Study of plasma polymer structures to induce composite layers[*]

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This study is designed to investigate the ability of plasma polymer films (PPHMDS), grown from the hexamethyldisiloxane (HMDS) monomer on stainless steel (SS) and silica glass (SG) substrates, to induce the deposition of composite layers from a mixture of saturated simulated body fluid (SBF) and detonation nanodiamond (DND) by a biomimetic process. Results from FTIR and XPS studies showed that the structure of the PPHDMS layers depends on the nature of the substrate, as well as on the deposition conditions and the influence of the subsequent deposition of the composite layers. The PPHDMS structure appears to be covalently bonded to SG, compared to those on SS. After their immersion in the mixture of SBF and DND, the layers grown on the SG_PPHDMS structure shows the existence of phosphate and carbonate groups. On the SS_PPHMDS, it shows a predominantly carbon enrich deposit, which indicates that the lack of functional polar groups of the SS_PPHMDS surfaces, and limits the process of precipitation of the SBF ions. The results emphasize the potential for tailoring a plasma polymer structure PPHMDS, by varying the deposition conditions and substrate, in order to use them as biocompatible materials.

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1. Introduction

Polymers are of increasing interest for utilizing as a matrix for calcium phosphate-based composites, with applications in hard tissue implants [1]. However, polymers with applications as heart valves, urea catheters and artificial vessels present a case where the formation of minerals (namely calcification) should be avoided. [1–2].

From a medical point of view, the formations of fibrous tissue and blood clotting are restrained upon implantation of carbon-based materials [3, 4]. In the experiment described in this paper, modification was made of the surfaces of stainless steel (SS) and silica glass (SG) substrates, by deposition of plasma polymer layers, grown from the monomer hexamethyldisiloxane (HMDS) [5, 6] (denoted as SS_PPHDMS and SG_ PPHDMS). A biomimetic (process of precipitation) method was utilized in this study, to deposit composite layers from a mixture of saturated SBF and DND on the already modified substrates. (SS_PPHDMS and SG_PPHDMS). The novelty in our work is the addition of nanodiamond particles (DND; 4-6 nm in size) to the SBF solution, which resulted in the reinforced deposition of SBF ions [7] and

can improve the mechanical properties of the HA itself and its adhesion to the metal surface [8].

2. Experimental

Substrates were prepared from austenitic stainless steel (AISI 316L) and SG 10x10x2 mm in a size that was subjected to standard treatment [9]. The polymerization of the monomer Hexamethyldisiloxane (HMDS) was carried out on the substrates by controlling two parameters of plasma polymerization: the flow rate of HMDS and the current density of the glow discharge [5, 6]. The characteristics of the obtained samples are described inTable 1.

The solution resembled the ion composition, concentrations and pH of the human blood plasma and is known as SBF [9]. The used DND particles were synthesized by detonation of trinitrotoluene and hexogen at high pressure and high temperature [10]. Subsequent purification from graphite by applying oxidation with potassium dichromate in sulphuric acid was carried out, and after several washings with HCl and water, the DND suspension was obtained. The as-obtained DND

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suspensions (41g/l) were added to the SBF solution and ultrasonically shaken for 20 min. The biomimetic process was performed at 37^0C, at pH values of 7 and 4, for 24 and 48 hours, applying permanent magnetic stirring. Two groups of samples were prepared by: (i) deposition on SS_PPHMD from SBF-DND for 24 and 48 h; samples denoted as SS_PPHMD_24(48); (ii) deposition on SG_PPHMD from SBF-DND for 24 and 48 h; samples denoted as SG_PPHMD_24(48)

Table 1. Parameters of the plasma process and the measured in situ thickness of PPHMDS films.

Sample	Monomer flow rate [l/h]	Current density [mA/cm^2]	Thickness [nm]
SS_PPHMDS_1 SG_PPHMDS_1	1.0	1.6	107
SS_PPHMDS_3 SG_PPHMDS_3	2.0	1.6	150

The samples were studied by AFM (NT-MDT Equipment, Uni Solver System), XPS (SCIENTA ESCA 200). FTIR (BRUKER, VECTOR 22) was used to investigate the bonding structure of PPHMDS and composite layers, grown on SG.

3. Results and discussion

The results of the AFM study are presented in Fig. 1. Roughness analysis (average roughness: Ra of scanned 5x5μm^2, 20x20μm^2 and 80x80μm^2 areas, respectively) showed that the deposition of thin PPHMD on SG resulted in the formation of smoother layer than that on the SS substrate. After their subsequent immersion in the SBF-DND for 24 and 48 hours this resulted in the deposition of the composite layers that had reduced average roughness
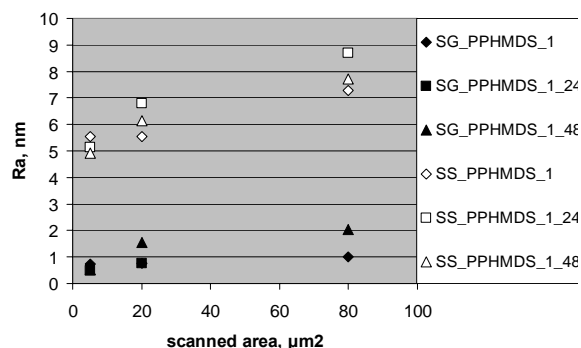

Fig. 1. Average roughness (Ra) of SS_PPHDMS_1 and SG_PPHMDS_1 depending on the soaking time and scanned area

of the initial plasma polymer (PPHDMS) surfaces, as following: the composite layer SG_PPHDMS_24(48) had a rougher surface than that grown on the SS (SS_PPHDMS_24(48)). The structure of the layers grown on the SG substrate (SG_PPHDMS_24(48)) was investigated by FTIR spectroscopy (not presented here). They
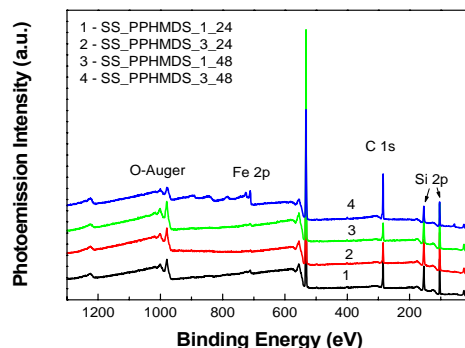

Fig. 2. Survey of SS_PPHDMS_1 and PPHDMS_3 samples after 24h (1,2) and 48h (3,4) soaking times, respectively.

show that no distinct hydroxylapatite (HA) layer was observed. However, an absorbance band at 870 cm^{-1} of acid phosphate and the triply degenerate asymmetric P-O bending vibration of the phosphate groups (PO_4^{3-} at 570, 602, and 632 cm^{-1}), as well as some carbonate bands (870 and 1420 cm^{-1}) were registered, the intensity of which increased with the time of precipitation [6]. Table 2 shows the semi-quantitative results from an XPS study, for the elements present on the surface of the samples, as obtained from the core levels. There was no preliminary surface cleaning. The percentage of each element was calculated using the atomic sensitivity factors, and does not represent the "real" content, but still is interesting in comparing the samples.

Table 2. Semi-quantitative results from an XPS study for the elements present on the surfaces of the samples (1-4, assigned in figures 2-6).

Sample	Fe (%)	O (%)	C (%)	N (%)	Si (%)
1	0.8	46.9	22.4	0.8	29.1
2	0.3	49.6	17.8	0.6	31.7
3	0.4	52.6	13.8	0.5	32.6
4	2.2	39.5	33.8	0.9	23.5

In Fig. 2, the survey of samples (1 – 4) are shown, and the assignation of each peak present in the spectrum. In Figures 3-5 the core levels of Fe 2p, O 1s and C 1s are shown for the samples 1- 4.

Fig. 3 shows that the iron content is practically the same in samples 2 and 3, double in sample 1, and more than five times higher in sample 4.

Iron is present both in the metallic and in the oxidised form. In Fig. 4, the O 1s line shape is pretty much the same for the entire sample, except for sample 4, where the tail at a lower binding energy is due to oxygen bound to iron. The peak at the higher binding energy is due either to O-Si and/or O-C bonds.

It has been shown that the polymer structure depends on the nature of the substrate and influences the composite layers subsequently grown from a SBF-DND mixture. In contrast to SS, the SG substrate could react by SG silanol
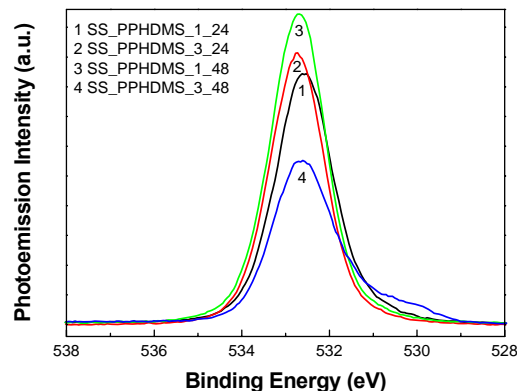

Fig. 4. Core line for O 1s of composite layers (1-4).

groups [6]. After immersion of a polymer structure grown on a SG substrate in the SBF-DND for 24 and 48 hours, this shows the existence of phosphate and carbonate groups. The process of precipitation of SBF ions is inhibited for the polymer structures grown on SS.
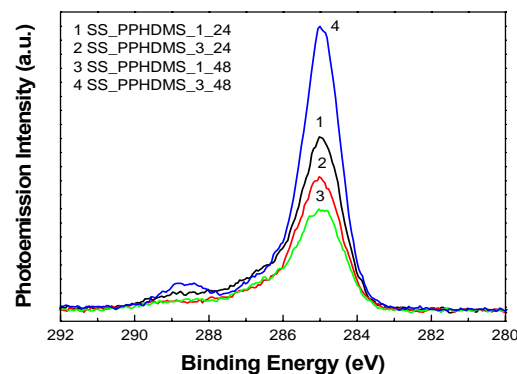

Fig. 3. Core line for Fe 2p of composite layers (1-4)

The C 1s lineshape in Fig. 5, consists of at least three peaks. The one at 285.0 eV, used to align all the spectra, is due to C-H and C-C bonds. The second one, around 187 eV, is due to C-N and C-O bonds, and the last one around 289 eV to COOH bonds. The amount of nitrogen is very small, and the measurements very noisy, making it difficult to perform a fit. The Si 2p core line (Fig. 6) shows that the position of the peak is the same in all the samples, and at the energy of SiO_2 bonds. The energy difference between Si 2p and O 1s (main peak) is that of SiO_2.

4. Conclusions

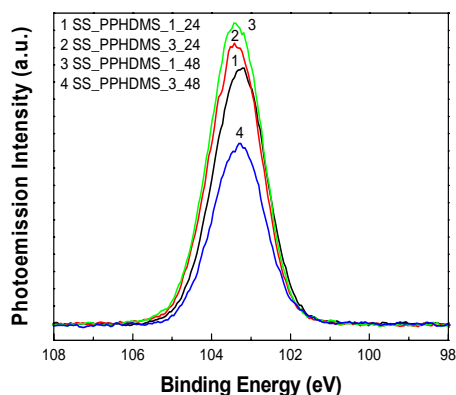*Fig. 5. Core lines for C1s of composite layers (1-4)*

Fig. 6. Core lines for Si2p of composite layers (1-4)

The results emphasize a potential for tailoring a plasma polymer structure of PPHMDS, by varying the deposition conditions and substrate, in order to use them as biocompatible materials for different medical applications.

Acknowledgements

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