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Layer-by-layer assembly of thin organic films on PTFE activated by cold atmospheric plasma

Abstract: An air diffuse coplanar surface barrier discharge is used to activate the surface of polytetrafluoroethylene (PTFE) samples, which are subsequently coated with polyvinylpyrrolidone (PVP) and tannic acid (TAN) single, bi- and multilayers, respectively, using the dip-coating method. The surfaces are characterized by X-ray Photoelectron Spectroscopy (XPS), Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Atomic Force Microscopy (AFM). The XPS measurements show that with plasma treatment the F/C atomic ratio in the PTFE surface decreases, due to the diminution of the concentration of CF_2 moieties, and also oxygen incorporation through formation of new C–O, C=O and O=C–O bonds can be observed. In the case of coated samples, the new bonds indicated by XPS show the bonding between the organic layer and the surface, and thus the stability of layers, while the gradual decrease of the concentration of F atoms with the number of deposited layers proves the creation of PVP/TAN bi- and multi-layers. According to the ATR-FTIR spectra, in the case of PVP/TAN multilayer hydrogen bonding develops between the PVP and TAN, which assures the stability of the multilayer. The AFM lateral friction measurements show that the macromolecular layers homogeneously coat the plasma treated PTFE surface.

Keywords: DCSBD plasma, Polytetrafluoroethylene surface, Polyvinylpyrrolidone and tannic acid layers, ATR-FTIR, XPS, AFM

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1 Introduction

Polymeric materials are used in several biomedical applications, such as implants – artificial skin [1], vascular grafts [2,3], artificial corneas [4], artificial organs [5] – along with tissue regeneration [6] and drug delivery systems [7]. In addition, they are broadly utilised for medical devices such as catheters and sutures [8,9]. Although many efforts have been made to improve these materials for biomedical applications, their biocompatibility is still a challenge. One way to achieve biocompatibility is coating the surface with natural molecules or covalent immobilization of biomacromolecules to the activated or subsequently grafted polymer surface [10-12]. The surface can be activated, i.e. the surface properties of polymers – including surface chemical composition and surface energy – can be modified by plasma treatment [13-15]. Plasma treatment can cause incorporation of polar functional groups, formation of dangling bonds, cross-linking and modification of surface roughness.

Our work focuses on the applicability of an atmospheric air plasma for the activation of PTFE surfaces, that are subsequently to be coated with organic materials. We have chosen two different macromolecules, i.e. polyvinylpyrrolidone (PVP) and tannic acid (TAN) and investigate the possibility of creating stable single- and multilayers of them. PVP is known for its wetting properties, therefore can be applied for hydrophilization of surfaces, and as being a good coating agent can be used as additive to coatings [16,17]. On the other hand, tannin coatings can exhibit antibacterial, antimutagenic or antimicrobial effects [18-20]. There has also been an increasing interest in H-bonded assembly of tannic acid with several neutral polymers, including poly(N-vinylpyrrolidone), for the development of physiologically stable thin films and hollow capsules for controlled drug

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release (since tannin can be a model polyphenolic drug) and other biotechnology applications [21-24].

2 Experimental

2.1 Plasma system

The plasma system used for surface activation is a diffuse coplanar surface barrier discharge (DCSBD) [25-27] (manufactured by Roplass s.r.o., Brno, Czech Republic). The DCSBD plasma panel consists of two systems of parallel strip-like electrodes (with typical dimensions of: 1.5 mm wide, ~0.5 mm thick, 1 mm strip to strip) embedded in alumina. The thickness of the ceramic layer between the plasma and electrodes is typically 0.4 mm. The plasma is ignited with sinusoidal high frequency, ~10–20 kHz, high voltage with peak-to-peak values of up to 20 kV. The diffuse plasma developed over the alumina surface is visually uniform, in fact it consists of sequences of H-shaped elementary discharges. The elementary discharge consists of a diffuse surface discharge developed over the metal electrodes and of a filamentary streamer discharge created between the electrodes giving its H shape [25]. With increasing the voltage and absorbed power, more and more elementary discharges are generated, thus the homogeneity of the DCSBD increases. Due to the applied high voltage, heating of the dielectric surface is expected, as well as that of the surrounding gas. To keep the system at the lowest possible temperature with a simple cooling system, oil is circulated over the system, which makes possible to keep the gas temperature around 370 K [26]. The discharge in the present study was operated in air at 300 W (which provided a quasi-homogeneous diffuse plasma surface). Fig. 1 shows the optical emission spectra recorded over the plasma surface. The emission is dominated by the N₂ second positive system, with a small contribution in the UV spectral range.

2.2 Sample preparation

In the present study polytetrafluoroethylene (PTFE) plates (size: 1200 mm x 1200 mm, thickness: 2 mm) produced by Quattroplast Ltd. (Budapest) were used. The PTFE was cut into 1 cm x 1 cm pieces, which were then treated with the DCSBD to activate their surface. The samples were brought in contact with the air plasma in tapping mode and exposed to it for 3 min. After plasma treatment, the PTFE samples were coated with Sigma-Aldrich polyvinylpyrrolidone

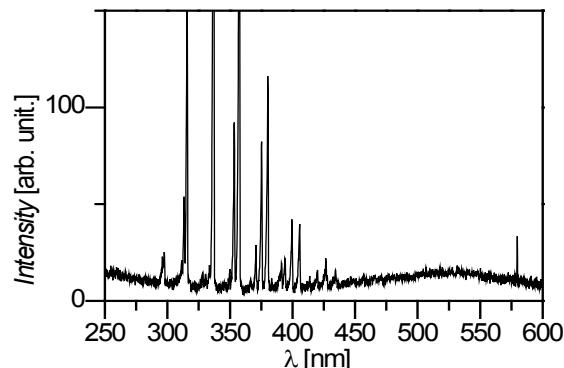


Figure 1: Optical emission spectra recorded over the plasma surface.

Table 1: The different samples prepared by treating the polytetrafluoroethylene (PTFE) and coating it with organic (PVP – polyvinylpyrrolidone, TAN – tannic acid) single- and multilayers.

Sample ID	Sample	Staying in reagent
PTF1	untreated PTFE	-
PTF2	activated PTFE with cold plasma	-
PTF3	activated PTFE with cold plasma	PVP for 12 hours
PTF4	activated PTFE with cold plasma	TAN for 12 hours
PTF5	activated PTFE with cold plasma	PVP and TAN for 1-1 hour
PTF6	activated PTFE with cold plasma	PVP and TAN and PVP for 1-1 hour
PTF7	activated PTFE with cold plasma	PVP and TAN for 1-1 hour repeated six times

(PVP, Molecular weight: ~10000, [C₆N₁O₁H₉]_n) and tannic acid (TAN, C₇₅O₄₆H₄₆) layers, respectively, by the layer-by-layer (LbL) technique, using the dip-coating method. For this purpose, solutions of PVP (5 g in 50 ml double distilled water) and TAN (5 g in 50 ml double distilled water) were applied alternately, with wash and heat treatment steps after depositions. The different type of single- and multilayer coated samples prepared during experiments are listed in Table 1. The soaking time in double distilled water after each deposition in PVP or TAN was generally 2 min, while the drying temperature after soaking was 80°C, except in the case of PTF6 sample, where 100°C was used.

2.3 Surface characterization

The surface structural, morphological and energetic properties of the systems were determined by Attenuated

total reflection – Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angle measurements.

The ATR-FTIR measurements were recorded using a Varian 2000 FTIR Scimitar Series (Varian, Inc, USA) spectrometer equipped with a liquid nitrogen cooled mercury-cadmium telluride (MCT) detector and fitted with a 'Golden Gate' single reflection diamond ATR accessory (Specac Ltd, UK). Interferograms were collected using 256 scans at a resolution of 2 cm^{-1} . The GRAMS/32 software package was used for the spectral analyses.

The XPS studies were performed by a Kratos XSAM 800 spectrometer using $\text{Mg K}\alpha_{1,2}$ excitation, with fixed analyser transmission of 80 and 40 eV pass energy, 0.5 and 0.1 eV step size for survey and high-resolution spectra, respectively. The spectra were referenced to the C1s line (binding energy, BE = 285.0 eV) of the hydrocarbon type carbon. The accuracy of binding energy determination was ± 0.2 eV. Data acquisition and processing were done with the Kratos Vision 2 program.

Atomic force microscopy (AFM) measurements were performed in a liquid AFM cell, in contact mode, at room temperature, under 100 mM MgCl_2 solution, using a NanoScope V microscope controller (Veeco Instruments, Inc., USA). The following parameters were applied: 9 different scan areas on each sample, scan size $10\text{ }\mu\text{m}$, scan rate 2 Hz, 256×256 pixel images. Silicon nitride cantilevers were used, with force constant of 0.12 N m^{-1} . The analysis was performed by the manufacturer's software Nanoscope 7.30.

3 Results and Discussion

The change in the chemical composition of the PTFE surface induced by the plasma treatment, as well as the composition of the coating layer, have been studied by X-ray photoelectron spectroscopy. Fig. 2 shows the XPS spectra recorded for the untreated and plasma-treated surfaces, as well as the plasma-treated surfaces coated with organic layer. The figures show the characteristic spectra of the different elements observed, i.e. fluorine (F 1s), oxygen (O 1s), nitrogen (N 1s) and carbon (C 1s). The composition of the surfaces determined, based on the measured spectra, are shown in Table 2. It is demonstrated that defluorination of the surface occurs due to plasma treatment, and while the F/C atomic ratio decreases, a significant amount of oxygen incorporates into the surface. The C 1s spectra indicates the decrease of the F

and CF_2 moieties' concentration – since the intensity of the characteristic peak at 292 eV binding energy decreases – and the formation of new functional groups such as C–O, C=O and O=C–O, with the appearance of the broad peak in the 283–290 eV binding energy range [28,29].

Concerning the organic layers, the XPS spectra indicates a further defluorination of the plasma treated surface when a single layer of PVP has been applied (PTF-3), while in the case of TAN (PTF-4), similar F concentrations are obtained as in the case of the uncoated plasma treated surface. This fact may indicate, that in the case of PVP, a stronger attachment to the surface can be achieved, than in the case of TAN. Nevertheless, the shift of the O 1s peak into direction of 533 eV in the case of TAN layers (PTF-4 on Fig. 2b) means the appearance of C–O–C functional groups, which can indicate the reaction between TAN ($\text{C}_{75}\text{O}_{46}\text{H}_{46}$) and PTFE. In the case of bi- and multilayers of PVP/TAN (PTF-5 – PTF-7) the gradual decrease of the F concentration originating from the substrate is observed, which indicates the increase of the organic layer thickness.

To obtain information on the interaction between the TAN and PVP molecules, and thus on the stability of the organic multilayer, the infrared spectrum of a self-assembled film was measured at room temperature. For this purpose, a multilayer (TAN/PVP) film was prepared on the plasma treated PTFE. The FTIR spectroscopic

Table 2: Surface composition (atomic %) of untreated and various plasma-treated PTFE samples, together with the theoretical and measured composition of compounds applied for organic layers formation. For identification of different ID samples please refer to Table 1.

Sample	F (%)	O (%)	N (%)	C (%)
PTF1	68.7	0.6		30.7
PTF2	53.1	4.3		42.6
PTF3	35.9	9.0	3.8	51.2
PTF4	53.8	6.7		39.5
PTF5	33.3	14.9	2.5	49.4
PTF6	25.5	13.9	4.4	56.0
PVP		13.2	11.0	75.8
TAN		40.1		59.9
Theoretical composition of basic materials				
PVP		12.5	12.5	75.0
TAN		38.0		62.0
PTFE	66.7			33.3

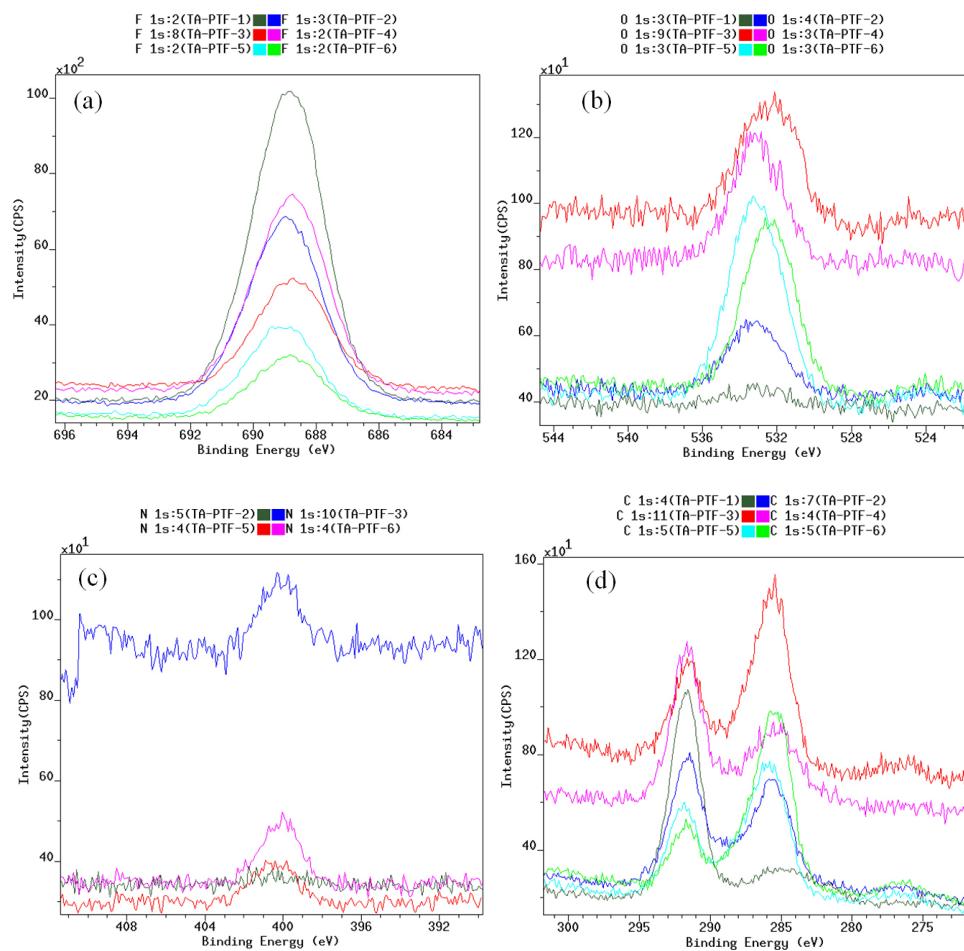


Figure 2: XPS spectra of untreated and plasma-treated PTFE samples.

method can reflect variations at the molecular level, providing information from the whole spectral region simultaneously. For comparison, the spectra of the pure PVP and TAN were also measured.

We focus our attention mainly on the vibrations associated with the carbonyl group in the 1750–1650 cm⁻¹ spectral region. As shown in Fig. 3a, the absorption band at 1653 cm⁻¹ in the spectra of PVP is assigned to the stretching vibration of carbonyl groups. This band shifts to 1692 cm⁻¹ in the spectra of the multilayer, suggesting the formation of intermolecular hydrogen bonds. The ester C=O stretching vibration at 1701 cm⁻¹ originating from TAN molecules is shifted towards higher wavenumbers, 1746 cm⁻¹, due to the formation of intermolecular hydrogen bonds between PVP and TAN molecules. Fig. 3b, shows also the vibrations at higher wavenumbers. The appearance of a new band at 2632 cm⁻¹ in the spectra of the multilayer, which is assigned to N-H stretching vibrations, also indicates the formation of intermolecular hydrogen bonds. On the other hand, the

bands appearing in the 3180–3400 cm⁻¹ spectral region are identified as the O-H stretching bands for the phenolic groups [22,30]. It can be also noticed that the absorption band of the hydroxyl groups in the TAN shifts from 3334 to 3280 cm⁻¹ (Fig. 3b). With the formation of new bonds, we can conclude that the two layers react with each other and form a stable assembly.

The surface properties of the treated PTFE and that of the coating layers have been investigated by AFM. The AFM measurements show that the average roughness (R_a) of the PTFE surface does not change significantly upon plasma treatment, but decreases upon layer deposition. The calculated average roughness data are shown in Fig. 4 for the untreated PTFE surface, for the plasma treated surface and that of the coated with PVP/TAN/PVP layer. The AFM can also give information about the quality of the surface through lateral force microscopy measurements, which images variations in surface friction, arising from chemical inhomogeneity in surface

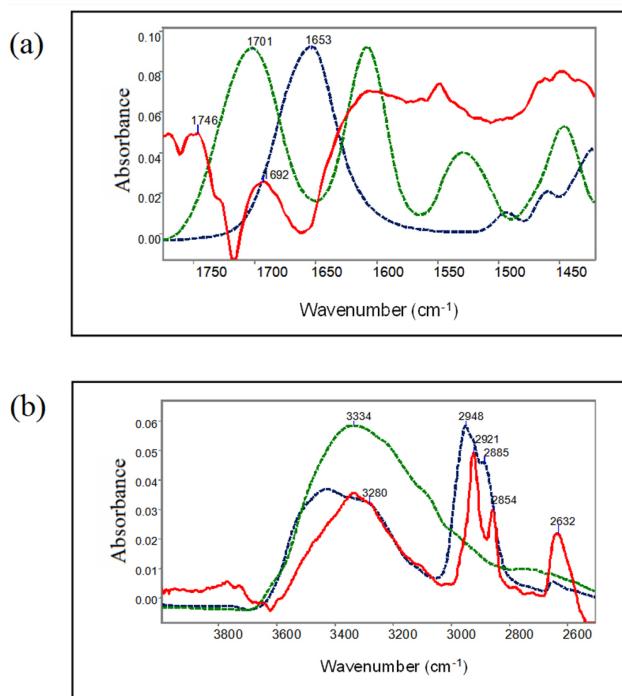


Figure 3: ATR-FTIR spectra of PVP (blue), TAN (green) and multilayer PVP/TAN film (red) for the carbonyl stretching (a) and the hydroxyl stretching regimes (b).

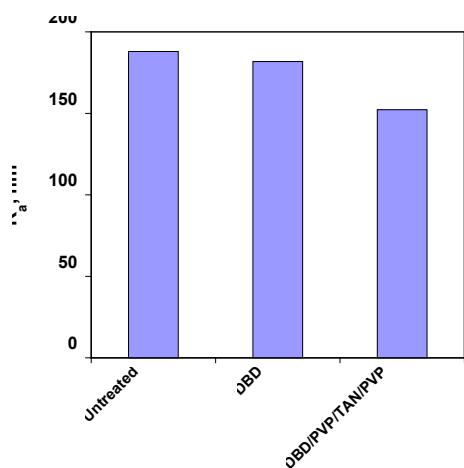


Figure 4: Average R_a surface roughness values of the untreated and treated surfaces.

material. Fig. 5 shows the friction images of the above mentioned surfaces, demonstrating, that the PVP/TAN/PVP layer homogeneously covers the plasma treated surface, which in turn is also more homogeneous than the untreated PTFE surface. Finally, the contact angle studies have shown that the wettability of PTFE increases upon air plasma treatment and with deposition of PVP and TAN layers.

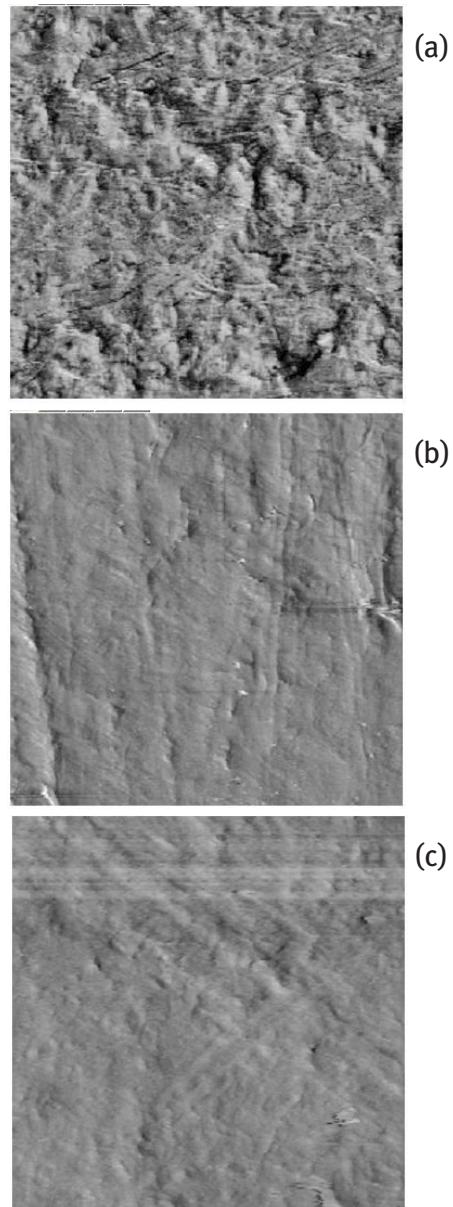


Figure 5: Friction images of the untreated (a), plasma-treated (b) surfaces, and plasma-treated surface coated with PVP/TAN/PVP layer (c), visualized by atomic force microscopy in aqueous environment.

4 Conclusions

In this work we investigated the possibility of creating stable organic bi- and multilayers on PTFE surfaces activated by an air diffuse coplanar surface barrier discharge (DCSBD). The PTFE surfaces were brought in contact with the plasma in tapping mode for about 3 minutes. Afterwards, organic single, bi- and multilayers were prepared on the plasma-activated surfaces by the layer-by-layer (LbL) technique, using the dip-coating method.

For this purpose, solutions of polyvinylpyrrolidone (PVP) and tannic acid (TAN) were applied alternately, with wash and heat treatment steps after depositions. The surface alterations induced by plasma to the PTFE surface, as well as the surface structural, morphological and energetic properties of the systems were determined by attenuated total reflection: Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angle measurements.

From the XPS measurements it has been concluded that both TAN and PVP attach to the surface by bonding, which gives stability to the coating layers. According to the ATR-FTIR results hydrogen bonding can develop between the TAN and PVP layers, which assures the creation of a stable PVP/TAN multilayer. The AFM friction measurements have demonstrated that the organic layers homogeneously coat the plasma treated surfaces.

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