

Atomic-Oxygen Induced Structural Changes in Polyphosphazene Films and Coatings

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Synopsis

Various polymers were exposed to atomic oxygen $O(^3P)$ and comparisons made of their stability. The rates of reaction and mass removal for polyphosphazenes exposed to atomic oxygen were found to be significantly lower than for other polymers evaluated in this study. Surface analysis of polyphosphazene films indicated that $O(^3P)$ induces rearrangements in the phosphorus–nitrogen backbone of the polymer resulting in crosslinking and cleavage of some pendant groups that are then replaced by oxygen.

INTRODUCTION

Low earth orbit (LEO) space missions have shown that materials interact with ambient atomic oxygen, $O(^3P)$, resulting in surface erosion.^{1–5} Planned space missions involving long duration vehicular activities in LEO will require materials that are resistant to $O(^3P)$ attack. Laboratory-based studies of $O(^3P)$ interactions with polymeric materials have concentrated on organic polymers and their mass removal rates in a plasma discharge.^{6,7} The most definitive study of the relationship of polymer structure versus mass loss rate from $O(^3P)$ was conducted by Hansen et al.⁷ on 36 selected polymers. Their study established that highly branched polymers and polyethers were susceptible to $O(^3P)$ attack whereas perfluorinated and aromatic polymers and sulfur vulcanized elastomers were considerably more resistant. The known resistance of polyphosphazenes to thermal oxidative degradation⁸ as well as a wide variety of other chemical and physical properties⁹ has stimulated investigations of their resistivity to $O(^3P)$ attack.¹⁰ The linear high molecular weight (10^6) poly(fluoroalkoxy phosphazenes) are flexible in the temperature range of -66 – 350°C , transparent to ultraviolet radiation, and resistant to oil and water. The characteristic bonding between the alternating phosphorus and nitrogen in the polyphosphazene backbone is directly related to their unique physical and chemical properties. These $3d_\pi$ – $2p_\pi$ bond interactions of the phosphorus and nitrogen approximate stabilized excited states⁹ permitting energy transmission along the phosphazene backbone without imposing any significant conformational restrictions.¹¹ This allows for a facile 360° rotation about the P–N bonds in the backbone resulting in a high degree of torsional mobility, thereby imparting to the poly(fluoroalkoxy phosphazenes) low glass transition temperatures (T_g).¹¹

In the present study, poly[bis(trifluoroethoxy)phosphazene], fluorophosphazene (PNF) elastomer, polyphosphazene-coated polyimide, poly(di-

OXYGEN PLASMA SOURCE

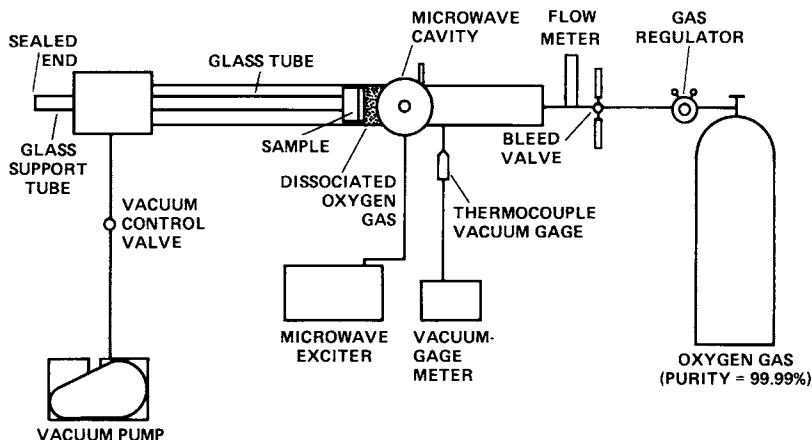


Fig. 1. Plasma discharge apparatus.

methylsiloxane, methylphenyl silane-*m*-carborane) elastomer, and Kapton H film (baseline material) were exposed in an oxygen plasma^{12,13} and to O(³P) beams.^{14,15} X-ray photoelectron spectroscopy (XPS or electron spectroscopy for chemical analysis, ESCA) of poly[bis(trifluoroethoxy) phosphazene] and phosphazene coatings was used to study the changes in surface composition resulting from interactions with O(³P).

EXPERIMENTAL

Poly[bis(trifluoroethoxy) phosphazene] was prepared by the nucleophilic substitution reaction of the linear poly(dichlorophosphazene) with sodium trifluoroethoxide.¹⁶ Film samples were prepared by solvent casting in dry redistilled methyl ethyl ketone in a 3.5-cm-diameter glass dish, dried, and stored in a desiccator prior to analyses. Fluorophosphazene elastomer was supplied by the Parker Seal Company (Culver City, California). Poly(fluoroalkoxy phosphazene) coating (0.013 mm) on 0.076-mm polyimide (Kapton H) supplied by Ethyl Corporation (Baton Rouge, Louisiana) was washed with Freon TF prior to use to remove surface contaminants. Poly(dimethylsiloxane, methylphenylsilane-*m*-carborane) was obtained from the Dexsil Corporation (Hamden, Connecticut). Kapton H film was supplied by the DuPont (Wilmington, Delaware). All samples were used as received except for the poly(fluoroalkoxy phosphazene)-coated Kapton H film as indicated.

Oxygen Atom Source

Microwave Discharge

The oxygen plasma was produced at ambient temperature by the previously described method of microwave discharge.^{6,7} The sample assembly consisted of

an adjustable quartz arm (35.5 cm length) with a sample attachment head (3.5 cm diameter) positioned inside the discharge tube (Fig. 1). The microwave generator, a magnetron 100 W at 2450 MHz was connected to a tunable resonant Hg-198 cavity. The samples were attached to the sample attachment head, the entire system evacuated, and 50–55 mtorr of oxygen (99.99% pure) was metered into the glow discharge tube. The discharge was initiated with a Tesla coil.

O(³P) and Ion Beam

Beam exposures of samples were conducted at the General Electric Space Simulation Facility at Valley Forge, Pennsylvania. The O(³P) beam was produced by electron impact ionization of high-purity oxygen in a broad beam ion source. The beam consisted of molecular ions and O(³P) as determined by mass analysis.¹⁴ A 15-cm-diameter beam was produced by the electron impact ionization of molecular oxygen in a broad beam ion source. This large diameter beam consists of atomic and molecular oxygen ions that pass through a fine mesh extraction electrode and into a space charge neutralization chamber [Fig. 2(a)]. Space charge neutralization is accomplished by electron injection. The

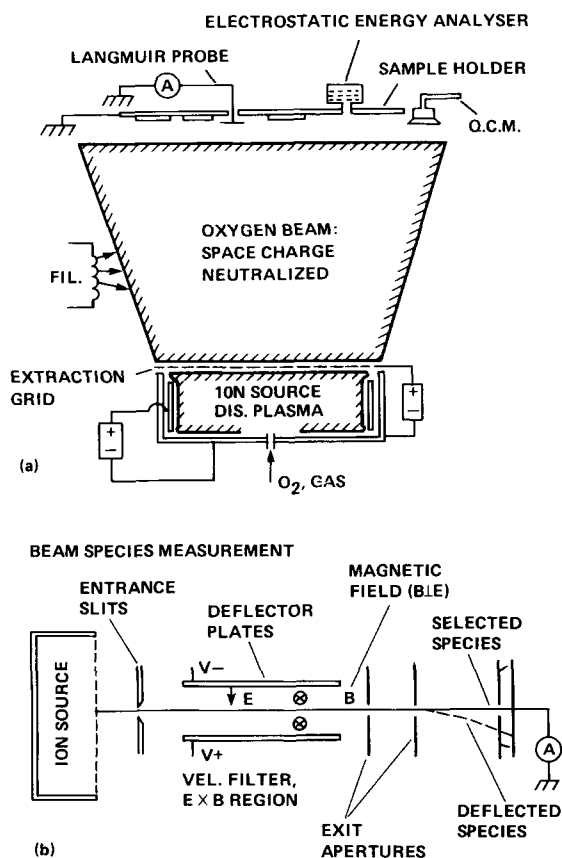


Fig. 2. Ion source and mass analyzer of O(³P) space simulator (GE).

directional aspects of the beam were modulated by magnetic and electric field adjustments to maintain a linear beam at the separator. The percentage of species in the ion beam was determined by a mass analyzer [Fig. 2(b)]. A symmetrical variable potential is applied to the deflection plates to generate an electric field and permanent magnets produce a 1900 G field. Collimated slits direct the beam through the analyzing area and into a Faraday cup. A negative potential of 20 V is applied to repel any electrons in the beam. The beam was generated at ambient temperature and 10^{-4} torr. The average energy of the beam was 5 eV at fluences of 5.2×10^{18} , 2.0×10^{19} , and 3.0×10^{19} atoms/cm². The percentage of neutral oxygen atoms is from 30 to 33% of the total amount (50%) of atomic species produced. It is assumed that the neutral oxygen atoms are in the ground (³P) state. Samples were run in identical sets of four and the exposure area was 2.5 cm diameter. Sample exposures to O(³P) beam were also conducted at the University of Toronto Institute for Aerospace Studies (UTIAS). A high-velocity O(³P) beam was produced by the microwave discharge of helium carrier gas containing 8% oxygen through a quartz nozzle into a vacuum chamber where the film is positioned [Fig. 3(a)]. The plasma was produced with a microwave generator (Microtom 200 Mk3) operating at a frequency of 2450 MHz and power range of 20–200 W. The plasma was initiated with a Tesla coil in the tunable cavity. The power was adjusted so as to obtain maximum glow and then adjusted to 40 W. The system pressure was from 2.0 to 4.5×10^{-5} torr at ambient temperature. The films were rectangular (2.6×0.6 cm) and run in duplicate. The percentage of oxygen dissociation was based on the mass spectra of O(³P) and O₂ based on their mass ratios 16 and 32 *m/e* [Fig. 3(b), Ref. 20].

Surface Characterization of Films (ESCA)

Pre- and post-exposure samples of (³P) were examined with a SSX-501 electron spectrometer. A 3.0-eV flood gun was used to neutralize sample charging. A survey scan from 0 to 1000 eV was run at 50 eV pass energy in order to establish elemental abundances. The analytical area on the surface was approximately a 100 Å top surface diameter with a sensitivity of one atom percent. The high-resolution spectra were curve fitted to resolve any multiple components.

RESULTS AND DISCUSSION

Before Exposure to the Plasma

A summary of ESCA examinations of poly (fluoroalkoxyphosphazene) films are listed in Table I. These examinations prior to O(³P) exposure revealed dimethyl silicone and hydrocarbon surface contaminants. Detectable also was sodium, a precursor or product from the substitution reaction of sodium trifluoroethoxide with poly (dichlorophosphazene).¹⁵ The most interesting of the ESCA findings in the preexposure and/or as-received samples was the presence of two forms of nitrogen (N_{1s}) bonding in the polymer backbone with binding

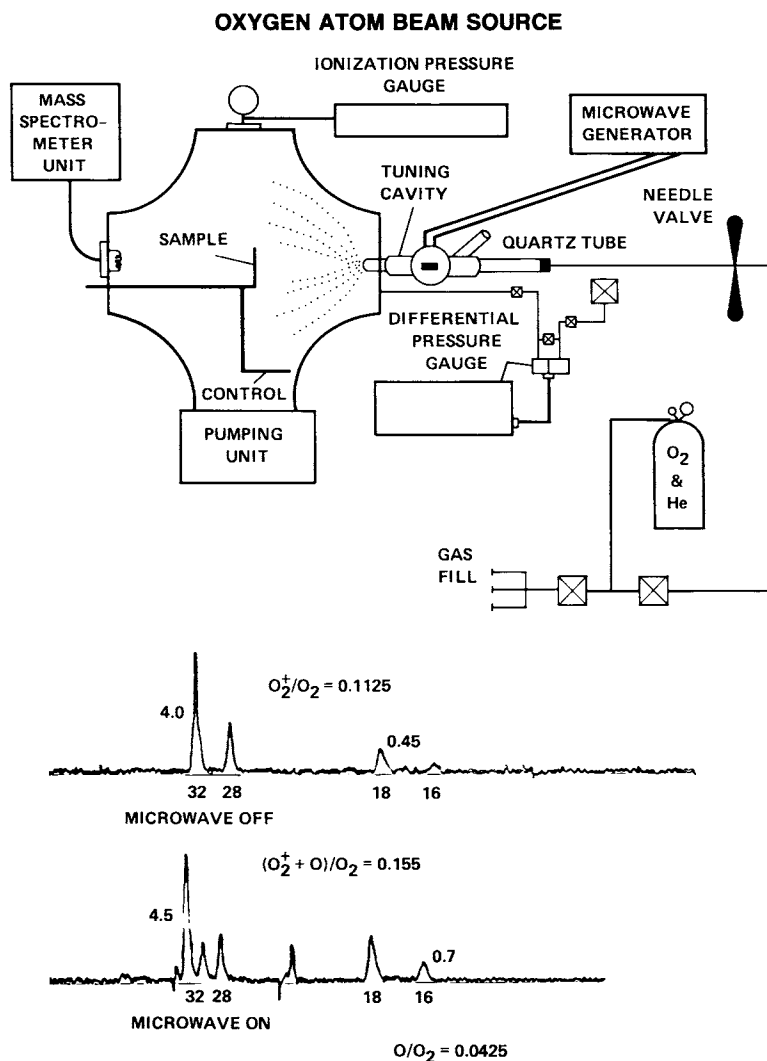


Fig. 3. O(³P) nozzle beam source (UTIA).

energies (BE) of 398.4 and 400 eV rather than one BE at 398.4 eV as evidenced in the ESCA survey of poly(dichlorophosphazene) (Fig. 4).

The nitrogen species at the higher BE probably corresponds to $-\text{P}=\text{N}-\text{N}=\text{P}-$ while the species with the binding energy of 398.4 eV corresponds to $-\text{P}=\text{N}-\text{P}-$. The $-\text{N}-\text{N}-$ bonding may be due to branching in the polymer during substitution reactions.^{17,18} The formation of active sites leading to branching in the polymer chain could also occur as the mixture nears the gelation point during thermal polymerization.¹⁹ The (O_{1s}) spectra also showed two peaks rather than one as expected. The extra peak (531.9 eV) arises primarily from an oxygen bound to a silicon atom caused by the silicon contaminant. The presence of dimethylsilicone was indicated in the ESCA

TABLE I
ESCA Peak Assignments, Binding Energies and Atomic Percentages
of Pre- and Post-Oxygen Plasma Exposures^a

	C ₁	C ₂	C ₃	O	N ₁	N ₂	N ₃	P	F
Poly[bis(trifluoroethoxy) phosphazene] film									
Binding energy (eV)	287.9	293.1		533.9	398.4	400.0		134.6	688.5
Atom percent	9.3	7.0		8.7	3.5	0.9		4.7	24.0
Exposure time (2 hr)									
Binding energy (eV)	288.3	293.4		533.8	398.8	401.6	402.3	134.8	688.9
Atom percent	9.7	8.0		9.5	4.1	2.8	0.3	8.6	24.0
Exposure time (45 hr)									
Binding energy (eV)	288.3	293.4		534.1	398.9	400.4	402.6	135.2	689.0
Atom percent	8.0	7.9		22.0	2.1	3.1	0.6	11.0	33.0
Poly(octafluoropentoxy) phosphazene coatings									
Binding energy (eV)	288.5	293.6	291.8	534.4	399.1	401.2		135.2	689.1
Atom percent	2.4	1.5	2.4	2.0	1.3	0.2		1.5	12.0
After washing with Freon TF									
Binding energy (eV)	288.5	293.7	291.7	534.5	399.0	400.6		135.3	689.1
Atom percent	8.0	5.2	8.4	9.2	3.8	0.5		4.0	37.0
Exposure time (2 hr)									
Binding energy (eV)	288.6	293.9	291.8	533.6	399.6	401.0		135.1	689.0
Atom percent	4.6	4.3	3.2	4.4	3.2	0.6		5.6	19.0

^a Assignments: C₁=O-C-CF₃, C₂=CF₃, C₃=CF₂, O=C-O-P, N₁=N=P, N₂=N-N, N₃=N-O, P=N=P, F=C-F₃, CF₂.

Note: Only elements related to polymer structure are listed. Contaminants not listed (dimethyl silicone, sodium and potassium).

survey by an additional O_{1s} peak (531.9 eV), which is an oxygen bound to a silicon atom. The high amount of surface contaminants (≥ 20%) on the poly(fluoroalkoxyphosphazene)-coated polyimide film made the sample unacceptable for ESCA examination. Washing the film with Freon TF resulted in the removal of 37% of the surface contaminants. Survey scans of the post Freon TF washed phosphazene coated polyimide film indicated the presence of fluorine, oxygen, carbon, nitrogen, phosphorus, and some silicon contaminant. The C_{1s} spectra (Fig. 5) indicates four major carbon functional groups: -CH-, O-C-CF₂, CF₂, and CF₃. Two forms of oxygen are present C-O-P and SiO(CH₃)₂. Nitrogen was present in two forms (Table I) instead of one as expected. The ratio of phosphorus to fluorine is 1 : 11 (Table III) and indicates mixed perfluorinated alkoxy side groups with the structure -[PN-(O-CH₂-CF₃)(O-CH₂-(CF₂)₃-CF₂H)]_n or poly(octylfluoropentoxy-trifluoroethoxy phosphazene).

After Exposure to Plasma

The poly[bis(trifluoroethoxy)phosphazene] film was exposed/etched in the oxygen plasma until the loss of film integrity or etch through (40-45 hr).

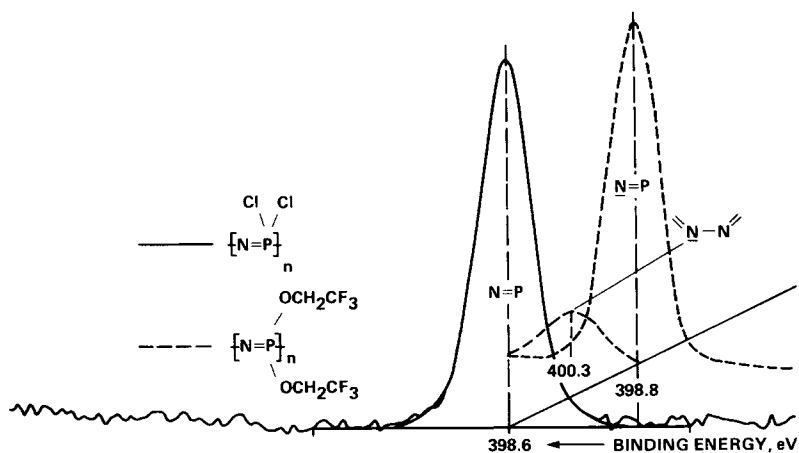


Fig. 4. ESCA spectra of N_{1s} binding energies in poly(dichlorophosphazene) and poly[bis(trifluoroethoxy)phosphazene] films.

Chemical species within the plasma have been characterized¹³ and found to be a rather complex mixture of O(³P), O₂(¹Δ_g), O(¹D), ionized species such as O₂⁺, O₂⁻, O⁺, O⁻, as well as electrons and ultraviolet radiation. The reactions of O(³P) at the surface of the polymer are responsible for the observed structural changes on the sample surface.¹⁻⁵ The most significant change occurred in the bonding characteristics of the nitrogen; three forms of nitrogen (N_{1s}) appear rather than the original two. The second nitrogen (N_{1s}) BE, (Fig. 6) because of a nitrogen doubly bonded to phosphorus (P_{2p}) and singly bonded to another nitrogen and/or rearrangement,^{20,21} has increased in a rather significant manner (atomic percent, Table I) compared to the nitrogen doubly bonded to phos-

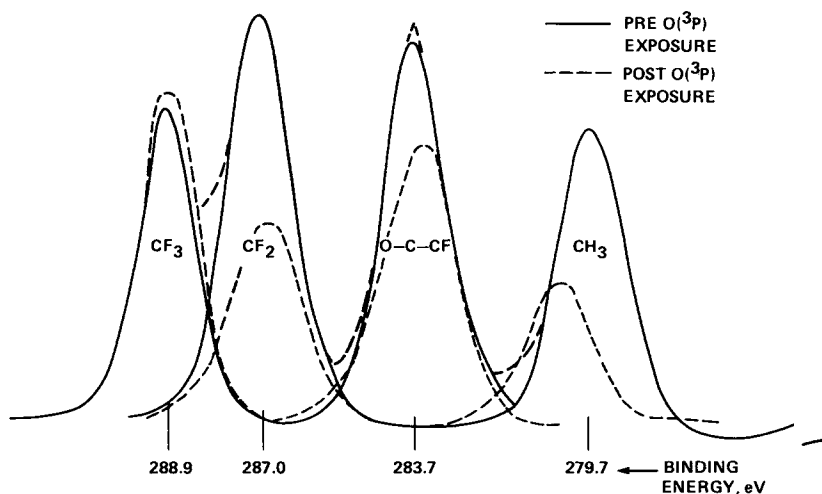


Fig. 5. ESCA spectra of pre- and post-O(³P) exposures of poly(octafluoropentoxy-trifluoroethoxy)phosphazene coated Kapton film.

ESCA SPECTRA OF CHANGES IN NITROGEN BONDING IN
POLY [BIS (TRIFLUOROETHOXY) PHOSPHAZENE] FILM INDUCED BY
O(³P) EXPOSURE

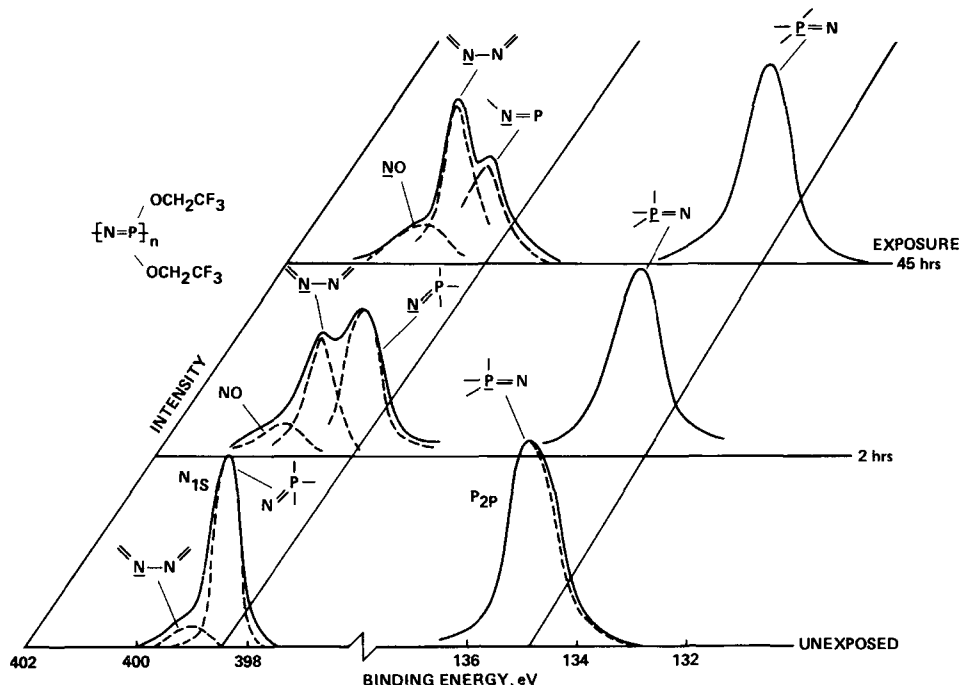


Fig. 6. ESCA spectra of O(³P)-induced changes in N_{1s} binding energies of poly[bis-(trifluoroethoxy)phosphazene] films after exposure in an oxygen plasma.

phorus ($-\text{N}=\text{P}-$) (Figs. 6 and 7). The third form of N_{1s} (BE of 401.9 eV) is nitrogen bound to oxygen,²² which indicates the possible cleavage or alteration of the nitrogen-phosphorus backbone brought about by exposure in the plasma.

The phosphorus signal intensity remained a single peak at BE of 135 eV that indicated no shifts in P_{2p} BE occurred during O(³P) exposures. Table III lists the stoichiometric changes resulting from O(³P) interactions with polyphosphazene films. After 2 hr of exposure, the phosphorus to nitrogen ratio has changed from 1 : 1 to 1 : 8/10 (5/10, 3/10, 3/100), representative of the three N_{1s} BEs. Changes in the phosphorus to carbon ratio also showed a decrease from 1 : 2 to 1 : 1, corresponding to C_{1s} BE in $-\text{CF}_3$ and $-\text{O}-\text{C}-\text{CF}_3$, respectively. Examination of the oxygen spectra indicated two O_{1s} peaks BE at 531 and 534.4 eV, the former BE resulting from an oxygen bound to the silicon contaminant and the latter BE being an oxygen atom bound to the phosphorus atom in the polymer backbone ($-\text{P}-\text{O}-\text{C}-$) and carbon. The phosphorus to oxygen ratio is now 1 : 1 rather than 1 : 2 as in the preexposure samples. Some of the pendant trifluoroethoxy groups are cleaved from the phosphorus atom by O(³P) and replaced by oxygen.

The effect of chain length of the perfluorinated alkoxy substituent groups on the phosphorus atom was observed in ESCA examinations of poly(octa-

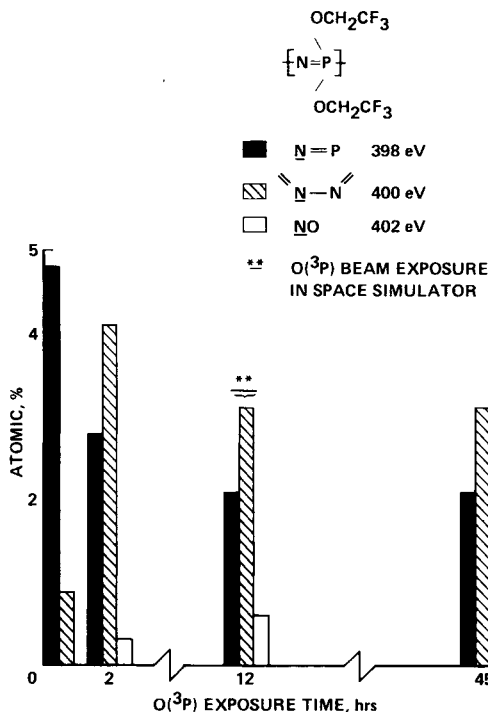


Fig. 7. Atomic percentages of nitrogen bonding forms induced by O(³P) exposure.

fluoropentoxy-trifluoroethoxy phosphazene) coated on Kapton H. After 2 hr of exposure in the plasma reactor²³ their surface compositions and mass loss rates ($1.44 \times 10^{-8} \text{ gm/cm}^2 \text{ s}$) were determined. The pattern of O(³P)-induced surface changes were the same as in previous samples, but it appears that long-chain octafluoropentoxy groups were particularly vulnerable to scission between CH₂ moieties by O(³P) (Fig. 5). The CF₂ moiety of the octafluoropentoxy pendant group appears to fragment during O(³P) attack more so than the trifluoroethoxy groups, which although cleaved from the phosphorus-nitrogen backbone remain intact. Examinations by ESCA of poly[bis(trifluoroethoxy)phosphazene] films after long-term exposures (40–45 hr) in the oxygen plasma indicated the same type of surface compositional changes as evidenced in short-term exposures. Examinations by ESCA were also conducted near the area of etch through to ascertain the magnitude as well as types of surface compositional changes of the thin film at the point of failure. The O(³P)-induced changes are best understood by their effects on the stoichiometry of the polymer. Further loss of nitrogen occurred as evidenced by the phosphorus to nitrogen ratio, which is now 1 : 1/2 (1/5, 1/4, and 1/20) for the three forms of N_{1s} BE. The N_{1s} BE (401.9 eV) is due to the nitrogen-oxygen bond, which causes a shift to a higher BE for nitrogen as a result of an increase in the charge density of oxygen and a resulting decrease in the nitrogen atom's charge density.²¹ The phosphorus to carbon ratio is 1 : 7/10 as compared to an initial ratio of 1 : 2. Ratios for P : F have changed from 1 : 6 to 1 : 3, but the P : O

ratio is unchanged at 1 : 2 (Table III). This indicates that the oxygen loss as a result of the cleavage of trifluoroethoxy groups from the polymer by $O(^3P)$ were replaced by oxygen. The polyphosphazene backbone has lost 50% of its nitrogen content; 65% of trifluoroethoxy groups have been cleaved from the polymer and replaced by oxygen.

After Beam Exposures

Poly[bis(trifluoroethoxy)phosphazene] films, fluorophosphazene (PNF) elastomer, poly(dimethylsiloxane, methylphenylsilane-*m*-carborane) elastomer, and Kapton H film were exposed to $O(^3P)$ and molecular oxygen ions/oxygen ions for 12 hr in the space simulator.¹⁴ Mass loss and reaction rates were determined for these samples (Figs. 8 and 9), but only the surface composition of the poly[bis(trifluoroethoxy)phosphazene] film was determined. Reaction rates versus oxygen atom fluence (Fig. 9) were not constant and suggest that other processes may be involved that predominate those leading to surface recession. Surface-induced reactions of $O(^3P)$ resulting in their adsorption on the film layer lead to the formation of oxidized products on the surface layer. The oxidized surface layer limits the rate of further oxidations at the surface.¹⁴ Surface recession caused by spalling of the oxidized layer would continue throughout the exposure time. ESCA revealed the same pattern of surface changes as evidenced in other polyphosphazene films previously exposed in the

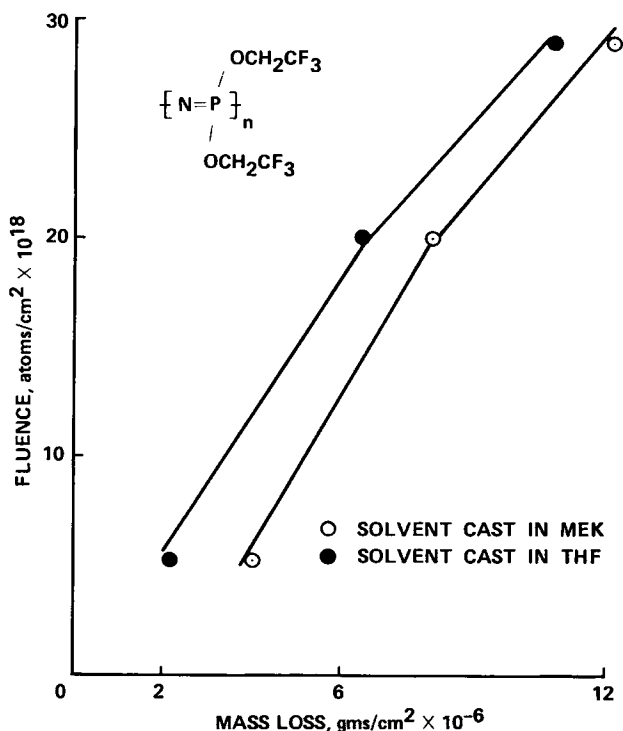


Fig. 8. Average mass losses of poly[bis(trifluoroethoxy)phosphazene] films vs. $O(^3P)$ fluence.

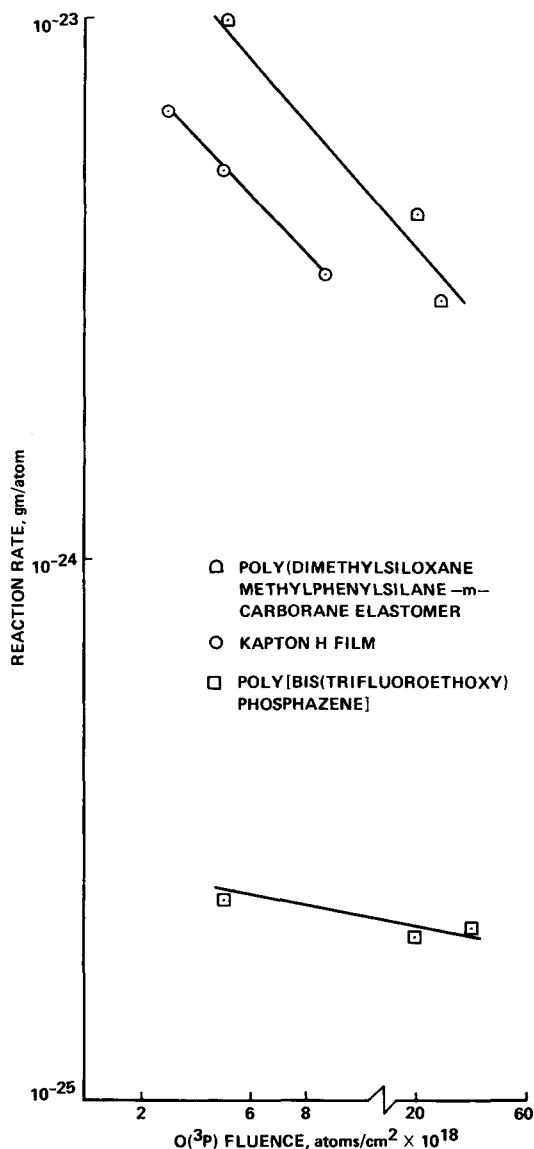


Fig. 9. Comparisons of the reaction rates of poly[bis(trifluoroethoxy)phosphazene], poly-carbosilane-siloxane copolymer and Kapton H film vs. O(³P) fluence.

plasma, namely three N_{1s} BE and the loss of some trifluoroethoxy pendant groups. However, exceptions were observed in the fluorine F_{1s} BE as indicated by two peaks, the first being at 688.8 eV (F_{1s} in CF₃) and the second peak at 686.1 eV, a shift caused by fluorine bonding to a sodium or silicon contaminant.²⁴ The magnitude of O(³P) reactions with the polymer are reflected in the change in the stoichiometry of polyphosphazene (Table III). The 12-hr beam exposure in the space simulator¹⁴ resulted in a P : N ratio of 1 : 3/5 (as compared to 1 : 1 in the unexposed film) and 1 : 1/2 in the films exposed 45 hr in an oxygen

TABLE II
O(³P)Beam Exposures ESCA Peak Assignments, Binding Energies, and Atomic Percentages^a

	C ₁	C ₂	C ₃	O	N ₁	N ₂	N ₃	P	F
Poly[bis(trifluoroethoxy) phosphazene] film									
Binding energy (eV)	288.3	293.4		534.3	398.8	400.2		135.0	688.9
Atom percent	14.0	14.0		7.4	6.0	0.8		7.2	39.0
Exposure time (12 hr)									
Binding energy (eV)	288.2	293.0		533.9	398.6	400.2	402.1	134.7	688.5
Atom percent	3.7	2.6		3.5	1.2	0.4	0.2	3.5	8.5
Exposure time (42 hr)									
Binding energy (eV)	288.2	293.4		534.0	399.1	400.3	402.3	134.7	688.9
Atom percent	9.4	9.9		14.0	2.3	2.7	1.3	12.0	26.0
Poly(octafluoropentoxy) phosphazene coating									
Binding energy (eV)	288.5	293.6	291.8	534.4	399.1	401.2		135.2	689.1
Atom percent	2.4	1.5	2.4	2.0	1.3	0.2		1.5	12.0
After Freon TF washing									
Binding energy (eV)	288.2	293.7	291.7	534.5	399.0	400.6		135.3	688.9
Atom percent	8.0	5.2	8.4	9.2	3.8	0.5		4.0	37.0
Exposure time (1.0 hr)									
Binding energy (eV)	288.2	293.8	291.8	533.7	399.2	400.5	402.3	134.8	688.9
Atom percent	4.3	3.8	3.6	27.0	1.7	1.7	0.3	6.6	19.0
Exposure time (4.0 hr)									
Binding energy (eV)	288.4	293.7	291.8	533.8	399.0	400.2	401.4	134.8	688.9
Atom percent	5.8	4.4	6.0	17.0	2.0	0.8	0.2	6.7	24.0

^a Assignments: See footnote to Table I.

Note: Only elements related to polymer structure are listed. Contaminants are not listed (dimethyl silicone, sodium).

TABLE III
Oxygen Plasma Exposure and Changes in the Stoichiometry of Polyphosphazene^a

	C ₁	C ₂	C ₃	O	N ₁	N ₂	N ₃	P	F
Poly[bis(trifluoroethoxy) phosphazene] film									
Predicted values	2.0	2.0		2.0	1.0			1.0	6.0
Unreacted	2.0	2.0		2.0	8/10	1/10		1.0	6.0
Exposure time (2 hr)	1.1	1.0		1.0	5/10	3/10		1.0	3.0
Preexposure	2.0	2.0		2.0	5/6	1/6		1.0	6.0
Exposure time (45 hr)	7/10	7/10		2.0	1/5	1/4	1/20	1.0	3.0
Poly(octafluoropentoxy) phosphazene coating									
Predicted values	2.0	2.0	3.0	2.0	1.0			1.0	11.0
Reacted ^b	2.0	1.7	1.7	1.4	9/10	1/10		1.0	8.6
After Freon TF washing	2.0	2.1	1.3	2.3	1.0	1/10		1.0	9.0
Exposure time (2 hr)	7/10	5/10	7/10	4.3	6/10	1/10		1.0	3.4

^a Assignments: See footnote to Table I.

Only elemental values associated with polymer are listed.

^b High level of surface contamination (> 20%).

plasma and after 42-hr exposure in an O(³P) nozzle beam generator (Table II, Ref. 15).

Despite stoichiometric differences, the pattern of O(³P)-induced structural changes are basically the same, varying only in degree. Long-term exposures (42 hr) of polyphosphazene films in a high-velocity O(³P) beam facility¹⁵ produced again the same pattern of changes as described in other O(³P) exposures. The same pattern of O(³P) attack on the octafluoropentoxy side groups of the phosphazene-coated Kapton H as seen in plasma exposures were also noted in beam exposures. Atomic oxygen, O(³P), attacks CF₂ at a greater rate than trifluoroethoxy groups, and O(³P) beam reactions with the poly[bis(trifluoroethoxy)phosphazene] resulted in the formation of a significant amount of N-O (Table III, Fig. 10). Long-term exposures of poly[bis(trifluoroethoxy)phosphazene] films in the O(³P) beam facility also resulted in the same amount of nitrogen removal from the polymer backbone (50%) as during long-term exposures in the oxygen plasma (Fig. 11, Table III). However, the stoichiometric relationships induced by the O(³P) beam are to an extent significantly different from those that resulted from long-term exposures in oxygen plasmas. The ratio of the nitrogen bonding forms (N_{1s}, 400.4 eV) considered to be the result of crosslinking, branching, and rearrangements^{20,21,25} is higher

PERCENTAGE OF N_{1s} BINDING ENERGIES vs.
O(³P) BEAM EXPOSURE TIMES OF
POLY[BIS(TRIFLUOROETHOXY) PHOSPHAZENE] FILM

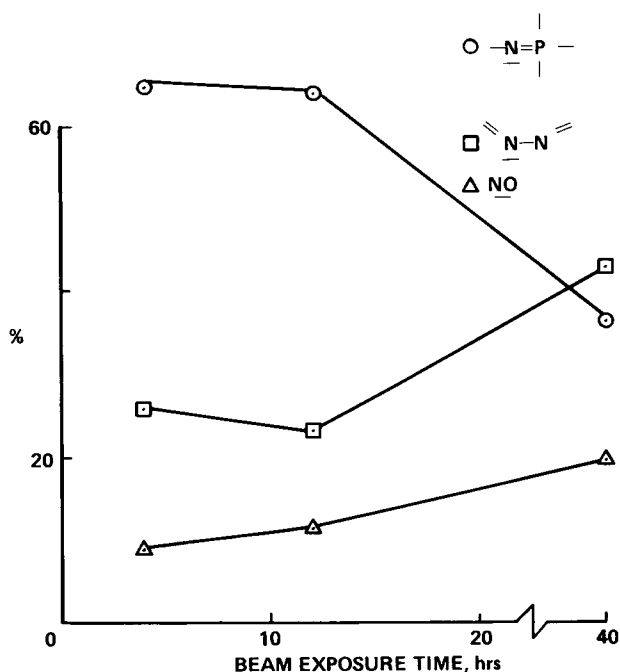


Fig. 10. Percentage of N_{1s} bonding forms in poly[bis(trifluoroethoxy)phosphazene] film as related to O(³P) beam exposure times.

$O(^3P)$ EXPOSURE TIME, vs. NITROGEN REMOVAL FROM POLYPHOSPHAZENE

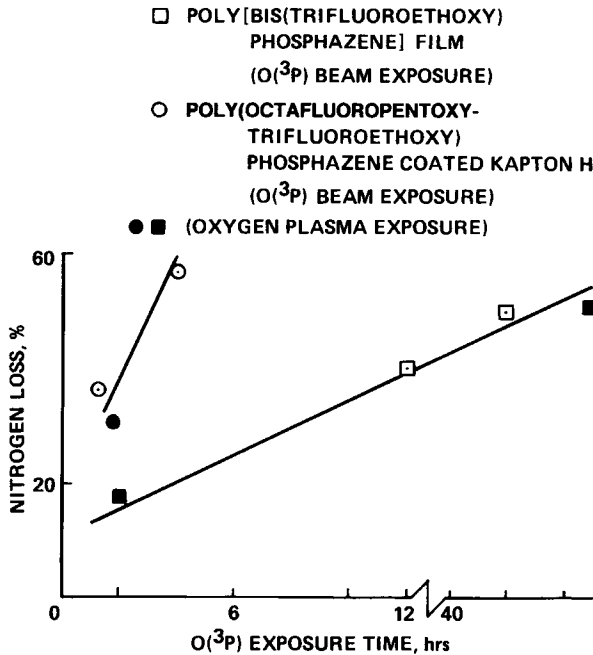


Fig. 11. Percentage nitrogen removal from polyphosphazene films as a function of $O(^3P)$ exposure time.

than N_{1s} BE (398.9 eV), which is nitrogen doubly bound to phosphorus. The beam induced a stoichiometric equivalency of $N=P$ (N_{1s} , 399 eV) and $-N-N-P=$ (N_{1s} , 400.3 eV). Also twice the amount of $N-O$ was formed in the polymer backbone (Fig. 11, Table III). The 42-hr $O(^3P)$ beam exposure resulted in no appreciable weight loss (3.2×10^{-6} g/cm² or 2.13×10^{-11} g/cm² s) at a fluence of 4.7×10^{22} atoms/cm² assuming a flux of 3.0×10^{14} $O(^3P)$ /cm² s, which is approximately the equivalent of 5 yr of exposure to $O(^3P)$ in LEO. These previously described surface-limited structural changes induced by $O(^3P)$ with polyphosphazene as determined by ESCA are summarized in Fig. 12.

CONCLUSIONS

Atomic oxygen, $O(^3P)$, induces the same patterns of surface structural changes in poly[(fluoroalkoxy)phosphazene] films and coatings independent of whether $O(^3P)$ was produced by microwave discharge or beam source. In this study $O(^3P)$ beam exposures resulted in differences in the stoichiometry of polyphosphazene in comparison to those that result from exposures in an oxygen plasma. Atomic oxygen, $O(^3P)$, beams resulted in an increased formation

**SURFACE COMPOSITION OF
POLY [BIS (TRIFLUOROETHOXY) PHOSPHAZENE] FILM AFTER
O(³P) EXPOSURE BASED ON ESCA**

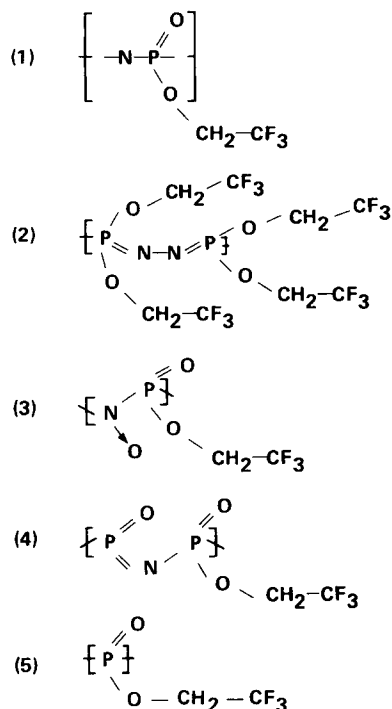


Fig. 12. Surface structures produced by O(³P) reactions with poly (fluoroalkoxy) phosphazene films based on ESCA.

of oxidized nitrogen (N → O) in the polymer. The ESCA analysis has established that O(³P) reactions with the polymer induces microstructural changes such as rearrangements in the phosphorus–nitrogen backbone characterized by shifts in the N_{1s} BE of the nitrogens, branching/crosslinking, loss of nitrogen (as much as 50%), no phosphorus is loss, and cleavage of some pendant groups followed by oxygen replacement. It was indicated by ESCA that O(³P) reacts with polyphosphazenes to form P=O (bond strength of 5.63 eV) and N=O (6.28 eV), which leads to increased bond strength in the polymer. The findings of this study suggest that resistivity to O(³P) attack is mainly a function of bond strengths and structural considerations. Based upon data from our oxygen plasma apparatus, the plasma reactor at Lockheed, O(³P) beam sources at General Electric's Space Simulator Facility, and the Nozzle Beam Facility at the University of Toronto indicated that poly[bis(trifluoroethoxy)phosphazene] films were resistant to O(³P) attack by mechanisms of backbone rearrangements, crosslinking, and by the formation of phosphorus–oxygen and nitrogen–oxygen moieties in the polymer. These time-dependent, O(³P)-induced structural changes on the film surface seem to enhance the resistivity of the polyphosphazene polymer to O(³P) attack.

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