

AO-resistant Properties of Polyimide Fibers Containing Phosphorous Groups in Main Chains^{*}

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Abstract A series of polyimide fibers containing phosphorus element derived from (3-aminophenyl) methyl phosphine oxide (DAMPO) diamine was exposed to an artificial atomic oxygen environment which simulated the space environment in low earth orbit (LEO). The mass loss, surface morphology, chemical composition, and mechanical properties of the fibers before and after atomic oxygen (AO) exposure were compared in detail with a blank sample. Results showed that the phosphor-containing fibers demonstrated lower mass change and less tensile strength reduction. SEM results showed that the fibers with phosphorous element had relatively dense surface after AO exposure. Meanwhile, XPS results indicated that a passivated phosphate layer, which could protect the following under-layer from attacking by AO, was formed on the surface of the fibers. These results indicated that the incorporation of diamine (DAMPO) into the main chains could protect the fibers for avoiding further erosion from AO exposure. Hence, the phosphor-containing PI fibers exhibits potential application in space fields.

Keywords: Atomic oxygen; Phosphorous; Polyimide Fibers; LEO environment.

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INTRODUCTION

Aromatic polyimides (PIs) have been widely used in the spacecraft and the air engine industries owing to their excellent thermal and mechanical properties^[1]. They serve as the matrix resins, membranes, and fibers that are applied in satellites, solar cells, and many other areas. Unfortunately, the PI-based materials have serious problems when used in the low earth orbit (LEO) environment (between 200–1000 km in altitude), where the materials are exposed to a dynamic mixture of different factors, such as charged particles, vacuum, micrometeoroids, radiation, temperature extremes, and man-made debris. Among them, atomic oxygen (AO) is considered as an crucial factor because it can seriously erode many materials commonly employed for spacecraft, which have been improved by the related reports^[2]. Generally, AO is formed by the photo dissociation of diatomic oxygen that is broken by short wavelength (< 243 nm) solar radiation with sufficient

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energy. Oxygen atom have a highly corrosive property once combined with the materials they mostly encounter. Furthermore, a spacecraft's orbital velocity of 7.8 km/s can expose itself to a stream of AO at an energy of approximately 5 eV. The erosion on surfaces, loss in mass, decrease in mechanical, thermal and optical properties, and changes in chemical compositions occur by the collision of AO. Hence, finding effective approaches to enhance the AO resistance of PIs for its application is a necessary research task.

There are three approaches to improve the AO resistance of the PI materials. First, inorganic surface coatings, including silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), aluminum (Al), copper, silver, are typically employed to protect the PI materials from AO erosion^[3]. However, this method requires precise instruments and there are many limitations on the shape and size of materials. Apart from these, the different thermal expansion coefficients between the substrate and the inorganic coating in continuous thermal cycling for LEO environment is another problem in this field. The second approach is the addition of inorganic fillers into the PI matrix. However, the dispersion and phase separation restrict the application of this method. Recently, a new concept of "self-healing", *i.e.*, incorporation of P (phosphor) or Si element component into the PI molecular structures, has been reported^[4]. This method is an intrinsic resistance to AO. Connell reported that the phenylphosphine oxide-containing polymers had a low weight loss with AO erosion, as less as 1% by weight^[5]. Meanwhile, the solar absorbance and solar emittance almost did not change^[6]. Timothy K. Minton reported that a POSS modified polyimide showed a perfect performance in AO resistance with as little as 1% erosion yield of Kapton^[7]. Zhang *et al.* reported that a PI/Si hybrid film had a good AO-resistant ability^[8]. Here, an inert inorganic oxide layer is formed on the surface of the materials through AO erosion. This method showed efficient protection effect on the PIs from further erosion by AO.

Recently, PI fibers as a part of high performance fiber, have been widely used in aerospace field, such as the antenna protection, the tension rope and the protective fabrics. However, the PI fibers also suffer the AO erosion when applied in LEO environment. Therefore, study on the materials with enhanced AO-resistance properties are very meaningful for the aerospace application. Due to the varieties and simple synthesis of the phosphorous-containing monomers, the phosphorous-containing PIs received much concern. Many polymers with phenyl phosphine oxide (PPO) groups were prepared as reported by Connell^[5, 9–12], which showed that the PPO groups could improve the AO-resistant for the PI materials. Furthermore, silicones^[13] can release vacuum condensable contaminants and cause the composite materials crack upon AO exposure. Consequently, in the current work, the PPO groups were introduced into the PI molecular structure and the novel PI fibers containing phosphorous groups were firstly prepared *via* a dry jet-wet spinning process. The AO-resistant properties of these fibers were systematically investigated, which provided valuable information for their application in the aerospace field.

EXPERIMENTAL

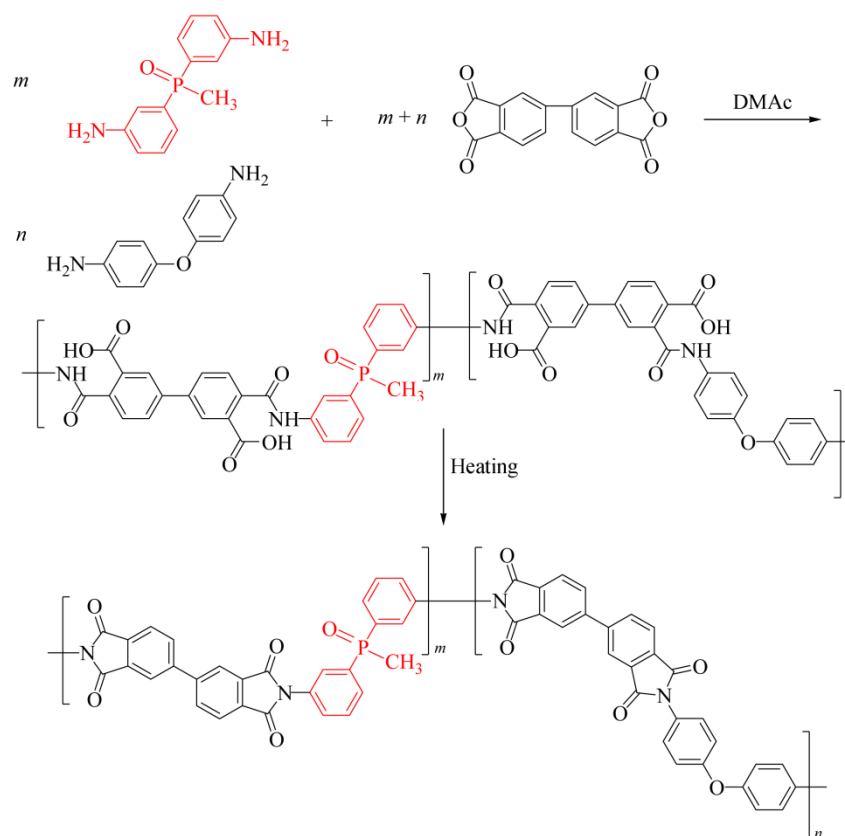
Materials

N,N'-dimethylacetamide (DMAc, analytical pure, $\geq 99.5\%$) was purchased from Tianjin Fine Chemical Co., Ltd. (Tianjin, China) and used as received. 4,4'-Oxydianiline (4,4'-ODA, $> 99.5\%$) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA) were purchased from Shanghai Research Institute of Synthetic Resins. *s*-BPDA was dried overnight in vacuum at 160 °C prior to use. Bis(3-aminophenyl) methyl phosphine oxide (DAMPO) was synthesized in our previous report^[14]. All the other solvents were used without further purification.

Preparation of the PI Fibers

The P-containing PI fibers were prepared by the polycondensation of DAMPO and ODA with equimolar dianhydride *s*-BPDA *via* a conventional two-step procedure^[15, 16], as shown in Scheme 1. The molar ratio of DAMPO/ODA varied from 0/10 to 6/4 with an increment of 20%. The polyamic acid (PAA) fibers were produced through the dry jet-wet spinning process (presented in Fig. S1 in supporting information, SI), corresponding to the two-step procedure. The PI fibers with PPO groups were obtained from PAA fibers by thermal imidization and heat drawing. Take PI-2 (DAMPO:ODA = 2:8 as molar ratio) as an example, to a

solution of 59.10 g (0.24 mol) DAMPO and 192.23 g (0.96 mol) ODA in DMAc, 353.06 g (1.20 mol) of *s*-BPDA was added in the equal stoichiometry. The solution was stirred at room temperature under N₂ for 48 h to obtain a viscous PAA solution. The PAA fibers were prepared from PAA solutions through the dry jet-wet spinning process, then were converted into the PI fibers by thermal imidization. The heat drawing of PI fibers was carried out. Other fibers (PI-0, PI-4, and PI-6) were also synthesized by the same method described above. The gel was formed when the molar ratio of DAMPO/ODA was higher than 6/4.



Scheme 1 A conventional two-step procedure for preparing the PI fibers

Atomic Oxygen Exposed Testing

AO exposure experiment was performed at Beihang University in a ground-based AO effects simulation facility, which was a type of Filament Discharging Plasma-type Atomic Oxygen (FDPAO) Simulation Facility) simulation facility, in which working air pressure was set to 0.15 Pa, discharge voltage was set to 118 V, and discharge current was set to 400 mA in the vacuum chamber), as shown in Fig. S2 (in SI). The oxygen was formed through the collision ionization and dissociation of oxygen molecules by electrons. The main components of the plasma were O₂, O₂⁺, O, O⁺, and e. The exposure conditions of the PI fibers are presented in Table 1.

Table 1. AO exposure conditions

Medial AO flux (atoms/(cm ² ·s))	Time (h)	Total fluence (atoms/cm ²)
AO fluence (atoms/cm ²)	0.5	2.08 × 10 ¹⁹
	1	2.92 × 10 ¹⁹
	2	5.33 × 10 ¹⁹
	4	9.29 × 10 ¹⁹
	6	1.46 × 10 ²⁰
Vaccum (Pa)	~0.15	

All the PI fibers with a length of 20 cm were placed on the platform for exposure to AO stream. Generally, the commercial Kapton film is used as a standard material for the estimation of AO flux. In this study, the Kapton films were cut into 2 cm × 2 cm pieces and randomly placed on the platform to obtain the average AO fluence. All the samples were weighted after exposure for 0.5, 1, 2, 4, and 6 h, respectively. The AO fluence was calculated from the mass loss of Kapton by the formula (1).

$$F = \Delta M / (\rho AE) \quad (1)$$

where F is the total AO fluence (atoms/cm²), ΔM is the mass loss of Kapton (g), and ρ is the density of Kapton (1.42 g/cm³). In addition, A is the exposure area of Kapton (4 cm²), and E is the erosion constant of Kapton (3×10^{-24} cm³/atom). The AO stream in the vacuum chamber was nearly uniform in our experiment. A single filament fiber was mounted on a paper holder. A schematic drawing of the sample fiber and its paper holder is illustrated in Fig. S3 (in SI). AO exposure fluences were controlled at 2.08×10^{19} , 2.92×10^{19} , 5.33×10^{19} , 9.29×10^{19} , and 1.46×10^{20} atoms/cm² at room temperature.

Measurements

The inherent viscosities of the PAA solutions were measured with an Ubbelohde viscometer at 30 °C in DMAc. FTIR spectra (KBr) were recorded on a VERTEX 70 spectrometer. The measurement of mechanical properties was carried out on the XQ-1 instrument with ASTM standards (D3379-75, edition 1987) at a drawing rate of 20 mm/min. Over 10 monofilaments for one sample were tested, and the average data were used to characterize the mechanical properties of the sample. The surface morphology and the aggregate structure of the fibers before and after AO exposure were observed through a field-emission environmental SEM (Micro FEI Philips XL-30-ESEM-FEG) operating at 15 kV. X-ray photoelectron spectra (XPS) were recorded on ESCALAB 250Xi with monochromatic Al K α X-ray source to analyze the element component and valence variation of the fibers before and after AO exposure. To eliminate charge effects, the XPS spectra were referenced with respect to the 284.8 eV carbon 1s level observed from the contaminated hydrocarbon to eliminate charge effects. The survey spectra were acquired over the binding energy range of 0–1200 eV. High-resolution region spectra were acquired for the C 1s, O 1s, N 1s, and P 2p photoelectron peaks. The peaks were then fitted using XPS software Avantage incorporated as described in NIST XPS database (<http://srdata.nist.gov/xps/Default.aspx>).

RESULTS AND DISCUSSION

Structure Characterization of the PI Fibers

All the PI fibers containing PPO groups were prepared from DAMPO, commercially available diamine (ODA) and dianhydride (*s*-BPDA) through the conventional two-step procedure. The polymerization was carried out by stoichiometric amounts of diamine and dianhydride at a concentration of 15% (solids) in DMAc. The chemical structure of PI fibers was characterized by FTIR spectra (Fig. 1) and elemental analysis. The absorption bands at 1712, 1652 and 1530 cm⁻¹ are corresponded to the absorption^[17] of C=O(COOH), C=O(CONH), and C—NH in the PAA fibers, respectively, as shown in Fig. 1(a). The bands at 1774 and 1710 cm⁻¹ are related to the C=O of aromatic dianhydride asymmetrical stretching, the peak at 1360 cm⁻¹ is attributed to the C—N stretching vibration of imide ring, and the peak at 734 cm⁻¹ is proven by the appearance of imide ring bending as shown in Fig. 1(b). The results indicated that the PI fibers containing PPO groups were successfully prepared. In addition, the elemental analysis results agreed with the calculated values for the proposed structures as presented in Table 2.

Mass Loss

The mass loss of the samples are shown in Table 3. The Kapton® film is used as a standard. The mass loss as a function of AO fluence is shown in Fig. S4 (in SI). The amounts of phosphorous compositions by weight were 0%, 1.32%, 2.60%, and 3.82% for PI-0, PI-2, PI-4, and PI-6, respectively. When the AO fluence was 2.08×10^{19} atoms/cm², the mass loss of PI-0, PI-2, PI-4, and PI-6 were 0.076, 0.074, 0.077, and 0.079 mg/cm², respectively. Compared with that of Kapton film, at an AO fluence of 1.46×10^{20} atoms/cm², the mass loss of PI-0, PI-2, PI-4,

and PI-6 were 88.6%, 81.6%, 72.0%, and 48.7%, respectively. As the AO fluence increase, the weight loss increased, especially for Kapton, PI-0, PI-2, and PI-4. Meanwhile, as shown in Fig. S5 (in SI), increasing the DAMPO content in the polymer resulted in the decrease of mass loss, particularly at a high AO fluence, where PI-6 exhibited better AO resistance. The AO-resistant property of the as-prepared fibers were equivalent to the phosphorous-containing copolyimides derived from bis[4-(3-aminophenoxy)phenyl] phenylphosphine oxide^[18], and better than those of the polyimide/containing-silicon hybrid thin films^[8]. Most of all, the ability of AO resistance was improved effectively owing to the introduction of the PPO groups into the polymer chains.

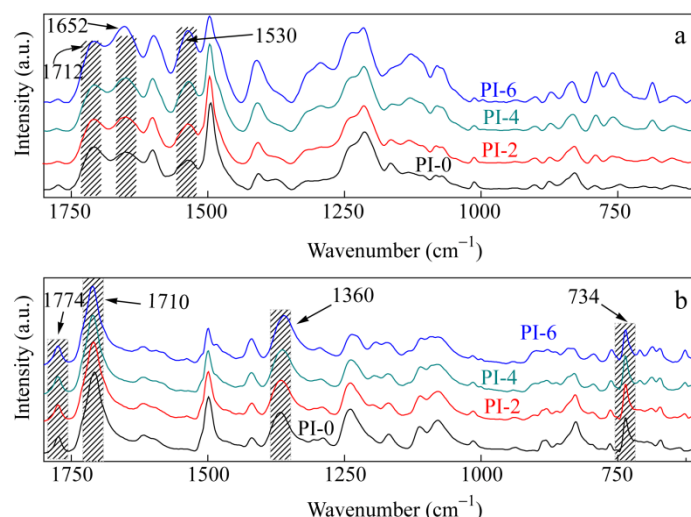


Fig. 1 FTIR spectra of the PAA (a) and PI (b) fibers

Table 2. Elemental analysis of the PI fibers

PI fibers No.	Inherent viscosity ^a (dL/g)	Repeating unit	Elemental analysis (%)			
				C	H	N
PI-0	1.77	$C_{28}H_{14}N_2O_5$	Calcd	73.36	3.08	6.11
			Found	73.17	3.02	5.98
PI-2	1.68	$C_{282}H_{146}N_{20}O_{50}P_2$	Calcd	72.43	3.15	5.99
			Found	72.61	3.25	5.93
PI-4	1.50	$C_{284}H_{152}N_{20}O_{50}P_4$	Calcd	71.54	3.21	5.88
			Found	71.45	3.28	5.72
PI-6	1.27	$C_{286}H_{158}N_{20}O_{50}P_6$	Calcd	70.68	3.28	5.76
			Found	70.50	3.24	5.60

^a The inherent viscosity is about PAA solution.

Table 3. Mass loss of the PI fibers versus AO exposure time

Films (Fibers) No.	Diamines ratio (m:n)	SEM sample No.	η_{inh} (dL/g)	Mass loss ^a 2.08×10^{19} atoms/cm ² (mg/cm ²)	Mass loss 2.92×10^{19} atoms/cm ² (mg/cm ²)	Mass loss 5.33×10^{19} atoms/cm ² (mg/cm ²)	Mass loss 9.29×10^{19} atoms/cm ² (mg/cm ²)	Mass loss 1.46×10^{20} atoms/cm ² (mg/cm ²)
Kapton	—		1.80	0.088	0.123	0.224	0.390	0.615
PI-0	0:10	0a-0d	1.77	0.076	0.120	0.189	0.366	0.545
PI-2	2:8	2a-0d	1.68	0.074	0.109	0.160	0.294	0.502
PI-4	4:6	4a-4d	1.50	0.077	0.100	0.154	0.278	0.443
PI-6	6:4	6a-6d	1.27	0.079	0.090	0.140	0.230	0.300

^a Using formula (1) to calculate the total AO fluence with Kapton® film in this Table;

^b The Number represented both of the fibers and the films with the same chemical structure.

Surface Morphologies

Figure 2 shows the surface morphologies of the fibers observed by SEM. Before AO exposure, the surfaces of the fibers were smooth and flat. When the AO fluence increased to 5.33×10^{19} and 1.46×10^{20} atoms/cm², the surfaces became very rough, as shown in Figs. 2(0c–6c) and 2(0d–6d), respectively. However, the diameter of the fibers almost kept constant (about 16 μ m). Furthermore, increasing DAMPO content resulted in a dense surface even at high AO fluence (Fig. 2, PI-6d).

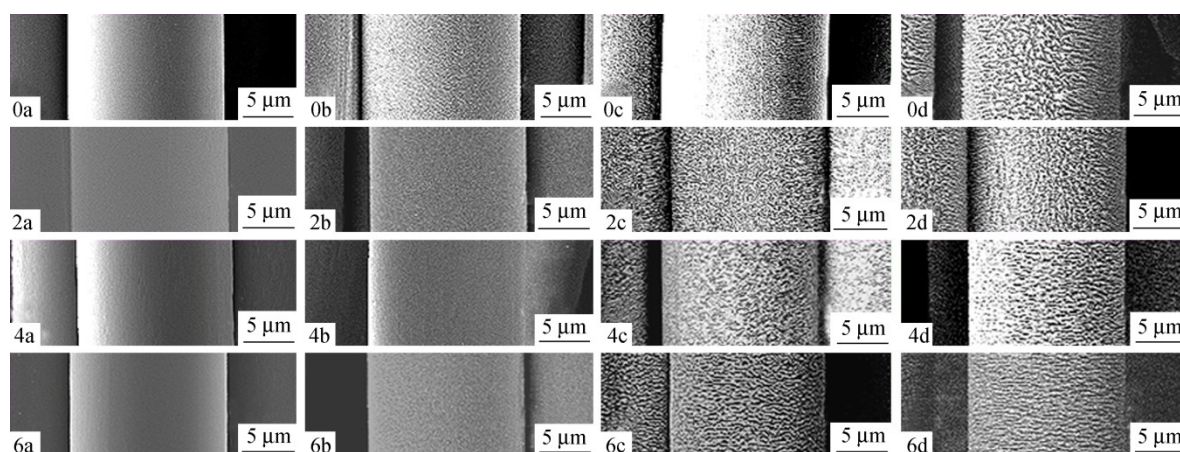


Fig. 2 Surface morphologies of the fibers after exposure to AO environment with fluence at (0a–6a) 0, (0b–6b) 2.08×10^{19} atoms/cm², (0c–6c) 5.33×10^{19} atoms/cm² and (0d–6d) 1.46×10^{20} atoms/cm²

Surface Elemental Analysis by XPS

In order to investigate the change in oxidation states of the surface atoms, the chemical compositions of the fiber surfaces as obtained *via* XPS are listed in Table 4. As can be seen, the relative carbon content reduced dramatically, oxygen content increased remarkably, and nitrogen and phosphor content increased significantly for all the samples after AO exposure. For example, the C content decreased from 77.65% to 62.55% for PI-0 and from 65.99% to 46.64% for PI-6; and the phosphor content increased from 1.17% to 8.87% for PI-6. These results suggested that AO erosion changed the surface composition; in particular, the phosphor content increased on the surface of the fibers. As discussed in the literature^[8, 19–21], this phenomenon indicated that some carbon element on the surface of fibers might be oxidized by AO and released from the surfaces as the volatiles; moreover, some AO might be incorporated into the surface as a new layer. Our observation is similar to the result reported by Yang *et al.*^[1], who found that a passivated layer of PI covered with phosphate formed after AO exposure.

Table 4. Surface chemical composition of the PI fibers before and after AO exposure

Sample element peaks	Element content (%)							
	PI-0		PI-2		PI-4		PI-6	
	Before AO	After AO	Before AO	After AO	Before AO	After AO	Before AO	After AO
C 1s	77.65	62.55	75.82	63.58	72.64	48.75	65.99	46.64
O 1s	17.99	26.28	19.73	25.57	20.49	35.12	29.78	35.23
N 1s	4.36	11.17	3.91	6.5	5.89	7.43	3.06	9.26
P 2p	–		0.53	4.35	0.98	8.7	1.17	8.87

Figure S6 presents the XPS survey spectra of the fibers before and after AO exposure. As can be seen, the P 2p peak emerged in the fibers with exposure, however, the peaks were not obvious in the fibers without exposure. Theoretical and experimental studies have been conducted concerning the XPS analysis of the polyimide^[22–25]. In the current study, XPS peaks were analyzed and fitted based on the experimental data obtained by Briggs and on the theoretical results by Silverman. Figure S7 presents C 1s spectra of the fibers before and after AO exposure. The C 1s spectra can be fitted with three peaks, *i.e.*, binding energies (BEs) at

284.8 eV for the C—C species, at 286.0 eV for the C—N or C—O species, and at 288.3 eV for the C=O species. These results coincided with the report by Duo *et al.*, who demonstrated the binding energy at 284.8 eV corresponding to the carbon atoms of benzene rings^[26]; the binding energy at 286.0 eV for C—O—C in ODA or to C—N—C in imide ring; and the binding energy at 288.3 eV from C=O in imide ring. As shown in Table 5, for PI-4 and PI-6, after AO exposure, the peak at 284.8 eV decreased obviously, whereas the peaks at 286.0 and 288.3 eV increased significantly. These results indicated that the degradation of the fibers came from the C—C bond in the benzene ring; simultaneously, the atomic oxygen combined with carbon atom formed C—O bond or C=O bond. As reported in the literature, oxygen atoms reacted with carbon atoms to generate CO₂, after which CO₂ degassed from the surfaces^[27–30].

Table 5. Fitted relative content for high resolution C 1s, O 1s, N 1s and P 2p spectra

Element peaks	Before AO exposure			After AO exposure		
	Binding energy (eV)	Assignments	Area (%)	Binding energy (eV)	Assignments	Area (%)
PI-0	284.8	C—C	78.5	284.7	C—C	70.0
	285.8	C—N, C—O	12.8	285.7	C—N, C—O	20.1
	288.3	C=O	8.7	288.3	C=O	9.9
	531.1	O=P	—	531.1	O=P	—
	532.0	O=C	81.7	532.0	O=C	87.6
	533.2	O—C	18.3	533.2	O—C	12.4
PI-2	284.7	C—C	76.8	284.7	C—C	57.8
	286.0	C—N, C—O	15.4	285.8	C—N, C—O	32.6
	288.3	C=O	7.8	288.4	C=O	9.6
	531.1	O=P	9.9	531.1	O=P	25.4
	532.0	O=C	70.5	532.0	O=C	63.0
	533.3	O—C, O—P	19.6	533.2	O—C, O—P	11.6
	132.2	P—(C ₆ H ₅)	63.8	132.2	P—(C ₆ H ₅)	—
	133.2	O=P	36.2	133.9	O=P(OR) ₃	100
PI-4	284.6	C—C	59.8	284.6	C—C	48.8
	286.0	C—N, C—O	34.3	286.1	C—N, C—O	41.3
	288.3	C=O	5.9	288.4	C=O	9.9
	531.1	O=P	10.7	531.1	O=P	27.0
	532.0	O=C	74.2	532.0	O=C	64.4
	533.2	O—C, O—P	15.0	533.2	O—C, O—P	8.9
	132.2	P—(C ₆ H ₅)	62.6	132.2	P—(C ₆ H ₅)	—
	134.0	O=P(OR) ₃	37.4	134.2	O=P(OR) ₃	100
PI-6	284.8	C—C	56.9	284.7	C—C	47.7
	285.7	C—N, C—O	38.5	285.4	C—N, C—O	41.4
	288.4	C=O	4.6	288.4	C=O	10.9
	531.1	O=P	11.1	531.1	O=P	32.8
	532.0	O=C	77.6	532.0	O=C	61.1
	533.2	O—C, O—P	11.3	533.2	O—C, O—P	6.09
	132.2	P—(C ₆ H ₅)	42.6	132.2	P—(C ₆ H ₅)	—
	133.7	O=P(OR) ₃	57.4	134.1	O=P(OR) ₃	100

Figure S8 shows the O 1s spectra of the fibers before and after AO exposure. The O 1s spectra can be fitted with three peaks, *i.e.*, binding energy at 531.1 eV for the P=O species, at 532.0 eV for the C=O bond, and at 533.5 eV for the P—O and C—O bonds. The detailed data are presented in Table 5, for PI-0, the content at 532.0 eV from C=O increased from 81.7% to 87.6%, while the content at 533.2 eV from C—O decreased from 18.3% to 12.4% after AO exposure. Regarding the fibers containing phosphor, PI-2, PI-4, and PI-6, the content at 531.1 eV from P=O increased greatly to 25.4%, 27.0%, and 32.8%, which are almost three times than those of the unexposed samples. The above results indicate that after AO exposure, the phosphor element obviously deposited to the surface of the samples.

The P 2p spectra of the fibers shown in Fig. S9 are fitted two peaks at 132.2 eV (P—Ar) and 133.2 eV (P=O) in the unexposed fibers except PI-0. After the fibers were exposed to the AO environment, the P 2p peak became one single peak at a higher binding energy $[O=P(OR)_3]$, whereas the peak at 132.2 eV binding energy disappeared, indicating that the PPO groups in the PI fibers might change to some of P oxides or phosphates, which could effectively protect the fiber surface from further AO erosion. This result is consistent with the increase of the O 1s peak at 531.1 eV (P=O). The above results confirmed that the surfaces formed a passivated layer with phosphate when the fibers were exposed to the AO beam in the vacuum. Such new P-passivated layer can effectively prevent the AO beam from eroding the surface of PI fibers further.

Mechanical Properties of the Fibers

A typical tensile test is shown in Fig. 3. As can be seen, the AO exposed fiber obviously exhibited low strength. The changes in tensile strength, initial modulus, and elongation of the PI fibers with AO fluence are plotted in Figs. 4, 5 and 6, respectively. For PI-0, PI-2, PI-4, and PI-6, at the AO fluence of 1.46×10^{20} atoms/cm², the tensile strength of the fibers decreased from 6.71, 5.71, 4.61, and 6.09 to 3.84, 3.96, 3.09, and 5.13 cN/dtex, respectively. These values corresponded to 57%, 76%, 80%, and 84% of the original values, respectively. The initial modulus also decreased significantly from 111.20, 134.00, 79.21, and 101.55 to 53.37, 86.75, 57.77, and 83.23 cN/dtex, respectively. These values corresponded to 48%, 64%, 73%, and 82% of the original values, respectively. Both tensile strength and the initial modulus decreased with the AO fluence. However, the elongation of the fibers either did not change or slightly increased after the AO exposure.

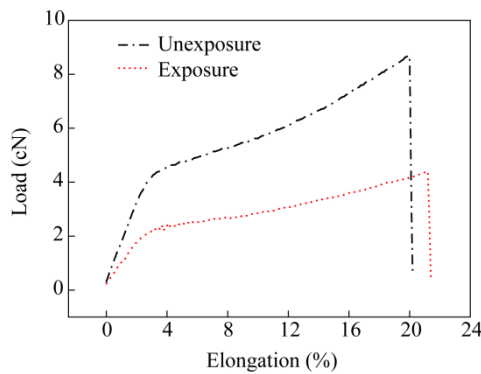


Fig. 3 Typical stress-strain curve of the PI fibers (AO fluence = 1.46×10^{20} atoms/cm²)

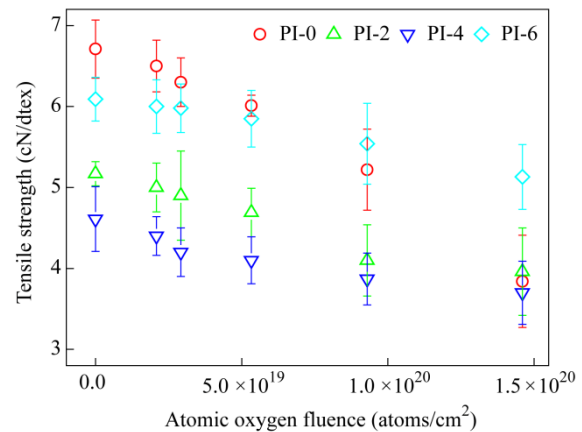


Fig. 4 Variation of the tensile strength with AO fluence

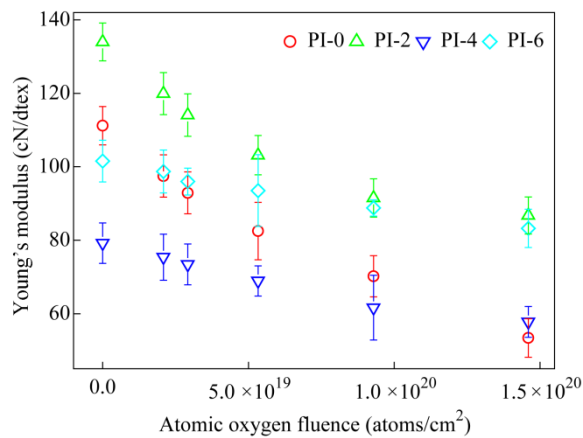


Fig. 5 Variation of Young's modulus with AO fluence

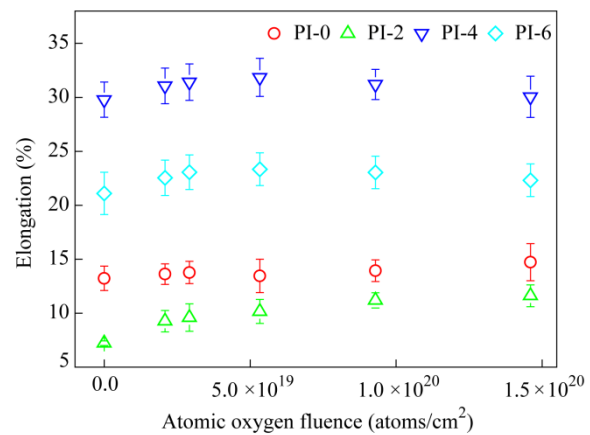


Fig. 6 Variation of the elongation with AO fluence

Resistance Mechanism to Atomic Oxygen Exposure

According to the above results, the mass loss of the PI fibers decreased when exposed to AO beams. However, with the increase of phosphorous content, the mass loss declined. Moreover, the surface became rough and dense after AO exposure. XPS results showed that the C content decreased, and the P and O contents increased dramatically, indicating that a passivated layer with phosphate was formed after AO exposure. The protecting layer reduced the mass loss and seemed like a dense surface. Previous literatures^[1, 7, 8, 19, 20, 22–26, 29, 30] have also implied that the hydrocarbon in the polymers was decomposed by AO, and some volatile products, such as CO or CO₂, have been removed from the surface, resulting to the decreased weight and the rough surfaces. However, some non-volatile P compounds formed and moved to the surface as a passivated layer, thus protecting the underlying structure from further eroding of AO beam, as illustrated in Fig. 7.

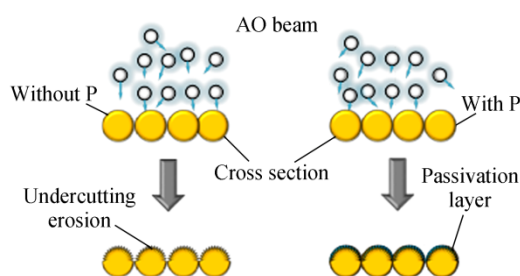


Fig. 7 Schematic diagrams of AO eroding fibers

CONCLUSIONS

A series of PI fibers containing phosphorous based on DAMPO monomer were successfully prepared and exposed to the atomic oxygen environment. The results indicate that the phosphorous-containing PI fibers display excellent AO-resistance at the fluence of 1.46×10^{20} atoms/cm². With the DAMPO content increased from 0% to 60%, the mass loss of the phosphorous-containing fibers after AO erosion decrease obviously from 88.6% to 48.7%. SEM results show that the phosphorus-containing PI fibers display a compact surface after AO erosion, whereas the pure PI fiber has a loose surface. XPS results confirm that most organic components of the fibers are eroded by AO and P atoms are oxidized approximately to phosphate ($\text{O}=\text{P}(\text{OR})_3$), which cause the fibers with the PPO groups self-passivated after AO erosion. Furthermore, the mechanical properties of the PI fibers are investigated before and after AO erosion. With the increase of DAMPO content in the polymer from 0% to 60%, the retention of the tensile strength and the initial modulus are improved dramatically from 57% to 84%, and from 48% to 82%, respectively. The passivated layer formatted on the surface of phosphorous-containing fibers prevented from further AO erosion, resulting in the decreased mass loss, dense surfaces, and the remaining of mechanical properties. These outstanding properties make these fibers promising polymers for potential application in the LEO environment.

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