Antimicrobial antiadhesive properties of nanostructured fluorocarbon films obtained under transient conditions using two-component gas mixtures

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Abstract. The main factors that determine the possibility of obtaining nanostructured fluorocarbon films with antimicrobial antiadhesive properties when forming them under the conditions of transient processes when using two-component gas mixtures are considered. An experimental test of the formed coatings for resistance to biodegradation was carried out.

The possibilities of creating polymeric materials with a wide range of physicochemical properties led to their successful use in microelectronics, radio engineering, the aerospace complex, etc. as construction materials, components of polytronics, discrete components. One of the main operational characteristics limiting the use of products from polymeric materials is low resistance to biodegradation [1, 2].

It is known [3] that the key stage in the formation of biofilms with which leads to biodegradation process is the adhesion of single microbial cells of microorganisms on the surface of polymers. Next, microcolonies are formed, then exomatrix appears and a mature biofilm with nomads gradually forms. To remove the formed biofilm it is necessary to use biocidal substances and materials.

In order to exclude the occurrence of these processes, barrier layers based on nanostructured fluorocarbon films with antimicrobial anti-adhesive properties were proposed in [4–6].

The antiadhesive properties of nanostructured fluorocarbon films are determined by two factors: the effect of fluorine and the appearance of a specific surface relief, at which the distance between the protrusions is commensurate with the size of the cells of the microorganisms. Such a nanorelief is formed on the surface of polymers under the conditions of transient processes (transition from deposition of films to etching) using two-component gas mixtures containing the component for applying films (C₆H₁₂) and the component for etching films (CF₄ or C₄F₈).

C₄F₈ is technologically safe, widely used in technologies for creating elements of microelectronics, in particular in Bosh - processes [7, 8]. CF₄ is also widely used in microelectronics technology [5, 6].

The purpose of this work is to identify and experimentally test the main factors that determine the possibility of forming nanostructured fluorocarbon films on the surface of various polymeric materials.

The formation of barrier layers was carried out on a vacuum unit EVD71-P3, equipped with two sources of ions II-4-0.15. At the first stage, the polymer surface was treated with tetrafluoromethane...
(CF₄) ions for 10 and 30 minutes using a single ion source to clean the surface, improve the adhesion of the fluorocarbon film, and create a preliminary nanorelief. At the second stage, a fluorocarbon film was deposited using two-component gas mixtures CF₄ + C₆H₁₂ and C₄F₈ + C₆H₁₂ with a different ratio of components using a second ion source.

Polyethyleneterephthalate (PET), polytetrafluoroethylene (PTFE) and polyethylene terephthalate-based track membranes were chosen as model polymers as one of the most widely used polymers in aviation, astronautics, electronics and medicine [1, 2, 4].

Fungus resistance studies were carried out according to GOST 9.049–91.

The results of the study of the fungus resistance of the formed fluorocarbon coatings on model polymer materials are presented in table 1. In any polymer materials presented, the formation of fluorocarbon coatings from a two-component gas mixture CF₄ + C₆H₁₂ leads to an increase in the antifungal activity, which is manifested in a decrease in fungus resistance for PET from 2 (untreated) to 0 points, both at 10 minute preprocessing, and at 30 - minute processing. A similar dependence is observed for PTFE, in which there is an increase in fungi resistance from 2-3 points to 0. It is also possible to increase the fungi resistance of PET membrane track membranes from 3 to 0 (30% CF₄).

A distinctive feature of the use of a two-component gas mixture of CF₄ + C₆H₁₂ is the presence of a transient process area, which manifests itself at 30-60% CF₄ in the gas mixture. This area combines a number of specific characteristics [4–6], which together lead to the appearance of anti-adhesive properties on the surface of microorganisms, which in turn leads to an increase in fungus resistance. This phenomenon is presented in table 1, which shows that on samples of PET, PTFE, when a fluorocarbon coating formed on the surface of a transient process forms on their surface, there is no adhesion of microbial cells (0 points). Similar effects are observed on the surface of polymer track membranes (PET TM).

| Treatment                  | PET | PTFE |
|----------------------------|-----|------|
| Untreated                  | 2   | 2-3  |
| Treatment CF₄, 10 min      | 1   | 1-2  |
| Treatment CF₄, 30 min      | 1   | 1    |

| CF₄ (%) | C₆H₁₂ (%) | CF₄ (%) | C₆H₁₂ (%) |
|---------|-----------|---------|-----------|
| 0       | 100       | 0       | 100       |
| 10      | 90        | 0       | 100       |
| 25      | 75        | 0       | 100       |
| 40      | 60        | 0       | 100       |
| 60      | 40        | 1       | 100       |
| 70      | 30        | 1       | 100       |
| 100     | 0         | 1       | 100       |

| Treatment CF₄, 30 min      | 1   | 1    |
| Treatment CF₄, 10 min      | 1   | 1    |
| Treatment CF₄, 30 min      | 1   | 1    |

Pretreatment of polymeric materials also plays a significant role. This treatment with CF₄ ions, apparently, can change the surface relief and shift the region of effective parameters (antifungal activity) of the coatings formed over the nanostructured surface.

When using a two-component fluorocarbon gas mixture C₄F₈ + C₆H₁₂ (table 2), an improvement in the antifungal properties on PET is also manifested when applying coatings with different C₄F₈ contents in the mixture. At the same time, the complete absence of growth of fungi is observed at the highest fluorine content in the gas mixture, at which it is possible to apply a coating, namely, at 60%
CF₄ in the gas mixture. With a higher content of octafluorocyclobutane in the gas mixture, etching processes occur [9].

When using CF₄ + C₆H₁₂ or C₄F₈ + C₆H₁₂, antifungal properties can be achieved (0 points), however, the content of the fluorine-containing component in gas mixtures is different.

| Treatment          | CF₄ + C₆H₁₂ | C₄F₈ + C₆H₁₂ |
|-------------------|-------------|---------------|
| Untreated PET     | 2-3         |               |
| Treatment CF₄/C₄F₈, 30 min | 1           | 2             |
| CF₄ (0%) / C₆H₁₂ (100%) | 1           | 1             |
| CF₄ (10%) / C₆H₁₂ (90%) | 0           | 1             |
| CF₄ (25%) / C₆H₁₂ (75%) | 0-1         | 1             |
| CF₄ (40%) / C₆H₁₂ (60%) | 0           | 1             |
| CF₄ (60%) / C₆H₁₂ (40%) | 1           | 0             |

The obtained results allow us to draw the following conclusions:

1. As a result of the work, the effect of the following factors on the antifungal properties of the fluorocarbon coatings formed is isolated and experimentally confirmed:
   - conditions for pretreatment of the polymer surface;
   - structure and composition of the fluorine-containing component;
   - the ratio of components for deposition and etching in a two-component gas mixture.

2. It is shown that the influence of the structure and composition of the polymer is relatively small and has little effect on the overall course of the dependence of the antifungal properties on the parameters studied.

3. The possibility of forming nanostructured fluorocarbon coatings with anti-adhesive properties against microorganisms, both on the surface of continuous polymeric materials and on the surface of track membranes using two-component gas mixtures CF₄ + C₆H₁₂ and C₄F₈ + C₆H₁₂, is shown.

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