SYNTHESIS AND CHARACTERIZATION OF POLYURETHANE-BASED BIOMATERIALS MODIFIED WITH CHITOSAN AND HYDROXYAPATITE

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Introduction

The tissue engineering offers new opportunities in regeneration of the damaged tissue in a human body when natural processes are impossible. One way to dissolve this problem is an introduction of a scaffold to give the cells the forming ability of new tissue [1,2]. Proper selection of physical and chemical properties of the scaffold material enables attachment and proliferation of cells. The polyurethanes are known to exhibit biodegradable, bioresorbable and non-toxic properties [3]. Polyurethanes are polymers composed of hard segments derived from a diisocyanates and chain extender, and soft segments formed from polyether or polyester. This type of microphase-separated structure proved different properties of polyurethanes depending on the ratio of soft and hard segments [4]. An alternative approach to achieve a bioactive polymer scaffold with appropriate mechanical quality is via incorporation of ceramics like hydroxyapatite (HAp) [5]. Along with biocompatible nature and non-toxic character of chitosan, that polysaccharide is applied as a chain extender/curing agent for PU. Chitosan has a significant impact on the enhancing thermal properties and biocompatibility of PU elastomers [6]

The aim of the research was to obtain polyurethanes, which may be used as bone cement and will show lower thermal effect during crosslinking, due to the introduced phase change materials (PCM) consisting of poly(ethylene glycol) and chitosan. Moreover, the introduction of hydroxyapatite to polyurethanesacharides was investigated towards the bioactivity of composite material.

Materials and Methods

The biodegradable polyurethanesaccharides containing phase change materials were obtained using bulk polymerization method. The prepolymerization of 1,6-hexamethylene diisocyanate (HDI) and poly(ethylene glycol) 2000 (PEG-2000) were carried out in a nitrogen atmosphere with dibutyltin dilaurate (DBTDL) as a catalyst. The obtained prepolymer was cured with 1,4-butanediol (BDO) and chitosan in different molar ratio. Hydroxyapatite was introduced to enhance biocompatibility and osteoconductivity. Differential scanning calorimetry (DSC), themogravimetric analysis (TG) and dynamic mechanical analysis (DMA) methods have been used to investigate the thermal properties of the material. The presence of hydrogen bonds was confirmed by Fourier-transform infrared spectroscopy (FTIR). The results of polyurethane hydrolytic degradation in a phosphate-buffered saline (PBS) and Ringer solution were presented. The formation of apatites on the polyurethane surface after incubation in simulated body fluid (SBF) was confirmed by scanning electron microscopy (SEM).

Results and Discussion

The influence of different molar ratio of chitosan and hydroxyapatite was analyzed. The thermal properties of the polyurethane were investigated using differential scanning calorimetry (DSC). The glass transition of soft segments has been found in the range of -47°C and –57°C. With the incorporation of chitosan to PU a slight decrease of melting temperature (T_m) (from 39 to 33°C) and the heat of phase transition (from 56 to 53 J/g) for soft segments from polyether component was observed. The TGA analysis showed multi-step decomposition of polyurethanes modified with chitosan and hydroxyapatite. Importantly, the initial decomposition temperature increased with a higher concentration of chitosan. The results from the FTIR and SEM studies prove the existence of chitosan and hydroxyapatite in polyurethane structure. FTIR spectrum of obtained polyurethanesaccharides showed the absorption bands at 1689 cm^{-1}(-C=O stretching) and 3310 cm^{-1} (-NH stretching) derived from urethane group in obtained polyurethanes.

Conclusions

Polyurethanesaccharides modified hydroxyapatite and chitosan were synthesized in a two-step polymerization method. It has been showed that chitosan as a chain extender improves the thermal stability of polyurethanes. The obtained materials have a potential for application as a replacement of acrylate bone cements.

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