THE STUDY OF POLY(ε-CAPROLACTONE)-BASED POLYURETHANES FOR BIOMEDICAL APPLICATIONS

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Introduction

Polyurethanes are a class of polymers composed mainly of isocyanates, polyol and chain extender units linked by urethane groups. Functionalization of polyurethanes through the addition of natural polysaccharides like chitosan has been performed to enhance biomedical applications of these polymers. Poly(ε-caprolactone) (PCL) is classified as a semicrystalline polymer characterized by melting temperature approximately 60°C and glass transition under room temperature [1].
Janik and co-workers reported successful modification of PU based on IPDI, PCL, and BDO via incorporation of chitosan. The inclusion of chitosan as a crosslinker has yielded polymer stable under sterilization conditions [2]. This solution offers materials suitable for heart valves. Mahmood et al. [3] have proposed the synthesis of chitosan-based polyurethane elastomers involving 2,4-toluene diisocyanate (TDI) and poly(ε-caprolactone) (PCL). Accordingly, chitosan-based polyurethane may link the properties of both components - chitosan and polyurethane.
The objective of the study is to demonstrate as a proof of concept an application of PCL as soft segments instead of PEG-2000. Moreover, we have used chitosan as a chain extender and hydroxyapatite to improve the bioactive character of polymer.

Materials and Methods

Poly(ε-caprolactone)-based polyurethane were synthesized using chitosan as a chain extender and hydroxyapatite as filler to enhance biocompatibility. The polyurethane prepolymer was prepared by the polymerization reaction of 1,6-hexamethylene diisocyanate (HDI) with poly(ε-caprolactone) (PCL) diol using dibutyltin dilaurate (DBTDL) as a catalyst. The synthesis was carried out under nitrogen atmosphere at 60°C. The bulk polymerization method was chosen as the synthetic way as it allows to avoid toxic solvents. The crosslinking process occurred via the reaction of urethane prepolymer with butanediol (BDO) and chitosan. The crosslinking process was conducted at 60°C for 24 hours.
Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) have been applied to determine the thermal properties of the PCL-based polyurethane. The Fourier transform infrared spectroscopy (FTIR) analyses were carried out to analyse the structure of PUs. The dispersion of hydroxyapatite in the polyurethane matrix was examined by scanning electron microscopy (SEM).

Results and Discussion

TG curves showed three-step degradation of polyurethane – FIG. 1.

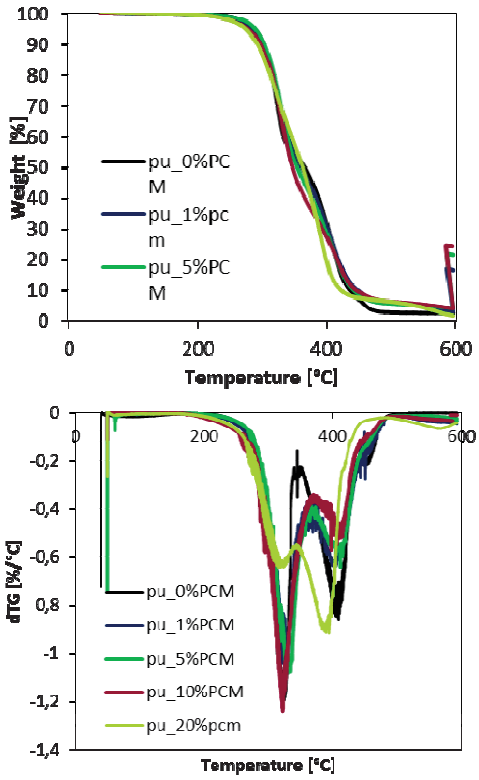

FIG. 1. The TG curves for polyuerthane samples.

The first one is associated with degradation of the hard segment of isocyanates. The second step is attributed to the degradation of polyol units. The third corresponds to the degradation of organic residues. The incorporation of PCL instead of PEG 2000 causes a decrease in the thermal stability.
The DSC profile showed a glass transition of soft and hard segments and there was an endothermic peak for melting of polyol units. The FTIR study confirms the completion of the polymerization reaction and crosslinking process of the obtained prepolymer. The SEM studies show the high degree of dispersity of hydroxyapatite in the polymer matrix.

Conclusions

FTIR analysis indicated the occurrence of the urethane bonds. The SEM photographs show good dispersion of hydroxyapatite in a polymer matrix. Thermal analysis techniques reveal that incorporation of PCL leads to a decrease in PU thermal stability.

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