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Durability of polymer-ceramics composite implants determined in creep tests

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Abstract

The polymer base composites are considered as one of the most promising groups of materials in medicine. Implants made of these materials have mechanical properties similar to natural tissues, show good biological compatibility, and also can be formed into various shapes. In living organism longterm working implants are subjected to mechanical stresses as well as aggressive body liquids. While aging, they can change their mechanical and biological properties. Investigations presented in this study show the influence of conditions simulating human body on the mechanical properties of two types of polymer composites such as: polysulphone–hydroxyapatite (PSU + HAP) and poly(lactide-co-glicolide)–hydroxyapatite (PGLA + HAP). Durability of investigated materials was estimated on the basis creep tests. The analysis of biological durability has been also performed, including the effects of modifying additives on the performance of examined composites. The biostable materials may be used as long-term implants with the stress level between 10% and 20% of initial strength. For resorbable polymers and their composites the time of resorption is a very important factor, and it depends on polymer's microstructure and the presence of modifying phases.

Keywords: A. Polymer-matrix composites; B. Mechanical properties; B. Durability; B. Creep; D. Scanning electron microscopy

1. Introduction

From the point of view of implant's application in bone-surgery, the most important properties of the material to be considered are: the ability of regeneration of surrounding tissues and the enhanced durability in biological environment [1]. The regeneration function may be assured by the application of bioactive ceramic materials, including primarily the calcium phosphates, bio-glasses as well as glass-ceramics [2,3]. The realization of biomechanical function requires on one hand the adjustment of Young's moduli of the implant and the surrounding tissue, and on the other, carrying the largest portion of stresses by the implant, according to the type of joint applied.

Depending on the role which the implant is supposed to play within the tissue, it is possible to use the long-term materials, with mechanical properties stable in function of time, as well as the materials undergoing partial biodegradation, the time of which should correlate with the time necessary to rebuild the regenerated tissue. The problem thus is to obtain bio-compatible material, which would be either biostable, or biosorbable, with increased mechanical properties and controlled durability, which at the same time would facilitate fixing of the implant/bone tissue interphase. Seen the complexity of requirements, the best solution seems to be the use of multifunctional composite materials copying the structure and the properties of the natural bone tissue (biomimetic materials). The trends of recent years in the development of biomaterials indicate the increasing role of polymer based composites in the implantology [4–7]. Use of modifying phases allows for improvement of the proper-

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ties of polymers, particularly the enhancement of their poor mechanical properties, particularly strength and the resistance to brittle fracture, with adjustment of Young's modulus to the values of the bone. The modifying phases allow also for introduction of variation in biological properties by assigning to them the bioactive properties [8].

The concept of polymer reinforcement using bioactive ceramic particles has been introduced in 1981 by Bonfield et al. [9]. Polyethylene reinforced with hydroxyapatite (PE/HA) was the first known by the commercial name of HAPEX™. The inner ear implant made of it in 1995 by Smith & Nephev Richard, Inc. had property characteristics close to natural bone [10]. Clinical successes brought about development of other bioactive composites based on polymer matrix. Researches from many countries of the world begun experiments with application of bioactive ceramic particles for reinforcement of various polymers. The particles of hydroxyapatite were applied as additives for polymer matrices such as poly(etheretherketone) (PEEK) [11], poly(hydroxybutyrate) (PHB) [12], polysulfone (PSU) [13], polylactide (PLLA) [14]. Other bioactive particles like bioglasses, or A/W (apatite/wollastonite) ceramics were also applied to reinforce polymer matrices [15,16].

In order to define the durability of polymers it is necessary to establish the stress levels in the liquid biological environment, in which they will remain biostable.

The majority of data cited in the literature relates mostly to mechanical properties defined in static tests [17–19]. This does not give the full picture of implant's behaviour in real conditions, where they are subjected to simultaneous action of mechanical stresses and aggressive environment of body fluids. This is particularly important in the case of polymer composites, which can change their properties substantially due to, among others, creep phenomena. Additionally, physiological fluids may penetrate inside the composite materials affecting the state of interphases, which results in deterioration of mechanical properties [20]. Disadvantageous changes of long-term mechanical properties were observed also in other composites. Zhang et al. [21] examined strength of PEEK/CF composites reinforced with continuous unidirectional fibres under in vitro conditions. They noted the strength decrease due to the changes of state of the interphases, which they interpreted as being due to the presence of physiological fluids.

Christtel et al. [22] were brought to similar conclusions in the case of PEEK/CF composites containing random packing of short carbon fibres. Interphase degradation due to both cyclic loading and artificial biological environment was observed in the cases of PSU/CF composites and also PSU/aromatic polyamid fibres [23]. The results obtained make the use of these composites doubtful in applications where substantial mechanical loads are present, like orthopedics, and such composites require further modifications and extensive research [24].

In the composites based on resorbable polymers it is important to define the time dependent effects of modifying additives during implant's degradation, as well as the effects on its biological properties (bioactivity). The goal of this work is to define the conditions in which the implants made of PGLA + HAP and PSU + HAP composites may play the roles of stress-bearing implants (biomechanical function), and also to determine the effects of HAP particles on their biological performance.

2. Materials and methods

The tests were carried out on paddle-shaped samples received by injection molding (at the temperature of 180 °C – PGLA and 340 °C – PSU) and made of PGLA (PLA:PGA-84:16, Mn = 85,000 Da), manufactured at the Centre for Polymer Chemistry in Zabrze (Poland) and PSU-by Aldrich Chemical Company, Inc. USA. $C_{27}H_{26}O_6S$, Mn = 26,000 Da, $T_g = 190$ °C, $d = 1.24$ (g/cm^3). Composites were made by the addition of 15%wt of natural origin (beef bone) hydroxyapatite (HAP) $Ca_{10}(PO_4)_6(OH)_2$, $d = 3.16$ g/cm^3, specific surface $S_w = 79.7$ m^2/g.

Samples were incubated at the temperature of 37 °C during 16 weeks in the Ringer Fluid made by Baxter Terpol Sp. z o.o. (of composition [g/cm^3]: $NaCl^-$, 8.60; KCl^-, 0.30; $CaCl^-$, 0.48; which simulated the biological environment. The material was additionally incubated in the SBF fluid (artificial serum), with the following ionic composition [mmol/l]: Na^+, 142.0; K^+, 5.0; Ca^{2+}, 2.5; Mg^{2+}, 1.5; Cl^-, 148.8; HCO_3^-, 4.2; HPO_4^{2-}, 1.0; SO_4^{2-}, 0.5.

The pH of solutions and the mass measurements were performed on a weekly basis using the pH-meter CP-315 ELEMETRON. After the 6th and the 12th week the microstructure was examined using scanning electron microscope (SEM) Jeol JSM-5400, and the phase composition was examined by transmission infrared spectroscopy (FTIR) using the Fourier Spectrometer BIO-RAD FTS-60V.

Mechanical properties were measured using universal testing machine Zwick 1435. The "in vitro" creep behaviour was examined according to standard PN-83/C-89041.

3. Results and discussion

The "in vitro" behaviour of the examined samples was determined on the basis of pH variations of the Ringer fluid during the polysulphone incubation, and variation of the weight of samples during 16 weeks solution immersion. Fig. 1(a) shows the lack of significant pH changes of the Ringer fluid during incubation of polysulphone, which proves its in vitro stability. The results confirm known from the literature stability of polysulphones under conditions simulating the life body environment [25]. In the case of PSU/HAP composites, the variation of pH can be observed, which is caused by the presence of hydroxyapatite's bioactive particles on the surface of this composite.

The beginning of degradation of PGLA incubated in Ringer fluid occurs during the 4th week (Fig. 1(b)), which is confirmed by the pH decrease. For the PGLA + HAP composite the pH variation can be observed after 10 weeks