Investigation of the surface properties of anti-adhesive antimicrobial coatings formed by ion-plasma technology on the surface of polyethylene terephthalate and polytetrafluoroethylene

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Abstract. The paper is devoted to the problem of fight with biodestruction, the presence of which defines the duration of effective exploitation of polymeric materials and wares. The results showed the possibility of creating a field of transient processes that prevent the adhesion of microbial cells on the surface of polymeric materials. The specified transient area is the result of the optimum fluorine content in the film and the formed relief, which together ensure the absence of adhesion of microbial cells. The relief characteristic for the field of transient processes is different for polymers of various chemical structure. The study of antifungal activity showed that the areas of transient processes in different polymeric materials, ensuring the absence of cell adhesion of microorganisms and fungi, almost coincide.

1. Introduction
The duration of effective operation of polymeric materials and products is determined by the speed of their destruction. A special role in these processes is played by the destruction under the influence of microorganisms (biodestruction). It is well known that biodestruction is the result of the formation and development of biofilms [1–3]. Figure 1 shows the stages of biofilm formation [3]. The first stage of biofilm formation is the formation of germ-free protein film (figure 1(a)). Then adhesion of single S.aureus cells occurs (figure 1(b)). Figure 1(c) shows the formation of microcolonies (after 24 and 48-hour incubation), in figure 1(d) – the beginning of the formation of the exomatrix, and in figure 1(e) – formation of a mature biofilm with nomads. For comparison, figure 1(f) shows a mature biofilm of Ps. Aeruginosa [4, 5]. Excluding the stage of adhesion, which plays a key role in the formation of biofilms, then it is possible thereby to exclude the formation of a biofilm and the subsequent biodestruction of products from polymeric materials. Thus, one of the most promising approaches to prevent biodestruction of polymeric materials is to create on the surface of polymers and products from them barrier layers that prevent the adhesion of microorganisms to the surface, which in turn prevents the formation of biofilms and subsequent biodestruction. The most active layers in this regard can be formed on the basis of fluorocarbon films [4].

2. Nanostructured fluorocarbon barrier layers deposition
The formation of nanostructured barrier layers consists of 2 stages. At the first stage, the initial polymer is treated with a stream of CF₄ ionized particles with the formation of a nanostructured
surface (NSS). At the second stage, the formed NSS is exposed to the gas mixture \( \text{CF}_4 + \text{C}_6\text{H}_{12} \), so the deposition of films, their etching and the release of products of ion-chemical etching. Nanostructured barrier layers (NBL) are formed on the polymer surface.

Nanostructured barrier layers [6, 7], formed by ion-plasma technology using a two-component plasma-forming mixture \( \text{CF}_4 + \text{C}_6\text{H}_{12} \), containing a component for film deposition (\( \text{C}_6\text{H}_{12} \)) and a component for etching (\( \text{CF}_4 \)) allows not only to apply films and etch them, but and adjust the relief of the film and the fluorine content in it. All these processes occurring simultaneously, allow us to form a transient area, which will be shown below.

The structure of the NBL formed on the surface of polytetrafluoroethylene (PTFE) [4, 6] was studied using a Quanta 200 3D dual-beam ion-electron scanning microscope (FEI Company, USA) in high vacuum mode, and the composition was studied using the Genesis XM 2 attachment (EDAX, USA) to a scanning electron microscope.

### 3. Analysis of the chemical composition, roughness and antifungal activity of barrier layers

Content of fluorine, carbon, and oxygen, as well as the surface relief, change dramatically with varying ratios of \( \text{CF}_4 \) and \( \text{C}_6\text{H}_{12} \) in the gas mixture (table 1). The atomic ratio (at at%) of carbon and fluorine at different ratios of \( \text{CF}_4 \) and \( \text{C}_6\text{H}_{12} \) in the gas mixture shows that the maximum fluorine content is observed for the initial sample, the sample with a nanostructured surface (without NBL) and when applying NBL from a gas mixture with 70% \( \text{CF}_4 \) content. For samples containing 10, 30, 40 and 60% \( \text{CF}_4 \) in the gas mixture, the carbon content increases with decreasing fluorine content. Samples containing 40 and 60% \( \text{CF}_4 \) in the gas mixture attract particular attention. They have a similar topography and very close composition.

The same samples are presented in figure 2 before incubation and after 5-day incubation of \( A. \text{Staphylococcus} \) [6]. This figure clearly shows that it is samples No. 4 and No. 5 that demonstrate the absence of adhesion of microorganisms on the surface of the NBL, and the remaining samples show
the formation of biofilms at various stages. The area of lack of adhesion, which is determined by the fluorine content in the film and the specific surface relief, is the “area of transient processes”.

Table 1. X-ray microanalysis of the surface of PTFE samples (element atomic content).

| Sample                                      | F, %  | C, %  | O, % |
|---------------------------------------------|-------|-------|------|
| PTFE untreated                              | 43.01 | 50.60 | 5.67 |
| PTFE + Treatment CF₄                        | 33.63 | 60.19 | 5.52 |
| PTFE + Treatment CF₄ + Film (10% CF₄ + 90% C₆H₁₂) | 32.37 | 61.55 | 5.34 |
| PTFE + Treatment CF₄ + Film (30% CF₄ + 70% C₆H₁₂) | 30.44 | 63.53 | 5.35 |
| PTFE + Treatment CF₄ + Film (40% CF₄ + 60% C₆H₁₂) | 42.11 | 53.92 | 3.22 |
| PTFE + Treatment CF₄ + Film (60% CF₄ + 40% C₆H₁₂) | 33.54 | 59.62 | 6.14 |
| PTFE + Treatment CF₄ + Film (70% CF₄ + 30% C₆H₁₂) | 48.17 | 45.75 | 5.22 |

Figure 2. Interaction of Staphylococcus aureus with NBL, formed on the surface of PTFE with different content of CF₄ in the plasma-forming mixture

The results presented in figure 3 show the presence of a peak of the mean square surface roughness (Rq) and the formation of a specific relief on the surface of polyethyleneterephthalate (PET) coated with NBL when the content of CF₄ in the gas mixture is from 40 to 60%.

Figure 3. Dependence of the root-mean-square surface roughness (Rq) for PET on the content of CF₄ in the plasma-forming mixture.
The obtained Rq results using AFM (NT MDT, SolverNext) indicate that the area of transient processes on polymers of various chemical structures almost coincide.

Table 2 shows the results of antifungal activity study in accordance with the state standard GOST 9.049-91 in points when using a suspension containing \textit{Penicillium expansum}, \textit{Penicillium aurantiogriseum}, \textit{Aspergillus versicolor}, \textit{Aspergillus sydowii} and \textit{Cladosporum cladosporioides}.

The study of antifungal activity showed that the areas of transient processes, demonstrating the absence of adhesion of fungi, almost coincide for polymers of different chemical nature.

Table 2. The results of the study of the antifungal activity of the NBL of various polymeric materials.

| Sample | Value |
|--------|-------|
| PTFE untreated | 2-3 |
| PTFE + Treatment CF$_4$ + Film (40% CF$_4$ + 60% C$_6$H$_{12}$) | 0 |
| PTFE + Treatment CF$_4$ + Film (60% CF$_4$ + 40% C$_6$H$_{12}$) | 0 |
| PET untreated | 2 |
| PET + Treatment CF$_4$ + Film (30% CF$_4$ + 70% C$_6$H$_{12}$) | 1-2 |
| PET + Treatment CF$_4$ + Film (40% CF$_4$ + 60% C$_6$H$_{12}$) | 0 |
| PET + Treatment CF$_4$ + Film (60% CF$_4$ + 40% C$_6$H$_{12}$) | 0 |

4. Conclusions
The obtained results allow drawing the following conclusions:

1. Possibility of creating a field of processes that prevent the adhesion of microbial cells on the surface of polymers of various chemical structures is shown.

2. The specified area of transient processes is the result of the optimum fluorine content in the film and the formed relief, which together ensure the absence of adhesion of microbial cells.

3. It was also shown that the relief characteristic of the transient process region and ensuring the absence of cell adhesion of microorganisms is different for polymers of various chemical structures.

4. The study of antifungal activity showed that the areas of transient processes that ensure the absence of cell adhesion of microorganisms and fungi almost coincide for different polymers.

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