

Effect of plasma treatment on the surface properties of polydimethylsiloxane

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ABSTRACT: In this work, the analysis of the plasma modification of polydimethylsiloxane (PDMS) substrates was conducted. The influence of the modification onto the changes occurred within the geometrical structure and chemical composition of the surface was analyzed. Due to the study of the atomic force microscopy, it was possible to determine the relationships between the surface development and applied process parameters, defining the conditions facilitating to obtain isotropic or anisotropic orientations of wrinkles. A precise analysis of the chemical composition of the surface, executed before and after the modification processes, enabled to define the changes in their elementary composition. Moreover, the modification influence onto the changes of the contact angle and the surface free energy were also analyzed. So, based on the research it was stated that the increase of value of the surface free energy is proportional to the sp^3 phase contents in the DLC coatings. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41635.

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INTRODUCTION

Polymers are the group of materials for which current material engineering dedicates the biggest amount of attention. So, considering that fact, we can observe a quick development in the field of both creation and modification of polymers. Research conducted in the laboratories all over the globe focus on the production or modification of already well-known polymer materials as well as assigning them completely new features. One of the most interesting solutions to modify the surface properties of polymers is based on the plasma method, benefiting from the ionized gas. There are numerous articles related to the application of plasma for polymers modification under the reduced^{1–6} as well as the atmospheric pressure.^{7–11} Independently from the way the properties are changed through a proper modification of materials surface, we are capable of assigning the appropriate properties, provided for a certain work environment. Polymer substrate modifications, applied in medicine and used in order to improve their biocompatibility, within their biological environment¹² can be regarded as the best example for the above. Due to the change of polymers properties it is possible to influence the following, *inter alia*: increase their resistance onto bacteria colonization,^{12–14} change the thrombogenicity in relation to the unmodified material,^{12,15} as well as obtain a better adhesion and proliferation¹⁶ of osteoblasts, endothelium cells,¹⁷ or fibroblasts.^{18,19}

Methods of plasma surface processing related to polymer materials can be applied in order to fulfill at least five different treatments: introduction of functional groups onto the surface, introduction of surface roughness (etching) which can be decisive for the certain parameters of the surface geometry, cross-linking, grafting of the chains of other polymers on the surface (surface graft polymerization), as well as creating thin coatings.²⁰ One of polymer materials used in both medicine and medical diagnostic, where its surface undergoes the plasma modifications, is polydimethylsiloxane. In the majority of applications of PDMS, the plasma processing is applied in order to improve the polymer surface adhesion in glass-encapsulation of chips, widely used in the medical diagnostics.²¹ However, there is also a wide application spectra in the microflow devices where microchannels come into being, for example, through the etching of PDMS in SF_6 plasma.^{1,22}

Plasma processing of PDMS substrates is based on their etching as well as on the production of thin layers. PDMS surface roughness can be controlled using plasma.¹ Literature data show that the inherent effect of such treatments is based on a specific surface configuration, most commonly defined as the wrinkles.^{5,23} Moreover, that phenomenon is also related to other polymers.²⁴ Wrinkled topography of the surface is connected with a major mismatch of the Young's modulus of polymer as well as the thin layer, created during the plasma processing.

Among thin layers most commonly deposited onto the polymer substrates we can distinguish the following coatings: diamond-like carbon DLC,^{24–26} gold layers,⁵ as well as silica-like layers^{27,28} created as the result of reactions taking place onto the PDMS surface throughout the plasma processing. Some of the scientists suggest that the process of wrinkles creation, particularly their wavelength and the amplitude, may be controlled.^{25,29} Accordingly, the possibility to apply the plasma processing for the change of the contact angle or surface free energy^{2–4,7,30} is often described as well. Unfortunately, values of these parameters can change and become similar to those gathered before the modification, as the result of the ageing process. Most often, such a process takes place at the PDMS processing in oxygen or argon plasmas where a thin layer of Si-OH polar groups (which influence the hydrophilicity of the surface) are formed, and then, considering a lower weight of the molecular particles, the migration inside the material occurs.^{2,11,31,32} Additionally, the kinetics of the ageing process depends on the outer environment as well as the temperature.^{3,4} So, the ageing process conducted after a performed plasma processing is also described for other polymer materials^{33–35} as well as for carbon layers deposited onto the substrates, made of the austenitic steel.³⁶

This work presents studies over the possibilities of changing both geometry and the chemical composition of the PDMS surface substrates through their plasma modification. Those processes were conducted in the atmosphere containing methane, oxygen, or their mixture. Obtained results were compared with the results achieved using the carbon-titanium nanocomposite coating. The ability to control the surface topography plays an enormous role in production of the super-hydrophobic surfaces, where an appropriate configuration guarantees to obtain the surface contact angles at over 150 degrees.^{37,38} Another, a very important issue, is to search for the optimal surface of devices, meant for cell cultures.^{16,17,19,20} The study presented in this work may be beneficial in the development of future PDMS based biomedical devices. They show the relationship between the chemical composition of the modified surfaces, and the wettability evolution, being the most important parameters, that may affect the biological properties, such as the cell culturing. Besides, the proposed surface modification of the PDMS is usually used to improve the biological characteristics. In the literature, we can find several reports related to the influence of oxygen plasma treatment on, among others, cell culturing on PDMS substrates,^{19,39} as well as the application of DLC coatings pure and doped with titanium for the same purpose.^{40,41}

EXPERIMENTAL

Preparation of PDMS Substrates

In this work, PDMS from Dow Corning Inc. company, under the name of Sylgard 184 was used. It was produced out of two components: base and the curing agent, mixed in the proportions of 10:1. After the process of degassing, liquid PDMS was poured out in Petri dishes and hardened at 80°C for 2 h. The thickness of PDMS was established at about 2 mm. Final samples of 15 mm in diameter were then cut off out of the film.

Before the modification, the substrates were cleaned in ultrasonic cleaner in isopropyl alcohol bath for 10 min and then dried using compressed air, and placed onto the water cooled RF electrodes in plasma-chemical reactors.

Substrate Modifications

Modifications of presented PDMS substrates were conducted using two different technologies: microwave/radio frequency plasma assisted chemical vapor deposition (MW/RF PACVD) and magnetron sputtering/radio frequency plasma assisted chemical vapor deposition (MS/RF PACVD). Details regarding the two technologies are described elsewhere.^{42,43} Dual-frequency technology was used in order to conduct the modification processes using pure oxygen, methane, and their mixture in the proportions of 50/50. Each time, the amount of introduced gases was equal to 40 sccm. Those processes were conducted at the pressure of 15 Pa and the RF and MW generators power at the same level of 500 W. Those parameters allowed to reach the negative bias (V_b) on the level of 600 V. The duration time of the process amounted to 5 min. In addition, PDMS modifications were also executed using the hybrid technology of the pulsed magnetron sputtering, conducted in the presence of the radio frequency discharge.^{44–46} Worked out technology facilitates the synthesis of nanocomposite coatings, consisted of Ti_xC_y carbides, uniformly distributed into the amorphous carbon matrix. The processes of the carbon-titanium nanocomposite coatings synthesis were conducted in the argon-methane atmosphere and the pressure of 1.3 Pa; the bias of RF electrode—300 V; magnetron sputtering power density 28 W/cm². Modified substrates were placed on the water-cooled RF electrode. In both presented techniques, methane, introduced into the chamber, was the basic source of carbon for the synthesis of DLC coatings. In case of the titanium-carbon based nanocomposite coatings, it was necessary to apply argon ions in order to sputter the titanium target. The duration of the process was chosen experimentally in order to compare the impact of the chemical composition of plasma with the changes on the PDMS surface. The selection of modification time amounting to 5 min was dictated by the necessity to reduce the significant surface development. Moreover, longer modification processes of PDMS substrates using the presented parameters also resulted in both deformation and degradation of the polymer.

Atomic Force Microscopy (AFM)

Observations of the morphology and the surface topography were carried out using the Veeco Multimode atomic force microscope, equipped with the Nanoscope V controller, operating in the tapping mode. The tests were performed in the environmental conditions. AFM tips made of silicone of a nominal resonance frequency 325 kHz, constant elasticity of 40 N/m, and the fillet radius <20 nm were used for measurements. For the data collecting the Nanoscope 7.3 software was applied, while the Mountains-Map 5 software was used for further image processing. Areas of two sizes 10 × 10 μm and 100 × 100 μm with the resolution of 512 × 512 pixels were scanned for each sample. For further analysis of the chosen geometrical structure parameters (R_a , R_z , RMS , $Rsm = \lambda$) their average values, taken from 512 scans in accordance with a certain directions, were used. Furthermore, a surface development, determined using the NanoScope Analysis, was examined.

X-ray Photoelectron Spectroscopy (XPS)

Studies of X-ray photoelectron spectroscopy (XPS) were carried out using ESCALAB-210 system (VG Scientific, UK) equipped with nonmonochromatic Al ($K\alpha = 1486.6$ eV) X-ray source operated at 14.5 kV and 20 mA. Considering the obtained

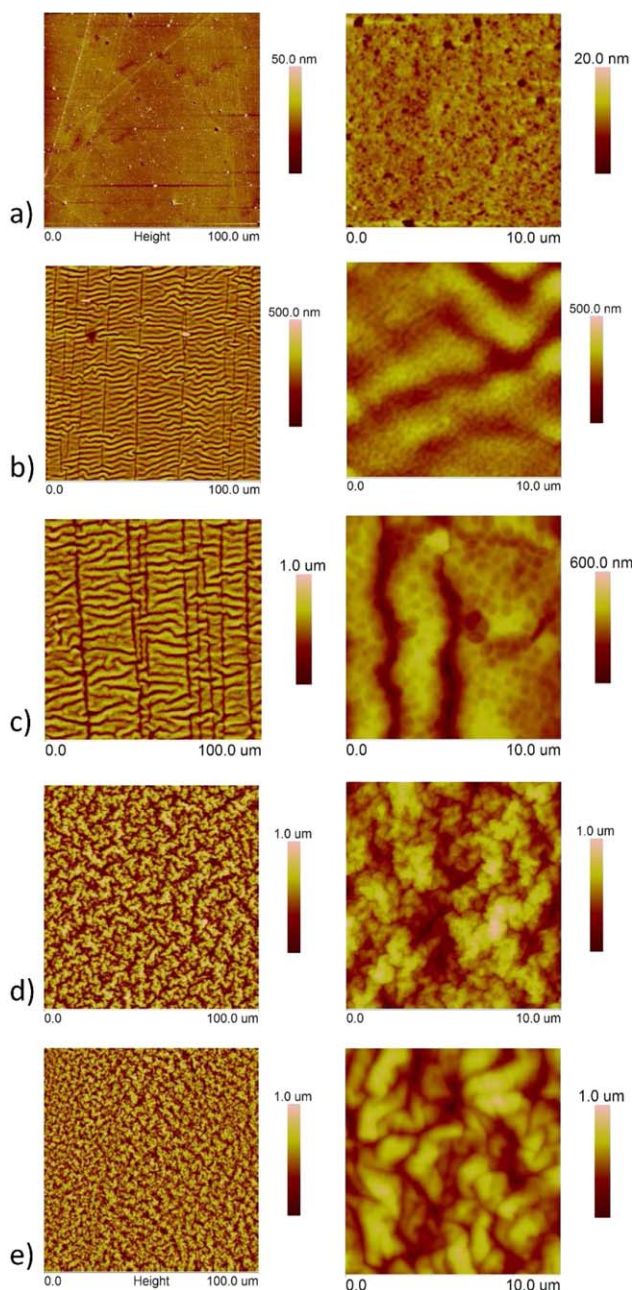


Figure 1. AFM pictures of: a) unmodified PDMS, b) modified in oxygen plasma, c) modified in methane/oxygen plasma, d) modified in methane plasma, e) nanocomposite carbon-titanium coatings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

results for carbon coatings, calibrations of the peak position were executed by taking the C1s peak at 284.8 eV.^{47,48} The C1s core level spectra were obtained at a pass energy of 25 eV. Experimental spectra were analyzed using the PEAK-FIT software. The C1s spectra were deconvoluted by Gauss-Lorentz curves, corresponding to the peaks of C-Ti (only in case of the carbon-titanium composite layers), C-Si, sp^2 phase, sp^3 phase, C-O, and C=O bounds. Obtained peak maxima were around 281.9 eV, 284.2 eV, 284.5 eV, 285.3 eV, 286.1 eV, 288 eV, respectively.^{49–51}

Contact Angle Measurement

A static contact angle was measured using the sessile drop technique, using the Kruss Easy Drop DSA15B device, at 25°C. Measures were carried out using 0.8 μ L drops of bidistilled and deionized water and diiodomethane. Presented results of the contact angles meant the average values obtained from five measurements. Based on the obtained values related to contact angle for water and diiodomethane drops, the polar and dispersive components of the surface free energy, according to the Owens-Wendt method, were calculated.^{52,53}

RESULTS AND DISCUSSION

The Analysis of Surface Geometry Changes

AFM pictures of PDMS substrates before and after the modification processes are shown in Figure 1. It was observed that when we used oxygen plasma or plasma containing the mixture of oxygen with methane, slight wrinkles on the PDMS substrate appeared, heading at one, privileged direction, while, on the contrary, in case of using methane plasma, the features of occurred wrinkles were the same, considering both vertical and horizontal directions. So, those observations also confirm data included in Table I. Coatings manufactured in methane plasma, not only DLC but also those nanocomposite (titanium-carbon), indicated the highest roughness parameters. However, the application of the pure oxygen plasma resulted in the lowest surface development (Figure 2). It was observed that the addition of oxygen into the mixture of CH_4/O_2 influenced the limitation of the values of roughness parameters of the modified surfaces. So, occurred wrinkles can assign the isotropic or anisotropic character to the surface. They are characterized by a different amplitude (λ), while, its lowest values were achieved for the privileged direction of the wrinkle propagation, when 100% of oxygen plasma was used. Similar results have been described in the literature, concerning the cases where a preliminary etching within the atmosphere of nitrogen was used.²⁵ Slight discrepancies in the value of λ , considering the two directions, for coatings modified using methane plasma, confirm the anisotropic surface geometry. In order to better illustrate the directionality of surface texture, from the two-dimensional AFM images presented in Figure 1, vertical and horizontal surface profiles were isolated (Figure 3). From the presented topography profiles is clearly visible, that the treatment of the substrates in oxygen and methane/oxygen plasma leads to the isotropic nature of the surface layer of PDMS [Figure 3(b,c)]. For other modifications [Figure 3(d,e)], the anisotropic character of the surface geometrical structure is visible. Note that the oxygen plasma treatment results in occurrence of wrinkles with lower amplitude and higher frequency, as compared with substrates treated with use of the methane/oxygen plasma.

The results of AFM investigation indicate a different modification character for methane and oxygen plasma. The differences in the observed surface topography, as indicated by Kim *et al.*,⁵⁴ arise from different values of residual strain (thermal and intrinsic), characteristic for oxidized and DLC layers. It seems that, in this experiment, the intrinsic strain plays a particular role. Considering the oxidized layer, they decide on the formation of wrinkles by close to one-way orientation, as the stiff

Table I. The Analysis of the Changes of the Surface Geometry of Modified and Unmodified PDMS Substrates Using the Plasma Techniques

Roughness parameters/SD (nm)	Type of modification				
	PDMS	O ₂	O ₂ /CH ₄	CH ₄	Ti/CH ₄
Ra ^a	2.62 ± 1.64; 2.91 ± 2.03	39.10 ± 6.81; 48.00 ± 6.24	80.70 ± 11.20; 101.00 ± 12.00	136.00 ± 11.10; 137.00 ± 11.40	122.10 ± 13.60; 116.00 ± 13.30
Rz ^a	42.50 ± 28.00; 46.50 ± 28.80	189.00 ± 37.20; 272.00 ± 40.90	448.00 ± 47.90; 586.00 ± 61.40	705.10 ± 52.20; 737.00 ± 61.10	712.00 ± 72.20; 681.00 ± 81.70
RMS ^a	5.42 ± 4.16; 5.82 ± 4.80	47.30 ± 8.65; 59.20 ± 6.73	101.26 ± 12.60; 128.00 ± 11.90	165.01 ± 12.4; 167.00 ± 12.90	151.10 ± 15.70; 144.00 ± 16.00
λ ^a	-	8.82 ± 1.66; 3.29 ± 0.61	9.72 ± 1.90; 5.33 ± 1.24	6.67 ± 0.90; 6.67 ± 0.89	5.68 ± 0.62; 5.75 ± 0.72

^aFirst values in each chart cell correspond to data heading into vertical direction, second ones – into horizontal direction.

created layer has no lateral strain.⁵⁴ However, if we consider DLC coatings, we can talk about the equibiaxial nature of compressive stress in the film,²⁶ which determines the two-dimensional wrinkles. The observed changes in the geometric parameters of PDMS surface are confirmed by the results of Kim *et al.*,²⁶ according to which the increasing thickness of the DLC coating results in an increase in the surface roughness. The coatings produced in the methane-oxygen plasma, of which the synthesis was limited by oxygen ion etching processes, are characterized by lower parameters of the surface geometrical structure, compared with the layers produced in methane plasma. In addition, based on the presented results, it can be concluded, that by decreasing the residual stress of the DLC coatings it is possible to reduce the surface geometrical parameters and the amplitude of surface wrinkles. It is, for example, clearly visible on the nanocomposite layer, where the residual stress was limited by the incorporation of Ti_xC_y inclusions into amorphous carbon matrix.

Chemical Composition Analysis

PDMS substrates before and after modification were characterized using XPS. Based on the obtained spectra, chemical composition of the examined surfaces was established (Table II) and basic relations between the surface chemical composition and the types and amounts of gases (methane and oxygen) introduced into the process were defined (Figure 4).

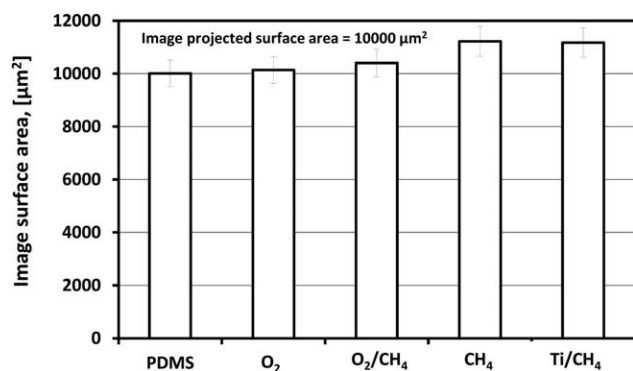


Figure 2. Comparison of the surface development of unmodified PDMS and modified PDMS using the plasma techniques.

Analyzing the chemical composition presented in Table II we can easily state that the bigger amount of methane introduced into the plasma-chemical reactor's chamber is, the smaller amount of oxygen occurs onto the modified surface. The smallest amount of oxygen was observed for samples modified in methane plasma as well as by titanium and carbon based nanocomposite coatings. These ratios are reverse if we consider the analysis of the surface carbon concentration. Coatings produced in methane plasma contained the largest amount of that element. Each of the applied plasma modifications of PDMS substrates resulted in implementing silicon into the coating, which could be derived only from the substrate, due to the fact that exclusively pure gases (methane and oxygen) were used for the modification. Nanocomposite coating synthesis procedure efficiently limited the etching processes of the substrate material, and therefore it was characterized by the lowest content of silicone. Moreover, other scientists²⁵ also observed the effect of implementing silicon into the carbon coatings. Ratios of carbon to silicon (C/Si) and oxygen to silicon (O/Si) for unmodified PDMS substrates amounted to 1.45 and 0.86, respectively. So, obtained data seem to be close to the theoretical values,

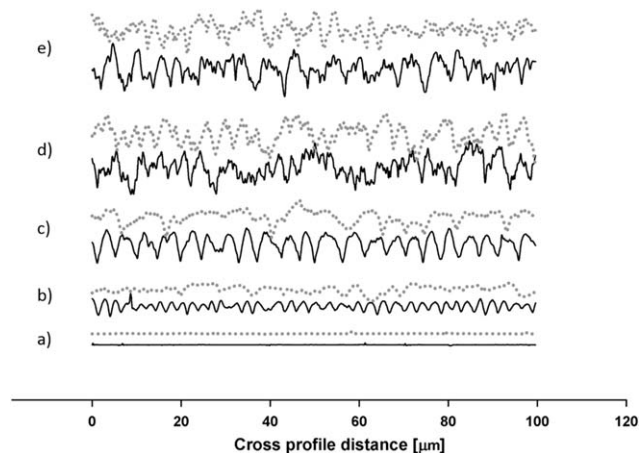


Figure 3. Cross profile evolutions of bare and modified PDMS substrate: a) unmodified PDMS, b) modified in oxygen plasma, c) modified in methane/oxygen plasma, d) modified in methane plasma, e) nanocomposite carbon-titanium coatings.

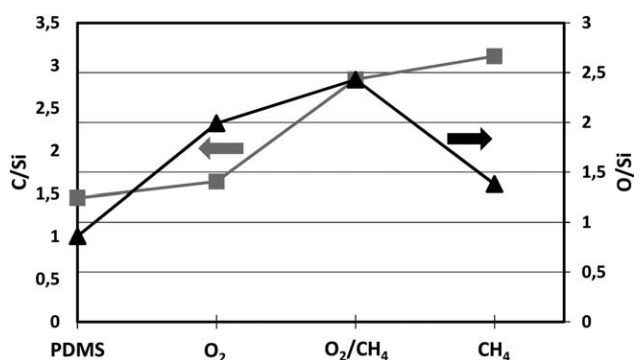
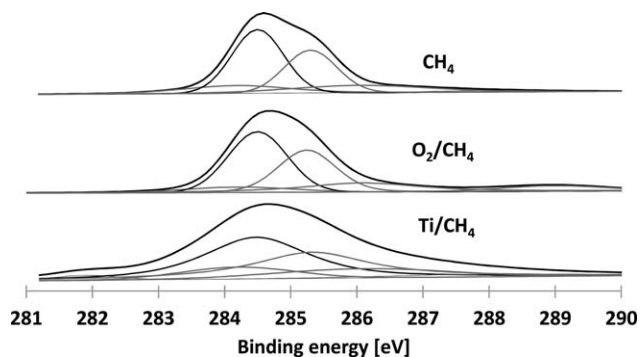
Table II. Chemical Composition of PDMS Surface, Before and After the Modification

	PDMS	O ₂	O ₂ /CH ₄	CH ₄	Ti/CH ₄
O1s	26.03	42.50	38.50	25.10	21.00
C1s	43.74	35.20	45.00	56.30	65.89
Si2p	30.23	21.40	15.80	18.10	8.34
N1s	-	0.90	0.70	0.50	0.41
Ti2p	-	-	-	-	4.36
C/Si	1.45	1.64	2.84	3.11	7.90
O/Si	0.86	1.99	2.43	1.38	2.52

characteristic for PDMS core, where each silicon atom is joined into two methyl groups. Little deviations were probably caused by joining the oxygen groups into the PDMS surfaces. Those results are in agreement with the data provided by the literature.²⁵ In case of modified substrates C/Si and O/Si ratios increase until the flow ratio of methane to oxygen reaches the value of 50/50. So, those data indicate that adding maximally 50% of methane to the working atmosphere results in strengthening the processes of oxidation of modified PDMS substrates. Considering a 100% of methane content within the working atmosphere, the highest ratio of C/Si was achieved and, simultaneously, the lowest ratio of O/Si was obtained among all described proportions. In such a way, the oxidation of the surface was efficiently decreased. In case of the titanium and carbon based nanocomposite coating, the values of the C/Si and O/Si ratios were formulated on the level of 7.9 and 2.52, respectively, being the highest among all the studied modifications.

For a more precise analysis of observed changes on the surface of carbon coatings, characteristic bonds appearing under the C1s peaks (Figure 5) were also investigated.

C1s peak was deconvoluted (Table III) on the peaks of which the maximum values oscillated around the following binding energies: 281.9 eV (corresponding to C-Ti bonds, occurring only in case of composite coatings), 284.2 eV (corresponding to C-Si bonds), 284.5 eV (characteristic for C=C bonds of sp² type) 285.3 eV characteristic for C-C bonds of sp³ type), 286.1

**Figure 4.** C/Si and O/Si content ratio for unmodified PDMS substrates and PDMS modified in the oxygen plasma, oxygen-methane and methane plasma.**Figure 5.** The view of deconvolution of C1s core level spectra for PDMS substrates, modified by the carbon coatings.

eV (characteristic for C-O bonds), 288 eV (characteristic for C=O bonds).

If we consider the coatings created using the MW/RF PACVD method, the lowest content of sp³ phase was achieved for coatings produced in the methane plasma, while, a higher one—for coatings obtained from methane-oxygen plasma. So, it is possible to assume that the addition of oxygen to methane plasma facilitates the process of etching of the graphite-like phase, allowing for reaching the highest sp³/(sp² + sp³) ratio.⁵⁵ Large amounts of sp³ phase were also noted for the nanocomposite carbon-titanium coatings. Considering that kind of modification, the amount of sp³ phase depends on both the value of a negative bias potential as well as the concentration of titanium into the coating (which facilitates the graphitization).^{44,56,57}

Contact Angle and Surface Free Energy Analysis

In Table IV, the results of contact angle measurements for deionized water and diiodomethane are presented. Based on those results and Owens-Wendt relationship, the calculations of the surface free energy SFE (Figure 6) were conducted using eq. (1).

$$(1 + \cos \Theta) \gamma_L = 2 \left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p} \right) \quad (1)$$

where γ_S^d and γ_S^p are the respective dispersion and polar terms of the solid surface free energy, γ_S , γ_L^d , and γ_L^p are the respective dispersion and polar terms of the liquid surface free energy, γ_L ; Θ is the contact angle between the solid and the analyzed liquid.

Table III. The C1s Core Level Spectra Deconvolution Analysis

	The percentage contents of C1s peak [%]		
	O ₂ /CH ₄	CH ₄	Ti/CH ₄
C-Ti (281.9 eV)	-	-	2.36
C-Si (284.2 eV)	6.50	11.96	9.62
sp ² (284.5 eV)	40.46	42.64	40.84
sp ³ (285.3 eV)	29.52	28.99	31.76
C-O (286.1 eV)	16.74	14.07	11.46
C=O (288 eV)	6.78	2.33	3.96
sp ³ /(sp ² + sp ³)	0.42	0.40	0.44

Table IV. Analysis of the Contact Angles of PDMS Surfaces Before the Modification and Modified by Plasma Techniques After the Period of 1 h Time After the Process was Conducted

	Contact angle (°)				
	PDMS	O ₂	O ₂ /CH ₄	CH ₄	Ti/CH ₄
Water	111.85 ± 0.34	41.30 ± 0.99	47.80 ± 0.17	128.80 ± 0.31	120.20 ± 0.52
Diiodomethane	74.75 ± 0.23	44.50 ± 0.4	41.70 ± 0.10	64.10 ± 0.22	95.52 ± 0.14

Obtained values of the contact angle for deionized water of unmodified PDMS substrate are adequate to the data found in literature.^{11,58–60} Thus, they are the proof for the hydrophobic properties of that polymer surface. Through the processes of plasma modification it is possible to influence the change of the wettability, either to strongly hydrophilic (what is clearly visible for the PDMS substrates modified using the oxygen plasma) or more hydrophobic, what is proved by the next modifications. The lowest values of the contact angle were obtained for modifications conducted in the oxygen plasma. In the literature, we are capable of finding the information about a possibility of decreasing the value of the contact angle after the process of oxygen plasma modification, even up to the value of a few degrees.^{59,60} However, the change of that angle toward higher values takes place very quickly, while the time between the removal of the sample from plasma-chemical reactor till the moment of the measurement is a determining factor for the values of obtained data. As presented in the Materials and Methods section, preliminary measurements of the contact angle were performed after 1 h after the process was conducted. In this way, the angle of 41.3 ± 0.99 for modification in the oxygen plasma was obtained. While, upon the introduction of methane and oxygen to the process in the 50/50 proportions, the contact angle increased to 47.8 ± 0.17 . Nevertheless, it is worth mentioning that in case of modification with oxygen, the value of the contact angle was changing, reaching the values around 90 degrees after few days (Figure 7).

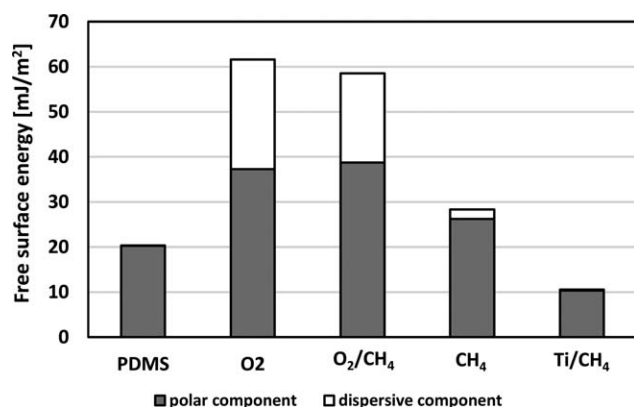
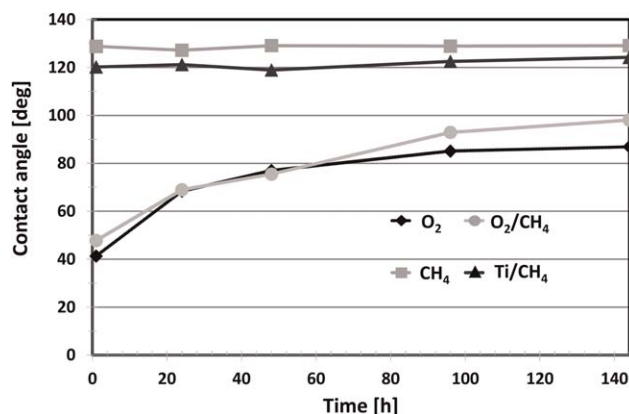
The highest values of the contact angle for deionized water were obtained for modifications performed using methane plasma (which means that the carbon coatings with their lowest

amount of sp³ phase), while for carbon and titanium based nanocomposite coatings, the values of contact angle remained already low (always indicating higher values in comparison to unmodified PDMS). Considering those modifications, the value of the contact angle within the period of time was stable, while the observed changes in the contact angle for carbon coatings can be explained by different ratios of sp³/sp² phases. Stability of contact angle of PDMS substrates, modified in methane plasma were also confirmed by other scientists.⁵⁹

Conducted research and the literature data⁶¹ indicate that, the carbon coatings are characterized by a constantly decreasing contact angle with a simultaneous growth of the sp³ phase content. The analysis of the surface free energy showed that its particularly high values can be achieved through the modification of PDMS in oxygen plasma. PDMS substrates modified by the titanium and carbon based composite coatings were characterized by the lowest surface free energy value.

CONCLUSIONS

In the presented work the analysis of the influence of the chemical composition of the working atmosphere used for the surface modification of PDMS substrates onto the changes in both their surface geometry and chemical composition was conducted. It was turned out that the wrinkles, produced onto the surface of modified PDMS can show uni- or multidirectional character, being precisely connected with the type of gas used in the modification process. The smallest surface development was characteristic for the modifications performed using oxygen plasma. In turn, application of titanium and carbon based layer resulted in the smallest amplitude. Surface chemical

**Figure 6.** Analysis of the surface free energy of PDMS substrates before and after the modification using plasma techniques.**Figure 7.** Analysis of the changes of the contact angle in time of the surfaces, modified by plasma techniques.

composition of substrates subjected the plasma modifications confirmed the presence of silicone onto the surface, being the result of etching the PDMS substrates. This process takes place simultaneously with the synthesis of carbon coatings. Obtained carbon coatings were characterized by about 40 to 44% of the sp^3 phase content within the total ratio of $sp^3/(sp^2 + sp^3)$. Proposed modification of the PDMS substrates allowed to change their properties from hydrophilic (with low stability in time) to hydrophobic (contact angles to over 115 degrees—stable in time). Moreover, the correlation between the sp^3/sp^2 phase ratio and values of contact angles for deionized water was also established. Values of the contact angles and the surface free energy were increasing according to the decrease of sp^3/sp^2 ratio. Despite clear differences in topography of modified PDMS surfaces, the parameters of geometrical surface structure did not play a significant role in the changes of contact angles. Presented results constitute the basis for conducting modification processes of PDMS substrates in order to achieve the best conditions provided for the cell cultures, where the biggest significance is related to a precise control of the surface roughness as well as the possibility to change the surface chemical composition through the implementation of appropriate functional groups.²⁰

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