

Microdomain Composition and Properties Differences of Biodegradable Polyurethanes Based on MDI and HDI

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The study of the effect of the diisocyanate structure on the microstructure and macroscopic properties of polyurethanes was the main aim of this work. Biodegradable segmented thermoplastic elastomeric polyurethanes based on a poly(hexamethylene carbonate-co-caprolactone)diol (PHM-co-PCL) as soft segment were synthesized using 1,4-butanediol (BD) as chain extender and both 4,4'-diphenylmethane diisocyanate (MDI) and 1,6-hexamethylene diisocyanate (HDI) as components of the hard segment by the two shoot synthesis procedure. Microphase structure and properties were analyzed using Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) as complementary techniques, used to characterize thermal transitions of the polyurethanes and to assign them to determinate functional groups interactions. Gaussian deconvolution technique was used to decompose carbonyl region in four peaks and to study the hydrogen bonding within the different polyurethanes. Both DSC and FTIR showed that MDI-based biodegradable polyurethanes were less phase segregated than to those based on HDI, and thus that diisocyanate structure has an important role on microdomain composition and polyurethanes properties. Macroscopic properties as hardness and water-polymer contact angles are related to polyurethanes microphase compositions. *POLYM. ENG. SCI.*, 48:519–529, 2008. © 2008 Society of Plastics Engineers

INTRODUCTION

Segmented thermoplastic polyurethane elastomers (STPUE) have drawn the attention of many researches working in different fields due to the tunable properties of these materials. These copolymers can be described with a $-[D-P-(D-C)]_x-$ structure, where P is the used polydiol, commonly a polyether, polyester or polycarbonate, D is the diisocyanate employed, and C is the chain extender,

generally a low molecular weight diol or diamine, and x is the average degree of polymerization of the hard segment, D-C, which can be controlled with the reactants ratio via a two shoot polymerization synthesis. STPUE based on poly(ester)urethanes and poly(carbonate)urethanes have been claimed to be promising biodegradable materials with potential utilities in biomedical sciences applications, as long or short term medical implants, mainly in blood contact devices [1–8]. These polyurethanes have received great attention as they possess a broad range of chemical and physical properties, good biocompatibility and can be designed to degrade in biological environments due to the possibility of easily varying their chemical composition. Aromatic diisocyanates have been claimed [1, 8] to produce aromatic diamines upon degradation, being these potentially toxic. Aliphatic diisocyanates in addition to biocompatibility also provide to the polyurethanes better light stability and better resistance to hydrolysis and thermal degradation. In this work, 1,6-hexamethylene diisocyanate (HDI), which is claimed as a not toxic amine producer during degradation of the corresponding polyurethanes [8], has been used. No catalyst was employed in the polyurethane synthesis for avoiding biocompatibility problems of the material.

As proposed by Cooper and Tobolsky [9] the versatile properties of STPUE are attributed to the micro-phase separated structure that these materials present. The hard domains generally formed by the union of diisocyanate-chain extender units, act as thermally breakable physical crosslinking sites, as well as reinforcement to the soft segment phase. Soft segment domains generally soften the material and provide elastomeric properties to the polyurethane along with other properties as susceptibility to degradation [1, 7].

Hydrogen bonding along with microphase composition is an important parameter when designing biostable or biodegradable materials. Hydrogen bonding of polyurethanes constituent segments has resulted to be a determining factor on their hydrolytic stability. Tang et al. [4] found that the range of the susceptibility to hydrolytic degradation of the different carbonyls present in polycarbonate-based polyurethane was as follows: nonhydrogen

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