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Oxygen plasma-resistant phenylphosphine oxide-containing polyimides and poly(arylene ether heterocycle)s: 2

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Phenylphosphine oxide-containing poly(arylene ether imide)s, poly(arylene ether quinoxaline)s, poly(arylene ether benzoxazole)s and poly(arylene ether benzothiazole)s were prepared by reacting the appropriate difluoro heterocyclic compound with bis(4-hydroxyphenoxy-4'-phenyl)phenylphosphine oxide. The polymers exhibited glass transition temperatures from 209 to 255°C and inherent viscosities from 0.35 to 1.34 dl g^{-1}. Thin-film tensile properties measured at room temperature and 177°C exhibited tensile strengths of 10.2–15.8 and 6.0–9.0 ksi (~70.3–108.9 and ~41.4–62.1 MPa), respectively, and tensile moduli of 340–381 and 204–365 ksi (~2.34–2.63 and ~1.41–2.52 GPa), respectively. Unoriented thin films of these phenylphosphine oxide-containing polymers were subsequently exposed to a radiofrequency-generated oxygen plasma under vacuum along with Kapton® HN. To assess the resistance of the materials to the oxygen plasma, the weight losses of the films were monitored as a function of exposure time. Phenylphosphine oxide-containing poly(arylene ether benzoxazole)s and poly(arylene ether benzothiazole)s exhibited weight-loss rates that were 38–190 (1–2 orders of magnitude) times slower than that of Kapton® HN. Phenylphosphine oxide-containing poly(arylene ether quinoxaline)s exhibited weight-loss rates only slightly slower (1–7 times) than those of Kapton® HN. The changes in surface chemistry of the exposed films were subsequently examined using X-ray photoelectron spectroscopy. In most cases, the phosphorus and oxygen near the surface exhibited increases in relative concentration and the photopeaks shifted towards higher binding energies. These changes are indicative of the formation of phosphate-type species. In addition, their limiting oxygen indices were calculated from char yields at 850°C in nitrogen utilizing a reported method. For the most part, the incorporation of phenylphosphine oxide groups did not substantially increase the limiting oxygen indices.

(Keywords: polyimides; poly(aryl ether heterocycle)s; phenylphosphine oxide polymers)

INTRODUCTION

As part of a cooperative materials development effort for atomic oxygen- (AO) and oxygen plasma-resistant materials, a series of phenylphosphine oxide-containing polymers were prepared, characterized and evaluated for oxygen plasma resistance. These materials have potential 'dual-use' applications on spacecraft in low Earth orbit (LEO) and as reactive ion etch barriers used in the fabrication of microelectronic circuity. The National Aeronautics and Space Administration (NASA) has needs for such light-weight, atomic oxygen-resistant (AOR) materials for use in the fabrication of flexible solar arrays and multi-layer thermal insulation blankets for potential use in LEO where AO is prevalent. Microelectronic industries have needs for oxygen plasma-resistant materials of this type to help simplify and improve certain microelectronic fabrication processes and aid in overall cost reduction.

The incorporation of silicon into organic materials is a recognized means of improving the AO/oxygen plasma resistance. Upon exposure to the AO/oxygen plasma, the silicon is converted to silicon oxide, which provides a protective surface layer for the bulk material. This phenomenon has long been recognized in the aerospace and microelectronic communities[1,2]. Similarly, the presence of phosphorus in polymers has also resulted in enhanced AO/oxygen plasma resistance, presumably by the formation of an inorganic phosphate-type species upon exposure. Phosphorus-containing materials that have exhibited good AO/oxygen plasma resistance include polyphosphazenes[3,4] and phosphine oxide-containing poly(arylene ether)s[5,6]. As a collaborative effort on AO/oxygen plasma-resistant polymers, phosphine oxide-containing poly(arylene ether imide)s, poly(arylene ether benzoxazole)s, poly(arylene ether benzothiazole)s and poly(arylene ether quinoxaline)s were prepared, characterized and subsequently exposed to a radiofrequency-generated oxygen plasma under vacuum[7]. The weight-loss rates of thin films of these polymers were compared

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with those of Kapton® HN polyimide film exposed simultaneously.

EXPERIMENTAL

Starting materials

Bis(4-hydroxyphenoxy-4′-phenyl)phenylphosphine oxide[6], 2,6-bis(4-fluoro)benzo[1,2;4,5]dithiazole[8], 2,2′-bis(4-fluorophenyl)-5,5′-bibenzoxazole[9], 1,4-bis(6-fluoro-3-phenyl-2-quinoxalinyl)benzene and isomers[10] and 2,3-bis(4-fluorophenyl)quinoxaline[11] were prepared as previously reported. High-purity reagents such as *N*-methyl-2-pyrrolidinone (NMP), *N*-cyclohexyl-2-pyrrolidinone (CHP), 4-fluorophthalic anhydride, 1,4-diaminobenzene, *N,N′*-(dimethyl)trimethylsilylamine, potassium carbonate and toluene were purchased from commercial sources and used without further purification.

Bis(4-trimethylsiloxyphenoxy-4′-phenyl)phenylphosphine oxide

A three-necked round-bottomed flask equipped with a condenser and nitrogen inlet was charged with bis(4-hydroxyphenoxy-4′-phenyl)phenylphosphine oxide (10.00 g, 20.2 mmol) and *N,N′*-(dimethyl)trimethylsilylamine (8.494 g, 60.7 mmol). The reactants were rinsed in with toluene and heated to 75°C for 48 h. Thin layer chromatographic analysis on silica gel using ethyl acetate/hexanes (3:1) as the mobile phase indicated quantitative conversion of the starting materials to a single product. The reaction mixture was concentrated to afford a quantitative yield of an amorphous glassy product. Proton nuclear magnetic resonance (^{1}H n.m.r.) spectroscopic analysis indicated quantitative conversion of the phenolic protons to trimethylsilyl groups. ^{1}H n.m.r. (ppm) δ7.51 (10H, m), 6.89 (11H, m) and 0.24 (18H, s). ^{13}C n.m.r. (ppm) δ116.3, 121.0, 124, 126.0, 128.2, 131.8, 133.8, 148.9, 151.9 and 161.7.

1,4-Bis(4-fluorophthalimido)benzene

A three-necked round-bottomed flask equipped with an overhead stirrer assembly and nitrogen inlet was charged with 4-fluorophthalic anhydride (14.048 g, 84.6 mmol), 1,4-diaminobenzene (4.590 g, 42.3 mmol) and a 1:1 mixture of NMP/CHP. The reaction mixture was heated to 190°C for 24 h. Upon cooling, the product crystallized from solution and was collected and washed with methanol. The product exhibited the expected ^{1}H n.m.r. spectral characteristics. ^{13}C n.m.r. (ppm) δ104.3, 106.1, 109.8, 117.8, 128.7, 130.1, 131.4, 133.3, 140.4, 150.6, 152.4, 157.0, 157.4, and 157.7.

Poly(arylene ether quinoxaline) and isomers (PPQ/PPO-1)

Into a 100 ml three-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, Dean–Stark trap and condenser were placed 1,4-bis(6-fluoro-3-phenyl-2-quinoxalinyl)benzene and isomers (4.4390 g, 8.5 mmol), bis(4-hydroxyphenoxy-4′-phenyl)phenylphosphine oxide (4.2005 g, 8.5 mmol), pulverized anhydrous potassium carbonate (2.70 g, 19.5 mmol), toluene (50 ml) and NMP (33 ml, 20% solids). The mixture was heated to ~145°C for ~4 h and the water generated was collected in the Dean–Stark trap. The toluene was removed from the system and the temperature was increased to ~180°C. After 1 h the solution had become viscous and was diluted with NMP (15 ml); heating was continued for an additional 2 h. The solution was poured into water/acetic acid mixture in a high-speed blender to precipitate the off-white, fibrous polymer. The polymer was washed successively in hot water and hot methanol and dried for ~3 h at 120°C in a forced air oven to give 99% of the theoretical yield of polymer.

Poly(arylene ether quinoxaline) (PPQ/PPO-2)

Into a 100 ml three-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, Dean–Stark trap and condenser were placed 2,3-bis(4-fluorophenyl)quinoxaline (2.9961 g, 9.4 mmol), bis(4-hydroxyphenoxy-4′-phenyl)phenylphosphine oxide (4.6529 g, 9.4 mmol), pulverized anhydrous potassium carbonate (2.156 g, 15.6 mmol), toluene (35 ml) and NMP (32 ml, 18.5% solids). The mixture was heated to ~155°C for 6–8 h and the water generated was collected in the Dean–Stark trap. The toluene was removed from the system and the temperature was increased to ~180°C for 20 h. Completion was estimated at the point where solution viscosity increased notably. The solution was poured into methanol in a high-speed blender to precipitate the polymer. The polymer was washed in hot methanol and dried for 24 h at 80°C under vacuum.

Poly(arylene ether benzoxazole) (PBO/PPO)

Into a 100 ml three-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, Dean–Stark trap and condenser were placed 2,2′-bis(4-fluorophenyl)-5,5′-bibenzoxazole (2.5827 g, 6.1 mmol), bis(4-hydroxyphenoxy-4′-phenyl)phenylphosphine oxide (3.0091 g, 6.1 mmol), pulverized anhydrous potassium carbonate (1.9 g, 13.7 mmol), toluene (50 ml) and NMP (21 ml, 20% solids). The mixture was heated to ~145°C for ~4 h and the water generated was collected in the Dean–Stark trap. The toluene was removed from the system and the temperature was increased to ~180°C. After 2.5 h the solution had become viscous and was diluted with NMP (21 ml); heating was continued for an additional 1 h. The solution was poured into water/acetic acid mixture in a high-speed blender to precipitate the fibrous polymer. The polymer was washed successively in hot water and hot methanol and dried for ~3 h at 120°C in a forced air oven to give 95% of theoretical yield of polymer.

Poly(arylene ether benzothiazole) (PBT/PPO)

Into a 100 ml three-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, Dean–Stark trap and condenser were placed 2,6-bis(4-fluoro)benzo[1,2,4,5]dithiazole (1.1094 g, 2.9 mmol), bis(4-hydroxyphenoxy-4′-phenyl)phenylphosphine oxide (1.4419 g, 2.9 mmol), pulverized anhydrous potassium carbonate (0.93 g, 6.7 mmol), toluene (50 ml) and NMP (10 ml, 20% solids). The mixture was heated to ~145°C for ~4 h and the water generated was collected in the Dean–Stark trap. The toluene was removed from the system and the temperature was increased to ~180°C. After 2.5 h the solution had become viscous and was diluted with NMP (20 ml); heating was continued for an additional 0.5 h. The solution was poured into water/acetic acid mixture in a high-speed blender to precipitate the yellow, fibrous polymer. The

polymer was washed successively in hot water and hot methanol and dried for ~3 h at 120°C in a forced air oven to give 95% of theoretical yield of polymer.

Poly(arylene ether imide)

Into a 50 ml three-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, Dean–Stark trap and condenser were placed caesium fluoride (0.15 g, 0.98 mmol, predried at 180°C for 20 h under vacuum), toluene (15 ml) and NMP (25 ml). The mixture was heated to ~155–165°C for ~7 h to dehydrate the catalyst further. The toluene was subsequently removed from the system and the reaction mixture allowed to cool to room temperature. Bis(4-trimethylsiloxyphenoxy-4′-phenyl)phenylphosphine oxide (2.7835 g, 4.35 mmol) and 1,4-bis(4-fluorophthalimido)benzene (1.7617 g, 4.35 mmol) were charged to the flask and the temperature was slowly increased to ~180°C for ~30 h to effect displacement. The solution was poured into a 10-fold excess of methanol/water (1/1) in a high-speed blender to precipitate the polymer. The polymer was washed in hot methanol and dried for 24 h at 80°C under vacuum. This synthetic method was first reported by Kricheldorf[12].

Films

NMP solutions (15% solids) of the polymers were centrifuged, the decantate doctored onto clean, dry plate glass and dried to a tack-free form in a low-humidity chamber. The films on glass were stage-dried up to ~50°C above their respective T_g for 1 h. Thin-film tensile properties were determined according to ASTM D882 using at least four specimens per test condition.

Oxygen plasma asher exposure

Oxygen plasma exposures were performed on thin films (0.5 inch × 0.5 inch, ~2 mil thick; approx. 13 × 13 mm^2 and 50 μm thick) of the polymers in a Tegal Plasmod asher. The asher was operated at 500 mTorr, 100 W of radiofrequency, oxygen pressure of 3 psi (~20.7 kPa) and a flow rate of 50 $cm^3 min^{-1}$. Since the asher was not calibrated, a simultaneous exposure of Kapton® HN film was performed with the experimental polymers. The Kapton® HN film served as a standard, allowing for direct comparison with the experimental polymer films. In each case, duplicate exposures were performed. The samples were periodically removed, weighed and replaced in the asher typically over a 23 h period, and the weight losses of the films were monitored as a function of exposure time.

Calculated limiting oxygen index

Thermogravimetric analyses (t.g.a.) were performed on a Seiko model 200/220 instrument on film samples at a heating rate of 40°C min^{-1} in nitrogen at a flow rate of 40 $cm^3 min^{-1}$. Char yields were determined by the amount (weight per cent) of material remaining at 850°C. Limiting oxygen indices (*OI*) were calculated following a reported procedure[13] using the equation:

$$OI = [17.5 + 0.4(CR)]/100$$

where *CR* is the char residue in weight per cent at 850°C in nitrogen.

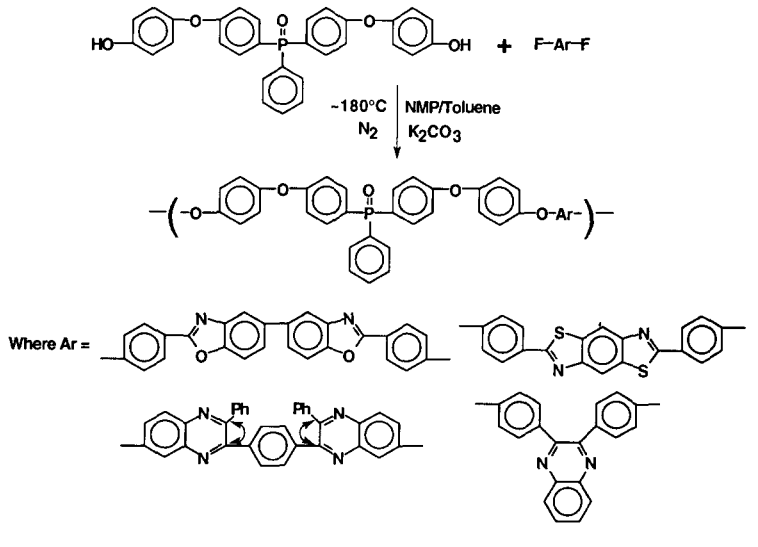
Other characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% solutions in NMP at 25°C. Differential scanning calorimetry was conducted on a Shimadzu DSC-50 thermal analyser at a heating rate of 20°C min^{-1} with the T_g taken at the inflection point of the ΔT *versus* temperature curve. Nuclear magnetic resonance (n.m.r.) spectra were recorded on an IBM WP250 instrument operating at 250.1 MHz (^1H) and 62.9 MHz (^{13}C). Tetramethylsilane was used as an internal standard with the reference peak being assigned 0.0 parts per million (ppm).

RESULTS AND DISCUSSION

Polymer synthesis

High-molecular-weight phenylphosphine oxide-containing poly(arylene ether quinoxaline)s, poly(arylene ether benzoxazole)s and poly(arylene ether benzothiazole)s were prepared from activated difluoro heterocyclic compounds with the bisphenolate of bis(4-hydroxyphenoxy-4′-phenyl)phenylphosphine oxide in NMP (*Scheme 1*). The chemical structures of the phenylphosphine oxide-



Scheme 1

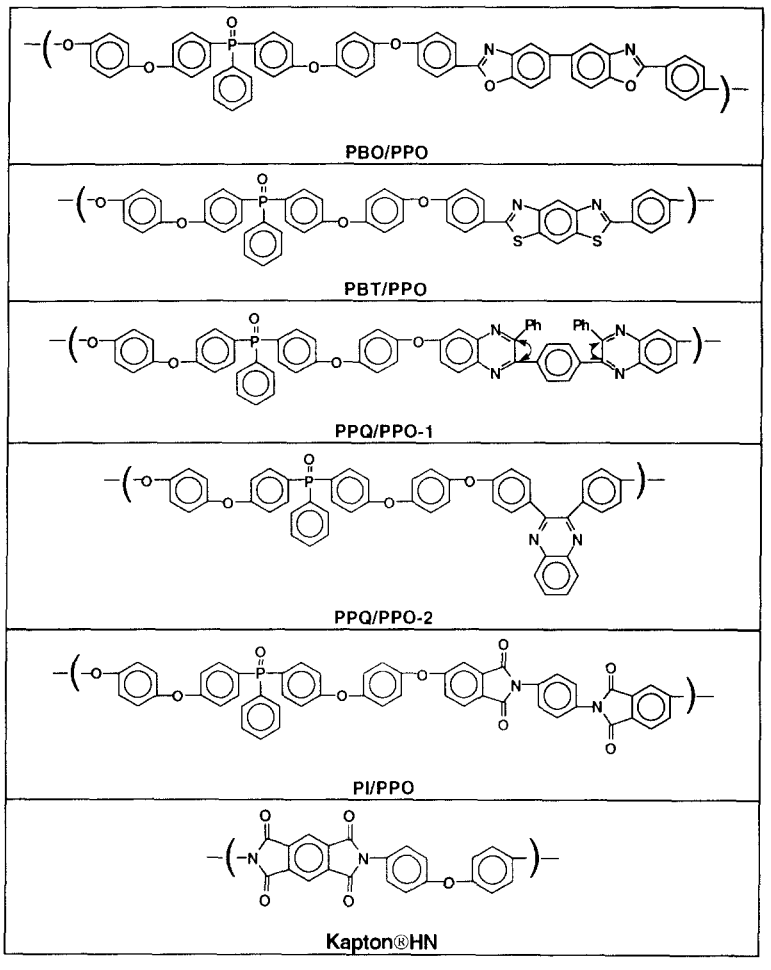


Figure 1 Chemical structures of polymers evaluated in this study

Table 1 Polymer characterization

Polymer	η_{inh}[a] (dl g^{-1})	T_g (°C)	Char yield[b] (%)	Calculated *OI*
PPQ/PPO-1	1.05	248	57.1	0.40
PPQ/PPO-2	0.35	209	45.3	0.36
PBO/PPO	0.97	223	33.3	0.31
PBT/PPO	1.34	255	50.0	0.37
PI/PPO	0.42	220		
Kapton® HN	–	–	57.3	0.40

[a] Inherent viscosity obtained on 0.5% solution in NMP at 25 °C
[b] Char yield at 850°C in N_2 by t.g.a., heating rate 40°C min^{-1}

Table 2 Unoriented thin-film tensile properties[a]

Polymer	Test temp. (°C)	Tensile strength (ksi)	Tensile modulus (ksi)	Elongation to break (%)
PPQ/PPO-1	23	12.3	360	7
	177	7.0	254	29
PPQ/PPO-2	23	10.2	340	6
	177	9.0	365	29
PBO/PPO	23	12.6	347	43
	177	6.0	223	100
PBT/PPO	23	15.8	381	64
	177	8.7	204	122

[a] 1 ksi ≃ 6.895 MPa

containing polymers are presented in *Figure 1*. The polymers exhibited T_g values ranging from 209 to 255°C and η_{inh} values from 0.35 to 1.34 dl g^{-1} (*Table 1*). The polymers formed light yellow, tough films, which exhibited tensile properties that were higher than those observed for amorphous poly(arylene ether)s of comparable chemical structure that do not contain heterocyclic rings[5]. Unoriented thin-film tensile properties are presented in *Table 2*.

The phenylphosphine oxide-containing poly(arylene ether imide) was prepared from bis(4-trimethylsiloxyphenoxy-4′-phenyl)phenylphosphine oxide and 1,4-bis(4-fluorophthalimido)benzene in NMP using caesium fluoride (*Scheme 2*). The polymer exhibited an η_{inh} of 0.42 dl g^{-1} and a T_g of 220°C (*Table 1*). The thin film cast from this polymer was brittle and consequently not tested for thin-film tensile properties or oxygen plasma resistance.

Calculated limiting oxygen index

The incorporation of phosphorus into polymers either chemically bound or as an additive is known to improve flame resistance. Thus, it was of interest to determine the *OI* values for several of the phenylphosphine oxide-containing polymers. The *OI* was calculated from a reported relationship[13].

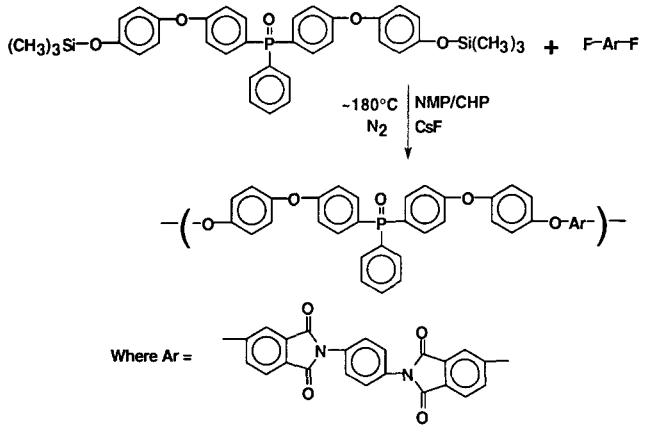
$$OI = [17.5 + 0.4(CR)]/100$$

where *CR* is the char residue (yield) determined by t.g.a.

at 850°C under a nitrogen atmosphere. The char yields and calculated *OI* values for the experimental polymers are presented in *Table 1*. The incorporation of phosphorus into these polymers did not dramatically improve the *OI* values. However, all of the materials exhibited *OI* values greater than 0.31. A material is considered flammable if the *OI* is less than 0.26. Kapton® HN exhibited a char yield of 57.3% and a calculated *OI* of 0.40 (*Table 1*).

Oxygen plasma resistance

Unoriented thin films (~2 mil thick; 50 μm) of the phenylphosphine oxide-containing poly(arylene ether quinoxaline)s, poly(arylene ether benzoxazole) and poly(arylene ether benzothiazole) were exposed simultaneously with Kapton® HN film of comparable thickness to an oxygen plasma under vacuum. Exposures were typically performed for up to 23 h with the samples being periodically removed, weighed and replaced in the asher. The weight losses of the films were monitored as a function of exposure time. Since the asher was not calibrated for atomic oxygen concentration (fluence), the weight losses of the experimental polymers were compared to that of the Kapton® HN film exposed simultaneously. In all cases, duplicate sample exposures were performed. The normalized results of the oxygen plasma exposures are represented graphically in *Figure 2* and compiled in *Table 3*. All of the phenylphosphine oxide-containing polymers exhibited lower weight-loss rates compared to Kapton® HN. However, the polymers containing quinoxaline groups exhibited weight-loss rates of ≤1 order of magnitude slower than that of Kapton® HN, whereas the other polymers exhibited rates of 1–2 orders of magnitude slower. The higher weight-loss rates exhibited by the poly(arylene ether quinoxaline)s were unexpected since earlier work with phenylphosphine oxide-based poly(arylene ether)s containing imide, 1,3,4-oxadiazole and benzimidazole units indicated weight-loss rates of 1–2 orders of magnitude less than that of Kapton® HN[12]. In addition, the phenylphosphine oxide-containing poly(arylene ether quinoxaline)s exhibited linear weight-loss rates, whereas the other phenylphosphine oxide-containing polymers exhibited non-linear weight-loss rates. Kapton® HN also exhibited a relatively constant, linear weight-loss rate throughout the duration of the oxygen plasma exposure.



Scheme 2

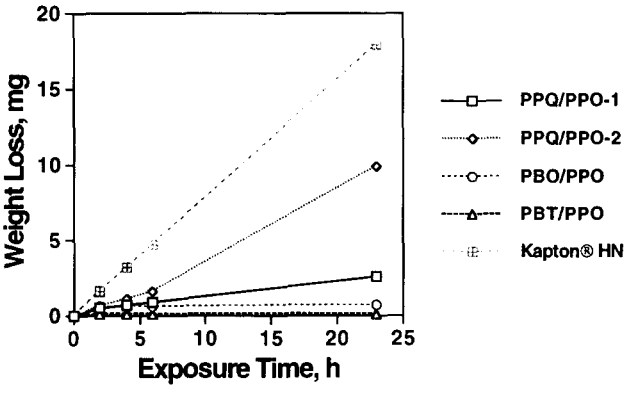


Figure 2 Weight loss *versus* exposure time in the oxygen plasma asher

The weight-loss rates of the phenylphosphine oxide-containing films during a 23 h exposure period ranged from 0.004 to 0.44 mg h^{-1} as normalized to the Kapton® HN weight-loss rate of 0.77 mg h^{-1} (*Table 3*). The poly(arylene ether quinoxaline)s exhibited weight-loss rates of 0.11 (PPQ/PPO-1) and 0.44 mg h^{-1} (PPQ/PPO-2) compared to that of Kapton® HN (0.77 mg h^{-1}).

The phenylphosphine oxide-containing poly(arylene ether benzoxazole) and poly(arylene ether benzothiazole) exhibited two distinct regions of differing weight-loss rates, as indicated by the change in slope of the weight-loss *versus* exposure time (*Figure 2*). The first region of weight loss occurred within the first 2 h of exposure to oxygen plasma with a subsequent decrease in weight-loss rate. The weight-loss rates of the poly(arylene ether benzoxazole) and poly(arylene ether benzothiazole) for the 2–23 h exposure were reduced (0.0074 and 0.0014 mg h^{-1}, respectively) compared to the 0–2 and 0–23 h weight-loss rates (*Table 3*). Presumably this change in weight-loss rate exhibited by the poly(arylene ether benzoxazole) and poly(arylene ether benzothiazole) is due to formation of a higher oxidized phosphate-type surface layer upon exposure, which has superior resistance to the oxygen plasma. An inorganic phosphate-type surface layer

Table 3 Oxygen plasma exposure results

	Weight-loss rate (mg h^{-1}) 0–2 h		Weight-loss rate (mg h^{-1}) 0–23 h	
Polymer	Experimental	Normalized[a]	Experimental	Normalized[a]
PPQ/PPO-1	0.28	0.26	0.11	0.11
PPQ/PPO-2	0.31	0.43	0.42	0.44
PBO/PPO	0.20	0.20	0.01	0.02
PBT/PPO	0.04	0.05	0.003	0.004

[a] Normalized to a Kapton® HN weight-loss rate of 0.77 mg h^{-1}

Table 4 X.p.s. analyses

Polymer	Photopeak	Binding energy (eV)		Atomic concentration (%)		
		Before	After	Before	After	Theory
PPQ/PPO-1	C 1s	285.0	285.0	67.2	36.2	78.7
	O 1s	532.6	533.2	18.8	45.4	8.2
	N 1s	400.0	400.0	2.0	3.7	5.7
	P 2p	132.7	134.5	0.6	4.6	3.2
	Si 2p	102.4	103.5	11.4	10.0	0
PBO/PPO	C 1s	285.0	285.0	78.3	47.6	76.5
	O 1s	532.8	533.3	15.9	39.6	12.7
	N 1s	400.0	400.7	1.7	2.9	3.2
	P 2p	132.7	134.8	3.2	8.9	3.5
	Si 2p	102.3	103.5	3.2	1.0	0
PBT/PPO	C 1s	285.0	285.0	76.2	47.8	71.9
	O 1s	532.7	532.5	16.3	39.8	9.6
	N 1s	400.0	400.0	2.3	2.9	3.3
	S 2p	164.4	169.5	1.2	8.4	7.7
	P 2p	132.4	134.6	0.7	2.1	3.7

has been shown to form on certain polyphosphazenes[3,4] and poly(arylene ether phosphine oxide)s[5,6] exposed to oxygen plasma. A similar change in surface chemistry of the phenylphosphine oxide-containing polymers after exposure to oxygen plasma is presumed to occur based upon previous observations and X.p.s. analyses.

During the oxygen plasma exposure experiments, the thin-film samples were periodically removed from the asher and weighed, thereby exposing them to the atmosphere. Earlier work has shown that similar weight-loss rates are obtained with this type of experiment regardless of whether the sample is removed periodically or not[6].

X-ray photoelectron spectroscopic analysis

To determine changes in oxidation states of the surface atoms, thin films of several experimental phenylphosphine oxide-containing polymers were analysed by X.p.s. before and after exposure. All photopeaks were referenced to that of carbon having a maximum taken at 285.0 eV. The following polymers were examined by X.p.s.: PPQ/PPO-1, PBO/PPO and PBT/PPO. The PPQ/PPO-1 and PBT/PPO control (unexposed) samples exhibited 0.6 and 0.7% of phosphorus, respectively whereas the PBO/PPO control exhibited 3.2% (*Table 4*). These materials have theoretical amounts of phosphorus ranging from 3.2 to 3.7%. The PPQ/PPO-1 and PBO/PPO control and exposed samples were contaminated with silicon from an unknown source, which could influence the weight-loss rates of these samples. This contamination could have had an advantageous effect on PPQ/PPO-1, which contained 11% silicon, since it exhibited a slightly lower erosion rate than Kapton® HN and PPQ/PPO-2. The PBO/PPO sample was contaminated with 3.2% silicon before exposure and only 1% silicon after exposure.

Both PPQ/PPO-1 and PBO/PPO exhibited increases in binding energies of the phosphorus and oxygen atoms near the surface and increases in relative concentrations of these two species. The control samples exhibited an oxygen photopeak around 532.7 eV and a phosphorus photopeak centred near 132.7 eV. After exposure to the oxygen plasma the binding energies exhibited an increase to 533.2 eV for oxygen and 134.6 eV for phosphorus. The ratio of oxygen to phosphorus of exposed PPQ/PPO-1 was ~10:1 while that of exposed PBO/PPO was 4.5:1. The different oxygen/phosphorus ratio and the higher weight-loss rates exhibited by PPQ/PPO-1 and PPQ/PPO-2 compared to other phenylphosphine oxide-containing polymers suggests that they may interact differently with the oxygen plasma.

The PBT/PPO exhibited different behaviour upon exposure to the oxygen plasma with regards to the change in binding energy of the oxygen atoms near the surface. The binding energies and relative concentrations of phosphorus and sulfur atoms near the surface exhibited increases while the binding energy of oxygen atoms remained unchanged. However, the relative concentration of the oxygen atoms did exhibit an increase after exposure. The control samples exhibited an oxygen photopeak around 532.7 eV and a phosphorus photopeak centred near 132.4 eV. After exposure to the oxygen plasma the binding energies were 532.5 eV for oxygen and 134.6 eV for phosphorus. The binding energy for sulfur changed from 164.4 to 169.5 eV and the relative concentration increased from 1.2 to 8.4%. This result implies that a thiophosphate species may form preferentially compared to a phosphate. The ratio of sulfur to phosphorus of the exposed PBT/PBO was ~4:1. In previous reports of oxygen plasma exposure of phenylphosphine oxide-containing polymers, the ratio of oxygen to phosphorus in the exposed samples has ranged from 4:1 to 5:1[6,14], with the one exception being the poly(arylene ether quinoxaline)s previously discussed.

The shifts in the binding energy and the broadening of the photopeaks for phosphorus and oxygen after exposure to an oxygen plasma have been reported to be indicative of the formation of a higher oxidized phosphorus species (i.e. phosphate-type)[5,6].

The Kapton® HN film used in this study was not analysed by X.p.s. Results from an X.p.s. study of both

LEO and oxygen plasma-induced chemical changes in Kapton indicate that there are some differences in erosion rate and oxygen uptake[15]. However, the chemical changes (oxidation) appeared to be uniform through the thickness of the Kapton film.

It should be noted that observed changes in the surface chemistry of both ground-based and space-flight material exposure experiments are potentially influenced by the exposure of the samples to atmospheric conditions prior to analysis.

CONCLUSIONS

Thin films of the phenylphosphine oxide-containing poly(arylene ether benzoxazole) and poly(arylene ether benzothiazole) exhibited significantly better weight retention after exposure to an oxygen plasma compared to Kapton® HN. In addition, they exhibited a non-linear weight-loss behaviour, presumably due to the formation of an inorganic phosphate-type species upon exposure to the oxygen plasma. The weight-loss rates measured over a 23 h exposure time ranged from 1 to 2 orders of magnitude less than that of Kapton® HN. The phenylphosphine oxide-containing poly(arylene ether quinoxaline)s exhibited linear weight-loss rates and only slightly slower weight-loss rates than Kapton® HN.

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The use of tradenames of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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