Multifunctional polymer materials with antifungal activity, modified by fluorocarbon films by methods of ion-plasma technology

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Abstract. The formation of fluorocarbon coatings from plasma-forming mixtures $\text{CF}_4 + \text{C}_6\text{H}_{12}$ and $\text{C}_4\text{F}_8 + \text{C}_6\text{H}_{12}$ on the surface of polyethylene terephthalate and polystyrene using ion-plasma technology are considered. Nanostructured polymer materials have increased fungicide resistance and high optical characteristics.

The use of polymeric materials in modern electronics, in particular, polytronics, leads to a complex of required characteristics: high transmittance in the visible wavelength range, flexibility, low moisture transmission, and high resistance to biodegradation, which allows increasing the life of products from polymeric materials [1].

Polymeric materials are adversely affected by the environment. One of the most significant influencing factors is biodegradation, which can lead to the formation of microcracks, plaque and darkening, which in turn leads to the failure of the product from a polymeric material [2].

In this regard, it is necessary to search for methods of modifying polymeric materials in order to increase the resistance to biodegradation. In [3, 4] the possibility of creating nanostructured barrier layers on the surface of polymeric materials based on fluorocarbon films formed in a gas mixture of $\text{CF}_4$ (etching component) and $\text{C}_6\text{H}_{12}$ (deposition component) using ion plasma technology was shown. The layers created in the field of transient processes (the transition from deposition of the film to its etching as the content of the fluorine-containing component in the plasma-forming mixture increases) have a specific relief and reduce the adhesion of microbial cells, which increases the resistance to biodegradation and increases the service life of products out of polymeric materials.

To expand the use of plasma-forming mixtures with a fluorine-containing component, it is possible to use octafluorocyclobutane ($\text{C}_4\text{F}_8$) as an etching component instead of $\text{CF}_4$, since $\text{C}_4\text{F}_8$ is widely used in the technology of creating microelectronics elements, in particular in Bosh processes [5].

Thus, the purpose of this work is to study the properties of nanostructured fluorocarbon coatings on the surface of PETF and PS, formed by ion-plasma methods using plasma-forming mixtures of $\text{CF}_4 + \text{C}_6\text{H}_{12}$ and $\text{C}_4\text{F}_8 + \text{C}_6\text{H}_{12}$, in particular, surface relief, optical characteristics, fungicide resistance.

The formation of barrier layers was carried out in a vacuum unit, equipped with two ion sources II-4-0.15 working in crossed magnetic and electric fields. At the first stage, ion treatment was performed from tetrafluoromethane ($\text{CF}_4$) for 30 minutes using a single ion source. At the second stage, a fluorocarbon film with different ratios of octafluorocyclobutane ($\text{C}_4\text{F}_8$) and cyclohexane ($\text{C}_6\text{H}_{12}$) in a gas mixture was deposited using a second ion source for 20 minutes.
The surface parameters were measured by NT MDT Solver Next scanning probe microscope with an AFM head (Russia) in the semi-contact mode. The optical characteristics of the formed fluorocarbon nanostructures on the surface of polymeric materials were studied on a CARY-5000 spectrophotometer (UV-VIS-NIR) manufactured by Agilent Technologies (USA). Fungi resistance studies were conducted according to GOST 9.049-91.

In the paper we used a method for describing graphs depending on the weight content of fluorine in the plasma-forming mixture, which makes it possible to generalize the approach to the description of the proposed results. In [6], an increase in the growth rate of the fluorocarbon coating in the range from 30 to 50 % C₄F₈ in the plasma-forming mixture C₄F₈ + C₆H₁₂ was found, which indicates the presence of a specific relief.

Figure 1 shows a graph of dependence of the standard deviation of roughness Rq on the fluorine content in plasma-forming mixtures, as well as relief parameters of PETF modified with the fluorocarbon film using a mixture of C₄F₈ + C₆H₁₂. When the PET surface is modified with a fluorocarbon film with a low weight fluorine content (up to 25 %), Rq increases, which is manifested in an increase in the heights of the heterogeneity peaks and, accordingly, an increase in the actual surface area relative to the geometric. A further decrease in Rq values is associated with the prevailing processes of surface etching and a decrease in peak heights and the distance between them. At 59.37% of fluorine in the mixture, the values of Rq again increase, which, apparently, is due to the formation of a specific relief. Specific relief was also observed at 35.51 and 52.73 % Wt (F) in the plasma-forming mixture C₄F₈ + C₆H₁₂.

![Graph](image.png)

**Figure 1.** Dependence of the roughness standard deviation (Rq) for PETF and PS on the weight content of fluorine (F) in plasma-forming mixtures C₄F₈ + C₆H₁₂ and C₄F₈ + C₆H₁₂: 1 – original sample; 2 – CF₄ treatment, 30 min; 3 – in the plasma-forming mixture CF₄ + C₆H₁₂; 4 – in a mixture C₄F₈ + C₆H₁₂.

From the graph of the dependence of Rq for PS on the fluorine content in the plasma-forming mixture C₄F₈ + C₆H₁₂ (figure 1), it can be seen that the minimum Rq is observed at 30% fluorine in the plasma-forming mixture, and the maximum at 50 %, which also indicates the formation of a specific relief.

Table 1 presents the integral coefficients of transmittance (T), reflection (R) and absorption (A) of PETF and PS, modified with a film formed from mixture containing C₄F₈. The values of the integral transmittance on the PS are close to the values of the transmittance of PETF. The transmittance of samples of polymers modified by fluorocarbon coatings with content of octafluorocyclobutane more than 60 % in the gas mixture has values that are acceptable for using modified polymers as elements of polytronics (T > 70 %).

From table 2 it can be seen that the increase in resistance to fungi is manifested when the PETF is modified with a fluorocarbon film with a different ratio of components. The fungi stop growing on modified PETF samples at 60 % of the fluorine-containing component in the plasma-forming mixtures CF₄ + C₆H₁₂; C₄F₈ + C₆H₁₂ (Wt (F) 52.73 and 59.37 %, respectively).
Table 1. Integrated optical coefficients for PET and PS.

| Sample                  | T, %  | R, %  | A, %  |
|-------------------------|-------|-------|-------|
|                         | PETF  | PS    | PETF  |
| Untreated sample        | 89.7  | 88.7  | 9     | 0.4  |
| Treatment CF$_4$, 30 min| 85.5  | 84.8  | 10.2  | 4.8  |
| C$_4$F$_8$ (0 %) + C$_6$H$_{12}$ (100 %) | 40.4  | 40.67 | 11.7  | 47.9 |
| C$_4$F$_8$ (10 %) + C$_6$H$_{12}$ (90 %) | 40.6  | 43.93 | 15.2  | 44.2 |
| C$_4$F$_8$ (25 %) + C$_6$H$_{12}$ (75 %) | 35.8  | 39.4  | 11.6  | 52.6 |
| C$_4$F$_8$ (40 %) + C$_6$H$_{12}$ (60 %) | 37.8  | 38.13 | 7.8   | 54.9 |
| C$_4$F$_8$ (60 %) + C$_6$H$_{12}$ (40 %) | 75.2  | 77.92 | 7.6   | 16.3 |
| C$_4$F$_8$ (75 %) + C$_6$H$_{12}$ (25 %) | 79    | 79.8  | 6.8   | 14.2 |
| C$_4$F$_8$ (90 %) + C$_6$H$_{12}$ (10 %) | 80.1  | 81.3  | 10.8  | 9.1  |

Table 2. Investigation of fungi resistance

| Sample                  | Wt(F), % | Value |
|-------------------------|----------|-------|
| PETF untreated          | –        | 2–3   |
| Treatment CF$_4$        | –        | 2     |
| Treatment CF$_4$ + film (30 % CF$_4$ + 70 % C$_6$H$_{12}$) | 27.31 | 1 |
| Treatment CF$_4$ + film (60 % CF$_4$ + 40 % C$_6$H$_{12}$) | 52.73 | 0 |
| Treatment CF$_4$ + film (0 % C$_4$F$_8$ + 100 % C$_6$H$_{12}$) | 0     | 1     |
| Treatment CF$_4$ + film (10 % C$_4$F$_8$ + 90 % C$_6$H$_{12}$) | 17.25 | 1     |
| Treatment CF$_4$ + film (40 % C$_4$F$_8$ + 60 % C$_6$H$_{12}$) | 46.61 | 1     |
| Treatment CF$_4$ + film (60 % C$_4$F$_8$ + 40 % C$_6$H$_{12}$) | 59.37 | 0     |

The obtained results allow drawing the following conclusions:

1). The presence of a transient process region was found when using the plasma-forming mixture C$_4$F$_8$ + C$_6$H$_{12}$, which is accompanied by the formation of a specific relief, a change in the film growth rate, as well as resistance to fungi.

2). Coatings formed with a C$_4$F$_8$ and CF$_4$ content of 60 % have integral transmittance values of more than 75 %, which makes it possible to use these coatings in polytronic elements.

3). It was found that fungus resistance manifests itself at 60 % fluorine-containing component in plasma-forming mixtures CF$_4$ + C$_6$H$_{12}$, C$_4$F$_8$ + C$_6$H$_{12}$. Apparently, fungi resistance is associated with a combination of various relief factors and the fluorine content in the gas mixture.

References

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