Adaptive bio-based polyurethane elastomers engineered by ionic hydrogen bonding interactions

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The intrinsic responsiveness properties of non-covalent interactions are appealing for the preparation of soft polymer networks with unique adaptive properties. The synthesis of supramolecular polyurethane elastomers is achieved using post-synthetic non-covalent cross-linking approach based on ionic hydrogen bonding interactions. The ionic networks are formed between the tertiary amino groups of side chain functional castor oil-derived polyurethane and small-molecular biological acids such as sebacic acid, suberic acid, oxalic acid, and citric acid. The obtained polymers have some promising material properties concerning energy dissipation through stress, shape-regeneration property, as well as recycling/reshaping and self-healing capabilities.

1. Introduction

Post-synthetic chemical modification of functionalized macromolecules can be used to alter or enhance desired properties and function in nearly any direction, and has enabled the preparation of unique materials for use in polymer science, medicine, and materials research [1,2]. Polyurethanes (PUs) are an essential class of synthetic polymers that have been used in a wide range of applications [3–5]. Large-scale production of these materials mainly relies on feeds of diisocyanates, diols and/or polyols in the presence of a catalyst [6]. However, despite the wide range of PUs available via step-growth polymerization, their scope is constrained because the lack of functionalities.

To address this, the major avenue is to directly incorporate side-chain functionalities during the polymerization process employing functionalized precursors. For example, hydroxyl- [7], amine- [8], alkyne-[9–14] alkene- [8,15–17], active/non-active ester [18,19] and furan [20]-functionalized PUs are available from functional diols although in some cases the use of protection/deprotection strategies, e.g. amine- and maleimide-containing diols are protected as the corresponding carbamate [8] and furan-adduct [21] prior to the polymerization, is mandatory. Similarly, as demonstrated by the synthesis of maleimide-functionalized copoly(urethane–urea)s, the reactive moiety can be introduced through a functionalized diisocyanate [22]. Alternatively, more environmentally attractive isocyanate-free methods, based on amine–thiol–ene conjugation [23] or cyclic carbonates were also elaborated [24].

Whilst the covalent post-synthetic modification of side-chain functionalized PUs have been widely studied during the past decade through the development of click reactions and lead to a variety of usages in polymer chemistry, [7,9–20] the non-covalent approach has received limited attention despite its modular character and ease of synthesis [25]. In this line, Zigon et al. [26] and others [27] designed liquid-crystalline polymers based on the non-covalent side-chain modification of PUs containing pyridine pendant groups taking advantage of the carboxylic acid-pyridine supramolecular association. Beyond modification, this approach is more appealing

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for the preparation of supramolecular polymer networks (SPNs) by crosslinking due to the reversibility and stimuli-responsiveness contributed by non-covalent interactions [28]. Compared to the strong non-reversible covalent bonds, the reversibility and low energy bonding of non-covalent bonds such as hydrogen bonding [29–33], metal coordination [34–36], electrostatic interaction [37–42], π-π stacking [43,44], or host–guest complexation [45] can endow SPN with plenty of unique properties such as improved processing, self-healing behavior, stimuli responsiveness as well as a mechanism for energy dissipation at the nanoscale through sacrificial bond scission [46–52]. Ionic hydrogen bonds are a particular type of hydrogen bond with potential proton transfer between organic cations (e.g. quaternary ammonium) and anions (e.g. carboxylates, sulfates) [53,54]. These bonds, which are facile accessible by simple mixing acid and base, i.e. the classical acid-base reaction [55,56], have recently used to construct supramolecular assemblies that in the majority of cases exhibit excellent self-healing capabilities [41,42,39,57–60].

Owing to their preparative ease and excellent properties, PUs are attractive frameworks for the preparation of supramolecular entities [61–63]. Herein, we present the synthesis and studies of novel adaptive elastomers constructed from a linear PU featuring tertiary amino groups as side chain functionalities and carboxylic acid as non-covalent crosslinkers. To enhance the sustainability level of our approach, the networks were assembled between two complementary components based on chemicals coming from renewable sources [64]. These materials exhibit some promising material properties such as effective energy dissipation upon deformation through unzipping the ionic hydrogen bonding network, combined with good shape-regeneration property and recycling/reshaping capability due to their recoverable nature. More importantly, the resulting biobased elastomers possess the inherent ability of self-healing which further extend their sustainability [65].

2. Experimental

2.1. Materials

The following chemicals were obtained from Sigma-Aldrich and used as received: N-allylmethylamine, boron trifluoride ethylamine complex, 1,4-butandithiol, 3-chloroperoxybenzoic acid, citric acid, diethylamine, 2,2-dimethoxy-2-phenylacetophenone (DMPA), hexamethylene diisocianate (HDI), tin(II) 2-ethylhexanoate, sebacic acid, suberic acid, succinic acid, oxalic acid and 10-undecen-1-ol. Tetrahydrofurane (THF) was distilled from sodium immediately before use. Other solvents were used as received. 10,11-Epoxyundecan-1-ol and 11-allylmethylaminoundecan-1,10-diol (diol II) was synthesized according to the literature [66].

2.2. Characterization

Attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR FTIR). ATR FTIR spectra were recorded on a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) device with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Tknokroma) was used.

Nuclear magnetic resonance (NMR). ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded using a Varian Gemini 400 spectrometer. Spectra were recorded at room temperature using 15–25 mg of sample, in CDCl$_3$ as solvent. Chemical shifts were reported in ppm relative to TMS as internal standards.

Size exclusion chromatography (SEC). SEC analysis in DMF was carried out with an Agilent 1200 series system equipped with three serial columns (PLgel 3 μm MIXED-E, PLgel 5 μm MIXED-D and PLgel 5 μm MIXED-C from Polymer Laboratories) and an Shimatzu RID-6A refractive-index detector working at 60 °C at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained with polystyrene (PS) standards.

Differential scanning calorimetric (DSC) analysis. DSC analysis was carried out on a Mettler DSC822 differential scanning calorimeter. Samples were accurately weighed (5.5 ± 0.5 mg) and sealed in hermetic aluminium pans. Dry nitrogen gas was purged into the DSC cell at a flow rate of 100 ml/min. DSC analysis was carried out in three cycles two of heating and one of cooling from −50 °C to 100 °C, from 100 °C to −50 °C and finally from −50 °C to 100 °C at scanning rate of 10 °C/min.

Thermogravimetric analysis (TGA). TGA studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N$_2$ as purge gas. The studies were performed in the 30–600 °C temperature range at a scan rate of 10 °C/min.

Electrical conductivity (EC) measurements. EC was determined using the Dielectric Analysis option (DETA) of the ARES Rheometer (TA Instruments) coupled to an Agilent E4980 Bridge (Agilent). Electrodes were 20 mm diameter stainless steel plates and the measurements were performed on samples of 1.0 mm thickness. Temperature sweeps were carried out in the temperature range from 30 to 80 °C using a voltage of 1 V. Test were performed at a frequency of 6.28 rad/s. Dielectric data were recorded as a function of the frequency (ν). The real part of the conductivity, σ′ (ν) is calculated from the imaginary part of the dielectric constant ε″(ν) through the relation: σ′ (ν) = 2π ν ε$_0$ ε″(ν) where ε$_0$ = 8.8510^{-12} F/m is de vacuum permittivity. The DC value calculated from the frequency independent conductivity associated to the low frequency regime accounts for the ionic conductivity.

Uniaxial tensile measurements. Tensile tests were used both to characterize the mechanical response of the materials and to evaluate their self-healing efficiency. For mechanical property measurement, 5 mm width, 45 mm gauge length, and about 2 mm thickness length specimens were tested using a 5942 Instron test machine at ambient temperature under the following conditions: cross-head speed = 100 mm min^{-1} and sample length between jaws = 30 mm. The deformation was evaluated from the crosshead displacement. At least three samples were tested per test condition. In order to evaluate the self-healing efficiency of the materials, the specimens (dimensions above) were cut in the middle of the gauge length, and the two cut surfaces were brought back in contact by hand pressure and by placing the sample in a hard Teflon mold to properly align the two sides. The samples were allowed to heal