

INJECTABLE BONE SUBSTITUTES BASED ON POLYURETHANE AND β -TCP

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Introduction

Structure of segmented polyurethanes (PU) determines their widespread properties. PU/ β -tri-calcium phosphate (β -TCP) open-celled foams may be used as three-dimensional scaffolds which successfully support cell adhesion, proliferation, angiogenesis, nerve and bone tissue regeneration [1]. The aim of this study was to investigate the influence of varying PEG/PCL ratios on properties of polyurethane hierarchical foams. Poly(ethylene glycol) (PEG) is an uncharged, hydrophilic and nonimmunogenic polymer used as component of blood-contacting devices [2]. Poly(ϵ -caprolactone) (PCL) is widely used in regenerative medicine due to good mechanical properties, nontoxicity and biocompatibility [3]. Li et al. developed hemocompatible PEG/PCL based PU which supported attachment, growth and proliferation of rat glial cells. The research carried out by Li et al. showed potential of PU based on PCL and PEG as nerve regeneration scaffolds [4]. PU synthesized by Gong et al. exhibited higher hydrophilicity with increasing PEG content. On the other hand higher PCL content prolonged degradation time [5]. This study focused on the relationship between composite structure and properties.

Materials and methods

β -TCP microparticles (with particle size ca 150 μ m) were produced by Fluka Chemie GmbH. Composites were manufactured with different mass fractions of β -TCP (0, 20, 40, 60 and 80%). 4,4'-diphenylmethane diisocyanate (MDI), poly(ethylene glycol) (PEG) of average molecular weight (Mw) of 2000, poly(ϵ -caprolactone) diol (PCL) of Mw amounting to 2000 and 1,4-butanediol (BDO) were purchased from Sigma Aldrich. Sulphonated castor oil (SCO) from Fluka Chemie GmbH and calcium stearate (CS) from POCH S.A. One-step synthesis was performed by mixing all the above mentioned substrates. SCO and CS were used for better porosity control and to obtain open porous systems. SCO played role of surfactant.

Fourier transform infrared (FTIR) spectra of the composites were obtained with a BIO-RAD FTS60V FTIR spectrometer in the middle infrared range with samples mixed with the KBr powder (about of 0.1-2% of the KBr amount) and pressed into pellets. The contact angles were measured by the sessile drop method using an automatic drop shape analysis system DSA 10 Mk2 (Kruss, Germany). Ultra high quality (UHQ) water droplets with a volume of 0.2 μ l were placed on each sample surface and the contact angles were obtained by averaging the results of ten measurements. Compressive tests were carried out with the aid of a mechanical testing machine Zwick on dry samples.

Results and discussions

The structure of obtained polyurethane was confirmed by FTIR method. The FTIR spectra (FIG. 1) revealed structure changes occurring by different PEG/PCL ratio. Characteristic absorptions corresponding to functional groups in PEG and PCL differ from each other. This allows to detect structural changes with aid of infrared spectroscopy.

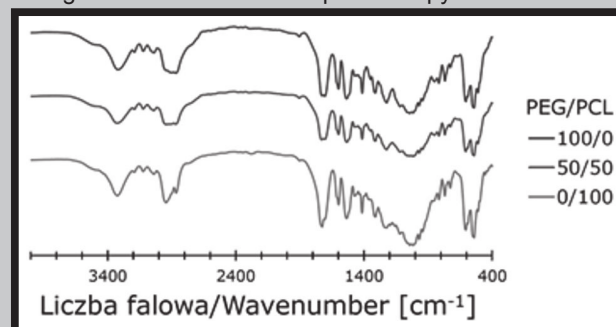


FIG. 1. FTIR spectra for PU/ β -TCP composite samples containing 80% β -TCP.

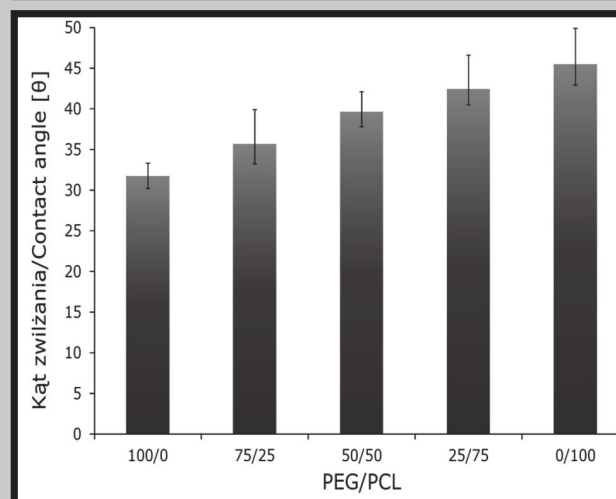


FIG. 2. Contact angle values measured on surface of the composites containing 80% β -TCP.

The characteristic peak at 1100 cm^{-1} corresponds to the ether linkage C-O-C present in PEG. The absorbance at 1730 cm^{-1} corresponds to the ester carbonyl linkage present in PCL. The band located at 3330 cm^{-1} proves presence of N-H stretching vibrations and band at 2934 and 2850 cm^{-1} is assigned to asymmetric and symmetric vibrations of group CH_2 . Backbone vibrations causing stretch of the C-C binding within aromatic ring absorb radiation in range 1600-1585 cm^{-1} and 1500-1400 cm^{-1} . Stretching vibration C-N, in turn, absorbs radiation of wavenumber 1222 cm^{-1} . The band at 1535 cm^{-1} is assigned to bending vibrations of N-H group. The bands at 570 cm^{-1} and 600 cm^{-1} are assigned to the O-P-O bending mode in β -TCP.

Contact angle was measured on surface of the samples to assess the contribution of PEG into hydrophilicity. The measured values are shown in the FIG. 2.

The values are average of measurements from 10 readings for each sample. The above results indicate that PEG is more hydrophilic than PCL. The increasing PCL content caused higher contact angle. This complies with previous research [6]. Different PEG/PCL ratios may be used to manipulate hydrophilicity of the composite samples. Additionally β -TCP influenced hydrophilic nature of the surface. Pure PU surface is more hydrophobic in comparison with composites containing β -TCP microparticles.

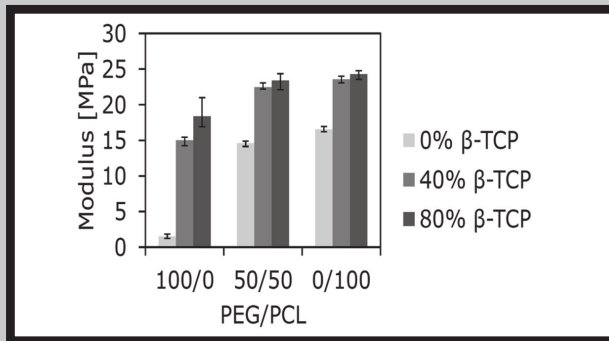


FIG. 3. Modulus of composite samples.

Compressive tests were carried out on dry samples. The modulus was calculated on basis of force-strain relationship curvatures. The results are shown in the FIG. 3.

The above results show an increase of modulus with increasing PCL and β -TCP content. These results comply with previously carried out research [7]. Both PCL and β -TCP can be used to manipulate mechanical properties. However the values are much lower than in case of cancellous bone of which Young's Modulus amounts to 60-260 MPa [8].

Conclusions

Porous composite materials containing bioactive ceramics were synthesized and characterized. They have potential to be applied as injectable biomaterials. However there is still need to investigate their properties considering tissue engineering application.

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APPLICATION OF INJECTION METHOD TO MODIFY TITANIUM ALLOY Ti6Al4V

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Abstract

In the present work, the samples were subjected to a comparative analysis of the titanium alloy Ti6Al4V prepared by various methods. The research included a comparison of the following properties of manufactured elements: microstructure, phase composition and surface roughness. The test results clearly showed that these properties are different when using different method of casting. These changes allows the use of prepared elements in medicine.

Keywords: biomaterials, titanium alloy Ti6Al4V, massive amorphous alloy

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Introduction

Long-term studies lasting over metallic materials suitable for biomedical applications have shown, that a group of alloys based on titanium is safe to implant applications. Since the forties of the last century there are attempts selecting the ideal chemical composition of the alloy, which would be completely neutral to the human body. One of the most widely used implant material is titanium alloy Ti6Al4V, although that alloy doesn't have only advantages [1,2]. Currently, studies are carried out of the attempt to obtain amorphous materials based on titanium, thereby resulting in improved mechanical properties, more developed surface, higher biochemical resistance. Obtaining materials with such properties allows the injection method, which the liquid is injected into the metallic copper mold cooled with a suitable rate [3,4].

Materials and methods

The first test sample was cut by waterjet from purchased rod made of titanium alloy Ti6Al4V, the second was produced by a novel method of injection. The chemical composition of materials tested are given in TABLE 1.

Samples were subjected to microscopic analysis, qualitative X-ray analysis, assessment of surface topography.

TABLE 1. Chemical composition of titanium alloy Ti6Al4V.

Chemical composition	Al	V	C	Fe	O	N	H	Ti
%	6	4	0,03	0,1	0,15	0,01	0,003	rest