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Characterization of sustainable polyhydroxyls, produced from bio-based feedstock, and polyurethane and copolymer urethane-amide foams



M. Stanzione^{a,1}, V. Russo^{b,1}, M. Oliviero^{a,1}, L. Verdolotti^{a,*},
A. Sorrentino^a, M. Di Serio^b, R. Tesser^b, S. Iannace^c,
M. Lavorgna^a

^a Institute of Polymers, Composites and Biomaterials, (IPCB-CNR) National Research Council, P.le E. Fermi 1, Napoli, Italy

^b Department of Chemical Sciences, University of Naples Federico II, Napoli, Italy

^c Institute for Macromolecular Studies (ISMAC-CNR) National Research Council, Milano 20133, Italy

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ABSTRACT

This manuscript presents data related to the research article entitled "Synthesis and characterization of sustainable polyurethane foams based on polyhydroxyls with different terminal groups" (DOI: [10.1016/j.polymer.2018.06.077](https://doi.org/10.1016/j.polymer.2018.06.077)) [1]. We provide [Supplementary data](#) on the chemical properties, in terms of FTIR characterization, of polyhydroxyls produced starting from bio-based feedstock (biosuccinic acid and 1,4 butandiol) and thermal properties (glass transition temperature-T_g and thermal degradation behavior) of polyurethane and copolymer urethane-amide foams manufactured from the aforementioned polyhydroxyls. The FTIR characterization elucidates the chemical structure of polyhydroxyls and allows to make some hypothesis on their reaction routes with the isocyanate molecules. The thermal characterization revealed that the addition of bio-based polyhydroxyls to the sample formulations improves both the glass transition and degradation temperature of the foams. These foamed products

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* Corresponding author. Fax: +39 081 7758850.

E-mail address: letizia.verdolotti@cnr.it (L. Verdolotti).

¹ These authors contributed equally to this work.

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exhibit potential performances to be applied as a substitute for conventional polyurethane foams.

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Specifications table

Subject area	<i>Materials science</i>
More specific subject area	<i>Bio-based materials</i>
Type of data	<i>Tables, text file, graphs, figures</i>
How data was acquired	<i>Data were acquired from: FT-IR spectrometer (Nicolet FT-IR, Thermo Scientific- Italy) in ATR mode, Differential Scanning Calorimetry (DSC-Q1000, TA Instrument-Italy), Thermogravimetric Analysis (TGA 2920, TA Instruments-Italy) instruments.</i>
Data format	<i>Raw, analyzed and plotted data</i>
Experimental factors	<i>Chemical and thermal properties of produced polyhydroxyls and polyurethane and copolymer amide-urethane foams, respectively.</i>
Experimental features	<i>The characterization of polyhydroxyls was assessed in liquid phase, the thermal characterization of produced foams was undergone in solid phase under inert atmosphere.</i>
Data source location	<i>Institute of Polymers, Composites and Biomaterials, National Research Council, P.le Enrico Fermi 1, Naples, Italy</i>
Data accessibility	<i>Data is supplied with this manuscript</i>

Value of the data

- This dataset presents a chemical-physical characterization of bio-based polyhydroxyls.
- The FTIR spectra related to the different polyhydroxyl precursors are reported.
- A thermal behavior in terms of the effect of several bio-based polyhydroxyls on T_g and thermal degradation behavior of manufactured polyurethane and copolymer urethane-amide foams are provided.

1. Data

The data provided here is Fourier Transform InfraRed (FT-IR) spectroscopy of polyhydroxyls produced by using succinic acid obtained via *Arundo donax* fermentation. These analyses were performed in order to evaluate the effect of molar ratio (succinic acid/1,4 butandiol) on the chemical structure (terminal functional groups) of polyhydroxyls.

Differential Scanning Calorimetry (DSC) and ThermoGravimetric Analysis (TGA) of the resulting *poly(urethane-amide)* foams are also reported. They show the effect of the quality and amount of the functional groups on the final properties of the resulting polymeric foams.

2. Experimental design, materials and methods

2.1. Materials

The chemicals used to produce polyhydroxyls are summarized in [Table 1](#). Raw materials used to produce foams are reported in [Table 2](#).

Table 1

Details of materials used to produce bio-based polyhydroxyls.

Material	Type	Supplied by
<i>Succinic Acid (SA)</i>	<i>Carboxylic Acid</i>	<i>Biomass fermentation</i>
<i>1,4 butanediol (BDO)</i>	<i>Diol</i>	<i>Catalyzed hydrogenolysis of SA</i>
Ru/C 5 wt. % loading	Catalyst	Sigma Aldrich
Titanium(IV)N-butoxide (TNB)	Catalyst	Sigma Aldrich

Table 2

Details of materials used to produce polyurethane and urethane-amide foams.

Material	Type	Supplied by
Biosuccinium Polyol-FF1	Commercial Polyol	Coim S.p.a
CH ₃ COOK	Catalyst	Momentive
Niax PM40	Catalyst	Momentive
Methylen diphenyl di-isocyanate	MDI	Huntsman

2.2. Methods

The production of polyhydroxyls, polyurethane and copolymer amide urethane foams is described in the following paragraphs.

2.2.1. Synthesis of bio-based polyhydroxyls

Bio-based polyhydroxyls were synthesized by tuning molar ratio of Succinic acid (SA) and 1,4 butanediol (BDO) (which were produced through the fermentation process of *Arundo Donax*) [2,3] through an esterification reaction by means of a suitable catalyst. Three molar ratio SA/BDO was used:

2/1 for the sample namely S_1 ; 1/1 for the sample namely S_2 and 1/2 for the sample namely S_3 (see Table 1) [1].

2.2.2. Synthesis of polymeric foams

One step reaction was employed to synthesize polymeric foams (polyurethane and urethane-amide copolymer) with different amount and typology of bio-based polyhydroxyls. The synthesized bio-based polyhydroxyls were used to replace a commercial bio-polyester polyol in the production of polymeric foams [1,4]. Materials used for the production of the foams are reported in Table 2.

2.3. FTIR-ATR characterization of polyhydroxyls

FTIR spectra were recorded at room temperature by using a Nicolet FT-IR spectrometer in Attenuated Total Reflectance (ATR) mode from 400–4000 cm^{-1} operating in single reflection [5]. The spectra were recorded at 4 cm^{-1} resolution and 64 scans of average. FTIR spectra are reported in Fig. 1.

In the spectrum of S_1 the characteristic peaks of the stretching vibration of carbonyl group, $\text{C}=\text{O}$, at 1708 cm^{-1} and 1720 cm^{-1} ascribed to carboxylic group ($-\text{COOH}$) with hydrogen intramolecular bonds and ester group (COO^-) respectively are observed. The OH stretching vibration peak around 3000 cm^{-1} and the corresponding bending at 1420 cm^{-1} are also observed [6]. For the S_2 sample the stretching vibration of $\text{C}=\text{O}$ related, to the overlapping of both carboxylic and ester functional groups are detected at 1716 cm^{-1} , furthermore, the OH stretching vibration band at 3400 cm^{-1} ,

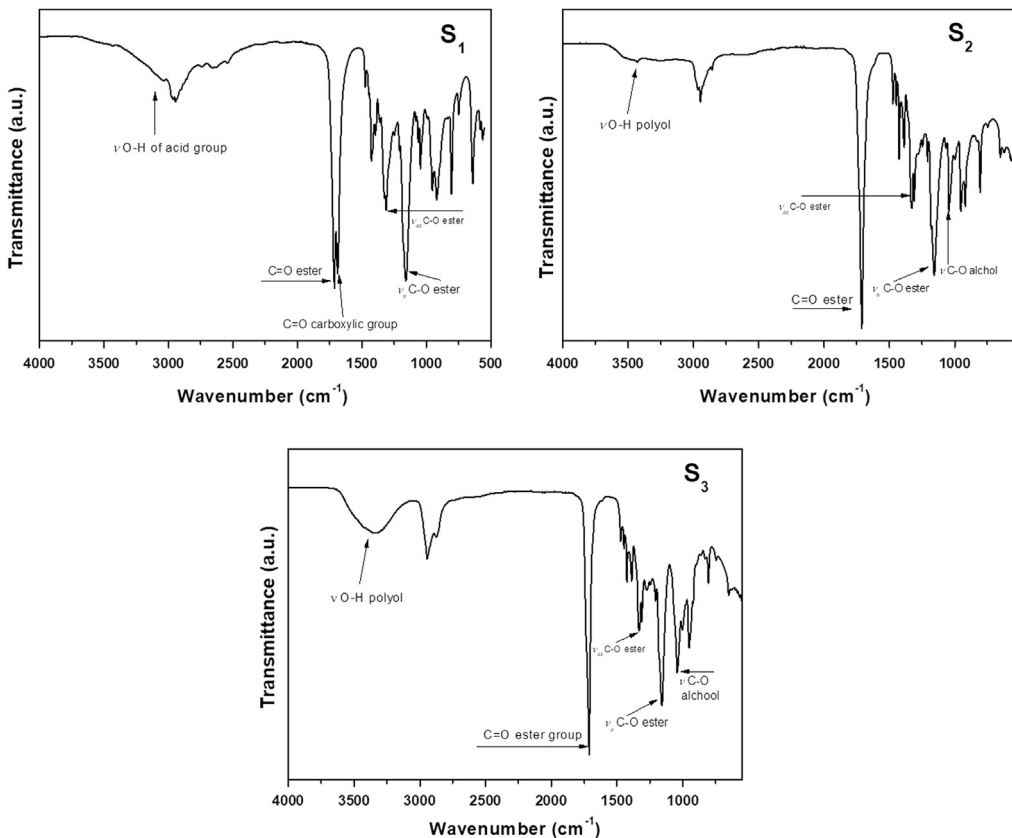


Fig. 1. FT-IR spectra of S_1 , S_2 and S_3 bio-based polyhydroxyls with ester groups assignment.

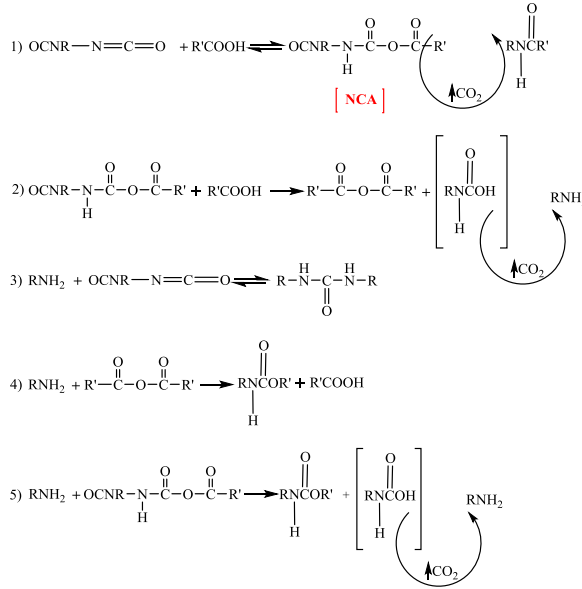


Fig. 2. Mechanism reaction of carboxylic group with isocyanate, NCO, functional group.

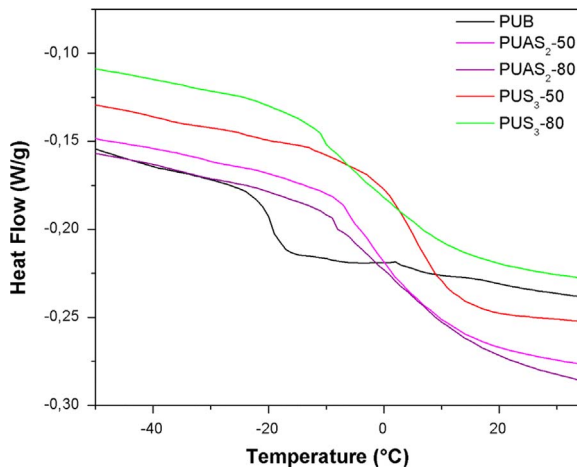


Fig. 3. DSC curves of polyurethane and copolymer amide urethane foams.

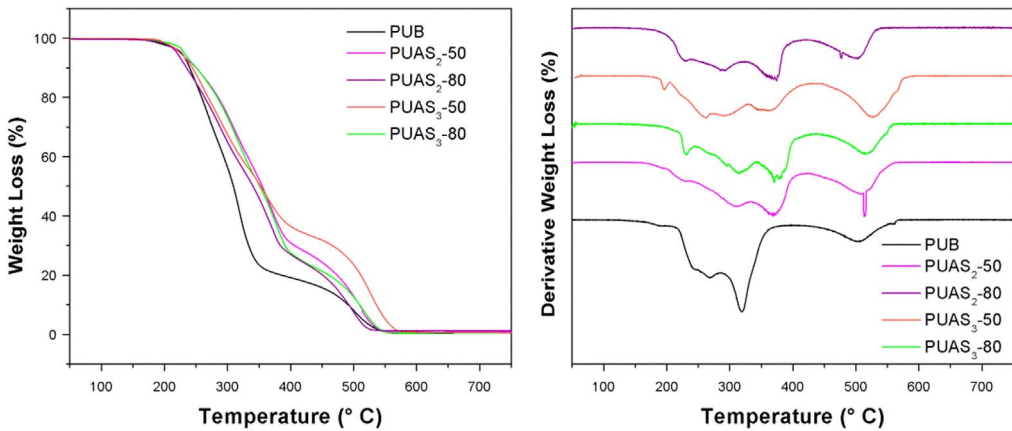
corresponding to the overlapping of O-H band ascribed to both carboxylic and alcoholic group, is also detected. The S_3 spectrum highlights a broad band, typical of alcoholic compounds, in the range $3100\text{--}3600\text{ cm}^{-1}$ due to O-H groups (free and H-bonded). The corresponding OH bending vibration at 1420 cm^{-1} is observed. Furthermore, the stretching vibration related to the ester carbonyl group $\text{C}=\text{O}$ was detected at 1718 cm^{-1} . The chemical structure of the produced polyhydroxyls allows making some hypothesis on their reaction routes with isocyanate. It is well known that the basis of polyurethane or polyamide chemistry is correlated to the high reactivity of isocyanates groups. Typically, the isocyanate reacts (under mild conditions and in presence of suitable catalysts and surfactants) with all chemicals that contain “active” hydrogen atoms: mainly alcohols, acid (OH group) and amines. In particular, the reaction of $-\text{NCO}$ group with alcohols, amines, carboxylic acids and/or water induce the formation of urethane [7], urea and amide linkages.

Table 3

Thermal data of polyurethane and copolymer amide urethane foams.

Samples	T _g (°C)	Td ₁ (°C)	Td ₂ (°C)
PUB	−19.8	320	504
PUAS ₂ -50	3.0	370	513
PUAS ₂ -80	2.1	375	516
PUS ₃ -50	5.1	362	528
PUS ₃ -80	2.0	369	502

* PUAS₁ samples were not analyzed due to the collapse of the foams [1].

**Fig. 4.** TGA and DTGA curves of polyurethane and copolymer amide urethane foams.

In particular, as well described by Schotman et al. [8], the mechanism reaction of carboxylic group with isocyanate involves several steps (see the reactions in Fig. 2).

These steps can be summarized in the formation of N-carboxylated anhydride (NCA) and the subsequent reaction with carboxylic group decomposes for producing amine and CO₂. The amine formed could react via several pathways with isocyanate (if present), anhydride or NCA to produce urea, amide/acid or carbamic acid/amide respectively. In our case, having different polyhydroxyls sources, i.e. carboxyl and hydroxyl terminated precursors, and Methylene Diphenyl di-isocyanate, as NCO source, both polyurethane and copolymer amide-urethane foams were obtained.

2.4. Thermal characterization of polyurethane and copolymer urethane-amide foams

Differential Scanning Calorimetry (DSC) tests of the foamed samples PUB, PUAS₂-50, PUAS₂-80, PUS₃-50 and PUS₃-80 were carried out in a heat-cool-heat mode. An amount of 8 to 10 mg of samples was placed in the DSC pan and heated from −50 °C to 100 °C at 10 °C/min. In Fig. 3 are reported the untreated enthalpic curves of the analysed samples in the range −50 to 30 °C. The curves show a typical transition corresponding to the glass transition temperature (T_g). It is important to note that this transition does not occur suddenly at one unique temperature but rather over a range of temperatures. In this case, the temperature in inflection points is taken as the T_g [9,10]. In Table 3 are reported the T_g values calculated from the previous curves. As evident, the T_g increased by addition of both S2 and S3. It is probably due to their high molecular weight that induced a reduction of mobility of the polymeric structures [11,12]. However, an additional increasing from 50% to 80% of the amount of S1 and S2 lead to a reduction of T_g. This effect could be due to the heterogeneity of synthesized polyhydroxyls which, as consequence, induce an increased network inhomogeneity within the foam structure [1].

Thermogravimetric analyses (TGA) of the foams were obtained by heated about 10 mg of sample from 30 to 800 °C in N₂ atmosphere at the heating rate of 10 °C/min.

TGA thermograms and the corresponding thermal degradation data are reported in Fig. 4 and in Table 2, respectively. In all thermograms, two main degradation stages are observed. The first step between 200 and 400 °C (with a maximum of derivative weight loss at around 320 °C, T_{d1}) is due to the breakage of urethane links. The second step between 440 and 550 °C (with a maximum of derivative weight loss around 520 °C, T_{d2}) is due to the decomposition of biosuccinium polyol or mixture polyhydroxyls-biosuccinium polyol [7]. By adding S₂ and S₃ an improvement in thermal stability of PUAS₂ and PUS₃ with respect pristine PUB was detected. Also in this case, the improvement in thermal stability is probably due to the higher molecular weight of polyhydroxyls.

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Transparency document. Supporting information

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