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NON-METALLIC COMPOSITE MATERIALS FOR BONE SURGERY

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Possibility of using non-metallic materials in biomedical applications was considered. The attention was focused mainly on polymer materials and both the carbon-carbon and carbon-reinforced polymer composites, their mechanical and biological properties. The obtained results indicate that some of these materials can be successfully used instead of metallic implants for biomechanical functions.

1. INTRODUCTION

Metallic implants commonly used in bone surgery, besides of their high strength, fracture toughness and relatively easy machining, have two important drawbacks. The first is corrosion in biological media, the second is overstiffening as a result of large difference in Young's modulus of metals and bone tissues [1, 2]. One of possible solutions of this problem is using non-metallic materials with controlled biological response and with mechanical properties ensuring fulfilment of biomechanical functions. Because of the microstructural similarity to bone tissue and the possibility of adjusting the mechanical properties, the most promising are fibre-reinforced composites [3, 4]. Development of such materials is however dependent on biocompatibility of both components, i.e. fibres and matrix. It is therefore possible to combine biocompatible fibres with carbon, ceramic and polymer matrices. Application of various matrices for the reinforcing elements can change not only the mechanical properties but also the biological ones, like capability of fixation with the bone tissue. In the present work, the mechanical and biological properties of the non-metallic composites are analysed mainly with reference to the results of our own studies.

2. Criteria for materials selection

In composite materials, different factors influence the mechanical and biological properties [5, 6] In the first group these are features of the fibres themselves, their orientation and the adhesion at the fibre-matrix interface. In the second group those are chemical and structural factors describing the material of fibres and the matrix (Table 1).

Table 1. Factors influencing the mechanical and biological properties of composites.

Properties of composites	Factors influencing the properties
Mechanical – σ, E, γ	fibre type
	adhesion at interface
	fibre orientation
Biological behaviour	material of matrix
	material of fibres adhesion

These materials exhibit very good combinations of mechanical properties, such as: strength (σ), Young's modulus (E), fracture energy (γ), and have a fibrous structure similar to that of natural tissues. It is very important that the composite materials give the possibilities to obtain implants with high strength, high fracture energy and low Young's modulus close to that of bone tissue (Fig. 1).

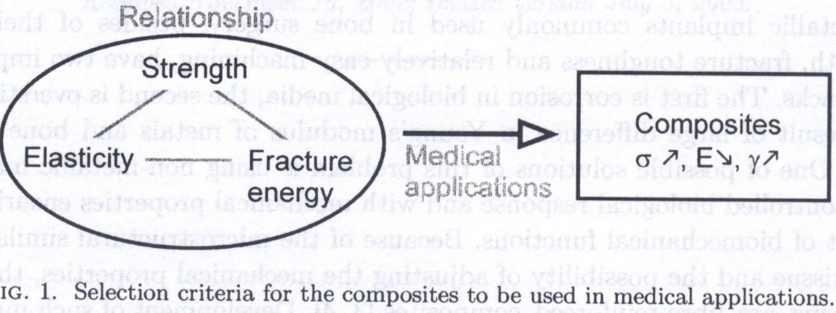

FIG. 1. Selection criteria for the composites to be used in medical applications.

Due to these properties, composite materials can be used as load–bearing implants, and as scaffolds for tissue regeneration [7–9]. In such composites the reinforcing phases can change the mechanical and biological properties. This can be related to changes in the microstructure of materials, mainly in porosity (pore size and distribution) and arrangement of the fibres. The porous system is decisive for both the biological reaction and fixation to bone tissue.

The fibre orientation influences Young's modulus, a very important factor for adequate stress distribution between the implant and bone [4, 10] As follows from Fig. 2, it is possible to obtain composite materials with various Young's moduli. For 2D, 3D, MD composites Young's modulus is similar to that of bone, i.e. about 20 GPa. This problem is unsolved for metallic implants because of their higher E values.

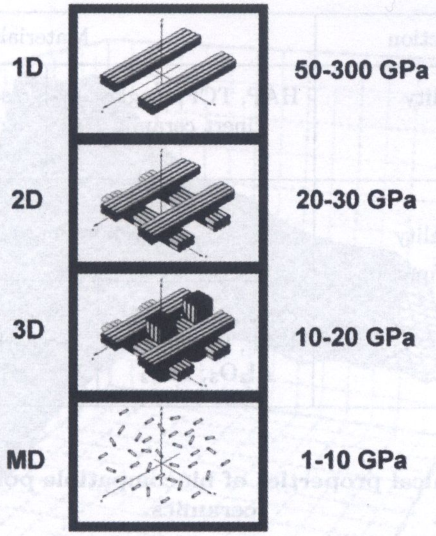

FIG. 2. Young's modulus of carbon composites (1D, 2D, 3D – 1-, 2-, 3-dimensional composite, MD – multidirectional composite).

The greatest difficulty in obtaining biocompatible composite materials is proper selection of biocompatible fibres. As it is well known, biocompatibility and biofunctionality are two main factors taken into account while selecting materials for medical applications. The first one is related to the chemical properties of materials, its surface state, structure and microstructure. The second one means that the properties of the material should possibly match those of natural tissue.

Among the biocompatible materials distinguished are the bioactive phases such as hydroxyapatite (HAP), tricalcium phosphate (TCP), bioglasses, inert ceramics, inert and resorbable polymers and carbon materials [11–14]. For the biomechanical function it is necessary to modify the properties of biocompatible materials by introducing the reinforcing phases such as ceramic particles and various biocompatible fibres (Table 2). Among biocompatible fibres there are at our disposal organic polymers like polylactide, whiskers of HAP and special carbon fibres [15–17].

Table 3. presents the mechanical properties of some biocompatible polymers and ceramics. It can be noticed that in order to satisfy the biomechanical requirements, it is necessary to modify the microstructure (reinforcing elements). In the case of polymers, the main objective of introducing the fibres is to raise the strength, while in the case of ceramics it is to raise the fracture toughness.

Table 2. Comparison of mechanical properties of composite implants.

Criteria of selection	Materials		
Biocompatibility	HAP, TCP, bioglasses, inert ceramics	resorbable and inert polymers	carbon materials
Biofunctionality (biomechanical function)	reinforcing phase:		
	ceramic particles: HAP, bioglasses, Al_2O_3, ZrO_2	whiskers and fibres: HAP, carbon, polylactide	

Table 3. Mechanical properties of biocompatible polymer materials and ceramics.

Material type	Properties		
	Tensile strength σ [MPa]	Young's modulus E [GPa]	K_{IC} [MPa·$m^{1/2}$]
PSU	72.8	2.1	2–5
PLA	32.5	1.9	1–3
P(GLA/PLA)	21.4	1.5	1–3
Epoxy resin	50.0	5.0	1–2
PEEK	139	8.3	2–5
HAP	95	50.0	1.1
Alumina	300	380	1–2

3. CARBON-CARBON COMPOSITES (CFRC)

In the case of carbon-carbon composites the fulfilment of biocompatible criteria limits the possibilities of obtaining the composites with the best mechanical properties. The relation of strength-failure strain of carbon fibres-ILSS (interlaminar shear strength) (Fig. 3) [18] shows that the best strength of these composites can be obtained with high-modulus carbon fibres, i.e. fibres with low failure strain. On the other hand, high-modulus carbon fibres exhibit limited biocompatibility [5, 15]. It is related to large size of graphite crystallites. This can lead to inflammations in biological environment after partial biodegradation. Similar situation appears in the case of carbon precursor. We can use a phenol-formaldehyde resin as the precursor only. Very important role is played by pyrocarbon coating on the carbon surface. It reduces biodegradation of carbon materials and facilitates the carbon particle removal by phagocytosis.

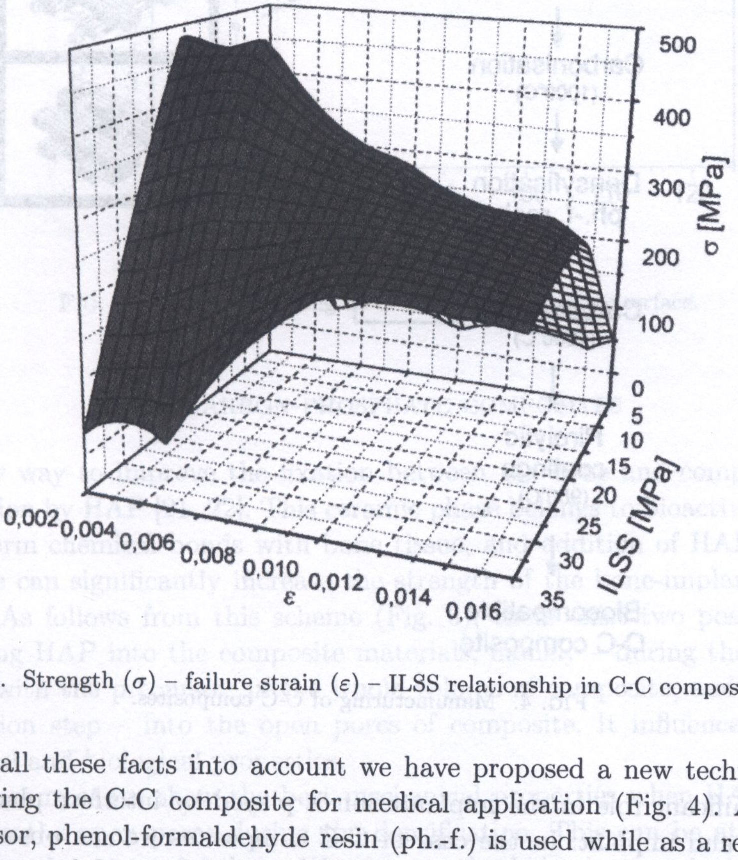

FIG. 3. Strength (σ) – failure strain (ε) – ILSS relationship in C-C composites.

Taking all these facts into account we have proposed a new technology of manufacturing the C-C composite for medical application (Fig. 4). As a matrix precursor, phenol-formaldehyde resin (ph.-f.) is used while as a reinforcing element, low-modulus carbon fibres with the possibility of changing their orientation. This gives a possibility to obtain both the one-directional and multidirectional composites. The final stage is carbonisation at 1000°C and coating with pyrocarbon.

Such composites were used in clinical practice in the form of screws, plates, stems of endoprosthesis and scaffold for tissue regeneration [5, 19, 20]. Taking into account mechanical properties we have prepared implants for various branches of medicine such as orthopaedy, laryngology, jaw surgery, urology and others.

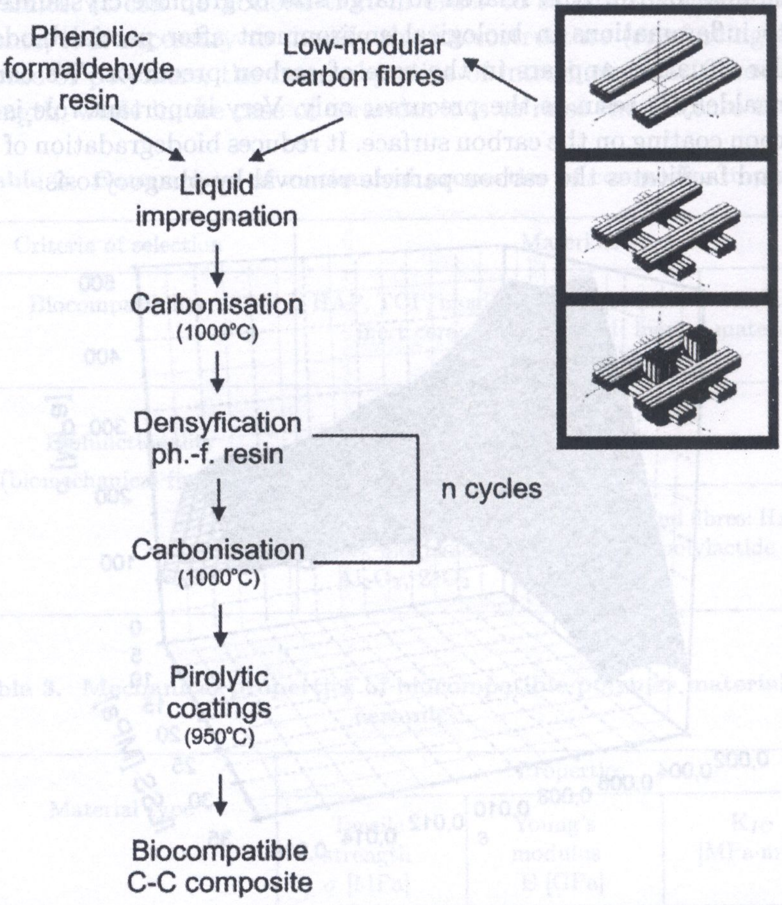

FIG. 4. Manufacturing of C-C composites.

A significant role in the implantation is played by interface phase between the bone and implant. In the case of C-C composites we can observe the formation of two types of interfaces (Fig. 5). Mechanism of fixation is related to the porous system: Bone tissue ingrowth occurs when the composite has larger pores and the pores create an open system of channels near the surface of implant. Such a type of microstructure can be achieved in 3D composite implants. For 1D composites with small open pores we observe formation of mechanical bonds at the interface. The situation may be unstable because in the living organism the composite undergoes gradual degradation. Open pores are, formed which are penetrated by the bone tissue increasing the shear strength at the bone/implant interface.

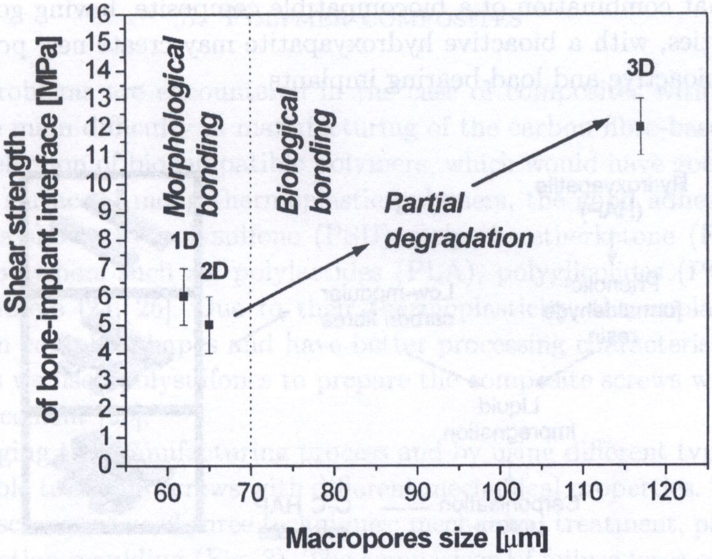

FIG. 5. Types of bonding at C-C composite/bone interface.

4. CARBON-PHOSPHATE COMPOSITES

A new way to improve the fixation between the bone and composite is its modification by HAP [21, 22]. This ceramic phase belongs to bioactive materials able to form chemical bonds with bone tissue, and addition of HAP to a C-C composite can significantly increase the strength of the bone-implant interface (Fig. 5). As follows from this scheme (Fig. 6), there exist two possibilities of introducing HAP into the composite materials; namely – during the first step, together with the precursor, in the whole volume of composite, and during the densification step – into the open pores of composite. It influences both the mechanical and biological properties.

These composites show the best mechanical properties when HAP is introduced into the open pores during the densification. This can be attributed to different mechanisms of failure. We observe the behaviour typical for fibrous composites while the composites with HAP introduced in the whole volume exhibit a mechanical behaviour similar to the brittle materials. In the first case, carbon-phosphate composites have the bending strength of about 200 MPa and work up to fracture four times higher than that of pure HAP (Fig. 7). The presence of amorphous carbon phase during carbonisation exerts a catalytic effect on the HAP-TCP transformation. The second important effect of this transformation is an appearance of carbonate phase responsible for the formation of a strong chemical bond with the bone tissue. On the basis of the obtained results it seems that combination of a biocompatible composite, having good mechanical properties, with a bioactive hydroxyapatite may create new possibilities of designing bioactive and load-bearing implants.

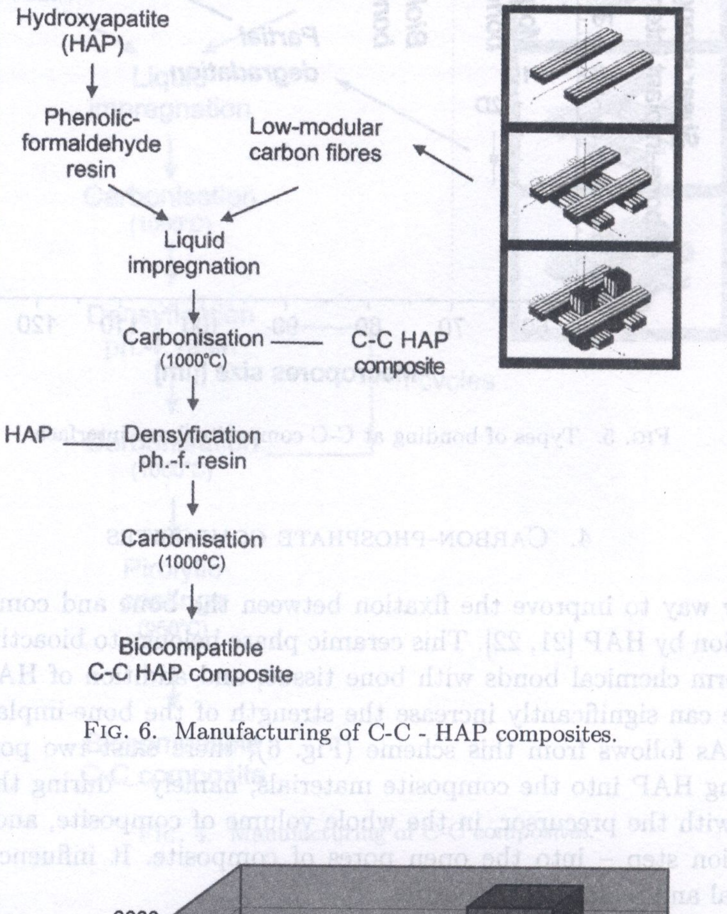

FIG. 6. Manufacturing of C-C - HAP composites.

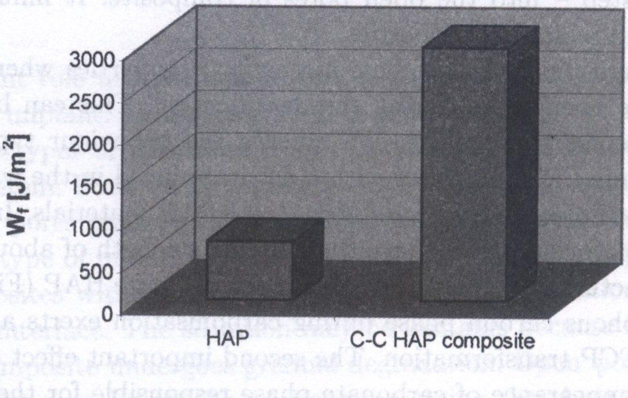

FIG. 7. Work up to fracture for pure HAP and for C-C-HAP composite.

5. Polymer composites

Other problems are encountered in the case of composites with a polymer matrix. The main difficulty in manufacturing of the carbon fibre-based composites is the selection of biocompatible polymers, which would have good adhesion to the fibre surface. Among thermoplastic polymers, the good adhesion to carbon fibres is shown by polysulfone (PSU), polyetheretherketone (PEEK) and resorbable polymers such as, polylactides (PLA), polyglicolides (PGLA)) and their copolymers [24, 25]. Due to their thermoplasticity, the implants can be fabricated in complex shapes and have better processing characteristics. In our experiments we used polysulfones to prepare the composite screws with carbon-fibre reinforcement [25].

By changing the manufacturing process and by using different types of fibres it was possible to obtain screws with different mechanical properties. To produce the uniting screws we used three techniques: mechanical treatment, plastic forming and injection moulding (Fig. 8). The comparison of failure force of thread for various techniques shows that screws obtained by plastic forming have the best properties. In this case, fibres are placed in accordance with the shape of the thread. Lower values were found for the screws obtained by injection moulding – with short fibres, however there were characterised by the best reproducibility. The screws prepared from the carbon-carbon composites exhibited the lowest strength due to brittleness. Depending on mechanical properties, the composite screws can be used in different types of uniting elements.

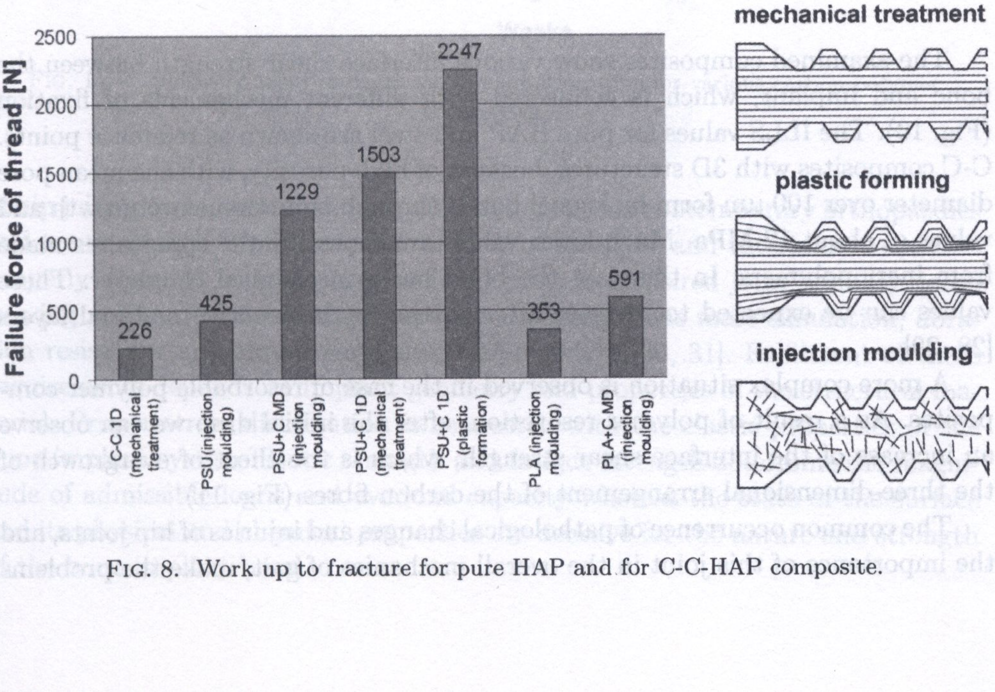

FIG. 8. Work up to fracture for pure HAP and for C-C-HAP composite.

More interesting are resorbable polymers such as polylactide and polyglicolide. They biodegrade in biological environment into non-toxic compounds [26]. Because of their low mechanical properties, such materials must be reinforced with particles or fibres. Introduction of fibres can change not only the mechanical properties but also the time of biodegradation, and mechanism of bonding with the bone tissue.

Figure 9 shows that the introduction of organic and carbon fibres enhances composite tensile strength and also accelerates biodegradation of polymer matrix [27]. This is a result of delamination occurring on the fibre-matrix interface resulting in increasing of the surface contact.

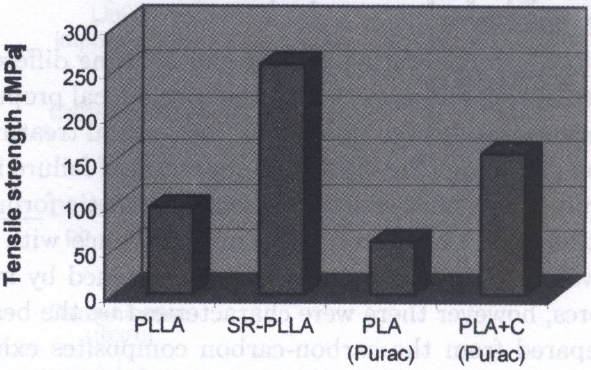

FIG. 9. Tensile strength of different polymer composites PLLA – poly-L-lactide SR-PLLA – self-reinforced poly-L-lactide PLA (Purac) – polylactide (prod. Purac) PLA+C – carbon reinforced polylactide (prod. Purac).

The examined composites show various interface shear strength between the bone and implant, which is connected with different mechanisms of fixation (Fig. 10). The ILLS values for pure HAP and steel are shown as reference points. C-C composites with 3D structures, because of high porosity, with the mean pore diameter over 100 μm form biological bonds through bone tissue overgrowth and values of about 12 MPa. Much lower values are shown by the composites made from inert polymers. In this case the bond has a mechanical character. These values can be expected to increase after coating with bioactive material layers [28, 29].

A more complex situation is observed in the case of resorbable polymer composites. As a result of polymer resorption, after the initial drop we can observe an increase of the interface shear strength, which is the effect of overgrowth of the three-dimensional arrangement of the carbon fibres (Fig. 11).

The common occurrence of pathological changes and injuries of hip joints, and the importance of this joint in the overall mechanics of gait, make the problems

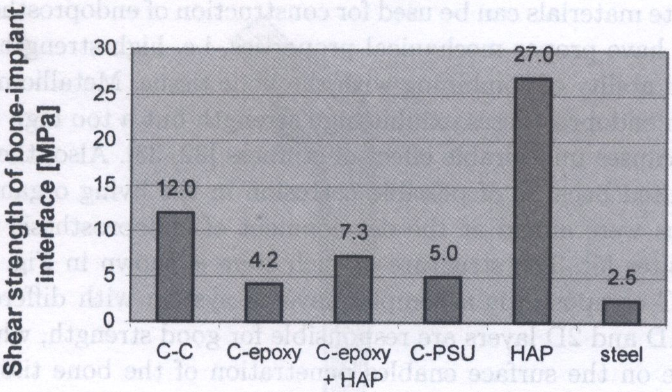

FIG. 10. Shear strength of bone-implant interface.

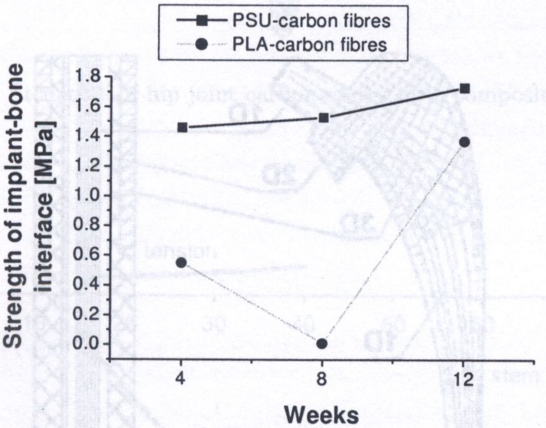

FIG. 11. Changes of shear strength vs. implantation time for various carbon-polymer composites.

of hip joint alloplasty rank among the leading ones in contemporary orthopaedics and traumatology. From the point of view of medicine and veterinary science, a properly designed endoprosthesis should provide a desired joint mobility, load-bearing and overload capacity, vibration damping, bone mass simulation, abrasion resistance and simple implantation procedure [30, 31]. Fulfilment of these requirements depends on implant geometry and properties of the structural material. Proper stress distribution is connected with the elastic properties of the bone-implant system. Static strength and fatigue strength determine the magnitude of admissible loads and overload capacity whereas the state of the surface and its physical and chemical properties are decisive for the nature and strength of the bone-implant bond.

Composite materials can be used for construction of endoprosthesis stem. The stem should have proper mechanical properties, i.e. high strength, low Young's modulus and ability of combining with the bone tissue. Metallic materials most often used in endoprostheses exhibit high strength but a too high Young's modulus, which causes undesirable effect of stiffness [32, 33]. Also, their biocompatibility is limited because of possible corrosion in the living organism. Our first investigations were aimed at the development of endoprosthesis stem made of C-C composites [5]. The structure of such stem is shown in Fig. 12. The stem made of C-C composite is a complex layered system with differently oriented fibres. The 1D and 2D layers are responsible for good strength, while the porous 3D structure on the surface enables penetration of the bone tissue and makes that the endoprosthesis is cement-less and self-fixing. A limitation of this solution is, however, low resistance to cyclic loading, much lower than for metallic endoprostheses.

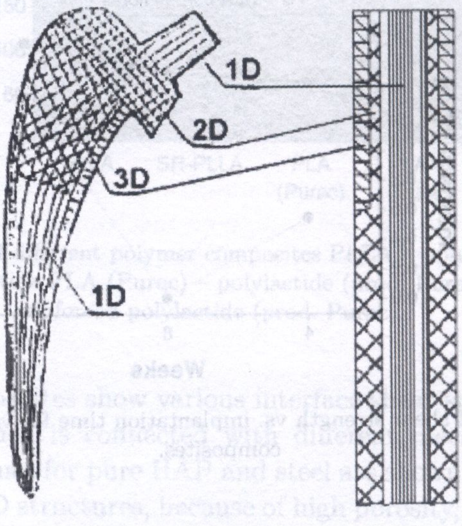

FIG. 12. Structure of hip joint C-C composite stem.

Thus, we embarked on research to develop endoprosthesis stems made of polymer composites reinforced with carbon fibres. The best results were received in the case of carbon fibre/epoxy resin composites (Fig. 13) [34]. In other investigations the carbon fibre/PEEK system was also used [35]. Particularly important is the possibility of obtaining gradient structures in which the value of Young's modulus, responsible for load bearing, can change in all directions within the loaded element. Such distribution is illustrated on the example of C-epoxy composite in Fig. 14.

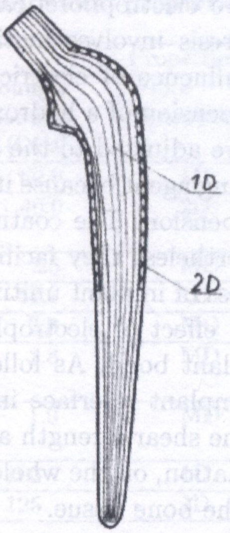

FIG. 13. Structure of hip joint carbon-epoxy resin composite stem.

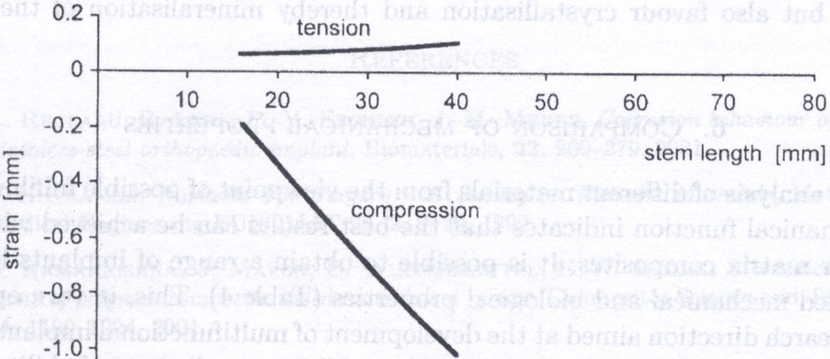

FIG. 14. Strain distribution on stem length in carbon-epoxy composite.

These composites perfectly conform to the biomechanical requirements but the problem of bond with the bone tissue remains unresolved. The discussed composites have low open porosity which practically disables the formation of biological bonds i.e. ingrowth of the bone tissue. One of possible remedies is to use coatings of bioactive HAP [36, 37].

Hydroxyapatite layers were electrophoretically deposited on the surface of composite stems. Electrophoresis involves motion of charged particles of the dispersed phase under the influence of electric field. The electrophoresis was conducted in an alcoholic suspension of a hydroxyapatite powder, with graining of 0.5 μm. The electrodes were adjusted to the shape of elements to be coated. Ethanol was used as a dispersing agent because its dielectric constant guaranteed sufficient stability of the suspension. The coatings obtained on endoprosthesis stems were not uniform; nevertheless they facilitated calcium phosphate nucleation and growth in the process of implant uniting with the surrounding tissues.

We examined *in vivo* the effect of electrophoretically deposited hydroxyapatite layer on the bone-implant bond. As follows from Fig. 10, the values of shear strength at the bone-implant interface indicate that the hydroxyapatite layer significantly improves the shear strength at the bone-implant interface.

According to SEM examination, on the whole circumference, there is a direct contact of the implant with the bone tissue.

This effect is not observed in the case of composites without the hydroxyapatite layer. Explanation of the advantageous effect of the electrophoretically deposited hydroxyapatite on the bone-implant bond, calls for evaluation of morphological features and density of bone tissue, growing around the implant. It seems that the hydroxyapatite layers not only are a source of bone-forming elements but also favour crystallisation and thereby mineralisation of the bone tissue.

6. COMPARISON OF MECHANICAL PROPERTIES

The analysis of different materials from the viewpoint of possible fulfilment of biomechanical function indicates that the best results can be achieved with the polymer matrix composites. It is possible to obtain a range of implants having controlled mechanical and biological properties (Table 4). This, in turn opens a new research direction aimed at the development of multifunctional implants that would transfer loads and at the same time exhibit controlled resorbability after fulfilment of that function. The modification with bioactive ceramics may significantly change the bone/implant interface, stimulating the formation of bonds of chemical nature. Another, not yet fully recognised area of application, is the use of carbon/polymer composites as structural elements in a variety of external stabilisers. In such applications, in addition to good mechanical properties, low density and X-ray permeability are of importance.

Summarising, it can be concluded that application of carbon fibres to various matrices changes their mechanical and biological properties and allows matching the microstructure and properties of composite implants and those of reconstructed or regenerated bone structure.

Table 4. Comparison of mechanical properties of composite implants.

Material type	Properties			
	Tensile strength σ_r[MPa]	Young's modulus E [GPa]	Fibre orientation	Biological behaviour
C-C	150	60.0	1D	partialy degradable
C-C – HAP	120	40.0	2D	partialy degradable, bioactive
PSU + C	94.2	2.5	MD	biostable
PSU + C	497	48.1	1D	biostable
PLA + C	80	2.3	MD	partialy resorbable
P(GLA/PLA) + C	75	2.8	MD	partialy resorbable
P(GLA/PLA) + bioglass	30.6	1.9	MD	partialy resorbable, bioactive
C-epoxy	1000-3500	100	1D	biostable
C-PEEK	1940	125	1D	biostable

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