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Oxygen plasma-resistant phenylphosphine oxide-containing polyimides and poly(arylene ether heterocycle)s: 1

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Phenylphosphine oxide-containing polyimides, poly(arylene ether 1,3,4-oxadiazole)s and poly(arylene ether benzimidazole)s were prepared and evaluated for resistance to an oxygen plasma. Thin films of the phenylphosphine oxide-containing polymers were exposed to a radiofrequency-generated oxygen plasma under vacuum along with Kapton® HN and polymers of similar chemical structure that did not contain the phenylphosphine oxide group. The stability of the materials to the oxygen plasma was assessed by monitoring the weight loss of the films as a function of exposure time. After 23 h oxygen plasma exposure the phenylphosphine oxide-containing polymers exhibited weight-loss rates that were 40 to 145 (1–2 orders of magnitude) times slower than that of Kapton® HN, whereas polymers of similar chemical structure that did not contain the phenylphosphine oxide group exhibited weight-loss rates about 1–3 times faster than that of Kapton® HN. The changes in surface chemistry of the exposed films were subsequently examined using X-ray photoelectron spectroscopy. 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, limiting oxygen indices were calculated from char yields at 850°C in nitrogen utilizing a known method. For the most part, the incorporation of the phenylphosphine oxide group did not substantially increase the limiting oxygen indices of these experimental polymers.

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

INTRODUCTION

The development of materials technology focused on improving environmental durability of light-weight materials for potential applications on spacecraft is an ongoing activity within the National Aeronautics and Space Administration (NASA). This activity is being driven by the design of future spacecraft with increased mission lifetimes (>10 years). The materials issue is complicated by the fact that the typical orbital environments, geosynchronous (GEO) and low Earth orbit (LEO), are quite different in their make-up and consequently the effects that they have on materials. Organic polymeric materials offer the advantage of being light-weight (low-density); however, their long-term environmental stability, particularly in LEO, is of concern. Atomic oxygen (AO) severely degrades most organic materials and can cause catastrophic erosion and mass loss in relatively short time periods[1–4]. This issue is of concern primarily in LEO, where AO is present in sufficient concentration and at sufficiently high energy levels to cause degradation. Certain perfluorinated polymers, such as copolytetrafluoroethylene, have exhibited good resistance to AO in both ground-based and space-flight exposure experiments. However, simultaneous exposure to AO and ultraviolet (u.v.) radiation dramatically increases the rate of degradation of this material[5,6]. Coatings of inorganic oxides such as aluminium oxide[7], silicon oxide[7], chromium oxide[8] and indium tin oxide[9] as well as decaborane[10] based coatings have been shown to protect organic materials from AO erosion. To provide maximum protection, the coatings need to be ~500–2000 Å thick, relatively uniform and defect-free. Although coatings have been used successfully to protect materials on spacecraft from AO, they possess some inherent shortcomings. The application of thin, uniform coatings to complex shapes can be difficult and quality control must be performed to assure the absence of pinholes and defects. Generally, the coatings are readily abraded, so care must be exercised during the fabrication of components. Presently there is concern that, on missions of long duration, impacts by micrometeoroids and debris that are prevalent in LEO will damage the protective coatings and expose the underlying material, which will subsequently be eroded by AO. Polymer materials with inherent AO resistance offer an added margin of safety. If desired, these materials could be coated for added AO protection; however, if the coating is imperfect or somehow damaged either in LEO or during fabrication, the exposed material would erode at a significantly slower rate as compared to the materials currently in use. Potential applications for polymer films on spacecraft include flexible solar array substrates and multi-layer thermal insulation blanket material.

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One method to improve the AO resistance of organic polymers has been to incorporate silicon into the material, which subsequently is converted to silicate/silicon oxide upon exposure to AO[11-18]. Similarly, the presence of phosphorus in polymers has also resulted in enhanced AO resistance, presumably by the formation of inorganic phosphate-type species upon exposure. Phosphorus-containing materials that have exhibited good AO resistance include polyphosphazenes[19,20] and phosphine oxide-containing poly(arylene ether)s[21,22]. As a continuation of our work on atomic oxygen-resistant (AOR) polymers, phosphine oxide-containing polyimides, poly(arylene ether 1,3,4-oxadiazole)s and poly(arylene ether benzimidazole)s were prepared and subsequently exposed to a radiofrequency-generated oxygen plasma under vacuum[23]. The weight-loss rates of thin films of these polymers were compared with those of Kapton^{R} HN polyimide film and polymers of similar chemical structure that do not contain the phenylphosphine oxide group.

EXPERIMENTAL

Polymers

The syntheses of the polymers evaluated in this study have been reported elsewhere. However, a detailed description is provided that is representative of each type of polymer.

Poly(arylene ether benzimidazole) (PAEBI), 3% stoichiometric offset and end-capped

Into a 5 litre three-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen gas inlet, thermometer, Dean–Stark trap and reflux condenser were placed 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole] (295.9 g, 0.707 mol), bis(4-fluorophenyl)phenylphosphine oxide (229.1 g, 0.729 mol), 2-(4-hydroxyphenyl)benzimidazole (9.196 g, 0.044 mol), pulverized anhydrous potassium carbonate (242 g, 1.75 mol), toluene (500 ml) and *N*-methyl-2-pyrrolidinone (NMP, 2.2 litre, 18.2% solids w/w). The water generated during the initial stage (phenolate formation) of the reaction was removed as an azeotrope with toluene. The reaction mixture was heated for ~4 h at 140–150°C and the water/toluene azeotrope was collected in the Dean–Stark trap. The toluene was subsequently removed from the reaction mixture via the Dean–Stark trap and the temperature was increased to 175–185°C. After ~5 h the solution had become extremely viscous and was diluted with hot NMP (1.4 litre, 12.0% solids). Heating was continued for an additional 2.5 h and subsequently stopped. To aid in the precipitation and work-up, the viscous solution was further diluted with NMP (1.5 litre). The polymer was precipitated in water/acetic acid (10/1) in a high-speed blender, washed successively in hot water and hot methanol and dried at 130°C in a forced air oven. The light tan powder, obtained in near-quantitative yield, exhibited a glass transition temperature (T_g) of 365°C. The inherent viscosity (η_{inh}) of a 0.5% solution in *N,N*-dimethylacetamide (DMAc) at 25°C was 0.77 dl g^{-1}. (For additional information see refs. 23 and 24.)

The poly(arylene ether benzimidazole) that contained 25 mol% phenylphosphine oxide was prepared as described above from 5,5′-bis[2-(4-hydroxyphenyl)benzimidazole], 1,3-bis(4-fluorobenzoyl)benzene (75 mol%), bis(4-fluorophenyl)phenylphosphine oxide (25 mol%) and 2-(4-hydroxyphenyl)benzimidazole in NMP at ~180°C. This polymer was prepared at a stoichiometric offset of 5 mol% and exhibited an η_{inh} of 0.90 dl g^{-1} (0.5% solution in DMAc at 25°C) and a T_g of 287°C.

Poly(arylene ether 1,3,4-oxadiazole)(PAEO)

Into a 500 ml three-necked round-bottomed flask equipped with a mechanical stirrer, thermometer, nitrogen gas inlet and reflux condenser were placed 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole (19.068 g, 0.075 mol), diphenylsulfone (200 g, 20% solids) and pulverized anhydrous potassium carbonate (23.9 g, 0.17 mol, 15% excess). The mixture was heated to ~180°C under nitrogen for ~0.5 h and 1,3-bis(4-fluorobenzoyl)benzene (24.167 g, 0.075 mol) was subsequently added. The temperature was increased to 210°C and maintained for 16 h under nitrogen. The viscous solution was cooled to ~175°C, diluted with NMP (150 ml) and precipitated into methanol/acetic acid mixture (20/1) in a high-speed blender. The polymer was washed successively in hot water and hot methanol and dried for 8 h at 120°C under vacuum to give 39.4 g (98%) of white fibrous polymer. The polymer exhibited a T_g of 182°C, a crystalline melting transition (T_m) of 265°C and an inherent viscosity (0.5% solution in *m*-cresol at 25°C) of 1.53 dl g^{-1}. (For additional information see ref. 25.)

Polyimide

Into a 100 ml three-necked round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet and drying tube ($CaCl_2$) were placed bis(4-aminophenoxy-4′-phenyl)phenylphosphine oxide (BAPPO, 3.2012 g, 0.0065 mol) and DMAc (20.0 ml). The mixture was stirred until the diamine dissolved and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, 2.0944 g, 0.0065 mol) was subsequently added and rinsed into the flask with DMAc (10.0 ml) to give a final concentration of 15% solids. The solution was stirred at room temperature under nitrogen overnight. The poly(amide acid) solution exhibited an inherent viscosity (0.5% solution in DMAc at 25°C) of 0.64 dl g^{-1}. The poly(amide acid) solution was used to cast a thin film, which was converted to the polyimide by heating for 1 h each at 100, 200 and 300°C in a forced air oven. The film exhibited a T_g of 258°C. (For additional information see ref. 26.)

Films

DMAc solutions of the PAEBIs or *m*-cresol solutions of the PAEOs (15–20% solids) 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 at up to ~50°C above their respective T_g for 1 h. Owing to the high T_g of PAEBI containing phenylphosphine oxide groups (365°C), those films were heated to 375°C for ~10 min. The poly(amide acid) films were cast from DMAc and thermally converted to the polyimide by heating for 1 h each at 100, 200 and 300°C in a forced air oven.

Oxygen plasma asher exposure

Oxygen plasma exposures were performed on thin films (0.5 inch × 0.5 inch, ~1–3 mil thick; approx. 13 mm × 13 mm and 25–75 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 monitored as a function of exposure time. In one case the exposure was performed for 88 h with periodic removal of the sample 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^{-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 indexes (OI) were calculated following a reported procedure[27] 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 were obtained on 0.5% solutions in DMAc (PAEBIs and poly(amide acid)s) or *m*-cresol (PAEOs) 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 and the crystalline melting temperature (T_m) taken at the minimum of the transition peak. X-ray photoelectron spectroscopic (X.p.s.) analyses were performed at Virginia Polytechnic Institute and State University.

RESULTS AND DISCUSSION

Polymer synthesis

Poly(arylene ether benzimidazole)s (PAEBIs) were prepared from 5,5'-bis[2-(4-hydroxyphenyl)benzimidazole] and bis(4-fluorophenyl)phenylphosphine oxide and end-capped with 2-(4-hydroxyphenyl)benzimidazole in NMP at ~180°C[23]. Phenylphosphine oxide-containing PAEBIs were prepared at stoichiometric offsets of 2 and 5 mol% using 2-(4-hydroxyphenyl)benzimidazole as the end-capper. In order to have polymers of similar chemical structure without phenylphosphine oxide groups, two molecular-weight-controlled and end-capped samples were prepared from 5,5'-bis[2-(4-hydroxyphenyl)benzimidazole], 1,3-bis(4-fluorobenzoyl)benzene and 2-(4-hydroxyphenyl)benzimidazole in DMAc at 160°C at stoichiometric offsets of 5 and 7 mol%[23,24]. In addition, a PAEBI containing 25 mol% phenylphosphine oxide was prepared from 5,5'-bis[2-(4-hydroxyphenyl)benzimidazole], bis(4-fluorophenyl)phenylphosphine oxide, 1,3-bis(4-fluorobenzoyl)benzene and 2-(4-hydroxyphenyl)benzimidazole in NMP at 180°C at a stoichiometric offset of 5 mol%.

Poly(arylene ether 1,3,4-oxadiazole)s (PAEOs) were prepared from 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole and bis(4-fluorophenyl)phenylphosphine oxide or 1,3-bis(4-fluorobenzoyl)benzene as previously reported[25]. These PAEOs were prepared at exact stoichiometry in diphenylsulfone at 210–280°C.

Polyimides were prepared from bis(4-aminophenoxy-4'-phenyl)phenylphosphine oxide (BAPPO) and both 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 3,3',4,4'-biphenylenetetracarboxylic dianhydride (BPDA) as previously reported[26]. These polyimides were prepared using exact stoichiometry. Imidization was achieved by heating a poly(amide acid) film for 1 h each at 100, 200 and 300°C in a forced air oven. The chemical structures of the polymers evaluated in this study are presented in *Figure 1*. Polymer characterization is presented in *Table 1*.

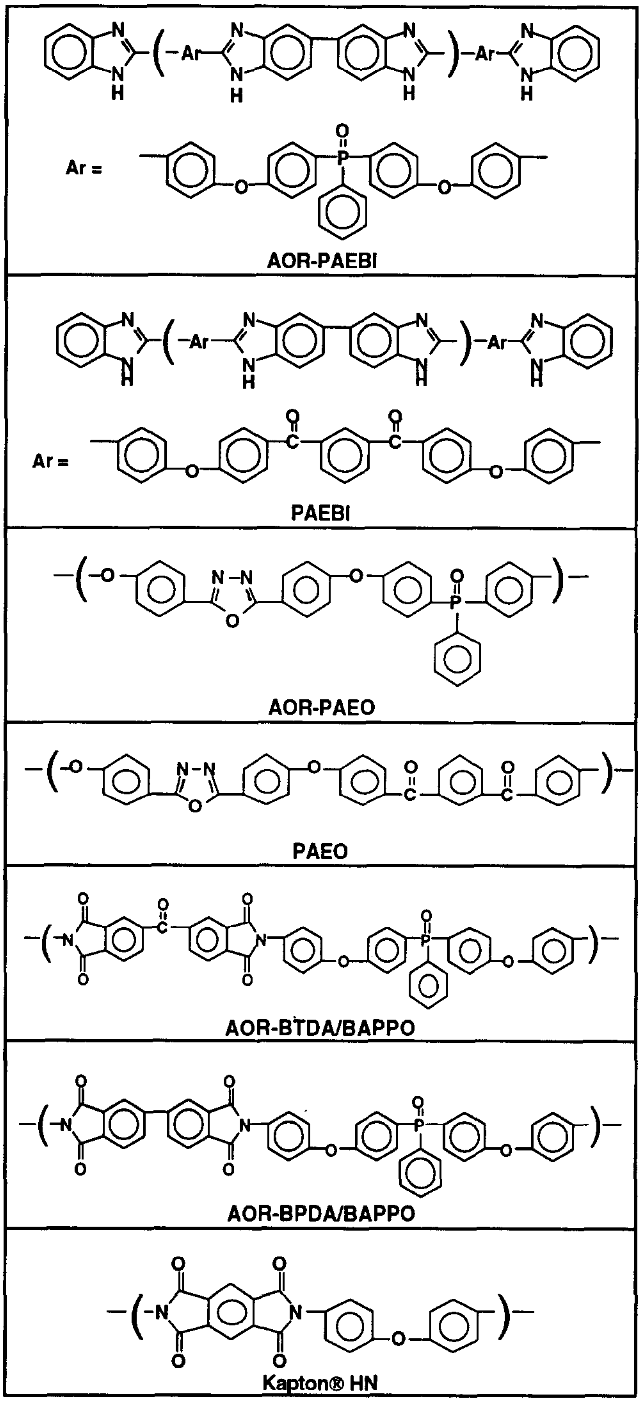

Figure 1 Chemical structures of polymers

Table 1 Polymer characterization

Polymer[a]	η_{inh} (dl g^{-1})	T_g (°C)	Char yield[b] (%)	Calculated *OI*
AOR-PAEBI-2%	0.91[c]	376	62.5	0.42
AOR-PAEBI-5%	0.41[c]	364	64.0	0.43
AOR-PAEBI-5% (75/25)	0.90[c]	287	–	–
PAEBI-5%	0.84[c]	269	–	–
PAEBI-7%	0.46[c]	265	71.8	0.46
AOR-PAEO	1.38[d]	242	40.5	0.34
PAEO	1.53[d]	182 (265)[e]	20.8	0.26
AOR-BPDA/BAPPO	0.64[f]	265	51.6	0.38
AOR-BTDA/BAPPO	0.43[f]	258	46.7	0.36
Kapton® HN			57.3	0.40

[a] Percent indicates stoichiometric offset
[b] Char yield at 850°C in N_2 by t.g.a., heating rate 40°C min^{-1}
[c] Inherent viscosity obtained on 0.5% solution in DMAc at 25°C
[d] Inherent viscosity obtained on 0.5% solution in *m*-cresol at 25°C
[e] Crystalline melting transition in parentheses
[f] Inherent viscosity obtained on 0.5% solution of poly(amide acid) in DMAc at 25°C

Table 2 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]
AOR-PAEBI-2%	0.23	0.24	0.010	0.011
AOR-PAEBI-5%	0.43	0.43	0.021	0.022
PAEBI-5%	1.73	1.77	1.44[b]	1.61[b]
PAEBI-7%	0.81	0.81	0.88[b]	0.95[b]
AOR-PAEBI (75/25)	0.48	0.65	0.37[b]	0.59[b]
AOR-PAEO	0.05	0.05	0.009	0.009
PAEO	1.84	2.18	2.09[b]	2.65[b]
AOR-BPDA/BAPPO	0.11	0.09	0.007	0.009
AOR-BTDA/BAPPO	0.21	0.25	0.013	0.018
AOR-PAEBI-2% (88 h exposure)	0.16	0.20	0.003	0.006

[a] Normalized to a Kapton® HN weight-loss rate of 0.85 mg h^{-1}
[b] Weight-loss rates determined on 0–6 h exposure times

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 experimental polymers. The *OI* was calculated from an established relationship[27]:

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

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* for the experimental polymers are presented in *Table 1*. The incorporation of phosphorus into the polymers gave mixed results with regard to improvement in *OI*. For example, PAEO exhibited a char yield of 20.8% and an *OI* of 0.26, whereas the phenylphosphine oxide-containing derivative (AOR-PAEO) exhibited a char yield of 40.5% and an *OI* of 0.34 (*Table 1*). Conversely, PAEBI-7% exhibited a char yield of 71.8% and an *OI* of 0.46, whereas the phenylphosphine oxide-containing derivative (AOR-PAEBI-5%) exhibited a char yield of 64% and an *OI* of 0.43 (*Table 1*). A material is considered flammable if the *OI* is less than 0.26. For comparative purposes, the *OI* for Udel® polysulfone is 0.30[27]. Kapton® HN exhibited a char yield of 57.3% and a calculated *OI* of 0.40 (*Table 1*).

Oxygen plasma resistance

Unoriented thin films of the various polymers were exposed to an oxygen plasma under vacuum. Since the asher was not calibrated, a simultaneous exposure of Kapton® HN film was performed with the experimental polymers. The Kapton® HN film serves as a standard allowing for relative comparison with the experimental polymers. Exposures were typically performed for up to 23 h with the samples being periodically removed and weighed. Generally, the polymers without phenylphosphine oxide groups began to disintegrate after ~6 h of exposure. In one case a phenylphosphine oxide-containing polymer was exposed for 88 h with periodic removal and weighing of the specimen. The weight losses of the films were monitored as a function of exposure time. The results are compiled in *Table 2* and represented graphically in *Figures 2, 3* and *4*. All of the phenylphosphine oxide-containing polymers exhibited excellent resistance

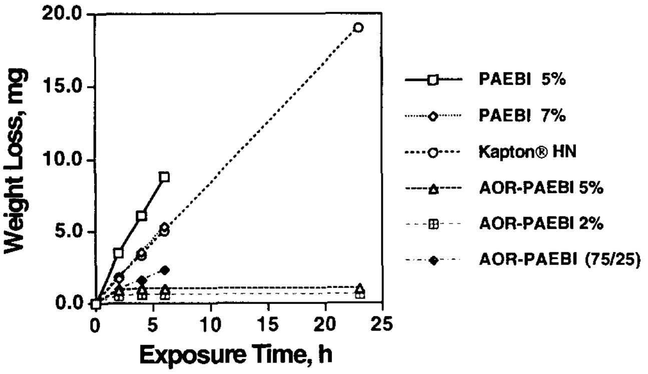

Figure 2 Weight loss *versus* exposure time in the oxygen plasma asher for the PAEBIs

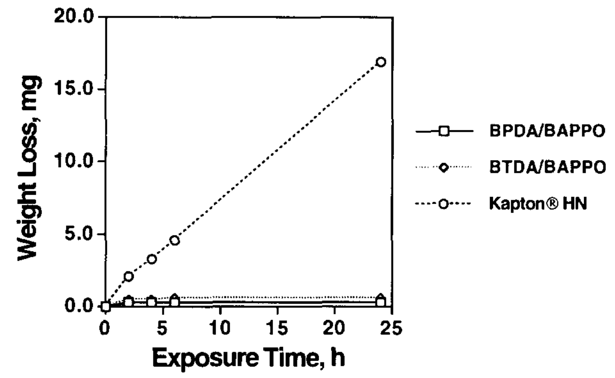

Figure 3 Weight loss *versus* exposure time in the oxygen plasma asher for the polyimides

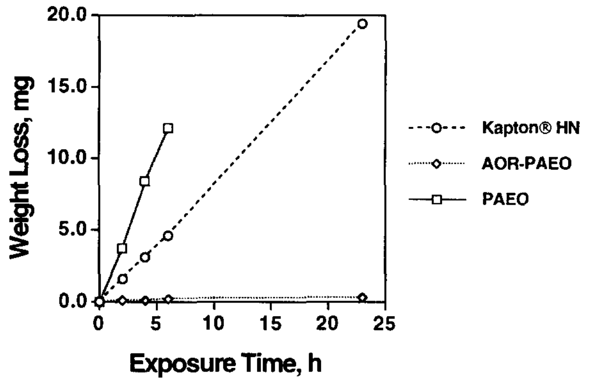

Figure 4 Weight loss *versus* exposure time in the oxygen plasma asher for the PAEOs

(i.e. weight retention) to the oxygen plasma. The phenylphosphine oxide-containing polymers exhibited nonlinear weight-loss rates. Typically, these polymers exhibited higher initial weight-loss rates with a subsequent decrease in rates after ~2 h of exposure. In general, the phenylphosphine oxide-containing polymers exhibited two distinct regions of differing weight-loss rates as indicated by the change in slope of the weight loss *versus* exposure time graphs (*Figures 2, 3* and *4*). The first region of weight loss occurred within the first 2 h of exposure to oxygen plasma with a subsequent decrease in weight-loss rates. In contrast, Kapton® HN and experimental polymers that do not contain the phenylphosphine oxide group exhibited relatively constant, linear weight-loss rates throughout the duration of the oxygen plasma exposure.

The second region of weight loss occurred from 2 to 23 h with weight-loss rates of the phenylphosphine oxide-containing polymers ranging from 0.0005 to 0.008 mg h^{-1} as compared to the weight-loss rate of 0.85 mg h^{-1} for Kapton® HN. The weight-loss rates of the phenylphosphine oxide-containing polymers decreased dramatically in this region (2–23 h) as compared to that of the initial 0–2 h exposure (*Table 2*). The phenylphosphine oxide-containing PAEBI with 25 mol% phenylphosphine oxide exhibited a relatively linear weight-loss rate over the 23 h exposure period (*Table 2*). This material exhibited a weight-loss rate of 0.59 mg h^{-1}, only slightly better than that of Kapton® HN (0.85 mg h^{-1}) but better than that predicted by a simple rule-of-mixtures relationship.

The weight-loss rates of the phenylphosphine oxide-containing films over the 0–23 h exposure period ranged from 0.006 to 0.022 mg h^{-1} as normalized to the Kapton® HN weight-loss rate of 0.85 mg h^{-1}, whereas polymers of similar chemical structure that do not contain the phenylphosphine oxide group exhibited weight-loss rates of 0.95–2.65 mg h^{-1} compared to the Kapton® HN weight-loss rate of 0.85 mg h^{-1}. Atomic-oxygen-resistant AOR-PAEBI-2% film was exposed for 88 h and exhibited a weight-loss rate of 0.006 mg h^{-1} (Kapton® HN 0.85 mg h^{-1}). This result is somewhat better than that exhibited by an identical specimen of AOR-PAEBI-2% exposed for only 23 h (0.011 mg h^{-1}). After 2 h of exposure the weight-loss rate decreases so that, the longer the exposure, the lower the overall weight loss rate. Presumably this change in weight-loss rate is due to formation of a higher oxidized phosphate-type surface layer upon exposure, which is resistant to the oxygen plasma. An inorganic phosphate-type surface layer has been shown to form on certain polyphosphanes[19,20] and poly(arylene ether phosphine oxide)s[21,22] exposed to oxygen plasma. A similar change in surface chemistry of he 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[22].

The use of oxygen plasma ashers to assess the stability of materials to atomic oxygen in LEO has been reviewed[28,29]. The LEO environment is not accurately simulated by an oxygen plasma asher. Conditions such as oxygen flux and energy level, high-energy particles, ultraviolet radiation and thermal cycling need to be addressed to assess material stability in LEO. However, the asher is useful for determining relative stabilities of materials to the oxygen plasma and thereby aids in determining structure–property relationships in polymers.

X-ray photoelectron spectroscopic analysis

To determine changes in oxidation states of the surface atoms, thin films of several of the experimental phenylphosphine oxide-containing polymers were analysed by X.p.s. before and after exposure. All photopeaks were

Table 3 X.p.s. analyses

		Binding energy (eV)		Atomic concentration (%)		
Polymer	Photopeak	Before	After	Before	After	Theory
AOR-PAEBI-2%	C 1s	285.0	285.0	74.3	52.9	72.3
	O 1s	532.2	533.2	17.6	35.6	6.9
	N 1s	399.9	401.3	5.6	3.1	8.1
	P 2p	132.6	134.6	1.2	8.4	4.5
AOR-PAEO	C 1s	285.0	285.0	76.0	66.6	72.7
	O 1s	532.8	533.2	17.6	23.3	12.1
	N 1s	399.7	400.0	1.0	4.9	5.3
	P 2p	132.6	134.6	3.7	4.6	5.9
AOR-BPDA/BAPPO	C 1s	285.0	285.0	73.9	52.9	73.6
	O 1s	532.5	533.2	18.0	35.6	14.5
	N 1s	400.3	401.3	2.5	3.0	3.7
	P 2p	132.5	134.6	0.7	8.4	4.1

referenced to that of carbon having a maximum taken at 285.0 eV. The following polymers were examined by X.p.s.: AOR-BPDA/BAPPO, AOR-PAEBI-2% and AOR-PAEO. The AOR-BPDA/BAPPO and AOR-PAEBI control (unexposed) samples exhibited < 1% of phosphorus whereas the AOR-PAEO control exhibited 3.7%. These materials have theoretical amounts of phosphorus ranging from 4.0 to 6.0%. The control samples typically exhibited an oxygen photopeak around 532 eV and a phosphorus photopeak centred near 132.5 eV. After exposure to the oxygen plasma the binding energies exhibited an increase to ~533 eV for oxygen and 134.6 eV for phosphorus with a broadening of both photopeaks. In addition, the concentration of phosphorus and oxygen increased while that of carbon decreased. The X.p.s. results are presented in *Table 3*. Generally, the exposed films exhibited ~2.0 eV increase in the binding energy of the phosphorus photopeak and ~1.0 eV increase in the binding energy of the oxygen photopeak. In addition, the ratio of oxygen to phosphorus after exposure ranged from 4:1 to 5:1. Similar results have been obtained for poly(arylene ether phosphine oxide)s exposed to an oxygen plasma[21,22]. 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)[21,22].

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[30]. 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 heterocyclic polymers exhibited significantly better weight retention after exposure to an oxygen plasma compared to Kapton® HN and polymers of similar chemical structure that did not contain the phenylphosphine oxide group. The phenylphosphine oxide-containing polymers 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 up to 88 h exposure time ranged from one to two orders of magnitude less than that of Kapton® HN.

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REFERENCES

1 Peters, P. N., Linton, R. C. and Miller, E. R. *J. Geophys. Res. Lett.* 1983, **10**, 569

2 Bowles, D. E. and Tenney, D. R. *Sampe J.* 1987, **23**(3), 49

3 Slemp, W. S., Santos-Mason, B., Sykes, G. F. Jr and Witte, W. G. Jr, AO Effect Measurements for Shuttle Missions STS-8 and 41-G, 1985, Vol. 1, Sec. 5, p. 1

4 LDEF—69 Months in Space. First Post Retrieval Symp., NASA Conf. Publ. 3134, Part 2 (Ed. A. Levine), 1991

5 Leger, L., Visentine, J. and Santos-Mason, B. *Sampe Q.* 1987, **18**(2), 48

6 Stiegman, A. E., Brinza, D. E., Anderson, M. S., Minton, T. K., Laue, G. E. and Liang, R. H. Jet Propulsion Laboratory Publ. 91-10, May 1991

7 Banks, B. A., Mistich, M. J., Rutledge, S. K. and Nahra, H. K. Proc. 18th IEEE Photovoltaic Specialists Conf., 1985

8 Leger, L. J., Spikes, I. K., Kuminecz, J. F., Ballentine, T. J. and Visentine, J. T. STS Flight 5, LEO Effects Experiment, AIAA-83-2631-CP, 1983

9 Smith, K. A. Evaluation of Oxygen Interactions with Materials (EOIM), STS-8 AO Effects, AIAA-85-7021, 1985

10 Packrisamy, S., Schwam, D. and Litt, M. *Polym. Prepr.* 1993, **34**(2), 197

11 Visentine, J. T., Leger, L. J., Kuminecz, J. F. and Spiker, I. K. AIAA-85-0415, AIAA 23rd Aerospace Conf., 1985

12 Arnold, C. A., Summers, J. D., Chen, Y. P., Bott, R. H., Chen, D. H. and McGrath, J. E. *Polymer* 1989, **30**(6), 986

13 Arnold, C. A., Summers, J. D., Chen, Y. P., Yoon, T. H., McGrath, B. E., Chen, D. and McGrath, J. E. in 'Polyimides: Materials, Chemistry and Characterization' (Ed. C. Feger), Elsevier Science, Amsterdam, 1989, pp. 69–89

14 Arnold, C. A., Chen, D. H., Chen, Y. P., Waldbauer, R. O., Jr Rogers, M. E. and McGrath, J. E. *High Perf. Polym.* 1990, **2**(2), 83

15 Connell, J. W., Working, D. C., St Clair, T. L. and Hergenrother, P. M. in 'Polyimides: Materials, Chemistry and Characterization' (Ed. C. Feger), Technomic, Lancaster, PA, 1992, pp. 152–164

16 Connell, J. W., Smith, J. G. Jr and Hergenrother, P. M. *J. Fire Sci.* 1993, **11**(2), 137

17 Young, P. R. and Slemp, W. S. LDEF Materials Workshop '91, NASA Conf. Publ. 3162, Part 1, 1991 pp. 376–378

18 Kulig, J., Jefferis, G. and Litt, M. *Polym. Mater. Sci. Eng.* 1989, **61**, 219

19 Fewell, L. L. *J. Appl. Polym. Sci.* 1990, **41**, 391

20 Fewell, L. L. and Finney, L. *Polymer* 1991, **32**(13), 393

21 Smith, C. D., Grubbs, H., Webster, H. F., Gungor, A., Wightman, J. P. and McGrath, J. E. *High Perf. Polym.* 1991, **3**(4), 211

22 Smith, J. G. Jr, Connell, J. W. and Hergenrother, P. M. *Polym. Prepr.* 1992, **33**(2), 241; *Polymer* 1994, **35**(13), 2834

23 Connell, J. W., Smith, J. G. Jr and Hergenrother, P. M. *Polym. Prepr.* 1993, **34**(1), 525

24 Hergenrother, P. M., Smith, J. G. Jr and Connell, J. W. *Polymer* 1993, **34**(4), 856

25 Connell, J. W., Hergenrother, P. M. and Wolf, P. *Polym. Mater. Sci. Eng. Proc.* 1990, **63**, 366; *Polymer* 1992, **33**(16), 3507

26 Hergenrother, P. M. and Havens, S. J. *J. Polym. Sci, Polym. Chem. Edn.* 1989, **27**, 1161; US Patent 5145937 (NASA), 1992

27 van Krevelen, D. W. *Polymer* 1975, **16**(8), 615

28 Koonz, S. L., Albyn, K. and Leger, L. J. *J. Spacecraft* 1991, **28**(3), 315 (May–June)

29 Banks, B. A., Rutledge, S. K., deGroh, K. K., Stidham, C. R., Gebauer, L. and LaMoreaux, C. M. Int. Conf. On Plasma Synthesis and Processing Materials Proc., 1993

30 Golub, M. A., Wydeven, T. and Cormia, R. D. *Polym. Commun.* 1988, **29**, 285