



Synthesis and properties of new crosslinked polyurethane elastomers based on isosorbide



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ABSTRACT

The purpose of this research is to formulate flexible polyurethane elastomers, with different crosslinkers from renewable resources that can be used into cast film materials. Isosorbide moieties were incorporated into the main chains by chain extending the diisocyanate prepolymer which was obtained from polyether diol and hexamethylene diisocyanate. The influence of the crosslinker structure on the polyurethane elastomers was evaluated. The thermal properties of the polymer films were investigated by differential scanning calorimetry and thermogravimetric analysis. These polymers have good thermal stability and increased glass-transition temperatures. The flexible nature of the crosslinkers from renewable resources decreases the rigidity of the elastomers due to of isosorbide moieties. The crosslinked polyurethanes present good mechanical properties with breaking strain in the range of 730–1100% and tensile stress in the range of 5–27 MPa. The crosslinked samples were thus found to be flexible, eco-friendly materials.

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1. Introduction

Elastomers are known because of their elastic deformability as results of the physical or chemical links between the molecular chains. Chemical crosslinks are strong bonds formed between the hard segments and provide the mechanical strength of the polymer materials. In recent times, more and more raw materials obtained from renewable resources are starting to be used in polymer formulations [1,2].

Due to their abundance, great functional diversity, biodegradability and biocompatibility, carbohydrate derivatives have started to be increasingly used in polymer synthesis. The use of carbohydrates with multiple functional groups contributes to decreased thermal stability, therefore in polymers synthesis is much more attractive the use of simplified or bi-functional carbohydrate-derived moieties. One of the bi-functional carbohydrate derivatives is isosorbide, whose characteristics - such as rigid structure and low toxicity - makes it attractive for usage in polymer formulations [3–5]. Isosorbide (1,4:3,6-dianhydro-D-sorbitol) is prepared by hydrogenation and subsequent dehydration from D-glucose. The two hydroxyl groups from its structure make isosorbide very suitable for polycondensation or polyaddition reactions [6,7]. Thus, for research purposes, poly(isosorbide carbonate) was obtained by polycondensation of the isosorbide with diphosgene in pyridine [8]. High performance applications have employed synthesized isosorbide-methacrylate monomers which were polymerized [9–12]. The incorporation of isosorbide into the polyesters backbone has been found to result in polymers with higher Tg and lower

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toxicity, which makes them useful in biomedical applications [13–15]. Isosorbide was also used in the synthesis of linear polyurethanes with different soft segment structures and different aliphatic or aromatic diisocyanates [7,16,17]. Additionally, isosorbide was also used to prepare water-borne polyurethane dispersions [18] or in the synthesis of isocyanate-free polyurethanes from isosorbide dicyclocarbonates and different commercial diamines [19].

This work presents crosslinked polyurethane elastomers that include isosorbide in their structure, a component derived from renewable resources. The scope of this study is to evaluate the influence of the renewable resource-based crosslinkers and of the rigid structure of the isosorbide on the properties of the resulting elastomer materials. The crosslinkers used in these formulations are based on renewable raw materials (glycerin, castor oil, sorbitan laurate, pyridoxine). In this work, we developed new advanced materials with improved, useful properties, by using isosorbide and natural crosslinkers.

2. Experimental

2.1. Materials

All chemicals used in this study were used as received from the suppliers. The polyether diol was poly(tetramethylene ether) glycol (Terathane 1400, with an average molecular weight of 1400 g/mol) which was obtained from Fluka (Fluka Chemie AG, Buchs, Switzerland) and was dried under reduced pressure at 120 °C for 2 h. Hexamethylene diisocyanate (HDI) was obtained from Fluka. The chain extender, dianhydro-D-glucitol (isosorbide, IS) and crosslinkers - glycerin (Gly), castor oil (CO), pyridoxine (PYR), sorbitan laurate (Span 20) (Fig. 1) and dimethylformamide (DMF) - were obtained from Aldrich (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany).

2.2. Polyurethane synthesis

The polyurethane with isosorbide moieties in the main chain and different crosslinkers were obtained while in DMF solution, in the presence of dibutyltin dilaurate as a catalyst, according to the following typical procedure (Fig. 2). The polymers were synthesized with molar ratios of poly(ether)-diol/HDI/diol and triol of 1:2:1 (Table 1). The ratio of isocyanate groups to hydroxyl groups, [NCO]:[OH] and the ratio of OH diol:OH triol was 1:1 in each of the polyurethane formulations.

The isocyanate end-capped prepolymer was prepared by reaction of the required amounts (14 g) of dried Terathane 1400 and HDI (3.7 mL), in a 250 mL glass reactor equipped with a mechanical stirrer, a drying tube connected to the vacuum pump and an oil bath, at 80 °C for 2 h. The prepolymer was then chain-extended using the required amount of IS (1.46 g) and 15 mL DMF as solvent at 80 °C for 2 h. The polyurethane resins were then cast onto cleaned glass plates and stored at 80 °C for 24 h in order to obtain flexible films. The crosslinked samples were prepared using a similar procedure, the chain extender and crosslinker combination being given in Table 1. The films thus prepared were used for the determination of surface and thermo-mechanical properties.

2.3. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 Instrument equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the range of 600–4000 cm^{-1} with a nominal resolution of 4 cm^{-1} , averaging 64 scans for each sample.

Thermogravimetric experiments took place in an air atmosphere through thermogravimetric analysis (TGA) using a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of the TGA scans was of 10 °C/min. The initial weight of the samples was about 50 mg and the temperature range 30–700 °C.

A differential scanning calorimeter (DSC) type DSC-7 Perkin-Elmer was used for the thermal analysis and was operated at a heating rate of 10 °C/min. The thermal transition behavior was studied in a temperature range of –50 °C to 150 °C.

The mechanical properties were determined using a Shimadzu EZTest (Japan), equipped with a 5 kN load cell. Dumbbell-shaped specimens were prepared using dies (75 × 12.5 × 4 mm; ISO 37 type 2). The tests were performed at room temperature (23 °C), with a cross-head speed of 50 mm/min. All the tests were conducted for five samples and the averaged values were reported. The standard deviation between the values obtained from all performed tests was less than 10%.

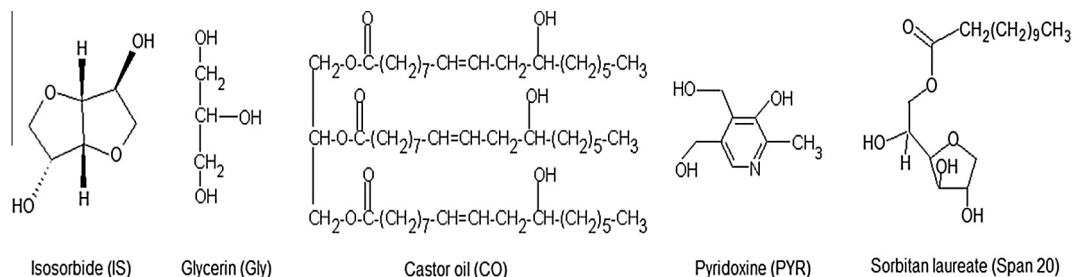


Fig. 1. Chemical structure of the isosorbide and natural crosslinkers.

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