Investigation of the surface relief of polyalkaneimide composites after treatment with oxygen plasma

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Abstract. The paper presents data on the treatment of the flow of oxygen plasma of polyalkanimmune and polyalkanimmune composites. The hydrophobic SiO$_2$ was used as a filler. The fluency of oxygen atoms was $5.4 \times 10^{18}$ at/cm$^2$ (equivalent to 10 years of exposure to atomic oxygen). Studies of the evolution of the surface relief of pure polyalkanimmune and a composite containing 65 wt% SiO$_2$ under the action of oxygen plasma were performed by the probe method. It was shown that after oxygen plasma treatment of a sample of pure polyalkanimmune or its composites, the surface acquires a peculiar grainy relief that was formed by depressions and elevated areas of conical and acicular shape oriented towards the flow of atomic oxygen. It has been established that the introduction of crystalline SiO$_2$ into polyalkanimmune significantly increases the resistance of the polymer to the action of the oxygen plasma flow. Data on the change in the contact angle of wetting of the surface of polyalkanimmune and polyalkanimmune composites after treatment with an oxygen plasma flow are presented.

1. Introduction

Today, most satellites are launched in low Earth orbit (LEO), from 200 to 1000 km. The natural or artificial space environment of the LEO have many obstacles to the successful performance of a spacecraft mission. The environment is destructive for polymers because it includes atomic oxygen (AO), ultraviolet (UV) radiation, ionizing radiation, ultrahigh vacuum, thermocycling, micrometeorites and orbital debris. Because of individual, combined or synergistic interactions with these cosmic hazards, polymers in particular are subject to erosion, structural modification and surface roughness [1-3]. This can lead to irreversible degradation of optical, thermal, electrical, and mechanical properties [4-5].

AO is produced by photo dissociation of molecular oxygen in the upper atmosphere by solar radiation with a wavelength less than or equal to 243 nm. AO is the main component of the residual atmosphere in the low orbit. Oxygen atoms have a density of $10^7$ to $10^8$ atoms/cm$^3$ at the International Space Station (ISS) (about 400 km) with a thermal energy of about 0.1 eV. Spacecraft rotate at a speed of 7.78 to 8 km/s at these altitudes. For a satellite-gas collision, this orbital velocity corresponds to the energies from the shock gas energies of 0.34, 4.40, and 5.03 eV for hydrogen, nitrogen, and oxygen atoms, respectively.

Collision of AO with the surfaces of space vehicles with this energy initiates numerous chemical and physical events on the surface. Erosion of the surface, loss of mass, deterioration of mechanical,
thermal and optical properties, and changes in the chemical composition of materials can be induced by collision with AO [6-7].

There are several methods for increasing the durability of polymers in space. Most methods of protecting polymers from AO involve applying a thin-film metal or metal oxide surface coating on the upper surface of polymers [8-9]. Possible coating materials include SiO$_2$, Al$_2$O$_3$, germanium, silicone, aluminium or gold [10-12]. These coatings form stable oxides, which serve to protect the lower layers of the polymer. Only a thin layer (~ 100 nm) of metal or metal oxide is required to protect against AO erosion. Care must be taken when implementing this method, because protective coatings can create their own new problems, such as silicone cracking. Applying a thinner coating thickness helps reduce the chance of breaking or splitting.

Surfaces of polymers can also be modified to make them more durable. This method involves the implantation of metal atoms in the polymer surface or chemical modification of the surface. For example, silicon atoms are implanted in the polymer inside and near its surface. Also, an alternative way to protect polymers can be to place metal atoms inside the polymer, which form a stable oxide when exposed to AO [13]. The methods listed are good for protecting polymers from AO effects, but they still may lead abnormal effects that result from the addition of other substances to the polymer. A solution to the problem of erosion from AO, which does not require a change of polymers, is the use of non-carbon polymers. An example of such a polymer is siloxane. The effectiveness of the reaction of siloxane with AO is much less than that of typical organic polymers; this reduces the need for protective coatings.

It is known that atomic oxygen acts synergistically with ultraviolet solar radiation. The Earth's atmosphere filters out UV radiation with a wavelength below 290 nm. Radiation in this wavelength range is called vacuum ultraviolet radiation or VUV. The shorter the wavelength of the radiation, the more energy it has (of the order of 6-12 eV for VUV). The VUV has sufficient energy to break atomic bonds in materials on the surface of spacecraft. When materials are exposed to AO and VUV in tandem, the VUV is able to break atomic bonds on the surface of materials [14-15]. The VUV leaves the atoms ready to react and to be oxidized with AO. Thus, AO and VUV act synergistically.

In this paper, the effect of AO on polymeric composites based on polyalkanimide combined with crystalline silicon dioxide was studied. A change in the morphology and in the contact angle of the wetting of the polymer composite after treatment with AO has been examined.

2. Materials and methods

2.1. Materials

As the polymer matrix for the synthesis of composites, a thermoplastic polyalkanimide obtained by polycondensation of dianhydride-pyromellitic acid with 1,12-dodecamethylene diamine was used. Silica (SiO$_2$) was used as a filler with a crystal structure. A hydroalcoholic solution of sodium methylsiliconate (30% aqueous solution) with the formula H$_3$CSi(OH)$_2$ONa was used for the surface modification of SiO$_2$ particles [16].

Composite discs were prepared as follows. The polyalkanimide was dissolved in a polar aprotic solvent (toluene). Dissolution of polyalkanimide was necessary for mixing the matrix and the modified filler in a liquid medium for ultrasonic cavitation (frequency 22 Hz). After evaporation of the solvent, a powder mixture of matrix and filler was obtained.

The resulting mixture of polyalkanimide and crystalline silicon dioxide was charged into a steel mold, heated to the softening point of the polyalkanimide, and kept at this temperature for an hour. After heating, pressing took place at a high pressure of 1 GPa. The resulting composite was a circular disk with a diameter of 3 cm and a thickness of 1-5 mm.

2.2. Installation for treatment with oxygen plasma, in conditions simulating outer space

The composites were irradiated with a beam of oxygen plasma formed in a magnetoplasmodynamic accelerator at the Skobeltsyn Institute of Nuclear Physics imitation unit Lomonosov Moscow State
University (SINP MSU). The scheme of the experimental stand based on the magnetoplasmodynamic accelerator is shown in figure 1.

Figure 1. Diagram of the SINP MSU plasma beam stand: 1 - vacuum chamber, 2 - partition, 3 - plasma source section, 4 - measuring section, 5 - accelerator, 6 - plasma flow, 7 - input window, 8 - sample, 9 - sample holder, 10 - ion sensor, 11 - neutral sensor, 12 - manipulator of sensors, 13 - quadrupole analyser, 14 - electronic block of mass spectrometer, 15 - computer registration system, 16, 17, 18 – cryopumps.

The fluency of oxygen atoms was $5.4 \times 10^{18} \text{ at/cm}^2$. This value of fluency is equivalent to 10 years of exposure to AO at an altitude of 800 km and at a speed of 10-12 km/s.

2.3. Research Methods

To study the change in the surface roughness of composites before and after treatment with oxygen plasma, a scanning probe microscope NanoEducator II was used. NanoEducator II is a microscope capable of operating as atomic force and scanning tunneling microscopes. A characteristic feature of NanoEducator II is the use of wire (tungsten, in particular) probes which are used in both STM and AFM.

The measurement range of linear dimensions is as follows: in the XY plane not less than 70 μm; along the Z axis, not less than 8 μm. The minimum step is 1 Å. The parameters of the probe are as follows: a range of resonance frequencies from 6 to 14 kHz, typically 8 kHz; quality factor - 20; the radius of curvature is 100 nm.

Contact-angle measurements were carried out at room temperature using a Krüss DSA30 Drop Shape Analysis System (Krüss GmbH, Germany). The substrate was laid in thin layer. The procedure involved the deposition of a 5 ml deionized water droplet on the surface of the sample, the subsequent acquisition of an image of the drop, and the computation of the contact-angles (both left and right) within 3 s using the software DSA4 (Krüss GmbH, Germany).

3. Result and discussion

Studies of the evolution of the surface relief of pure polyanilimide and a composite containing 65 wt% SiO$_2$ under the action of oxygen plasma were performed by the probe method. Figure 2 shows AFM images in the topography mode for sections of the initial polyanilimide and composite, as well as for sites subjected to oxygen plasma processing. A strongly pronounced amorphous structure with a smooth surface was observed for the surface of the initial polyanilimide (Fig. 2a) (average roughness (Ra) 1047 nm, rms roughness (Rq) 1292 nm). Differences in the local elastic characteristics of the initial polyanilimide surface were not revealed. After processing a sample of pure polyanilimide with an oxygen plasma, its surface acquired a peculiar grainy relief (Fig. 2c). Analysis of the figure shows that an erosion relief develops after irradiation of the surface of pure polyanilimide. The depth of this relief is ~ 3-6 μm (Ra = 4233 nm, Rq = 5645 nm).
It can be noted that AO causes a non-uniform destruction of the surface of pure polyalkanimide. A relief arises formed by depressions and elevated areas of conical and acicular shape that are oriented towards the flow of AO (Fig. 2c).

When an oxygen plasma is irradiated along the normal surface of the polyalkanimide, a relief is formed from the columnar nano-formations located close to each other and joined to the crests and cones (Fig. 2c). The nano-formations are oriented in the direction of plasma flow. The distance between the columns is ≤ 300 nm, and between cone tops ~ 2-4 μm. The thickness of single columnar nanostructures is ~ 216 nm. Separate extended fibrillar formations of the same thickness are observed that connect the apices of adjacent cones or ridges in the plane of the erosive surface of pure polyalkanimide. It can be noted that the action of oxygen plasma on polyalkanimide led to an intensive destruction of its surface layer without significant crosslinking.

The formation of a granular relief of the surface of pure polyalkanimide after irradiation with an oxygen plasma can be explained by the destruction of polymer chains when they interact with AO. As a result of this interaction, gaseous products (NO, NO₂, CO₂, H₂O, CO, H₂) are formed which are removed from the material and this is one of the factors leading to the formation of the surface structure (Fig. 2c).

Analysis of the initial surface of the composite (Fig. 2c) showed that, compared to pure polyimide, the surface of the composite is rougher and has minor irregularities. Insignificant differences in the local elastic characteristics of the surface of the initial composite with 65 wt% SiO₂ containing were
revealed. This was also confirmed by the numerical values of the surface roughness parameters: \( \text{Ra} = 2494 \text{ nm}; \text{Rq} \) is 3121 nm. It is noticeable that these values are more than 2 times greater than the roughness of pure polyalkanimide. This is because pure polyalkaneimide has an amorphous-crystalline character, while the SiO2 filler introduced has a fully crystalline structure. Therefore, the increase in roughness with the introduction of the filler can be explained by the features of the technological process of synthesizing the composite, which consists of mixing components of different density and crystal structure.

It is noticeable that the surface of the composite changes after exposure to the oxygen plasma. Just as in the treatment of pure polyalkanimide, a granular relief was formed, characterized by depressions and elevated areas of conical and acicular shape and oriented toward the flow of atomic oxygen. However, according to the basic parameters of the surface roughness of the composite after exposure to AO (\( \text{Ra} \) - 3124 nm, \( \text{Rq} \) - 3536 nm), the average roughness increased by 25% and the root-mean-square roughness by 13%, which is much lower than for pure polyalkanimide samples. On the basis of the data obtained, it can be concluded that the introduction of crystalline SiO\(_2\) in polyalkanimide significantly increases the resistance of the polymer to the effects of oxygen plasma flow and atomic oxygen. Since the treatment with an oxygen plasma flow resulted in a significant change in the surface relief of the polyalkanimide and the composite, studies were carried out to change the hydrophobicity of the surface of the samples before and after treatment with oxygen plasma. Table 1 shows data for the contact angles of the surfaces.

| Type of sample | Contact angle, ° (degrees) |
|---------------|---------------------------|
| Polyalkanimide | 73±3                      |
| Composite     | 115±3                     |
|               | 19±6                      |
|               | 56±3                      |

The value of the contact angle of the initial surface of polyalkanimide (73 ± 3°) indicates the hydrophilic nature of the surface, which is due to the presence of functional polar groups with high affinity for water (such as C-O, O=C = O). Polyalkanimide is a nonpolar polymer, it does not contain chemical groups capable of forming hydrogen bonds with water. After treatment of oxygen plasma, the contact angle of wetting decreases by 3.8 times, i.e. the liquid completely wet the surface of the polymer. The increased wetting characteristic may be the result of morphology changes.

The contact angle of the composite (115°) is much larger than that of pure polyalkanimide. This is explained by the modification of the hydrophilic SiO\(_2\) to give it a hydrophobic property in order to improve the compatibility of the nonpolar matrix and filler. After the modification, the coated SiO\(_2\) particles are more hydrophobic and the wetting contact angle is 126°. After processing the composite with oxygen plasma, the surface acquires a hydrophilic character (contact angle 56 ± 3°).

In all experiments, the water droplets had a symmetrical shape, and there was no spreading or penetration of the liquid into the sample volume within two minutes after the drop application. The experimental error for polyalkanimide treated with an oxygen plasma stream was ± 6°, whereas in all other experiments the error is much lower (± 3°). This is due to the peculiar morphology of the surface of this sample, in particular to the more heterogeneous (according to figure 2) surface structure.

4. Conclusion
The paper presents data on the change in the surface relief of polyalkanimide and polyalkanimide composites by treatment with oxygen plasma. It was shown that after the oxygen plasma treatment of a sample of pure polyalkanimide or of its composites, the surface acquires a peculiar grainy relief formed by depressions and elevated areas of conical and acicular shape that are oriented towards the
flow of AO. It can be noted that the action of oxygen plasma on polyalkanimide led to an intensive destruction of its surface layer without significant crosslinking. It has been established that the introduction of crystalline SiO$_2$ into polyalkanimide significantly increases the resistance of the polymer to the action of oxygen plasma flow.

The initial surface of polyalkanimide has hydrophilic properties (contact angle 73 ± 3°). After treatment with oxygen plasma, the wetting angle was significantly reduced by (19 ± 6°) and the liquid practically completely wet the surface of the polymer. The contact angle of the composite (115°) is much larger than that of pure polyalkanimide, and after processing the composite with oxygen plasma, the surface acquired a hydrophilic character (contact angle 56 ± 3°).

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