Influence of the Composition of the Hybrid Filler on the Atomic Oxygen Erosion Resistance of Polyimide Nanocomposites

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Figure S1. Chemical structure of polyimide. Polymer with $M_w=10.7 \times 10^5$ was synthesized by one-step high-temperature polycondensation of the relevant monomers in m-cresol. A reduced viscosity of 0.97 dL/g was measured for the polymer solution in N-methyl-2-pyrrolidone at 25 °C.
**Figure S2.** Structural formulas of precursors.

**Table S1.** Compositions of films based on PI.

| Sample   | Precursor Concentration [wt.%] | Precursor Solution Weight [g] | Filler Content [wt.%] | Filler Content [mmol/g]** |
|----------|--------------------------------|-------------------------------|-----------------------|---------------------------|
| PI-Al    | 3                              | 0.062                         | 1.6                   | 0.065                     |
| MDES     | 14                             | 0.323                         | 8.0                   | 0.341                     |
| PI-Fe    | 3                              | 0.063                         | 1.7                   | 0.06                      |
| MDES     | 14                             | 0.329                         | 8.1                   | 0.313                     |
| PI-Cr    | 3                              | 0.073                         | 2.3                   | 0.066                     |
| MDES     | 14                             | 0.384                         | 10.7                  | 0.346                     |
| PI-Zr    | 3                              | 0.063                         | 1.8                   | 0.046                     |
| MDES     | 14                             | 0.324                         | 10.0                  | 0.285                     |
| PI-Hf    | 3                              | 0.060                         | 1.8                   | 0.039                     |
| MDES     | 14                             | 0.325                         | 10.7                  | 0.249                     |
| PI-Nb    | 3                              | 0.067                         | 1.8                   | 0.040                     |
| MDES     | 14                             | 0.352                         | 8.3                   | 0.210                     |

*The 5 wt.% precursor solution in chloroform was added to 0.10 g PI solution in 4 ml of chloroform with stirring in an argon stream. **mmol of filler per gram of PI.

**Preparation of filled films**

A precursor solution in chloroform was added to 0.10 g PI solution in 4 ml of chloroform with stirring in an argon stream. The detailed formulations are listed in Table S1. The precursor concentration was 3 and 14 wt%. The resulting solution was poured into a teflon form and dried at room temperature for 3 days. Afterwards, the polymer film was heat treated in a drying oven with a gradual increase in temperature from 50 to 200 °C for 6 hours.

The thickness of the obtained films was 110-120 μm. The filler contents, according to calculations carried out under the assumption of 100% conversion of the ethoxy groups, are presented in Table S1.
For analyses of filled films, the polymer film and the film of 100% precursor, obtained under identical conditions, served as samples for comparison.

AO Beam Exposures

The facility consists of an evacuated vessel in which a plasma accelerator is placed. The vessel has a specimen holder and beam diagnostic equipment. Using vacuum pumping by cryogenic pumps with a rate of 5 m$^3$/s, the vessel maintains a pressure of (0.5-2)×10$^{-2}$ Pa with a plasma-supporting gas-oxygen requirements of 0.5 L Pa/s. The beam components are atoms, molecules and oxygen ions with a predominance of atomic ions. The power flux density absorbed by the specimen was 15 mW/cm$^2$, which approximately corresponds to the heating of the specimen by solar radiation in space.

Film samples 20×20 mm in size were used. The specimens were degassed beforehand and held for 24 hours at a temperature of 20 °C in a vacuum of 10$^{-4}$ Pa.

Specimens were irradiated by an oxygen plasma beam from a plasma accelerator, simulating low-earth orbit conditions. To ensure the same exposure, the analysed specimens and the reference specimen were mounted on a rotating disk, placed normally to the plasma flow. The specimens’ masses were measured outside the evacuated vessel on an analytical microbalance HR-202i (AND, Japan) with a scale multiplier of 10$^{-5}$ g, before and after each irradiation cycle with plasma flow.

In the experiment, the effective fluence method was used to determine the intensity of AO exposure [1]. The equivalent AO fluence, F (O atoms cm$^{-2}$), was determined by the change in weight of a reference sample (Kapton H polyimide film, DuPont) with an erosion yield of $E_K = 3 \times 10^{-24}$ cm$^3$/atom:

$$F = \frac{\Delta m_K}{S \rho_K E_K}$$

where $\Delta m_K$ is the reference sample weight loss (g) during AO exposure, S is the exposed surface area (cm$^2$) and $\rho_K$ is the density of the reference sample (1.42 g/cm$^3$). The effective AK flux density in polyimide equivalents was (3-4)×10$^{16}$ atom/cm$^2$s.

The erosion yield coefficient ($E_y$, cm$^3$ atom$^{-1}$) of research samples is defined as the volume loss caused by one AO attack, calculated by Eq. (2)

$$E_y = \frac{\Delta m}{S \rho F}$$

where $\Delta m$ is the sample weight loss (g) during AO exposure, S is the exposed surface area (cm$^2$), and $\rho$ is the density of sample (1.38 g/cm$^3$).

\[ M \left[ \text{OSi(CH}_3\text{)(OC}_2\text{H}_5)\right]_n \xrightarrow{\text{atmospheric \ moisture}} \text{-C}_2\text{H}_5\text{OH} \rightarrow M \left[ \text{OSi(CH}_3\text{)(OH)}\right]_n \]

(a)

\[ mM \left[ \text{OSi(CH}_3\text{)(OH)}\right]_n \xrightarrow{-\text{H}_2\text{O}} \left( M \left[ \text{OSi(CH}_3\text{-O)}\right]_n \right)_m \]

(b)

**Figure S3.** Assumed scheme of metalloalkoxysiloxane hydrolysis (a) and condensation (b), where M= Al, Fe, Zr, Hf, Nb and n=3-5.
Figure S4. IR spectra of the films (on KBr plates) in the region 800-1800 cm\(^{-1}\): the PI – 14 wt.% Cr-MDES (1), the PI (2) and the difference spectrum (3), proving the presence of Cr-MDES in the composite (a broad band 900-1150 cm\(^{-1}\) in the difference spectrum).
Figure S5. The proposed scheme of the reaction the amine group of the precursor with the imide group of the matrix polymer.

Reference

1. ASTM E. 2089-00. Standard practices for ground laboratory atomic oxygen interaction evaluation of materials for space applications, Annual book of ASTM standards, 2000.

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