Surface charge of polymer materials modified by nanostructured fluorocarbon coatings

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Abstract. The paper presents the results of a study of the surface charge of polymer materials modified with fluorocarbon films formed by ion-plasma technology at different CF$_4$ contents in the CF$_4$ + C$_6$H$_{12}$ plasma mixture. Nanostructured fluorocarbon films formed on the surface of polyethylene terephthalate and polystyrene have a positive charge in the region of "transient" processes, and films on the surface of polytetrafluoroethylene have a negative charge, which is associated with different topology of the relief on the surface of these polymers, as well as their polarity.

1. Introduction

One of the most important factors limiting the use of polymeric materials in various fields of science and technology is low resistance to biodegradation, which accounts for more than 20 % of all damaged materials. Characteristic signs of polymer biodegradation are: surface tarnishing, change in dielectric properties, decrease in mechanical strength, swelling, shape change, cracking, etc. The formation of biofilms, for example, on implantable equipment (catheters, artificial heart valves and other implants, lenses, etc.) also leads to the development of a number of severe, difficult to treat chronic diseases [1, 2]. In this regard, an important task is to find ways to modify the surface of polymers in order to increase resistance to biological damage and subsequently to increase the service life of products made of polymeric materials.

In works [3, 4] it was shown that one of the most rational and economically justified methods of combating biofilms is the formation of antiadhesive barrier layers (BL) with respect to microorganisms on the polymer surface using ion treatment and subsequent deposition of fluorocarbon films from a plasma-forming mixture CF$_4$ + C$_6$H$_{12}$, formed in the field of "transient" processes (transition from film deposition to their etching), by methods of ion-plasma technology. In recent years, works [3, 5] have appeared, indicating that the presence of fluorine in the gas mixture, when using ion-plasma technology, significantly reduces the surface energy, which reduces adhesion and complicates the formation of biofilms, because adhesion is the initial stage of surface colonization by microorganisms.

Ion-plasma treatment makes it possible to modify the surface layer of the material without affecting its main volume and to impart new properties to the surface. Thus, it became necessary to study the characteristics of the surface, which to the greatest extent affect the anti-adhesive properties of fluorocarbon films. These factors are: surface relief, chemical composition, and surface charge.
The aim of this work is to study the surface charge of fluorocarbon nanostructures on the surface of polymeric materials.

2. Materials and research methods

The formation of nanostructured surfaces was carried out on a UVU71-P3 vacuum unit equipped with two II-4-0.15 ion sources. At the first stage, treatment was performed with directed ionized flows of particles in order to form a nanostructured surface using tetrafluoromethane (CF$_4$) for 10 and 30 minutes. At the second stage, a nanometer-thick fluorocarbon film with different ratios of CF$_4$ and C$_6$H$_{12}$ in a gas mixture was formed for 10 or 20 minutes.

Polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE), and polystyrene (PS) were chosen as model polymers. The choice of materials is due to their widespread use in the manufacture of electronic products, medicine, biotechnology, etc. [2, 6].

The electrostatic properties of polymer films in the electret state were studied in accordance with GOST 25209-82 “Plastics and polymer films. Methods for determining the surface charges of electrets”. For this, an IPEP-1 meter of electrostatic field parameters (figure 1) was used, designed for non-contact measurement of the surface density of electric charges ($\sigma$, $\mu$C/m$^2$).

![Diagram of the IPEP-1 device](image)

Figure 1. Diagram of the IPEP-1 device with a nozzle: 1 – nozzle; 2 – nozzle disk (measuring plate); 3 – surface of the measured object; 4 – rack.

The principle of operation of the IPEP-1 device is based on the method of periodic screening of the recording electrode. For this, a rotating grounded shield (shutter) is used, which periodically covered the recording electrode from the electrostatic field. The voltage across the electrode was periodically changed from zero (when the electrode is closed) to a value proportional to the potential of this point (when the electrode is open). To study the effect of technological modes of processing and deposition of a plasma-forming mixture (CF$_4$ + C$_6$H$_{12}$) on the magnitude and stability of the charge, the charge of the films was measured at three points. 30 days after the formation of the coatings, when the charge state was stabilized, readings of the surface density of electric charges were taken.

3. Results and discussion

Microorganisms (S. aureus 29213 ATCC) adhered to a lesser extent to surfaces treated with CF$_4$ for 30 minutes than to samples that were treated for 20 minutes, where signs of bacterial cell division and small accumulations were found. Upon further application of a fluorocarbon film with 40 % and 60 % CF$_4$ to the sample with a 30-minute treatment, no microorganisms were detected in the gas mixture on the surface of the samples, which indicates the absence of adhesion of microorganisms to the surface). When the CF$_4$ content was from 10 to 30 %, rare single cells were found on the surface, no accumulations of cells and the formation of a continuous biofilm were found.

The graph (figure 2) shows that pre-treatment of PET with CF$_4$ ions for 30 minutes leads to an increase in the surface charge. When a fluorocarbon film is deposited at 10 % CF$_4$ content in the gas mixture, the surface charge changes its sign to positive. At 30 % CF$_4$, this charge increases slightly. Then, in the region of "transient" processes (40–60 % CF$_4$), a decrease in the surface charge to values close to zero is observed. With an increase in the CF$_4$ content to 70 %, the charge slightly increases,
which is associated with the surface etching processes and the effect of positive ions in the gas mixture.

Figure 2. Dependence of the surface charge of PET films on the CF$_4$ content in the plasma-forming mixture (30 min treatment).

Figure 3. Dependence of the surface charge of PET films on the CF$_4$ content in the plasma-forming mixture (10 min treatment).

When PET is treated with CF$_4$ ions for 10 minutes and the film is applied for 10 minutes (figure 3), the general view of the graph is preserved, but the surface charge is less in magnitude.

The graph (figure 4) shows that pre-treatment of PS with CF$_4$ ions for 30 minutes leads to a decrease in the value of the negative surface charge. When a fluorocarbon film is deposited at 10 % CF$_4$ content in the gas mixture, the surface charge changes its sign to positive.

The graph (figure 5) shows that pre-treatment of PTFE with CF$_4$ ions for 30 minutes leads to a decrease in the negative surface charge. When a fluorocarbon film is applied at 10 % CF$_4$ content in the gas mixture, the surface charge changes its sign to positive. At 30 % CF$_4$ content and in the area of "transient" processes (40–60 % CF$_4$), the PZ sharply becomes negative. The negative charge on the PTFE surface can be associated with the effect of static electricity due to a more developed relief, as well as due to an increase in the content of fluorine atoms on the PTFE surface due to competing
etching and deposition processes when using a fluorine-containing gas mixture. Under the action of a surface discharge plasma in PTFE films, the formation of a stable electret state is observed, which is associated with the injection of electrons from the plasma into the surface layers of the material and their localization in traps.

![Surface charge vs. CF4 content](image)

**Figure 4.** Dependence of the surface charge of polystyrene films on the CF4 content in the plasma-forming mixture.

![Surface charge vs. CF4 content](image)

**Figure 5.** Dependence of the surface charge of PTFE films on the CF4 content in the plasma-forming mixture.

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

- Based on measurements of the surface charge, it was found that nanostructured fluorocarbon films formed on the surface of PET and PS have a positive charge in the region of "transient" processes, and negative on the surface of PTFE, which is apparently associated with the different topology of the relief on the surface of these polymers as well as their polarity. The negative charge on the PTFE surface can be associated with the effect of static electricity due to the more developed relief, as well as the more pronounced dielectric properties of this polymer.

- When a fluorocarbon coating is applied, electret states are formed on the surface of polymeric materials.

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