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Effect of hydroxylated soybean oil and bio-based propanediol on the structure and thermal properties of synthesized bio-polyurethanes

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ABSTRACT

The aim of this work was to obtain bio-polyurethanes using synthetic compounds and bio-components, i.e. bio-glycols. Bio-polyurethanes were prepared by means of the prepolymer method. Prepolymers were synthesized from 4,4′-diphenylmethane diisocyanate (MDI) and a polyol mixture containing 75% by weight of commercial polyether and 25% by weight of hydroxylated soybean oils (H2 or H3), the latter being obtained in the reaction with bio-glycol during the hydroxylation process. Bio-components were also used as chain extenders of prepolymer, i.e. bio-based 1,2- or bio-based 1,3-propanediol (1,2bioPDO or 1,3bioPDO). The reaction was catalyzed by 1,4-diazabicyclo[2.2.2]octane (DABCO). The influence of the content of low molecular chain extenders on the structure and thermomechanical properties of the obtained bio-polyurethanes was investigated. The FTIR analysis demonstrated that different types of bio-propanediol change the chemical structure of the obtained bio-polyether urethanes. The results of thermomechanical analysis showed that the application of 1,2-bio-propanediol as a chain extender was advantageous in comparison to bio-based 1,3-propanediol; the polyurethanes produced with 1,2-bio-propanediol exhibited higher storage modulus and lower loss modulus.

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1. Introduction

Polyurethanes (PUs) are mainly synthesized from components which are derived from nonrenewable resources. One of the aims in research on PU is the application of modified vegetable oils in their synthesis due to the fact that the resources of petroleum oils are near exhaustion. Synthetic polyols can be replaced, either partially or entirely, by chemically modified plant oils such as linseed oil, sunflower oil, palm oil, cotton oil, soybean oil, tung oil, cashew nut oil (Datta and Głowińska, 2012, 2014) or by other recycled semiproducts (Czub, 2008; Datta and Janicka, 2007). The properties of bio-based polyols derived from vegetable oils depend on the methods of their synthesis, which significantly influence the final properties of polyurethanes (Datta and Głowińska, 2012). Polyurethanes prepared from vegetable oils have numerous advantageous properties due to the hydrophobic nature of triglycerides (Monteavaro et al., 2005). In comparison to the extraction process of petroleum oils, the production of plant oils is environment-friendly. Moreover, natural oils are cheap, readily available and derived from renewable resources.

In terms of chemical structure, plant oils are triglycerides, i.e. they are mixtures containing esters of glycerin, and saturated and unsaturated fatty acids. The content of unsaturated groups per molecule influences the functionality of obtained oil, while the length of alkyl fatty acid chain in the oil molecule influences the elasticity of prepared or modified polymer. Plant oils and the products of their modification are a valuable source of natural polyols. The modified oils, derived from plants, are used in the synthesis of rigid and semi-rigid polyurethane foams, but seldom in thermoplastic or elastomer polyurethanes. The modification methods of plant oils are well described in literature (Chasar and Hughes, 2003; Datta and Balas, 2003; Hassan et al., 2011;Meffert et al., 1989; Suppes et al., 2010). Among the well-known methods of synthesis of bio-based polyols are epoxidation and ring opening reaction, hydrogenation, halogenation, transesterification, and microbiological methods. The triglyceride compound must be isolated, purified and functionalized to obtain the required reactivity (Li et al., 2010).

Soybean oil is an abundant renewable resource, which is inexpensive and readily available; it possesses attractive properties that allow for converting it to polyols that are used to produce polyurethanes (PUs) and useful polyester semiproducts. Soybean oil triglycerides contain both saturated and unsaturated (80%) fatty

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acids depending on the variety and climatic conditions of harvest (John et al., 2002; Sun et al., 2012). Examples of soybean oil utilize in polyol production are soy polyols as formiated epoxy soy polyols, having functionalities from 1.9 to 3.2, which can be prepared through a one-step reaction using the method of in situ performic acid generation. Depending on the functionality, the hydroxyl number changes from 104 to 166 mg KOH/g (Monteavaro et al., 2005).

Very important group of components used during polyurethane productions are chain extenders e.g. glycols or amines. Polyurethanes used in the industry usually have got multiblock structure, consisting of soft segments (oligomers component) and hard segments (isocyanates and chain extender components). Use of a chain extender in polyurethane synthesis has got significant impact on polyurethane properties despite that their mass content is slight. The role of the chain extender is to produce an "extended" sequence in the copolymer consisting of alternating chain extenders and diisocyanates. These extended sequences, or hard segments, act both as filler particles and physical crosslink sites to increase mechanical strength. Chain extenders provide to increase of hard segments and density of hydrogen bonding and molecular weight. A polyurethane-urea is obtained when a diamine is used while polyurethane results when adiol is used. As a chain extender usually are used low molecular weight, di-functional substance which possesses groups with active hydrogen atoms, especially glycols. Tri or more functional compounds are described as cross-linking or branching compounds (Castonguay et al., 2001; Wirpsza, 1991). The properties of polyurethane can be modified and significantly improved by the addition of chain extender. Influence of chain extenders, used in polyurethane synthesis, on their properties is a subject of many research works, e.g. the effect of chain extender, different type of polyols and different amount of blowing agents on mechanical and morphological properties of the rigid foam was studied by Firdaus (2011). Commonly as the crosslinking agents are used reactants derived from nonrenewable sources. For a few last years are developed the research of production of glycols derived from natural components. Well known are novel bioglycols of DuPont products: Susterra®, Zamea® and new Zamea® USP which are 1,3-propanediols. Different types of bio-based glycols (1,2-propanediol) are offered by ICSO Blachownia (Poland).

Susterra® 1,3-propanediol, the product of DuPont Tate & Lyle Bio Products, is a specialty glycol manufactured via a proprietary corn sugar fermentation process, that offers a non-petroleum alternative for end uses that desire a bio-based product – without sacrificing performance or quality (Van Gorp et al., 2010). Susterra® can easily be used to replace part or the entire glycol component used in the polyester reaction, e.g. Susterra® is applied as the glycol portion in the manufacturing of unsaturated polyester resins where it has been formulated and commercialized globally in a wide variety of products. These resins incorporating Susterra® propanediol have found use in the construction, marine and automotive industry worldwide with end users that require high performance polymers with a more sustainable footprint. In polyurethane applications like coatings, adhesives, sealants, and microcellular elastomers, thermoplastic polyurethanes, and aqueous polyurethane dispersions, Susterra® 1,3-propanediol can be used in a polyester polyol production and also as a chain extender. Susterra® reacts with MDI to yield linear urethane domains with low melt energies at room temperature in thermoplastic urethane elastomers. An example of the use of polyester polyol adipates can also successfully replace the mixed BDO/EG adipates in solvent borne polyurethane systems. Adipates made with Susterra® crystallize slowly at room temperature. Mixed Susterra®/EG polyester adipates are liquids at room temperature. Improved handling, clear or transparent polyurethanes, and polyurethanes with improved low temperature properties are expected to result from mixed glycol Susterra® based adipates (Miller, 2010; Van Gorp et al., 2010).

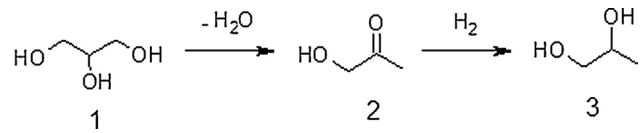

Fig. 1. Conversion of glycerin to propylene glycol.

Zemea® bio-derived propanediol, manufactured by DuPont Tate & Lyle Bio Products, can be used to replace petroleum based glycols such as propylene glycol (PG), butylene glycol (BG) or glycerin in cosmetic and personal care formulations. Zemea® propanediol is a natural, 100% bio-based ingredient made through fermentation of corn glucose. It is currently being used as a humectant, emollient, and/or natural solvent in skin and hair care products and as a solvent for botanical extraction and dilution. It is a high-performance, environmentally sustainable alternative to petroleum-based glycols and glycerin in which the product's lack of skin irritation, improved moisturization, antimicrobial efficacy and excellent esthetic properties are benefits (Miller and Durham, 2012).

Different environment-friendly technology for manufacturing of bioglycol – propylene glycol – is offered by ICSO Blachownia (Poland), which is an innovation on a national and world scale. Biopropylene glycols (1,2-biopropanediol) are produced by innovative technology through hydrogenation of glycerol deriving from biodiesel production from fatty raw material. The technological line process comprises three stages: glycerin purification through distillation under reduced pressure, hydrogenation of glycerol to propylene glycol on the catalysts in a heterogeneous flow reactor and purification of the product through distillation (Fig. 1).

Process has got many advantages. As particularity innovative in the proposed technology must be considered: the use of renewable and easily available resource for production which is glycerin fraction (a by-product in the used on wide scale biodiesel production technologies). The method for purifying of the glycerol fraction dedicated specifically for the needs of the process and providing glycerin with the desired quality and favorable price. During the process, developed by ICSO heterogeneous catalyst is used in hydrogenation of glycerol to propylene glycol with high selectivity and activity, produced from easily available raw materials and with high regenerative qualities (waste-free). To obtain an environmentally friendly product with high added value, the most important merits in the process are not using solvents and toxic substances. Optimized flow of the process streams for the total utilization of the raw material and energy. Implementation of this novel technology of biopropylene glycol production provide to solve problem of develop glycerin wastes and propylene shortage. Higher supply of propylene glycol leads to eliminate or limit the application of toxic ethylene glycol (ICSO, 2010).

The application of environment-friendly components in polyurethane synthesis influences on the physicochemical properties and chemical structure of the produced materials. Functionality, hydroxyl number of modified oils, and the type of OH groups (primary or secondary) affect the properties of polyurethanes (Badri et al., 2001; Guo et al., 2006; Petrovic et al., 2002, 2010). Polyols produced from vegetable oils can be used in the same way as synthetic commercial polyols to prepare polyurethane materials for different applications. Veronese et al. (2011) prepared rigid foam using modified castor and soybean oil based polyols. The polyols were characterized by using OH number (393–477 mg KOH/g oil) and molecular weight (894–1205 g/mol). The Brookfield viscosity at 25 °C ranged widely from 51 to 2187 cP. The foams from modified vegetable oils exhibited mechanical properties that were

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