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# Using the High-Dispersity [Alpha]-$Al_2O_3$ as a Filler for Polymer Matrices, Resistant Against the Atomic Oxygen

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**Abstract:** The work is devoted to studying the possibility of synthesizing a polymer composite, filled with high-dispersity modified [alpha]-$Al_2O_3$ and analyzing the resistance of its surface against the oxygen plasma oncoming flow. The main technologic phases of synthesizing the high-dispersity low-admixture aluminum oxide have been detailed. To make [alpha]-$Al_2O_3$ compatible with polymer it was modified with organosilicon compound-HSF-11 (hydrophobic silicone fluid), which provided the aluminum oxide with hydrophobic properties. According to physical and mechanical properties there was selected an optimal composition, containing to 70 mas. % of modified [alpha]-$Al_2O_3$ and possessing the optimum properties, as, if the loading of the filler is continued, the properties of the material begin to deteriorate. The paper also presents the results of treating the received composite with an oxygen plasma beam, formed in the magnetoplasmadynamic accelerator. The relief of the composite before and after treating was researched by the scanning electron microscopy. It was found out that during the oxygen plasma treating erosion processes on the surface of filled composite are not as intensive as on the surface of pure polystyrene.

**Key words:** [alpha]-$Al_2O_3$ · Modification · Polystyrene composite · Atomic oxygen · Oxygen plasma · Scanning electron microscope (SEM) image

## INTRODUCTION

Atomic oxygen (AO), which is characterized by the high chemical activity, is the main component of the Earth atmosphere at heights of 200-700 km, where there operate about half of all the space vehicles of various assignments [1]. The impact of the AO oncoming flow results in the intensive sputtering of the vehicle's outer surface matter. The influence of AO can also lead to substantial alteration of mechanical, optical, electrophysical, thermophysical and other performance properties of materials, which results in losing the important functional parameters [2,3].

The polymeric materials are most liable to this effect. For them, the layer thinning after the year of a space vehicle's flying in the mentioned range of heights can amount to 10-100 µm. In this regard there are developed different methods of improving the polymers' resistance against the atomic oxygen impact, particularly by modifying the near-surface layers of materials by introducing oxygen-resistant microparticles and nanoparticles of various compositions, from whence the material acquires actually the structure of a matrix composite [4].

This work is devoted to studying the possibility of synthesizing a polymer composite, filled with high-dispersity modified [alpha]-$Al_2O_3$ and analyzing the resistance of its surface against the oxygen plasma oncoming flow.

**Methodology:** There were studied polystyrene composites with various concentration of [alpha]-$Al_2O_3$. The process of receiving the high-dispersive powder of [alpha]-$Al_2O_3$ includes several basic technological phases:

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- Dissolving of aluminum chloride in water solution:

$$AlCl_3+H_2O \rightarrow [Al(OH_2)_6]^{3+}$$

- Receiving the white residuum of aluminum hydroxide, which has amorphous structure:

$$[Al(OH_2)_6]^{3+}+OH^- = [Al(OH)(OH_2)_5]^{2+}+H_2O$$
$$[Al(OH)(OH_2)_5]^{2+}+OH^- = [Al(OH)_2(OH_2)_4]^{+}+H_2O$$
$$[Al(OH)_2(OH_2)_4]^{+}+OH^- = [Al(OH)_3(OH_2)_3]^{0}+ H_2O$$
$$[Al(OH_2)_6]^{3+}+3\ OH^- = Al(OH)_3\downarrow$$

- Receiving the aluminum oxide by heating its hydroxide:

$$Al(OH)_3\ (t>1000°C) \rightarrow Al_2O_3$$

- To receive the aluminum oxide with low quantity of admixtures, which substantially improves its technological properties, there was used a method, described in [5]. The aluminum oxide was ground in the planetary mill within 35 minutes and then admixtures were removed with salt acid. The grinding was done with steel balls, 4 mm in size; and the admixtures were removed alternately with salt acid with concentration no less than 10 mas. % and alkali solution with concentration no less than 5 mas. % and then with salt acid again. The admixture removing with acid and alkali was done at heating to the temperature of about 85°C.

The received [alpha]-$Al_2O_3$ was presented by a white high-dispersive powder 3,89 g/cm$^3$ of density. To make [alpha]-$Al_2O_3$ compatible with polymer it was modified with an organosilicon compound-HSF-11 (hydrophobic silicone fluid), which provided the aluminum oxide with hydrophobic properties [6].

The granulometric analysis of the received aluminum oxide was done with a laser particle size analyzer «Microsizer 201C». The infrared study of the modified aluminum oxide was carried out with an « FT-IR spectrometer Verteõ70» in the wave numbers range 4000-350 cm$^{-1}$.

The modified filler ([alpha]-$Al_2O_3$) and the matrix (polystyrene) were mixed in the planetary mill. The composites were synthesized by solid-phase compaction method at specific pressure 200 MPa. The content of the filler in the composite material varied from 0 to 70 mas. %.

Bombardment with the oxygen plasma (OP) beam, formed in the magnetoplasmadynamic accelerator (Fig. 1), was carried out at the simulation unit of SRINP of Lomonosov Moscow State University. The beam of accelerated oxygen plasma consisted of atomic and molecular ions, fast atoms and oxygen molecules with energy up to 40 eV and of plasma electrons with energy 1-5 eV. The fluence density of atoms was ~10$^{15}$ at/cm$^2$•s and the fluence of atoms ~ 6,7•10$^{22}$ at/cm$^2$, the operating vacuum (0,5-2)•10$^{-2}$ Pa.

Three asymmetrical electrodes-cathode (3), ferromagnetic intermediate electrode (2) and anode (1) are located coaxially within the internal channel of a short solenoid (4). Between the hollow cathode, having the high thermionic property and anode the externally heated discharge is allowed within the discharge gap, into which the plasma-supporting gas $O_2$ is fed through pipe (7). The discharge gap is comprised of plasma, consisting of electrons, ions, neutral and activated atoms and operating oxygen molecules. Besides, the plasma is bound to contain particles of electrode matter due to its erosion.

The surface topography research and elemental microanalysis before and after oxygen plasma treatment were carried out with scanning electron microscope (SEM) EVO-40 by company Zeiss, provided with X-ray microanalysis detector Rontec XFlash.

**The Main Part:** In figure 2 there is shown the FT-IR spectrum of the received modified $Al_2O_3$. Absorption bands 740, 620 and 480 cm$^{-1}$, which are components of [alpha]-$Al_2O_3$, correspond to symmetrical ([neu]$_s$ Al-O) and asymmetrical ([neu]$_{as}$ Al-O) deformation and valence ([delta]$_{as}$ Al-O) vibrations of aluminum-oxygen bond [7]. Treating the aluminum oxide with an organosilicon fluid (HSF-11) results in appearing of absorption bands in the range of 2350 and 2380 cm$^{-1}$, which characterize, according to [8] valence vibrations of bond in organosiloxane compound and indicating the chemical inoculation of organosilicon groups to the surface. The weak absorption band at 2850 cm$^{-1}$ and the intensive absorption band at 3300-3600 cm$^{-1}$ correspond to the valence vibrations of O-H bond, which indicates the presence of undecomposed $Al(OH)_3$ residues in the material.

The wetting angle of the received modified [alpha]-$Al_2O_3$ is 125°, which indicates the high hydrophobic properties of the synthesized powder and its high compatibility with nonpolar polymeric matrices.

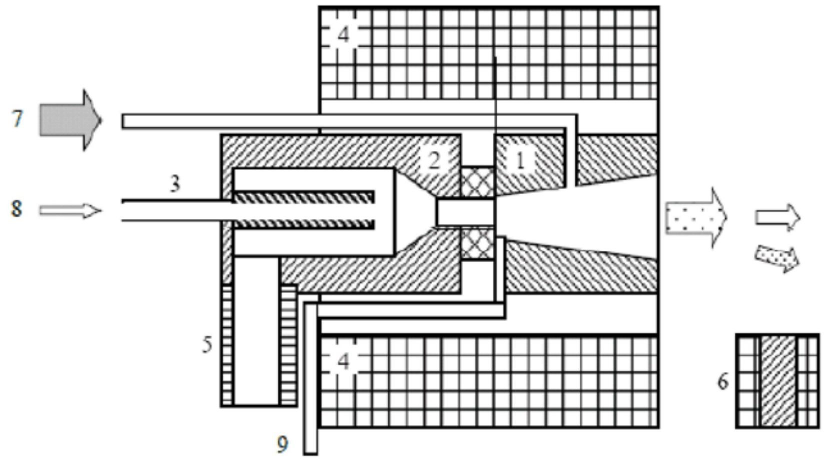


Fig. 1: Scheme of magnetoplasmadynamic accelerator: 1-anode; 2-ferromagnetic intermediate electrode; 3-hollow hot cathode; 4-solenoid; 5-additional vacuum pumping duct; 6-deflection electromagnet; 7-plasma-supporting gas pipe; 8-inert gas pipe; 9-feed route of protective gas $H_2$

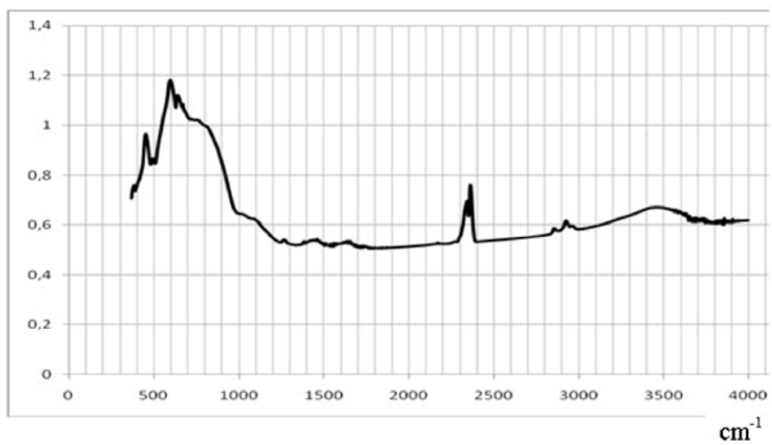


Fig. 2: FT-IR spectrum of the synthesized modified [alpha]-$Al_2O_3$

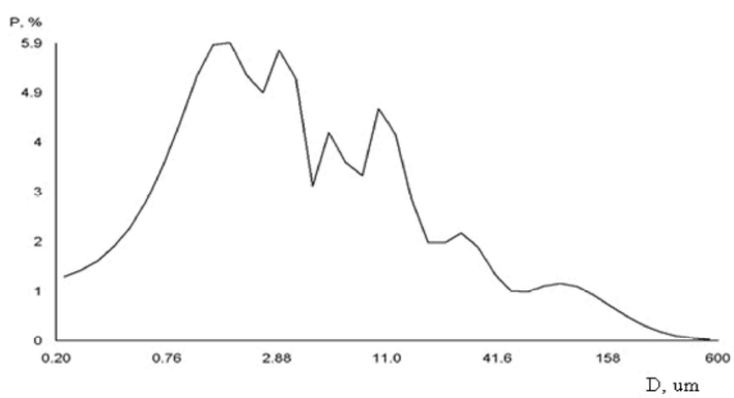


Fig. 3: Granulometric composition of the synthesized modified [alpha]-$Al_2O_3$

The granulometric analysis of the received modified [alpha]-$Al_2O_3$ (Fig. 3) indicates the high dispersity of the received oxide. The size of the biggest [alpha]-$Al_2O_3$ particle doesn't exceed 3 µm (Fig. 3).

The physical and mechanical properties of polystyrene-based composite with different content of the filler-modified [alpha]-$Al_2O_3$-are presented in table 1.

Table 1: Physical and mechanical properties of polystyrene composite with different content of modified [alpha]-$Al_2O_3$

| Content of modified [alpha]-$Al_2O_3$, mas. % | Parameter | | |
|---|---|---|---|
| | Density, kg/$m^3$ | Sound velocity, m/s | Modulus of elasticity, Å•$10^{-4}$, MPa |
| 0 | 1056 | 2197 | 0,510 |
| 30 | 1283 | 2314 | 0,687 |
| 50 | 1490 | 2383 | 0,846 |
| 70 | 1675 | 2616 | 1,146 |
| 90 | 1895 | 2356 | 0,789 |

The density of polystyrene composite increases by linear function with increasing the amount of introduced filler (Table 1).

According to physical and mechanical characteristics data, the optimum properties are shown by the composite, containing to 70 mas. % of modified [alpha]-$Al_2O_3$, as, if the loading of the filler is continued, the properties of the composite begin to deteriorate measurably. The decrease of elasticity modulus is connected with reducing the compatability of matrix and filler at the high concentration of the filler. In these circumstances the stoichiometric ratio in topochemical reactions between matrix and filler is altered, which results in the rapid change of polystyrene composite phase composition and as a consequence, decrease of elasticity parameter. So, the elasticity modulus value can be an orienting point at evaluating the composite material quality.

The samples of the designed composites were bombarded with oxygen plasma beams consisting of atomic and molecular ions, fast atoms and oxygen molecules with average energy 20 eV and of plasma electrons with energy of several eV. The value of atomic oxygen equivalent fluence was measured by alteration of KaptonH witness sample film thickness, with known values of mass erosion coefficient:

$$F = \Delta m_k / R_k \quad (1)$$

where $R_ê$=4,4•$10^{-24}$ g/atom O, the erosion coefficient of KaptonH witness sample [9]. All samples were treated with oxygen plasma within 3 hours, the fluence of atomic oxygen was ~ 6,7•$10^{22}$ at/$cm^2$.

After the oxygen plasma treating the surface morphology of polymeric composite was studied by method of scanning electron microscopy (SEM) combined with elemental analyses of the surface. In figure 4 there is shown the surface of pure polystyrene sample after treating it with oxygen plasma. In figure 4 we can see the surface relief, formed after bombardment with oxygen plasma; the surface has acquired the fibrous structure, typical for most of polymer materials [10, 11].

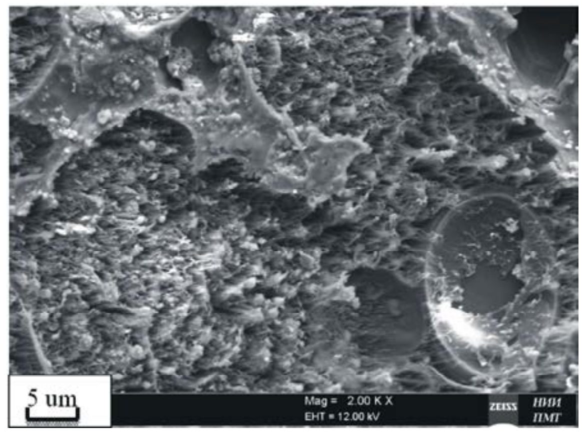


Fig. 4: SEM-image of the surface morphology of polystyrene, treated with oxygen plasma beam

During the normal oxygen plasma bombardment, on the surface there is formed a relief, consisting of closely-spaced separate or coalesced into ridges and cones columnar nanoformations (Fig. 4), oriented towards the plasma flow, i.å. perpendicularly to the surface. The space between columnar formations = 100 nm and between vortexes of cones ~ 1-2 μm. The thickness of separate columnar nanoformations is ~ 150 nm. There are observed the separate extended fibrillar formations of the same thickness, which connect vortexes of neighboring cones or ridges in the plane of pure polystyrene erosion surface.

The oxygen plasma effect on polystyrene results in the intensive destruction of its surface layer, without substantial crosslinking. At the disrupture of polymeric chains there are generated gaseous products ($CO_2$, $H_2O$, CO, $H_2$), which are removed from the material (carry-over) and become one of the factors of the characteristic surface structure forming [12].

In figure 5à there is given the image of a border between the oxygen-treated and untreated areas of pure polystyrene sample; and in figure 5b-the image of a border between the oxygen-treated and untreated areas of the composite containing 70 mas. % of modified [alpha]-$Al_2O_3$.

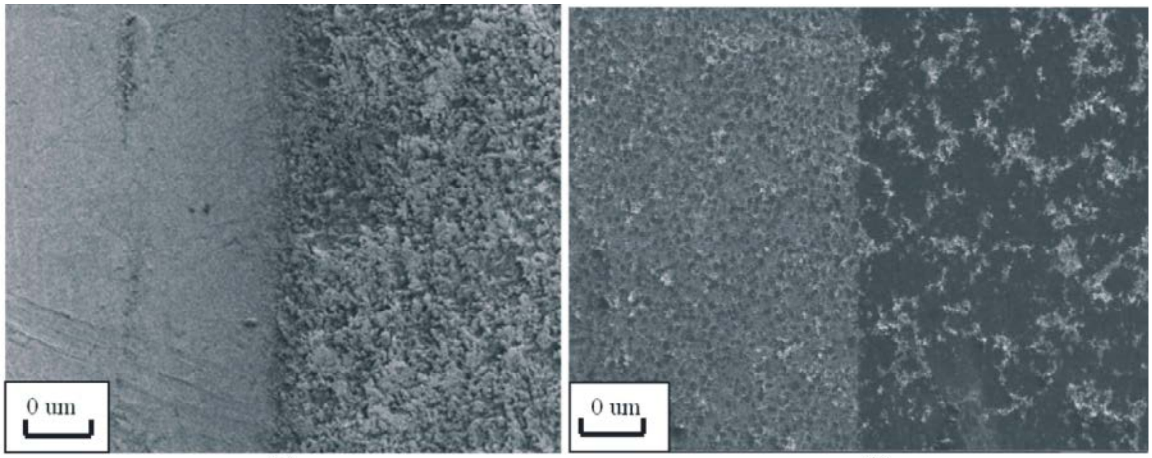


Fig. 5: The image of the border between the untreated area and area treated with oxygen plasma flow: à-pure polystyrene sample; b-polystyrene composite with 70 mas. % of modified [alpha]-$Al_2O_3$.

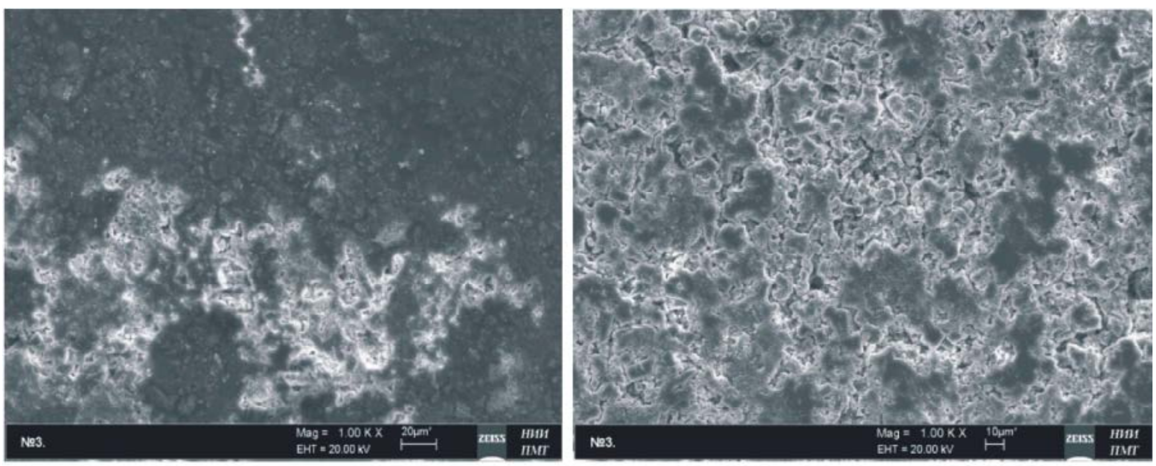


Fig. 6: The SEM-image of the surface morphology of composite with 70 mas. % of modified [alpha]-$Al_2O_3$ à) untreated and b) treated with oxygen plasma flow

After treating polystyrene with oxygen plasma the border between treated and untreated area is strongly pronounced (Fig. 5à) and on the treated surface there forms the erosional relief ~ 4-5 µm deep. Atomic oxygen induces the nonuniform destruction of the composite surface and there is formed the relief, presented by indents and protruding areas of conical and needle shape, oriented towards the oncoming atomic oxygen flow (Fig. 5).

The analysis of figure 5 has shown that during the oxygen plasma treating erosion processes on the surface of filled composite are not as intensive as on the surface of pure polystyrene. It is known, that aluminum oxides and nitrides are chemically inert to atomic oxygen, so their sputtering by oncoming flow is negligible [13].

The initial surface of the composite has smooth uniform structure with nanoscale roughness (Fig. 6à). After oxygen plasma treating on the surface of the composite there forms the erosional relief, ~ 2-3 µm deep (Fig. 6b). In figure 6b we can see crystals of [alpha]-$Al_2O_3$ and in figure 6à they are covered with amorphous structure (polystyrene).

It is known that materials containing certain chemical elements (Al, Si, P etc.), in their structure are characterized by increased resistance against the atomic oxygen flow, as these elements play a key role in forming on the surface of the materials the stable protective structures in the form of involatile oxides or glasslike substances when these materials are placed in the aggressive medium [14]. The increased resistance of these materials against strong oxidizing agents (including atomic oxygen) is based on the surface conversion mechanism, i.e. protective layer forming. When atomic oxygen hits polystyrene particles, part of oxygen atoms form the $O_2$ molecules, which leave the surface, another part (30-50 %) of O atoms are springily reflected and the third part (10-50 %) penetrate into the material and chemically interact with it, inducing series of conversions (chemical destruction) [15] and when oxygen atoms hit the particles of the filler ([alpha]-$Al_2O_3$) they are springily reflected. So, the structure formed on the composite surface prevents further degradation of the composite, reducing the material's wear.

At forming such a surface structure the erosion coefficient is minimal and doesn't alter at increasing the time of oxygen treating.

## CONCLUSION

There have been developed the main technologic phases of synthesizing high-dispersity low-admixture aluminum oxide. According to the granulometric analysis of the received modified [alpha]-$Al_2O_3$, the size of its biggest particle doesn't exceed 3 µm, which indicates the high dispersity of the received oxide. Treating the aluminum oxide with organosilicon fluid (HSF-11) results in chemical inoculation of organosilicon groups to the surface, which provides the aluminum oxide with hydrophobic properties and good compatibility with polymeric non-polar matrices. According to physical and mechanical properties there was selected an optimal composition, containing to 70 mas. % of modified [alpha]-$Al_2O_3$ and possessing the optimum properties, as, if the loading of the filler is continued, the properties of the composite begin to deteriorate. The relief of the received composite before and after treating it with oxygen plasma oncoming flow has been studied by method of scanning electron microscopy. It has been found out that during the oxygen plasma treating erosion processes on the surface of filled composite are not as intensive as on the surface of pure polystyrene.

**Conclusions:** According to the experimental data, the designed polystyrene composite, filled with the modified [alpha]-$Al_2O_3$ in the amount of 70 mas. % is highly resistant against the atomic oxygen, formed in the magnetoplasmadynamic accelerator. The further research should be aimed at studying the integrated effect of the near space negative impacts on the designed polystyrene composite, filled with the modified [alpha]-$Al_2O_3$.

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