM characterization of polymer surfaces which has been exposed to pure CF_4 plasmas.[24]

Discussion

A range of energy transfer mechanisms are in operation within a low pressure RF discharge; these include electron acceleration in the bulk of the plasma, electron deflection from sheath potentials, and ion and electron acceleration in the wall boundary sheaths.[25] In terms of surface modification, the most important criteria of a glow discharge are the nature, the arrival rates, and the angular and energy distributions of the species impinging upon the surface.[26] Electron impact processes influence the density of ions, radicals, metastables, and photons contained within the plasma.

Inert gas plasmas interact with organic substrates via a direct energy transfer component arising from ions and metastables down to ~10 Å, and a radiative transfer component consisting of vacuum ultraviolet (VUV) photoirradiation which can penetrate up to ~10 μm below a polymer surface.[27-29] Typically, ion densities lie in the range 10^8–10^{10} cm^{-3} with energies of 0–100 eV,[30-33] while mean electron energies $\langle \epsilon \rangle$ span 0–20 eV with a high energy tail reaching out to 100 eV due to reflections at sheath boundaries.[30,34] Crossed-beam electron impact induced fluorescence studies with argon atoms have shown that the most intense VUV emission lines appear at 104.8 and 106.7 nm; these give rise to the Ar I transitions between the lowest lying electronically excited states and the ground state of the atom (i.e. $3s^23p^54s^1 \rightarrow 3s^23p^6$).[35,36] The excited ion Ar II resonance lines at 91.98 and 93.21 nm also emit strongly and correspond to the $3s^13p^6 \rightarrow 3s^23p^5$ transitions. Spin–orbit coupling results in pairs of lines.[29] The aforementioned Ar I lines display a maximum excitation cross section at ~30 eV electron energies, whilst this occurs at ~50 eV for the Ar II lines.[35] In general, the M I emission

Table 5. Most Intense Vacuum UV Emission Lines for Inert Gas Plasmas[29,37]

noble gas (M)	M I emission lines/nm	M II emission lines/nm	M_2* continuum emission/nm
He	58.4	30.4	58–110
Ne	73.3, 74.4	46.1, 46.2	74–100
Ar	104.8, 106.7	92.0, 93.2	105–155

lines are the most intense for low pressure noble gas plasmas (where M is the noble gas);[29,37] these are listed in Table 5. The background consists of a radiation continuum arising from excited inert gas molecules M_2*. There is also emission in the UV/visible, but the intensity is at least 2 orders of magnitude lower than for the vacuum UV region. Vacuum UV photons typically possess energies corresponding to the order of first ionization potentials of polymers.[29]

On moving to heavier noble gas atoms, the observed trend in the degree of sulfur retention and the level of surface roughening for poly(ether sulfone) is contrary to what might be expected in terms of a direct energy transfer standpoint.[38] However it is consistent with the radiative energy transfer model,[29,38,40] since the M I resonance lines becomes less energetic on descending the inert gas series, resulting in lower photochemical ablation. In the case of the heavier noble gas atoms, momentum transfer effects will make a greater contribution toward surface roughness.

Although a large number of chemical reactions are possible in an oxygen plasma, oxygen atoms are generally regarded as being the primary reactive species in conjunction with vacuum UV surface activation.[4,41,42] This combination produces the most oxidized PES surface in this study. Such a high level of surface oxidation during oxygen plasma treatment has been reported for a number of phenyl containing polymers, e.g. poly(ether ketone),[43], polystyrene,[44,45] poly(ether ether ketone),[17] poly(*p*-phenylene),[46] etc. The level of oxidation is always much greater for phenyl containing polymer repeat units and can be attributed to the vacuum UV photoexcitation of the aromatic centers.[18,45]

A pure CF_4 glow discharge can be regarded as a source of fluorine atoms with a small concentration of CF, CF_2, and CF_3 radicals.[47–51] This is supported by electron impact experiments with CF_4, which indicate that F atoms are the primary species.[52] Substitution of hydrogen atoms in C—H bonds (bond strength = 3–4 eV) by fluorine to yield HF (bond strength = 5.9 eV) and fluorinated polymer (bond strength $\sim$ 5 eV) is energetically favorable.[53–55] A pure CF_4 plasma displays poor etching behavior.[56] The extent of fluorine incorporation into the poly(ether sulfone) surface is found to be greater than theoretically predicted on the basis of a straightforward swop of hydrogen atoms for fluorine atoms. CF_4 glow discharges are also capable of imparting cross-linking.[57] The slightly higher carbon content compared to the expected theoretical value following substitution of hydrogen by fluorine is consistent with a small degree of cross-linking. Hydrogen and sulfur atoms are probably removed from the poly(ether sulfone) surface as HF and SF_6, respectively. However the reaction of fluorine atoms with oxygen will be energetically less favorable ($OF^\bullet$ bond strength = 2.4 eV).[58] Poly(ether sulfone) is structurally related to poly(ether ketone) ($-[C_6H_4-O-C_6H_4-C{=}O]_n-$), the only difference between these two polymers being the replacement of the sulfone group by a ketone functionality along the polymer backbone. CF_4 plasma treatment of both polymers is virtually identical;[43] for poly(ether ketone) 12.2% is CF_3 (293.6 eV), 49.8% is CF_2 (291.2 eV), 3.9% is C_xH_y, and there are also some $CF-CF_n$ (289.5 eV) functionalities which overlap in binding energy with oxygenated carbon centers.[12] This is consistent with fluorine atoms attacking the aromatic group in phenyl containing polymers.[49,59,60]

Conclusions

Nonequilibrium glow discharge treatment of poly(ether sulfone) using nonpolymerizable gases results in surface modification. Oxygen plasma treatment gives rise to the highest level of oxidation. A hydrogen glow discharge treatment causes simultaneous loss of both oxygen and sulfur from the surface. Inert gas plasma treatment promotes the formation of a uniform columnar texture, while substitution of C—H bonds by C—F bonds in the poly(ether sulfone) structure takes place during CF_4 glow discharge treatment.

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References and Notes

(1) Babari, T. A.; Koros, W. J.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 709.
(2) Clark, D. T.; Dilks, A. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 15.
(3) Gerenser, L. J. *J. Adhesion Sci. Technol.* **1987**, *1*, 303.
(4) Hollahan, J. R., Bell, A. T., Eds. *Techniques and Applications of Plasma Chemistry*; Wiley: New York, 1974; Chapter 1.
(5) Beonig, H. V. *Fundamentals of Plasma Chemistry and Technology*; Technomic Publishing Co. Inc.: Lancaster, PA, 1988.
(6) Shard, A. G.; Munro, H. S.; Badyal, J. P. S. *Polym. Commun.* **1991**, *32*, 152.
(7) Ehrlich, C. D.; Basford, J. A. *J. Vac. Sci. Technol.* **1992**, *A10*, 1.
(8) Zhong, Q.; Inniss, D.; Kjoller, K.; Elings, V. B. *Surf. Sci.* **1993**, *290*, L688.
(9) Clark, D. T.; Dilks, A.; Peeling, J.; Thomas, H. R. *J. Chem. Soc., Faraday Trans.* **1975**, *60*, 183.
(10) Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 791.
(11) Evans, J. F.; Gibson, J. H.; Moulder, J. F.; Hammond, J. S.; Goretzki, H. *Fresenius Z. Anal. Chem.* **1984**, *319*, 841.
(12) Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*; J. Wiley & Sons: Chichester, U.K., 1992.
(13) Clark, D. T.; Adams, D. B.; Dilks, A.; Peeling, J.; Thomas, H. R. *J. Electron Spectrosc.* **1976**, *8*, 51.
(14) Yasuda, H.; Marsh, H. C.; Brandt, E. S.; Reilley, C. N. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1975**, *16*, 142.
(15) Clark, D. T.; Feast, W. J.; Ritchie, I.; Musgrave, W. K. R.; Modena, M.; Ragazzini, M. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1049.
(16) Clark, D. T. *Makromol. Chem., Macromol. Symp.* **1993**, *75*, 1.
(17) Munro, H. S.; Clark, D. T. *Polym. Degrad. Stab.* **1985**, *11*, 225.
(18) Wells, R. K.; Drummond, I. W.; Robinson, K. S.; Street, F. J.; Badyal, J. P. S. *Polymer* **1993**, *34*, 3611.
(19) Brauman, S. K. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 1247.
(20) Yamashita, T.; Tomitaka, H.; Kudo, T.; Horie, K.; Mita, I. *Polym. Degrad. Stab.* **1993**, *39*, 47.
(21) Kim, C. Y.; Goring, D. A. I. *J. Appl. Polym. Sci.* **1971**, *15*, 1357.
(22) Strobel, J. M.; Strobel, M.; Lyons, C. S.; Dunatov, C.; Perron, S. J. *J. Adhes. Sci. Technol.* **1991**, *5*, 119.
(23) Overney, R M.; Guntherodt, H.-J.; Hild, S. *J. Appl. Phys.* **1994**, *75*, 1401.
(24) Kogoma, M.; Kasai, H.; Takahashi, K.; Moriwaki, T.; Okazaki, S. *J. Phys. D: Appl. Phys.* **1987**, *20*, 147.
(25) Egitto, F. D.; Matienzo, L. J. *Soc. Vac. Coaters, Annu. Tech. Conf. Proc., 36th* **1993**, 10.
(26) Chapman, B. *Glow Discharge Processes*; Wiley: New York, 1980.
(27) Clark, D. T.; Dilks, A. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2321.
(28) Clark, D. T.; Dilks, A. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *16*, 911.
(29) Clark, D. T., Dilks, A. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *18*, 1233.
(30) Seebock, R. J.; Kohler, W. E.; Romheld, M. *Contrib. Plasma Phys.* **1992**, *32*, 613.
(31) Winters, H. F. *Top. Curr. Chem.* **1980**, *94*, 69.

(32) Janes, J.; Huth, C. *J. Vac. Sci. Technol.* **1992**, *A10*, 3522.

(33) Hopwood, J. *Appl. Phys. Lett.* **1993**, *62*, 940.

(34) Godyak, V. A.; Piejak, R. B. *Phys. Rev. Lett.* **1990**, *65*, 996.

(35) Ajello, J. M.; James, G. K.; Franklin, B.; Howell, S. *J. Phys. B: At. Mol. Opt. Phys.* **1990**, *23*, 4355.

(36) Kelly, R. L. *J. Phys. Chem. Ref. Data* **1987**, *16*, 1.

(37) Samson, J. A. R. *Techniques of Vacuum Ultraviolet Spectroscopy*; Wiley: New York, 1967.

(38) Wells, R. K.; Ryan, M. E.; Badyal, J. P. S. *J. Phys. Chem.* **1993**, *97*, 12879.

(39) Liston, E. M. *Proc. Int. Symp. Plasma Chem., 9th* **1989**, L7.

(40) Takacs, G. A.; Vukanovic, V.; Tracy, D.; Chen, J. X.; Egitto, F. D.; Matienzo, L. J.; Emmi, F. *Polym. Degrad. Stab.* **1993**, *40*, 73.

(41) Shard, A. G.; Badyal, J. P. S. *J. Phys. Chem.* **1992**, *95*, 9436.

(42) Joubert, O.; Pelletier, J.; Arnal, Y. *J. Appl. Phys.* **1989**, *65*, 5096.

(43) Onyiriuka, E. C. *J. Vac. Sci. Tchnol.* **1993**, *A11*, 2941.

(44) Wells, R. K.; Drummond, I. W.; Robinson, K. S.; Street, F. J.; Badyal, J. P. S. *J. Adhes. Sci. Technol.* **1993**, *7*, 1129.

(45) Shard, A. G.; Badyal, J. P. S. *Macromolecules* **1992**, *25*, 2053.

(46) Tepermeister, I.; Swain, H. H. *J. Vac. Sci. Technol.* **1992**, *A10*, 3149.

(47) Zheng, J. S. *J. Appl. Polym. Sci.* **1993**, *48*, 231.

(48) Occhiello, E.; Morra, M.; Garbassi, F.; Bargon, J. *Appl. Surf. Sci.* **1989**, *36*, 285.

(49) d'Agostino, R.; Cramarossa, F.; DeBenedictis, S. *Plasma Chem. Plasma Process.* **1982**, *2*, 213.

(50) Truesdale, E. A.; Smolinsky, G. *J. Appl. Phys.* **1979**, *50*, 6594.

(51) Plumb, J. C.; Ryan, K. R. *Plasma Chem. Plasma Process.* **1986**, *6*, 205.

(52) Kay, E. *Proc. Int. Ion Eng. Congr.* **1983**, 1657.

(53) Inagaki, N.; Tasaka, S.; Mori, K. *J. Appl. Polym. Sci.* **1991**, *43*, 581.

(54) Strobel, M.; Corn, S.; Lyons, C. S.; Korba, G. A. **1985**, *23*, 1125.

(55) d'Agostino, R.; Cramarossa, F.; Fracassi, F.; Illuzzi, F. In *Plasma Deposition, Treatment, and Etching of Polymers*; d'Agostino, R., Eds.; Academic Press Inc.: San Diego, 1990; Chapter 2.

(56) Egitto, D. F.; Vukanovic, V.; Taylor, G. N. In *Plasma Deposition, Treatment and Etching of Polymers*; d'Agostino, R., Eds.; Academic Press Inc.: San Diego, 1990; Chapter 5.

(57) Inagaki, N.; Kobayashi, N.; Matsushima, M. *J. Membr. Sci.* **1988**, *38*, 85.

(58) Egitto, F. D.; Matienzo, L. J.; Schreyer, H. B. *J. Vac. Sci. Technol.* **1992**, *A10*, 3060.

(59) Strobel, M.; Lyons, C. S. *Polymeric Materials Science and Engineering*; ACS Symposium Series No. 56; American Chemical Society: Washington, DC, 1987; p 232.

(60) Yasuda, T.; Okuno, T.; Yoshida, K.; Yasuda, H. *Polymeric Materials Science and Engineering*; ACS Symposium Series No. 56; American Chemical Society: Washington, DC, 1987; p 240.