



Promising mechanical and adhesive properties of isocyanate-free poly(hydroxyurethane)

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ABSTRACT

A series of poly(hydroxyurethane) (PHU) materials were synthesized by step growth polymerization of cyclic carbonates and diamines. Trimethylolpropane tris-carbonate and various poly(propylene oxide) bis-carbonates were copolymerized with EDR-148 or 1,3-cyclohexanebis(methylamine) (CBMA). Thermal, mechanical and thermo-mechanical properties of PHU materials were characterized by DSC, TGA, durometer, dynamometer and DMA. Moreover, for the first time, we report adhesive properties of PHU synthesized without isocyanate on wood, aluminum and glass supports. All these properties were compared to reference polyurethane materials, synthesized from poly(propylene oxide) triol polymerized with hexamethylenediisocyanate (HDI) or 1,3-bis(isocyanatomethyl)cyclohexane (CBMI), in order to compare the materials properties of similar chemical structure. PHUs exhibit outstanding adhesion properties due to the presence of hydroxyl groups hanging off the main polycarbonate chain.

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1. Introduction

Since the discovery of the synthesis reaction of Polyurethanes in 1947 by Otto Bayer and coworkers [1], between diisocyanates and polyols, the polyurethane (PU) production have not stopped to increase to reach a global production of 18 million tons in 2016 [2]. PU ranks 6th among all polymers based on annual worldwide production. Owing to the facile variation of structure of polyols and diisocyanates, PU were readily tailored for diversified applications ranging from flexible and rigid foams, elastomers, thermoplastics, thermosets, adhesives, coatings, sealants, fibers... [3–5].

Despite this undeniable success, increasing concerns related to the use of (poly)isocyanate monomers as key reagents for the synthesis of PU have stimulated the search for alternative synthetic strategies that could afford macromolecules with similar properties without requiring the use of toxic isocyanate building blocks. In fact, the European regulation REACH is very vigilant on the harmfulness of PU synthesis [6]. Actually, the two most widely used isocyanates in PU industry, methylene diphenyl 4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), are classified as CMR (Carcinogen, Mutagen and Reprotoxic) [7].

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Therefore, this context has led to the development of non-isocyanate polyurethane (NIPU). Thus, one first routes relies on the ring opening polymerization of aziridines with carbon dioxide. This route is the less dependent on isocyanates, but its main problem concerns the high toxicity of aziridines [8]. Another way to produce NIPU consists in the rearrangement of acyl azide followed by polycondensation with alcohol functions. However, during the polymerization, isocyanates are formed in situ [9,10] which cannot fully prevent any toxicity. Other ways emerged, especially the polycondensation by transurethanization between diols and bicyclic carbonates, which still leads to the release of by-products during polymerization [11–15]. Hence, the reaction between a bicyclic carbonate and a diamine represents one of the most promising alternatives to the conventional synthesis of PUs [12,15–37]. The resulting materials are called polyhydroxyurethanes (PHUs). Indeed, the macromolecular chain contains one hydroxyl group hanging off the chain for each generated urethane group.

The main problem concerning the synthesis of PHU relies on the low reactivity of carbonate/amine reaction and low molar masses of synthesized thermoplastic PHUs. Many studies reported in the literature have been conducted to enhance the reactivity of cyclic-carbonates with electro-withdrawing substituents [26,34,36,38–44] or by using six-, seven-, eight-membered or thio-cyclic carbonates. But the synthesis of these compounds requires the use of harmful and toxic products such as phosgene or its derivatives for six-, seven- or eight-membered cyclic carbonates or carbon disulfide for thio-cyclic carbonate. Hence, in order to increase the kinetic reactions, Blain et al. [45] and Lambeth and Henderson [46] describes, in their works, the synthesis of PHU from 5-membered cyclic carbonate in presence of catalysts such as thiourea and 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD). However, despite numerous studies dedicated to enhance the reactivity of carbonate/amine reaction, actually, the preparation of the PHU materials with total conversion of carbonate at room temperature has been reported only for the synthesis of PHU foams [47]. Indeed, during the formation of PHU, hydrogen bonds are created between hydroxyl groups and carbamate groups, fixing the reaction mixtures. The use of blowing agent allows homogenizing the reaction and reaching total conversion of cyclic-carbonates. However, this is only valid for the foams and not for the other types of PHU materials.

Since the PHU thermoplastics do not exhibit high molar masses from five member carbonates and amines, cross-linking of PHU by polyfunctional carbonate cross-linker with di- or poly-amines can be envisaged to afford PHU thermoset rubbers [48,49]. So far, PHU materials were reported for various applications such as coatings and the barrier properties [50], thermosets or thermoplastics [48,49], rigid [51] and flexible [47,52] foams. The only study in literature which reports adhesive properties is based on hybrid PHU-PU materials with TDI [53]. Moreover, only a handful of studies report mechanical characterizations of PHU materials [48,49] and particularly the team of Torkelson who reported interesting tensile properties of structured PHUs and PHU elastomers [54,55]. To the best of our knowledge, the preparation and the characterization of PHU adhesives without isocyanate was never reported in literature. Therefore, we aspired to synthesize and characterize the first PHU adhesives. This pioneered work is very interesting since it is important to study for the first time the influence of hydroxyl groups of PHUs on adhesion properties and compare to PUs in order to assess potential interest for adhesive applications.

To synthesize a series of various PHUs, we chose five-membered cyclic carbonates since their synthesis does not require any phosgene derivative, in combination with diamines. We selected three commercially available five-membered cyclic carbonates: trimethylolpropane tris-carbonate (TMPTC) used as cross-linking agent, and two polypropylene oxide bis-carbonate of different molar masses (PPOBC380 and -640). PHUs were obtained by step growth polymerization of this three five-membered cyclic carbonates, in combination with aliphatic (EDR-148) or cycloaliphatic (CBMA) diamines. We characterized the thermal and mechanical properties of synthesized PHUs prior the characterization of the adhesive properties on wood, aluminum and glass substrates. All these properties were compared to structural analogous PU reference synthesized from polyols and diisocyanate.

2. Experimental

2.1. Materials

Poly(propylene oxide) diglycidyl ether ($\bar{M}_n = 380 \text{ g mol}^{-1}$ PPO-DGE-380 and $\bar{M}_n = 640 \text{ g mol}^{-1}$ PPO-DGE-640), trimethylolpropane triglycidyl ether (TMPTGE), lithium bromide (LiBr), dimethylformamide (DMF), 1,3-cyclohexanebis(methylamine) (CBMA), dibutyltin dilaurate (DBTDL), hexamethyldiisocyanate (HDI), 1,3-bis(isocyanatomethyl)cyclohexane (CBMI), ethyl acetate, tetrahydrofuran (THF) and toluene were purchased from Sigma Aldrich. 2,2'-(ethylenedioxy)diethylamine (EDR-148) was obtained from Huntsman. Poly(propylene oxide) triol (Triol 420) was obtained from Dow Chemical. Deuterated solvents (CDCl_3 and $\text{DMSO}-d_6$) were purchased from Eurisotop (Saint-Aubin, France).

2.2. Nuclear magnetic resonance

Chemical structures of the molecules were determined by ^1H , ^{13}C and ^{19}F NMR spectroscopy using a Bruker Advance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. External reference was tetramethylsilane (TMS). Shifts were given in ppm. NMR samples were prepared as follows: around 10 mg of product for ^1H , ^{13}C and ^{19}F experiment in around 0.5 mL of CDCl_3 or $\text{DMSO}-d_6$.

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