MEASUREMENT OF SURFACE PROPERTIES OF PYROLYTIC GRAPHITE FOR BIOMEDICAL APPLICATIONS

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Introduction

In recent years, a great number of biomaterials have come into routine use for constructing medical devices. Biomaterials should fulfill certain requirements, namely the following:
biofunctionality, i.e., suitable mechanical properties for replacing the tissue,
biocompatibility, i.e., no negative interactions between biosystem and biomaterial,
given stability, i.e., the material is either inert to biosystem corrosion or degradable by the biosystem.

Carbon materials are generally well tolerated by animal cells. The possibility of applying carbon fiber reinforced carbon (CFRC) composite materials is given by their excellent biocompatibility and porosity, coupled with a modulus which can be tailored to be similar to that of bone. This makes them an attractive material for bone plates and implants in orthopaedic and dental surgery. It is known the volume properties of a material usually have little or no influence on the surrounding tissue (e.g.,osteogenic,MG63 line cells). In general, biocompatibility is controlled mainly by the interface between biomaterial and living tissue cells.

The literature and our preliminary study [1,2] indicate that the interaction at the interface is specifi-cally controlled by the surface morphology, (i.e., especially by surface roughness), and by the chemical state of the surface - by hydrophobia (wettability) [3], free chemical bonds and present chemical groups [4], etc. Unfortunately, the results are slightly contradictory. Nevertheless, biocompatibility can be im-proved by a suitable change of these parameters. There are several possible methods for influencing the roughness and chemical state of the surface. One way to change the surface properties is by preparing a suitable coating. The properties of the surface are controlled by process technology, and the grinding and polishing of the substrate and/or of the surface layer can be used for roughness control. Parameters de-scribing the mechanical properties of the layer - its surface roughness, adhesion to the substrate, wear resistance, etc., are studied in the paper by Hornik et al., which is submitted together with this paper.

On the other hand, the chemical state of the surface is usually checked by a range of physical methods. Reflexion goniometry is usually employed for measuring the wettability of the surface [3]; the free polar energy can be deduced from these measurements. Infrared spectroscopy (e.g., in the Fourier Transform modification) and Raman spectroscopy can give some information on the state of a layer just below the surface, especially on the concentration of conjugated double bonds which are closely related to degree of graphitization and the presence of other carbon groups [3]. More sophisticated methods of surface analysis are employed in sequence, e.g., X-ray photoelectron spectroscopy (XPS) and electron spectroscopy for chemical analysis (ESCA) [5]. The disadvantage of these methods is the difference between the surface state at measurement (usually ultrahigh vacuum) and at cell life (plasma or serum, i.e., water with several type of salts and proteins).

We prepared a surface coating of CFRC using a layer of pyrolytic graphite (PyG). The purpose of this paper is to define the surface of CFRC and of PyG and its chemical state as measured by reflexion goniom-etry, FTIR and ESCA, and to correlate the results with several parameters of tissue cell growth. The main topic of this work is therefore the proper characterisation of the surface parameters.

Experimental

The investigated composites were manufactured at the Institute of Rock Structure and Mechanics, AS CR. Commercially available plain-weave carbon fabric made of the general purpose ex-PAN carbon fibre Toray T800 was used. A stack of 8 layers of the fabric, soaked in an ethanol solution of phenol-formaldehyde resin Umaform LE (SYNPO Ltd., Pardubice, CR), was cured at 120°C. During its carbonization at 1000°C in nitrogen, conversion of the resin matrix to glass-like carbon was accompanied by the release of volatile pyrolysis products. The open porosity of the carbonized specimens (as measured by the water penetration technique) was about 25 %. High-temperature treatment of the samples took place at 2200°C in an argon environment. Samples of pure glassy carbon (from matrix material), annealed at vari-ous temperatures, were also prepared.

The surface of CFRC, ground by metallographic paper of 4000 grade, was covered with PyG in vacuum furniture (working gas C_4H_{10}, presure 4 Torr, temperature 1900°C, time 325 min) in TESLA Vršov-ice, Ltd., Prague, CR. Some of the samples were annealed to 2200°C. The roughness of CFRC and PyG was modified by grinding and polishing by usual metallographic methods, firstly by metallographic paper followed by polishing using a diamond paste of 3/2 and finally of 1/0 grade (PRAMET, Šumperk, CR).

In this way, we had several types of samples with various surface chemical states (matrix with various heat treatments, CFRC and CFRC/PyG) and also several types of samples with different roughness but with the same chemical nature of the surface (CFRC/ PyG).

Results and discussion

The thicknesses of the PyG films were 0.4 - 0.7 mm, with strong lamellar growth and a polycrystalline structure revealed by SEM and XRD. By reflexion goniometry we compared the wetting angle q both of samples with various chemical natures (CFRC, CFRC/PyG unanneled and that annealed at 2200°C, and of pure glassy carbon, which annealed at 850, 950, 1950 and 2200°C, respectively), and of samples of CFRC/ PyG with various surface roughnesses. In the case of glassy carbon, q increases with annealing tempera-ture; for CFRC θ = 75 deg, for CFRC/PyG with the same roughness θ = 88.8 deg. Contrary to expecta-tion, the θ of samples with the same chemical nature depends on the quality of polishing (FIG.1). The com-parison shows that

the free polar energy and biological parameters are correlated. The question is now whether the different values of θ (and of the free po!ar surface energy) can be related with the real chemi-cal state given by FTIR and ESCA. The preliminary results of FTIR show that there is a different intensity of IR reflection indicating different occupation of the surface by the carbonyl and carboxyl group at CFRC in comparison with CFRC/PyG. No differences in FTIR spectra were found on surfaces with the same chemical nature but

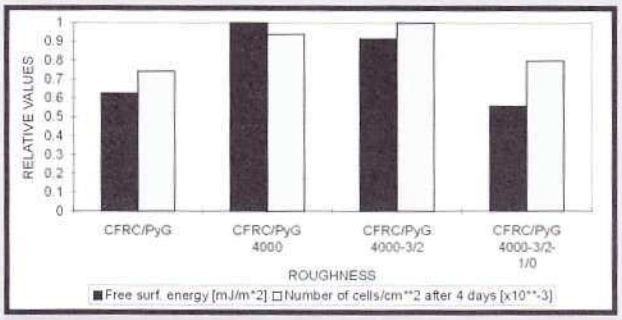

FIG.1. Dependence of free surface energy and cell density on surface roughness.

	CFRC	CFRC/PyG
Free surf. energy [mJ/m^2]	13.1	6.0
Cell density -1 day [1e3/cm^2]	5.8	9.3
Cell density - 4 day [1e3/cm^2]	77.8	130.6

TABLE 1. Comparison of the chemical and biological response of surfaces with the same roughness.

different roughness. One reason for the differences in surface free energy may be con-nected with the change in the ratio of the real area to the geometrical area of the surface in question.

Conclusion

The results indicate a different relation between biological response and free surface energy for roughness (with the same chemical state) and for chemical state (with the same roughness). The results of reflection goniometry, FTIR, and ESCA need to be compared.

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References

[1] Bačáková L., Starý V., Kofroňová O., Inzynieria Biomaterialow I (No.4), (1998) 22.
[2] Bačáková L., Starý V., Glogar P., Inzynieria Biomaterialow I, (No.2), (1999) 3.
[3] Švorčík V. et al., J. Mater. Chem., 5 (1995), 27-30.
[4] Smetana K. Jr. et al., Clinical Materials 13 (1993), 47.
[5] Chen J.-X. et al, Proc. of 1995 MRS Fall Meeting, Thin Films and Surfaces for Bioactivity and Bio-medical Applications, Materials Research Society Symposium Proceedings V. 424, (1996), 45.

OSTEOBLAST-LIKE MG63 CELLS IN CULTURES ON CARBON FIBRE-REINFORCED CARBON COMPOSITES

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Carbon fibre-reinforced carbon composites (CFRC) have been widely used in technical and industrial applications because of their unique physical properties, such as specific strength, thermal resistance, and thermal and electrical conductivity [Fitzer *et al.* 1987, Bosdorf *et al.* 1995]. In addition, these materials seem to be promising for biomedical applications, particularly for hard tissue surgery. The mechanical properties of CFRC, namely the density, porosity and modulus of elasticity, can be tailored to be very close to those of the bone. The CFRC could be used, therefore, for bone and dental root replacements, external and intenal bone fixation, and the construction of artificial intervertebral plates [Blazewicz *et al.* 1997, Pesakova *et al.* 2000]. The chemical nature of CFRC is very close to that of pure carbon, so these materials can be well tolerated by the surrounding tissue. As follows from our earlier studies, the CFRC support adhesion and growth of osteogenic and vascular cells, both important components of the bone [Bacakova *et al.* 1998a,b,c; 2001). Colonization of an artificial bone implant with these cells types is desirable for its good integration with the surrounding bone tissue [for review see Bacakova *et al.* 2001]. However, the physicochemical surface properties of CFRC composites in their native, unmodified state usually are not ideal for optimal adhesion, subsequent growth and differentiation of bone-derived cells. As revealed by scanning electron microscopy, the surface roughness of CFRC seems to be too high, which is due to the prominence of carbon fibres over the carbon matrix [Bacakova *et al.* 1998c, 2001]. This study focuses on modifications of CFRC by grinding, polishing and coating with pyrolytic carbon in order to obtain a surface roughness optimal for interaction with osteogenic cells.

Two-dimensionally reinforced CFRC were prepared in the Institute of Rock Structure and Mechanics, Acad. Sci. CR, Prague. Commercially available woven fabric made of carbon fibres Toray T 800 was arranged in layers, infiltrated with a carbon matrix precursor (phenolic resin UMAFORM LE, Synpo Ltd, Pardubice, CR), pressed, cured, carbonised at 1000°C, and finally graphitised at 2200°C. The following groups of samples of various surface roughness were prepared:
#1: control untreated
#2: ground by metallographic paper of 4000 grade
#3: coated with pyrolytic carbon in Tesla Vrsovice Ltd., Prague, CR
#4: ground and coated with pyrolytic carbon