Research of the dielectric properties of polyethyleneterephthalate modified by fluorocarbon films formed by ion-plasma technology methods

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Abstract. The paper presents the results of a study of polyethyleneterephthalate (PET), modified by nanostructured fluorocarbon films formed by vapor deposition in a vacuum using a two-component gas mixture containing a film coating component ($C_6H_{12}$) and an etching component ($CF_4$). The dependence of the dielectric loss tangent and permittivity on the ratio of the components of the gas mixture is established. The obtained data were correlated with the physicochemical characteristics of the materials used.

Last year’s carbon materials, in particular, polymers and composites based on them, have found wide application in electronics, mechanical engineering, aviation and space complex, medicine, etc. Good dielectric properties allow their use as insulating and constructing materials in electrical and electronic devices, as well as in the manufacture of cases for capacitors and load-bearing elements.

Surface modification of polymer and composite materials allows us to expand the range of their properties [1]. Modification of polymeric materials with nanostructured fluorocarbon films makes it possible to add such characteristics as environmental resistance, including increased moisture resistance and resistance to microbial influences [2, 3], which significantly expands the possibilities of their practical use.

The aim of the work is to study the effect of modifying nanostructured fluorocarbon films on the dielectric properties of polymer materials using the example of polyethyleneterephthalate (PET), the choice of which is due to its widespread use in the manufacture of electronic devices, medicine, etc.

The formation of fluorocarbon films was carried out in a vacuum chamber with a residual pressure of hydrocarbons of 0.2 – 0.4 Pa, equipped with two ion sources. At the first stage, using one ion source, the PET surface was treated using tetrafluoromethane ($CF_4$) ions with an energy of 3 keV for 3 min to clean the polymer surface, increase the adhesion of the fluorocarbon film, and also create a preliminary relief on the surface of PET. At the second stage, a fluorocarbon film was applied using a second ion source using a two-component gas mixture $CF_4 + C_6H_{12}$ with a different ratio of components.

In [4, 5] the possibility of creating antimicrobial, and at a certain ratio of $CF_4$ and $C_6H_{12}$ in a gas mixture (for these conditions 40 – 60%) and anti-adhesive anti-microbial films, opening up the possibility of creating fundamentally new materials for photoelectronics, devices and devices used in aerospace equipment, medicine, etc.
In this work, we studied the dielectric properties of structures of a PET-nanostructured fluorocarbon film in order to identify patterns of behavior of experimental samples in an alternating electric field. During the experiments, such material parameters as the dielectric loss tangent $\tan \delta$ and the relative dielectric constant of the samples $\varepsilon$ were studied.

For this purpose, an E7-20 immittance meter was used, the operation of which is based on the method of measuring the current passing through the object under study and the voltage drop across it. Using the obtained values, the software part of the apparatus calculates the resistance and conductivity of the sample.

The voltage of the operating frequency from the generator is supplied to the measured object. The converter generates two voltages, one of which ($U_T$) is proportional to the current flowing through the measured object, the other ($U_H$) – to the voltage on it. The ratio of these voltages is equal to the complex conductivity ($Y$) or the complex resistance ($Z$) of the object.

The measurement of the stress ratio is carried out by a hardware-software logometer, the result of the work of the software part of which is the calculation of the stress ratio. The projections of the vectors $U_T$, $U_H$ on the reference voltage $U_o$ and $jU_o$ are distinguished by a synchronous detector and are measured at some arbitrary scale by an integrating type meter.

The following transformations are used in the calculations:

$$Y = G + jB' = \frac{U_T}{U_H} = \frac{A+jB}{C+jD},$$

(1)

where $Y$ is the conductivity of the sample; $G$ is the active component of conductivity; $B'$ is the reactive component of conductivity.

$A$, $B$, $C$, $D$ are the projections of the vectors $U_T$ and $U_H$ on the reference voltage $U_o$ and $jU_o$, whence

$$G = \frac{AC+BD}{C^2+D^2},$$

(2)

$$B' = \frac{BC-AD}{C^2+D^2}.$$  

(3)

Similarly to the expression (1) we have for resistance:

$$Z = R + jX = \frac{U_H}{U_T} = \frac{C+jD}{A+jB},$$

(4)

where $Z$ is the resistance of the sample; $R$ is the active component of the resistance; $X$ is the reactive component of the resistance;

Wherein:

$$R = \frac{AC+BD}{A^2+B^2},$$

(5)

$$B' = \frac{AD-BC}{A^2+B^2}.$$  

(6)

And further from the relations:

$$X = \frac{1}{2\pi fC} \rightarrow C = \frac{1}{2\pi fX},$$

(7)

$$tg\delta = \frac{1}{Q} = \frac{R}{X}$$

(8)

the capacitance and tangent of the dielectric loss angle of materials are calculated, where $C$ is the sample capacity; $f$ is the signal frequency; $Q$ – figure of merit of the measured object.

Based on the results of the experiments, the relative permittivity values were calculated and the dependences of the dielectric loss tangent $\tan \delta$ and permittivity $\varepsilon$ of the samples on the percentage of
CF$_4$ in the modifying gas mixture and frequency $f$ of the applied voltage were plotted, shown in figures 1 – 4.

In samples treated with mixtures of 10% CF$_4$ + 90% C$_6$H$_{12}$, 25% CF$_4$ + 75% C$_6$H$_{12}$, 40% CF$_4$ + 60% C$_6$H$_{12}$, a decrease in its value relative to pure PET is observed. This effect is especially pronounced at 200 kHz and 1 MHz. At a frequency of 750 kHz, the value of relative dielectric constant has a maximum at any ratio of the components of the modifying mixture.

The increase in the dielectric loss of PET after treatment with high-energy ions and the deposition of fluorocarbon films on the surface of the material can be explained by the formation of large charge complexes in the surface layer of the sample. These complexes are formed due to the cleavage of the weakest covalent bonds in PET molecules (C – O and C – C with sp3 hybridization), as well as in C$_6$H$_{12}$ (C – H with sp3 hybridization).

It is known that the most durable are sp2-hybridized bonds forming cyclic elements, as well as C = O groups on the linear sections of PET and cyclohexane molecules. It can be assumed that it is these bonds that are retained during the processing of the sample, and the rupture occurs on the linear sections of PET molecules. Probably, as a result, cyclic groups form massive dipole groups that absorb part of the energy at frequencies up to 50 kHz.

![Figure 1. The dependence of the dielectric loss tangent tanδ on frequency for PET samples modified in a CF$_4$/C$_6$H$_{12}$ mixture with a CF$_4$ content of 25%.

![Figure 2. The dependence of the dielectric loss tangent tanδ of PET samples modified in a CF$_4$/C$_6$H$_{12}$ mixture on the CF$_4$ content at a frequency of 1 MHz.](image-url)
Figure 3. Frequency dependence of dielectric constant $\varepsilon$ for PET samples modified in a CF$_4$/C$_6$H$_{12}$ mixture with a CF$_4$ content of 25%.

Figure 4. The dependence of the dielectric constant $\varepsilon_{\text{max}}$ of PET samples modified in a CF$_4$/C$_6$H$_{12}$ mixture on the content of CF$_4$ at a frequency of 1 MHz.

With increasing frequency of the external field, the influence of the above-described charge complexes weakens due to the fact that they do not have time to navigate the field due to the significant mass. In the frequency range 500 kHz - 1 MHz, the dielectric loss tangent of the modified structure decreases, which may indicate that during ion processing large polymer molecules in the surface layer are fragmented into large cyclic groups and smaller fragments of linear sections of PET molecules with greater mobility, than the molecules themselves, which is confirmed by the calculation of the relative dielectric constant of the obtained samples.

In the frequency range up to 50 kHz and at 750 kHz, maximums $\varepsilon$ are observed, indicating the cessation of the influence of certain types of polarization on the dielectric properties of the film. In particular, this can be a dipole-segment polarization, which manifests itself at frequencies up to 105 Hz and is caused by the large dipole groups described above in the surface layer of the material, as well as a dipole-group polarization observed at frequencies up to 106 Hz, and probably caused by segments of the PET substrate itself lying in the bulk of the film.

An increase in the tan\(\delta\) value with an increase in the CF$_4$ content from 10% and higher in the gas mixture is associated with a change in the topology and an increase in the concentration of charge complexes in modified near-surface layers, which are a consequence of the manifestation of
competing processes of deposition and etching of fluorocarbon thin films. This is confirmed by measurements of the relative permittivity \( \varepsilon \) depending on the composition of the working gas mixture \( \text{CF}_4 + \text{C}_6\text{H}_{12} \) (Fig. 4). In the range of \( \text{CF}_4 \) concentration from 10% to 40%, there is a significant decrease in \( \varepsilon \) (from 3.6 to 3.0) and a significant increase (up to 3.5) of this parameter with an increase in the concentration of \( \text{CF}_4 \) up to 60%, which is also associated with a more developed surface topology as a result of competing deposition and etching processes.

Thus, the dielectric properties of PET, including the level of dielectric losses and the relative permittivity of the material, correlate with a change in the composition of the modifying gas mixture \( \text{CF}_4 + \text{C}_6\text{H}_{12} \).

Conclusions:
1. The dielectric loss tangent in a modified PET film in the frequency range up to 50 kHz is slightly higher than in the original film. With increasing frequency, its value decreases and a minimum is observed at 750 kHz.
2. At frequencies up to 50 kHz, the minimum \( \tan \delta \) levels are observed for samples with 100% \( \text{C}_6\text{H}_{12} \) in a modifying gas mixture. With increasing frequency, minima appear in samples treated in 10% \( \text{CF}_4 \) + 90% \( \text{C}_6\text{H}_{12} \).
3. The relative dielectric constant of the modified PET film in the frequency range up to 50 kHz is slightly higher than in the unmodified one. Further, as the frequency increases, its value decreases, and already in the frequency range 500 or 750 kHz a new drop appears.
4. The relative dielectric constant of the modified PET film increases significantly with a content of 100% \( \text{C}_6\text{H}_{12} \) in the gas mixture.
5. The simultaneous growth of the studied dielectric characteristics: \( \tan \delta \) and \( \varepsilon \) in the concentration range of 40% - 60% \( \text{CF}_4 \) confirms the appearance of a special state on the modified PET surface, which manifests itself in the form of release properties [4,5] as a result of competing deposition and etching processes.

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