Synthesis and characterization of sustainable polyurethane foams based on polyhydroxyls with different terminal groups

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Abstract

Several *bio*-based polyhydroxyls are successfully synthesized by using succinic acid, obtained via *Arundo donax* fermentation and characterized by ^{1}H-NMR, GPC, and FT-IR analyses. Furthermore, the *bio*-based polyhydroxyls, consisting of a wide spectrum of compounds in terms of chemical structure and molecular weight, are used as substitute of conventional polyol in the formulations of Polyurethane and random Urethane-Amide Copolymer *bio*-based foams. The influence of both amount and typology of *bio*-based polyhydroxyls on *bio*-based foam properties is investigated through kinetic analysis, thermo-mechanical characterization, and morphological analysis. The results highlight that the replacement of conventional polyol with the *bio*-based polyester polyhydroxyls affects the foaming process and consequently the final properties of the free-foamed materials. In particular, the compressive modulus increases by about 140% for a bio-based polyester content of 50 wt% together with an increase in foam density. A further increase of these adducts results in a decrease of the glass transition temperature and the mechanical performances. However, the experimental results demonstrate the potentiality of these bio-based foams as commodity in several applications.

Keywords: *Sustainable polyurethane foam, Sustainable random Urethane-Amide Copolymer foam, bio-based polyhydroxyls, morphological properties, mechanical properties.*

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1. Introduction

Renewable sources are getting great attention from the governance, the industrial sector as well as by current scientific literature [1]. Most of the actual research programs (i.e.: Horizon 2020) have planned actions toward the development of bioenergy and/or *bio*-based chemicals [2]. The diversification towards renewable resources and/or sustainable processing is expected to contribute to a more sustainable chemistry and thus to a more sustainable and ethical society [3-5].

Unfortunately, despite the huge effort spent the integration of renewable raw materials (rather than fossil fuels) with sustainable technologies in the production of base chemicals is still a key opened issue.

In this context, biomass represents a renewable, abundant and cheap source of chemicals for the synthesis of *bio*-based polymers [4,6]. Vegetable oils and lignocellulosic biomass are extensively studied for their uses in producing *bio*-based polyols [7,8]. Epoxidation/oxirane ring opening, ozonolysis, hydroformylation, and esterification/amidation are currently used to convert vegetable oils to polyols [9,10]. On the other side lignocellulosic biomass, which is highly rich in hydroxyl groups, need first to be converted into liquid by oxypropylation or liquefaction [11,12]. Often these technologies require the use of expensive petroleum-based solvents [13,14].

Recently, succinic acid has gained great scientific and industrial interests as replacement of a large number of intermediates and specialty chemicals derived from petrochemical sources [15]. They can be produced by bacterial fermentation of lignocellulosic biomass [16,17]. The fermentative production is itself a "*greener*" production process. Succinic acid represents one of the chemical building block that could be used as bio-precursor to synthesize several alcoholic derivatives such as alcohol (1,4 butandiol) and polyhydroxyls [18,19].

Polyurethanes (PUs) are one of the most versatile classes of polymeric materials [20,21] with round 18 million tons of worldwide annual production in 2016 [22]. Most commonly, they are used for flexible and rigid foams, but they also have significant applications in coatings, adhesives, sealants, and elastomers [23].

The synthesis of PUs is based on a polyaddition reaction between a polyol and a di-isocyanate such as Methylen Di-phenyl di-isocyanate or Hexa Methylen isocyanate [24-26]. PUs structure can be tailored to fit specific requirements by a correct selection of the precursors. Thanks to the high variety of molecular structures of polyols, it is possible to modulate the final properties of Pus [24-26]. Furthermore, the presence of certain functional

groups such as carboxylic groups may allow the production of poly(urethane-amide) foams (PUAs) with improved thermal stability. Few studies are present in the literature on the synthesis of PUAs. Most of these involve the combined use of acid and conventional polyol for the formation of urethane and amide linkages [27,28,29].

PUs are industrially produced from petrochemical resources, but the environmental regulations drives this sector in the use of sustainable resources. Thus, several "sustainable strategies" ought to be implemented to obtain greener PUs with mechanical and functional properties comparable to the conventional ones [30]. To date, greener PUs could also be produced without using isocyanates precursor through reactions of amines, cyclo-carbonates as well as phenol sulphonic with conventional polyol [31, 32]. Alternatively, the most common examples of greener PU are based on the partial replacement of conventional polyol with polyols mainly produced from vegetable oils (castor oil, palm oil, soybean oil etc.). However, the process technology to produce these innovative PUs has not yet reached a "sustainable" level [33].

Lee et al. [29] draw the basis on the realization of PUs using succinic acid and 1,4-butanediol to obtain green foams composed by polyethylenglucol and polybutylensuccinate. These authors also investigated the stability of the obtained products. Moon et al. [30] synthesized nanocomposites based on PUs/montmorillonite from crystalline polyols using 1,4-butanediol and organoclays as chain extenders.

In our knowledge, only few studies on the use of polyol "*as it is*" without purification processes are known [12]. In this paper, we evaluated the effect of un-purified sustainable polyhydroxyls, produced by chemicals from biomass fermentation, on the synthesis of PUs and PUAs foams and their final properties. The novelty of this approach is twofold to evaluate the effect of un-purified sustainable polyhydroxyls, produced by chemicals from biomass fermentation, and to deepen the previous investigation, by verifying the effect of the succinic acid/1,4-butanediol molar ratio on the final foams properties. To that purpose three different *bio*-based polyhydroxyls were synthesized from esterification and poly-condensation reactions between succinic acid (SA) and 1,4 butanediol (BDO). SA was obtained via sustainable fermentation process of lignocellulosic biomass (*Arundo donax)* whereas BDO was synthesized through hydrogenation of SA in aqueous medium. The molar ratio of SA to BDO (for polyester synthesis) was varied in order to obtain polyhydroxyls with different terminal functional groups. No purification process was applied. The polyhydroxyls "*as obtained*" were used to replace a commercial *bio*-polyester polyol in the production of polymeric foams. Chemico-physical and mechanical properties of PUs and PUAs foams were evaluated and correlated to the chemical structure of *bio*-based polyhydroxyls.

2. Materials and Methods

2.1 Raw materials

Pyrometallic dianhydride 97% (PMDA, Mw = 218.12 g/mol), N, N dimethylformamide 99.8% anhydrous (DMF, Mw = 73.09 g/mol; d = 0.944 g/ml), Imidazole (IMA, Mw = 68.08 g/mol), phenolphthalein solution 2% ethanol (Mw = 318.32 g/mol) and sodium hydroxide solution 0.5 N were purchased by Sigma Aldrich, Italy.

Platinum on carbon extent of labelling: 5 wt% loading, matrix activated carbon support (Pt/C) and titanium(IV)N-butoxide (TNB) catalysts, were purchased by Sigma Aldrich, Italy. Commercial polyester polyol, succinic acid based, "*Biosuccinium Polyol-FF1*" (BP, Mn: 2000 g/mol; functionalities: 3-4; OH index: 61.5 mgKOH/g; η(25°C): 132300 mPa·s; Acidity: 1.12 mgKOH/g) was kindly provided by Coim Spa, Italy.

CH_3COOK and Niax PM40 as catalysts for polymerization and blowing reactions, respectively, were kindly provided by Momentive, Italy. Methylen diphenyl di-isocyante (MDI, Suprasec 2085 - NCO value = 30.5%) were provided by Huntsman, Italy. All materials were used as received.

2.2 Succinic acid and 1,4 Butandiol

A broth containing succinic acid (SA) was produced by a pilot fermentation scale in the separate hydrolysis and fermentation experiments on *Arundo Donax* [16]. Through several ultrafiltration processes on active carbon (without using solvent) in different temperature values SA was obtained as chemical to produce 1,4 butandiol [34].

1,4 Butandiol (BDO) was synthetized under mild reaction conditions (pressures and temperatures) through hydrogenolysis of succinic acid catalyzed by highly active, stable and reusable supported metal nanoparticles, Ru/C [8].

The synthesis of BDO was carried out in a fed-batch reactor, where H_2 was fed at constant pressure to a 0.3 L vessel. An AISI 316 stainless steel net was installed at the bottom of the withdrawn pipe to avoid any catalyst loss. Temperature and H_2 flow were measured of a National Instruments DAQ device, equipped with homemade acquisition software written in LabView 2013. In a representative hydrogenation of SA to BDO, the catalyst powder of Pd/C was previously pre-reduced in a dedicated packed-bed under 0.1 min^{-1} H_2 flow, 1 bar and a fixed temperature for 3h. The pre-reduced catalyst was cooled at room temperature under H_2 flow and then quickly charged to the vessels. Subsequently, 25 g of SA was diluted into 200 mL of deionized water and the mixture was added to the fed-batch reactor along with 1 g of .Pd/C. The solution was stirred briefly prior to assembling on the reactor head. The reactor was purged with 40 bar nitrogen to evacuate the

dissolved O_2, prior to filling with hydrogen and the magnetic stirrer was kept at a constant 1000 rpm. The reactor was firstly pressurized at 20 bar, heated until to 200° C, and after about 10 washes and temperature stabilization, H_2 was fed to the reactor at 40 bar, and reaction started. Samples were periodically withdrawn from the reactor vessel, to evaluate the evolution with time of both SA conversion and BDO selectivity. In the Scheme 1 the hydrogenation of SA to BDO is reported.
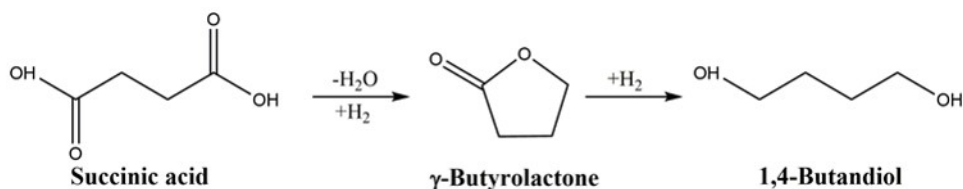
Scheme 1. SA hydrogenation to BDO.

2.3 Synthesis of bio-based polyhydroxyls

The *bio*-based polyhydroxyls have been synthesized by using a lab-scale discontinuous reactor with a volume capacity of 0.25L (see device sketch in Fig. 1) [10]. The vessel is equipped with an external oil bath, whose temperature is regulated by a PID system connected to a thermocouple placed in the vessel itself. The reactants/products were continuously mixed at a fixed rate of 750rpm. A valve for a sample withdrawn/catalyst or reactant loading is placed on the reactor head. A fitting is placed to connect the vessel to a glass condenser, which is useful to condensate water that is formed as the reaction proceeds. The refrigerator is connected first to a graduated closed cylinder, used to collect and measure the amount of water produced by the reaction. A vacuum trap made by an acetone/CO_2 bath, and a vacuum pump provided with a dedicated regulation valve was used to adjust the system vacuum.
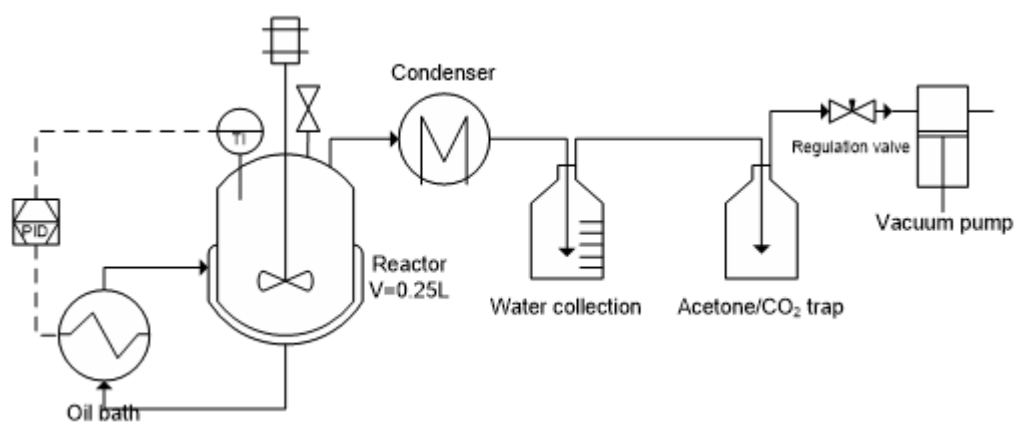

Fig. 1. Sketch of the experimental apparatus developed to perform for the synthesis of the *bio*-based polyhydroxyls.

The reactor was loaded with 180g of the SA/BDO mixture at 150°C. The reaction time was measured since temperature became constant and catalyst was added. All the experimental tests were performed by fixing the reaction time at 90 min. This time was found necessary to achieve good conversion in preliminary investigations. Both temperature (equal to 150°C) and catalyst concentration (for instance xTNB (wt%/SA) equal to 1.0) were kept constant for all tests. By varying the molar ratio of SA/BDO, it is possible to produce generic bio-based polyhydroxyls with specific SA/BDO molar ratio (S_n), characterized by (i) acid terminal groups (S_1); (ii) mixed acid/alcohol terminal groups (S_2); (iii) alcohol terminal groups (S_3) (see the reactions in the Scheme 2).

The reaction path is acid catalysed esterification, where the carboxylic group of SA is esterified by the alcoholic group of BDO. The reaction occurs in the presence of a classical homogeneous catalyst (TNB). Its concentration was chosen in agreement with our previous experience. As the reaction proceeds, water is formed. Being the esterification of a carboxylic group an equilibrium reaction, water was removed from the reaction medium in order to increase the overall conversion. Particular attention was paid to collecting water produced during the synthesis in order to be sure that the reactions were completed. Afterword the reaction product was discharged and quickly quenched in order to stop the reaction. Samples were stored at room temperature and then submitted to a chemical characterization analysis.
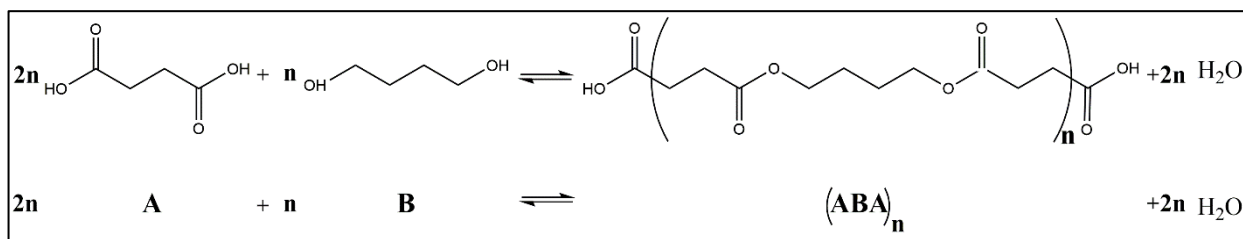
(i)
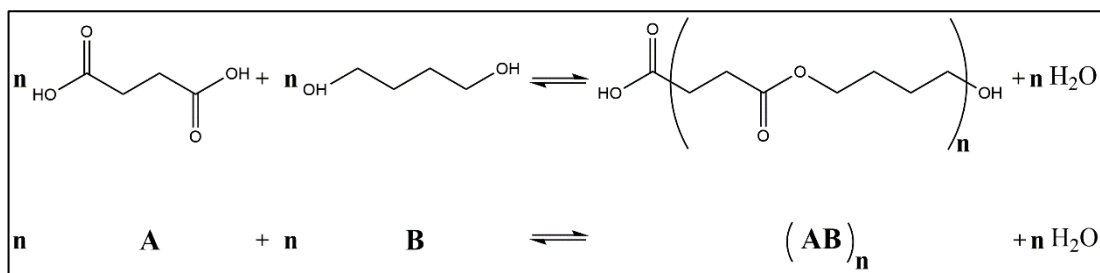
(ii)
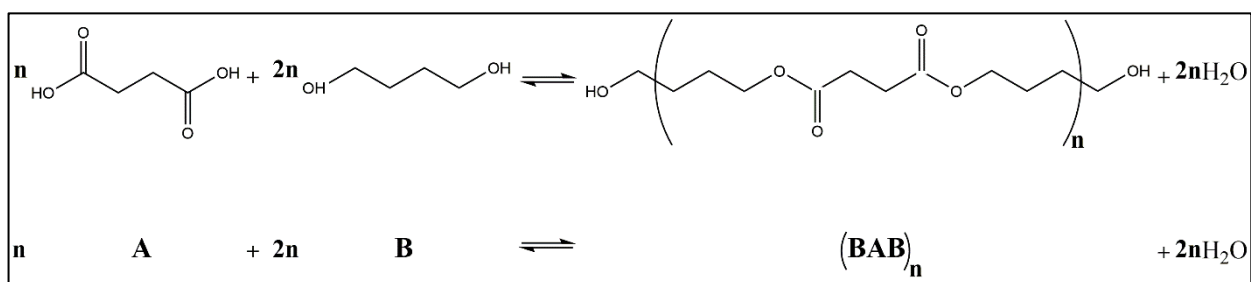
(iii)

Scheme 2. Chemical reactions related to the different molar ration of SA and BDO.

Both equations (i) and (iii) lead to the formation of a trimer if n=1, only if a stoichiometric reaction occurs. If n=1, in equation (i) 2 molecules of succinic acid (A) react with 1 molecule of 1,4-butanediol (B), leading to a trimer (ABA) where the middle location is occupied by the diol. In equation (iii), 1 molecule of succinic acid (A) reacts with 2 molecules of 1,4-butanediol (B) leading to the formation of a trimer (BAB) were 1,4-butanediole molecules are placed as terminal respect to the succinic acid. Finally, according to equation (ii) a dimer can be formed.

2.4 Synthesis of polymeric foams

Flexible polymeric foams with different amount and typology of *bio*-based synthesized polyhydroxyls, S_n, and a commercial polyester polyol (BP) were synthesized by using a one-step reaction.

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The bio-based polyols are characterized by a solid-like consistency which limits their reactivity with poly-isocyanate. For this reason in the synthesis of polyurethane, BP is used as a sort of diluent. In details different mixtures of S_n-BP (at different concentrations) were prepared and heated at 150°C for 10 minutes under stirring in order to allow an homogeneous mixing between the two components. After that, a suitable amount of additives, catalysts and silicone surfactants (1wt% with respect to the total amount of Total Polyhydroxyls), were added and mechanically stirred to ensure a complete homogenization. Subsequently, MDI reagent (NCO/OH ratio equal to 1.5 for all formulations) was added to the aforementioned mixture and mechanically mixed for 7s and then poured into a mold ($10 \times 10 \times 4$ cm^3). The formulations of *bio*-based polymeric foams are reported in Table 1, according to the following nomenclature: PUB as polyurethane prepared from BP, PUS$_n$ and PUAS$_n$ respectively as polyurethane and urethane-amide copolymers obtained by a reaction of bio-based carboxylic and alcohol terminated polyhydroxyls with MDI. All components were dehydrated in vacuum oven at 70 °C for 24 hours prior to use. Distilled water was added as chemical blowing agent only for the PUB sample.

Table 1. *Bio*-based polymeric foams formulations.

Samples	*S_1 (wt%)	*S_2 (wt%)	*S_3 (wt%)	H_2O (wt%)
PUB				1
PUAS$_1$-50	50	-	-	-
PUAS$_1$-80	80	-	-	-
PUAS$_2$-50	-	50	-	-
PUAS$_2$-80	-	80	-	-
PUS$_3$-50	-	-	50	-
PUS$_3$-80	-	-	80	-

* The amount of S_n (wt%) was calculated with respect to 100 parts of Total Polyhydroxyls (Total Polyhydroxyls = BP + S_n).

2.5 General methods and analysis

Acid titration: In order to verify the final succinic acid conversion, the produced *bio*-based polyhydroxyls were characterized in terms of acidic groups. The S_n products were dissolved in THF solution and then the acid groups were titrated with a standard methanolic solution of NaOH (0.1M) by using phenolphthalein as an indicator.

Hydroxyl Index: The hydroxyl number (I_{OH}) of synthesized *bio*-based polyhydroxyls (S_1, S_2, and S_3) was evaluated according to ASTM D4274-05, E Method.

Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR): The 1H-NMR analysis were recorded in DMSO for S_1 and CDCl3 for the systems S_2 and S_3 on Bruker spectrometer operating at 400MHz. Tetramethylsilane (TMS, Chemical shift: δ=0.00 ppm) is used as internal standard.

Fourier transform infrared spectroscopy (FT-IR): FTIR spectra were recorded at room temperature by using a Nicolet FT-IR spectrometer (Thermo Scientific, Italy) in Attenuated Total Reflectance (ATR) mode from 400–4000 cm^{-1} operating in single reflection. The ATR spectra were collected in reflectance mode by pressing the solid foam on the crystal. The spectra were recorded at 4 cm^{-1} resolution, and the reported results are the average of 64 scans. Furthermore, the spectra were normalized (for a qualitative comparison) by using as invariant peak, the peak vibration of the aromatic ring at 1597cm^{-1}.

Foam process: In order to analyse the foaming process in details, FOAMAT 281 equipment from Format, Messtchnik GmbH(Germany) with the software "FOAM" version 3.8 x, was used. This device records height, changes of the temperature and dielectric polarization of the foaming samples. Three samples of each formulation were tested. The software also calculates several parameters as start, rise, gel and curing times, the maximum temperature reached in the analysed system, shrinkage of the sample, etc. The start time is calculated as the time at which the ratio between the instantaneous rise velocity and the maximum rise velocity is equal to 0.15. The gel time criterion is set as the time at which the dielectric polarization reaches the 85% of its maximum value.

Scanning electron microscopy (SEM): The morphologies of the foams were analysed with a Leica model S440 (Leica Microsystems GMbH, Germany) scanning electron microscope operating at 20 kV. Small specimens were cut from the middle of the foams in the direction of growth. The pieces were coated with gold with a sputter coater (Emscope SC500, UK) before they were observed under the microscope.

Density measurements: The density of the foams was calculated as the ratio between the weight and volume of parallelepiped specimen. The weight was measured by an analytical balance with a precision of 0.001 g and sample linear dimensions by a high-resolution calliper with an accuracy of 0.01 mm. The obtained values were averaged among four samples.

Compression tests: Mechanical tests were performed in compression mode by means of a Q800 Dynamic Mechanical Thermal Analyser (TA Instruments). The tested samples were cubes with dimensions 10x10x10mm^3. Compression tests have been performed at ambient temperature, with a strain rate of 1mm/min^{-1}.

3. Results and Discussion

3.1 Characterization of bio-based polyhydroxyls

The *bio*-based polyhydroxyls have been characterized from the chemical point of view. In particular, the residual content of carboxylic groups was measured by an acid-base titration with 0.1M NaOH in CH_3OH. It was performed by dissolving about 0.1g of the sample in 10g of THF and using phenolphthalein as indicator. At the equivalent point, the moles of the carboxylic acid groups ( ) were measured. The percentage residue is expressed by dividing this value with the initial acidity moles ( ), obtained by titrating the prepared reaction mixture (see Equation 1).

$$R_{COOH} = \frac{n_{COOH}}{n^0_{COOH}} \cdot 100$$
                                                                                            (*Eq.1*)

In order to have a clear idea about the overall conversion, it is important to compare the content of carboxylic acid with the theoretical carboxylic acid residue at the total conversion of the limiting reagent. The results are reported in Table 2.

Table 2. Results of the residual acid content for the synthetized *bio*-based polyhydroxyls obtained both by acid-base titration and by the water collected as the reaction proceeded.

Samples	SA:BDO (mol:mol)	R_{COOH} (%)	V_{H2O} (cm^3)	$R_{COOH, H2O}$ (%)
S_1	2:1	55.1	9.0	54.9
S_2	1:1	54.8	4.5	54.9
S_3	1:2	1.5	9.8	1.72

As the reactants ratio is different for each experiment, it is difficult to define a unique conversion degree. Hence, we decided to report the experimental data in terms of residual carboxylic acid content. Sample S_1 was obtained by using SA in excess (2:1). Ideally, when the reaction ends it is possible to obtain a polyhydroxyl where both end groups are carboxylic (see the reaction (**i**) - Scheme 2). This means that starting from four COOH groups the reaction achieve final stage with two, which corresponds to a 50% residual content. Sample S_2 was prepared by using a 1:1 SA:BDO ratio. This means that when the reaction ends it is possible to get stoichiometrically a residual content of 50%, corresponding to the carboxylic acid end group of the obtained polymer (see the reaction (**ii**) – Scheme 2). Finally, S_3 was prepared with a diol excess. This means that ideally the polymer terminals

are characterized by hydroxyl groups (see the reaction (**iii**) – Scheme 2), which would lead to a 0% carboxylic acid residual content.

From the results reported in Table 2, it can be seen that a quite complete conversion is achieved in every case. The obtained residual content is comparable with the theoretical ones. A further validation of this data can be made by measuring the amount of collected water during the reaction (values reported in Table 2). As the reaction proceeds, considering that the experiments are performed under vacuum, the water is continuously formed and stripped through the condenser in a graduated cylinder (Fig. 1). Thus, it is possible to quantify the water produced. From this value, it is possible to calculate the residual content of carboxylic acid as in Equation 2.

$$R_{COOH,H_2O} = \left(1 - \frac{n_{H_2O,reacted}}{n^0_{COOH}}\right) \cdot 100 = \left(1 - \frac{V_{H_2O} \, \rho_{H_2O}}{MW_{H_2O}} \frac{1}{n^0_{COOH}}\right) \cdot 100 \qquad (Eq.2)$$

The results, reported in Table 2, confirm that the residual contents calculated by both the titration and the stripped water are comparable. The hydroxyl numbers of *bio*-based polyhydroxyls, evaluated according to the ASTM D4274-05 E Method, are reported in Table 3.

Table 3. Hydroxyl number synthesized *bio*-based polyhydroxyls.

Samples	I_{OH} (mgKOH/g)
S_1	261.80
S_2	430.10
S_3	607.75

In order to verify the chemical structure of the obtained products, ^{1}H-NMR analysis was performed. In Fig. 2, the ^{1}H-NMR spectra for all the synthesized *bio*-based polyhydroxyls are shown. In the case of S_1 the singlet present at δ=1.61ppm is characteristic of the CH_2CH_2 carbon chain protons. It is possible to observe at δ=2.39ppm the $(CH_2)_2COOCH_2$ singlet and at δ=2.53ppm the $(CH_2)_2COOH$, while at δ =4.00 ppm the $(CH_2)_2OCO$ singlet. The resonance peak at δ=12.0 is assigned to the COOH singlet. For S_2, both doublets of $(CH_2)_2CH_2OH$ at δ=1.61-1.68 ppm and of CH_2COOCH_2 at δ=2.60 ppm groups can be observed. Finally, S_3 shows resonance peaks at δ=1.65-1.68 ppm (t($CH_2)_4CH_2OH$), at δ=2.6 ppm (s($CH_2)_2COOCH_2$), at δ=3.63ppm (s($CH_2)_2OH$) and at δ=4.09 ppm (s($CH_2)_2OCOCH_2$). All the mentioned shifts are in agreement with the structures reported in the Scheme 2.
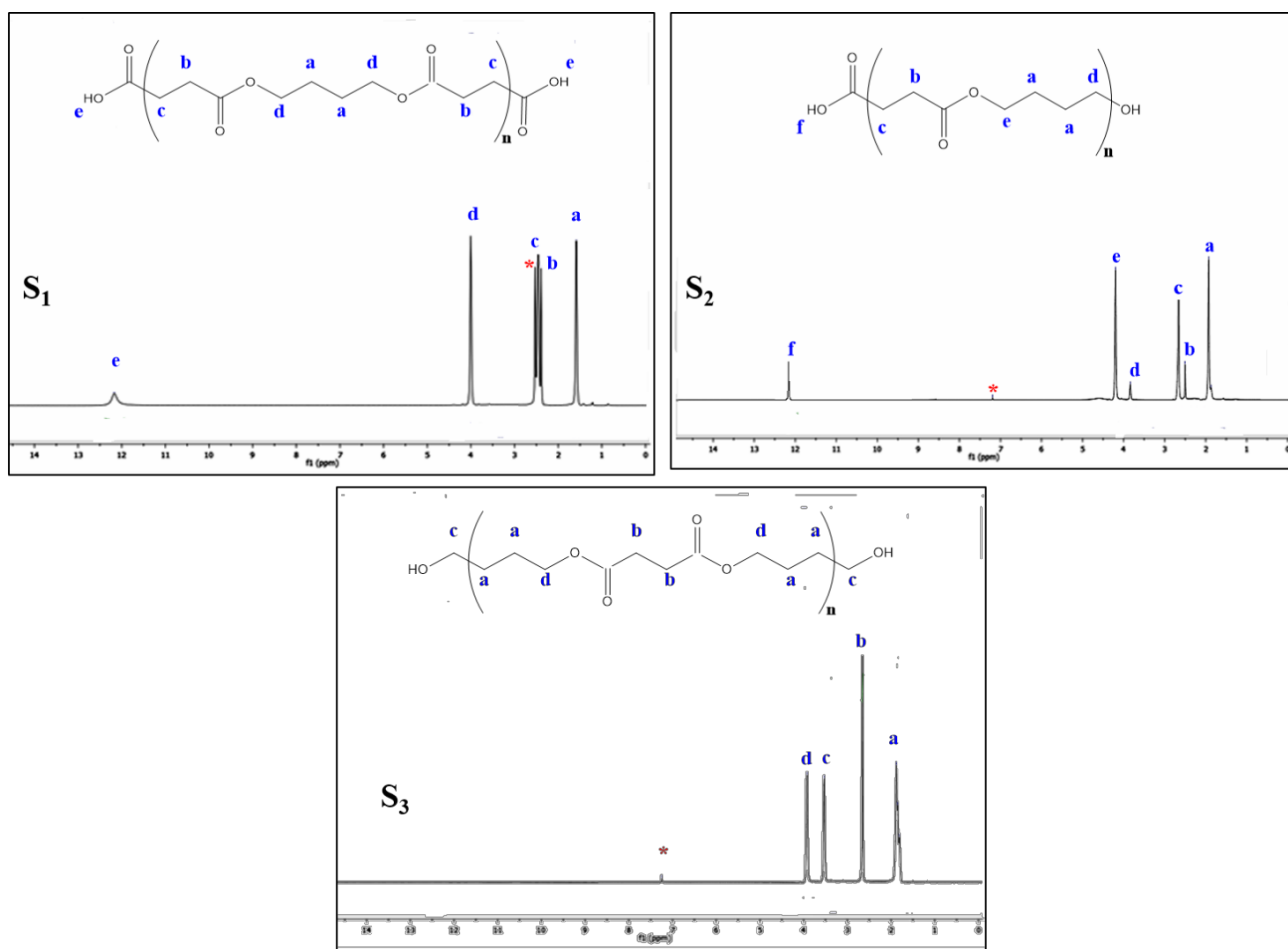
Fig. 2. ^{1}H-NMR spectra collected for S_1 [* δ=2.62 (DMSO)], S_2 and S_3 [* δ=7.26 (CDCl$_3$)] *bio*-based polyhydroxyls.

The GPC measurements give information about the average molecular weight and the polydispersity of the synthesized bio-based polyhydroxyls. The average molar mass (Mw) and Polydispersity (PDI) of S_n, expressed by an index calculated as the ratio between the weight average (Mw) and number average (Mn) molar mass of the polymer, are reported in Table 4. The GPC curves of S_1, S_2 and S_3 polyhydroxyls are shown in Fig. 3. The GPC curves for the bio-based polyhydroxyls S_1 and S_3 revealed a unimodal and moderately polydispersed distribution type (single peak and polydispersity index in the range 1.2-1.4). The GPC curve of bio-based polyhydroxyls S_2 showed, instead, a bimodal shape with a higher polydispersity index of 1.62.
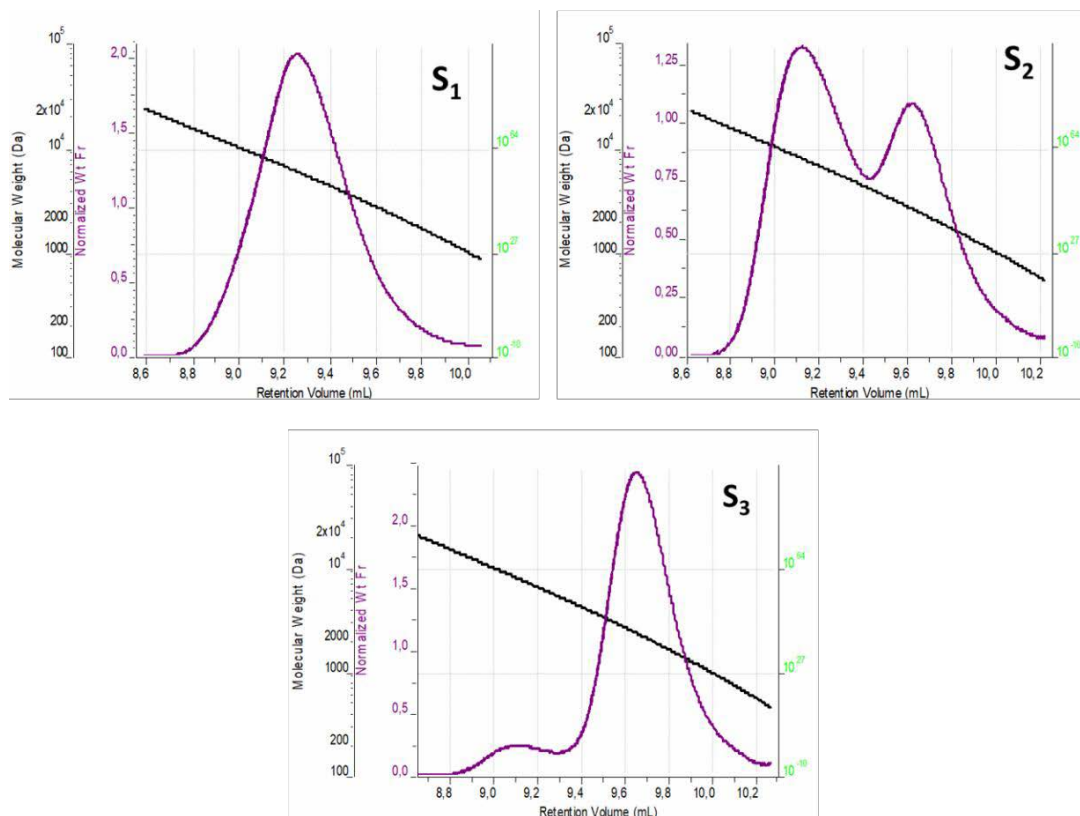
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Fig. 3. GPC curves of S_1, S_2 and S_3 bio-based polyhydroxyls

Table 4. Weight average molar mass (Mw) and Polydispersity (PDI) of S_1, S_2 and S_3.

Samples	Mw (g/mol)	PDI
S_1	5795	1.28
S_2	5292	1.62
S_3	2770	1.37

The highest PDI value was obtained for S_2 sample, whereas the lowest molecular weight was computed for the S_3 sample, where a diol excess was used. The most important information resulting from the GPC analysis is represented by the high molecular weight, which surely leading to n>1, thus proofing that achieved product are oligomers.

FTIR spectroscopy analysis was carried out to confirm the chemical structure of synthesized *bio*-based polyhydroxyls. The FTIR spectra (see Fig. 1, in Ref. [35]) have revealed the characteristic stretching vibration peaks of *bio*-based polyhydroxyls related to carboxylic and alcoholic terminal groups.

3.2 Characterization of bio-based polymeric foams, PUS and PUAS

As the *bio*-based polyhydroxyls are carboxylic and alcohol terminated, they can react with isocyanate compounds via polyaddition mechanism producing different polymers such as polyurethanes (PUs) and copolymers amide-urethane (PUAs).

Typically, isocyanate functional group reacts (under mild conditions and in presence of suitable catalysts and surfactants) with all chemicals containing "active" hydrogen atoms: mainly alcohols, water, acid (OH group) and amines and produces urethane, urea and amide linkages respectively. The reaction mechanism of polyhydroxyls with "NCO" was previously described by Verdolotti et al. [25]. The reaction mechanism of carboxylic group with isocyanate, as described by Schotman [36] evolves through several steps (see the reactions schematized in Fig. 2, in Ref. [35]): formation of N-carboxylated anhydride (NCA) which subsequently reacting with carboxylic group decomposes to produce amine and CO_2. The amine formed could react via several pathways with isocyanate, anhydride or NCA to produce urea, amide/acid or carbamic acid/amide, respectively. By FTIR-ATR investigation, it is possible to derive the absorption peaks of different chemical groups. For instance, Fig. 4 reports both the FTIR spectra of all foams containing the 50 wt% of S_n and deconvoluted spectra of carbonyl region (C=O). The corresponding assignments are provided in Table 5. In the Fig. 4, the labels related to the absorption peaks of the "urethane" and "amide" units were highlighted for clarification purpose. For all samples, the absence of the asymmetric stretching of "NCO" group at 2270 cm^{-1} indicated that the isocyanate was totally consumed during the blowing reactions. As expected, the foams produced starting from *bio*-based polyhydroxyls with terminated carboxylic groups (S_1 and S_2) show the presence of amide units in the polymeric structure.

In fact, from the PUAS$_1$-50 and PUAS$_2$-50 spectra the characteristic amide vibrations centered around 1660 cm^{-1}, 1558 cm^{-1} and 1262 cm^{-1} corresponding to the C=O stretching vibration, N-H bending and C-N were detected. In addition, C=O stretching vibration of urethane units at 1725 cm^{-1} was observed too. However, in the PUS$_3$-50 spectrum, only the absorption peaks related to the urethane units were detected. These outcomes confirm that the presence of carboxylic groups (-COOH) in S_1 and S_2 samples have induced the formation also of the amide units during the synthesis of the polymeric foams. Conversely, S_3 sample, that is a polyhydroxyl polyol, has brought the formation of urethane linkages. Same results were obtained for the samples PUS$_n$-80 data not reported for brevity.
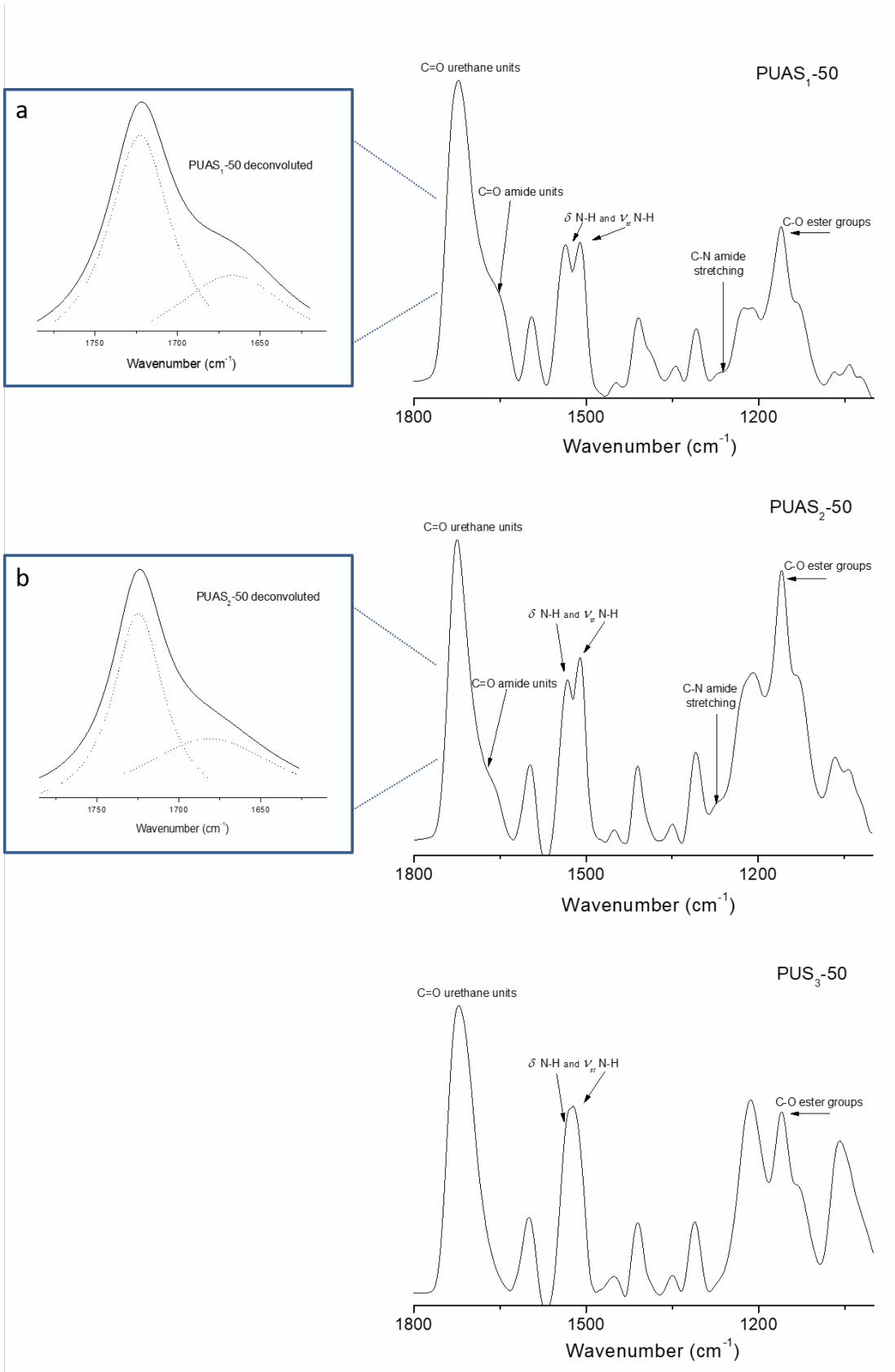
Fig. 4. FTIR spectra of produced foams (PUAS$_1$-50, PUAS$_2$-50 and PUS$_3$-50) and deconvoluted carbonyl region for PUAS$_1$-50 (a) and PUAS$_2$-50 (b).

Table 5. Assignments of the main IR bands of produced foams.

Assignment	Groups assignment	Wavenumber (cm^{-1})		
		$PUAS_1$	$PUAS_2$	PUS_3
υ_{st} C-O	Ester group (from Polyol)	1160	1160	1160
υ_{st} C-N	Amide	1270	1273	-
δ-CH_2	Ester group (from Polyol)	1450	1452	1452
υ_{st} N-H	Urea	1510	1509	1510
δ-N-H	Amide	1535	1530	1528
υ_{st} C=C	Aromatic ring vibration	1600	1600	1600
υ_{st} C=O	Amide	1670	1675	-
υ_{st} C=O	Free urethane	1725	1728	1720

The kinetic curves of the tested foams are shown in Fig. 5. Table 6 reports some parameters, acquired by the Foamat software, for all samples. The cream time is defined as the time taken for the reaction mixture to change from a clear to a creamy colour [36]. The end of rising time represents the time it takes for the foaming mixture to reach the maximal height [37].

The replacement of BP with S_n influences the foaming behavior in terms of induction time, end of rising time and maximal height values. In all foams with S_n, the expansion starts almost immediately after catalyst addition and mixing. As reported by Marcovich et al. [38], this behavior can be attributed to the lower viscosity of the systems with S_n mixed at a higher temperature that allowed the exothermic reaction to initiate faster.

The end of rising time depends, instead, on the type of *bio*-based polyester polyol and the maximal height is lower than that of PUB. In the synthesis of $PUAS_1$ foam the reaction between carboxylic groups and isocyanate (see the reaction reported in Fig. 2, in Ref. [35]), releases a large amount of carbon dioxide gas. Therefore, the production of gas proceeds more quickly than the crosslinking reaction, the polymer has not enough strength to maintain the solid phase of cellular structure and thus the foam collapses (Fig. 5a, black curve) [38,39]. The presence of both carboxylic and hydroxyl groups in S_2, involves a lower production of CO_2 and a right balance between both blowing and crosslinking reaction rates. Therefore, the $PUAS_2$ foam shows a stable cellular structure (Fig. 5a, blue curve). The expansion reaction of PUS_3 foam is due to the decarboxylation (CO_2 production) of unreacted succinic acid (carboxylic groups) present as residual in the *bio*-based polyhydroxyl S_3 (see Table 2). The maximal height of the PUS_3 foam is lower than those of

other samples, because of a small amount of blowing agent (Fig. 5a, green curve). In all experiments with S_n, water was not added as a chemical blowing agent. Therefore, the CO_2 cannot be obtained by the reaction between water and isocyanate, as generally occurs for the production of polyurethanes. The dielectric polarization for selected samples (Fig. 5b) reflects the progress of the reactions taking place between functional groups as a function of the reaction time [40]. Therefore, it gives an indication of reactivity of studied *bio*-based polyhydroxyls. Dielectric polarization is essentially determined by chain-like molecules with a large dipole moment due to their polar ending groups (COOH, OH, and NCO) [41,42]. Chain formation precedes the crosslinking reaction that ultimately suppresses all dipole mobility during curing [42]. All the dielectric polarization curves show two-step decrease at short times. The first step is related mainly to the initial foam formation, while the second step is associated with the formation of crosslinks. The foams modified with *bio*-based polyhydroxyls are characterized by the slower decrease of the dielectric polarization indicating a lower reactivity as compared with the PUB foam. Such effect could be associated with the chemical structure of the *bio*-based polyhydroxyls. It is known in the literature that the reaction of an isocyanate group with a carboxylic acid group is more complex and slower than with hydroxyl groups [43,44].
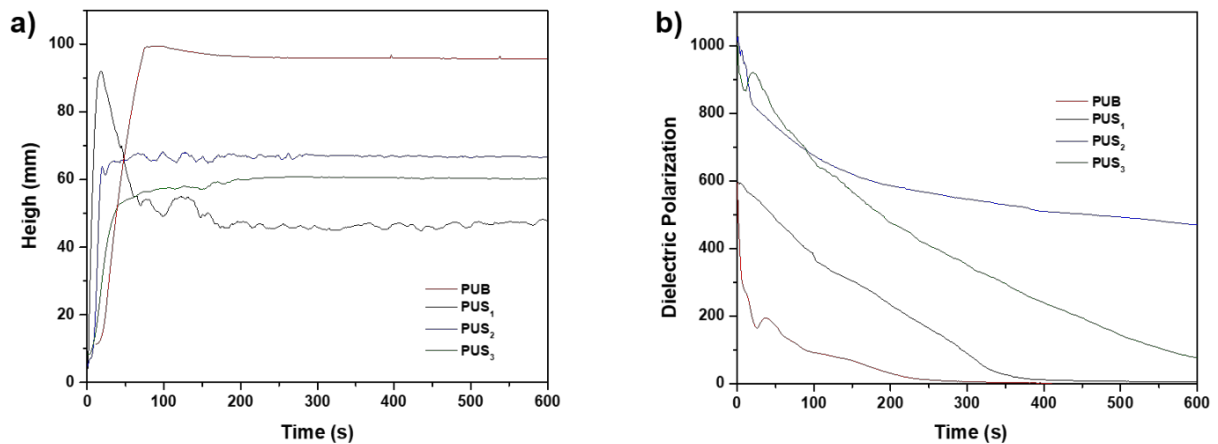

Fig. 5. Kinetic curves of PUB, PUAS$_1$, PUAS$_2$ and PUS$_3$ foams: a) Height vs Time, b) Dielectric Polarization vs Time.

Table 6. Characteristic Times during the foaming experiment.

Samples	Cream time (s)	End of rising time (s)	Foam average density (Kg/m^3)
PUB	15	78	45 ± 0.31
PUAS$_1$-50	5	19	*
PUAS$_1$-80	5	20	*
PUAS$_2$-50	8	68	65 ± 0.35
PUAS$_2$-80	8	70	61 ± 0.14
PUS$_3$-50	6	212	76 ± 0.09
PUS$_3$-80	6	214	71 ± 0.60

* Not evaluated because of the collapsed foams.

At longer times, the curves display the final curing of the foam giving a constant signal after the chemical reaction is completed. Increasing the content (80%) of S$_n$, the foaming behavior is not influenced. On the other hand, the attempts to replace more than 80% of the commercial polyol with one of the *bio*-based polyhydroxyls were unsuccessful and led to the spontaneous collapse of the foam after a few hours.

Fig. 6 shows low-magnification SEM images of samples cut from the middle of the foams in the direction of foam growing. The PUAS$_1$-50 and PUAS$_1$-80 foams reveal a large portion of cells collapsed, confirming the results obtained by Foamat measurements. All of the others foams present, instead, a mix between a closed and open cellular structures with small pores and a greater tendency for incomplete cell opening, as compared with the reference foam PUB. There are not preferential orientations in the cells. However, the partial replacement of BP with S$_2$ or S$_3$ led to smaller cells with a narrow distribution of size. In general, the reduction of cell sizes can be favored by a decreased gas diffusion [45,46].

For our systems, the decrease of cell sizes is due to a lower production of CO_2, which in turn can be associated with a limited expansion of the modified foams, in agreement with the higher densities of the foams (see density values reported in Table 6). The average density of the reference foam PUB was 45 Kg/m^3 and it increased with the replacement of BP with S$_2$ and S$_3$. This is associated with the lower reactivity of the S$_2$ and S$_3$ *bio*-based polyhydroxyls, which decreases the volume expansion of the foams. The morphology of the foams is not influenced significantly by *bio*-based polyhydroxyl content.
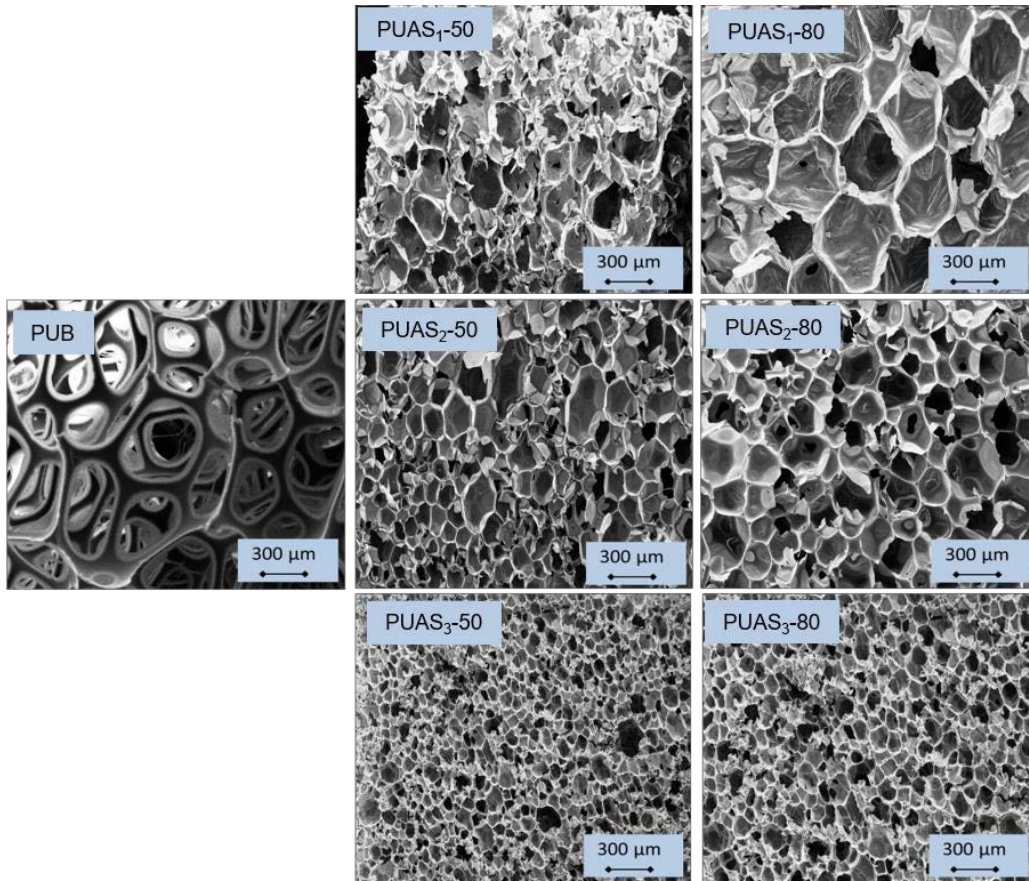
Fig. 6. SEM images of PUB , $PUAS_n$ and PUS_n foams.

The compressive stress-strain curves of reference foam and modified foams are reported in Fig. 7. Curve **a** is related to PUB foam, whereas curves **b** and **c** refer to foams synthesized from *bio*-based polyhydroxyl S_2 at 50 and 80 wt%, respectively. The curves related to PUS_3-50 and PUS_3-80 foams are reported as curves **d** and **e**, respectively. Curves **a**, **b** and **d** represent the typical behavior of plastic foams characterized by an initial linear portion, related to the elastic deformation of cells, a plastic yield, and a densification part characterized by a progressive increase of the stress versus strain. This behavior has been observed in both open and closed cell structures [47,48]. The related values of the modulus, calculated as the slope of the linear part, are reported in Table 7. The partial substitution of BP with S_2 produces an initial increase of the modulus from 0.23 KPa to 0.54 KPa when S_2 is added at 50 wt% (curve **b**), in agreement with the foam density values reported in Table 5 [49]. As is stated in the literature, the reduction of the open cells content, by adding S_2 polyhydroxyl, contributes to this result due to the effect on the modulus of the closed cell walls stretching, improved by the *bio*-polyol content addition [38].

An increase of the glass transition temperature (Tg) (see Table 3, in Ref. [35]) is usually accompanied by an increase of the material modulus [50]. This trend is followed by a reduction of this value to 0.19 KPa, when the content of S_2 reaches 80 wt%. This decrease cannot be related to the foam density values or to open cells content since that the morphology of the foams is not influenced by *bio*-based polyhydroxyls content. The mechanical behavior at 80 wt% of S_2 can be explained, instead, by the thermal and structural considerations. The presence of higher amount of S_2 bring a reduction of Tg (see Table 3, in Ref. [35]) of the foam and an increased network inhomogeneity consistent with the heterogeneity of the *bio*-based polyhydroxyl employed and, as a consequence, an increase of the segmental mobility of the polymer chains, as shown by the modulus value reported in Table 7 and by curve **c** in Fig. 7. Similar results were found by Tan et al. [51], Ribeiro da Silva [52] and Septevani et al. [53]. The same mechanical behavior has been evaluated for the PUS$_3$ foams. However, the compressive properties of the all studied foams are comparable to that of flexible polyurethane foams prepared from commercial polyol [6].
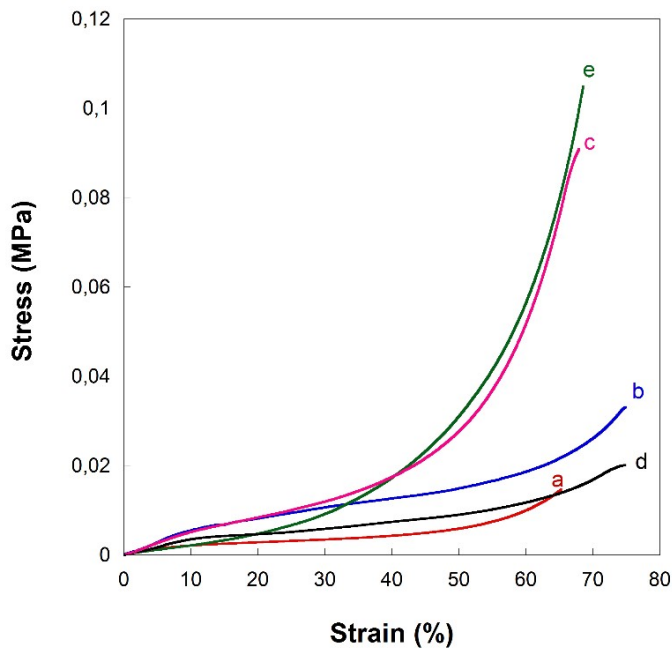

Fig. 7. Stress-strain curves of the foams: (a) PUB, (b) PUAS$_2$-50, (c) PUAS$_2$-80, (d) PUS$_3$-50 and (e) PUS$_3$-80.

Table 7. Compressive modulus of PUB, PUAS$_2$ and PUS$_3$ foams.

Samples	Modulus (KPa)
PUB	0.23±0.02
PUAS$_2$-50	0.54±0.015
PUAS$_2$-80	0.19±0.05
PUS$_3$-50	0.55±0.018
PUS$_3$-80	0.31±0.03

The morphological (open cells) and the mechanical results (modulus comparable to conventional foams) highlight that the "*as obtained*" polyhydroxyls can be proposed as potential substitute of conventional polyols in the production of flexible PUs foams in the packaging and load absorbing sector.

4. Conclusions

A new generation of bio-based polymeric foams was successfully synthesized by using sustainable polyhydroxyls, derived from succinic acid and 1,4 butanediol. In particular, the materials have been designed by trying to reduce the costs and the environmental impact connected with the preparation of bio-based polyhydroxyls and the corresponding foams. Succinic acid was obtained via sustainable fermentation process of lignocellulosic biomass (Arundo donax) whereas 1,4 butanediol was synthesized through hydrogenation of succinic acid in aqueous medium. The molar ratio of succinic acid to 1,4 butanediol was varied in order to obtain polyhydroxyls with COOH and OH-terminated functional groups. Chemical structure, OH value and molecular weight of these products were used as parameters to formulate, in presence of MDI and suitable catalysts and surfactant, different polymeric foams (i.e. polyurethanes and copolymer amide-urethane foams). The morphological structure and mechanical performances, of produced foams, were found to depend on the content of bio-based polyhydroxyls. The best performances in terms of fine and homogeneous cellular structures and high compressive modulus were obtained with 50 wt. % of bio-based –COOH/OH terminated (S$_2$) and –OH terminated (S$_3$) polyhydroxyls. In fact, the compressive modulus increased by about 140% for a and S$_3$ content of 50 wt% together with an increase in foam density.

The presence of higher amount of S$_2$ and S$_3$ brought, instead, a reduction of compressive modulus. This result can be correlated to the effect of higher amount of S$_2$ and S$_3$ on both thermal and structural properties. In fact, the copolymers amide-urethane PUAS$_2$-80 and PUS$_3$-80 obtained respectively with a partial replacement (80%) of S$_2$ and S$_3$ were characterized by a lower glass

transition temperature and an increased network inhomogeneity. It is consistent with the heterogeneity of the bio-based polyhydroxyl employed with a consequently decrease of mechanical performances. However, these bio-based foams should fulfill the requirements for a wide range of applications from packaging to load absorbing materials.

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Highlights

1) *Bio-based* were polyhydroxyls successfully synthesised by using bio-based feedstock.

2) Polyurethane and urethane-amide foams were produced from *bio-based* polyhydroxyls.

3) The foams exhibit chemico-physical performances comparable to conventional foams.

Data in Brief

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