PLASMA SURFACE MODIFICATIONS OF POLYMERIC SUBSTRATE FOR APPLICATIONS IN BIOMEDICINE

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Introduction

Polymeric materials have a significant role in medicine, in particular as parts of orthopaedic prosthesis, cardiovascular grafts (*i.e.* artificial heart valves), and artificial organs, *etc.*. Unfortunately, surface properties of these materials such as wear resistance, hardness or wettability do not meet requirements for biomaterials. Therefore, physicochemical properties, as well as biological activity, have to be improved, for instance using thin layer technology [1-3].
Many research groups have obtained coatings on polymeric substrates (*i.e.* polyethylene, polyurethane) using various deposition methods [4-5]. However, in the case of modification of polymeric surfaces for use in implantology, plasma-based techniques are the most suitable ones, especially the chemical vapour deposition (CVD) methods.
In this study, the various types of DLC coatings (as well doped with Si or N atoms) on polyethylene, were deposited under plasma conditions in order to improve mechanical and biological properties of the substrate.

Materials and Methods

Carbon-based coatings were deposited on polyethylene (PE) substrate by RF CVD (*Radio Frequency Chemical Vapour Deposition*) method. Firstly, substrates were functionalization in argon plasma. Then, four experimental series of coatings were obtained: (*i*) single layer: a-C:H or a-CN:H and (*ii*) multil-layer coatings: a-CN:H/a-C:H or a-CN:H/a-SiC:H. All plasma processes were carried out at room temperature and under pressure of gas mixture in reactor chamber below 60 Pa.
Characterization of surfaces were conducted with application of typical engineering methods: (*i*) microstructure and composition of the obtained coatings were determined using scanning electron microscopy (Nova NANO SEM 200, FEI USA) with EDS analyser, (*ii*) topography and atomic structure characterization of the resulting coatings were revealed by AFM and IR-ATR spectroscopic methods, respectively, (*iii*) wettability and surface free energy (SFE) of tested samples were investigated using an automatic drop shape analysis system DSA 10 Mk2 (Kruss, Germany), (*iv*) hardness and Young modulus of unmodified and modified samples were evaluated by Nanoindenter G200 (Agilent Technologies, MTS Nano Instruments), (*v*) cytotoxicity of the resulting materials was assessed *in vitro* by MTT assay.

Results and Discussion

SEM images confirmed the structure without visible defects and delamination of obtained coatings. In case of sample with a-SiC:H deposition, the EDS analysis revealed the high value of silicon content (*ca.* 27 at. %). This should cause the decrease of internal stresses in the obtained structure and assure low bacterial adhesion.
The most homogenous surfaces were obtained for the deposition of two-layers (a-CN:H/a-SiC:H). The AFM image (FIG. 1B) of two-dimensional surface confirmed the granular and nanometric structure of the deposited coatings.

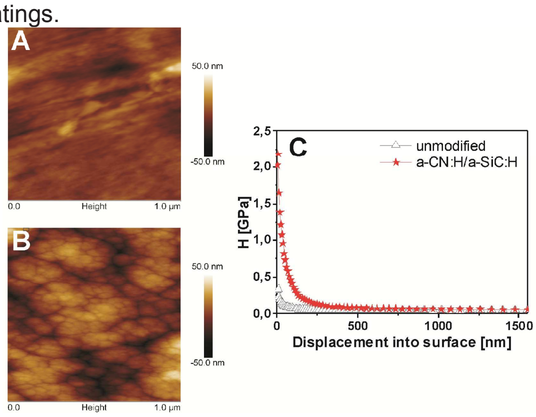

FIG. 1. Surface topography of the PE substrate: A) unmodified surface, B) after a-CN:H and a-SiC:H coatings deposition. C) Hardness profile of the modified PE in comparison with untreated substrate.

All types of plasma modifications significantly improved hardness of the polymeric substrates in comparison with the untreated samples. The highest hardness (*ca.* 2.2 GPa) was observed for the series after the process of modification with two layers deposition (FIG. 1C).
Furthermore, it was demonstrated that for all the tested modified samples with DLC, N-DLC and Si-DLC coatings the characteristic bands' positions in IR spectra were observed at 2750 cm^{-1}÷3050 cm^{-1}, 3300 cm^{-1}÷3400 cm^{-1} and 1250 cm^{-1}, respectively.
For all series of surface modifications after plasma treatment, significant decrease of contact angle was observed, compared to untreated polymeric substrate (up to *ca.* 57^{o}, diiodomethane).
What is noteworthy, for all obtained surface modifications no significant cytotoxicity against osteoblast cell line (MG-63) *in vitro* was observed (less than 20 % reduction of surviving fraction). These preliminary results suggest that the resulting materials may demonstrate a promising biocompatibility.

Conclusions

In conclusion, in this study it was demonstrated that for all plasma-based surface modifications of PE substrate psychochemical properties such as wettability, hardness, and wear resistance were improved. The most significant improvement was observed in case of bilayer deposition of a-CN:H and a-SiC:H coatings. Importantly, all plasma modified samples do not exhibit significant cytotoxicity *in vitro*.

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