The study of relief parameters of fluorocarbon coatings antiadhesive to microorganisms formed on polymer materials

V M Elinson¹, E D Kravchuk¹ and P A Schur¹,²

¹ Moscow Aviation Institute (National Research University), Volokolamskoe sh. 4, 125993 Moscow, Russia
² All-Russian Institute of Aviation Materials (VIAM), Radio 17, 105005 Moscow, Russia

E-mail: shur-pavel@mail.ru

Abstract. The problems of the formation of fluorocarbon coatings in a plasma-forming mixture CF₄ + C₆H₁₂ on the surface of polyethylene terephthalate and polytetrafluoroethylene by ion-plasma technology are considered with the aim of increasing mushroom resistance, in particular, the relief parameters of the formed coatings (root-mean-square deviation of the roughness, average high heterogeneity peaks, average distance between peaks) and their influence on mushroom resistance.

The problem of destruction of polymeric materials under the influence of microorganisms becomes more relevant with the growth of their production and variety. Equipment failure, failure of various systems, destruction of structural elements, crew safety in a confined space - this is only a small part of what undesirable activity of microorganisms can lead to. This problem also carries serious economic losses, which are estimated at 2-5% of the gross domestic product of countries with developed industry [1].

Natural and synthetic polymeric materials, metals, inorganic minerals are subject to biodestruction. During operation and storage, they are adversely affected by various microorganisms, among which the most aggressive are microscopic fungi. Damage to polymers by mold fungi occurs not only as a result of mechanical destruction by expanding mycelium, but also from exposure to polymers of fungal metabolism products [2, 3]. Such significant damaging activity of molds is due to their ability to adapt to materials of various chemical nature.

In this regard, it is necessary to create barrier layers on the surface of polymeric materials in order to increase their resistance to biodegradation. The method of two-stage surface treatment by the methods of ion-plasma technology was presented in [4, 5], which allows to create nanostructured barrier layers (NBL) on the surface of polymer materials based on fluorocarbon films from a CF₄ gas mixture (a component that etches the surface) + C₆H₁₂ (component for film deposition). The layers created in the field of transient processes (the area in which competing processes of film deposition and its simultaneous etching take place) have a specific relief and can reduce the adhesion of microbial cells, which increases the resistance to biodegradation and allows to increase the service life of products made of polymeric materials. To obtain the clearest character of the surface topography, it is advisable to use the following parameters: Rq (root-mean-square deviation of the roughness), Hav (average height of the inhomogeneity peaks) and Dav (average distance between the peaks).
Thus, the aim of this work is to study the relief of nanostructured fluorocarbon coatings formed on polymeric materials by the methods of ion-plasma technology using a two-component gas mixture $\text{CF}_4 + \text{C}_6\text{H}_{12}$ and to reveal the dependence of the mushroom resistance of the samples on the relief parameters.

The two-stage formation of the NBL was carried out on a UVN71-P3 vacuum unit equipped with two ion sources II-4-0.15 («Radical»). At the first stage, using a first ion source, ion treatment was carried out using an ionized beam of tetrafluoromethane ($\text{CF}_4$) for 30 minutes in order to improve the adhesion of the fluorocarbon layer, clean the polymer surface and create a preliminary relief. At the second stage, using a second ion source, a fluorocarbon film was deposited in a gas mixture with a different ratio of tetrafluoromethane ($\text{CF}_4$) and cyclohexane ($\text{C}_6\text{H}_{12}$) for 20 minutes [6].

The surface parameters were measured using an NT MDT Solver Next scanning probe microscope with an AFM head in the tapping mode. Mushroom resistance studies were carried out according to GOST 9.049 - 91. To study the adhesive properties, strains of fungi Aspergillus niger van Tieghem, Aspergillus terreus Thom, Penicillium funiculosum Thom, etc. were used. Material samples were examined using a Stemi 2000 stereo microscope.

As model polymers, polytetrafluoroethylene (PTFE) and polyethyleneterephthalate (PET) were chosen as one of the most used polymers in aviation, astronautics and electronics. PET is of great interest in the production of flexible printed circuit boards, it has also been widely used as a chemically resistant insulating material, a material for the manufacture of cases and parts of products, PET films are used as a substrate for photosensitive materials and in the manufacture of capacitors [2, 3]. PTFE has been widely used as insulation for wires, which does not deteriorate in a wide temperature range, as anti-adhesive and non-stick coatings, and also as filters [2, 7].

![Figure 1](image.png)

**Figure 1.** The dependence of the $R_q$ on the $\text{CF}_4$ content in the plasma-forming mixture during the formation of the fluorocarbon layer after the surface treatment of PET with $\text{CF}_4$ ions.

Figure 1 shows that surface treatment with $\text{CF}_4$ ions increases the $R_q$ index by almost 2 times, compared with the initial sample. With the subsequent deposition of the fluorocarbon film, the root-mean-square deviation of the roughness $R_q$ increases up to the boundary of the transient region; in this region, a monotonic decrease in the mean-square deviation of the $R_q$ profile occurs. A further increase in the $\text{CF}_4$ content in the plasma-forming mixture and going beyond the boundary of the transient region leads to the fact that the $R_q$ returns to values with the $\text{CF}_4$ content from 10 to 30%.
Figure 2. Dependence of the average height of the inhomogeneity peaks on the CF$_4$ content in the plasma-forming mixture during the formation of the fluorocarbon layer after the surface treatment of PET with CF$_4$ ions.

A similar situation is observed for the average peak height (figure 2). Surface treatment with CF$_4$ ions leads to a significant increase in the index (from 9.9 nm to 27.5 nm). When depositing a fluorocarbon film with a CF4 content of 20-30%, the height of the inhomogeneity peaks continues to increase and reaches a maximum value for this relief of 38 nm. However, in the transient area, by analogy with the root-mean-square deviation of the roughness $R_q$, a monotonic decrease in the average height of the inhomogeneity peaks occurs with the CF$_4$ content in the gas mixture approaching 60%, that is, to the “upper” boundary of the transient area. Outside the “upper” boundary of the region, the peak height returns to values with a CF$_4$ content of 20 to 30%.

Figure 3. Dependence of the average distance between the peaks of heterogeneity on the CF$_4$ content in the plasma-forming mixture during the formation of the fluorocarbon layer after the surface treatment of PET with CF$_4$ ions.
For the average distance between the inhomogeneity peaks (figure 3), the inverse relationship is the dependence of the root-mean-square deviation of the roughness Rq or the average height of the inhomogeneity peaks. When treating the surface with CF₄ ions, the distance between the peaks decreases from 150 nm to 67 nm. The application of the fluorocarbon layer first leads to an increase in the distance (up to 350 nm), and with an increase in the content of CF₄, to a sharp decrease in the distance. In the transient area (30-60% CF₄), the average distance between the peaks of the inhomogeneity increases with a simultaneous decrease in the height of the peaks, which indicates smoothing of the surface topography. With a subsequent increase in the CF₄ content over 60%, the distance between the peaks of the inhomogeneity decreases and tends to a value when the surface is treated with CF₄ ions, which indicates the prevailing etching processes [8].

![Height of peaks, nm](image)

**Figure 4.** Dependence of the height of the inhomogeneity peaks on the CF₄ content in the plasma-forming mixture during the formation of the fluorocarbon layer after surface treatment of PTFE with CF₄ ions.

The nature of the change in the surface parameters of PTFE modified with fluorocarbon coatings is similar to the dependence of the surface parameters on the content of tetrafluoromethane on PET (figure 4).

| Treatment CF₄, 30 min. | CF₄ (%) | C₆H₁₂ (%) |
|-----------------------|--------|-----------|
| Initial sample        | 2      | 2-3       |
| Treatment CF₄, 30 min. | 1      | 1         |
| 0                     | 100    | 1         | 2         |
| 10                    | 90     | 1         | 1         |
| 25                    | 75     | 0-1       | 0         |
| 40                    | 60     | 0         | 0         |
| 60                    | 40     | 0         | 0         |
| 70                    | 30     | 1         | 0         |
| 100                   | 0      | 1         | 1         |

**Table 1.** Fungi resistant.

Figure 3 shows the size distribution of mesopores. The size distribution curves of mesopores for both samples are almost identical and have a pronounced peak corresponding to the presence in the samples of a large group of pores with a size of about 40 Å.
To study the microporous structure, the initial parts of the nitrogen adsorption isotherm was fixed at the relative pressure \( p/p_0 = 0.0001 - 0.01 \). The micropore distribution by size is shown in figure 4. Quantitative characteristics of the microporous structure are shown in table 2.

From table 1 it is seen that the ion surface treatment leads to an increase in resistance to biodegradation of both polymeric materials. It was found that the growth of fungi on modified PET samples ceases in the transient area from 40% to 60% of the fluorine-containing component in the plasma-forming mixture \( \text{CF}_4 + \text{C}_6\text{H}_{12} \).

The results obtained allow us to draw the following conclusions:

1) Treatment with \( \text{CF}_4 \) ions of the PET surface increases its mushroom resistance to 1 point. Rq and the average height of the peaks of heterogeneity increase when depositing a fluorocarbon coating, and the distance between the peaks of the heterogeneity decreases.

2) In the transient area, the dependences of the parameters on the \( \text{CF}_4 \) content in the plasma-forming mixture change their character to the opposite, Rq and the average height of the inhomogeneity peaks decrease, and the average distance between the inhomogeneity peaks increases.

3) On PET samples with a 30-minute treatment with \( \text{CF}_4 \) ions and a fluorocarbon coating with 40% and 60% \( \text{CF}_4 \) content in the plasma-forming mixture, mold growth was not detected, which indicates the formation of release coatings in relation to mold fungi.

4) The nature of the change in the surface parameters of PTFE modified by fluorocarbon coatings is similar to the dependence of the surface parameters on the content of tetrafluoromethane on PET.

5) Apparently, there is a region of parameters in which release coatings in relation to mold fungi are formed. This area requires further study in order to clarify.

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