HIGHLY POROUS POLURETHANE-BASED GRADIENT SCAFFOLDS FOR TISSUE ENGINEERING OF OSTEOCHONDRAL DEFECTS

PATRYCJA DOMALIK-PYZIK*, KAROLINA KOSOWSKA, MARTYNA HUNGER, KINGA PIELICHOWSKA, JAN CHŁOPEK

DEPARTMENT OF BIOMATERIALS AND COMPOSITES,
FACULTY OF MATERIALS SCIENCE AND CERAMICS,
AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY
*E-MAIL: PDOMALIK@AGH.EDU.PL

[ENGINEERING OF BIOMATERIALS 158 (2020) 66]

Introduction

Polyurethanes (PU) are known for their versatility and diversity of properties that can be tailored to a specific application by playing with PU building blocks and chemical composition. They can be volume- or surface-modified to create polymer-matrix composite systems with improved properties. Also, studies have shown that introduction of chitosan, a natural polysaccharide, can positively affect biocompatibility of PU. Bearing in mind that polyurethanes are generally known for their superior (when compared especially to natural polymers) mechanical properties and susceptibility to various modifications, including these responsible for enhanced bioactivity/biocompatibility, one can safely state that their potential for application as biomaterials is extensive. Among many others, they can be used as scaffolds in regeneration of osteochondral defects. Tissue engineering applications are demanding in many ways and impose certain material- and scaffold-related criteria, like biodegradability, nontoxicity or high porosity to name a few. In this study, a series of highly-porous polyurethane-based composite scaffolds modified with chemically-grafted hydroxyapatite (HAp) and graphene oxide (GO) was developed and characterized.

Materials and Methods

Highly porous polyurethane-based scaffolds were obtained in a one-step bulk polymerization method. First, dry poly(ethylene glycol) (PEG, M_W=2000 g/mol and poly(ε-caprolactone) diol (PCL, M_W=2000 g/mol) with a molar ratio of 1:3 were melted under 60°C, followed by addition of a medical-grade chitosan (CS, DDA = 85%, HMC+). All the reagents were heated. When the reaction system reached 90°C, a chain extender, 1,4-butanediol (BDO), was added and finally, melted 4,4'-diphenylmethane diisocyanate (MDI) was injected under 60°C. The system was mixed thoroughly, left for approx. 4 h in 80°C and subsequently for 12 h in 80°C (120°C for GO samples). The synthesis was carried out under nitrogen atmosphere. For PU-based composites, HAp or GO were dispersed through sonication in the melted polyols. The obtained samples were as follows: PU1 (ref sample), PU2 – PU4 with added 1, 5, and 10% of HAp, respectively, PU5 and PU6 with 0.1 and 1% of GO, respectively. Gradient scaffolds were obtained by gradual synthesis of different PU on top of each other. Physicochemical properties of the materials were examined using various methods.

Results and Discussion

As shown in FIG. 1, all of the non-modified and HAp-modified PU were highly porous (PU1-4). Microstructure of the GO-modified samples was more dense, but still with open porosity. With higher GO content (0.1% vs 1%) some nonhomogeneity was observed.

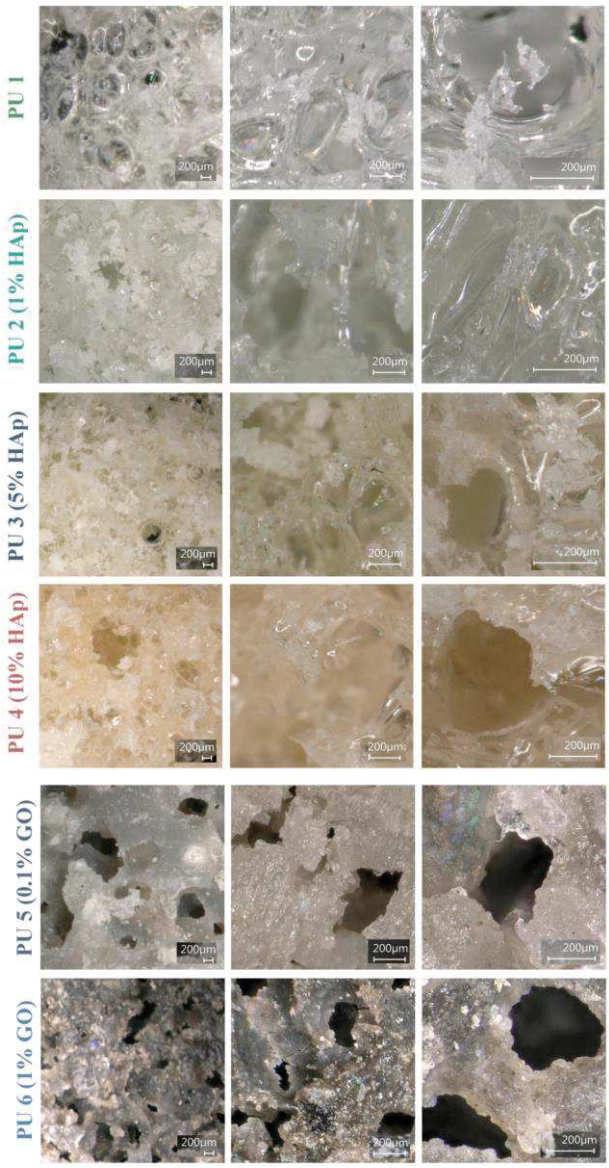

FIG. 1. Digital microscope images of the cross-section of the samples.

Improved mechanical properties (compressive strength and Young's modulus) were observed for samples modified with HAp and GO (especially for samples PU4 and PU5, respectively. Addition of HAp positively affected also wettability of the materials. After incubation in simulated body fluid (2 and 4 weeks, 37°C), apatite-like structures were formed on the surface of all the samples. Gradient scaffolds had three distinct zones designed for to fit the osteochondral defects requirement: (i) thin layer (approx. 3 mm) of PU/GO, non-modified intermediate zone (as PU1) and HAp-rich lower zone destined for subchondral bone area.

Conclusions

Polysaccharide (chitosan) containing polyurethanes were successfully synthesized. They were further modified with hydroxyapatite and graphene oxide. It was possible to obtain gradient scaffolds for soteochondral defects regeneration.

Acknowledgments

This research was funded by the National Center for Research and Development, Poland (BioMiStem grant No. STRATEGMED3/303570/7/NCBR/2017).