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Surface Texturing of PTFE Film Using Non-equilibrium Plasmas

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ABSTRACT: Surface treatment of poly(tetrafluoroethylene) by O_2, H_2, N_2, He, Ne, Ar, and CF_4 non-isothermal glow discharges has been investigated by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The chemical and topographical modification of the polymer surface is found to be strongly influenced by the type of feed gas employed.

Introduction

The inherent good dielectric properties, high thermal stability, low surface energy, and chemical inertness of poly(tetrafluoroethylene) (PTFE) makes it virtually impossible to bond without some form of surface pretreatment. Common activation methods include electrochemical reduction,[1] sodium solution etching,[2] and glow discharge modification.[3−5]

Non-isothermal glow discharge treatment of polymer surfaces can give rise to desirable adhesive and wettability characteristics.[6,7] The active plasma medium consists of atomic and molecular species, as well as ions, electrons, and a broad electromagnetic spectrum.[8] This highly reactive and complex mixture can offer a low cost and attractive route for altering the surface properties of a polymer at ambient temperatures.[9]

This study examines the chemical and topographical changes encountered during the glow discharge treatment of PTFE using a variety of non-polymerizable gases.

Experimental Section

Small strips of poly(tetrafluoroethylene) (Goodfellows) were ultrasonically washed in an isopropyl alcohol/hexane mixture for 30 s and dried in air. High purity oxygen (99.6%), hydrogen (99.99%), nitrogen (99.995%), helium (99.995%), neon (99.999%), argon (99.999%), and carbon tetrafluoride (99.7%) gases were used for the different types of electrical discharge treatment.

Electrical, inductively coupled plasmas were ignited in a cylindrical glass reactor (4.5 cm diameter, 460 cm^3 volume, base pressure of 1.0×10^{-3} Torr, and with a leak rate better than 4.0×10^{-3} cm^3 min^{-1}) enclosed in a Faraday cage.[10] This was fitted with an externally wound copper coil (4 mm diameter, 9 turns, spanning 8−15 cm from the gas inlet), a gas inlet, a Pirani pressure gauge, and a 27 L min^{-1} two-stage rotary pump attached to a liquid nitrogen cold trap. An L-C matching network was used to match the output impedance of the RF (13.56 MHz) generator to that of the partially ionized gas load, this was achieved by minimizing the standing wave ratio (SWR). All joints were grease-free. Gas flow and leak rates were calculated by assuming ideal gas behavior.[11] A typical experimental run comprised initially scrubbing the reactor with detergent, rinsing with isopropyl alcohol, and oven drying; this was followed by a 30 min high-power (50 W) air plasma cleaning treatment. Next, the reactor was opened to atmosphere, a strip of polymer was inserted into the center of the RF coils, and then the system was evacuated back 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 1.0 cm^3 min^{-1} (i.e. at least 99.6% of the reactor contents). After allowing 5 min 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 flushed with feed gas for 5 min prior to venting to atmospheric pressure. Each sample was characterized immediately after electrical discharge treatment by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

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

gas	% C	% F	% O	% N
PTFE	33.3 ± 0.6	66.8 ± 0.6		
O_2	33.0 ± 0.2	65.4 ± 0.2	1.7 ± 0.4	
N_2	33.2 ± 0.0	64.0 ± 0.6	1.6 ± 0.3	1.3 ± 0.4
H_2	56.1 ± 1.1	37.7 ± 0.4	4.7 ± 0.7	1.5 ± 0.1
He	38.7 ± 0.4	55.8 ± 2.0	4.1 ± 1.4	1.5 ± 1.0
Ne	34.6 ± 1.3	62.0 ± 1.0	2.6 ± 0.4	0.9 ± 0.0
Ar	37.2 ± 0.5	56.8 ± 0.8	4.3 ± 0.2	1.8 ± 0.1
CF_4	32.8 ± 0.6	67.2 ± 0.6		

A Kratos ES200 electron spectrometer equipped with an unmonochromatized Mg Kα X-ray source (1253.6 eV) and a hemispherical analyzer was used for XPS surface analysis. Photo-emitted core level electrons were collected at a take-off 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):N(1s):F(1s) equals 1.00:0.55:0.74:0.53. XPS was used to check the cleanliness of the PTFE substrate and for the absence of any surface-active inorganic additives. Gross and experimental errors were calculated for each surface treatment.

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 PTFE surface prior to and after electrical discharge exposure. All of the AFM images were acquired in air using the Tapping model[12] 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

(a) Clean PTFE. The C:F ratio for untreated PTFE film obtained from XPS is in good agreement with the theoretically expected value of 1:2, Table 1. C(1s) XPS spectra were fitted with Gaussian peaks of equal full widths at half-maxima (FWHM),[13] using a Marquart minimization computer program, and showed only a

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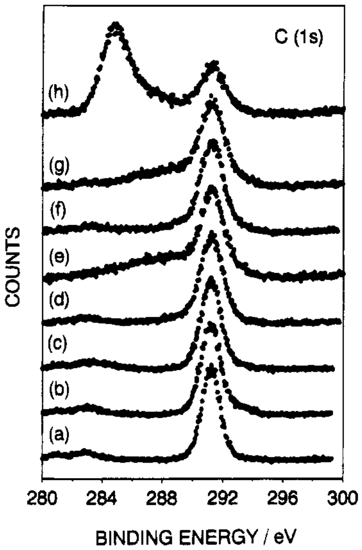


Figure 1. C(1s) XPS spectra of PTFE: (a) clean, (b) CF_4 plasma treated, (c) O_2 plasma treated, (d) N_2 plasma treated, (e) He plasma treated, (f) Ne plasma treated, (g) Ar plasma treated, and (h) H_2 plasma treated.

main $>\underline{C}F_2$ peak at 291.2 eV and the corresponding Mg $K\alpha_{3,4}$ satellite at a lower binding energy,[14] Figure 1a.

A common method for making PTFE film is by compaction and sintering of PTFE granules.[15] The constituent particles and surface voids are clearly discernible in the AFM micrograph of untreated PTFE, Figure 2a. Furthermore, uniaxial alignment of the surface texture is indicative of the substrate having undergone tribological deformation during manufacture.[16]

(b) Oxygen Plasma Treatment. XPS shows that there is virtually no change in the chemical nature of the PTFE substrate during oxygen plasma treatment, Figure 1c and Table 1.

However there is a substantial degree of surface roughening, which is discernible in the form of a microroughness superimposed upon the original macroroughness of the starting material, Figure 2b.

(c) Hydrogen Plasma Treatment. Hydrogen plasma treatment of PTFE results in the defluorination of the surface,[17] Table 1. The C(1s) envelope has shifted to lower C(1s) binding energy values, which are more typical of hydrogenated carbon centers,[14] Figure 1h. A small amount of oxygen and nitrogen was detected on some treated PTFE 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.

In many ways the hydrogen and oxygen glow discharge treated PTFE surfaces are topographically very similar in appearance, except that the level of macroroughness is less extensive for the former, Figure 2c.

(d) Nitrogen Plasma Treatment. Nitrogen glow discharge treatment of PTFE results in a small amount of nitrogen incorporation together with a slight broadening of the C(1s) envelope,[3,18-20] Figure 1d and Table 1.

Atomic force microscopy shows a fine globular texture which has wiped out the original parent polymer microstructural features, Figure 2d. This is consistent with previous scanning electron microscopy (SEM) studies where the PTFE topography was reported to undergo change to a fibrous pattern.[20]

(e) Inert Gas Plasma Treatment (Helium, Neon, and Argon). Inert gas plasma treatment of PTFE results in a small amount of oxygen and nitrogen incorporation into the surface,[3,21,22] Table 1. This can be accounted for as previously in terms of the activated surface undergoing reaction with the atmosphere during substrate transfer to the XPS spectrometer.[22,23] The relative order of surface defluorination is He > Ar > Ne. This is accompanied by the emergence of a low binding energy shoulder on the main $>\underline{C}F_2$ C(1s) peak, which is characteristic of Mg $K\alpha_{1,2}$ components corresponding to $-\underline{C}F-CF_n-$ (289.5 eV), $-\underline{C}F-$ (288.3 eV), $-\underline{C}-CF_n-$ (286.6 eV), and $-\underline{C}_x-$ (284.6 eV) environments,[24] Figures 1e–g.

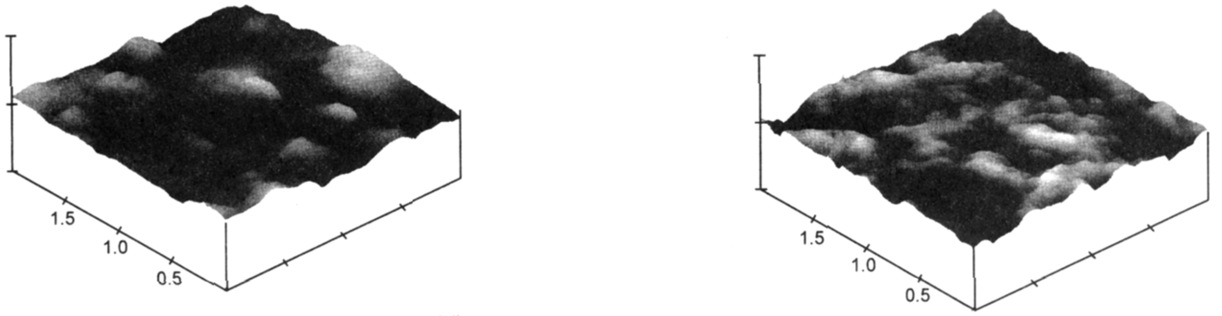
The atomic force micrographs following inert gas plasma treatment are in many ways similar to the surface texture previously seen following nitrogen glow discharge modification, Figures 2e–g. Fine globular features are evident in all cases. However, the way in which these are distributed varies a great deal depending upon the gas used. On moving from helium-to-neon/nitrogen-to-argon glow discharges, there appears to be a local ordering phenomenon taking place which gives rise to the formation of fibrils. These results are in contradiction with previous SEM studies which mentioned that Ar plasma treatment does not alter the PTFE surface morphology.[21] This discrepancy could be attributed to the masking of any topographical features during the metallization of the substrate prior to SEM characterization.

(f) CF_4 Plasma Treatment. CF_4 plasma treatment of poly(tetrafluoroethylene) effectively produces very little chemical change in the PTFE substrate, except for a small amount of fluorine incorporation. This leads to a slight shoulder at higher C(1s) binding energy (293.6 eV), which can be assigned to the $-\underline{C}F_3$ environment, Figure 1b.

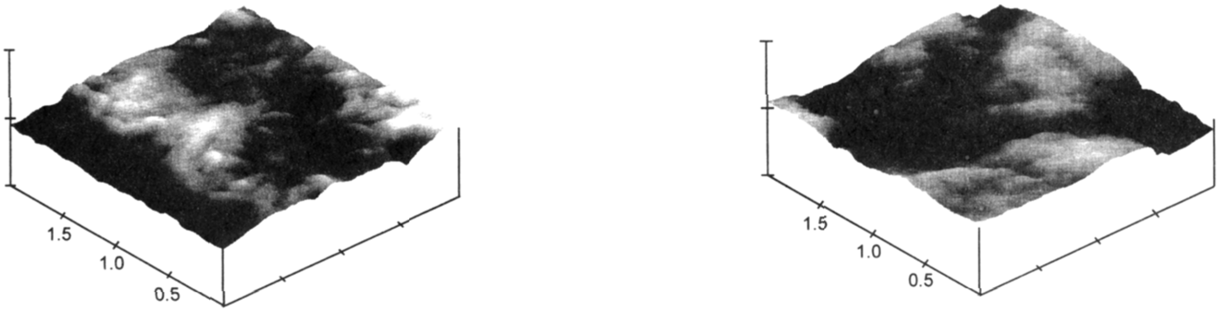
Contrary to what might have been expected in terms of the highly reactive nature of CF_4 glow discharges, the treated PTFE surface exhibits the smoothest texture amongst the series of feed gases under investigation, Figure 2h. Similar behavior has been previously observed by SEM for other polymer substrates which have been exposed to pure CF_4 plasmas.[25]

Discussion

Differing rates of physical sputtering between amorphous and crystalline regions of PTFE cannot solely account for the observed changes in surface topography for the various plasma treatments.[26,27] 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, formation of energetic neutrals by charge exchange and elastic collisions between ions and neutral gas species, and ion and electron acceleration in the wall boundary sheaths.[28] 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.[29] Electron impact processes influence the density of ions, radicals, metastables, and photons contained within the plasma. The energy distributions for neutral and ionic species contained within a non-equilibrium plasma correspond to approximately ambient temperature, while the electron temperature is considerably higher.

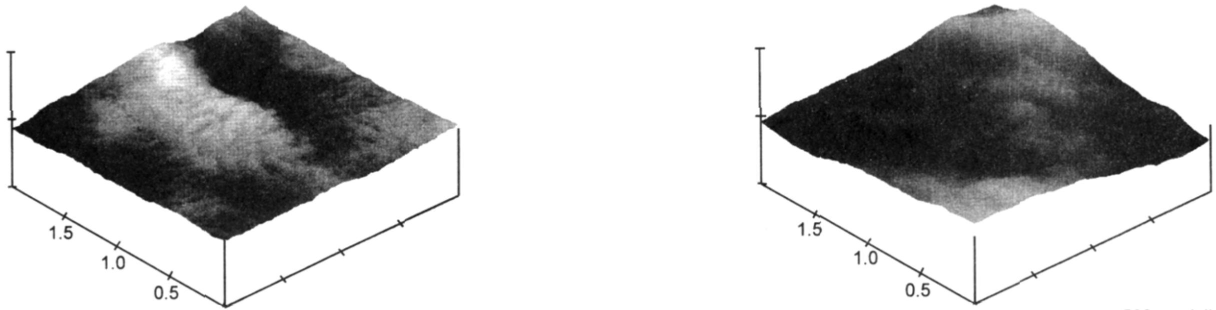


(a) CLEAN PTFE (b) OXYGEN PLASMA



(c) HYDROGEN PLASMA (d) NITROGEN PLASMA

(e) HELIUM PLASMA (f) NEON PLASMA



(g) ARGON PLASMA (h) CF_4 PLASMA

Figure 2. Atomic force micrographs of PTFE: (a) clean, (b) O_2 plasma treated, (c) H_2 plasma treated, (d) N_2 plasma treated, (e) He plasma treated, (f) Ne plasma treated, (g) Ar plasma treated, and (h) CF_4 plasma treated.

Non-isothermal 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) photo-irradiation which can penetrate up to ~10 μm below a polymer surface.[30-32] Typically, ion densities lie in the range 10^8-10^{10} cm^{-3} with energies of 0–100 eV,[33-36] 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.[33,37] Within the glow region, the plasma exists at a positive potential with respect to the substrate surface; this results in positive ions contained in the plasma being accelerated through a space charge sheath toward the substrate.[38]

Prolonged oxygen plasma treatment of PTFE results in a morphologically spongy-like surface.[21,39,40] Pure O_2 plasmas yield a much rougher surface in comparison to CF_4 glow discharge treatment of PTFE.[41] 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.[8,42,43] Also the average potential difference between the plasma and the substrate (plasma sheath potential) is much greater for an oxygen plasma than for a CF_4 plasma.[41] Therefore a greater level of substrate etching can be expected for the case of an oxygen plasma. The most likely initiation step during O_2 plasma treatment of PTFE is reported to be polymer radical formation during ion/photon/electron bombardment[41] to yield either

$$-CF_2-CF_2- \rightarrow -CF_2-CF^{\bullet}- + F^{\bullet} \qquad (1)$$

or

$$-CF_2-CF_2- \rightarrow -CF_2^{\bullet} + {}^{\bullet}CF_2- \qquad (2)$$

The reaction of O atoms or O_2 with a polymer radical will inhibit cross-linking, leading to scission of the polymer backbone.[44] Fluorine abstraction from PTFE by oxygen radicals to form $OF^{\bullet}$ is energetically unfavorable,[41] and studies using atomic oxygen ($O(^3P)$) have exhibited negligible etching.[45]

A comparison of H_2^+ and He^+ ion bombardment of PTFE has shown that the former is better at defluorination of the surface, and this can be attributed to a chemical effect.[46] However the level of surface defluorination is not as great as observed during H_2 plasma treatment of PTFE.[17] Low-energy electron impact of H_2 produces photons in the vacuum ultraviolet region,[47] but this also cannot solely account for the high level of surface defluorination observed. Defluorination of the PTFE surface by a hydrogen glow discharge must therefore be governed by the chemically reducing nature of the constituent hydrogen atoms,[17] whereas for the other gases, any loss of surface fluorine can only be attributed to vacuum ultraviolet (VUV) photons,[48,49] ion beam bombardment,[50] or electron impact dissociation.[51,52] Fluorine abstraction from PTFE by hydrogen atoms to form HF is energetically favorable[17,41] and has been previously identified by IR emission spectroscopy:[53]

$$RF + H^{\bullet} \rightarrow R^{\bullet} + HF^{54}$$

Ion beam modification of PTFE is known to induce topographical and chemical changes at the surface.[55-57] The floating potential of the substrate can be calculated to be approximately the same for the three noble gases used in this study.[58] On moving from He to Ne to Ar plasmas, the observed trend in the degree of PTFE defluorination is contrary to what might be expected in terms of a direct energy transfer perspective, where momentum transfer to the substrate should become more predominant with rising noble gas atom mass.[59] Therefore radiative energy transfer must also be taken into consideration.[30,60,61] Crossed-beam electron impact induced fluorescence studies with inert gas atoms have shown that intense VUV MI emission lines are produced which correspond to transitions between the lowest lying electronically excited states and the ground state of the atom (e.g. for Ar: $3s^23p^54s^1 \rightarrow 3s^23p^6$).[62,63] These display a maximum excitation cross section at electron energies of $\approx$30 eV.[62] Such VUV photons typically possess energies corresponding to the order of first ionization potentials of polymers.[32] The emission 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 VUV region. Therefore, the anomalously high defluorination of PTFE by the helium glow discharge can be accounted for, since the MI resonance lines become less energetic on descending the inert gas series,[32,64] whereas momentum transfer effects will make a greater contribution for the heavier noble gas plasmas. Primary processes during inert gas plasma treatment of PTFE will include rupture of the C−F bond, and main chain C−C scission followed by the chain fragments undergoing cross-linking or desorption.[65] Polymer radicals located on adjacent chains will cross-link,[30] while radicals on neighboring carbon atoms will form double bonds.[66] Greater fragmentation at the surface should produce a greater number of molecular fragments, with their respective mobilities decreasing with increasing chain length and cross-linking. The C−C bond distance along a polymer backbone is much shorter than the intermolecular C−C separation between adjacent polymer chains; therefore the net effect of cross-linking is to effectively cause surface shrinkage[30] and internal stress. This could contribute to the observed reorganization of surface texture during noble gas glow discharge treatment of PTFE. The observed morphology in these studies is markedly different from the fine cone-like structures observed during ion sputter-etching of PTFE[67,68] and therefore cannot be ascribed to just a manifestation of ion bombardment in the conventional sense. However, since ion bombardment is dependent upon the plasma sheath and the constituent ions, any macroroughness and/or localized charge buildup will cause a strong perturbation upon the local electric field experienced by the incident ions, leading to higher kinetic energy ions reaching the protruding and/or charged polymer regions. This can give rise to heterogeneous etching at the surface[69] and will be expected to become more evident with the increasing mass of the incident noble gas ion. Furthermore, agglomeration and orientation of charged low molecular weight species at the surface[70] may be influenced by such local surface electric fields. This effect would be expected to be greatest for an argon plasma, since the heavier argon ions will incur more polymer chain rupture, while its relatively weaker vacuum UV emission will yield less subsurface cross-linking, and therefore one would expect a more mobile surface in this case.

Nitrogen plasma treated PTFE experiences comparable physical and chemical changes to those observed during neon glow discharge modification. Atomic nitrogen and neon are very close to each other in the periodic table, thereby giving rise to similar momentum transfer behavior (small difference in atomic mass) and VUV emission spectra (virtually equivalent atomic orbitals).

A 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.[71-75] This is supported by electron impact experiments with CF_4, which indicate that F atoms are the primary species.[76] The identification of $-CF_3$ centers following CF_4 plasma treatment can be taken as evidence for the main PTFE backbone undergoing cleavage followed by fluorination of the $-CF_2$ radicals. The alternative explanation of $-CF_3$ functionalities attached to the main PTFE backbone can be ruled out since there are no corresponding cross-linked carbon centers present in the C(1s) spectrum at lower binding energy values from the main $-\underline{C}F_2$ peak. The contact angle of water increases during CF_4 plasma treatment.[77] This cannot be attributed to morphological changes (since Wenzels Law states "on roughening a wettable surface becomes more wettable and a non-wettable surface becomes more non-wettable")[78,79] and therefore must be due to the extra $-CF_3$ groups. CF_4 plasmas are widely used for polymer etching, in a way similar to O_2 plasmas. However, Egitto[41] has suggested that different etching mechanisms apply, since SEM characterization of CF_4 treated PTFE is very smooth (almost the same as that for clean PTFE) compared to the rough surface noted after O_2 glow discharge exposure. Pure CF_4 plasmas are not as efficient etchants as CF_4/O_2 mixtures[54,80] since fluorine abstraction from PTFE by fluorine radicals to form F_2 is energetically unfavorable,[41] while recombination or termination of polymer radicals with fluorine atoms will favor the formation of stable fluorocarbons species with inherently poor etch characteristics.[41,54]

Conclusions

Non-equilibrium glow discharge treatment of PTFE using nonpolymerizable gases results in surface modification. Oxygen plasma treatment gives rise to the highest level of surface roughening together with virtually no change in chemical composition. Hydrogen glow discharge treatment causes the greatest loss of fluorine from the surface. Nitrogen and noble gas plasma treatment promotes the formation a fibrillar microtexture, while CF_4 glow discharge treatment of PTFE causes polymer chain rupture followed by fluorine atom capping to yield $-CF_3$ end groups.

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