MECHANICAL AND BIOLOGICAL PROPERTIES OF CARBON FIBER-REINFORCED PEEK COMPOSITE MATERIALS INTENDED FOR LARYNGEAL PROSTHESES

Wojciech Smółka[1], Michał Dworak[2], Bartłomiej Noworyta[3], Maciej Gubernat[3], Jarosław Markowski[1], Marta Błażewicz[3]*

[1] Medical University of Silesia in Katowice, School of Medicine in Katowice, Laryngology Department, ul. Medyków 18, 40-752 Katowice, Poland
[2] University of Silesia, Faculty of Computer Science and Materials Science, Institute of Materials Science, ul. 75 Pułku Piechoty 1a, 41-500 Chorzów, Poland
[3] AGH University of Science and Technology, Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30-059 Krakow, Poland
*e-mail: mblazew@agh.edu.pl

Abstract

The work deals with the mechanical properties and biological behaviour of composite materials made of polyether ether ketone (PEEK) polymer and carbon fibers (CF) designed for laryngeal biomaterials. Two types of PEEK–based matrix composites containing carbon fibers in the form of cloth (2D) and short fibers (MD) were made. The composite samples were obtained via hot molding of PEEK/CF prepregs. Mechanical durability of the composite samples aging in Ringer's solution at 37°C was analyzed. The samples were dynamically loaded under bending force up to 10^6 cycles. The ultrasonic wave propagation method was applied to study changes in the composites. The mechanical changes were analyzed, taking into consideration the anisotropic structure of the composite samples. The layered composite samples were modified with multiwalled carbon nanotubes (CNTs). The changes in mechanical stability of the composite samples were not significant after fatigue testing up to $1 \cdot 10^6$ cycles. The biological tests were carried out in the presence of hFOB-1.19-line human osteoblasts and HS-5-line human fibroblasts. The level of type I collagen produced from both types of cells was determined by ELISA test. The tests showed differences between the samples with regard to the viability of the cells.

Keywords: *composite materials; PEEK, mechanical properties, cells viability*

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Introduction

Larynx is a key element of the upper respiratory tract that ensures free airflow towards the trachea and bronchi. It also plays an important role in creating voice and speech. Larynx cancer is the most common squamous cell carcinoma in the head and neck area (Head and Neck Squamous Cell Carcinoma - HNSCC). It is the seventh most frequently occurring malignant tumor in the male population in Poland, and according to the National Cancer Registry data in 2010, 2,200 new cases of this cancer were found, and more than 1,500 people died [1].

In the case of patients with high clinical advancement of larynx cancer, the most common treatment is total laryngectomy, i.e. removal of the larynx. After the surgery, the respiratory tract is changed. The airflow begins at the trachea level, and the inhaled air is not cleaned, as it is during its natural flow through the nose and throat. In addition, without larynx, a patient is deprived of the basic organ to create the voice.

For many years, voice prostheses have been used to rehabilitate the speech of laryngectomized patients. The prosthesis implantation involves creating a fistula communicating the trachea with the esophagus, which enables the development of tracheoesophageal speech. Within the obtained fistula a voice prosthesis is placed which functions as a unilateral valve system. The esophagus oscillations caused by the airflow are then transmitted to the throat and mouth where they are transformed into intelligible speech [2-4]. In Poland, the most commonly used silicone prostheses are Provox (Atos Medical AB, Hörby, Sweden) and Blom-Singer (InHealth Technologies, Carpinteria, CA, USA). The voice prosthesis functionality in the specific environment of tracheal mucosa and esophagus is characterized by limited "vitality". Implanted prostheses require periodic replacement due to their deteriorated quality and reduced functioning. The prosthesis lifetime, voice quality and ease of voicing are important factors when choosing the voice prosthesis. According to literature data, the average lifetime of an implanted prosthesis is 3-6 months [2,4,5]. After this time, the prosthesis needs to be replaced. The limitation in the functioning of the prosthesis is caused by the following factors: the properties of the prosthesis itself, i.e., mechanical dysfunction of the valve system resulting from the biofilm formation, and the properties of tissues surrounding the fistula, such as superinfection of the implantation site, formation of granulation tissue around the prosthesis or the fistula enlargement leading to its expulsion to the esophagus or trachea, which involves the risk of bronchial aspiration and life-threatening complications [2,6,7].

The basic features that determine the prosthesis viability include the quality of the material (usually silicone) and the efficiency and strength of the valve system. The most disadvantageous phenomenon impairing the voice prosthesis functionality is the biofilm formed on the silicon surface of the prosthetic valve which changes its kinetic properties. The biofilm is a specialized colony of bacteria and/or fungi that produce an extracellular matrix.

Therefore, the inhibition of biofilm formation is researched to improve the durability of voice prostheses. One of the considered solutions is using silicone enriched with a 7% addition of silver oxide which is known for its bactericidal properties. An example of the prosthesis endowed with bacteriostatic properties of silver oxide is Blom-Singer® Dual Valve™ [8]. The tracheal mucosal damage can lead to granulation around the tracheo-esophageal fistula. Therefore, the appropriate design of the prosthesis that minimizes the risk of mucosal damage may extend its lifetime. Such a modification is used in Provox® Vega™ prostheses which are made of PTFE polymers [9].

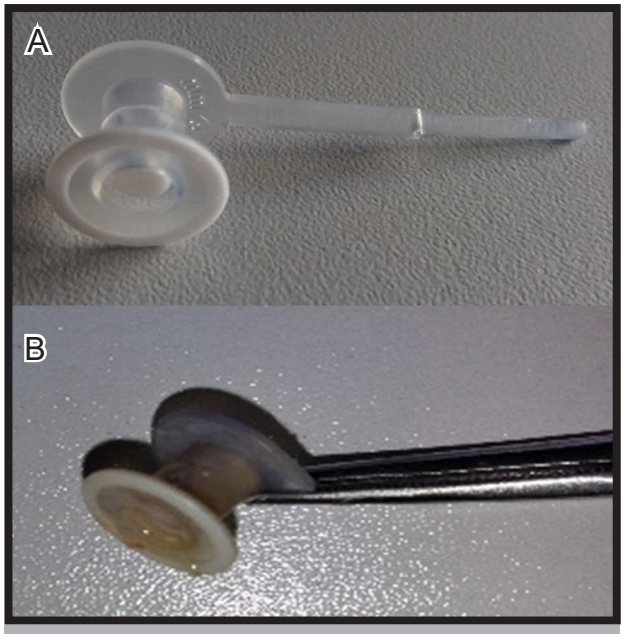

FIG. 1. Voice prostheses used in laryngology: A - Blom-Singer voice prosthesis before surgery; American company INHEALTH®I, B - Worn off Blom-Singer voice prosthesis after removal from tracheoesophageal fistula.

FIG. 1 shows the voice prosthesis before surgery (A) and after removal from the larynx (B).

The prosthesis dysfunction caused by losing the proper airflow pressure in the valve system impairs the effective formation of the tracheo-thoracic speech. The Provox® ActiValve™ prosthesis, which uses a magnet-enhanced valve mechanism, is designed to counteract the persistent early loss of such optimal kinetic values [8].

One of the possible developments of the voice prosthesis may be fibrous composite materials with appropriate fibers added to the polymer matrix. Proper manufacturing methods may also ensure the desired mechanical and biological properties. Polymer composites are compatible with modern diagnostic techniques (CT, NMR). Non-metallic composite materials seem to be a particularly good candidate to replace both pure polymer-based implants and the metallic ones used in various medical areas [10-13]. Studies have shown that the PEEK polymer matrix is endowed with properties inhibiting the biofilm formation at the implantation site [14,15]. The composites manufactured from various types of carbon fibers and PEEK matrix offer several opportunities to design and develop implants better suited for the specific treatment. As light materials, the composites can provide a high degree of anisotropy, due to physical properties similar to the replaced tissue. Optimal physical and mechanical properties of the composite which replaces the tissue or enhances the impaired organ functionality can be significantly improved by using fibrous reinforcement of roving or woven fabrics, braided fibers, fibrous sleeves, as well as chopped fibers. All those forms of the carbon fiber reinforcements appear to be beneficial for various structural applications, such as tubular implants, components of total hip prostheses, laryngeal implants and for fracture fixation joints [16-19].

However, there have not been enough experimental studies on the mechanical durability of PEEK/CF-based composites in the biological environment. In particular, the durability of such composites under dynamic loads in biological environment is a challenge that should be assessed to recognize their potential as structural implants.

The aim of the study was to manufacture composites of PEEK and carbon fiber reinforcements and to assess their mechanical strength under dynamic loading conditions and biological behavior *in vitro*. Cloths made of commercially available carbon fibers and mats of laboratory prepared PAN-based carbon fibers - were used as reinforcements. The target shapes of the composite samples were plates for laryngology. The study continues the hitherto research on the PEEK-reinforced carbon fibers composites as structural composite materials for general surgery and orthopaedics [19,20].

Materials and Methods

Manufacture of composite samples

The following material components were used to manufacture the composite samples:

- powder of polyether ether ketone (PEEK 150PF) delivered by Victrex was used as the matrix (TABLE 1). The Victrex polyether ether ketone for medical applications is available on the market under the separate InviBio brand as the PEEK Optima product line. The polymer is characterized by a high chemical purity and is certified by the FDA (Food and Drug Administration), and CE (a sign of compliance with the European Union New Approach Directives in the field of Active Medical Implants) to be used in implantable medicine. The polymer used in our study, under the trade name Victrex PEEK 150 PF, has identical mechanical properties and purity as the polymer for medical applications.
- (2D) carbon fiber cloths delivered from Porcher Industries Composites, code-named Pi preg® 3106-P17. The cloths in the form of prepregs were made from (2D) 3K,5H- Satin (3000 elemental fibers in roving) (TABLE 2).
- mats of laboratory manufactured PAN-based chopped carbon fibers; the thickness of the mat was 3 mm, the average fiber length in the mat was 9 mm and the tensile strength of single fiber was 0.3 GPa.
- multiwalled carbon nanotubes (CNT) provided by NanoAmor, USA. The nanotubes had diameters in the range of 10-30 nm and were 1-2 μm long.

TABLE 1. Victrex PEEK 150PF Product characteristics.

Tensile Strength	100 MPa
Tensile Elongation	15%
Melting Point	343°C
Glass Transition (T_g)	143°C
Melt Viscosity (400°C)	130 Pa·s
Density	1.3 g/cm^3
Bulk Density	0.3 g/cm^3
Processing Temperature	380-400°C

TABLE 2. Prepreg PEEK/2D/CF carbon cloth characteristics.

Prepreg thickness	0.6 mm
Mass per square meter	490 g/m^2
Polymer fraction in prepreg Polymer fraction in prepreg	50vo% 43wt%
Melting Point	343°C
Glass Transition (T_g)	143°C
Processing Temperature	380-400°C

The PEEK/CF composite was processed via hot compression molding, by stacking carbon cloths. The compression molding was performed using a hydraulic press and a heated mold. 10 layers cut from the prepreg PEEK/2D cloth (0/90°) were placed in a performing mold to make the composite samples of 3.5 mm in thickness. The compression molding was carried out under the following conditions: temperature 400°C, pressure 1.5 MPa, compression time about 3 min and free cooling in the air (about 3°C/min). The optimum molding conditions were established in earlier experiments [19-21].

A part of the composite samples was additionally modified by covering the prepregs' surface with CNTs. These composite samples were manufactured, as follows: the CNTs were introduced into dimethylformaldehyde (DMF) to prepare a suspension. The suspension was homogenized with ultrasound and CNTs were spread on the carbon fiber cloths by spraying and evaporating the solvent in a laboratory dryer. The CNTs weight fraction was determined basing on the weight difference of the composite samples and the CNT amount used to produce the composite samples. Samples with the following CNT weight fraction in the composite were obtained: 0.2wt%, 0.75wt% and 1.2wt%. The composites with chopped carbon fibers were obtained by placing the reinforcement mat and spreading the predetermined amount of PEEK powdered polymer alternately. The assumed volume fraction of the matrix in the composite was about 50%. The excess of the polymer was removed from the mold during compression molding. As a result of the compression molding, the composite plates measuring 15 mm x 3 mm x 80 mm were obtained.

The following types of composite samples were manufactured:

- PEEK/2D/CF – the composite samples made of 2D carbon fiber cloths;
- PEEK/2D/CF/CNT – the composite samples made of 2D carbon fiber prepregs additionally modified with CNTs;
- PEEK/MD/CF – the composite samples made of chopped carbon fibers- reinforced PEEK.

Methods

The mechanical properties of the composite samples were tested on a universal testing machine (Zwick 1435) controlled by TestXpert (v.8.1) software, in a bending mode. To determine the bending strength and modulus the tests were performed on the composite plates. The samples were placed on supports set 50 mm apart. The samples for bending tests measured 4 mm x 3 mm x 60 mm. The interlaminar shear strength (ILSS) of the composite samples was determined in the bending mode by short beam method with the span-to-depth ratio of 4:1. The composite plates for ILSS tests measured 3.5 mm x 3 mm x 35 mm. All the tests were conducted with a strain rate of 1 mm/min. For each type of the composite samples, 5 individual measurements were taken. The results are presented as a mean ± SD.

The fatigue properties under dynamic conditions were examined by subjecting the samples to a cyclic bending load in Ringer's solution at 37°C. The changes in the velocity of ultrasonic wave propagation in the sample were measured between consecutive cycles on the ultrasonic probe. The tests were conducted under a constant force amplitude conducted in the bending force-control mode, i.e. bending-bending mode. The level of the maximum force amplitude was established to be 50% of the strength determined in the static bending test. The samples were placed in a special reservoir containing a physiological fluid of 6.5 pH. The solution was continuously circulated by a pump system. The samples were subjected to 10^6 cycles. The ultrasonic measurements were taken after each $2x10^4$ cycles. At the beginning of the tests and between the successive stages, the wave velocity was measured. An ultrasonic tester - Ultrasonic Unipan-CT3 with heads of 1 MHz was used to measure wave propagation velocities. The mean and standard deviations of velocities were measured from 3 samples for each experimental group. For each measuring point, the velocity of the longitudinal wave propagation (CL) was determined and the value of the dynamic elastic modulus was determined from the dependence:

$$E = C_L^2 \cdot \rho \cdot K$$

where: C_L is the velocity of the longitudinal wave propagation in the sample in [m/s], E is dynamic longitudinal elasticity modulus in [GPa], and ρ is sample density, [kg/m^3], K - constant, was taken to be 1. The apparent density of composite samples was determined from the weight and size measurements. The water contact angle (θ) of the surface samples was measured at room temperature using a DSA10, Kruss apparatus (Germany). The roughness of the surface samples was determined by the surface profilometry technique (Hommel Tester T1500). The maximum of the surface roughness height, R_z as the mean and standard deviations from 3 measurements was determined.

Biological tests

In vitro experiments were carried out in the presence of hFOB-1.19-line human osteoblasts and HS-5-line human fibroblasts (ATCC, University Boulevard, Manassas, Canada). MTT tests were to determine the viability of both types of cells in the presence of the composite samples. The level of type I collagen produced from both types of cells was determined by ELISA test. The composite samples were prepared in the form of discs, 12 mm in diameter. Prior to testing, the samples were washed in 70% ethanol solution and sterilized under UV for 30 min on each side. Then, the samples were placed in the wells of the 48-well culture plates. The positive control was the polystyrene bottom of an empty culture plate well (TCPS). Cells viability was determined after a 7-day incubation, and the results were expressed as a percentage, assuming 100% of the absorbance value determined spectrometrically, at 570 nm wavelength, for the cells without the presence of the composite material.

The results were statistically analyzed using the t-test from Excel software. The p-values equal to or less than 0.05 were considered significant.

Results and Discussion

The parameters characterizing the obtained composite samples are presented in TABLE 3.

The composite samples are characterized by similar density values and volume fractions. A slightly lower density was obtained for the composites containing short fibers. The table also presents the values of surface wettability and surface roughness of the tested materials. The surface wettability, measured as the contact angle of the samples, depends on the type of carbonaceous components and indicates that the samples with carbon fibers have higher wettability, as compared to the pure polymer. The PEEK has the θ value characteristic for hydrophilic materials (64.4°). The composites modified with CNTs exhibit the distinctly higher values of water contact angle, i.e. 97.2-101.4°, bringing about a hydrophobic nature of the sample surface.

The mechanical properties of all types of composite samples determined in the bending test are collected in TABLE 4.

TABLE 3. Composites characteristics.

Samples	Fiber volume fraction [%]	Density [g/cm^3]	Surface roughness [μm]	Water contact angle [°]
PEEK	-	1.3	8.4 ± 2.5	64.4 ± 1.3
PEEK/2D/CF	50%	1.5	46.3 ± 11.8	89.3 ± 2.3
PEEK2D/CF/CNT(0.2%)	50%	1.5	42.4 ± 8.3	97.2 ± 2.3
PEEK2D/CF/CNT(0.75%	50%	1.5	39.4 ± 7.3	99.1 ± 3.3
PEEK2D/CF/CNT(1.2%)	50%	1.5	36.4 ± 4.3	101.4 ± 2.3
PEEK/MD/CF	45%	1.4	26.1 ± 1.2	77.3 ± 2.1

TABLE 4. Mechanical properties of PEEK- based samples.

Sample	Bending strength [MPa]	Bending modulus [GPa]	Work up to fracture [Nm]	ILSS [MPa]
PEEK	67.3 ± 5.3	2.7	-	-
PEEK/2D/CF	967.4 ± 88.7	68.6 ± 9.1	0.75 ± 0.13	57.2 ± 7.8
PEEK/2D/CF/CNT (0.2%)	887.2 ± 66.4	59.4 ± 4.8	0.82 ± 0.12	48.5 ± 3.9
PEEK/2D/CF/CNT(0.75%)	890.3 ± 26.6	65.7 ± 3.9	0.85 ± 0.06	67.3 ± 1.1
PEEK/2D/CF/CNT(1.2%)	826.6 ± 49.2	55.4 ± 4.3	0.76 ± 0.09	59.1 ± 1.1
PEEK/MD/CF	123.5 ± 17.3	5.4 ± 0.2	0.16 ± 0.1	27.8 ± 1.4

The results prove that the CNT addition causes a slight reduction in mechanical parameters, and the standard deviations of the mean values are significantly lower in the case of CNT-modified composites. It may prove a better homogeneity of these composites, especially for the samples containing 0.75% of CNTs. However, the reported content of nanotubes refers to the volume of the entire composite sample, whereas they were only deposited on the surfaces of the prepregs. For this reason, it can be assumed that nanotubes quantities at the interface boundaries between (2D) layers are higher than in the entire sample volume. The significantly lower mechanical properties were noted for the samples reinforced with short fibers. This is due to the fact that the mats of carbon fibers are characterized by low mechanical properties (tensile strength of 0.3 GPa).

For further fatigue tests, the composite samples containing 0.75wt% CNT and the unmodified composites were selected.

The manner of ultrasonic measurements of the composite plates is shown in FIG. 2. In the case of measurements along the sample (L direction), the ultrasonic heads were applied to the front surfaces of the sample. For measurements in the "a" and "b" directions, the heads were applied at three sites of the sample (FIG. 2), and the average value of 3 measurements was taken to calculate the dynamic elastic modulus.

FIG. 3 shows the changes in the dynamic elastic modulus of the CNT-modified composite plates (a) and the unmodified samples (b), respectively.

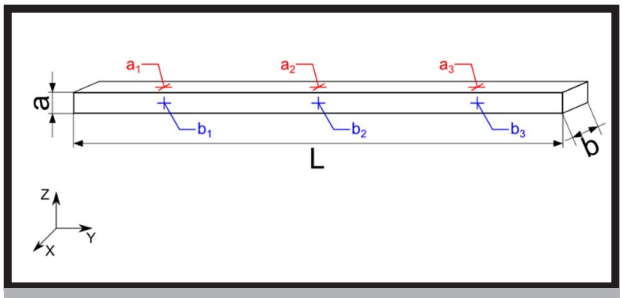

FIG. 2. Configuration of ultrasonic measurements of composite plate: L - along the length of plate, a - perpendicular to the thickness of plate, b - along the width of plate.

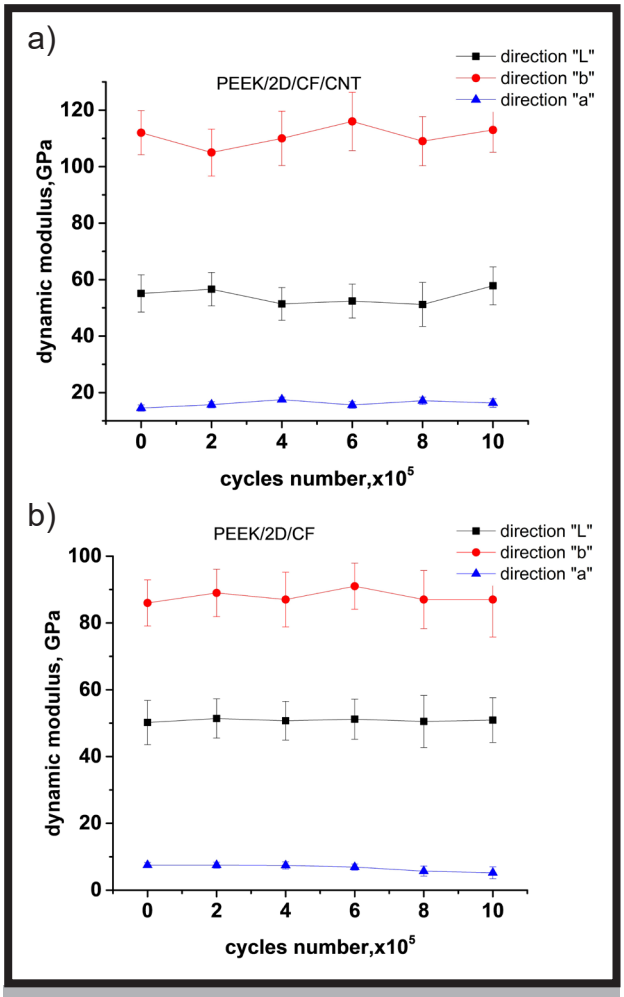

FIG. 3. Variations in dynamic elastic modulus of composite samples modified with CNT (a) and without CNT (b) as a function of cyclic load.

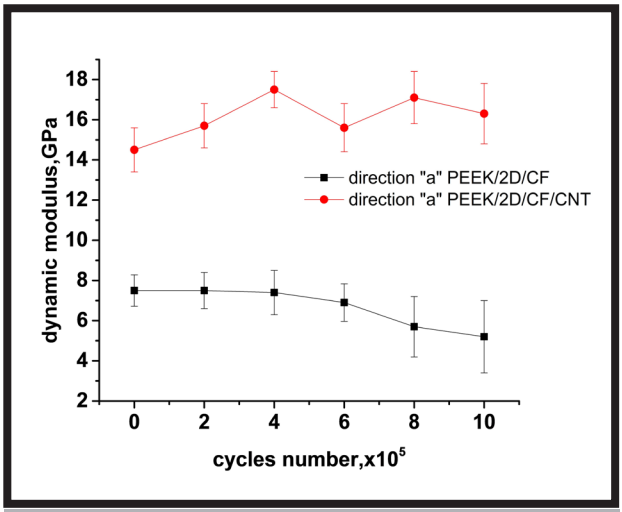

FIG. 4. Variations in dynamic elastic modulus of composite samples perpendicular to the carbon fiber layers as a function of cyclic load.

The changes in the dynamic modulus indicate that the composite samples do not degrade during dynamic loads. Due to the layered structure of the composite, it can be expected that the degradation may occur at the interlayer boundaries, which are represented by ultrasonic measurements referring to the "a" direction. The changes in the modulus in this direction do not reveal significant differences between the initial materials and after their dynamic loading to 10^6 cycles. However, the detailed analysis of these changes, taking into account the magnitude of the standard deviation of the ultrasonic wave propagation in the "a" direction, indicates some differences, which is shown in FIG. 4. For the composite without CNT a slight increase in SD after $6x10^5$ cycles (5.2 ± 1.8 GPa), as compared to CNT-modified composite (16.3 ± 1.5 GPa), can be observed. This may indicate the beginning of the samples' degradation. Yet, this observation requires further studies with the increased value of the load amplitude maximum.

FIGs 5-8 show the results of biological tests run on the composites with both types of carbon fibrous reinforcements and on the pure polymer samples. Cell viabilities were determined on day 7 after seeding cells on the studied materials.

In vitro viability tests revealed differences between the pure polymer, the composite materials, and the control. The viabilities of both types of cells were generally more favourable for the control, as compared to the pure polymer and the composite samples. Viability values for the control were taken as 100% and are not shown on the diagrams. The highest fibroblasts viability was observed on the pure polymer surface (FIG. 5), and in the case of osteoblasts the highest viability was noted for the cells cultured on the composites modified with CNT (FIG. 6). On the contrary, the lowest viability values were observed for the composites containing short carbon fibers (PEEK/MD/CF).

FIGs 7 and 8 show the level of collagen I produced by fibroblasts and osteoblasts in the presence of various composite samples.

All the PEEK-based samples were found to have a higher level of collagen I produced by osteoblasts (FIG. 8) in comparison to the control, whereas the level of collagen produced by fibroblasts was lower (FIG. 7).

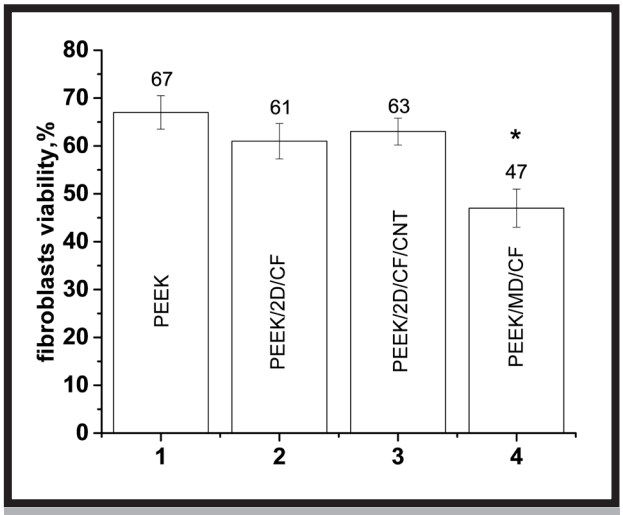

FIG. 5. Viability of HS-5-line human fibroblasts on composite surfaces on day 7 after seeding.
*** statistically significant difference of PEEK-based composites on day 7 *vs* pure PEEK; (p≤0.05)**

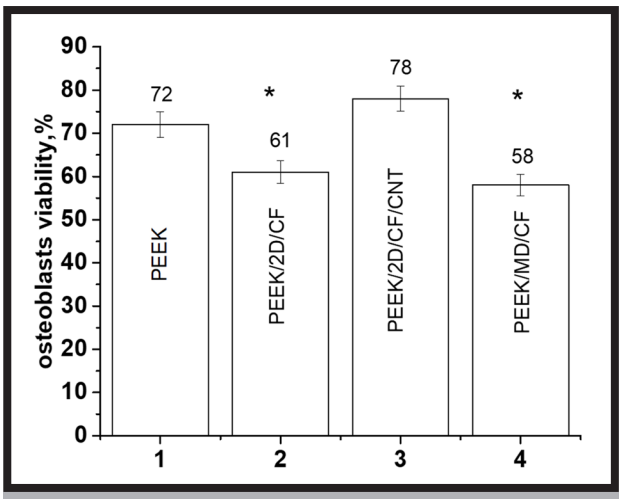

FIG. 6. Viability of hFOB-1.19-line human osteoblasts on composite surfaces on day 7 after seeding.
*** statistically significant difference of PEEK-based samples on day 7 *vs* pure PEEK; (p≤0.05)**

This assessment may be considered as a bioactivity test of the composite samples with respect to different cells. The results prove the influence of composite materials on osteoblasts and fibroblasts viability. The differences in viability and the level of collagen I produced by the cells may stem from the differences in the chemical and physical states of the samples' surface. The surface energy of the carbon-polymer composites is different from the pure polymers probably due to the reaction of carbon fibre surfaces with the polymer structure. The tests indicate that both types of cells are sensitive to the surface state of the composite samples.

The water contact angle measurements were performed to evaluate chemical nature of the materials surfaces. The calculated θ values for the pure polymer material was about 64.4° (TABLE 3), which is characteristic for hydrophilic materials [25]. The polymer samples exhibit smaller values of the water contact angle when compared to the composite samples. The composite materials modified with CNT exhibit slightly higher values in comparison to the composites without CNT.

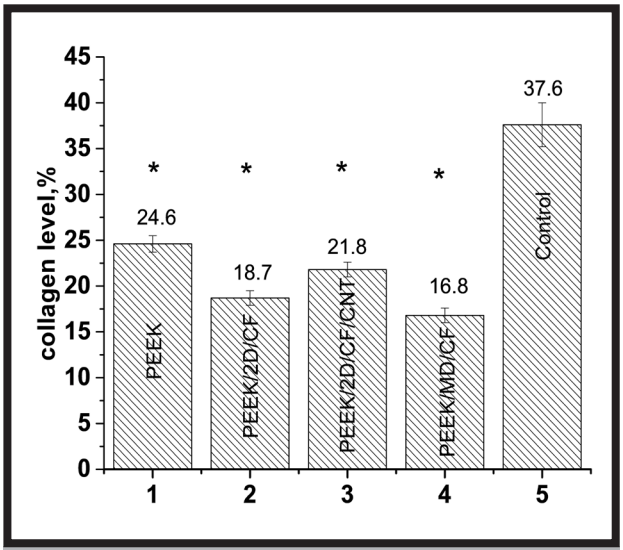

FIG. 7. Levels of collagen I produced by fibroblasts on PEEK-based sample surfaces, normalized to the level of the control.
*** statistically significant difference of PEEK-based samples on day 7 *vs* control; (p≤0.05)**

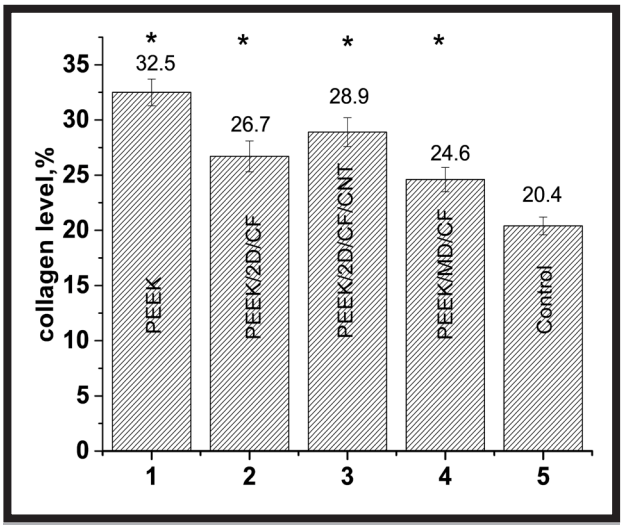

FIG. 8. Levels of collagen I produced by osteoblasts on PEEK-based sample surfaces normalized to the level of the control.
*** statistically significant difference of PEEK-based composites on day 7 *vs* control; (p≤0.05)**

The mechanical properties of the composites differ, depending on the form of carbon fiber reinforcement. Short fibers significantly reduce the mechanical parameters of the obtained composites. Nevertheless, this type of composite can be used to manufacture composites whose layers containing chaotically arranged fibers are combined with layers containing continuous filaments. In this way, the composite structures with properties suited to a specific application can be designed. In our research, we studied two distinctly different types of composites in terms of strength properties. The use of a fibrous carbon component modifies not only the mechanical parameters of the polymer matrix, but also affects other physical and chemical properties, such as electrical properties, surface structure, and the interaction with a biological environment. Numerous findings proved that fibrous carbon components could act as chondrogenic materials [22-24]. The carbonaceous materials, including carbon fibers and carbon nanotubes, were successfully applied in the treatment of cartilage defects. CNTs added to the polymer nanofibers improved biological and physical properties of fibrous scaffolds used for tissue engineering [25].

The study showed that the use of carbon nanotubes to modify the interface boundary between 2D layers did not enhance the mechanical properties of the composite materials. Yet, it improved the composites homogeneity, which was revealed by lowered values in the standard deviation of mechanical parameters, while the mechanical stability was maintained under dynamic loading. The fatigue bending tests at the level of variable loads (50% of maximum amplitude at which the composite fractures) indicated that such composites are durable and meet the requirements of mechanical durability for voice prostheses. Still, further tests are necessary, in particular on designing and manufacturing of the complete structure of a composite voice prosthesis.

The surface roughness, measured as the maximum of the surface roughness height, depends on the type of a carbon component and its arrangement in the polymer matrix (TABLE 3). The highest roughness was observed for the composite samples containing carbon fibrous cloths, and this parameter was significantly higher in comparison with the pure polymer.

The results of the biological tests are more complex and ambiguous. The obtained results indicate that the modification of the biocompatible polymer matrix with carbon fibers can induce significant changes in the cellular response. The research has also shown that the carbon fibers addition significantly changes the surface roughness and wettability values of the composite samples. The changes in surface properties brought about by the presence of fibers can affect the cell viability on the surface of the modified composite materials. The nanotubes introduced between the composite laminate layers increase the material hydrophobicity. Considering its prospective application for a voice prosthesis, a highly hydrophobic surface of the composite biomaterial may ensure the lack of undesirable interaction with the biological environment. Many studies on surface modification of biomaterials indicate that the use of nanometric components, e.g. various carbon nanoforms, can lead to the formation of superhydrophobic surface properties [26]. The conducted research indicated that an increase in the hydrophobicity of the composite surface may enhance the proper fixing of the biomaterial in situ. Studies have also shown that a carbon fibrous component in the polymer matrix may affect the wettability of the composite, which facilitates more efficient fitting of the composite biomaterial to the site. Another important requirement for a voice prosthesis is the ability to inhibit bacterial biofilm formation. The previous study has shown that the chemically modified PEEK surface has favorable surface properties inhibiting the development of bacterial biofilms [15].

The biological tests have shown a distinct influence of the carbon fibrous reinforcements on cells responses, and further research on the manufacturing of the composite for a voice prosthesis will be continued.

Conclusions

The composite samples containing carbon fibers were fabricated via the compression molding method. Two combinations of carbon fiber reinforcement, i.e. carbon fiber cloth and short fibers, in the PEEK matrix were used. The composite samples were modified with CNTs. The static and fatigue properties of the composites under dynamic cyclic tests were compared for both types of materials. The samples modified with carbon nanotubes improved their homogeneity in the interlayer polymeric phase between the carbon cloths, which was demonstrated by a decrease in standard deviations of the mean strength and modulus values. The results of the mechanical tests under dynamic bending loads indicated that ultrasonic wave propagation in the composite materials depended primarily on the elasticity of the carbon fibers themselves and their orientation to the propagation direction. The composite materials subjected to dynamic load amounting to 10^6 cycles retained their mechanical integrity when the maximum amplitude (deflection) of bending was 50% of the failure load. In the (2D) layered composites without CNTs a small increase in the standard deviation of dynamic elastic modulus was noted after the fatigue test.

The biological tests revealed that the viability of fibroblasts and osteoblasts determined in the MTT test after one week was slightly different from the control and the pure polymer. The value of viability was influenced by both the type of the material and the type of a cell line. Of the cells studied, osteoblasts displayed a higher survival level. The amount of collagen I produced by osteoblasts in contact with PEEK- based composites was higher than the amount of collagen I produced by these cells in the case of the control.

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ORCID iDs

W. Smółka: https://orcid.org/0000-0003-4074-9705
M. Dworak: https://orcid.org/0000-0002-6962-9283
M. Gubernat: https://orcid.org/0000-0002-5424-1091
J. Markowski: https://orcid.org/0000-0003-3416-7354
M. Błażewicz: https://orcid.org/0000-0001-9138-5409

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