J Mater Sci (2006) 41:5764–5766
DOI 10.1007/s10853-006-0109-5

LETTER

Phosphazene-based polymers as atomic oxygen resistant materials

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Received: 18 June 2005 / Accepted: 24 October 2005 / Published online: 16 May 2006

Spacecraft materials in low earth orbit environment (LEO; 200–700 km) are subjected to the combined effects of thermal cycling, far ultraviolet radiation, hard vacuum, micrometeoroid and debris impact, charged particle bombardment, spacecraft charging and atomic oxygen (AO). Of these the dominant chemical constituent of LEO environment is AO formed by the photodissociation of molecular oxygen [1, 2]. AO causes erosion of polyimide films, advanced composites and engineering thermoplastic materials which are extensively used for the construction of satellites and space stations placed in LEO and hence, these materials need protection. Metal oxides, which have negligible erosion rates, can be used as AO resistant protective coatings for materials that are susceptible to AO attack. However, these coatings lack flexibility and are susceptible to pin hole defects and easily crack on thermal cycling due to thermal expansion mismatch of the coating and the substrate [1, 2]. To overcome the above problems, several inorganic and organometallic polymers are considered for AO resistant protective coatings and also as AO resistant material [3–6].

In recent years, there has been considerable interest on the use of polymers based on phosphazene as AO resistant materials [7–11]. The incorporation of phosphorus has some advantages compared to the incorporation of organosilicon, i.e., less phosphorus is required to bring about the desired effect [10]. Earlier exposure experiments with polymers containing phenylphosphine oxide groups in the backbone suggest that the incorporation of such groups significantly increases the resistance to erosion by AO [11].

In the present work, cyclomatrix phosphazene–bismaleimide, cyclomatrix phosphazene-triazine–bismaleimide and a vinylic polymer containing fluoroalkoxy-substituted phosphazene as pendant groups were evaluated as AO resistant materials. Cyclomatrix phosphazene–bismaleimide polymer (PZ-BMM) was synthesized by the Alder-ene reaction between tris(2-allylphenoxy)triphenoxycyclotriphosphazene (TAP) and bis(4-maleimidophenyl) methane (BMM) [12]. TAP was synthesized from hexachlorocyclotriphosphazene by sequential reaction with sodiumphenolate and sodium (2-allylphenolate). Cyclomatrix phosphazene-triazine based polymers (PZ-TZ-BMM) with varying bismaleimide content were synthesized by co-curing a blend of TAP and tris(2-allylphenoxy)triazine (TAT) (1:1 mole ratio) with bis-(4-maleimidophenyl) methane (BMM) by the method of Nair and Ninan [13]. The phosphazene based film prepared from TAP and bis (4-maleimido-phenyl)methane (BMM) with allyl to maleimide content 1:2.5 is referred to as PZ-BMM-25 and cyclomatrix phosphazene-triazine based ones with allyl to maleimide content 1:1.5 and 1:2.5 are referred to as PZ-TZ-BMM-15 and PZ-TZ-BMM-25 respectively. The structures of phosphazene and phosphazene-triazine based polymers are given in Figs. 1 and 2 respectively. A vinylic polymer, VCP-1, in which fluoroalkoxy-substituted phosphazene is present as pendant groups, was synthesized from $N_3P_3Cl_5(OC_6H_4\text{-p-CH=CH}_2)$ and sodium trifluoroethanolate [14, 15] and this polymer has M_n of 1,20,000 and M_w of 5,60,000. The structure of VCP-1 is given in Fig. 3.

AO resistance of polymeric materials can be understood by studying the mass loss of the samples on exposure to AO at different time intervals. The material

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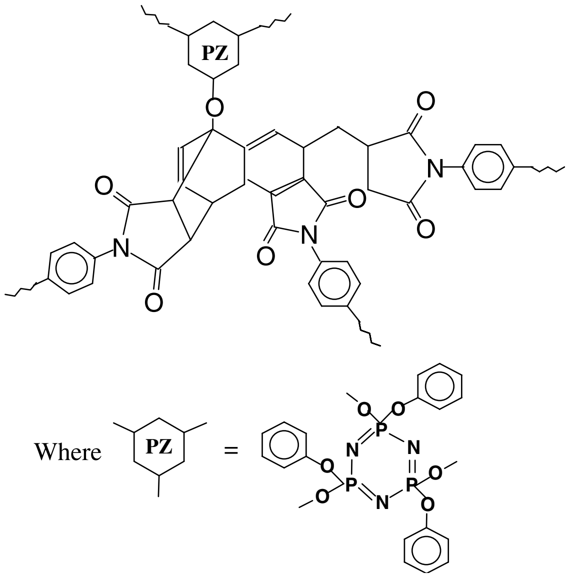
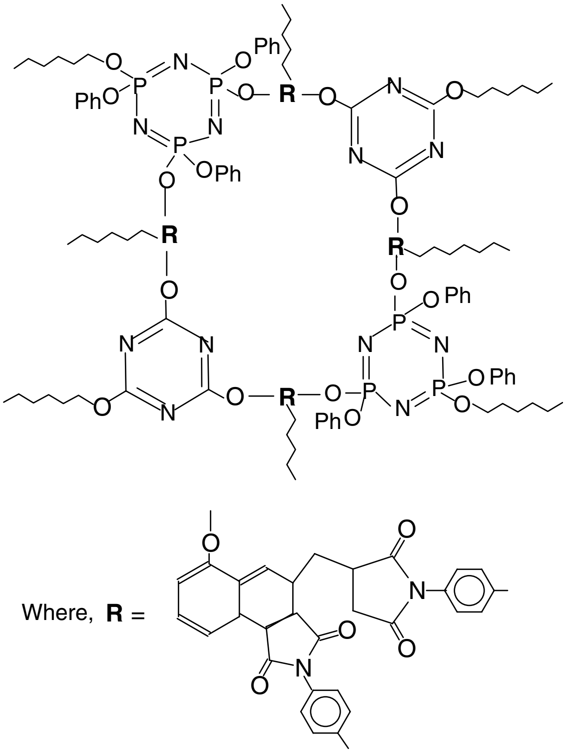


Fig. 1 Structure of phosphazene based polymer(PZ-BMM)



(for allyl/ BMM = 1/2)

Fig. 2 Structure of phosphazene-triazine based polymers(PZ-TZ-BMM)

that has the least mass loss will have higher resistance to AO erosion when compared to other materials. For ascertaining AO resistance, the material can be made into a film and exposed to AO or alternately a uniform coating of the material can be given on a quartz plate and the coated plate can be exposed to AO. In the latter case,

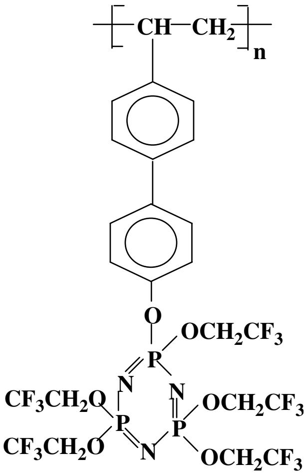


Fig. 3 Structure of vinylic phosphazene based polymer (VCP-1)

as quartz plate is not attacked by AO, mass loss, if any, on exposure to AO would be due to AO erosion of the polymeric material. Free standing films of size 2.5 cm × 1.5 cm and thickness ~200 μm from PZ-BMM-25, PZ-TZ-BMM-15 and PZ-TZ-BMM-25 were prepared by melt curing the required monomer mixtures on glass plates following the cure schedule: 150 °C for 1 h, 180 °C for 4 h, 200 °C for 1 h and 230 °C for 1.5 h.

As it was difficult to prepare a freestanding film from VCP-1, a 10% solution of this polymer in toluene was applied on a quartz plate using a brush to obtain a film of size 2.5 cm × 1.5 cm and thickness of ~40 μm. The coated quartz plate was then dried in an air oven under vacuum at 60 °C for 10 h. For studying AO erosion, films of PZ-BMM-25, PZ-TZ-BMM-15 and PZ-TZ-BMM-25 and VCP-1 coated quartz plate were exposed to AO in a plasma barrel system (March Plasmod Plasma Barrel System) operating at RF frequency of 13.56 MHz and 75 Watts current input. The system was operated under oxygen flow of 7.23 standard cubic centimeter per min (SCCM). Along with these samples, a Kapton® (polyimide) film of thickness 125 μm was also exposed to measure the AO fluence i.e., total number of incident AO per unit area expressed in atoms/cm^2. The mass loss of all the samples was measured at different time intervals using a Mettler Toledo balance and exposure of the samples to air during weighing was kept to the minimum to prevent rehydration. From the mass loss of the uncoated Kapton® film AO fluence can be calculated using the equation,

$$\text{Fluence } (F) = \frac{\Delta M}{A\rho E}$$

where M = initial mass of the sample − mass of the sample at that time of measurement (in g), A = area in cm^2, = density in g/cm^3 and E = erosion yield in cm^3/atom.

Erosion yield of Kapton®, as obtained from AO exposure study in space environment, is 3×10^{-24} g/cm^3. Density of Kapton® is 1 g/cm^3. From these measurements, the fluence for a given period of exposure can be calculated by substituting the above values. Plots of mass loss versus AO fluence of the samples are given in Fig. 4. Comparison of mass loss data with that of the phosphorus-containing polymers suggests that the phosphorus-containing polymers are resistant to AO attack. Phosphorus present in phosphazene ring would undergo oxidation on reaction with AO forming a protective phosphate layer, which would prevent further oxidation. Among the phosphazene ring containing polymers evaluated in the present study, VCP-1 exhibits better AO resistance. This is attributed to the following reasons:

(i) Phosphorus content is the highest for this polymer.
(ii) Unlike in PZ-BMM and PZ-TZ-BMM polymers where phosphorus is present in the polymer backbone, in VCP-1 phosphorus is present in the pendant group and hence, concentration of phosphorus on the surface of the film is expected to be more in the case of VCP-1.
(iii) VCP-1 contains fluoroalkoxy groups in addition to phosphazene group. C–F bond is resistant to AO when compared to C–C and C–H bonds [16]. Thus, presence of fluoroalkoxy group would contribute towards improving the AO resistance of VCP-1.

In the case of PZ-BMM and PZ-TZ-BMM polymers, AO resistance is found to dependent on both the structure and phosphorus content of the polymer (Table 1). It is interesting to note that PZ-TZ-BMM-15 which has less phosphorus content (3.4%) has better AO resistance when compared to PZ-BMM-15 which has higher phosphorus content (4.5%) and this observation is attributed to the presence of triazine moieties in the former. PZ-TZ-BMM-15 has better AO resistance when compared to PZ-TZ-BMM-25. Both these polymers have the same amount of triazine moieties and better AO resistance of PZ-TZ-BMM-15 is attributed to higher phosphorus content (3.4%) when compared to that of PZ-TZ-BMM-25 [phosphorus content, 2.4%].

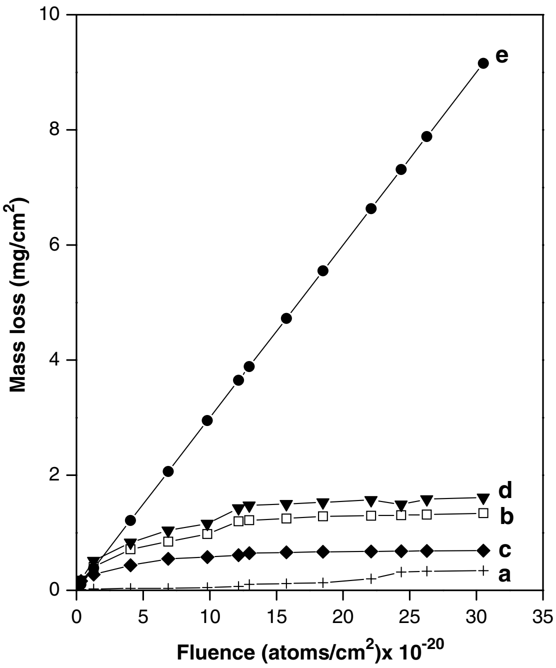


Fig. 4 Mass loss versus AO fluence for phosphazene-based polymers (**a**) VCP-1, (**b**) PZ-BMM-25, (**c**) PZ-TZ-BMM-15, (**d**) PZ-TZ-BMM-25 and (**e**) Kapton® film

Table 1 Phosphorus content of polymers

Polymer code	% of phosphorus[a]
VCP-1	11.3
PZ-BMM-25	4.5
PZ-TZ-BMM-15	3.4
PZ-TZ-BMM-25	2.4

[a] Calculated based on structures given in Figs. 1–3

Acknowledgements The authors thank the authorities of VSSC for granting permission to publish this work. One of the authors (D.D.) is thankful to CSIR, New Delhi for a senior research fellowship. The authors acknowledge Professor V. Chandrasekhar, IIT, Kanpur for supplying the vinylic polymer, VCP-1.

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