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The effect of thiolation on the mechanical and protein adsorption properties of polyurethanes

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Abstract

Segmented polyurethanes are important polymers for a number of industrial and technological applications. The purpose of this work was to synthesize polybutadiene-based polyurethanes and subsequently graft carboxylate and sulfonate side chains via thiol-ene reaction. Spectroscopic investigations showed that grafting yielded good conversion for the vinyl unsaturation of the polybutadiene soft segment. DSC and tensile testing revealed that grafted polyurethanes had a better segmental compatibility and superior mechanical properties than the control polyurethane without grafting. The carboxylic side chains of the soft segment were responsible for the observed improved mechanical properties. Initial protein adsorption tests on these polymers were found to be higher than the control surface. The polyurethanes of the current study could be used for biomedical applications where protein attachment to the surface is needed for specific cell adhesion and tissue repair.

Keywords: Polyurethanes; Thiol-ene reaction; Mechanical properties; Protein adsorption

1. Introduction

Segmented polyurethanes are among the important classes of thermoplastic elastomers with a unique combination of toughness, durability and flexibility, biocompatibility and biostability that makes them suitable materials for use in a diverse range of implantable medical devices [1]. The availability of different soft segment macrodiols (polyesters, polyethers, hydrocarbons), a wide range of isocyanates (aromatic and aliphatic with varying chain lengths) and chain extenders (diamines and diols of different chain lengths) made them versatile polymers for a multitude of applications. Segmented polyurethanes are made by covalently joining two dissimilar segments along the polymer backbone; and their two-phase nature is related to

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the limited thermodynamic compatibility of the hard urethane segment (formed from a diisocyanate and chain extender) with the macrodiol soft segment [2]. Segmental incompatibility is caused by a large difference in the polarity of the soft and hard segments, which can be quantified by their solubility parameters, block lengths, crystalizability of either of the segments and overall composition [3]. At the polymer service (application) temperature, the soft segment component is viscous or rubbery while the hard segment is glassy or semicrystalline. Their unique properties are the result of these combinations with hard segments acting as reinforcing fillers and a thermally reversible physical crosslinks whereas the soft segment acts as flexible matrix [4]. However, the degree of microphase separation required for optimum mechanical properties is dependent on the relative polarity differences between the two segments [5].

Although segmented polyurethanes based on polybutadiene soft segment exhibit excellent hydrolytic stability, good low-temperature characteristics, high elasticity, and superior chemical resistance; they have considerably poor mechanical properties compared with polyurethanes based on other soft segments [6]. It was suggested that this phenomenon was due to a very sharp interface boundary (tens of angstroms in size) causing poor adhesion between the soft segment matrix and the dispersed hard segment. As a consequence, there is often an interfacial gap between the matrix and the dispersed phase, resulting in insufficient stress transfer from the polymer soft segment to the hard domain [7]. In order to improve the mechanical properties of these highly phase-separated polyurethanes, chemical crosslinking is often carried out [8,9]. Crosslinking, mostly introduced via the double bonds of the polybutadiene, is not however beneficial since the polymer is no longer processable by solvent casting or melting. In addition, when these polymers are used as biomaterials, surface modification to impart the required biological responses is often needed since polybutadiene-based polyurethanes are not considered biocompatible [10]. Thus, crosslinking polybutadiene-based polyurethanes could potentially reduce the available functionality for such modifications.

The objective of this work was to synthesize polybutadiene-based polyurethane biomaterials containing carboxylate groups with improved segmental compatibility and mechanical properties via thiol-ene reaction. The long-term goal is to immobilize biological molecules for specific cell targeting.

2. Materials and methods

2.1. Materials

Hydroxy terminated polybutadiene (HTPB) ($\overline{M}_n = 2000$ g/mol, hydroxyl value of 0.88 meq/g) was kindly supplied by Sartomer Company Inc. (Exton, PA). Dicyclohexylmethane 4,4′-diisocyanate (H_{12}MDI), 1,4-butane diol (BD), thioglycolic acid (TGA), mercaptopropionic acid (MPA), sodium 2-mercaptoethanesulfonate (MESNA), dimethylpropionic acid (DMPA), toluene, dimethylformamide (DMF), triethylamine and dibutyltin dilaurate (DBTDL) were purchased from Sigma–Aldrich (Milwaukee, WI). 2,2′-Azobis-(2-methylpropionitrile) (AIBN) was purchased from Toronto Research Chemical Inc. (Toronto, Ont.). DMF and toluene were purified by distillation, under reduced pressure. HTPB was dried at 80 °C and reduced pressure prior to the experiment. All other chemicals were the highest purity available and used without further purification.

The proteins used for adsorption studies were bovine serum albumin (~99% agarose gel electrophoresis), lysozyme from chicken egg white, fibrinogen from human plasma (60% protein; >80% clottable protein) and all were purchased from Sigma (St. Louis, MO).

2.2. Synthesis of segmented polyurethanes

Segmented polyurethanes were synthesized from HTPB, H_{12}MDI and 1,4-butane diol as a chain extender according to a standard two-step solution polymerization described elsewhere [11]. Briefly, H_{12}MDI was reacted with HTPB at 2:1 molar ratio in the presence of 0.2% DBTDL (based on the isocyanate content) for 2 h at 75 °C. Since HTPB was not soluble in most polar solvents, a mixture of DMF/toluene (1:1 v/v) was used as a reaction medium. After 2 h reaction, the prepolymer was chain extended with 1,4-butane diol for 2 h at 75 °C.

2.3. Grafting of carboxylate and sulfonate groups onto the soft segment of polyurethanes

In order to graft thioglycolic acid (TGA), mercaptopropionic acid (MPA) and sodium 2-mercaptoethanesulfonate (MESNA) onto the HTPB lateral double bonds, thiol-ene reaction (Scheme 1a) was carried out at 80 °C for 6 h using AIBN as an initiator. Three AIBN/HTPB molar ratios (0.17, 0.25