SYNTHESIS AND CHARACTERIZATION OF NOVEL CALCIUM PHOSPHATES/ POLYURETHANE COMPOSITES FOR BONE TISSUE ENGINEERING

Piotr Szczepańczyk*, Jan Chłopek, Kinga Pielichowska

AGH University of Science and Technology
Faculty of Materials Science and Ceramics
Department of Biomaterials
30 Mickiewicza Av. 30-059 Kraków
*e-mail: pszczepa@agh.edu.pl

[Engineering of Biomaterials, 122-123, (2013), 71-72]

Introduction

Biodegradable materials for bone tissue engineering are currently intensively developed due to increasing number of injuries against background of sport or cancer. There are still many problems to solve connected with bioactivity, biocompatibility, vascularization etc.

There is an increasing demand of, which ideally biodegrade in register with controlled, progressive osseous regeneration [1] [2]. Autografts pose currently the gold standard therapy in bone healing though in many cases this method is not sufficient and the harvest of graft tissue leads to donor site morbidity. In turn, allografts are clinically limited due to eventuality of immune rejection and lack of donor sources [3] [4]. Regenerative medicine reposes hope in tissue engineering of which approaches have demonstrated potential solutions for bone tissue regeneration [3] [5]. The objective of this study was to fabricate PUR-based composite scaffolds filled with β-TCP nanoparticles with potential to be applied as injectable, resorbable biomaterials.

Materials and methods

The PUR foam was synthesized by one step bulk polymerization method, using water as expanding agent, methylene diphenyl diisocyanate (MDI), polyethylene glycol (PEG). Composite scaffolds have been obtained by addition of β-TCP nanoparticles to the polymerization mixture.

On the basis of microscope observations of samples, the area of hollow spaces and whole visible composite surface was determined. The pore-to-volume ratio in the scaffolds, also called porosity, was determined from the ratio of the nonsolid volume (pores) to the total volume of material including the solid and nonsolid parts. 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 SEM microphotographs were measured on NanoNova SEM (FEI) scanning microscopy. Investigation of compressive resistance were carried out with the aid of a mechanical testing machine Zwick on samples before and after incubation in phosphate buffered saline.

Results and discussions

The structure of obtained the polyurethane was confirmed by FTIR method. The FTIR spectra are shown in the FIG. 3.

The characteristic absorption band for ethers in range 1150-1085 cm^{-1} is caused by asymmetric stretching vibrations C-O-C. 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. Bands at 1700 and 1730 cm^{-1} attest to presence of stretching vibrations of carbonyl group. 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. The intensities of absorption of these bands increased with an increase of concentration of β-TCP in PUR composite.

The porosity was determined from the ratio of the nonsolid volume (pores) to the total volume of material including the solid and nonsolid parts. The calculated results are put in the TABLE 1.

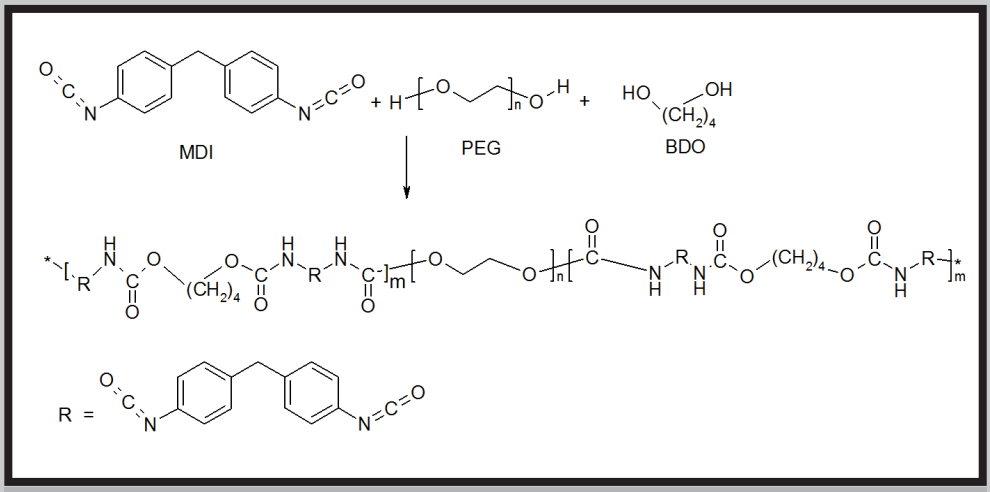

FIG.1. Mechanism of reaction of synthesis of polyurethane

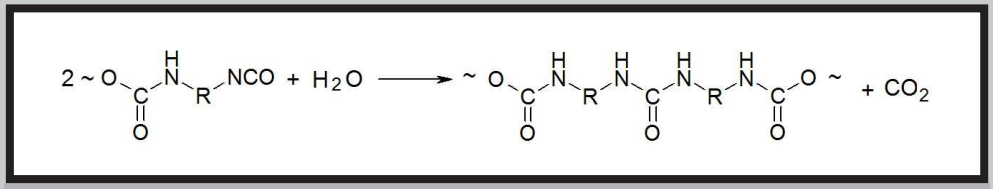

FIG.2. Mechanism of reaction of foaming of polyurethane

TABLE 1. Porosity determined for samples with different concentrations of β-TCP.

Concentration of β-TCP	0%	5%	10%	15%	20%	25%	30%
Porosity	41%	27%	38%	33%	44%	53%	46%

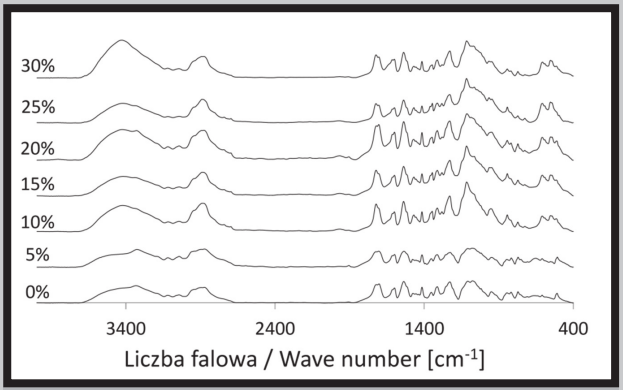

FIG.3. FTIR spectra for PUR/ β-TCP composite samplestrochlear groove filled with the implant material (b).

The influence of β-TCP on the bioactivity of PUR-based scaffolds was investigated by immersion tests in acellular simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma according to procedure described in work [6]. There is shown a SEM microphotograph of investigated samples after incubation and the EDX analysis results in the FIG. 4.

Measures of compressive strenght were carried out on samples before and after incubation in phosphate buffer saline (PBS). The modulus was calculated on basis of force-strain relationship curvatures. The results are shown in the TABLE 2.

The above results show a decrease of modulus of samples after incubation what proves hydrolysis of β-TCP during incubation [7]. There is additionally an observable increase in modulus with increasing concentration of β-TCP in PUR composite samples, what a result is of big contribution of ceramics in mechanical strength of composite [8].

Conclusions

Porous composite materials containing bioactive ceramics were obtained through synthesis. Summarizing, these biomaterials bode well in orthopaedic applications' terms and the obtained results indicate purposefulness of further investigations.

Acknowledgements

This work was financed by statutory research 11.11.160.256 of Faculty of Materials Science and Ceramics, AGH University of Science and Technology.

TABLE 2. Calculated modulus results for PUR/β-TCP composite samples.

Before PBS incubation		After PBS incubation	
Concentration of β-TCP	Modulus [MPa]	Concentration of β-TCP	Modulus [MPa]
0%	0,53±0,08	0%	0,33±0,08
5%	0,55±0,09	5%	0,35±0,07
10%	0,60±0,05	10%	0,40±0,08
15%	0,64±0,03	15%	0,49±0,04
20%	0,73±0,04	20%	0,54±0,06
25%	0,75±0,05	25%	0,60±0,05
30%	1,00±0,10	30%	0,86±0,08

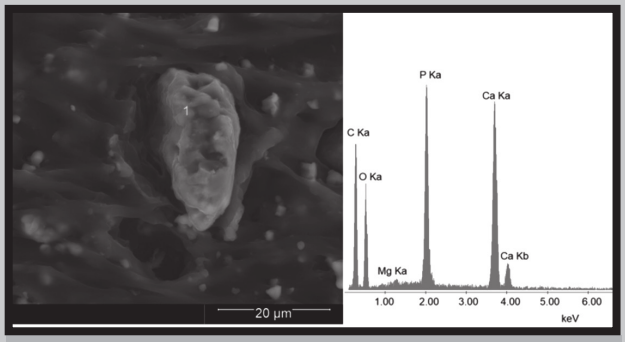

FIG.4. SEM microphotograph of PUR/ β-TCP composite surface.

References

[1] Zhang J, Doll BA, Beckman EJ, Hollinger JO, „A biodegradable polyurethane-ascorbic acid scaffold for bone tissue engineering," *Journal of Biomedical Materials Research,* pp. 389-400, 1 November 2003.

[2] Doll B, Sfeir C, Winn S, Huard J, Hollinger J, „Critical aspects of tissue-engineered therapy for bone regeneration," *Critical Reviews in Eukaryotic Gene Expression,* pp. 173-198, 2001.

[3] You Z, Bi X, Fan X, Wang Y, „A functional polymer designed for bone tissue engineering," *Acta Biomaterialia,* 11 November 2011.

[4] D. Puppi, F. Chiellini, A.M. Piras, E. Chiellini, „Polymeric materials for bone and cartilage repair," *Progress in Polymer Science,* pp. 403-440, 2010.

[5] Rezwan K, Chen QZ, Blaker JJ, Boccaccini AR, „Biodegradable and bioactive porous polymer/inorganic composite scaffolds for bone tissue engineering," *Biomaterials,* 28 February 2006.

[6] Kokubo T, Takadama H, „How useful is SBF in predicting in vivo bone bioactivity?," Biomaterials, pp. 2907-2915, 31 January 2006.

[7] Kobayashi S, Sakamoto K, „Effect of hydrolysis on mechanical properties of tricalcium," The Journal of Materials Science: Materials in Medicine, pp. 379-386, 21 September 2008.

[8] M. Bagheri Hossein Abadi, I. Ghasemi, A. Khavandi, M.A. Shokrgozar, M. Farokhi, S.Sh. Homaeigohar, A. Eslamifar, „Synthesis of Nano β-TCP and the Effects on the Mechanical & Biological Properties of β-TCP/HDPE/UHMWPE," Polymer Composites, pp. 1745-1753, 2010.