



Synthesis, structure and properties of fully biobased thermoplastic polyurethanes, obtained from a diisocyanate based on modified dimer fatty acids, and different renewable diols

M. Charlon^{a,b}, B. Heinrich^c, Y. Matter^{a,b}, E. Couzigné^c, B. Donnio^{c,d}, L. Avérous^{a,*}

^a BioTeam/ICPEES-ECPM, UMR 7515, Université de Strasbourg, 25 Rue Becquerel, 67087 Strasbourg Cedex 2, France

^b Soprema, 14 Rue de Saint-Nazaire, 67025 Strasbourg, France

^c Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 (CNRS-Université de Strasbourg), 23 rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France

^d Complex Assemblies of Soft Matter Laboratory (COMPASS), UMI 3254 (CNRS-Solvay-University of Pennsylvania), CRTB, 350 George Patterson Boulevard, Bristol, PA 19007, USA

ARTICLE INFO

Article history:

Received 13 August 2014

Received in revised form 16 October 2014

Accepted 19 October 2014

Available online 24 October 2014

Keywords:

Dimer fatty acids

Biobased

Isosorbide

Polyurethane

Differential scanning calorimetry

Small-angle X-ray scattering

ABSTRACT

Different innovative macromolecular architectures have been elaborated and characterized. The synthesis of a set fully biobased thermoplastic polyurethanes (TPUs) was contingent on different renewable or potentially renewable building blocks such as 1,4-butanediol (BDO), isosorbide (ISO), and 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentyl-cyclohexane, the latter obtained after the chemical modification of a dimer fatty acid. These TPUs were prepared in a one-step bulk process using different hard segment (HS) species with varying ratios of ISO/BDO contents. The final molar masses were found to decrease when BDO was progressively exchanged by ISO, presumably due to the high dissymmetry and lesser reactivity of the latter species (bearing exo and endo groups) with respect to the former. This substitution (BDO vs. ISO) altered the crystallinity, the thermal transitions and the stability of the resulting polymers. TPUs with low ISO content present good mechanical performances with high elongation and Young's Modulus. The deformation is however fully plastic, despite the "hard-soft" phase segregation proven by small-angle X-ray scattering analysis. These novel biobased materials are very attractive since they present highly tailorable properties by selecting appropriate HS content and suitable chemical structure.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The discovery of polyurethanes by O. Bayer and coworkers in 1937, via the reaction of a polyester diol with a diisocyanate, has permitted to develop a new family of valuable polymers. Nowadays, polyurethanes are one of the most consumed families of polymers in the world. They

are widely used as components in paints, coatings, foams, adhesives and packaging in numerous fields such as the automotive industry, consumer or domestic equipment, construction engineering and biomedical applications [1]. The performances and properties of polyurethanes are extensively tailored by the chemical nature of the reacting components as well as the processes used. Thermoplastic polyurethanes (TPUs) in particular exhibit many useful properties, including modulable flexibility, elasticity, strength, good abrasion resistance and often, high

* Corresponding author. Tel.: +33 3 68852784; fax: +33 3 68852716.

E-mail address: luc.averous@unistra.fr (L. Avérous).

transparency. TPUs are block copolymers with a specific organization of hard and soft segments, (HS) and (SS), respectively. The HS segments are typically made of a rigid diisocyanate and a chain extender (e.g., a short polyol), whereas the SS segments mainly consist of a long polyol. Such systems usually segregate into microphases or domains [1]. Different parameters such as e.g., the molar mass of the long polyol and the concentration of HS segments in the polymeric matrix, permit to finely tailor and control the physicochemical and mechanical properties of the final TPUs [2,3].

Nowadays, the use of renewable biobased carbon feedstock is highly taken into consideration because it offers the intrinsic value of a reduced carbon footprint and an improved life cycle analysis (LCA), in agreement with a sustainable development. Hence, the forthcoming materials for daily uses will be generated more and more from the biomass. For instance, the production of partially biobased polyurethanes from vegetable oils and animal fats has largely grown during the last decade [4,5]. Most of them are thermosets [4,6–8], however biobased TPUs (thermoplastics) have been also investigated and recently developed [2,3,5,8–16]. But, the corresponding TPUs are only partially renewable, since they are prepared with conventional fossil-based diisocyanates (e.g., methylene diphenyl diisocyanate and toluene diisocyanate, MDI and TDI, respectively) [1].

However recently, some pathways have been studied to produce biobased diisocyanate e.g., from fatty acid [16]. The oleo-chemistry is very rich [17]. As an example, at high temperature, the double bonds of the fatty acids can migrate within the chains to form conjugated structures, facilitating their dimerisation by a Diels–Alder mechanism. This reaction leads to a mixture of dimers and trimers of fatty acids [18,19]. After purification by distillation, these oligomers can be used as raw chemicals for the production of e.g., diisocyanates, after further chemical transformations. Also, a consecutive hydrogenation process can be applied to eliminate residual double bonds of the dimers to decrease the polymer sensitivity (UV, temperature, oxidation, etc.) and its degradation tendency, during long term applications (automotive, building, etc.).

In this study, we report the synthesis of an innovative family of fully biobased TPUs. They were elaborated with a biobased diisocyanate obtained from the chemical modification of a hydrogenated dimer from fatty acids, which were born to act as the SS part of the final macromolecular structure. As for the HS segment, they were based on isosorbide (ISO), a well-known and recently widely studied rigid building block [20], obtained by bioproduction from polysaccharide (starch). A short diol, 1,4-butanediol (BDO) is usually used as chain extender and is mainly integrated in the HS part. Biobased BDO is now easily produced at industrial scales by fermentation e.g., by Genomatica (USA), or metabolized from sugar (molasses) by genetically engineered *Escherichia coli* [21].

This study is aimed at (i) evaluating the effects of a dimerized acid-based diisocyanate, as soft building block, on the final properties of TPUs, and (ii) at analyzing the substitution of a common diol, BDO, usually integrated in the HS part, by the less common one, ISO, and the

consequences of such a progressive exchange onto the final chemical structures, morphologies, mechanical and thermal properties of the corresponding macromolecular architectures. The global percentage of ISO has been varied from 0 to 20 wt%.

2. Experimental

2.1. Materials

Isosorbide (abbreviated as ISO, molar mass = 146 g/mol, purity 99.8%) was offered by Roquette Frères-France (tradename Polysorb P). 1,4-Butanediol (BDO, molar mass = 90 g/mol, purity higher than 99%) was supplied by Merck. 2-Heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane (abbreviated as DDI, molar mass = 587 g/mol, purity higher than 92% according to the provider, and recent publications [22,23]) was kindly supplied by Cognis-BASF (tradename DDI1410). Dibutyltin dilaurate (DBDTL) was purchased from Aldrich. All reagents unless otherwise specified were used without further purification, except a thorough drying prior to usage.

2.2. Synthesis of the copolymers

Five different TPUs were prepared in a one-step bulk process with an isocyanate/hydroxyl contents ratio equal to one, to promote the formation of polyurethane chains with the highest molar masses. The hard segment (HS) content of these five polymers ranges between 0 and 20 wt%, corresponding mainly to increasing amounts of ISO. To maintain the isocyanate/hydroxyl ratio, the amount of ISO cannot overcome the threshold of 20 wt%. Table 1 gives the main reactants contents and the materials designations, which are related to the ISO content (in wt%).

A typical synthesis of a TPU was carried out as follows. DDI was mechanically stirred and heated to 70 °C in a 250 mL disposable container. To prevent the reaction of the isocyanate groups with air moisture, the synthesis was performed under a vigorous flow of dry nitrogen. The appropriate amount of ISO was then slowly added to the diisocyanate, and the temperature allowed to stabilize at 75 °C, temperature at which it melts rapidly. After full homogenization of the reactive mixture, the chain extender BDO and approximately 0.1 wt% of catalyst (dibutyltin dilaurate) were added dropwise. After the exothermic reaction (up to 135 °C max. for compositions with 0 and 5 wt% of ISO, respectively), the reaction mixture was continuously stirred at 80 °C until a significant increase in viscosity was detected. These reaction conditions were optimized to yield polymers with the highest conversion rates and molar masses. The corresponding polymer was then poured in a thin layer of silicon paper and post-heated at 70 °C overnight to ensure the complete reaction of the isocyanate groups, which was further monitored by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR). For further characterization, polymer sheets (thickness: 1 ± 0.1 mm) were prepared by compression molding (LabTech Engineering Company Ltd) at 120 °C for 5 min and at 160 ± 10 bars. A typical compression cycle comprises the pre-heating of the polymer without pressure

Download English Version:

<https://daneshyari.com/en/article/1398011>

Download Persian Version:

<https://daneshyari.com/article/1398011>

[Daneshyari.com](https://daneshyari.com)