CARBON FIBERS-BASED COMPOSITES FOR THE TREATMENT OF HARD TISSUE INJURIES

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Introduction

Fibrous composites are ranked among the materials, which, owing to the similarity to some tissue structures, can play a role of implants to fill, substitute or unite those structures. Particularly interesting seems their application in bone surgery. Due to good mechanical properties they can work as load-bearing implants. In the evaluation of biomechanical functions the mechanical properties and biological behavior both should be taken into account. The crucial problem in designing the composite materials for medical applications is to properly select the fibers and the matrix. The analysis of biocompatibility of different implant materials indicates that the most suitable ones are ceramics based on hydroxyapatite and calcium phosphates, resorbable polymers representing the polyhydroxyacid group and carbon materials [1-3]. Because of the unfavorable mechanical properties of these matrices it is necessary to modify them with dispersions or fibers. In this paper analyzed is the effect of microstructure on the mechanical and biological properties of composites reinforced with carbon fibers.

Experimental

The carbon-carbon composites were prepared from low-modulus carbon fibers and phenolformaldehyde resin or pitches, as matrix precursor. The manufacturing method was described elsewhere [4]. Two types of polymers were used: biostable polysulphone PSU ($M_n=26000$, $\eta=0.48$ -0.52dL/g, $T_g=120^{\circ}$ C, from Aldrich Chem. Comp, Germany) and bioresorbable poly-L-lactide PLA ($M_n=390000$, $\eta=6.9dL/g$, $\Delta H_m=41.4J/g$, from Purac Biochem Gorinchem, Holland), which were reinforced with short and long carbon fibers (Torayca T300) chemically modified according to the method described previously [5].

The composite samples were subjected to mechanical testing and to biological evaluation *in vitro* and *in vivo*. Their behavior in physiologic fluids was examined by measuring the pH variations and electrical conductivity of these fluids. The push-out method was employed to evaluate the shear strength of the composite-bone interface after the implantation into the femoral bone of rabbits.

Results and discussion

Owing to good mechanical properties and advantageous physico-chemical properties carbon fibers can be used in medicine in the form of bundles, plaited fabrics, fibrins or reinforcements in the composite materials. Extended studies [6] enabled formulation of the requirements to be met by carbon fibers applicable in medical practice. The best biocompatibility is observed in the case of lowmodulus fibers with small graphite crystallites (several nm in size) with low percentage of oxygen and with basic functional groups on the surface. In this study the carbon-carbon composites were prepared from phenol-formaldehyde resins or pitches as precursors of the carbon matrix. As a result of thermal treatment in an inert atmosphere they transformed into carbon phases significantly differing in carbon crystallite size and porosity. These parameters are important for the interactions with the biological environment. The carbon phases obtained from the phenol-formaldehyde resin were amorphous (size of crystallites $L_c=3$ nm) and more prone to biodegradation. In the case of pitch precursor the size of crystallites in the carbon phase was on the order of 30 nm. This restricted biodegradation and unfavorably affected the tissue reaction.

Application of thermoplastic polymers as composite matrices opened new possibilities in the manufacturing of implants. With respect to biocompatibility the most promising are inert polysulphones and resorbable polymers belonging to polyhydroxyacids. However, they also require modification with dispersions or fibers. Table 1 presents mechanical properties of the investigated composites along with some microstructural parameters. Different properties of the composites are mainly related to fiber orientation. In the case of carbon-carbon composite the long fibers were parallel (1D) while the polymeric composites were reinforced both with long and short fibers. These composites were used in the manufacturing of uniting screws by different methods such as mechanical working, plastic forming or injection. The results of shear tests for the screw thread show that the best shear strength was observed in the case of screws prepared by plastic forming of polysulphone. Lower values were found for the screws obtained by injection, however these were characterized by the best reproducibility. The screws prepared from the carbon-carbon composites, due to brittleness exhibited the lowest strength.

Complete evaluation of the usefulness of these screws in bone surgery calls for the analysis of behavior in a biological medium. As can be seen in Fig.1 the greatest pH changes were observed in the case of composites with a polylactide matrix incubated in physiologic fluids. The distinct pH drop results from the degradation of the polymer in water solution. Other composites did not show any significant pH changes, which may indicate their inert behavior. The obtained composites also differ in the degree of fixation with the bone tissue. As follows from Fig.2, the best strength of the boneimplant interface, as determined by the push-out method, was observed in the case of carbon-carbon composites. This is related to the presence of open pores with the diameters exceeding 100 µm, which are penetrated by bone tissue. Much lower values were recorded for the composites from the inert polymers. Their interfacial strength can be improved by using bioactive ceramic coatings (HAP).

A more complex situation occurred when the implant was made of a polylactide matrix reinforced with carbon fibers. The presence of fibers affects both resorption time of the polymer and the mechanism of fixation with the bone tissue. After the initial drop, being a result of polymer resorption, the interfacial strength increased due to fiber penetration with the bone tissue.

Conclusions

Carbon or polymer-matrix composites reinforced with carbon fibers can be used for bone uniting screws and plates with controlled mechanical and biological properties.

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Table 1. Properties of different materials

Tensile strength σr [MPa] Young's modulus E [GPa]	screw threadF _s [N] Open porosity [%]	Fibers orientation (manufacturing)
C-C 150.0 60.0 22	26.9 6.58	1D (M)
PSU 72.8 2.1 62	25.9 2.30	- (I)
PSU + C 94.2 2.5 12	29.0 1.98	MD (I)
PSU + C 497.0 48.1 15	03.0 -	1D (M)
PSU + C - 22	47.0 -	1D (P)
PLA 32.5 1.9 35	53.5 2.20	- (I)
PLA + C 80.2 2.3 59	01.0 2.30	MD (I)

M – mechanical treatment, I – injection moulding, P – plastic forming



Figure 1. Variations of pH during incubation time in water solution



Figure 2. Strength of bone – implant interface