

# Oxygen plasma resistant phenylphosphine oxide-containing poly(arylene ether)s

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Phenylphosphine oxide-containing poly(arylene ether)s were prepared by the aromatic nucleophilic displacement reaction of a new phenylphosphine oxide-containing bisphenol with activated aromatic difluorides in the presence of anhydrous potassium carbonate in *N,N'*-dimethylacetamide at 155°C or in sulfolane at 200°C. The phenylphosphine oxide-containing bisphenol was prepared in two steps from bis(4-fluorophenyl)phenylphosphine oxide and 4-methoxyphenol. The polymers exhibited inherent viscosities of 0.57–0.75 dl g<sup>-1</sup> and glass transition temperatures of 177–213°C. Thermogravimetric analyses showed 5% weight loss in the ranges of 447–471°C in air and 480–512°C in nitrogen. Unoriented thin films exhibited tensile strengths, moduli and break elongations at 23°C of 8.1–11.1 ksi, 275–370 ksi and 42–109%, respectively. Limiting oxygen indices of 0.30–0.33 were calculated based on polymer char residues at 850°C in nitrogen. Phenylphosphine oxide-containing poly(arylene ether)s exhibited excellent resistance to an oxygen plasma environment with weight loss rates of one to two orders of magnitude lower than that of Kapton<sup>®</sup> HN. The chemistry, and physical and mechanical properties of these polymers, as well as their oxygen plasma resistance, are discussed.

(Keywords: poly(arylene ether)s; oxygen plasma resistance; limiting oxygen index)

## INTRODUCTION

In low earth orbit (LEO), which extends from 200 to 500 km above the earth's surface, atomic oxygen (AO) is a prevalent species and has been observed to cause substantial erosion and degradation of uncoated non-fluorinated organic polymers<sup>1–4</sup>. The effect of AO erosion was especially apparent on materials flown on the long duration exposure facility for ~5.8 years at altitudes of 333–476 km<sup>4</sup>. Perfluorinated materials, such as copoly-(fluoroethylene propylene), displayed good resistance to AO, but dramatic increases in the erosion rate (mass loss) were observed when the polymer was exposed simultaneously to AO and u.v. radiation<sup>5,6</sup>. Current methods to eliminate or reduce the erosion due to AO involve coating materials with fluorinated polymers (i.e. polytetrafluoroethylene<sup>7</sup>) or inorganic oxides such as aluminium oxide<sup>8</sup>, silicon dioxide<sup>8</sup>, chromium oxide<sup>7</sup> and indium-tin oxide<sup>9</sup>. Recently, an organic coating based on decaborane-containing polymers has been reported to exhibit oxygen plasma resistance<sup>10</sup>. For the coating to be effective, it must be free from defects and pin-holes, relatively uniform, and ~500–2000 Å thick. The use of coatings for AO protection can pose problems since the coating of complex shapes can be difficult, and quality control is at best qualitative. In addition, damage can occur due to fabrication and/or handling on the ground or from micrometeoroid and debris impacts in space, exposing the underlying material to AO. NASA has needs for lightweight, AO resistant materials for potential use on spacecraft in LEO. Organic polymers which are intrinsi-

cally AO resistant would overcome the problems associated with coated materials since the AO resistance is inherent in the material and would provide through-the-thickness protection. For an added degree of safety, these materials could likewise be coated; however, if the coating is 'imperfect' or damaged, the underlying exposed surface would possess inherent AO resistance.

High performance polymers, such as polyimides, have been modified by the incorporation of silicon in the form of siloxane groups, either in the polymer backbone or pendent on the polymer chain. In addition to other advantageous effects, the incorporation of silicon-containing groups into these polymers has been observed to enhance oxygen plasma/AO resistance through the formation of inorganic silicon (i.e. silicates, silicon dioxide) species by interacting with oxygen plasma or AO<sup>3,5,11–17</sup>. Other polymers containing silicon, such as poly(carborane siloxane)s, have also exhibited excellent oxygen plasma resistance<sup>18</sup>.

Certain phosphorus-containing polymers have exhibited notable resistance to oxygen plasma erosion. Several polyphosphazenes<sup>19,20</sup>, poly(arylene ether phosphine oxide)s<sup>21,22</sup>, poly(arylene ether phosphine oxide)s containing heterocyclic groups<sup>23,24</sup> and polyimides containing the phenylphosphine oxide group<sup>24</sup> have shown excellent resistance to AO and oxygen plasma environments. Upon exposure to AO and oxygen plasma environments, an increase in the oxidation state of phosphorus near the surface has been observed using X-ray photoelectron spectroscopy (X.p.s.)<sup>19–21</sup>. The resultant structure formed from this change in surface chemistry apparently protects the underlying material from further erosion. Other benefits derived from the

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incorporation of phosphorus in polymers, either in the backbone or as additives, include flame retardance, increased adhesion to metals, enhanced metal-ion binding characteristics and increased polarity<sup>25</sup>.

Phosphorus in the form of the phosphine oxide group has been incorporated in poly(arylene ether)s (PAEs) via either the dihalide<sup>21,23,26-29</sup> or bisphenol<sup>22,24,26,27</sup>. PAEs are a class of high performance engineering thermoplastics useful in a variety of applications. One method of PAE synthesis is by the aromatic nucleophilic displacement reaction of an activated aromatic dihalide or dinitro compound by an alkali metal bisphenolate in a polar aprotic medium<sup>30-33</sup>. The work reported herein discusses the synthesis, physical, and mechanical properties of phenylphosphine oxide-containing PAEs prepared by the nucleophilic displacement reaction of activated aromatic difluorides and a new phenylphosphine oxide-containing bisphenol. The limiting oxygen index and oxygen plasma resistance of thin polymer films were determined and are discussed.

## EXPERIMENTAL

### Starting materials

4,4'-Difluorobenzophenone (Chemical Dynamics Corp.) and bis(4-fluorophenyl)sulfone (Aldrich Chemical Co.) were recrystallized from ethanol (m.p. 104–105°C and 98–99°C, respectively). 1,3 and 1,4-Bis(4-fluorobenzoyl)benzene (m.p. 178–179°C and 215–217°C, respectively) were prepared as previously described<sup>33</sup>. Bis(4-fluorophenyl)phenyl phosphine oxide (m.p. 123°C) was prepared following a known procedure<sup>21</sup>. 4-Methoxyphenol (Aldrich Chemical Co.) was used as received. Sulfolane (Aldrich Chemical Co.) was vacuum distilled prior to use. *N,N*-Dimethylacetamide (DMAc) (Fluka Chemika) was used as received.

### Bis(4-methoxyphenoxy-4'-phenyl)phenylphosphine oxide

A mixture of bis(4-fluorophenyl)phenylphosphine oxide (36.02 g, 0.115 mol), 4-methoxyphenol (28.91 g, 0.233 mol), pulverized anhydrous potassium carbonate (40.00 g, 0.290 mol), DMAc (75 ml), and toluene (130 ml) was heated under a nitrogen atmosphere for 12 h at 150°C. Toluene was used as an azeotroping agent to remove the water generated. The toluene was removed and the temperature increased to and maintained at ~160°C for 36 h. The cooled reaction mixture was filtered and the crude product precipitated in distilled water to afford a tacky solid. The tacky solid was dissolved in ethanol, treated with activated charcoal, and the ethanol subsequently removed under vacuum to afford a viscous oil. The oil was dried under vacuum for 1.5 h at 180°C to afford 50.6 g (85% yield) of an opaque amorphous solid. No melting point was detected by differential scanning calorimetry (d.s.c.). The amorphous solid liquified at 60°C, as determined visually by Fisher-Johns. Analysis: calcd for C<sub>32</sub>H<sub>27</sub>O<sub>5</sub>P: C 73.56%; H 5.21%; P 5.93%; found: C 72.09%; H 5.31%; P 5.90%. Mass spectroscopy: (*m/e*) 520 (calcd molecular weight, 522.54 g mol<sup>-1</sup>).

### Bis(4-hydroxyphenoxy-4'-phenyl)phenylphosphine oxide

A mixture of bis(4-methoxyphenoxy-4'-phenyl)phenylphosphine oxide (12.3 g, 0.0235 mol), 48% hydrobromic acid (65 ml, 0.5745 mol), and glacial acetic acid (38 ml) was refluxed for 24 h. As the solution cooled to room temperature, the crude product precipitated as a tacky

solid. The hydrobromic acid/acetic acid mixture was decanted and the tacky solid stirred in distilled water at room temperature to afford a grey-white solid. The crude solid was washed several times in warm distilled water and dried under vacuum at room temperature to afford 11.6 g (~100% yield) of a grey-white solid. The solid was dissolved in acetone, treated with activated charcoal, and filtered. Hot distilled water was added until the solution became turbid. The mixture was allowed to cool with stirring to precipitate a solid. The product was recovered by filtration and dried under vacuum at 90°C to afford 9.95 g (86% yield) of a grey-white solid, m.p. (d.s.c.) 263°C (broad); (Fisher-Johns) 270°C (broad). Analysis: calcd for C<sub>30</sub>H<sub>23</sub>O<sub>5</sub>P: C 72.87%; H 4.69%; P 6.22%; found: C 72.43%; H 4.93%; P 6.16%.

### Polymers

Phenylphosphine oxide-containing poly(arylene ether)s (PAE-PPO)s were prepared by reacting stoichiometric quantities of the phenylphosphine oxide-containing bisphenol monomer with an activated aromatic difluoride in the presence of potassium carbonate in sulfolane or DMAc at ~19% solids. Toluene was used as an azeotroping agent to remove the water generated. The reaction mixtures were stirred at ~155°C (DMAc) or at ~200°C (sulfolane) under a nitrogen atmosphere. Most of the reaction mixtures became viscous after 1–4 h. The mixtures were diluted to ~13% solids and stirring was continued for an additional 1–3 h. The cooled reaction mixtures were precipitated in a water/acetic acid mixture (10/1), washed successively in hot water and methanol and subsequently dried at 120°C to afford the polymers in >95% yields.

### Films

DMAc 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 dried at 50, 100, 150°C for 0.5 h each and ~50°C above their respective glass transition temperatures (*T<sub>g</sub>*) for 1 h. Thin-film tensile properties were determined according to ASTM D882.

### Oxygen plasma asher exposure

Oxygen plasma exposures were performed on thin films (12.7 mm × 12.7 mm, ~25.4–76.2 μm thick) of the phenylphosphine oxide-containing polymers in a Tegal Plasmod Asher. The asher was operated at 66.6 Pa, 100 W of radio frequency, oxygen pressure of 20.7 kPa and a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>. Since the asher was not calibrated, a simultaneous exposure of Kapton<sup>®</sup>HN film was performed with the phenylphosphine oxide-containing polymers. The Kapton<sup>®</sup>HN film served as a standard, allowing direct comparison with the phenylphosphine oxide-containing polymer films. The samples were periodically removed, weighed, and replaced in the asher over a 23 h period, and the weight loss of the films was monitored as a function of exposure time. In order to assess the effect of periodic removal and exposure of the film samples to atmospheric conditions, one sample was exposed for a 23 h period prior to removal for weighing.

### 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<sup>-1</sup> in nitrogen at a flow rate of

$40 \text{ cm}^3 \text{ min}^{-1}$ . Char yields were determined by the amount (wt%) of material remaining at  $850^\circ\text{C}$ . Limiting oxygen indices (OI) were calculated following a known procedure<sup>34</sup> using the equation:

$$\text{OI} = 17.5 + 0.4\text{CR} \quad (1)$$

where CR is the char residue (wt%) at  $850^\circ\text{C}$  in nitrogen.

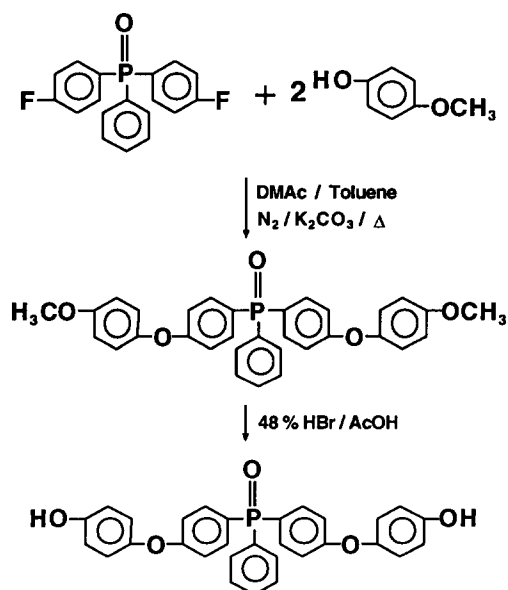
#### Other characterization

Inherent viscosities ( $\eta_{\text{inh}}$ ) were obtained on 0.5% solutions in DMAc at  $25^\circ\text{C}$ . Differential scanning calorimetry (d.s.c.) was conducted on a Shimadzu DSC-50 thermal analyser at a heating rate of  $10^\circ\text{C min}^{-1}$  with the melting point taken at the endothermic peak, and at a heating rate of  $20^\circ\text{C min}^{-1}$  with the  $T_g$  taken at the inflection point of the  $\Delta T$  versus temperature curve. T.g.a. were performed on a Seiko Model 200/220 instrument on powder samples at a heating rate of  $2.5^\circ\text{C min}^{-1}$  in air and nitrogen at a flow rate of  $15 \text{ cm}^3 \text{ min}^{-1}$ . Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

## RESULTS AND DISCUSSION

#### Monomer synthesis

Although a novel phenylphosphine oxide-containing bisphenol was initially prepared from bis(4-fluorophenyl)phenylphosphine oxide and excess hydroquinone, the yield was only 30%. A more efficient synthesis of the bis(4-hydroxyphenoxy-4'-phenyl)phenylphosphine oxide monomer was from bis(4-fluorophenyl)phenylphosphine oxide and 4-methoxyphenol (Scheme 1). The dimethoxy intermediate was easily prepared and obtained as an amorphous solid in  $\sim 85\%$  yield after purification. Attempts to obtain a narrow melting crystalline material proved unsuccessful, thus the compound was used as isolated. Demethylation of the dimethoxy compound by hydrobromic acid/acetic acid proceeded smoothly and afforded an 86% yield of a grey-white powder after recrystallization from aqueous acetone. The overall yield for this two-step synthesis was  $\sim 70\%$ . Even though the bis(4-hydroxyphenoxy-4'-phenyl)phenylphosphine oxide



Scheme 1

Table 1 Polymer characterization

X	Polymer	$\eta_{\text{inh}}^a$ ( $\text{dl g}^{-1}$ )	$T_g^b$ ( $^\circ\text{C}$ )	Temp. of 5% weight loss ( $^\circ\text{C}$ ) <sup>c</sup>	
				Air	N <sub>2</sub>
O	PPO-1	0.57	213	462	497
$\parallel$ P(C <sub>6</sub> H <sub>5</sub> )	PPO-2	0.75	207	447	480
SO <sub>2</sub>	PPO-3	0.64	187	468	511
CO					
	PPO-4	0.62	187	471	512
	PPO-5	0.90	177	467	503

<sup>a</sup> 0.5% (w/v) DMAc solutions at  $25^\circ\text{C}$

<sup>b</sup> D.s.c. at a heating rate of  $20^\circ\text{C min}^{-1}$

<sup>c</sup> T.g.a. on powdered samples at a heating rate of  $2.5^\circ\text{C min}^{-1}$

monomer exhibited a broad melting point, both visually and by d.s.c., the elemental analysis agreed well with the calculated values, and high molecular weight polymers were obtained as implied by the inherent viscosity data (Table 1).

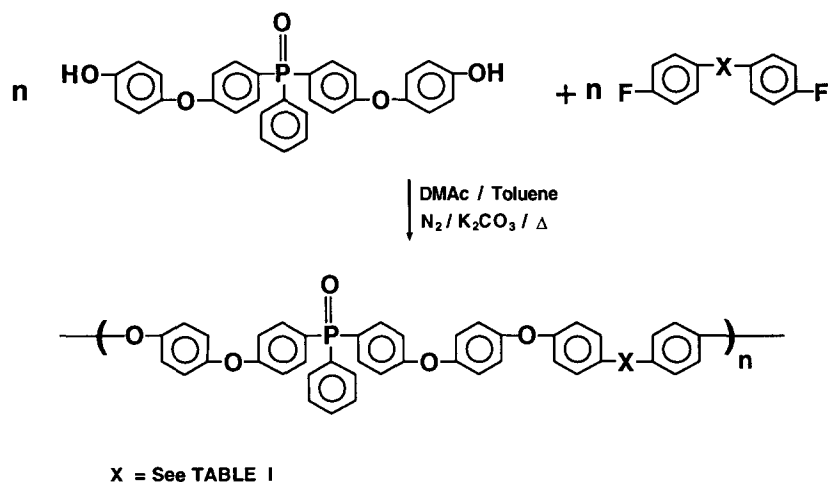
#### Polymer synthesis

High molecular weight PAE-PPOs were prepared from activated aromatic difluorides and the alkali metal bisphenolate of bis(4-hydroxyphenoxy-4'-phenyl)phenylphosphine oxide in DMAc or sulfolane under a nitrogen atmosphere (Scheme 2). The polymerizations generally proceeded rapidly and required dilution with additional solvent after 1–4 h, depending on the system, so as to maintain efficient stirring. The polymers were isolated in  $>95\%$  yields with no insoluble ('gel') material present. The inherent viscosities ranged from 0.57 to  $0.75 \text{ dl g}^{-1}$  and  $T_g$ s ranged from 177 to  $213^\circ\text{C}$  (Table 1). The trend for the  $T_g$ s was phenylphosphine oxide  $>$  sulfone  $>$  carbonyl  $>$  terephthaloyl  $>$  isophthaloyl. A similar trend has been observed for other PAEs<sup>32</sup> and PAEs containing heterocyclic groups<sup>35,36</sup>. As-isolated polymer powders exhibited no weight loss to  $300^\circ\text{C}$  by t.g.a., with 5% weight losses occurring at  $\sim 465^\circ\text{C}$  in air and  $\sim 500^\circ\text{C}$  in nitrogen (Table 1).

Thin films cast from DMAc were tough and transparent. The unoriented thin film properties at  $23^\circ\text{C}$  are presented in Table 2. The average tensile strength, tensile modulus, and percent elongation (break) were 11.0 ksi, 325 ksi and 95%, respectively. The tensile strength, tensile modulus, and percent elongation (break) for PPO-5 at  $121^\circ\text{C}$  were 6.9 ksi, 291 ksi and 145% (Table 2). These values are similar to other non-heterocyclic-containing PAEs<sup>33</sup>.

#### Calculated limiting oxygen index

Phosphorus incorporated in polymers, either as an additive or in the polymer backbone, is known to impart excellent flame resistance. Thus, it was of interest to



Scheme 2

determine the OI for several of the PAE-PPOs. The OI was calculated from equation (1). The char yields for unoriented thin PAE-PPO films ranged from 31 to 38% with calculated OI ranging from 0.30 to 0.33. As a comparison, the OI for polysulfone<sup>34</sup> is 0.30 and for PEEK<sup>®</sup><sup>37</sup> is 0.35. A material is considered fire resistant if the OI is >0.225 and self-extinguishing<sup>38</sup> if the OI is >0.27. The self-extinguishing characteristic of the PAE-PPOs has been observed for poly(arylene ether phosphine oxide)s evaluated in a qualitative flame test<sup>21</sup>. The OI trend for the PAE-PPO films was isophthaloyl > phenylphosphine oxide ≥ sulfone. The polymers containing the terephthaloyl and carbonyl groups were not tested. However, the OI and char yields would be expected to be similar to that of the isophthaloyl-containing PAE-PPO. The polymer PPO-1, containing the greatest amount of phosphorus by weight (~8 wt%), surprisingly did not exhibit the highest OI and char yield. The other PAE-PPOs contain ~4 wt% phosphorus.

#### Oxygen plasma resistance

Excellent resistance to AO and/or oxygen plasma environments has been observed for several polymers containing phosphorus in the form of phosphazene and phosphine oxide groups<sup>19–24</sup>. Upon exposure to these environments, the materials were reported to form a surface layer containing higher oxidized species of phosphorus, which subsequently protected the underlying material from further erosion. This surface layer was proposed to be composed of highly oxidized phosphate-type groups<sup>21</sup>.

Thus it was of interest to evaluate the oxygen plasma resistance of unoriented thin films of the PAE-PPOs. Since the asher was not calibrated, a simultaneous exposure of Kapton<sup>®</sup>HN film was performed with the PAE-PPOs. The Kapton<sup>®</sup>HN film served as a standard, allowing direct comparison with the PAE-PPOs. Exposures were performed for up to 23 h with the samples being periodically removed and weighed. The weight loss of the films was monitored as a function of exposure time. The weight loss rates for the PAE-PPOs were normalized to that of Kapton<sup>®</sup>HN film exhibiting the greatest weight loss rate (0.88 mg h<sup>-1</sup>) and are presented in Table 3. All of the PAE-PPOs exhibited excellent resistance (i.e. weight retention) to an oxygen plasma environment. The polymers generally exhibited a higher initial weight loss

Table 2 Unoriented thin film tensile properties at 23°C

Polymer	Strength (ksi) <sup>a</sup>	Modulus (ksi) <sup>a</sup>	Elongation (%)
PPO-1	10.8	370	109
PPO-2	8.1	277	42
PPO-3	9.8	275	96
PPO-4	11.1	287	96
PPO-5	10.9 (6.9) <sup>b</sup>	322 (291) <sup>b</sup>	79 (145) <sup>b</sup>

<sup>a</sup> To convert to MPa divide ksi by 0.145

<sup>b</sup> Film specimens tested at 121°C

Table 3 Oxygen plasma etching

Polymer	Weight loss rate (mg h <sup>-1</sup> )		
	0–2 h, exp. (normalized) <sup>a</sup>	2–23 h, exp. (normalized) <sup>a</sup>	Kapton <sup>®</sup> HN 0–23 h
PPO-1	0.11 (0.15)	0.026 (0.0352)	0.65
PPO-2	0.040 (0.048)	0.0022 (0.0027)	0.73
PPO-3	0.13 (0.13)	0.0065 (0.0065)	0.88
PPO-4	0.090 (0.10)	0.0086 (0.0098)	0.79
PPO-5	0.055 (0.068)	0.0078 (0.0097)	0.71

<sup>a</sup> Normalized values determined by adjusting to a Kapton<sup>®</sup> HN weight loss rate of 0.88 mg h<sup>-1</sup>

rate with a subsequent decrease in rate. In contrast, the Kapton<sup>®</sup>HN film exhibited a relatively constant weight loss rate (Figures 1 and 2). A similar type of behaviour was observed for poly(arylene ether phosphine oxide)s compared with Udel<sup>®</sup> (polysulfone), bisphenol A derived PEK, and Ultem<sup>®</sup> [poly(ether imide)]. In that study the surface recession was monitored with respect to exposure time instead of weight loss<sup>21</sup>.

In general, the PAE-PPOs exhibited two regions of differing weight loss rates. The first region of weight loss occurred during the initial 2 h of exposure to oxygen plasma. The weight loss rates of the PAE-PPO films ranged from 0.048 to 0.15 mg h<sup>-1</sup> as normalized to Kapton<sup>®</sup>HN, which had a weight loss rate of 0.88 mg h<sup>-1</sup>. The trend of decreasing weight loss rate was phenylphosphine oxide > carbonyl > terephthaloyl > isophthaloyl > sulfone. It was surprising that the polymer

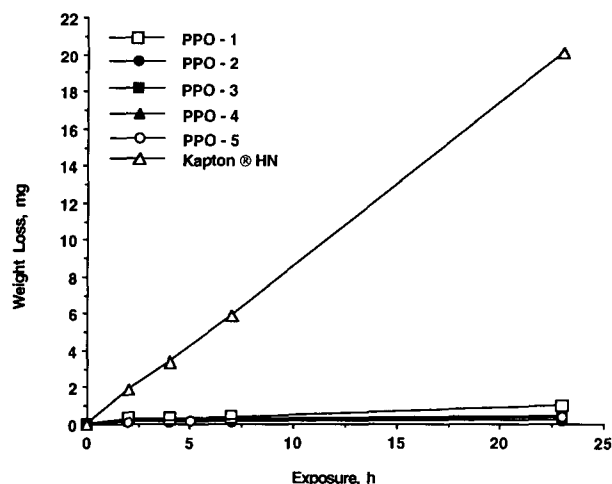


Figure 1 Weight loss versus exposure time: 0–23 h oxygen plasma exposure

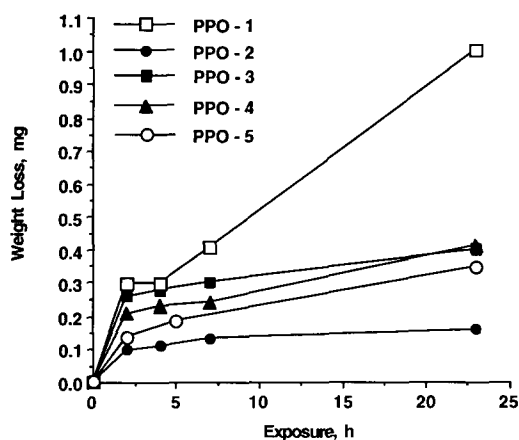


Figure 2 Weight loss versus exposure time: 0–23 h oxygen plasma exposure of PAE-PPOs

containing the greatest amount of phosphorus (PPO-1, ~8 wt%) exhibited the greatest weight loss rate during the initial 2 h of exposure ( $0.15 \text{ mg h}^{-1}$ ) as compared to other PAE-PPOs, which contain ~4–4.5 wt% phosphorus. This initial weight loss region (Figures 1 and 2) is presumably due to the formation of an inorganic phosphate-type surface layer which subsequently protects the underlying material and thereby reduces the weight loss rate. The inorganic phosphate-type surface layer has been shown to form on polyphosphazenes<sup>19,20</sup> and poly(arylene ether phosphine oxide)s<sup>21</sup> exposed to an oxygen plasma environment. A similar change in surface chemistry of the PAE-PPOs after exposure to oxygen plasma is presumed to occur based upon previous observations and X.p.s. analyses.

The second region of weight loss occurred from 2 to 23 h, with weight loss rates of the PAE-PPOs ranging from  $0.0027$  to  $0.0352 \text{ mg h}^{-1}$  as compared to the weight loss rate of  $0.88 \text{ mg h}^{-1}$  for Kapton®HN. As expected, the weight loss rates of the PAE-PPOs decreased in this region (2–23 h) as compared to that of the initial 0–2 h exposure. The trend of decreasing weight loss rate for this second region was phenylphosphine oxide > terephthaloyl > isophthaloyl > carbonyl > sulfone. After a non-measurable weight loss from 2 to 4 h exposure, polymer PPO-1 exhibited a third region of weight loss,

Table 4 X.p.s. analysis before and after oxygen plasma exposure of 23 h

Polymer	Photopeak	Binding energy (eV)		Atomic conc. (%)	
		Before	After	Before	After
PPO-2	C1s	285.0	285.0	74.1	55.3
	O1s	532.0	533.4	19.0	33.0
	S2p	168.1	168.5	0.9	0.7
	P2p	132.4	134.6	1.1	7.2
PPO-3	C1s	285.0	285.0	79.7	50.8
	O1s	532.8	533.8	14.6	37.3
	P2p	132.5	134.9	0.8	9.4

with a weight loss rate of  $0.037 \text{ mg h}^{-1}$  (4–23 h exposure time period).

In order to determine the effect of periodic sample removal and exposure to atmospheric conditions, polymer PPO-5 was exposed in the asher for a 23 h period prior to removal for weighing along with Kapton®HN. The weight loss rates of PPO-5 and Kapton®HN after the 23 h continuous exposure were  $0.0096$  and  $0.59 \text{ mg h}^{-1}$ , respectively. The normalized weight loss rate for PPO-5 was  $0.0144 \text{ mg h}^{-1}$ . Comparatively, the normalized weight loss rate for the step-wise exposed PPO-5 film from 0 to 23 h was  $0.0124 \text{ mg h}^{-1}$ . The ~15% difference in weight loss rates between the step-wise and continuous exposures can be attributed to the number of data points used to calculate the weight loss rates. The normalized weight loss rate for the step-wise exposed PPO-5 film using only the data point at 23 h was  $0.0151 \text{ mg h}^{-1}$ , which is in good agreement with the weight loss rate obtained for the continuous exposure.

#### X-ray photoelectron spectroscopic analysis

Thin films of PPO-2 (sulfone) and PPO-3 (carbonyl) were examined by X.p.s. before and after 23 h exposure to oxygen plasma (Table 4). All photopeaks were referenced to that of carbon having a maximum taken at 285.0 eV. Polymers not exposed to oxygen plasma had ~1% atomic concentration of phosphorus with a peak maximum at 132.4 eV and 14.6% (PPO-3) and 19.0% (PPO-2) atomic concentration of oxygen, with a peak maximum of 532.8 eV. After exposure to an oxygen plasma environment, the carbon content was found to have decreased while the oxygen and phosphorus contents increased. The exposed films exhibited ~2.3 eV increase in the binding energy of the phosphorus photopeak and ~0.8 eV increase in the binding energy of the oxygen photopeak, with a broadening of both photopeaks. Similar results have been obtained for poly(arylene ether phosphine oxide)s exposed to an oxygen plasma<sup>21</sup>. The shifts in the binding energy and the broadening of the photopeaks have been reported to be indicative of the formation of a higher oxidized phosphorus species (i.e. phosphate type)<sup>21</sup>. However, care should be exercised in the interpretation of both ground-based and space flight material exposure results, as observed changes in surface chemistry are likely to be influenced by exposure of the samples to atmospheric conditions prior to analysis.

#### DISCRETION

Weight loss data alone as a means of assessing material stability can be misleading, as materials which form

non-volatile oxides can exhibit weight gain. Other means of assessing material stability, such as surface erosion, have been used. In order to substantiate the results obtained using an asher, several of the PAE-PPOs will be exposed to the atomic oxygen environment in LEO on an upcoming space flight experiment.

The use of oxygen plasma ashers as tools to assess the stability of materials to atomic oxygen in LEO has been critiqued<sup>39,40</sup>. Although oxygen plasma ashers may be useful as screening devices for relative degradation of materials in that environment, the LEO environment is significantly different in several important respects, most notably oxygen atom flux and energy, and the presence of low/high energy particles, u.v./vacuum u.v. radiation and thermal cycling. These combined factors can dramatically increase the actual degradation process compared to that predicted by exposure to only one LEO environmental component. Thus it may not be reasonable to extrapolate material degradation data obtained from an oxygen plasma asher to predict behaviour in LEO.

## CONCLUSIONS

A novel phenylphosphine oxide-containing bisphenol was prepared and subsequently reacted with activated aromatic difluorides to prepare phenylphosphine oxide-containing poly(arylene ether)s. The polymers exhibited physical and mechanical properties which were comparable to other poly(arylene ether)s. Thin films of the phenylphosphine oxide-containing poly(arylene ether)s exposed to an oxygen plasma environment for up to 23 h had weight loss rates which were one to two orders of magnitude lower than that of Kapton<sup>®</sup>HN film.

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