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Hot pressed hydroxyapatite–carbon fibre composites

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Abstract

Composite samples were obtained from hydroxyapatite powder and carbon fibres by hot pressing at 1100°C and 25 MPa for 15 min in argon atmosphere. Two types of cut carbon fibres produced in a carbonisation process of polyacrylonitrile (PAN) precursor were used both in non-coated or coated form. The coatings of calcium phosphate were applied by sol–gel technique. The highly sintered composite with the best strength properties was obtained from coated carbon fibres with basic character of the surface. The existence of hydroxyl groups on fibre surface makes possible formation of bonds with the calcium phosphate layer formed as a result of polycondensation following the sol–gel procedure. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Because of the role of bone implants, the ceramic composites used for re-construction of bone defects should exhibit high biocompatibility and bioactivity as well as very good mechanical properties. It is worth to underline, that among the implant composites applied nowadays there is no one which meets — to the full extent — the requirements defined for implants. Therefore intensive investigations aiming the improvement of the hitherto existing bio-composites and elaboration of completely new materials is still continued. Certain research activity is directed to the experiments on both particulate and fibre reinforced composites for medical purposes.

For sure some of the most prospective bio-ceramic materials are composites based on calcium phosphates[1–8] in which the highly bio-compatible but mechanically weak matrix made of hydroxyapatites or TCP is reinforced with metal,[9] ceramic,[10] organic,[11] carbon fibres[12] or even with HAp whiskers.[13]

Park and Vasilos[12] applied the hot pressing technique to produce the composite material: TCP matrix reinforced with carbon fibres. Bending strength of 23.6 MPa has been reached for 5 vol% fibre content.

The present paper reports the investigations on hot pressing process of composites containing HAp reinforced with 20 vol% of carbon fibres.

2. Materials and methods

Four types of hydroxyapatite–carbon fibre composites have been investigated. The raw materials were: powdered hydroxyapatite (specific surface ca. 20 m^2/g) obtained in wet process from CaO and H_3PO_4[14] and carbon fibres obtained as a result of carbonisation of polyacrylonitrile (PAN) fibres at 1000°C.[15]

Two types of cut carbon fibres (with different surface properties) have been used to produce these composites.

On the surface of F-type and T-type carbon fibres applied-hydroxyl groups and acidic groups were dominating, respectively (see Table 1). The amount of acidic and basic groups on the surface of fibres was determined by neutralisation with 0.01 N NaOH and 0.01 N KCl, respectively.[16]

The above-mentioned fibres were applied in two forms: non-coated or coated, with calcium phosphates.

The coatings were applied following the sol–gel procedure. The surface of fibres was treated using a methoxyethanol solution of in-situ produced orthophosphoric acid esters — $(CH_3OC_2H_4O)x(OH)_{3\text{-}x}OP$ ($x=1$, 2) and calcium alcoholates $(CH_3OC_2H_4O)_2Ca$. The

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Table 1
Characteristic properties of carbon fibres used in production of composite materials with hydroxyapatite matrix

Type of fibres	Properties					
	Origin	Carbonisation temperature of PAN precursor (°C)	Chemical treatment after carbonisation	Diameter of fibres (μm)	Concentration of acidic groups (g ionH^+/g of carbon fibres)	Concentration of hydroxyl groups (g ionOH^-/g of carbon fibres)
Carbon fibres F	Carbon felt	1000	–	12÷13	0.2×10^{-4}	5.6×10^{-4}
Carbon fibres T	Carbon tissue	1000	Oxidation in HNO_3	8÷9	3.38×10^{-4}	1.1×10^{-4}

required solution has been synthesised by subsequent dissolution of taken in excess P_2O_5 (p.a. Merck) and metallic Ca (99%, Aldrich) in $CH_3OC_2O_4OH$ (A.C.S. reagent, 99.3%, Aldrich, additionally distilled before usage). The substrates were used in such a proportion as to guarantee molar ratio Ca:P = 1.67. The operations of proportioning by weighing of P_2O_5 and Ca have been carried out in a glove-bag in nitrogen atmosphere. At room temperature the reaction of P_2O_5 and $CH_3OC_2H_4OH$ was completed after ca. 24 h of intensive mixing. The Ca amount added after P_2O_5 dissolution reacted after subsequent 150 h of mixing. The final product was a clear, pale yellow, stable solution. After longer period of storage its colour became amber.

In order to coat the carbon fibres with calcium phosphates, the fibres were initially mixed with methoxyetanol solution for 15 min at room temperature. Afterwards they were put on a soft filter paper and dried in a laboratory dryer at 115°C for ca. 2 h.

The batches were prepared from individual types of fibres and hydroxyapatite powder. The fibres:matrix volume ratio was kept constant and equal to 1:4. After thorough mixing, the batches were dry grinded for 20 min in a rotary-vibrating pulveriser and afterwards sieved through a 0.2 mm screen. Subsequently, the composites were fabricated by hot pressing at 1100°C and 25 MPa for 15 min in argon atmosphere. The sintered samples were cooled to room temperature and then machined into rectangular bars 50×5×5 mm. The base-line samples have been prepared in the same way using the matrix material, i.e. hydroxyapatite (Table 2).

The carbon fibres used in our study were initially investigated using scanning electron microscope (Model 5400 JEOL) and the chemical composition of their surface was analysed by energy-dispersive spectrometry (EDS) using a microanalyser (Model AN 10000, Link). The phase composition of these coatings was X-rayed for 2Θ angle ranging from 10° to 60° (Dyfractometer XRD7, Seifert-fpm). The apparent density and open porosity of the samples were measured by Archimedes method. Bending strength was tested in a three-point bending test on a span of 40 mm at a crosshead speed of 0.1 mm/min (Zwick 7005, Model 1435). Investigations of each material were carried out on 10 samples. The results were statistically tested (Dixon test). Mean values and standard deviations were calculated.

The fractured surfaces were observed using scanning electron microscopy (SEM). Non-destructive ultrasonic investigation was carried out to measure the velocity of the longitudinal ($f = 10$ MHz) and transverse ($f = 2$ MHz) waves within the samples (UZP-1 device, manufactured by INCO, Poland). The condition of a three-dimensional body was fulfilled at indicated frequencies.[17] The material constants: Young's modulus (E) and modulus of rigidity (G) were determined.

3. Results and discussion

The sol–gel procedure of coating carbon fibres applied in our experiments was efficient after optimisation of test conditions. The applied practical procedure allowed the authors to eliminate almost completely the inconveniences resulting from significant difference in electronegativity of phosphorus and calcium (in Pauling scale: $\chi_p = 2.91$; $\chi_{Ca} = 1.00$, respectively). The sol–gel procedure is successful if the substances acting as calcium and phosphorus precursors guarantee the start of polycondensation processes (in which products containing both these elements are formed) already in the

Table 2
HAp–carbon fibre composites

Composition	Description
F/c	20 vol% carbon fibres obtained from carbon felt and coated with calcium phosphates 80 vol% HAp
F	20 vol% carbon fibres obtained from carbon felt (non-coated) 80 vol% HAp
T/c	20 vol% carbon fibres obtained from carbon tissue and coated with calcium phosphates 80 vol% HAp
T	20 vol% carbon fibres obtained from carbon tissue (non-coated) 80 vol% HAp
H	Base-line samples — monophase hydroxyapatite ceramics

solution. In the case of application of aqueous medium, the polycondensation does not occur at all (phosphorus remains mainly in a form of $[H_x(PO_4)]^{(3-x)-}$ anions (where $x=0$, 1, 2) while calcium still exists in a form of Ca^{2+} cations) or an appropriate calcium phosphate sediment precipitates quickly just after the beginning of polycondensation.[18] On the other hand, the desired polycondensation products can be formed in non-aqueous media (first of all in alcohols) following the nucleophilic substitution mechanism, provided that the attacking groups are related to phosphorus and calcium is contained in the solution in a non-ionic form, i.e. mainly in the form of an alcoholate.

As a result of the reaction of P_2O_5 with $CH_3OC_2H_4OH$, the orthophosphoric acid hydroxoesters are formed. The partial charge of the OH group in $(CH_3OC_2H_4O)_2(OH)OP$ hydroxyester is equal to 0.23 while this in the $(CH_3OC_2H_4O)(OH)_2OP$ is equal to 0.18. Therefore these groups can attack the calcium atom in $(CH_3OC_2H_4O)_2Ca$ because it has the highest positive charge in the mixture containing $(CH_3OC_2H_4O)_x(OH)_{3-x}OP$ ($x=1$, 2) and $(CH_3OC_2H_4O)_2Ca$ [$\delta_{Ca} = +1.01$, compared with $\delta_p = +0.15$ and $+0.18$ in $(CH_3OC_2H_4O)(OH)OP$ and $(CH_3OC_2H_4O)(OH)_2OP$, respectively]. Therefore, $(CH_3OC_2H_4O)_2Ca$ formed in the reaction of Ca with $CH_3OC_2H_4OH$ can immediately react with orthophosphoric acid esters. In such solution there exists a "competition" in the process of coordinative polymerisation of calcium alcoholate, which leads to the forms insoluble in the initial alcohol, i.e. useless in sol–gel processes.

The appropriate reactions between $(CH_3OC_2H_4O)_2Ca$ and $(CH_3OC_2H_4O)_x(OH)_{3-x}OP$ ($x=1$, 2) can be formulated as follows:

$$\begin{aligned}&PO(OH)(OR)_2 + Ca(OR)_2\\&\Longleftrightarrow (RO)_2PO(OH)\ldots Ca(OR)_2 \Longleftrightarrow\\&\Longleftrightarrow (RO)_2POOCaOR + ROH\end{aligned} \tag{1}$$

$$\begin{aligned}&PO(OH)(OR) + Ca(OR)_2\\&\Longleftrightarrow (RO)(HO)PO(HO)\ldots Ca(OR)_2 \Longleftrightarrow\\&\Longleftrightarrow (RO)(HO)POOCaOR + ROH\end{aligned} \tag{2}$$

$R = CH_3OC_2H_4$

In both reactions (1) and (2), the charge of $CH_3OC_2H_4OH$ molecule in transient complexes $(CH_3OC_2H_4O)PO(OH)\ldots Ca(C_2H_4OCH_3)_2$ and $(CH_3OC_2H_4O)(HO)PO(HO)\ldots Ca(OC_2H_4OCH_3)$ is positive ($+0.26$ and $+0.28$, respectively). Thus, according to the partial charge model[19] it appears that the $CH_3OC_2H_4OH$ molecule can be split off and, consequently, the process of polycondensation between orthophosphoric acid esters and calcium alcoholate can be commenced.

The existence of hydroxyl groups on fibre surface makes possible creation of bonds with the products of polycondensation of esters of orthophosphoric acid and calcium alcoholate following the nucleophilic substitution mechanism, in which the hydroxyl groups connected with fibre surface play the role of attacking agent; the phosphorus atoms in products of polycondensation of esters of orthophosphoric acid and calcium alcoholate is the subject of attack, while the alcohol or water molecule is the leaving group. Since the products of polycondensation of orthophosphoric acid esters and calcium alcoholate include non-hydrolysed alcoxyl groups — $OC_2H_4OCH_3$ — connected with phosphorus (furthermore, they contain even a certain small amount of OH groups), the corresponding quasi-reactions can be formulated as follows:

$$\begin{aligned}&\ldots C{-}OH + CH_3OC_2H_4OP\ldots\\&\qquad\Longleftrightarrow \ldots C{-}O{-}P\ldots + CH_3OC_2H_4OH\end{aligned} \tag{3}$$

$$\begin{aligned}&\ldots C{-}OH + HO{-}P\ldots\\&\qquad\Longleftrightarrow \ldots C{-}O{-}P\ldots + H_2O\end{aligned} \tag{4}$$

The initial SEM investigations as well as EDS tests of the coated with calcium phosphates and non-coated carbon fibres proved existence of a significant difference in the shape and chemical composition of their surface. The non-coated fibres are smooth along its length and carbon only was detected on their surface (Fig. 1). Numerous beads, closely adhering to the fibre have been found on fibre surface treated chemically with calcium phosphates. These beads constitute the foreign phase precipitation (Fig. 2) The EDS investigations confirmed that in spite of elementary carbon, also calcium, phosphorus and oxygen are present on the entire surface of coated fibres (not only within the areas of these beads). This fact confirms that these fibres are coated by calcium phosphate (Fig. 3). It follows from SEM investigations that distinctly better results of coating were achieved in the case of fibres obtained from carbon felt. It confirms that presence of hydroxyl groups supports

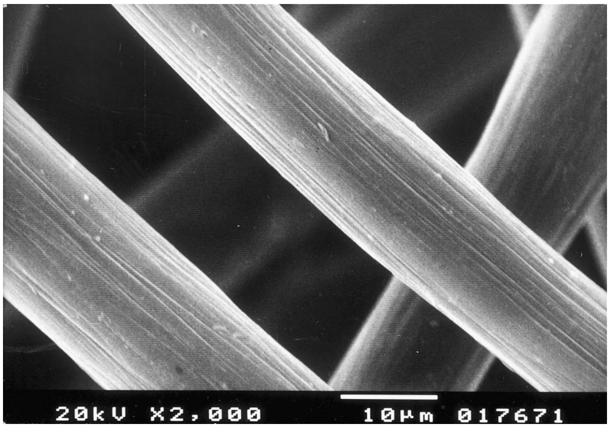

Fig. 1. Non-coated carbon fibres.

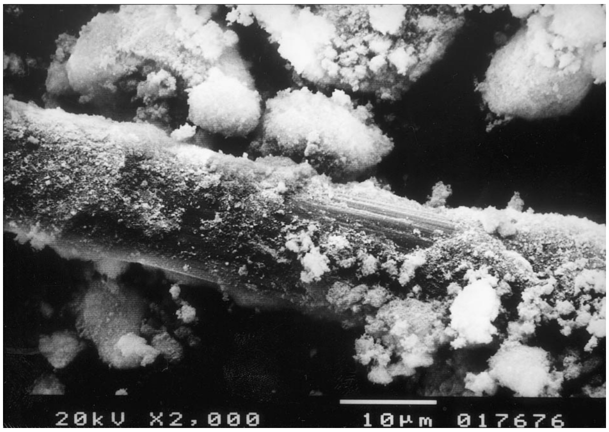

Fig. 2. Carbon fibre with basic character of the surface, covered with calcium phosphates.

formation of calcium phosphate layers applied following sol–gel procedure in liquid environment. This fact can be explained taking into account the possible formation of hydrogen bonds between hydroxyl groups occurring on fibre surface and those originated from the coating layer.

The X-ray studies proved the amorphic character of coatings before heat processing. During firing the calcium phosphates deposited on fibres underwent transformation into highly crystallised β-TCP (sharp peaks on X-ray diffractogram) with very insignificant $Ca_2P_2O_7$ admixture. Consequently the coating formed on carbon fibres following the sol–gel process constitute a non-stoichiometric hydroxyapatite (ns-HAp) with HPO_4^{2-} ions included in its structure. The ns-HAp decomposition during heating results in formation of β-TCP. The apparent density of produced composite materials was ranging between 2.85 and 3.04 g/cm^3.

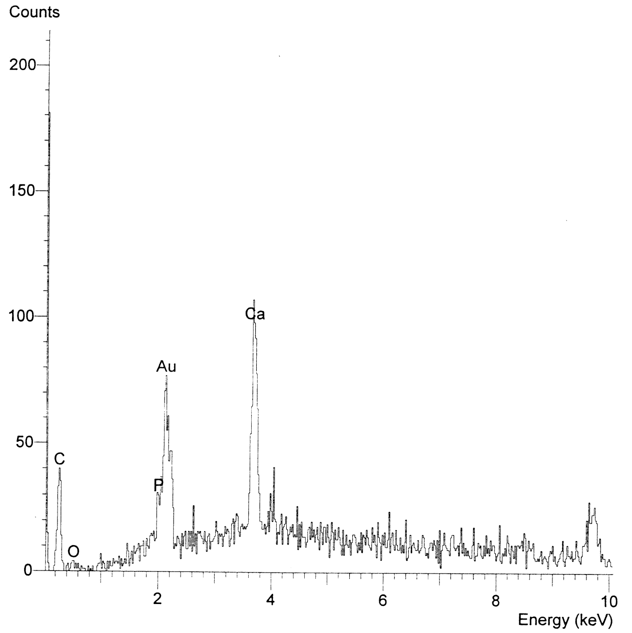

Fig. 3. EDS graph of the surface of carbon fibre after sol–gel treatment.

The apparent density of mono-phase hydroxyapatite base-line samples was 3.14 g/cm^3 (Fig. 4).

Open porosity of composite sinters was ranging from 0.31% (F/c material) to 2.30% (T/c material). The best sintered composite has been obtained in the case of coated fibres with basic character of the surface. The oxygen bridges are based on hydrogen bonds created earlier and they assure good connection of fibres with calcium phosphate layer covering their surface. Such coated fibres are closely connected with hydroxyapatite matrix of the composite material.

Significant difference in coefficients of heat expansion of different phases co-existing in HAp–non-coated carbon fibres composites (1×10^{-6} and 11.6×10^{-6} K^{-1} for carbon fibres and hydroxyapatite, respectively) causes generation of high stresses during cooling of sintered samples. It may result in matrix cracking and even in complete destruction of the samples. Such phenomena have been really stated in the case of HAp–non-coated fibres of carbon tissue material (T samples). Heat stress generated in this composite during hot pressing process was so strong that the HAp matrix crashed. The samples completely disintegrated after removing them from a graphite mould.

These problems have been eliminated when coated fibres were applied for production of HAp–carbon fibre composites. It can be supposed that formation of β-TCP mid-layer (heat expansion coefficient of β-TCP = 13.1×10^{-6} K^{-1}) resulted in reduction of the gradient of thermal stress on its phase boundary with HAp matrix and consequently caused improvement of mechanical properties of the material, comparing with these of a composite with non-coated fibres.

The investigated materials demonstrate distinct differentiation of bending strength (Fig. 5). It has been stated that their bending strength is closely connected

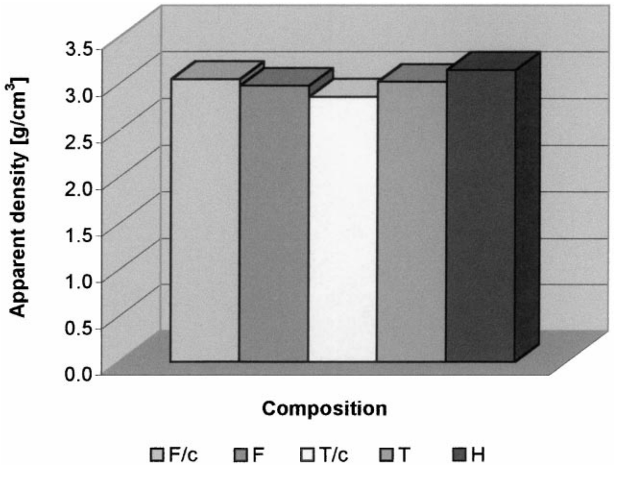

Fig. 4. Apparent density of hot pressed HAp–carbon fibre composites.

with the character of the surface of fibres used and with the resulting quality of the coating. Maximal bending strength (69 MPa) has been measured in the case of the composite: 80 vol% HAp–20 vol% carbon fibres of basic character of the surface, coated with a calcium phosphate layer (F/c samples). Although this value is three times higher than this obtained for another similar material: carbon fibre–reinforced calcium phosphate composite,[12] but it is still too low when compared with bending strength required for materials to be used for re-construction of bone defects. It is probably caused by the phase composition of the coatings. In our opinion the volume changes accompanying β-TCP polymorphic transformation at ca. 1125°C to α-TCP may have negative effect on mechanical properties of the composites.

The non-destructive ultrasonic investigations evidenced that composite materials based on fibres coated with calcium phosphates are significantly more homogeneous than materials containing non-coated fibres. It is testified by lower difference in the rate of ultrasonic wave propagation between the edge and the middle part of the samples (Fig. 6).

The material constants: Young's modulus (*E*) and modulus of rigidity (*G*) determined basing upon the ultrasonic investigations are presented in Fig. 7. The *E*

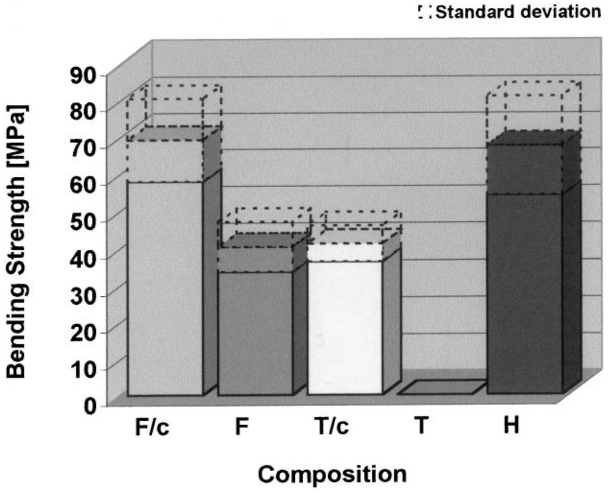

Fig. 5. Bending strength of hot pressed HAp–carbon fibre composites.

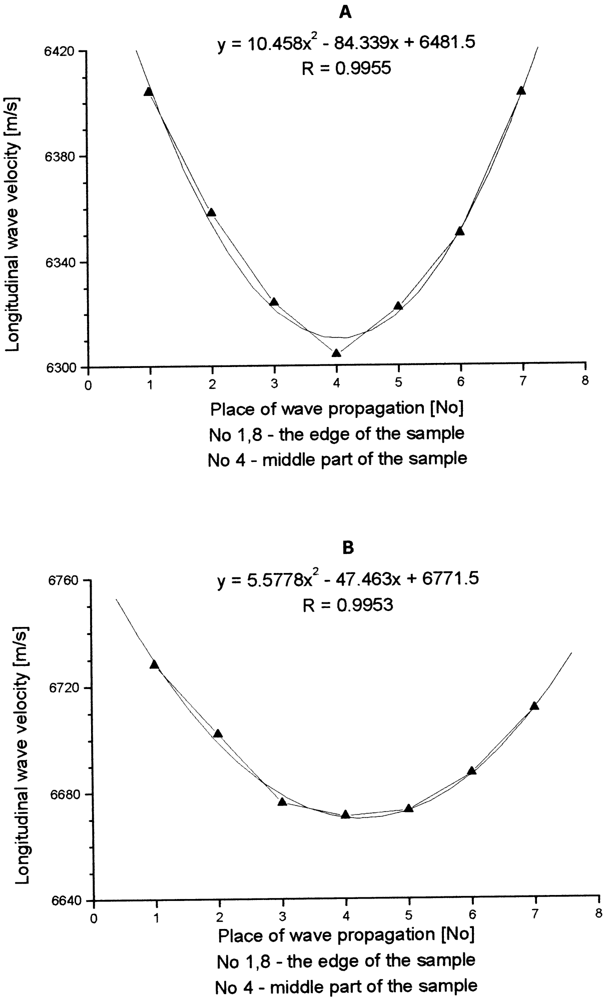

Fig. 6. Rate of propagation of the longitudinal ultrasonic wave in composites: HAp–carbon fibre: with non-coated fibres: (a) with non-coated fibres; (b) with coated fibres.

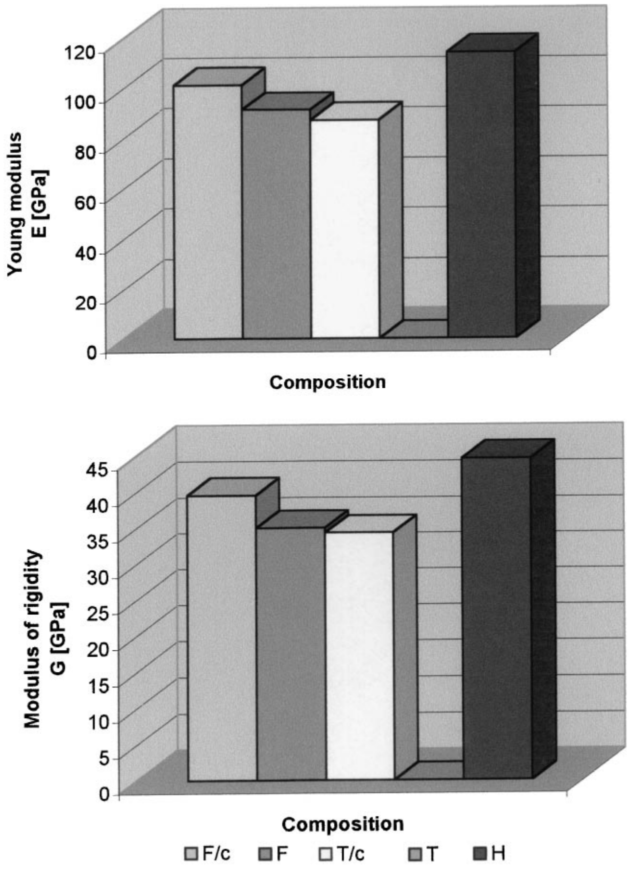

Fig. 7. Materials constants of the HAp–carbon fibre composites: *E*, Young modulus, *G*, modulus of rigidity.

and G values obtained for the composite material having the highest mechanical strength equal 101.4 and 39.5 GPa, respectively, and they are lower by ca. 13% than the values characteristic for dense hydroxyapatite ceramics produced following the hot pressing process.

The presented investigations should be treated as initial stage. In our opinion they should be followed by experiments on formation of HAp coatings on carbon fibres as well as on the evaluation of the change of K_{IC} of the investigated composites.

4. Summary

Following the hot pressing procedure we obtained in our investigations a new type of composite material consisting of ceramic hydroxyapatite matrix and carbon fibres produced from polyacrylonitrile (PAN).

The properties of HAp–carbon fibre composites depend significantly on the characteristics of initial fibres and especially on the type of functional groups existing on their surface. Fibres containing hydroxyl groups on the surface are preferred.

Better adhesion of carbon fibres on hydroxyapatite matrix is reached when the fibre surface is coated with a calcium phosphate layer. The sol–gel method applied in these investigations appeared to be suitable for making this coat layer. This method consists in treatment of fibre surface with metoxyetanol solution of orthophosphoric acid esters and calcium alcoholate obtained in-situ.

The best homogeneity of the sample in its entire volume, the best sintering grade and the best strength properties were stated in the case of composites produced from carbon fibres coated with calcium phosphates, with basic character of the surface.

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