Physical, chemical and antimicrobial properties of polyethylene terephthalate surface nanostructured by ion-plasma treatment.

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Development of technologies, which permit to change polymer surface for providing new functional properties, in particular, antimicrobial activity (AA), without affecting the bulk properties of material is a vital and perspective problem. One of approaches to solving this problem is nanostructurization of polymer surface by ion-plasma treatment (IPT). First results related to preparation of antimicrobial materials by IPT were reported at PSE 2008 [1] and in [2.] Further results devoted to study of physical, chemical and antimicrobial properties of polyethylene terephthalate (PET) surface nanostructured by IPT and subsequently modified by deposition of nanoscaled carbon films are under discussion in the present work.

PET (GOST 24234-80, Russia), which is a polar synthetic polymer, with thickness of 30 μm was used in this work. Nanostructured surfaces (NSS) were formed by ion beams of reactive and inert gases and gas mixtures, such as CF_4, $Ar+O_2$ and N_2+O_2.

The next stage of treatment involved modification of NSS by ion-plasma deposition of carbon films (thickness of 5-120 nm) using C_6H_{12} vapour. Surface topography of the prepared samples was investigated with scanning probe microscope "FemtoScan" (MSU, Moscow). Horizontal size R, peaks height H and mean square value of the surface roughness Rq were uses as main parameters for surface characterization.

Contact angle measurements using water and ethylene glycol were used for calculation of surface energy and its polar and dispersive components. The surface chemical composition was analysed using X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out using XSAM-800 instrument (Kratos, UK). Measurements of surface charge value were carried out by method of dynamic condensator. AA was measured by application method using gram-positive (*Staphylococcus aureus* ATCC 29213) and gram-negative (*Escherichia coli* ATCC 54383 and *Pseudomonas aeruginosa* ATCC 27853) strains, and funguses (*Candida albicans*). The results were estimated by sight using growth and counting microorganisms colony grown in differential-diagnosis dense nutrient media. An effective decrease in titre (DIT) for every microorganism was averaged over four dilutions. It was supposed that DIT was an evidence of AA of polymer coatings.

The results of surface study by scanning probe microscope (AFM mode), in particular, R, H and Rq values for different conditions of NSS formation and modification by a-C:H with different film thickness are presented in Table 1.

As shown in Table 1, using different gases and gas mixtures permit to obtain Rq, H and R values in the ranges of 2.7-6.3, 8-22 and 103-166 nm, respectively. It was established, that a-C:H film deposition increases H and R till 40 and 215 nm, respectively. The values of total surface energy σ_s (Table 1) calculated on the base of measurement of contact angles strongly depend on treatment conditions and film thickness. The most remarkable results are observed at film thickness of 20 and 50 nm.

Fig. 1 shows that NSS formation induces large surface charge till 5.5 μC/m (Fig.1, a) and it may be controlled by film deposition (Fig.1, b). At film thickness of 20 nm, the least surface charge has been measured.

3D DIT dependencies on σ_s and time of nanostructurizing of PET surface in relation to different microorganisms (Fig. 2) and DIT on surface charge and time of nanostructurizing (Fig. 4)

Table. 1. Surface properties of samples NSS.

№	Object for research			Rq, nm	R, nm	H, nm	σ_s
	Material	Treatment conditions	α-C:H film thickness, nm				
1	PET	control	-	2.7	103	8	40.3
			10	5.2	151	18	42.2
2			20	12.8	135	27	42.7
3			30	10.8	167	28	38.8
4			50	13.8	188	41	42.7
5			100	11.2	186	34	38.0
6		N_2+O_2, 3 min	-	3.9	166	8	37.4
			10	2.8	120	17	34.3
7			20	1.9	162	13	36.0
8			40	1.7	–	–	–
9			50	4.0	121	20	33.0
10			70	2.2	–	–	–
11			100	2.9	98	16	36.0
12		N_2+O_2, 5 min	-	2.9	143	6	33.6
			10	11.4	149	15	37.2
13			20	4.6	189	13	37.3
14			50	5.6	174	17	36.8
15			100	9.9	215	30	36.1
16		N_2+O_2, 10 min	-	4.5			35.7
			10	4.8	–	–	–
17			20	6.6	–	–	42.6
18			50	8.9	167	21.2	
19			100	9.4	158	34.2	38.1
20		CF_4, 5 min	-	6.3	144	22	–
			10	5.3	88	40	–
21			40	10.8	111	6.2	–
22			70	13.4	107	6.4	–
23		CF_4, 10 min	-	5.7			2.7
			10	7.2	95	4.1	–
24			40	13.4	103	10.8	–
25			70	15.1	98	6.8	–

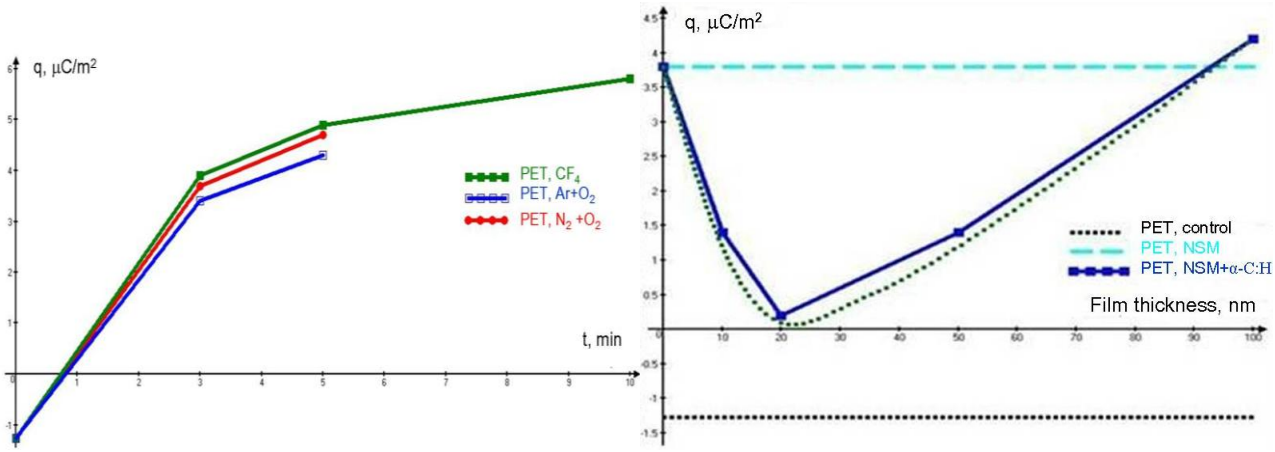
demonstrate a threshold character, which underlines by projection of 3D dependence of DIT on σ_s and time of nanostructurizing of PET surface in relation to different microorganisms (Fig. 2) onto DIT-time plane (Fig. 3)

3D dependence of DIT on Rq and time of nanostructurizing of PET surface in relation to different microorganisms was also obtained. This dependence has more complex behaviour, which is likely related to size and type of microorganisms. Nevertheless, it was established that antimicrobial activity was not observed at Rq value less than 40 nm. The obtained results briefly summarized here.

1. Threshold character of dependencies of DIT on total surface energy σ_s, mean square value of the surface roughness Rq, as well as on value of surface charge shows, on one hand, existence of dimensional biological effects, in particular, AA for 2D materials just the same as for 3D materials,

which was reported previously [3]. On the other hand, the results made clear the mechanism of AA appearance.

2. The results demonstrate the possibility of preparation of multifunctional medical and other items, which besides functional properties may possess desirable antimicrobial properties as well.



a b

Fig. 1. a- dependence of surface charge upon time of nanostructurizing for PET surface; b-dependence of surface charge upon carbon film thickness for PET nanostructured in N_2+O_2 during 3 min.

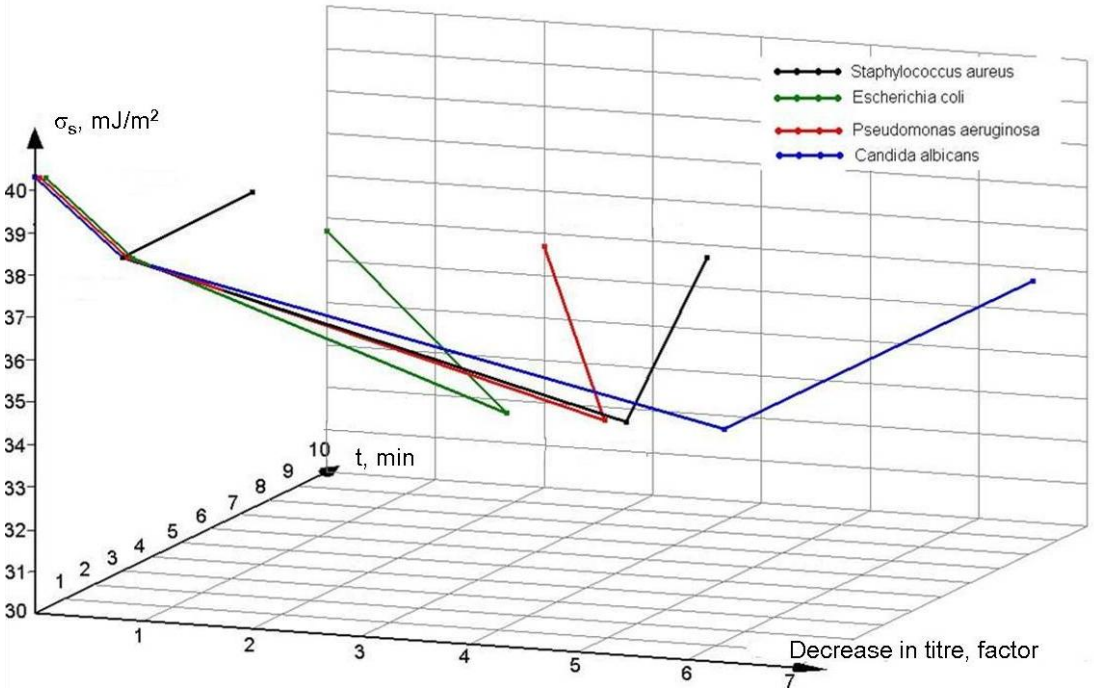


Fig. 2. 3D-dependence of DIT on total surface σ_s and time of nanostructurizing of PET surface in relation to different microorganisms.

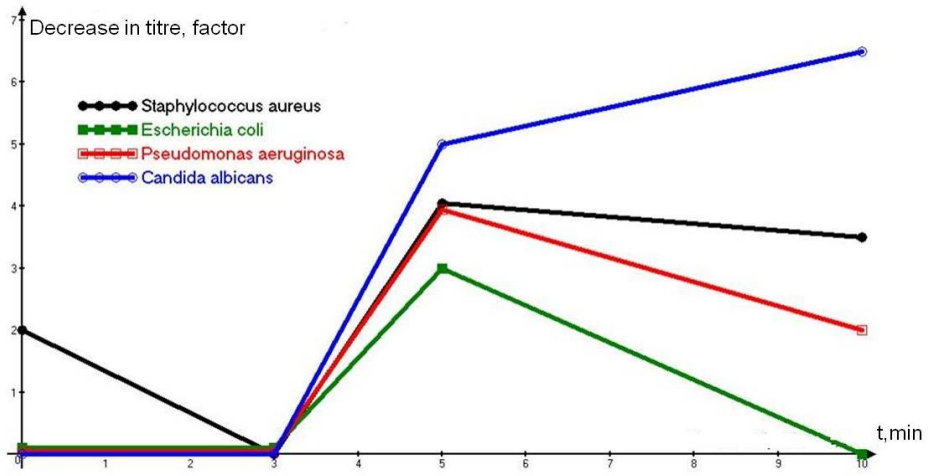


Fig. 3. Dependence of DIT on time of nanostructurizing of PET surface in relation to different microorganisms (Projection of 3D dependence of fig. 2 onto DIT-time plane).

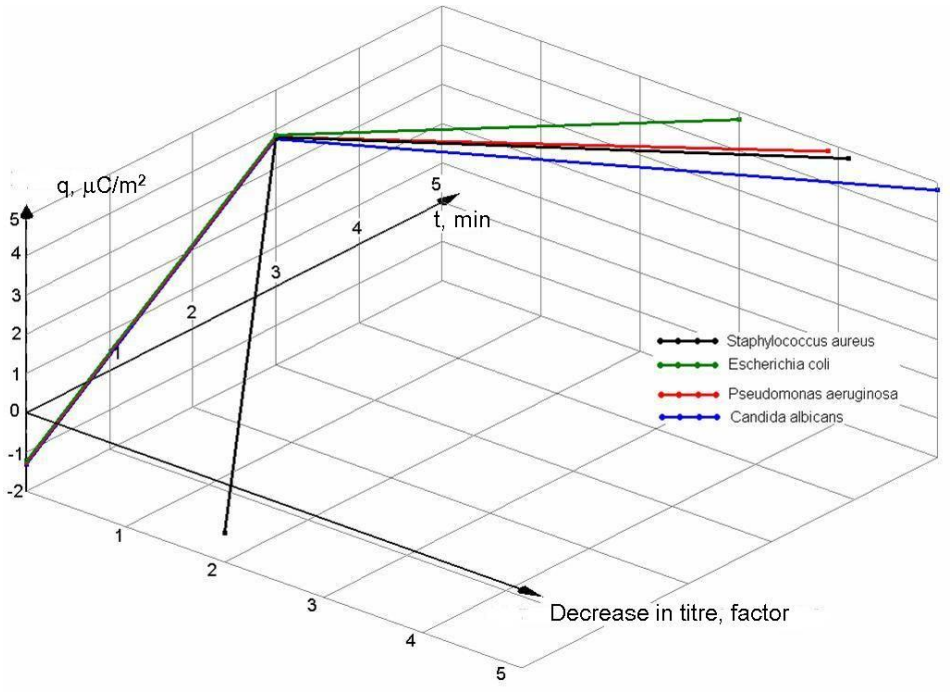


Fig 4. 3D dependence of DIT on surface charge and time of nanostructurizing of PET surface in relation to different microorganisms.

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