



Crystallization and thermal properties in waterborne polyurethane elastomers: Influence of mixed soft segment block



Suzana M. Cakić^{a,*}, Ivan S. Ristić^b, Ivan Krakovský^c, Dragan T. Stojiljković^a, Petr Bělský^d, Lucie Kollová^d

^a Faculty of Technology, University of Niš, Bulevar oslobođenja 124, 16000 Leskovac, Serbia

^b Faculty of Technology, University of Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

^c Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University of Prague, V Holešovičkách 2, 18000 Praha 2, Czech Republic

^d University of West Bohemia, New Technologies Research Centre, Univerzitní 8, 30614 Plzeň, Czech Republic

HIGHLIGHTS

- Biodegradable polyurethane elastomers were synthesized by replacing polycaprolactone diol with polyether type polyol.
- The thermal stability of polyurethane elastomers was influenced by the length and oxygen content of polyether polyol.
- The highest degree of crystallinity showed polyurethane elastomer, based on the longest polyether polyol.

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ABSTRACT

A series of nontoxic biodegradable waterborne polyurethane (WBPU) elastomers were synthesized by two-step polymerization, using isophorone diisocyanate (IPDI), 1,4-butanediol (BDO) and ι -lysine as a chain extender and a range of soft segments with various macrodiols composition. The soft segment was formed by replacing polycaprolactone diol (PCL) as a polyester type polyol with hydrophilic polyether type polyol. Hydrophilic poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG) different block lengths were used to this purpose.

Fourier-transformed infrared spectroscopy (FTIR) was used for evaluation of degree of phase separation. The effect of the soft segment composition on the thermal properties of polyurethane elastomeric films was investigated by means of thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). The thermal stability of materials is influenced by composition of soft segments and it was explained by the effect of oxygen content of polyether polyols, the length polyether block and interaction between the soft and hard segment. The wide-angle X-ray scattering (WAXS) is used to investigate the degree of crystallinity of PCL in soft segment of WBPU. It was found that the polyether polyol length in the soft segment had a significant influence on degree of microphase separation in the soft and hard segment and crystallization behaviour of the materials. The restriction of the crystallization of the PCL soft segment depends on the hard segment content and length of the polyether polyol.

The results show that the properties of polyurethanes prepared are directly related to the soft segment composition and can be varied easily for a different set of properties that are significant for biomaterial application.

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1. Introduction

Synthesis of new biocompatible and biodegradable waterborne polyurethane (WBPU) elastomers is of great interest for medical

applications. The high versatility of polyurethane chemistry allows the synthesis of novel biomaterials across a broad range of chemical, physical and biocompatible properties [1]. Synthesized polyurethane elastomers must have good physico-mechanical properties similar to properties of natural tissues. Cardiac valves and ocular implants are examples of permanent implantable devices prepared by polyurethanes [2]. The waterborne polyurethane elastomers consist of an alternating flexible component or

* Corresponding author. Tel.: +381 16247203; fax: +381 16242859.

E-mail address: suzana_cakic@yahoo.com (S.M. Cakić).

macrodiol, called soft segment, and a stiff component derived from diisocyanate and a chain extender, called hard segment. WBPU properties are determined by the ionic group content, segments structure, molecular weight of polyols, the type of chain extender and hard/soft ratio. Poly(ethylene glycol) (PEG) is also often introduced as a co-monomer for soft segment of polyurethane backbone. Besides, PEG has many attractive properties, such as hydrophilicity, solubility in water, absence of antigenicity and immunogenicity, and non-toxic degradation products. PEG is a biocompatible hydrophilic and highly flexible polymer, non-biodegradable but able to be eliminated from the body by the renal system. In polyurethanes, polycaprolactone diol (PCL) usually enhances crystallinity and elastomeric mechanical properties of the polyurethanes, while PEG hydrophilicity and the absorption of water. PCL is a semi-crystalline resorbable polyester which is biodegradable due to ester bonds susceptible to hydrolysis [3].

The majority of biodegradable polyurethanes produced commercially are based on polyesters, mainly because of their mechanical properties. However, they are susceptible to hydrolytical degradation when implanted in the body, even for short periods of time. Thus, when looking for more biostable materials, ether based polyols have been used, although they are still susceptible to degradation via scission of the urethane and $\text{CH}_2\text{-O}$ links. The combination of ether and ester groups, include both hydrophilic and hydrophobic characteristics, respectively [4].

WBPU shows high elasticity with specific micro-structure determined by rigid chain segments (hard) and flexible chain segments (soft). The changes in the soft segment structure can bring different levels of phase separation. Polyurethanes can form hydrogen bonds using hydrogen atom in urethane group by donating proton with carbonyl and adjacent oxygen atom in the urethane linkage (interurethane hydrogen bonding) as with ester linkage (polyester soft segment) or ether oxygen (polyether soft segment). The extent of hydrogen bonding in polyurethanes can be investigated using infrared spectroscopy (FTIR), and it has been used as an indication of phase separation. The extent of phase separation depends on the content and nature of soft and hard segment [5–7].

Biodegradable polyurethanes were mainly synthesized using aliphatic diisocyanate, various chain extenders and various soft segment compositions. For example, Jiang and co-workers have developed a series of biodegradable waterborne polyurethanes based on isophorone diisocyanate (IPDI), 1,4-butanediol (BDO) and L-lysine as chain extender with various amounts of poly(ϵ -caprolactone) (PCL) and poly(ethylene glycol), PEG (MW 1450), as soft segment by two-step polymerization. Depending on the amount of PEG in the polymers, waterborne polyurethanes with different tensile properties and biodegradability were synthesized [2]. The other kinds of biodegradable polyurethanes were also prepared with different molar ratio and molecular weight of PCL (MW 2000) and PEG (MW 2000) and 1,6-hexamethylenediisocyanate (HMDI), by one-step bulk polycondensation. In this article, the rates and mechanisms of degradation and mechanical properties of the obtained biodegradable polyurethanes were investigated [3]. Study concerning the influence of PCL soft segment with different molecular weight, hard segment content and total molecular weight on crystallizability of segmented poly(ester-urethanes), based on an aliphatic hard segment has been published previously [8]. Generally, when the length of soft segment increasing and the concentration of the hard segment decreasing, the crystallizability of the polyurethanes increased. Biodegradation of polymeric biomaterials, mainly depends on hydrolytic degradation of polymer chain. The primary mechanism for degradation in these polymers is hydrolysis, where the water absorption is an important parameter for evaluation. Water equilibrium sorption depends on the

intermolecular density of polymer, and density depends on chain flexibility. Since the water molecules, can easily diffuse into the amorphous region of the polymer, the hydrolytic degradation occurs preferably in the amorphous region rather than crystalline region. The effects of different composition of mixed soft segments based on polycaprolactone diol on hydrolytic degradation have been investigated by Mondal et al. [1]. This study demonstrated that hydrolytic degradation behaviour of polyurethanes depends on the backbone structure of the soft segments which could find utility in engineering field of soft tissue.

From the above discussion about the importance the structure of soft segment on hydrolytic degradation of polymeric biomaterials and considering the lack of studies in the existing literature about the influence of polyether block length and hard segment content on properties of WBPU and the crystallinity of soft segment, in the present study, series of biodegradable polyurethane elastomers was prepared by two-step polymerization. In this paper, materials prepared by reaction of isophorone diisocyanate (IPDI), 1,4-butanediol (BDO) and L-lysine as hard segment and different ratio PEG or PPG and PCL as soft segment were studied. Comparison of the soft segment crystallinity and other physical properties of WBPU with respect to the PEG or PPG length and hard segment content, were also studied. Hydrophilic poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG) of increasing length were used, namely PEG400, PEG1000, PPG2000 and PEG6000, where the numbers indicate the molecular weight of the polyether polyol in materials. In order to understand the effects of molecular weight PEG or PPG on properties of the materials prepared, WBPU with PCL soft segment was also synthesized.

The current work demonstrated a new approach to investigate of the physical properties of the biocompatible and biodegradable WBPU with respect to soft segment composition would be important in the further considerations about proper application as degradable materials.

2. Experimental

2.1. Materials

Polycaprolactone diol (PCL) of molecular weight of 2000 g mol^{-1} was dried at $100\text{--}108^\circ\text{C}$ under vacuum for 12 h. PEG400, PEG1000, PPG2000 and PEG6000 were dried under vacuum at 80°C for 12 h. All polyols were obtained from Aldrich. Isophorone diisocyanate (IPDI, 98 wt.% purity), L-lysine and 1,4-butanediol (BDO) were supplied by Aldrich and used as received. All other chemicals are reagent grade and used without further purification.

2.2. Synthesis of nontoxic biodegradable waterborne polyurethanes elastomer

The biodegradable waterborne polyurethane elastomers were prepared by two-step polymerization process. The PCL and appropriate polyether type of polyol were mixed at 70°C for 30 min to obtain a homogeneous mixture. In the first step, IPDI and 1% stannous octoate as a catalyst were added to the stirred PCL and polyether polyol for 60 min at 70°C . The isocyanate content in the prepolymer during and at the end of the synthesis was determined with the standard dibutyl amine back-titration method (ASTM D 1638). Theoretically, the NCO values of the sample WBPU1 to WBPU5 were 9.34; 5.51; 6.29; 5.5 and 6.29 (wt.%), respectively. In the second step chain extender 1,4-butanediol (0.85 mol) was added to the reaction mixture and the reaction continued for 2 h at 62°C . When the practical NCO value reached half of theoretically calculated values, L-lysine (0.85 mol) in dimethyl sulfoxide (DMSO)

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