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Atomic Oxygen-resistant Phosphorus-containing Polyimides Derived from Bis(4-aminophenoxy)phenylphosphine Oxide and Aromatic Dianhydrides

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A series of phosphorus-containing polyimides are prepared from p-DAPO$_3$ and corresponding dianhydrides by two-stage polycondensation, and properties such as AO resistance are discussed in detail.

Nowadays, numerous spacecraft are traveling in low earth orbit (LEO) altitudes, ranging from 200 to 800 km. Most structure of such spacecraft comprise polymeric materials. The degrading factors for polymers in LEO include atomic oxygen (AO), ultraviolet (UV) and ultrahigh vacuum, thermal cycles, and orbital debris. AO is the most hazardous factor present in the LEO, causing failure of the materials.[1–4]

Polyimides (PIs) are useful as high-temperature polymers due to their excellent thermal stability, chemical resistance, mechanical and dielectric properties.[5–7] However, atomic oxygen erosion will result in the degradation of the polyimide and affect the lifetime of spacecraft. Recently, a promising approach AO resistant is to incorporate phenylphosphine oxide (PPO) groups into the polyimide chains. Previous work showed that PPO-containing polyimides have significantly lower erosion yields compared to Kapton®HN. A report about AO resistance of PPO-containing PIs by NASA revealed that the formation of inorganic phosphate layer protects the underlying polyimide from further AO attack.[8,9]

Based on knowledge of PPO-containing polyimides, the P element in PPO-containing diamine converted to the higher oxidation state of phosphate upon AO exposure.[10,11] Thus, the higher oxidation state P-containing diamine could be a kind of valid monomer to prepare AO resistant polyimide. The purpose of this work is to perform a study of the AO resistance properties of polyimide films prepared from higher oxidation state P-containing diamine, bis(4-aminophenoxy)phenylphosphine oxide (p-DAPO$_3$) and corresponding dianhydrides.

In this study, we synthesized an intermediate dinitro compound, bis(4-nitrophenoxy)phenylphosphine oxide (p-DNPO$_3$, **1**) first, and then reduced to a diamine monomer, p-DAPO$_3$ (**2**), by catalytic hydrogenation, as shown in Scheme 1 (Supporting Information; SI[13]). The structure of **1** and **2** were characterized by FT-IR, ^{1}H NMR, and elemental analysis (SI[13]). Phosphorus-containing polyimides were prepared by reacting **2** with an equivalent of dianhydrides (**a**–**d**) followed by thermal condensation as shown in Scheme 2 (SI[13]).

The FTIR spectra of PI are shown in Figure 1. The characteristic peaks of polyimide were observed at 1770 (C=O asymmetric stretch), 1720 (C=O symmetric stretch), 1370 (C–N stretch), and 724 cm^{-1} (C=O bending), indicating the PI films had successfully synthesized. The characteristic absorption peaks at 920 (P–O–Ph) and 1200 cm^{-1} (P=O) were observed in all spectra.

The transparency and cutoff wavelength of all polyimides were measured by UV–vis spectroscopy as shown in Figure 2. Figure 2 shows the UV–vis spectra of the polyimide films with average thickness of 35 µm, in which the cutoff wavelength ranged from 344 to 380 nm. Diamine p-DAPO$_3$ containing electron-withdrawing P=O, and a bulky pendant –Ph group affords an irregular structure to the polyimide. This was expected to disrupt the formation of CTC and lead to low color polyimide films. The values of cutoff wavelengths of polyimides showing dark color higher than 400 nm is due to the phenyl group being not bulky enough.

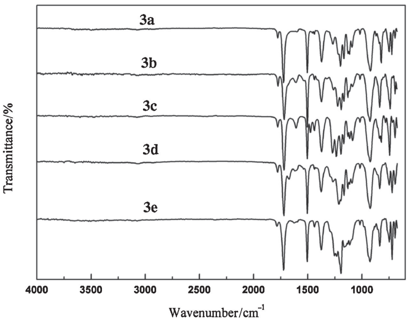

Figure 1. FTIR spectra of PI films **3a**–**3e** before and after AO exposure.

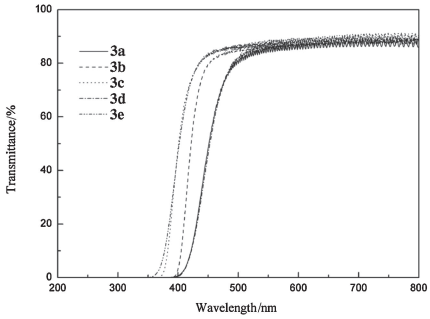

Figure 2. UV–visible spectra of polyimides **3a**–**3e**.

As listed in Table 1, the T_g obtained from the peak temperature of DSC is 270, 227, 198, 216, and 221 °C for **3a**–**3e**, respectively. Among the PIs, **3a** showed the highest T_g due to the rigid pyromellitic moieties. In contrast, **3c** displayed the lowest T_g because of the flexible ether linkage.

The thermal stability of polyimides **3a**–**3e** was evaluated by TGA as shown in Table 1. The 5 wt % degradation temperatures of PIs **3a**–**3e** in nitrogen atmosphere range from 475 to 518 °C, and the char yields are in the range of 33–67 wt %. On heating, the decomposition of the P–Ph bond decreases the molecular weight rapidly. However, the phosphorus-rich char retarding the degradation of the main chain of polyimides when the open O=P–Ph chain decomposes at high temperature.

Table 1. Thermal properties of PI films

PI	$T_g{}^a$/°C	$T_{5\%}{}^b$/°C	$R_{w700}{}^c$/%
3a	270	489	60
3b	227	518	67
3c	198	490	61
3d	216	488	63
3e	221	475	33

[a]T_g: glass-transition temperature was obtained from DSC curves. [b]$T_{5\%}$: temperatures at 5% weight loss. [c]R_{w700}: residual weight ratio at 700 °C in nitrogen.

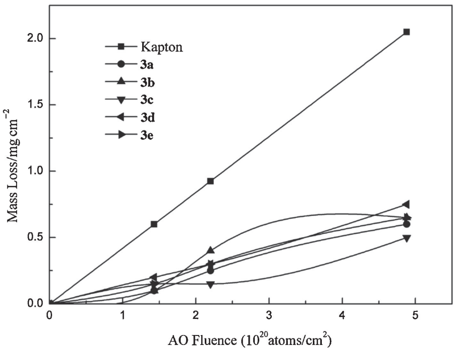

Figure 3. Mass loss versus AO fluence during the AO exposure for the phosphorus-containing films.

Figure S1 shows the SEM photograph of the phosphorus-containing polyimide films **3a** before and after exposure to AO for 5 and 20 h (SI[13]). It shows that the sample surface is smooth before exposure to AO. However, these surfaces were eroded and exhibited a rough texture attributed to AO attacks after exposure to AO for 5 h (the fluence is 1.43×10^{20} atoms/cm^2). After 20 h exposure to AO, the fluence is 4.88×10^{20} atoms/cm^2. It is obvious that the surface is not "carpet-like" but "relief-like" morphology, indicating that the AO did not severely erode the film. It is attributed to the observation that the organic molecules on the surface were eroded at the early stage which resulted in P–Ph bond scission and phosphate formation.

To study the effect of the introduction of P=O group on the AO resistant properties of the phosphorus-containing polyimides, ground-based AO exposure experiments were carried out. The Kapton®HN film serves as a standard for relative comparison with the AO exposure films. The results of weight losses of the films as a function of AO fluence are shown graphically in Figure 3. All of the phosphorus-containing films exhibited excellent resistance (i.e., weight retention) to the AO. As AO fluence of 4.88×10^{20} atoms/cm^2, the mass loss of **3a** is approximately 29% that of Kapton®HN film. The Kapton®HN film sample exhibited a yellow opaque area whereas visual examination of the phosphorus-containing films revealed no evidence of frosting appearance and remained transparent.

It is important to note that the phosphorus-containing films exhibited a nonlinear mass loss over the 20 h exposure period, while the Kapton®HN film undergo relatively constant, linear mass loss rate during exposure to AO. Which means the mass loss relative to Kapton®HN film of **3a** could lower than 26% with the increasing of AO fluence. As previously reported,[12] the mass loss of PPO-containing PI is approximately 26% that of Kapton®HN film as AO fluence of 7.5×10^{20} atoms/cm^2. It might be concluded that the AO resistance of film **3a** and **3c** are better than PPO-containing PI film if we ignore the difference of AO generating source. However, further studies should be needed to verify the accuracy of above resulting. It is interesting that the phosphorus-containing polyimide films do not exhibit linear weight loss due to the formation of a phosphate surface layer upon exposure to AO.

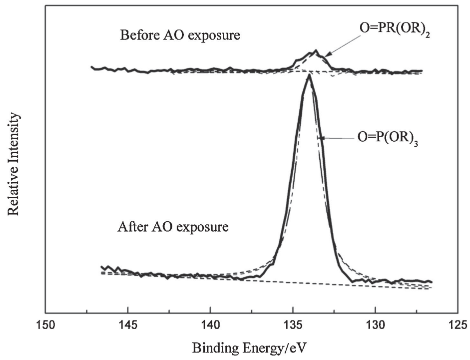

Figure 4. P 2p high resolution XPS spectra of **3a** film before and after exposure to AO for 20 h.

According to the shape of P 2p XPS spectra of **3a** film before and after exposure to AO, the XPS spectra were deconvoluted. The curve fitting results were in accordance with the P 2p of Table S1 (SI[13]). As can be seen from Figure 4, before exposure to AO, the peak at 133.6 eV is assigned to O=PR(OR)$_2$. However, the peak at BE of 133.6 eV shifted slightly to high energy (i.e., 133.9 eV) and intensity increased significantly after exposure to AO. The results corresponded to P 2p of **3a** in Table S1.[13] The P element concentration increased from 0.63% to 7.55%. It is convincing that a phosphate layer had formed on the surface of the film.

In summary, the phosphorus-containing polyimide films were successfully prepared by thermal condensation of p-DAPO$_3$ and commercially available dianhydrides, and exhibited T_g in the range of 198–270 °C with thermal stability up to 518 °C. These PIs can be good candidates as promising polymers for potential space application in LEO.

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