BIO-BASED POLYURETHANE FOR SURGICAL APPLICATIONS – INFLUENCE OF PEG MOLAR MASS, BIOLOGICAL AND THERMAL PROPERTIES OF POLYURETHANE COMPOSITES

KLAUDIA ORDON^{*}, PIOTR SZATKOWSKI, KINGA PIELICHOWSKA

DEPARTMENT OF BIOMATERIALS AND COMPOSITES, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KRAKOW, POLAND *E-MAIL: ORDON@AGH.EDU.PL

[ENGINEERING OF BIOMATERIALS 153 (2019) 59]

Introduction

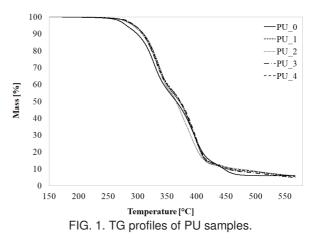
History of medicine shows that due to the constant development of modern operational techniques, as well as an increasingly broad range of available biomaterials interest in using of synthetic materials in surgical is constantly growing. Polymeric materials, due to their properties, are quickly unique replacing other biomaterials, such as ceramics or metals and theirs alloys in medical applications. Polyurethanes (PURs) are a group of polymers with interesting properties and the broadest range of applications. The main substrates for the preparation of PURs are isocyanate, chain extender and polyol. Isocyanate and chain extender create in the PUR so-called rigid segment while the polyol - flexible segment [1]. So far, Poly(ɛ-caprolactone) (PCL) - based PURs has been most widely studied because the PCL soft segment is characterized by a high modulus and also ultimate tensile stress. PCL is a biocompatible, semicrystalline and biodegradable aliphatic polyester having promising thermal properties [2,3]. It is degradable enzymatically and hydrolytically. The biodegradability and mechanical properties of PCL-PUR can be tailored for various applications by varying the chemistry or molecular weight of its components [2].

Materials and Methods

Poly(ɛ-caprolactone) diol with a 2000 average molar mass was used as a soft segment. 1,6-hexamethylene diisocyanate (HDI) was used in stoichiometric amounts. Dibutyltin dilaurate (DBTDL) was used as a catalyst. PURs were synthesized with starch (SA) and 1,4butanediol (BD) as a chain extender. In order to improve the mechanical properties and bioactivity of the biomaterial, hydroxyapatite (HAp) was applied, while poly(ethylene glycol) (PEG) with a 4000, 6000, 8000 and 10000 average molar mass was used as phase change material (PCM) for storing curing thermal energy. PUR biomaterials were obtained using a two-step bulk polymerization method. PCL, SA, BD, PEG and HAp were dried before synthesis, while the other reagents were used as supplied. PEG was introduced into a flask, HDI and DBTDL were added and stirred under nitrogen to obtain the pre-polymer. The BD, SA, PEG and HAp were dispersed by sonication. In the second stage, a chain extension process was performed. After thorough mixing of ingredients at RT, the samples PUR were cured at 80°C for 24 h [4]. Differential scanning calorimetry (DSC). scanning electron microscopy (SFM). thermogravimetry (TG), dynamic mechanical analysis (DMA) and Fourier transform infrared spectroscopy (FT-IR) techniques were used for characterization of the obtained PURs.

Results and Discussion

The thermal degradation of PUR is characterised by the decomposition of urethane bonds and the degradation of soft segments as well as the evolution of volatile components. Thermogravimetric analysis TG/DTG of biodegradable polyurethanes before (FIG. 1) and after incubation in a solution of phosphate buffered saline (PBS) at 37°C show that incubation changes degradation pathways of PUR.



The SEM images indicate that the surface of the PURs after exposure in PBS is defected. The SEM images and EDS analysis confirmed the incorporation of hydroxyapatite and starch components into the PUR matrix. The structure of PURs was confirmed by FTIR method. The absorption bands from –OH groups in at 3570 cm⁻¹ confirms that HAp was chemical bonded to PUR chains.

Conclusions

In this work polyurethane modified with PCL, poly(ethylene glycol) as PCM and hydroxyapatite were obtained using a two-step bulk polymerization method. The structure of the synthesized PURs was confirmed by FTIR technique. The mechanical properties of biodegradable PUR with PEG were better in comparison to the polyurethanes without PEG. The degradation of polyurethanes with PEG at the temperature of 37°C in a solution of phosphate buffered saline (PBS) seems to be faster, what was confirmed by TG method and SEM observations.

Acknowledgments

Authors are grateful to the Polish National Science Centre for financial support under the Contract No. UMO-2016/22/E/ST8/00048.

References

[1] A. Domanska, A. Boczkowska, Polym. Degrad. Stabil. 108 (2014) 175-181.

[2] H. Ji Hye, J. Hyun Jeong et al., Polym. Degrad. Stabil. 92 (2007) 1186-1192.

[3] J. Hyun Jeong, K. Jin Sook et al., Appl. Surf. Sci. 254 (2008) 5886-5890.

[4] K. Pielichowska, J. Bieda et al., Renewable Energy, 91 (2016) 456-465.