Computer Modeling of Polymer Structures Degradation Under the Atomic Oxygen Exposure

N. Chirskaya
Lomonosov Moscow State University, Faculty of Physics, Moscow, Russian Federation.

M. Samokhina
Lomonosov Moscow State University, Skobeltsyn Institute of Nuclear Physics (SINP MSU), Moscow, Russia.

Abstract. The surface of the spacecraft is exposed to the damaging effects of the upper atmosphere atomic oxygen (AO). In this paper, a Monte Carlo method is used to model the erosion process of polymer structures under the influence of AO. Also polymer materials with AO-resistant fillers are investigated. The results of mathematical modeling are compared with experimental data.

Introduction
Atomic oxygen (AO) of the upper atmosphere is one of the most important space factors that can cause degradation of spacecraft surface. On the height between 200 and 800 km concentration of AO prevails in the atmosphere. The energy of atoms in the flux is 5 eV relatively to spacecraft [Novikov and Chernik, 2008].

Polymer materials and polymer composites, including micro- and nano-composites, are widely used in space technology. Polymers have a number of unique mechanical properties; they can be used for electric insulation of conductors, devices and detectors. Polymer films with metal cover, polyimide and fluoropolymer films are used for thermoregulation of the spacecraft. Therefore, an actual problem is to study the AO impact on different materials used in space technology with an emphasis on polymers and composites. In this work mathematical and laboratory modeling of the AO interaction with polymeric materials (polyimide samples and epoxy-based composites) were carried out.

Monte-Carlo method implemented in software package GEANT3 [Apostolakis et al., 1993] was used for mathematical modeling of the polymer etching process. There were two types of modeled material: polymer with a protective coating and polymeric composite with fillers resistant to AO. Laboratory experiments were made on magneto-plasma dynamic accelerator of the oxygen plasma, SINP MSU [Novikov and Chernik, 2008]. This accelerator allows producing fluxes of fast neutral and ionized AO. The irradiated samples were investigated with atomic-force and electron microscopes.

Computational model
The two-dimensional model of material sample is used in the computations. Sample is divided into equal square cells by computational grid similar to one used in the work of Yang et al. [2010]. By this method samples with a protective coating were investigated (Fig. 1).

A thick lower layer shown in Fig. 1 consists of polymer, which reacts chemically with oxygen atoms. Upper layer represents the protective coating, resistant to AO. The model contains two types of cells: polymer cells, which can be removed after the AO impact and protective coating cells. Upper protective layer contains a hole, or defect, through which AO can penetrate inside the model.

Calculations were carried out using Monte-Carlo method and “large particles” approximation. In this approximation one large particle (one event) corresponds to $10^4$ atoms of oxygen. Linear size of the cell equals to 1 micron.

The following assumptions were used:

— “large particles” don’t react with protective coating. If particle touches the coating, it stops;
— atoms O do not recombine into O$_2$ because the mean free path between collisions is too large.

Processes included in the simulation:

— chemical reaction which results in the volatile products formation. Polymer cell is removed;
— specular reflection from the surface. Energy of the particle after reflection remains the same;
— diffuse isotropic scattering. Energy of the particle is fractionally reduced until particle is thermally accommodated.
Figure 1. The two-dimensional model of polymer with protective coating.

Diffuse isotropic scattering can occur inside the volume of the polymer. In this case volatile oxides which are produced by chemical reactions recombine quickly and do not leave the bulk of material. Therefore, we use the following assumption: diffuse scattering occurs only from the surface of the polymer, i.e. when particle is scattered within the volume of the polymer, it stops and is no longer involved in the calculations. Parameters of the large particle interaction with material, such as the chemical reaction, reflection and scattering possibilities, are selected on the basis of the experiments. The criteria of selection are the agreement between calculated and experimental data. The initial energy of the particle was set as \(5\) eV, which corresponds to the AO energy in the flow relatively to the spacecraft surface in the low Earth orbital environment.

Experimental

In order to validate computational model, laboratory simulations were provided. To modeling, the impact of the AO flow the accelerator of plasma was used (Fig. 2).

Oxygen plasma produced in the discharge gap is accelerated by the electric field arising in a diverging magnetic field of the solenoid. Average ion energy in the flow is regulated in the range of 20–80 eV. To reduce to an energy of \(5\) eV in polyimide equivalent flux density of ions and neutral particles of oxygen on the surface of the sample is \((0.6–8)\times10^{17}\) cm\(^{-2}\) s\(^{-1}\). Those energies are much higher than in the natural environment. For that reason the fluence is defined as it would be in the space environment for the same damage of sample. The damage is defined by the mass loss or thickness reduction of the sample, the fluence is calculated using the data from space experiments. The influence of other space factors on the process of erosion is not yet fully researched and is the subject of special studies. In this paper, it is assumed that other space factors are negligible when focus of research is on the chemical scattering.

Samples of coated polyimide film with a crack and polymer nanocomposites based on epoxy were irradiated by AO flow. The fluence of irradiation in different experiments were \(0.5\times10^{18}\); \(1.1\times10^{19}\) and \(1.3\times10^{21}\) atom/cm\(^2\). After irradiation samples were investigated by atomic force microscope MT MDT Ntegra Spectra and electron microscope Mira 3 FEG-SEM. The CSG01 cantilevers were used in measurements with a tip height 14–16 µm and typical curvature radius 6–10 nm.

Results and discussion

The results of polymer etching process modeling for the sample with a protective coating (see Fig. 1) are shown in Fig. 3. The conditions were: The transverse dimension of the sample—100 micron, the thickness of the protective layer—10 micron, the diameter of the hole in the protective layer—30 micron and the angle of the AO particles incidence 30 degrees.

The cavity profile, produced by etching process simulation for the “single specular reflection, single diffuse scattering” mode is shown in Fig. 3a. The chemical reaction probability for this case—\(Q = 0.5\); the probability of specular reflection—\(R = 0.15\); the probability of diffuse scattering—\(D = 0.25\). The result shown in Fig. 3b is obtained for the case of multiple diffuse scattering, for which the particle energy is decreased exponentially after each bounce until the particle is thermally accommodated (the terminate value of the particle energy is \(\approx 0.025\) eV) [Yang et al., 2010].
A set of laboratory experiments, where polyimide samples with perforated protective coating were irradiated with a real AO flux (Figs. 4, 5), was produced. After a low AO fluence ($0.5 \cdot 10^{18}$ atom/cm$^2$) exposure the cavity with a typical nap-like structure is observed (Fig. 4a). Increased fluence of $1.1 \cdot 10^{19}$ results in a deeper cavity and the smoothing of the profile (Fig. 4b). In both cases, the AO flow fell with normal incidence on the sample surface.

It is assumed that the profiles asymmetry is produced by particles scattering from the rough edges of the hole in the protective screen. To eliminate this effect, the hole in the protective screen—aluminum foil—was made by a laser beam. As it seen in Fig. 5, the shape of the defect profile after exposure in this case is quite symmetrical and more convenient to calibrate the mathematical model (Fig. 5). The fluence of $1.3 \cdot 10^{21}$ atom/cm$^2$ was provided.
In addition to the coated samples, polymer composites with nanofillers resistant to AO were investigated. Such composites are widely used in aerospace technology, as they demonstrate sustainability to the upper atmosphere environment [Novikov et al., 2010]. The composite consists of polymer matrix and particles mixed into matrix in the stage of material production. While the erosion during the oxygen plasma irradiation fillers act as a shield, which protects the underlying polymer from removal. The stability of the polymer composite to the damaging effect of AO depends on the dispersion degree of the filler particles in the polymer matrix. We have previously carried out mathematical modeling of the etching process for polymer samples with spherical filler particles injected into subsurface monolayer [Voronina et al., 2011].

In Fig. 6, the dependence of removed polymer cells number from filler particles diameter for different angles of AO incidence is presented. In the model, the number of filler particles N was chosen so that the total amount of matter remained the same for all possible sizes of filler. The following data were obtained in a model that takes into account a single specular reflection and single diffuse scattering of a given AO particle from the polymer cells. In Fig. 6, we can conclude that the composite resistance to the atomic oxygen impact is defined by filler dispersibility degree. The polymer composite degradation reduces with the decrease of particle size and increase of oxygen flow incidence.

The erosion of polymer composites based on polyimide matrix with TiO₂ (rutile) and Al₂O₃ (alumina) fillers was experimentally investigated. The average size of rutile and alumina particles was 30–40 nm and 40–80 nm respectively. The surface images of samples after the AO exposure were obtained by means of electron scanning microscopy and are shown in Fig. 6. Structures consisting of “shields” (AO resistant filler particles) and “legs” (polymer under the “shield,” protected from the erosion) are observed.

The results of mathematical modeling for the same experiment are exposed in Fig. 8a. The distribution of fillers in the upper quarter of polymer matrix was set as a random. The diameter of filler particles was varied. Structures shown in Fig. 8a are quite resembling to those observed in experimental data (Figs. 7, 8b).

Figure 5. Cavity profile in the protected polyimide with a 30 micron hole in the coating (fluence F=1.3·10²¹ atom/cm²).

Figure 6. Removed cells number dependency on filler particles diameter for different atomic oxygen flow incidence. The dashed line shows the erosion level for pure polymer without protective filler.
Figure 7. Structure of the composites with different fillers after atomic oxygen exposure: a – filler is TiO$_2$; b – filler is Al$_2$O$_3$.

Figure 8. Results of mathematical (a) and laboratory (b) modeling of modified polymer etching process. Structures in the surface layer consist of AO-resistant particles and polymer “leg,” which is shielded from the impact of atomic oxygen.

Conclusion

Polymer materials are important research object due to their wide implementation in aerospace industry and sufficient degradation in space environment. In our experiments mathematical model of atomic oxygen interaction with polymer materials was created. First test calculations were made. The effects of atomic oxygen on protected polymers and microfiller containing composites were experimentally investigated and mathematically simulated.

If the polymer surface is protected with a resistant coating and the layer has a defect, or a hole, there is an intensive destruction of polymer through defect beneath the coating. This leads to significant deterioration of material properties. In polymer composites, fillers resistant to atomic oxygen can significantly reduce the mass loss of the material under the atomic oxygen irradiation. It is found that the intensity of erosion process decreases while the filler particles size decreases and filler uniformity in the polymer matrix increases. It is also found that the polymer composite degradation reduces with the increase of atomic oxygen flow incidence.

Acknowledgments. We are grateful to our research advisor L.S. Novikov for his supervision and to V. N. Chernik for technical support in experiments.

References

Novikov L.S., Chernik V.N. Primenenie plasmennih uskoreitelei v kosmicheskom materialovedenii [Application of plasma accelerators in space material science], M. Universitetskaya kniga, p. 90., 2008
Voronina E.N., Novikov L.S., Samokhina M.S., Chirskaya N.P. Matematicheskoe modelirovanie vozdeistvija atomarnogo kisloroda na polimerne kompozity [Mathematical modeling of atomic oxygen effects on polymer composites], Materials of XII interuniversity scientific school for young specialists “Koncentrirovannie potoki energii v kosmicheskoj tehnike, elektronike, ekologii I medicine” [“Strong fluxes of energy in space technology, electronics, ecology and medicine”], Moscow, SINP MSU, November 21–22, pp. 87–94, 2011.