Nanostructured fluorine-containing surfaces: physicochemical properties and resistance to biodestruction

V.M. Elinson¹, L.V. Didenko², N.V. Shevlyagina³, G.A. Avtandilov³, A.N. Lyamin¹, O.A. Silnitskaya¹

¹Moscow Aviation Institute (National Research University), 125993, Volokolamskoe Shosse, 4, Moscow, Russia
²Gamaleya Research Center for Epidemiology and Microbiology Ministry of Healthcare, 123098, Gamaleya str, 18, Moscow, Russia
³Moscow State Medical and Stomatological University Ministry of Healthcare, Delegatskaya str, 20 bld.1, Moscow, Russia

Biodestruction of materials is one of the main problems limiting the application of polymeric materials and wares in biological aggressive medium. It is possible to cite a great numbers of instances from various fields of science and technique which demonstrate the importance of the problem for fight with the biodestruction of polymeric materials and wares. In present chapter on the base of scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX) data and research of total surface energy and surface relief parameters of various nanostructured fluorine-containing surfaces, formed by means of ion-plasma technology, the study of the processes of colonization by *Staphylococcus aureus* cells of different fluorine-content surfaces are under discussion. It was shown that the intensity of colonization is connected with fluorine content on the surface, as well as with the relief type of treated samples. It was also established, that nanostructures formation, accompanying by sharp decrease of surface energy, prevents *Staphylococcus aureus* cells adhesion on the fluorine-containing surfaces.

**Keywords:** Biodestruction; colonization; adhesion; *Staphylococcus aureus*; nanostructured fluorine-containing surfaces; ion-plasma technology; SEM-EDX; relief type; surface energy

1. Introduction

Biodestruction of materials is one of the main problems limiting the application of polymeric materials and wares in biological aggressive medium. The actuality of the fight with biodestruction suitably to polymers constantly increases because the input of polymers and polymeric wares also increases and their assortment is widening. It is possible to cite a great numbers of instances from various fields of science and technique which demonstrate the importance of the problem for fight with the biodestruction of polymeric materials and wares [1-4].

In electronic technique now the field of electronics, named polytronic, is highly growing, where the active elements are formed on the base of organic polymeric materials [5].

In medicine a wide use of artificial implanted devices has developed new ecological niche for microorganisms which colonize surfaces and form biofilms. Biofilms formation promotes to survival of bacteria, provides the increase of their resistance to antibacterial and disinfection means, effect to unfavorable factors of media and immunity protection of organism-host. Biofilms formation on implanted devices (catheters, artificial heart valves and other implants) leads, from one hand, to the progress of heavy hardly cured chronic diseases and from another one – to biodestruction of materials and wares, where they have formed [6,7].

Now a number of industrial protective fluorine-containing materials is well known, the sample of which is PROTECTGUARD FT®, possessing the low value of surface energy and, as a consequence, high hydro- and oleophobic characteristics, high water and vapor resistance and other properties [8]. The coatings with low surface energy also related to them: one-layered on the base of perfluoroethers [9] and two-layered systems on the base of polystereone block-copolymers, modified by liquid crystals with fluorine-containing groups [10]. Such materials are of great interest in relation of study of colonization of their surfaces by microorganisms and resistance to biodestruction.

The stability of materials to microbial colonization and their resistance to biodestruction determines the safety and durability of their use. The adhesion of microorganisms to the materials surface is a key step for the realization of all subsequent processes of biodestruction. In this connection, the important task is a search the ways to modify the surface of different kind material that can provide stability to microbial adhesion and resistance to biodestruction.

One of the perspective approaches for creation of such materials is formation of antimicrobial nanostructured barrier layers by means of various methods of ion-plasma technology [7,11-13], the use of which permits to form nanostructured barrier layers on the surface of polymeric materials no touching the main material and to combine the aim functional properties of materials and wares with providing their surface antimicrobial properties.

The aim of the present research was a study of surface energy and relief parameters of nanostructured fluorine-containing surfaces based on polytetrafluoroethylene (PTFE), surface of which was modified by different methods of ion-plasma technology and detection of biodestruction under influence of *Staphylococcus aureus*. 
2. Materials and methods

For research in the present work samples of PTFE, samples of PTFE, formed by ions CF$_4$ treatment of PTFE during 30 minutes with the following modification of nanostructured surface by deposition of fluorine-containing films under the use of gas mixture CF$_4^+$ C$_6$H$_{12}$ with different content of CF$_4$ have been used. The choice of the samples was defined by the necessity to study the influence of fluorine content, the influence of the mode for forming of fluorine-containing film and the mode for surface treatment. The samples under research are presented in Table 1. Methods for surface treatment and films formation are written in [7,11-13] in details.

*Staphylococcus aureus* was chosen as biodestructioner because, as it was shown before, this microorganism possesses high destructive potential in relations to some polymeric materials [3,4].

2.1 Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX)

The samples of the fluorine-containing materials were incubated in LB (Luria-Bertani) nutrient together with *Staphylococcus aureus* ATCC 25923 during 5 days at room temperature. Additional enrichment of LB nutrient during incubation with materials was not carried out. After incubation samples of fluorine-containing materials were fixed in 10% neutral aqua solution of formalin, were drying at room temperature during 10 minutes and were mounted onto aluminum stubs.

Estimation of the samples surface structure was carried out in the dual-beams scanning electron microscope Quanta 200 3D (FEI Company, USA) in high vacuum mode at accelerating voltage 5 and 10 kV after sputtering with gold (999) in the SPI-Module Sputter/Carbon Coater System (SPI Inc., USA). Analysis of chemical elements was realized by method of energy dispersive X-ray analysis (EDX) using the attachment Genesis XM2 (EDAX, USA) to the scanning electron microscope Quanta 200 3D. Mapping of elements was performed at accelerating voltage at 10 kV in high vacuum mode, magnification 2000x, counts per second=2000, dead time=20-40% and working distance 15 mm. The combination of the original image with the image with signals of elements was performed using LiveSpecMap Viewer (EDAX; USA) software application.

2.2 Study of total surface energy.

Study of total surface energy was carried out on the base of measurement of contact wetting angles. Values of contact wetting angles were obtained on horizontal microscope “MG” with honiometer attachment in conditions of leakage of two liquids – water and octane. All measurements were fulfilled at 20°C. Angles measurement accuracy was ± 1°. Total specific surface energy of solid state $\sigma_S = \sigma_P^S + \sigma_D^S$ was calculated on the base of solving the equations system given in [14].

\[
\begin{align*}
(1 + \cos \theta_{L1}) \sigma_{L1} &= 2 \sqrt{\sigma_{LV1}^d \cdot \sigma_{S}^d + 2 \sqrt{\sigma_{LV1}^p \cdot \sigma_{S}^p}} \\
(1 + \cos \theta_{L2}) \sigma_{L2} &= 2 \sqrt{\sigma_{LV2}^d \cdot \sigma_{S}^d + 2 \sqrt{\sigma_{LV2}^p \cdot \sigma_{S}^p}},
\end{align*}
\]

where $\theta_{L1}$ and $\theta_{L2}$ – wetting angles the leakage rate of test liquids; $\sigma_{LV1}^P$, $\sigma_{LV1}^D$, $\sigma_{S}^P$, $\sigma_{LV1}^D$ и $\sigma_{LV2}^D$, $\sigma_{S}^D$ – polar and dispersive components of the surface tension of the test liquid (L) and solid (S).

Table 1. Experimental samples on the base of PTFE.

<table>
<thead>
<tr>
<th>Sample title</th>
<th>Sample description</th>
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<tbody>
<tr>
<td>Control</td>
<td>PTFE (polytetrafluoroethylene)</td>
</tr>
<tr>
<td>№1</td>
<td>PTFE, treated by CF$_4$ ions beam during 30 minutes</td>
</tr>
<tr>
<td>№2</td>
<td>PTFE, treated by CF$_4$ ions beam during 30 minutes and modified by fluorocarbon film, containing 10% CF$_4^+$ 90% C$<em>6$H$</em>{12}$ in plasma forming mixture</td>
</tr>
<tr>
<td>№3</td>
<td>PTFE, treated by CF$_4$ ions beam during 30 minutes and modified by fluorocarbon film, containing 30% CF$_4^+$ 70% C$<em>6$H$</em>{12}$ in plasma forming mixture</td>
</tr>
<tr>
<td>№4</td>
<td>PTFE, treated by CF$_4$ ions beam during 30 minutes and modified by fluorocarbon film, containing 40% CF$_4^+$ 60% C$<em>6$H$</em>{12}$ in plasma forming mixture</td>
</tr>
<tr>
<td>№5</td>
<td>PTFE, treated by CF$_4$ ions beam during 30 minutes and modified by fluorocarbon film, containing 60% CF$_4^+$ 40% C$<em>6$H$</em>{12}$ in plasma forming mixture</td>
</tr>
<tr>
<td>№6</td>
<td>PTFE, treated by CF$_4$ ions beam during 30 minutes and modified by fluorocarbon film, containing 70% CF$_4^+$ 30% C$<em>6$H$</em>{12}$ in plasma forming mixture</td>
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3. Results and discussion

3.1 SEM-EDX

Using SEM it was shown that the treatment of PTFE surfaces by CF<sub>4</sub> ions beam during 30 minutes leads to the sharp alteration of relief. Surface structure of control sample PTFE; sample PTFE, treated by CF<sub>4</sub> ions beam during 30 minutes, and samples PTFE, treated by CF<sub>4</sub> ions beam during 30 minutes and modified by fluorocarbon films with different content of CF<sub>4</sub> and C<sub>6</sub>H<sub>12</sub> are presented on fig.1.

The further modification of formed nanostructured surface by means of deposition of fluorocarbon film, containing 10% and 30% CF<sub>4</sub> in plasma forming mixture, leads to smoothing of relief after films deposition with high content of carbon. For samples № 4 and № 5 (40 и 60% CF<sub>4</sub> content in gas mixture) the relief again changes radically and then for sample № 6 becomes more smooth because of flowing of competing with deposition of fluorocarbon film the etching process, that is demonstrated in relief alteration of the surface of sample № 6. Results of quantitative X-rays microanalyses of experimental samples confirm presented before argumentations. Fluorine content is maximal on the surface of inner PTFE, while content of carbon on this sample is minimal. After treatment of PTFE surface by CF<sub>4</sub> ions beam during 30 minutes fluorine content decreases till 40,35% and carbon content increase to 48,94%. At the further modification of surface by ions of gas mixture CF<sub>4</sub>+C<sub>6</sub>H<sub>12</sub> fluorine content continues to increase till 48,94% and carbon content - to increase to 48,94 %, when containing of CF<sub>4</sub> is increasing to 30%. Then a small splash is observed at increasing of CF<sub>4</sub> to 40%. After that the fluent increase of fluorine content on the surface and fluent decrease of carbon content are observed. It’s necessary to note that in the defect area fluorine content repeats the same dependence, but at the greater values. Obtained results are presented on fig.2, which demonstrates the diagrams of results of quantitative energy-dispersive X-rays analysis of samples, based on PTFE: a-atomic %, d-weight %. It’s important to note, that for atomic% the content of carbon more than the content of fluorine in the area of competing processes, but for weight % the content of carbon less than the content of fluorine.

Figure 3 demonstrates a mapping of carbon, oxygen and fluorine in samples, which are in agreement with fig.2. We can see that at the content of CF<sub>4</sub> in gas mixture 70% carbon on the film surface is practically absent.

Obtained results confirm the presence of competing processes: deposition of fluorocarbon film up to content of CF<sub>4</sub> about 30% in plasma forming mixture and surface etching at content of CF<sub>4</sub> more 60% in plasma forming mixture. Apparently, at the content of CF<sub>4</sub> in the range 40-60% in plasma forming mixture we may observe competing processes.

As a result of incubation the fluorine-containing materials with Staphylococcus aureus ATCC 25923 it was shown that the bacteria were adhered to the surface of control sample and experimental samples № 1, 3, 5, 6. Bacteria were not adhered to the surface of samples № 2 and № 4. Despite the fact of the adhesion of bacteria to certain samples, biodestruction was found only in the control sample (without treatment). Biodestruction of the control sample after incubation with the bacteria was determined in the form of cracks and pores that were not found on the surface of others samples.

Fig. 1. SEM images of the control sample (without treatment) and experimental samples № 1-6 (Table 1) at instrumental magnification 10000x.
Fig 2. Diagrams of results of quantitative energy-dispersive X-ray analysis of samples based on PTFE; a – atomic % of carbon and fluorine; b – weight % of carbon and fluorine.

Fig 3. EDX mapping of elements: carbon (red), oxygen (green) and fluorine (blue); a – control; b – sample № 1; c - sample № 2; d - sample № 3; e - sample № 4; f - sample № 5; g - sample № 6.
3.2 Study of total specific surface energy.
Calculations of total specific surface energy on the base of measurement of contact wetting angles have shown sharp decrease of surface energy at the content of CF₄ in the gas phase in the range 20-50%, testifying about the increase of hydrophobicity, which may also lead to decrease of *Staphylococcus aureus* adhesion (Fig. 4).

![Graph showing total surface energy vs. CF₄ content in gas mixture](image)

Fig.4. Dependence of total surface energy of fluorine-containing surfaces on CF₄ content in the gas phase for samples on the base of PTFE

On fig. 4 also was seen that surface energy after treatment PTFE by CF₄ ions was increased more than 10 mJ/ m². Deposition of carbon film increased the surface energy more than 150 mJ/m². At the enlarging of CF₄ content in the gas phase up to 20% sharp decrease of surface energy almost till 100 mJ/ m² and further slow decrease were observed.

4. Conclusion
Investigations permitted to conclude the following:
1. Obtained results confirmed the presence of competing processes after treatment of PTFE surface with use of gas mixture CF₄⁺ C₆H₁₂: deposition of fluorine-containing film till the content of CF₄ in gas mixture 30-40% and surface etching at the content of CF₄ in gas mixture more than 60% at the used regimes. Apparently, at the content of CF₄ in gas mixture in the range 40-60% the competing processes are following.
2. Study of the interaction processes of *Staphylococcus aureus* ATCC 25923 with PTFE surface, formed by CF₄ ions beam treatment and deposition of fluorocarbon film with the use of gas phase CF₄⁺ C₆H₁₂ have shown, that, apparently, optimal combination of fluorine concentration and definite surface relief promotes the resistance of coating to biofouling and biodestruction.
3. On the base of measurements of contact wetting angles and calculation of specific surface energy it was established, that the formation of nanostructures, providing the absence of *Staphylococcus aureus* cells adhesion, was accompanying by sharp decrease of surface energy.

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References