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New bio-based thermoplastic polyurethane elastomers from isosorbide and rapeseed oil derivatives

Héloïse Blache[a], Françoise Méchin[a,*], Alain Rousseau[a], Étienne Fleury[a], Jean-Pierre Pascault[a], Pierre Alcouffe[a], Nicolas Jacquel[b], René Saint-Loup[b]

[a] Univ Lyon, INSA-Lyon, CNRS UMR 5223, Ingénierie des Matériaux Polymères, F- 69621, Villeurbanne Cedex, France
[b] Roquette Frères, Polymer Chemistry Department, 62136 Lestrem, France

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ABSTRACT

Thermoplastic polyurethanes (TPUs) from fatty acids dimer-based polyester polyols, 4,4′-methylene bis(phenyl isocyanate) (MDI) and isosorbide (ISO) as chain extender were successfully synthesized by a two-stage synthesis. TPUs obtained from isosorbide were compared to the model 1,4-butanediol (BDO) −based materials. Differential scanning calorimetry revealed the phase-separated structure of these materials that displayed a typical thermoplastic elastomer behavior by dynamic mechanical analysis. Samples were further analyzed by transmission electronic microscopy, atomic force microscopy and compression set; hardness and water uptake were also monitored. Isosorbide was found to slightly increase the glass transition and melting temperatures of MDI-based hard segments, and to slightly decrease the stability and quality of phase segregation. This resulted in an increase in rubber modulus and hardness, shape retention, in a slight increase in the temperature of the α relaxation of the soft segment domains and in a characteristic microphase morphology. Moreover the use of the rather hydrophobic fatty acid-based soft segment allowed to keep the water uptake at a rather low level, in spite of the presence of isosorbide in the formulation.

1. Introduction

Sustainability has become a key factor in the development of technologies in the late 20th century. As such, finding alternatives to the use of petroleum-based chemicals in the elaboration of plastics is one of the main challenges of modern-day chemistry. Easily accessible replacements usually include molecules derived from vegetable oils and sugars. In this context, isosorbide (ISO) is a green monomer from the group of 1,4:3,6-dianhydrohexitol isomers. It is obtained from starch through a three-step synthesis route (Flèche and Huchette, 1986). In addition to its sustainable origin, isosorbide is also a non-toxic, aliphatic, chiral and rigid molecule. These structural properties have been known to induce a high glass transition temperature, and higher hardness in several types of polycondensates such as polycarbonates, polyamides or polyesters (Fenouillot et al., 2010). As such, its use as a chain extender for thermoplastic polyurethanes has a huge impact on the thermal and mechanical properties of such materials compared to more classical petroleum-sourced molecules, and increases the bio-sourced content of these polymers. The secondary nature of the hydroxyls and the H-bond formed by the endo-hydroxyl with the adjacent oxygen atom (Fig. 1) decreases a lot the reactivity of isosorbide compared to classical primary di-alcohols such as 1,4-butanediol. It has however been shown that when paired with a much more reactive aromatic isocyanate function such as those displayed by phenyl isocyanate, p-tolyl-isocyanate or 4,4′-diphenylmethylene diisocyanate (MDI), both hydroxyl functions of isosorbide can be considered quasi-equireactive (Cognet-Georjon et al., 1995, 1996; Ionescu et al., 2011; Li et al., 2014).

The first use of isosorbide for the synthesis of polyurethanes was reported in the mid-80's (Dirlikov and Schneider, 1984; Thiem and Lueders, 1986), however the first report of a thermoplastic polyurethane containing isosorbide originates from Cognet-Georjon (Cognet-Georjon et al., 1996) and the interest in those materials has only been renewed around the year 2010 (Marìn and Muñoz-Guerra, 2009; Tsui and Gogolewski, 2009; Park et al., 2013; Kim et al., 2014; Oh et al., 2015; Javni et al., 2015a; Lee et al., 2009). In order to obtain thermoplastic polyurethanes, it is required to synthesize linear multi-block copolymers composed of alternating hard and soft segments, the soft segments (SS) being composed of a flexible oligomer diol with a molar mass generally between 500 and 3,000 g mol^{-1}, while the hard segments (HS) are composed of an alternating pattern of diisocyanates and short diols. In this prospect, poly(tetrahydrofuran) (PTMEG)

* Corresponding author at: IMP, INSA-Lyon, Bâtiment Jules Verne, 17 avenue Jean Capelle, 69621 Villeurbanne Cedex, France.
E-mail address: francoise.mechin@insa-lyon.fr (F. Méchin).

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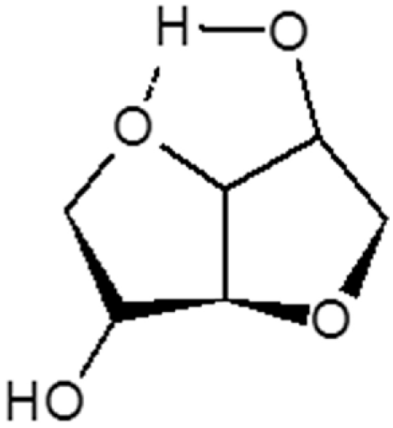

Fig. 1. Spatial structure of isosorbide.

(Cognet-Georjon et al., 1996; Kim et al., 2014; Javni et al., 2015a) or polycaprolactone (PCL) diols (Marìn and Muñoz-Guerra, 2009; Tsui and Gogolewski, 2009; Park et al., 2013) were very often used as soft segments in combination with hard segments composed of isosorbide and either MDI (Cognet-Georjon et al., 1996; Marìn and Muñoz-Guerra, 2009; Javni et al., 2015b) or 1,6-hexamethylene diisocyanate (Marìn and Muñoz-Guerra, 2009; Tsui and Gogolewski, 2009; Park et al., 2013; Kim et al., 2014; Oh et al., 2015), mainly for applications requiring biodegradation, biocompatibility or good mechanical properties. Isosorbide is intended to be used in such PU formulations as a new green building block and as an alternative for the very common and widely spread 1,4-butanediol (BDO), in order to bring new properties (Marìn and Muñoz-Guerra, 2009; Javni et al., 2015b; Marìn et al., 2012; Charlon et al., 2014). It appears that this replacement by ISO often induces smaller molar masses, but greatly increases the glass transition temperature of the hard segments (Lee et al., 2009; Oulame et al., 2015). It was moreover shown (Marìn et al., 2012) that the use of ISO as a chain extender affects both crystallization degree and crystal form compared to BDO in PCL-based polyurethanes. It is expected as well that the phase segregation will be impacted as the combination of macrodiol, diisocyanate and chain extender strongly influences the microphase morphology (Yilgör et al., 2015). Finally recently, isosorbide was also successfully incorporated in novel polyhydroxyurethanes, PHUs, obtained by an isocyanate-free route (Besse et al., 2013). For this purpose the authors prepared isosorbide dicyclocarbonates and these new precursors were then reacted with various diamines. Once again the presence of isosorbide induced interestingly high Tgs by comparison with what is usually observed for PHUs, and this method could represent a promising alternative to more traditional processes once the issues related to low molar masses can be worked out.

Increasing the bio sourced content can also be achieved by using bio-sourced soft segments and di-isocyanate, particularly vegetable oil-derived building blocks. Thus, fatty acid dimer-derived polyester soft segments used to synthesize TPUs were reported (Bueno-Ferrer et al., 2012a, 2012b; Carré et al., 2014, 2015, 2016). However, most materials obtained were amorphous except when associated with MDI and BDO, resulting in poor mechanical properties. Some authors (Charlon et al., 2014) were able to synthesize an entirely bio-based PU containing isosorbide and a partially bio-sourced di-isocyanate obtained from fatty acid dimers, called 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane (DDI). However, the mechanical properties of the obtained material were rather poor due to the lack of rigid and crystallization prone di-isocyanate. Other authors (Calvo-Correas et al., 2016) also used DDI in formulations with castor oil and isosorbide and obtained materials displaying phase segregation and a melting temperature around 60 °C.

In this study, we report the synthesis of several new TPUs based on ISO/MDI hard segments associated with a rapeseed oil-issued polyester polyol, with a number average molar mass 2,200 g mol^{-1}. In order to obtain insight into the effects of the hard segment content and the phase segregation quality, stoichiometry between SS and HS was varied. Model TPUs containing BDO as a chain extender were as well synthesized following the same method in order to compare the properties brought by ISO.

2. Materials and methods

2.1. Materials

The bio-based polyester macrodiol, Radia 7282 (FADM) used in this study was a gift from Mérylithe (France). It is produced by Oleon and made of dimeric fatty acids from hydrogenated rapeseed oil, adipic acid and hexanediol with renewable content 43% and number average molar mass (M_n) around 2,200 g mol^{-1} according to the supplier. Hydroxyl and acid values as measured by the supplier were 55 and 0.5 mg. $(g_{KOH})^{-1}$, respectively. The ^{1}H NMR characterization of the hydrogenated rapeseed oil-derived polyester polyol (FADM) can be found in the Supplementary Content, and one of the main possible chemical structures is shown in Scheme 1.

4,4′-diphenylmethylene diisocyanate (MDI) and dibutyltin dilaurate (DBTDL) were purchased from Sigma-Aldrich and used as received. Isosorbide (ISO), sold under the trade name Polysorb P, was kindly supplied by Roquette (France) and dried under nitrogen flux at 100 °C. 1,4-butanediol (BDO) was purchased from Sigma-Aldrich and dried under nitrogen flux at 100 °C. The hydroxyl number of both chain extenders were determined by chemical titration and found in perfect agreement with the theoretical values.

2.2. Synthesis of polyurethanes

Eight different TPUs were prepared in bulk with a slight excess of NCO (NCO/OH ratio = 1.02) and HS content ranging from 25 wt% to 50 wt%, by a two-stage synthesis process as shown in Scheme 1.

The synthesis was optimized in order to obtain polymers with sufficiently high molar masses to allow a subsequent correct assessment of their physical properties. In a first step, a prepolymer was obtained by reaction of the polyol with an excess of MDI for 45 min, under vacuum, in a reactor equipped with mechanical stirring and an inlet for nitrogen flushing, with an oil bath at 80 °C. The chain extender was subsequently added, in liquid state with a syringe, either at room temperature in the case of BDO or at 80 °C in the case of ISO. For ISO-based compositions, DBTDL catalyst was used. A solution of 0.07 wt% of DBTDL was made in the melted ISO. The reaction was then performed at 80 °C under vacuum with mechanical stirring until a clouding in the reaction mixture was observed, indicating the beginning of phase segregation. At this point the viscous polymer liquid was poured from the reactor into molds to form either 2 mm-thick square sheets, or 10 mm-thick cylinders. Sheets were placed at 110 °C under a 10 bar pressure for 2 h before being moved to an oven (110 °C) for 16 h. Cylinders were simply placed in the oven at 110 °C for 18 h (higher curing temperatures cannot be considered given the thermal reversibility of the urethane bond). Samples were then removed from the oven and left to cool on ceramic benches with unopened molds. When cooled, molds were finally opened to obtain 150 × 150 × 2 mm polymer sheets.

2.3. Characterization methods

Proton 1H NMR spectroscopy was used to study the structure and composition of the fatty acid dimer based macrodiol, as well as a mean to monitor synthesis. The 1H spectra were recorded at 400 MHz, in deuterated chloroform ($CDCl_3$) with a Bruker Avance III 400 (5 mm), at 298 K, acquisition time 2 s, pulse delay 4 s, and 128 scans.

Size Exclusion Chromatography was performed in a 0.01 M solution