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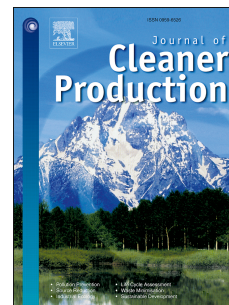
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**Article title:** The role of hydrogen bonding on tuning hard-soft segments in bio-based thermoplastic poly(ether-urethane)s

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28 **Keywords:** phase separation, thermoplastic polyurethanes, bio-based monomers, thermal properties,  
29 crystalline structure

## 30 1. Introduction

31 The increase in public environmental awareness, and consequent increase in regulation  
32 restrictions, has led to replacement of petrochemical monomers used in polyurethane industry by  
33 alternative monomers obtained from renewable sources, e.g., biomass, sugars or vegetable oils  
34 (Landim et al., 2019; Parcheta and Datta, 2017). There is plenty of motivation for that since the fossil-  
35 based thermoplastic polymers alone are responsible for about 13 million metric tons/year of direct  
36 contamination by polymeric solid residues. Moreover, besides been hard to degrade they also undergo  
37 incomplete degradation caused by ultraviolet (UV) radiation, mechanical abrasion, and biological  
38 processes, producing microplastic polymer particles (Donato and Mija, 2019). Additionally, the  
39 substitution of the petrochemical components allows for economic volatility reduction by the decrease  
40 in fossil fuel stock utilization. As a result, there is an improvement in economic stability in the countries  
41 without access to fossil fuels (Parcheta and Datta, 2017), since bio-based monomers production  
42 provides a decrease in the synthesis cost with an increasing amount of production. Moreover, they  
43 allow the reduction of energy consumption during production, the reduction of greenhouse gases'  
44 emissions (including decreased CO<sub>2</sub> emissions), and the biodegradability improvement (Muellhaupt,  
45 2013). This caused a search for renewable monomers that can replace the usual synthetic monomers,  
46 for materials synthesis, without worsening the properties of the final products (de Oliveira et al., 2019;  
47 Lligadas et al., 2013).

48 Thermoplastic polyurethanes (TPUs) are important groups of polyurethanes, obtained by the  
49 reaction of polyols, diisocyanates, and chain extenders - usually glycols (Król, 2007). The  
50 petrochemical chain extenders and polyols can be replaced by bio-derived compounds such as 1,3-  
51 propanediol (PDO), 1,4-butanediol (BDO), and bio-based poly(trimethylene glycol), which are  
52 produced by environmentally friendly biotechnological syntheses. PDO is obtained from glucose  
53 conversion using a patented microorganism under specific conditions (Adkesson et al., 2003; Emptage  
54 et al., 1999), and bio-based polyols, such as poly(trimethylene glycol) (PO3G), for TPU synthesis can  
55 be produced by the polycondensation of PDO. BDO is also obtained via a microbiological process by



56 the direct fermentation of sugars using the metabolic engineering of *Escherichia coli*, which is a  
57 patented fermentation technology from Genomatica (Burk et al., 2008).

58 TPU display excellent properties; such as high abrasion resistance, good thermal stability,  
59 high tensile strength, and flexibility (Kasprzyk and Datta, 2019). They have increased attention both in  
60 basic and applied research because these materials can be easily processed by various methods  
61 such as injection molding, extrusion, and blow molding (Lee et al., 2009; Verstraete et al., 2016). The  
62 melt flow index is an essential parameter influencing the melt processability, which depends on the  
63 number and weight average molecular weight, and polymer structure (Ferg and Bolo, 2013; Guerreiro  
64 et al., 2012). Moreover, TPU processability is also facilitated by their good thermal stability and phase  
65 transition temperatures (Xie et al., 2019).

66 TPUs contain repeating units of hard (HS) and soft segments (SS), where HS are derived from  
67 diisocyanate and short organic diols, and SS are built by polyols. As a result of thermodynamic  
68 incompatibility between the two types of segments, phase separation occurs (Yilgor et al., 2006).  
69 Materials with a high degree of microphase separation are characterized by the presence of two glass  
70 transition temperatures related to SS ( $T_{gSS}$ ) and HS ( $T_{gHS}$ ) (Kasprzyk and Datta, 2018). However, it is  
71 worth noting that TPUs never display a complete phase separation, and HS are always partially mixed  
72 with SS (Kasprzyk et al., 2019). As a result, the properties of TPUs are sensitive to many factors, such  
73 as synthetic (polymerization) procedure, processing method, thermal history, chemical structure,  
74 characteristics of the precursors used (e.g. polyols, diisocyanates, chain extenders), solubility  
75 parameters, volume fractions of HS and SS, intermolecular interaction between HS and SS, and  $T_{gSS}$   
76 (Buckley et al., 2010). This vast property tunability turns TPUs into promising materials for additive  
77 manufacturing (AM), which can produce end-use solid objects via layered stacking (Xu et al., 2020).  
78 The AM is known as the “third industrial revolution”, since it presents considerable production benefits,  
79 including the dramatic reduction of production waste by optimally utilizing materials and energy to  
80 produce final components (Ma et al., 2018).

81 This work explores the use of bio-polyols and bio-glycols to synthesize bio-based  
82 thermoplastic poly(ether-urethane)s (TPUs) with controlled ratios of HS and SS, via a two-step  
83 solvent-free method. The influence of different  $[NCO]/[OH]$  molar ratio and the type of bio-glycols on  
84 the TPUs' properties and processability were studied. Variable TPU compositions significantly affected  
85 hydrogen bonding interaction between HS and SS, which allowed us to obtain materials with a wide

86 range of thermo-mechanical properties and melt flow indexes. The influence promoted by the  
87 [NCO]/[OH] molar ratio and the type of bio-glycols on the TPUs' morphology and interphase bonding  
88 was also studied, to tune these characteristics by varying simple synthetic parameters and obtaining  
89 bio-TPUs with a good balance between processability and final properties.

90

## 91 **2. Materials and methods**

### 92 **2.1. Materials**

93 The bio-based poly(trimethylene glycol) (PO3G) ( $M_n = 2000$  g/mol, hydroxyl number 59.1 – 53.4  
94 mgKOH/g) was provided by Allesa (Germany). 4,4'-diphenylmethane diisocyanate (MDI) (NCO  
95 content: 33.5%, purity 99.5%) was purchased from Borsed Chem (Hungary). The bio-based glycols:  
96 1,4-butanediol (bio-BDO) (purity 99.8%) and 1,3-propanediol (bio-PDO) (purity 99.7%), were supplied  
97 by BASF (Germany) and DuPont Tate&Lyle, respectively. The catalyst 1,4-diacabicyclo[2.2.2]octane  
98 (DABCO) was purchased from Sigma-Aldrich (Poland).

99

### 100 **2.2. Thermoplastic poly(ether-urethane)s (TPUs) synthesis**

101 TPUs were prepared using a two-step prepolymer method. Initially, a prepolymer was  
102 synthesized by reacting to the PO3G polyol with an excess amount of diisocyanate at 85°C for 3 h  
103 under vacuum. The percentage of the unreacted NCO groups in prepolymer was equaled 7%, which  
104 was determined according to the ISO 14896:2010 standard. Secondly, a chain extender and a catalyst  
105 (0.3% DABCO) were added to the prepolymer, and the mixture was stirred for 30 s. For TPU  
106 syntheses, molar ratios of [NCO]/[OH] groups of 0.9, 0.95 and 1.0, and two bio-glycols (BDO and  
107 PDO) were used. Finally, the materials were post-cured in a laboratory oven at 100°C for 24h. A  
108 summary of the synthetic procedures is presented in Figure 1.

109 The materials were encoded as follows; the first part of the symbol corresponds to the bio-  
110 glycol used (B for bio-BDO glycol and P for bio-PDO glycol), while the second part refers to the  
111 [NCO]/[OH] molar ratio during the prepolymer chain extending step, e.g., the sample coded as P\_0.9  
112 was obtained using bio-PDO and presents a [NCO]/[OH] molar ratio of 0.9.



113

114 **Figure 1.** The synthesis of bio-based thermoplastic TPUs.

115

### 116 **2.3 Methods**

117 Size exclusion chromatography (SEC) was performed to determine the number ( $M_n$ ) and weight  
118 average ( $M_w$ ) molecular weights, as well as the dispersity. A chromatographic system equipped with a  
119 refractive index detector (Shodex, Japan), UV-Vis detector ( $\lambda = 254$  nm, LCD 2084, Ecom, Czech  
120 Republic) and a set of three columns (PLgel with a particle size of  $10 \mu\text{m}$ , pore size: 50/10E3/10E4 Å,  
121 300x7.5 mm, Polymer laboratories, UK) was used. Tetrahydrofuran was applied as the eluent at a 1  
122 ml/min flow rate, and the calibration was done on polystyrene standards.

123 Fourier transform infrared spectroscopy (FTIR) was carried out using a Nicolet 8700 FTIR  
124 spectrophotometer (Thermo Electron Co., USA) on attenuated total reflection (ATR) mode. The  
125 spectra were recorded at the room temperature for wavenumbers ranging from  $500$  to  $4000 \text{ cm}^{-1}$  at  $4$   
126  $\text{cm}^{-1}$  nominal resolution with 64 scans, using the normalized spectra for analysis. To calculate the  
127 degree of phase separation, spectra were analyzed in the  $1760 - 1680 \text{ cm}^{-1}$  region by deconvolution  
128 of the carbonyl peaks using Origin software. The degree of phase separation (DPS) and the degree of  
129 phase mixing (DPM) were calculated according to the equations (1-3):

$$130 \quad DPS = \frac{R}{R+1} \quad (1)$$

$$131 \quad R = \frac{A_b}{A_f} \quad (2)$$

$$132 \quad DPM = 1 - DPS \quad (3)$$

133 Where:  $R$  is the carbonyl hydrogen bonding index;  $A_b$  is the absorption intensity of hydrogen-bonded  
134 carbonyl;  $A_f$  is the absorption intensity of free carbonyl.

135 Thermogravimetric analysis (TGA) coupled with Fourier transform infrared spectroscopy (FTIR) of  
136 released gases was performed using a Pyris 1 TGA (PerkinElmer) coupled with an IR spectrometer  
137 Spectrum 100T FT-IR (PerkinElmer) through a transfer line TL 8000 (PerkinElmer). The analyses were

138 performed under a  $25 \text{ mL min}^{-1}$  nitrogen flow within the temperature range of  $35 - 700 \text{ }^\circ\text{C}$  and at a  
139 heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . The infrared spectroscopic cell and the coupling system to TGA were kept  
140 at  $270$  and  $260 \text{ }^\circ\text{C}$ , respectively, to prevent the condensation of evolved gases or vapors. FTIR  
141 spectra were continuously collected during the whole analysis, and they were recorded within the  
142 range of  $650 - 4000 \text{ cm}^{-1}$ , at 2 scans per spectrum at  $4 \text{ cm}^{-1}$  resolution.

143 Dynamic mechanical and thermal analysis (DMTA) was carried out, under the flexural mode, following  
144 ASTM D4065:2012 using the DMA Q800 analyzer (TA Instruments) within the temperature range of  
145  $100$  and  $150 \text{ }^\circ\text{C}$ , at a heating rate of  $4 \text{ }^\circ\text{C/min}$  and the frequency of  $10 \text{ Hz}$ . The measurements provided  
146 information about the systems' storage ( $E'$ ) and loss ( $E''$ ) moduli, and the glass transition temperatures  
147 of the SS based on the maximum  $\tan \delta$  peak ( $T_\alpha$ ).

148 Differential scanning calorimetry (DSC) was performed using a Q 2000 calorimeter (TA Instruments).  
149 The measurements were carried out in the heating-cooling-heating cycle from  $-90$  to  $250 \text{ }^\circ\text{C}$ , and the  
150 heating rate was  $10 \text{ }^\circ\text{C/min}$  and under a nitrogen purge of  $50 \text{ ml/min}$ . The sample weight was  
151 approximately  $6 \text{ mg}$ , and the data was collected from the first cooling ramp and the second heating  
152 ramp to exclude the samples' thermal history. Analyses were performed twice to ensure the data  
153 consistency within the thermal range performed.

154 X-ray diffraction (XRD) was performed with a high-resolution diffractometer Explorer (GNR Analytical  
155 Instruments, Italy) equipped with a one-dimensional silicon strip detector Mythen 1K (Dectris,  
156 Switzerland). The  $\text{CuK}\alpha$  radiation (wavelength  $\lambda = 1.54 \text{ \AA}$ ) was produced by a sealed X-ray tube  
157 operated at  $40 \text{ kV}$  and  $30 \text{ mA}$  and monochromatized with Ni foil ( $\beta$  filter). The measurements were  
158 performed in Bragg-Brentano geometry in the range of  $2\theta = 5 - 70^\circ$  with a step  $0.1^\circ$ . The exposure  
159 time at each step was  $15 \text{ s}$ .

160 The mechanical properties in static conditions were investigated on Zwick Z020 tensile testing  
161 machine, according to ISO 37:2007 standard. The dumbbell specimens were stretched at a cross-  
162 head speed of  $100 \text{ mm/min}$ , at room temperature. The hardness measurements were carried out  
163 using an electronic Shore type A Durometer, following ISO 868:2005 standard. The results were  
164 determined as the average of ten measurements.



165 Melt flow index (MFI) of bio-based thermoplastic polyurethanes were measured using Zwick/Roell  
166 plastometer, under ISO 1133. The evaluations were conducted with a 5.0 kg load at three different  
167 temperatures, i.e. 170, 175, and 180 °C.

168 Polarized light optical microscopy (POM) images were obtained, to differentiate the soft and hard  
169 segments present before and after a thermal treatment up to 250 °C (under vacuum) followed by a  
170 controlled cooling at 2 °C/min down to the room temperature. The images were obtained with a Canon  
171 EOS 650D camera coupled with a Zeiss Opton Photomicroscope III, using Planapo 63 objective  
172 lenses. The POM images were analyzed using ImageJ software for quantitative evaluation of the HS domain  
173 sizes and area contribution. Image areas of 150 x 150 µm areas were analyzed, where the  
174 measurements were repeated five times and averaged for ensuring the reliability of the results.

175 MALDI-TOF mass spectra were acquired with Ultraflex (Bruker Daltonics, Bremen, Germany) in the  
176 positive ion reflection mode, using delayed extraction. The spectra were the result of 30 000 shots with  
177 a DPSS, Nd: YAG laser (355 nm, 1000 Hz). External calibration was used. The samples were  
178 prepared by the dried droplet method. Chloroform solutions of the samples (10 mg/mL), the matrix:  
179 DHB (2,5-dihydroxybenzoic acid; 20 mg/mL), and the cationization agent: sodium trifluoroacetate  
180 (NaCF<sub>3</sub>COO; 10 mg/mL) were mixed in the respective volume ratio 4:20:1.1 µL. The mixture was  
181 deposited on a ground-steel target plate, and the analyzed drop was dried at an ambient atmosphere.

182

### 183 3. Results and discussion

184 The weight ( $M_w$ ) and number ( $M_n$ ) average molecular weights and the dispersity ( $\mathcal{D}$ ) indexes,  
185 as obtained by SEC, together with the chemical compositions and the hard segment (HS) contents of  
186 all TPU samples were displayed in Table 1. The formation of TPUs with high  $M_w$  and  $M_n$  was observed,  
187 with broad molecular weight distribution, where both the molecular weight and the dispersity  
188 proportionally increasing with [NCO]/[OH]. Consequently, samples B\_1.0 and P\_1.0 presented both  
189 the highest molecular weights and dispersities, however, the samples with the lowest [NCO]/[OH]  
190 during the prepolymer chains extending step displayed the highest contents of HS.

191 **Table 1.** Molar ratio, HS content, molecular weights, and dispersity of synthesized bio-based TPUs.

Label	[NCO]/[OH]	HS	$M_n$	$M_w$	$\bar{D}$	$M_n$
		[%]*				theoretical
<b>B_0.9</b>	0.9	34.6	20	44 300	2.21	10365
<b>B_0.95</b>	0.95	34.3	24	59 900	2.45	19374
<b>B_1.0</b>	1.0	34.1	31	84 500	2.66	86648
<b>P_0.9</b>	0.9	34.1	18	38 300	2.06	10182
<b>P_0.95</b>	0.95	33.8	23	50 500	2.14	18928
<b>P_1.0</b>	1.0	33.5	30	71 800	2.35	85470

192 \***[NCO]/[OH]**—the molar ratio of NCO and OH groups during the prepolymer chains extending step; **HS** – the  
 193 content of hard segments defined as the ratio of the mass of non-polyol components to the total mass of the  
 194 polymer;  $M_n$  – number average molecular weight;  $M_w$  – weight average molecular weight,  $\bar{D}$ —dispersity,  $M_n$   
 195 **theoretical** – calculated using Carothers equations (Yilgor et al., 2003).

196

197 The influence of the bio-glycol type and [NCO]/[OH] on the chemical structure, and the DPS of  
 198 the TPUs obtained were examined by FTIR and the spectra were presented in **Figure 2a**. Without  
 199 spectra normalization, all synthesized materials showed the characteristic groups for polyurethanes,  
 200 suggesting a quite similar chemical structure. The absorption bands related to NCO ( $2270\text{ cm}^{-1}$ ) and  
 201 OH groups ( $3300 - 3500\text{ cm}^{-1}$ ) were not observed, thus suggesting the complete monomer  
 202 consumption. The –NH stretching vibrations of the urethane groups were shifted to a characteristic  
 203 area representative to H-bond formation at the wavenumbers between  $3411$  and  $3210\text{ cm}^{-1}$ , with the  
 204 maxima at  $3320\text{ cm}^{-1}$  (Prisacariu et al., 2013). This band's intensity increased with decreasing the  
 205 [NCO]/[OH] molar ratio (Figure 2a), which would represent an increase of H-bonded groups.  
 206 Additionally, the maximum at  $3320\text{ cm}^{-1}$  was generally more intense for the materials based on bio-  
 207 BDO. The bimodal band with the maxima at  $2857\text{ cm}^{-1}$  and  $2960\text{ cm}^{-1}$  was assigned to the CH  
 208 asymmetric and symmetric stretching in the  $\text{CH}_2$  groups, respectively, while the deformation vibrations  
 209 of the C-H groups were observed at  $1410\text{ cm}^{-1}$ . The carbonyl groups (C=O) stretching vibrations were  
 210 observed in the range between  $1660$  and  $1740\text{ cm}^{-1}$  (Kopczyńska and Datta, 2016; Mizera and  
 211 Ryszkowska, 2016). In this region, three bands were usually observed, which were associated with: I)  
 212 H-bonded carbonyl groups in ordered HS( $1685 - 1706\text{ cm}^{-1}$ ); II) H-bonded carbonyl groups in a  
 213 disordered region ( $1714-1719\text{ cm}^{-1}$ ); III) free carbonyl groups ( $1730\text{ cm}^{-1}$ ) of SS (Niemczyk et al.,  
 214 2017). Moreover, bands associated with the urethane groups' N-H out-of-plane bending ( $1599\text{ cm}^{-1}$ )  
 215 and C–N stretching vibration ( $1520\text{ cm}^{-1}$ ), and with the polyether polyol's free ether bond (strong,  $1100$   
 216  $\text{cm}^{-1}$ ) were also observed. In the latter, two characteristic bands were visible and were associated with:

217 I) antisymmetric stretching vibration of non-associated ether groups ( $1100\text{ cm}^{-1}$ ); II) H-bonding  
 218 between N-H and C-O-C groups ( $1062\text{ cm}^{-1}$ ). The multiple bands in the range  $1180 - 1280\text{ cm}^{-1}$  was  
 219 connected with C-O stretching vibrations of the urethane groups in the amide III region (Saralegi et al.,  
 220 2013). Generally, with the increasing  $[\text{NCO}]/[\text{OH}]$  the band maximum was shifted towards higher  
 221 values. Once again, a correlation between band intensity and  $[\text{NCO}]/[\text{OH}]$  was observed, where the  
 222 carbonyl band increases with increasing  $[\text{NCO}]/[\text{OH}]$  during the prepolymer chains extending step (see  
 223 **Figure 2** and Supplementary Information **Figure S1**), and yet again the TPUs based on bio-BDO  
 224 displayed higher intensity than the ones based on bio-PDO.

225  
 226 **Figure 2.** a) FTIR-ATR spectra of bio-based TPU systems, b) Gauss model fitting of sample B\_0.95.  
 227 The solid line represents the sum of the overlapped peak-components (I – III), and the dashed lines  
 228 represent the deconvoluted distributions.

229 The band intensities and wavenumber shifts in the C=O region provided useful information  
 230 about the microphase separation within the bio-TPUs. **Figure 2b** shows the deconvoluted carbonyl  
 231 peak areas with band positions at  $1731$ ,  $1717$  and  $1700\text{ cm}^{-1}$  (marked as Peak I, II, and III) related to  
 232 free and H-bonded C=O within SS and HS, respectively. The calculated area fractions of the  
 233 deconvoluted bands were given in **Table 2**. The exact band positions indicated only small differences  
 234 among the materials containing different glycols and  $[\text{NCO}]/[\text{OH}]$  values. It could be concluded that  
 235 more than 70% of the HS was microphase separated, while only 30% of the HS seemed to be mixed  
 236 within the polyether polyol matrix. The bio-TPUs prepared by using bio-BDO presented a higher  
 237 fraction of H-bonded carbonyl groups than ones with bio-PDO, as a probable consequence of the  
 238 symmetric structure of bio-BDO. Additionally, materials prepared with lower  $[\text{NCO}]/[\text{OH}]$  had a higher  
 239 fraction of H-bonded C=O groups. However, the amount of H-bonded carbonyl groups was affected  
 240 not only by the content of HS but also by the symmetry of the chain extender used.

241 **Table 2.** Deconvolution of the FTIR absorbance bands in the range between  $1750$  and  $1660\text{ cm}^{-1}$ ,  
 242 occurring in the prepared TPUs.

Symbol	-C=O band			DPS	DPM
	Peak I: free C=O	Peak II: H-bonded amorphous region	Peak III: H-bonded in ordered HS		



	$\nu$ [cm <sup>-1</sup> ]	f [%]	$\nu$ [cm <sup>-1</sup> ]	f [%]	$\nu$ [cm <sup>-1</sup> ]	f [%]		
<b>B_0.9</b>	1730.51	23.93	1716.85	4.85	1699.81	71.23	0.715	0.285
<b>B_0.95</b>	1730.62	25.83	1717.19	4.42	1699.98	69.75	0.690	0.310
<b>B_1.0</b>	1730.68	27.14	1717.25	4.21	1700.11	68.65	0.675	0.325
<b>P_0.9</b>	1730.10	23.94	1716.23	9.72	1702.38	66.35	0.776	0.224
<b>P_0.95</b>	1730.15	28.05	1716.28	9.13	1702.10	62.83	0.736	0.264
<b>P_1.0</b>	1730.68	30.29	1717.65	8.50	1702.02	61.22	0.718	0.282

243 \* $\nu$  - location of maximum absorbance; f – fraction; **DPS** – degree of phase separation; **DPM** – degree of phase  
244 mixing.

245 Regarding the TPUs' thermal properties, five thermal events (one glass transition temperature,  
246 two exotherms, and two endotherms) could be distinguished from the DSC runs (Figure 3), and the  
247 results are summarized in **Table 3**.

248 The  $T_{gSS}$  were detected around -61°C and were slightly increased for TPUs with higher  $M_w$ .  
249 Moreover, since  $T_{gSS}$  is strongly dependent on the degree of miscibility between HS and SS (Eceiza et  
250 al., 2008; Niemczyk et al., 2017), TPUs with higher [NCO]/[OH] values displayed higher  $T_{gSS}$ .  
251 Consequently, the TPUs encoded B\_1.0 and P\_1.0 presented the highest  $T_{gSS}$  values, as higher  
252 contents of HS are embedded in the SS, thus decreasing the DPS as confirmed by FTIR-ATR.

253 The DSC cooling curves gave information about the TPUs' crystallization behavior. The  
254 decrease in [NCO]/[OH] promoted considerably the crystallization kinetics of the bio-based TPUs,  
255 while higher [NCO]/[OH] displayed broader peaks (higher DPM), as evidenced by the DSC's  
256 exothermic crystallization peaks. Sample B\_0.9 displayed a 20 °C higher crystallization temperature  
257 ( $T_c$ ) and a higher crystallization enthalpy change ( $\Delta H_c$ ), in comparison to samples B\_0.95 and B\_1.0.  
258 Additionally, TPUs prepared using bio-PDO as chain extenders generally showed higher  $\Delta H_c$  than the  
259 bio-BDO-based ones.

260 The second heating curves of DSC exhibited a relatively sharp exothermic peak at about -  
261 20°C resulting from the cold-crystallization of the SS (Righetti, 2017), followed by the endotherm at  
262 10°C associated with their melting temperature ( $T_m$ ). This phenomenon was exclusive to TPUs with  
263 [NCO]/[OH] = 0.9 and 0.95, suggesting the ability of these TPU formulations to form molar ratio-  
264 dependent ordered structures. The  $T_m$  (displayed upon heating) of SS was slightly increased as  
265 [NCO]/[OH] was also increased (within the temperature range between 0 to 12°C). The  $T_m$  at higher

266 temperatures (170 - 240°C) were connected with the dissociation of a long-range ordering, which was  
 267 related to the mixing between HS and SS. These multiple endotherms at higher temperatures were  
 268 also associated with the melting of HS crystallites, phase-separated into different domain sizes, and  
 269 microcrystalline structures upon cooling (Hossieny et al., 2017; Niemczyk et al., 2017). A similar  
 270 phenomenon was also observed by Eceiza *et.al.*, which prepared model rigid segments based on MDI  
 271 and BDO and observed three endotherms at high temperatures (200 - 240°C) related to the melting of  
 272 HS (Eceiza et al., 2008). The registered melt-endotherms confirmed the formation of the broad size  
 273 distribution of HS crystallites, as also observed in the  $T_c$  profiles at the cooling curves (Figure 4).  
 274 Especially samples B\_0.9, B\_0.95 and P\_0.9 displayed increased high-temperature endothermic  
 275 peaks, and their shift to higher temperatures, as a result of better HS ordering and formation of  
 276 stronger and more stable HS domains. Moreover, the samples B\_0.9 and B\_0.95 also presented  
 277 defined bimodal  $T_c$  behaviors, indicating the formation of more than one crystallite type.

278 For this reason, these two systems were analyzed using polarized light optical microscopy  
 279 (POM) for observing the HS size and distribution, before and after being thermally treated above the  
 280  $T_m$  followed by controlled slow cooling (2°C/min). This procedure was applied to induce different  
 281 crystallization behavior. This thermal treatment considerably increased the number of HS within the  
 282 TPU network, however, no considerable change in HS size was observed (Figure 3c and d). Similar  
 283 results have been previously described by other authors, where the HS aggregate diameters were  
 284 between 0.4 and 1.5 $\mu\text{m}$  (areas ~ 0.502 - 7.080  $\mu\text{m}^2$ ) and HS aggregates volume fraction between 8  
 285 and 21% (Lvii et al., 2012). Altogether, the bio-based TPUs that presented higher microphase  
 286 separation showed higher total  $\Delta H_c$  and  $\Delta H_m$ , also showing a greater tunability during the  
 287 crystallization processes.

288

289 **Table 3.** Summary of DSC results of the bio-based TPUs.

Sample	$T_{gSS}$ (°C)	$T_c$ (°C)	$\Delta H_c$ (J/g)	Total $\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)	Total $\Delta H_m$ (J/g)
<b>B_0.9</b>	-62.1	-12.1	3.3	9.3	8.6	3.5	9.7
		122.4	6.1		178.5	4.9	
					193.0	0.6	
					212.5	0.6	

<b>B_0.95</b>	-61.4	118.5	8.7	8.7	9.7	0.5	7.3
					181.4	6.2	
					203.8	0.5	
					221.0	0.1	
<b>B_1.0</b>	-59.6	104.6	7.0	7.0	2.0	0.03	5.5
					173.2	5.4	
					204.8	0.1	
<b>P_0.9</b>	-63.3	-10.2	7.1	15.9	9.8	9.2	13.7
		162.4	8.8		176.7	2.1	
					227.0	2.2	
<b>P_0.95</b>	-61.6	-5.4	0.8	8.5	11.5	1.0	8.6
		128.2	8.5		193.4	7.6	
<b>P_1.0</b>	-60.1	129.1	6.5	6.5	1.0	0.1	6.1

290 \* $\Delta H_m$  – melting enthalpy;  $\Delta H_c$  – crystallization enthalpy;  $T_c$  – crystallization temperature;  $T_m$  – melting  
 291 temperature;  $T_{gSS}$  – glass transition temperature of the soft segments.

292

293 **Figure 3.** DSC thermal transition curves of the second heating (a) and first cooling (b) ramps of the  
 294 bio-based TPUs. POM microphotographs of samples B\_0.9 (c), and B\_0.95 (d), before (left) and after  
 295 (right) a thermal treatment at 250 °C (under vacuum) followed by a controlled cooling at 2 °C/min.  $A_{HS}$   
 296 is the area and  $A_{\%HS}$  is the area fraction (and an estimation of the volume fraction) of HS aggregates.

297

298 The TGA results were displayed in **Figure 4** and **Table 4**, where  $T_{5\%}$  was assessed as the  
 299 initial degradation temperature. As a general trend, bio-BDO-based systems presented  $T_{5\%}$  10 °C  
 300 higher than bio-PDO ones. TPUs often present two decomposition stages (Lei et al., 2017): a first  
 301 degradation step with a maximum at 330-350 °C, referring to the HS decomposition; and a second  
 302 degradation step around 425 °C, connected to the SS decomposition. All TPUs prepared in this work  
 303 followed this characteristic, and the rate of weight loss was dependent on [NCO]/[OH]. With the  
 304 increase of [NCO]/[OH] the maximum weight loss rate for the first decomposition step decreases,  
 305 while the one for the second decomposition step increases. This could be correlated with the HS  
 306 content in both bio-BDO- and bio-PDO-based systems since all TPUs with a higher HS content also

307 presented a higher weight loss rate for the first decomposition step and a lower weight loss rate for  
 308 second decomposition step (Table 4).

309 Thermal stability depended on [NCO]/[OH] and the type of bio-glycols during the chain  
 310 extender step. With the increase of [NCO]/[OH] the thermal stability slightly increased. TPUs based on  
 311 bio-BDO displayed higher thermal stability than the ones based on bio-PDO, which could be related to  
 312 a more symmetric structure of bio-BDO in comparison to bio-PDO. All the prepared systems were  
 313 thermally degraded and carbonized above 500°C leaving only char residue, which varied negligibly for  
 314 bio-BDO and only slightly more for bio-PDO.

315

316 **Table 4.** Thermal degradation profiles of the bio-based TPUs obtained by TGA.

Sample	T <sub>5%</sub> [°C]	T <sub>10%</sub> [°C]	T <sub>50%</sub> [°C]	T <sub>90%</sub> [°C]	Char (wt.% at 650°C)	I step degradation		II step degradation	
						T <sub>max</sub> [°C]	DTG <sub>max</sub> [%/min]	T <sub>max</sub> [°C]	DTG <sub>max</sub> [%/min]
<b>B_0.9</b>	325.8	338.1	403.0	437.4	3.13	349.5	-6.72	422.2	-15.07
<b>B_0.95</b>	326.1	339.0	403.9	437.6	2.77	348.4	-6.70	423.4	-15.13
<b>B_1.0</b>	327.3	339.5	407.5	441.9	3.21	348.1	-6.39	423.2	-15.29
<b>P_0.9</b>	315.9	327.6	413.8	444.1	3.29	332.4	-4.95	427.2	-16.24
<b>P_0.95</b>	316.5	328.7	415.8	458.1	4.97	333.3	-4.82	427.4	-16.61
<b>P_1.0</b>	317.4	331.0	416.0	457.2	4.89	332.2	-4.71	427.6	-17.00

317

318 **Figure 4.** TGA and DTG curves of the bio-based TPUs.

319

320 Coupled TGA-FTIR analysis provided a more detailed description of the degradation  
 321 processes, by the continuous monitoring of the thermal degradation products by FTIR. The spectra  
 322 were recorded at the maximum evolution rate for each decomposition step of systems composed of  
 323 different bio-polyols (B\_0.95 and P\_0.95) (Figure 5). There are three main thermal decomposition  
 324 pathways for the urethane linkages: I) the dissociation to isocyanates and alcohols; I) the dissociation  
 325 to primary amines, olefins and carbon dioxide, and; III) the formation of secondary amines with the  
 326 elimination of carbon dioxide (Pielichowski and Leszczy, 2004).

327 Taking that into account, the spectra corresponding to the volatile products recorded during  
328 the first and second mass loss steps of systems B\_0.95 and P\_0.95 were very similar. The spectra  
329 collected at 348 and 333°C (first degradation step) showed multiple bands associated with the  
330 symmetric and asymmetric C-H stretching vibration from isocyanate and hydrocarbons (2860 – 2970  
331  $\text{cm}^{-1}$ ), with carbonyl groups (1720  $\text{cm}^{-1}$ ), and with C-O-C vibrations (1070  $\text{cm}^{-1}$ ). The bands within the  
332 range 4000 – 3500  $\text{cm}^{-1}$  are related to the N-H and O-H stretching vibrations (Cervantes-Uc et al.,  
333 2009), while the bands at 918 and 647  $\text{cm}^{-1}$  are associated with the C-H bending vibrations of aromatic  
334 rings (Yang et al., 2012). At the second degradation step (423 and 427°C), more intense bands at  
335 3641-3786  $\text{cm}^{-1}$ , 2670 – 2960  $\text{cm}^{-1}$ , 1730  $\text{cm}^{-1}$ , 1510 – 1340  $\text{cm}^{-1}$ , 1100  $\text{cm}^{-1}$  and 911 – 995  $\text{cm}^{-1}$  were  
336 observed. They were mainly connected to the SS thermal decomposition, indicating that their volatile  
337 decomposition products were aliphatic ethers, aldehydes, and carbon monoxide. The bands at 2780,  
338 2745, and 2810  $\text{cm}^{-1}$  were connected with C-H stretching vibrations, the multiple peaks in the range  
339 1660 – 1760  $\text{cm}^{-1}$  with C=O stretching vibrations, and the band at 954  $\text{cm}^{-1}$  with C-H bending vibrations  
340 of aldehyde groups. The band at 1100  $\text{cm}^{-1}$  was attributed to C-O stretching vibrations, and the bands  
341 at 2960 – 2860  $\text{cm}^{-1}$  to C-H stretching vibrations of the ether groups. The multiple peaks with several  
342 maxima at 1479, 1429, 1335  $\text{cm}^{-1}$  originated from the  $\text{CH}_2$  and  $\text{CH}_3$  groups from polyols. Finally, the  
343 band in the range 3573 – 3768  $\text{cm}^{-1}$  was attributed to O-H stretching vibrations from alcohol  
344 (Cervantes-Uc et al., 2009; Herrera et al., 2002).

345

346 **Figure 5.** FTIR spectra recorded during the 1<sup>st</sup> and 2<sup>nd</sup> mass loss step for the bio-TPU systems B\_0.95  
347 and P\_0.95.

348

349 Since the DSC analyses of the TPU systems indicated some degree of ordering, XRD  
350 characterizations were also performed. Considering that broad Gaussian peaks correspond to less  
351 ordered arrangements and defined sharp peaks correspond to crystalline domains (Lei et al., 2017), all  
352 bio-TPUs displayed an overall amorphous profile with the presence of some ordered/crystalline  
353 structures (**see SI, Fig. S2**). The crystallinity seems to be originated from the bio-polyols used since  
354 the neat polyol precursors presented crystalline peaks at  $2\theta \sim 14.4, 19.4, 20.6, 22.6, 23.7, 24.5^\circ$ . The  
355 TPU exhibited three weak diffraction patterns at about 11.5, 20.2 42.4 $^\circ$ , among which could be



356 observed a series of small peaks at  $2\theta \sim 11.0, 19.2, 20.6,$  and  $24.3^\circ$ . It worth noting that the crystalline  
 357 structures observed herein are provided only by the SS since it is necessary to anneal the TPUs for  
 358 observing also the HS (Fang et al., 2014; Lei et al., 2017), which was not the case in this study.

359 Regarding the TPUs' mechanical properties, the DMTA results were presented in **Table 5** and  
 360 the shifts in storage modulus ( $E'$ ), loss modulus ( $E''$ ) and the  $E''/E'$  ratio ( $\tan \delta$ ) (as a function of the  
 361 temperature) were displayed in **Fig. 6**. The transition temperatures detected by DMTA presented a  
 362 good correlation with the DSC data. Initially, the  $E'$  decreased significantly at temperatures higher than  
 363  $-30^\circ\text{C}$ , matching with the  $T_{gSS}$  observed by DSC. Subsequently, it could be observed the maximum  
 364 peak in the  $\tan \delta$ , referring to the  $T_g$  of the SS, herein also denoted as  $T_{gSS}$  (Table 5). Additionally,  
 365 above the  $T_{gSS}$  the  $E'$  decreased steadily up to  $-20^\circ\text{C}$ , followed by a sudden  $E'$  increase coinciding with  
 366 the cold crystallization of the SS observed for the same systems. Moreover, DMTA detected a weak  
 367 secondary thermal transition in the temperature range from  $75$  to  $100^\circ\text{C}$ , which was connected with  
 368 the glass transition of hard segments ( $T_{gHS}$ ).

369 The value and shape of the  $\tan \delta$  curve (vs. temperature) provided information about the  
 370 damping capacity (Beniah et al., 2016; Prisacariu, 2011). The TPUs prepared using bio-PDO as chain  
 371 extenders displayed the highest  $\tan \delta$  values. Moreover,  $\tan \delta$  also depended on  $[\text{NCO}]/[\text{OH}]$  and  
 372 decreased with increasing  $[\text{NCO}]/[\text{OH}]$ . Therefore, TPUs with lower H-bond content and higher  $M_w$   
 373 were less effective for damping vibrations. Although all TPUs had similar  $\tan \delta$  peak widths, the ones  
 374 with  $[\text{NCO}]/[\text{OH}] = 0.9$  and  $0.95$  presented an additional peak above  $75^\circ\text{C}$ , which was connected to the  
 375  $T_{gHS}$ .

376

377 **Table 5.** DMTA results of prepared TPUs.

Sample	$T_{gSS}$ [ $^\circ\text{C}$ ] (DMTA)	$\tan \delta$	$E'_{\max}$ [MPa]	$E'$ [MPa] at temp.			$T_{\max}$ of $E''$	$E''_{\max}$ [MPa]
				$T_{gSS}$	$25^\circ\text{C}$	$100^\circ\text{C}$		
<b>B_0.9</b>	-37.8	0.42	3020	420	42	14	-46.2	458
<b>B_0.95</b>	-36.4	0.47	2989	389	41	18	-46.1	449
<b>B_1.0</b>	-35.7	0.50	3010	370	40	20	-45.4	418
<b>P_0.9</b>	-38.2	0.49	3214	405	40	13	-46.6	434
<b>P_0.95</b>	-36.7	0.52	3198	381	39	12	-46.2	430

*P\_1.0*            -35.9        0.54        3276        372        38        16        -45.7        411

378 \* $T_{gss}$  – glass transition temperature of the soft segment;  $E'_{max}$  – maximum value of storage modulus;  $E'$  –  
379 storage modulus;  $E''$  – loss modulus.

380

381 **Figure 6.** DMTA curves of the TPUs based on (a) bio-BDO and (b) bio-PDO as a function of the  
382 temperature.

383            Regarding the general mechanical properties, the young's modulus ( $E$ ) of the TPUs increased  
384 with decreasing [NCO]/[OH]. TPUs based on bio-BDO presented the best mechanical performances  
385 with  $E$  ranging between 33.4 and 38.5 MPa, while for bio-PDO-based ones it ranged from 29.9 to 33.2  
386 MPa (**Table 6**). As shown in Tables 1 and 2, the materials prepared with bio-BDO presented a higher  
387 content of H-bonded carbonyl groups and HS. Thus,  $E$  increased proportionally with increasing the  
388 interfacial H-bonding, which also explained the higher stiffness observed by DMTA (Figure 6 and  
389 Table 5), caused by the more restricted mobility within the TPU networks (Saralegi et al., 2013).  
390 However, although increasing [NCO]/[OH] caused a reduction in  $E$ , the tensile strength ( $TS_b$ ) and the  
391 elongation at break ( $\epsilon$ ) increased, reaching tensile properties comparable to those of highly stretchable  
392 TPU-based composites applied as strain sensors (Duan et al., 2018). The  $TS$  and  $\epsilon$  of bio-PDO-based  
393 TPUs ranged from 7.2 to 24.6 MPa and from 189 to 680%, respectively, while bio-BDO-based ones  
394 ranged from 7.7 to 28.2 MPa and from 200 to 768%, respectively. Moreover, system B\_0.9 displayed  
395 higher hardness than systems B\_0.95 and B\_1.0, which could be explained by the more abundant H-  
396 bonding and HS caused by the lower [NCO]/[OH] during the prepolymer chain extension step. The  
397 same relationship was also found concerning the hardness of TPUs prepared with bio-PDO. The  
398 TPUs densities were strongly dependent on the monomer densities, where TPUs prepared with bio-  
399 PDO had a higher density than the ones with bio-BDO. Moreover, for synthesizing TPUs with  
400 [NCO]/[OH] = 0.9 it was necessary the use of larger glycol amounts (chain extenders) associated with  
401 the prepolymer, consequently, decreasing the density with increasing [NCO]/[OH].

402

403 **Table 6.** Summary of mechanical properties ( $TS_b$  and  $\epsilon$ ), hardness, and density of the bio-TPUs.

Sample	$TS_b$ [MPa]	$\epsilon$ [%]	$E$ [MPa]	$H$ [°ShD]	$d$ [g/cm <sup>3</sup> ]
--------	--------------	----------------	-----------	------------	--------------------------

<b>B_0.9</b>	7.7 ± 0.2	200 ± 21	38.5 ± 0.2	80.1 ± 0.4	1.138 ± 0.012
<b>B_0.95</b>	20.0 ± 1.5	621 ± 18	37.0 ± 0.9	82.6 ± 0.1	1.135 ± 0.003
<b>B_1.0</b>	28.2 ± 1.3	768 ± 23	33.4 ± 1.1	83.3 ± 0.2	1.131 ± 0.011
<b>P_0.9</b>	7.2 ± 1.2	189 ± 14	33.2 ± 1.1	80.6 ± 0.3	1.162 ± 0.010
<b>P_0.95</b>	18.4 ± 1.0	589 ± 31	30.7 ± 0.2	82.0 ± 0.2	1.160 ± 0.009
<b>P_1.0</b>	24.6 ± 2.1	680 ± 20	29.9 ± 0.8	84.1 ± 0.2	1.157 ± 0.009

404 \***TS<sub>b</sub>**– tensile strength; **ε**- elongation at break; **E** – Young moduli; **H** – hardness; **d** – density.

405

406 To prospect the TPUs applicability in processes demanding specific melt-behavior, such as  
 407 injection molding or additive manufacturing, the materials' melt flow indexes (MFI) were characterized  
 408 (**Table 7**). As expected, the MFI values were dependent on the TPUs' molar mass, [NCO]/[OH] and  
 409 the temperature, decreasing with increasing [NCO]/[OH]. The  $M_w$  (Table 1) has probably a major role  
 410 in this case since it is well-described that materials presenting higher  $M_w$  will also be more viscous  
 411 (Wirpsza, 1993), requiring higher reprocessing temperatures. Bio-PDO-based TPUs presented  
 412 generally higher MFIs than bio-BDO-based ones, showing also a dependency on the polymer  
 413 backbone formed by the different polyols. Almost in a complementary fashion, at 170°C both MFI and  
 414 the melt volume flow rate (MVR) increased in the following order: B\_1.0 < B\_0.95 < B\_0.9 < P\_1.0 <  
 415 P\_0.95 < P\_0.9 (Table 7).

416 Interestingly, many of the TPU systems presented MFI values close to the ideal for fused  
 417 deposition modeling (FDM) additive manufacturing, which for the most commonly used thermoplastic  
 418 polymer, poly(lactic acid), is MFI = 10g/10min (Wang et al., 2017). Moreover, a sufficiently high MFI is  
 419 required for an acceptable FDM printing quality, which can be obtained by altering the melting set  
 420 point. However, from an industrial point of view, materials within this MFI range are preferred,  
 421 especially if they allow control over the crystallinity and plasticizer type. Since the sole focus on MFI is  
 422 insufficient, and the plasticizer type and crystallinity also play a role after the polymer melt deposition,  
 423 we carefully analyzed the bio-TPUs with the best crystallinity controls (B\_0.9 and B\_0.95) using SEC  
 424 and MALDI-TOF mass spectroscopy. These analyses enabled us to detect any monomeric/oligomeric  
 425 residue that could promote the self-plasticization of the bio-TPUs, also acting as coupling agents  
 426 between HS and SS (Fig. 7).

427

428 **Table 7.** Temperature-dependent MFI and MVR results of the bio-TPUs.

Sample	170 °C, 5kg		175 °C, 5kg		180 °C, 5kg	
	MFI[g/10min]	MVR [g/10min]	MFI[g/10min]	MVR [g/10min]	MFI[g/10min]	MVR [g/10min]
<b>B_0.9</b>	16.2 ± 0.2	16.4 ± 0.3	38.2 ± 0.4	38.3 ± 0.2	62.8 ± 0.2	63.2 ± 0.2
<b>B_0.95</b>	10.2 ± 0.3	10.5 ± 0.2	12.5 ± 0.2	12.8 ± 0.3	26.3 ± 0.1	26.6 ± 0.3
<b>B_1.0</b>	7.2 ± 0.2	7.4 ± 0.5	10.6 ± 0.3	10.9 ± 0.4	21.2 ± 0.1	21.5 ± 0.1
<b>P_0.9</b>	37.3 ± 0.4	37.5 ± 0.3	56.1 ± 0.1	56.4 ± 0.4	89.1 ± 0.9	90.2 ± 1.0
<b>P_0.95</b>	25.6 ± 0.3	25.4 ± 0.8	32.5 ± 0.5	33.0 ± 0.1	61.3 ± 0.7	61.5 ± 0.6
<b>P_1.0</b>	17.7 ± 0.1	18.2 ± 0.3	28.7 ± 0.2	29.2 ± 0.2	41.2 ± 0.5	41.5 ± 0.7

429 **MFI** - the melt (mass) flow index, **MVR** - melt volume flow rate

430

431 **Figure 7.** MALDI-TOF spectra of systems a) B\_0.9 and b) B\_0.95 highlighting the repetitive low  
 432 molecular mass units representing monomeric/oligomeric species in the final TPUs, and c) SEC  
 433 results of systems B\_0.9 and B\_0.95, where  $M_{pn}$  represents  $M_n$  (g/mol) of the nth peak.

434

435 The MALDI-TOF analyses confirmed the presence of several repetitive mass units below  $m/z$   
 436 = 3000, presenting a bimodal repetition representative of the TPU's SS ( $m/z \sim 58$ ) and HS ( $m/z \sim$   
 437 340), in both systems B\_0.9 (Fig. 7a) and B\_0.95 (Fig. 7b). These results suggest that small fractions  
 438 of these TPUs only reach the oligomeric state or form cyclic structures during the polymerization  
 439 process. The presence of oligomers or cyclic structures was also detected by SEC (Fig 7c)  
 440 constituting about 4% of the total mass in B\_0.90 and 3% in B\_0.95. These are considerable amounts  
 441 when concerning plasticization and compatibilization, increasing the interphase between the HS and  
 442 SS within the bio-TPUs. The presence of these oligomers could help to explain both the relatively high  
 443 MFI values (Table 7) and the thermal dependent variation of phase-separated HS (Fig. 3). However,  
 444 these oligomeric species seem to be strongly H-bonded within the HS-SS interphase, allowing the  
 445 sustenance of good mechanical properties even with occurring plasticization. Taking that into account,  
 446 the system B\_0.95 seemed to be a good example of properties balance for the application in FDM 3D

447 printing, since it presented an ideal MFI value (10.2g/10min) at a moderate printing temperature (170  
448 °C), and would produce a printed TPU part with good E (37 MPa),  $TS_b$  (20 MPa) and  $\epsilon$  (621%).

449

#### 450 4. Conclusion

451 Bio-based TPUs with [NCO]/[OH] molar ratios ranging from 0.9 to 1.0 were successfully  
452 synthesized using a two-step method, where the molecular weight of the TPUs was inversely  
453 proportional to [NCO]/[OH]. Also, the type of bio-glycol used (bio-butanediol, BDO or bio-propanediol,  
454 PDO) and [NCO]/[OH] affected the degree of phase separation (DPS) and the H-bonding within the  
455 TPU matrix. Although all the synthesized TPUs exhibited (micro)phase-separated morphology, the  
456 highest DPS was observed for the bio-BDO-based TPUs. Moreover, the Bio-BDO-based TPUs  
457 displayed the highest tensile strengths and elongations at break, but at the same time, the lowest melt  
458 flow indexes (MFI) due to the presence of oligomers (residual from the synthetic process) acting as  
459 plasticizers and hard (HS) / soft (SS) segment coupling agents. Interestingly, this allowed obtaining  
460 bio-TPUs with a broad range of MFI values, including within the ideal range for FDM 3D printing.  
461 Additionally, all prepared TPUs presented good thermal stability (up to 315°C), with a two-step thermal  
462 degradation associated with the decomposition of their HS and SS.

463 Altogether, the integrated control of the H-bonding, phase-separation, and  
464 plasticization/compatibilization via simple synthetic parameters allowed obtaining bio-TPU materials  
465 that present good thermomechanical properties in the solid-state while also presenting ideal  
466 processability parameters. Consequently, this work not only evaluated the optimum synthesis  
467 conditions but also correlated them with the resulting structural effects and the systems' processability,  
468 prospecting their applications. Moreover, it was demonstrated that the most application-effective TPU  
469 systems are not necessarily the ones with the best bulk thermomechanical properties, hopefully  
470 allowing for competitive applications of these bio-based systems into the emerging market of additive  
471 manufacturing.

472 The next challenge to be addressed, associated with these systems, is the formulation of a  
473 fully (100%) bio-based TPU that is specifically designed for 3D printing. This would further decrease

474 the environmental impact of additive manufacturing, while still being competitive with currently  
475 commercially available petroleum-based TPUs.

476

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481 measurements.

#### 482 **Conflict of interest**

483 The authors declare that they have no conflict of interest.

#### 484 **Founding**

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#### 489 **References**

- 490 Adkesson, D.N., Alsop, A.W., Ames, T.T., Chu, L.A., Disney, J.M., Dravis, B.C., Fitzgibbon, P.,  
491 Gaddy, J.M., Gallagher, F.G., Lehnhardt, W.F., Lievense, J.C., Luyben, M.L., Seapan, M.,  
492 Trotter, R.E., Wendt, G.M., Yu, E.K., 2012. Purification of biologically-produced 1,3-  
493 propanediol. US8183417B2.
- 494 Beniah, G., Liu, K., Heath, W.H., Miller, M.D., Scheidt, K.A., Torkelson, J.M., 2016. Novel  
495 thermoplastic polyhydroxyurethane elastomers as effective damping materials over broad  
496 temperature ranges. *Eur. Polym. J.* 84, 770–783.  
497 <https://doi.org/10.1016/J.EURPOLYMJ.2016.05.031>
- 498 Buckley, C.P., Prisacariu, C., Martin, C., 2010. Elasticity and inelasticity of thermoplastic polyurethane  
499 elastomers: Sensitivity to chemical and physical structure. *Polymer.* 51, 3213–3224.

- 500 <https://doi.org/10.1016/j.polymer.2010.04.069>
- 501 Burk, M.J., Burgard, A.P., Osterhout, R.E., Sun, J., 2015. Microorganisms for the production of 1,4-  
502 butanediol. US20130109069A1.
- 503 Cervantes-Uc, J.M., Moo Espinosa, J.I., Cauich-Rodríguez, J.V., Avila-Ortega, A., Vazquez-Torres, H.,  
504 Marcos-Fernández, A., San Roman, J., 2009. TGA / FTIR studies of segmented aliphatic  
505 polyurethanes and their nanocomposites prepared with commercial montmorillonites. *Polym.*  
506 *Degrad. Stab.* 94, 1666–1677. <https://doi.org/10.1016/j.polymdegradstab.2009.06.022>
- 507 de Oliveira, S.A., Nunes de Macedo, J.R., Rosa, D. dos S., 2019. Eco-efficiency of poly (lactic acid)-  
508 Starch-Cotton composite with high natural cotton fiber content: Environmental and functional  
509 value. *J. Clean. Prod.* 217, 32–41. <https://doi.org/10.1016/j.jclepro.2019.01.198>
- 510 Donato, R.K., Mija, A., 2019. Keratin Associations with Synthetic, Biosynthetic and Natural Polymers:  
511 An Extensive Review. *Polymers.* 12, 32. <https://doi.org/10.3390/polym12010032>
- 512 Duan, L., D'Hooge, D.R., Spoerk, M., Cornillie, P., Cardon, L., 2018. Facile and Low-Cost Route for  
513 Sensitive Stretchable Sensors by Controlling Kinetic and Thermodynamic Conductive Network  
514 Regulating Strategies. *ACS Appl. Mater. Interfaces* 10, 22678–22691.  
515 <https://doi.org/10.1021/acsami.8b03967>
- 516 Eceiza, A., Martin, M.D., de la Caba, K., Kortaberria, G., Gabilondo, N., Corcuera, M.A., Mondragon,  
517 I., 2008. Thermoplastic Polyurethane Elastomers Based on Polycarbonate Diols With Different  
518 Soft Segment Molecular Weight and Chemical Structure: Mechanical and Thermal Properties.  
519 *Polym. Eng. Sci.* 48, 297–306. <https://doi.org/10.1002/pen>
- 520 Emptage, M., Haynie, S.L., Laffend, L.A., Pucci, J.P., Whited, G.M., 2003. Process for the biological  
521 production of 1,3-propanediol with high titer. US6514733B1.
- 522 Fang, C., Zhou, X., Yu, Q., Liu, S., Guo, D., Yu, R., Hu, J., 2014. Synthesis and characterization of low  
523 crystalline waterborne polyurethane for potential application in water-based ink binder. *Prog.*  
524 *Org. Coatings.* 77, 61–71. <https://doi.org/10.1016/j.porgcoat.2013.08.004>
- 525 Ferg, E.E., Bolo, L.L., 2013. A correlation between the variable melt flow index and the molecular  
526 mass distribution of virgin and recycled polypropylene used in the manufacturing of battery



- 527 cases. *Polym. Test.* 32, 1452–1459. <https://doi.org/10.1016/J.POLYMERTESTING.2013.09.009>
- 528 Guerreiro, S.D.C., João, I.M., Pimentel Real, L.E., 2012. Evaluation of the influence of testing  
529 parameters on the melt flow index of thermoplastics. *Polym. Test.* 31, 1026–1030.  
530 <https://doi.org/10.1016/J.POLYMERTESTING.2012.07.008>
- 531 Herrera, M., Matuschek, G., Kettrup, A., 2002. Thermal degradation of thermoplastic polyurethane  
532 elastomers (TPU) based on MDI. *Polym. Degrad. Stab.* 78, 323–331.  
533 [https://doi.org/10.1016/S0141-3910\(02\)00181-7](https://doi.org/10.1016/S0141-3910(02)00181-7)
- 534 Hossieny, N., Shaayegan, V., Ameli, A., Saniei, M., Park, C.B., 2017. Characterization of hard-  
535 segment crystalline phase of thermoplastic polyurethane in the presence of butane and glycerol  
536 monostearate and its impact on mechanical property and microcellular morphology. *Polymer.* 112,  
537 208–218. <https://doi.org/10.1016/J.POLYMER.2017.02.015>
- 538 Kasprzyk, P., Datta, J., 2019. Novel bio-based thermoplastic poly(ether-urethane)s. Correlations  
539 between the structure, processing and properties. *Polymer.* 160, 1–10.  
540 <https://doi.org/10.1016/j.polymer.2018.11.032>
- 541 Kasprzyk, P., Datta, J., 2018. Effect of molar ratio [NCO]/[OH] groups during prepolymer chains  
542 extending step on the morphology and selected mechanical properties of final bio-based  
543 thermoplastic poly(ether-urethane) materials. *Polym. Eng. Sci.* 58, E199 - E206.  
544 <https://doi.org/10.1002/pen.24874>
- 545 Kasprzyk, P., Sadowska, E., Datta, J., 2019. Investigation of Thermoplastic Polyurethanes  
546 Synthesized via Two Different Prepolymers. *J. Polym. Environ.* 27, 2588 - 2500.  
547 <https://doi.org/10.1007/s10924-019-01543-7>
- 548 Kopczyńska, P., Datta, J., 2016. Single-phase product obtained via crude glycerine depolymerisation  
549 of polyurethane elastomer: structure characterisation and rheological behaviour. *Polym. Int.* 65,  
550 946–954. <https://doi.org/10.1002/pi.5128>
- 551 Król, P., 2007. Synthesis methods, chemical structures and phase structures of linear polyurethanes.  
552 Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and  
553 ionomers. *Prog. Polym. Sci.* 52, 915–1015. <https://doi.org/10.1016/j.pmatsci.2006.11.001>



- 554 Landim, L.B., Miranda, E.O., de Araújo, N.A., Pinto, J.C., Cabral-Albuquerque, E.C.M., Cunha, S.,  
555 Fialho, R.L., 2019. Solvent-free mechanochemical polymerization of urea-succinic acid and urea-  
556 succinic acid-glycerol mixtures. *J. Clean. Prod.* 238.  
557 <https://doi.org/10.1016/j.jclepro.2019.117742>
- 558 Lee, Y.-H., Kang, B.-K., Kim, H.-D., Yoo, H.-J., Kim, J.-S., Huh, J.-H., Jung, Y.-J., Lee, D.-J., 2009.  
559 Effect of hot pressing/melt mixing on the properties of thermoplastic polyurethane. *Macromol.*  
560 *Res.* 17, 616–622. <https://doi.org/10.1007/BF03218918>
- 561 Lei, W., Fang, C., Zhou, X., Cheng, Y., Yang, R., Liu, D., 2017. Morphology and Thermal Properties of  
562 Polyurethane Elastomer Based on Representative Structural Chain Extenders. *Thermochim.*  
563 *Acta.* 653, 116 - 125. <https://doi.org/10.1016/j.tca.2017.04.008>
- 564 Lligadas, G., Ronda, J.C., Galia, M., Cadiz, V., 2013. Renewable polymeric materials from vegetable  
565 oils : a perspective. *Mater. Today.* 16, 337–343. <https://doi.org/10.1016/j.mattod.2013.08.016>
- 566 Lvii, T., Ryszkowska, J., Urea-urethane, S., 2012. Supermolecular structure , morphology and physical  
567 properties of urea-urethane elastomers. *Polimery.* 12, 775–902.
- 568 Ma, J., Harstvedt, J.D., Dunaway, D., Bian, L., Jaradat, R., 2018. An exploratory investigation of  
569 Additively Manufactured Product life cycle sustainability assessment. *J. Clean. Prod.* 192, 55–70.  
570 <https://doi.org/10.1016/j.jclepro.2018.04.249>
- 571 Mizera, K., Ryszkowska, J., 2016. Polyurethane elastomers from polyols based on soybean oil with a  
572 different molar ratio. *Polym. Degrad. Stab.* 132, 21–31.  
573 <https://doi.org/10.1016/j.polymdegradstab.2016.05.004>
- 574 Niemczyk, A., Piegat, A., Sonseca Olalla, Á., El Fray, M., 2017. New approach to evaluate microphase  
575 separation in segmented polyurethanes containing carbonate macrodiol. *Eur. Polym. J.* 93, 182–  
576 191. <https://doi.org/10.1016/j.eurpolymj.2017.05.046>
- 577 Parcheta, P., Datta, J., 2017. Environmental impact and industrial development of biorenewable  
578 resources for polyurethanes. *Crit. Rev. Environ. Sci. Technol.* 47, 1986–2016.  
579 <https://doi.org/10.1080/10643389.2017.1400861>
- 580 Pielichowski, K., Leszczy, A., 2004. TG-FTIR study of the thermal degradation of polyoxymethelene



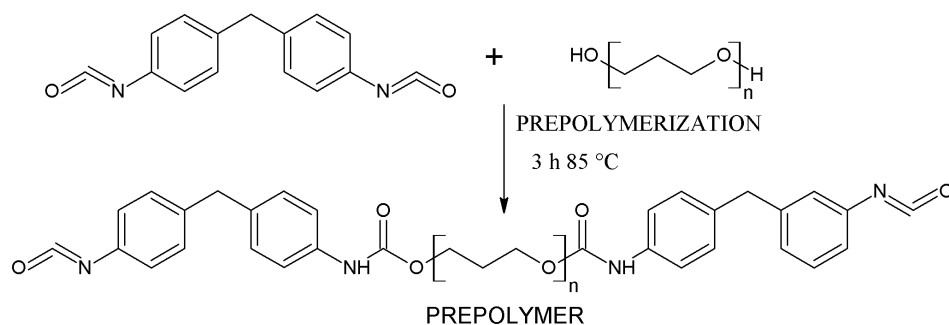
- 581 (POM)/ thermoplastic polyurethane (TPU) blends. *J. Therm. Anal. Calorim.* 78, 631–637.
- 582 Prisacariu, C., 2011. Thermal behaviour of polyurethane elastomers, in: *Polyurethane Elastomers*.  
583 Springer Vienna, Vienna, pp. 61–101. [https://doi.org/10.1007/978-3-7091-0514-6\\_3](https://doi.org/10.1007/978-3-7091-0514-6_3)
- 584 Prisacariu, C., Scortanu, E., Agapie, B., 2013. *Journal of Industrial and Engineering Chemistry Effect*  
585 *of the hydrogen bonding on the inelasticity of thermoplastic polyurethane elastomers. J. Ind. Eng.*  
586 *Chem.* 19, 113–119. <https://doi.org/10.1016/j.jiec.2012.07.012>
- 587 Righetti, M.C., 2017. Crystallization of Polymers Investigated by Temperature-Modulated DSC.  
588 *Materials.* 10, 442–464. <https://doi.org/10.3390/ma10040442>
- 589 Saralegi, A., Rueda, L., Fernández-D'Arlas, B., Mondragon, I., Eceiza, A., Corcuera, M.A., 2013.  
590 Thermoplastic polyurethanes from renewable resources: Effect of soft segment chemical  
591 structure and molecular weight on morphology and final properties. *Polym. Int.* 62, 106–115.  
592 <https://doi.org/10.1002/pi.4330>
- 593 Verstraete, G., Van Renterghem, J., Van Bockstal, P.J., Kasmi, S., De Geest, B.G., De Beer, T.,  
594 Remon, J.P., Vervaet, C., 2016. Hydrophilic thermoplastic polyurethanes for the manufacturing  
595 of highly dosed oral sustained release matrices via hot melt extrusion and injection molding. *Int.*  
596 *J. Pharm.* 506, 214–221. <https://doi.org/10.1016/j.ijpharm.2016.04.057>
- 597 Wang, S., Capoen, L., D'hooge, D.R., Cardon, L., 2017. Can the melt flow index be used to predict the  
598 success of fused deposition modelling of commercial poly(lactic acid) filaments into 3D printed  
599 materials? *Plast. Rubber Compos.* 47, 1–8. <https://doi.org/10.1080/14658011.2017.1397308>
- 600 Wirpsza, Z., 1993. *Poliuretany: chemia, technologia, zastosowanie*. WNT, Warszawa.
- 601 Xie, F., Zhang, T., Bryant, P., Colwell, J.M., Laycock, B., 2019. Degradation and stabilization of  
602 polyurethane elastomers. *Prog. Polym. Sci.* 90, 211–268.  
603 <https://doi.org/10.1016/j.progpolymsci.2018.12.003>
- 604 Xu, J., Wang, K., Sheng, H., Gao, M., Zhang, S., Tan, J., 2020. Energy efficiency optimization for  
605 ecological 3D printing based on adaptive multi-layer customization. *J. Clean. Prod.* 245, 118826.  
606 <https://doi.org/10.1016/j.jclepro.2019.118826>



- 607 Yang, H., Wang, X., Yu, B., Song, L., Hu, Y., Yuen, R.K.K., 2012. Effect of borates on thermal  
608 degradation and flame retardancy of epoxy resins using polyhedral oligomeric silsesquioxane as  
609 a curing agent. *Thermochim. Acta.* 535, 71–78. <https://doi.org/10.1016/j.tca.2012.02.021>
- 610 Yilgor, E., Atilla, G.E., Ekin, A., Kurt, P., Yilgor, I., 2003. Isopropyl alcohol: An unusual, powerful,  
611 “green” solvent for the preparation of silicone-urea copolymers with high urea contents. *Polymer*  
612 44, 7787–7793. <https://doi.org/10.1016/j.polymer.2003.10.048>
- 613 Yilgor, I., Yilgor, E., Guler, I.G., Ward, T.C., Wilkes, G.L., 2006. FTIR investigation of the influence of  
614 diisocyanate symmetry on the morphology development in model segmented polyurethanes.  
615 *Polymer.* 47, 4105–4114. <https://doi.org/10.1016/j.polymer.2006.02.027>
- 616

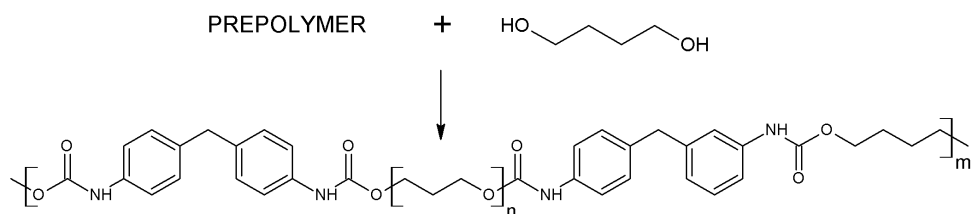
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## I STEP

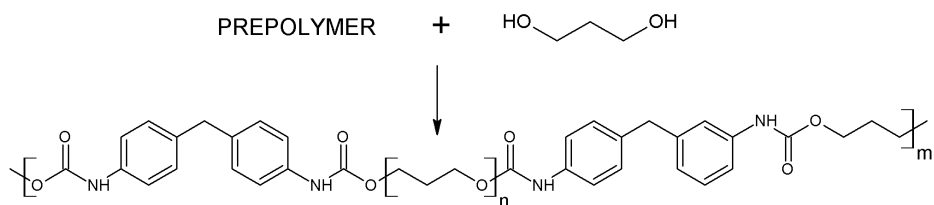


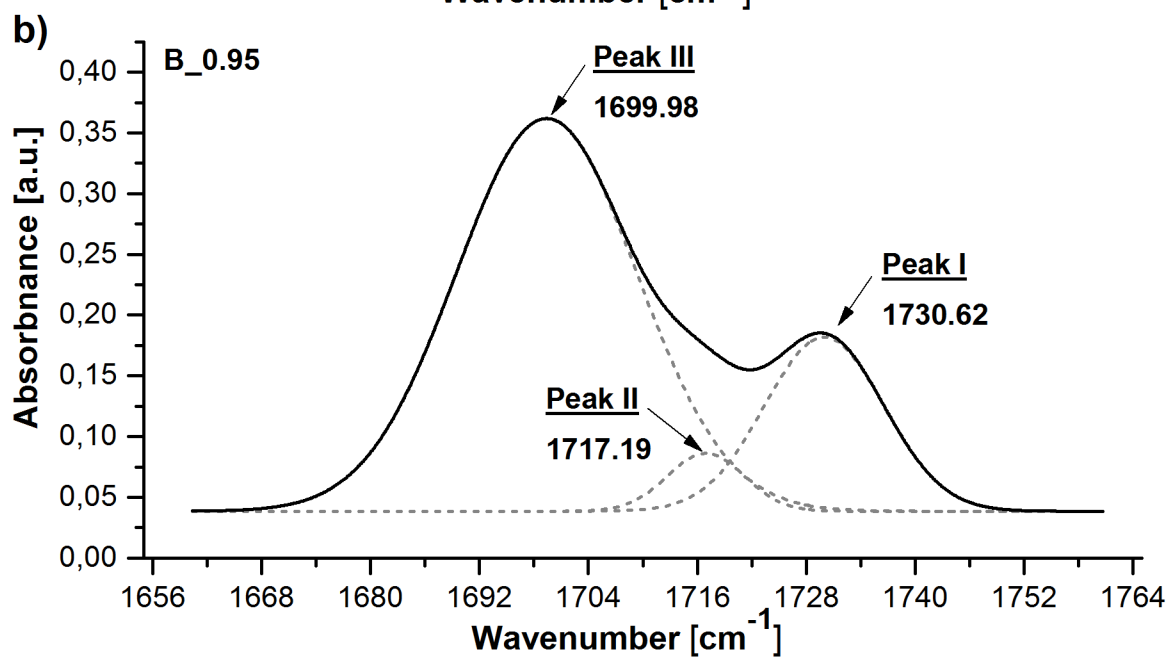
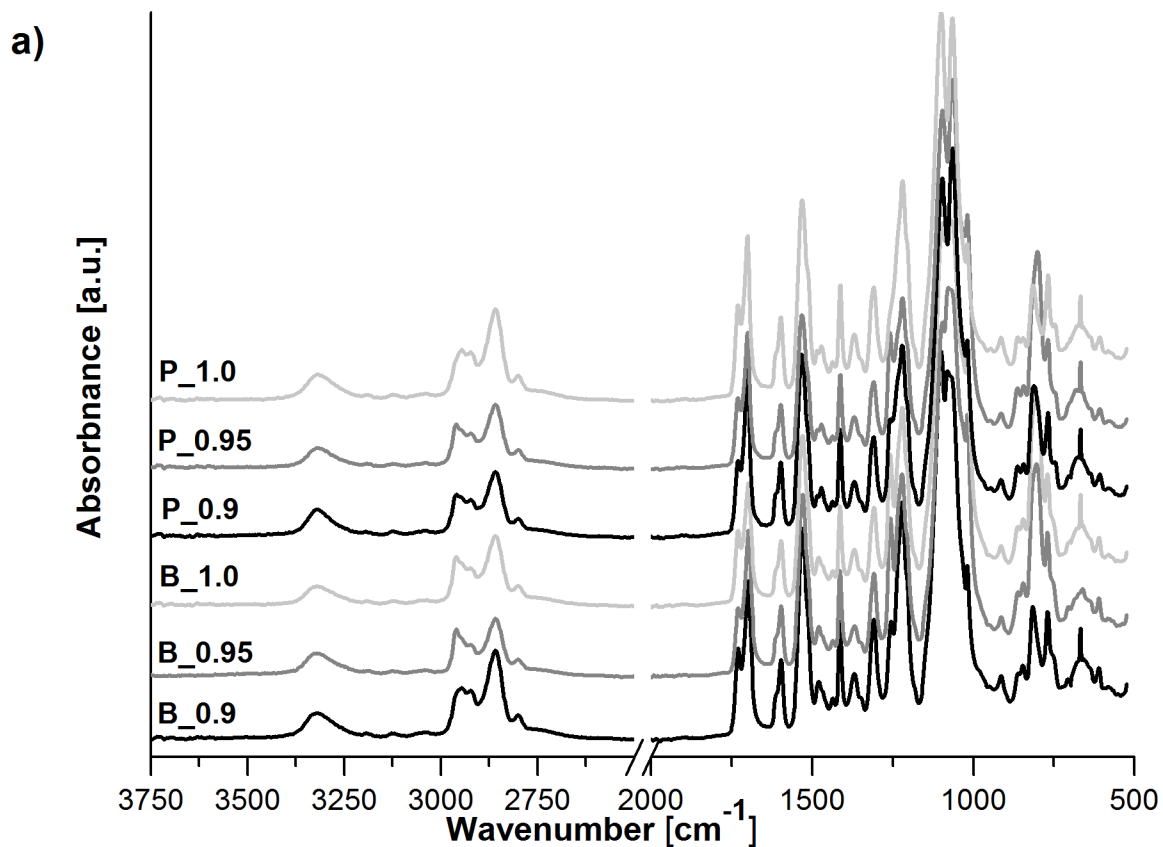
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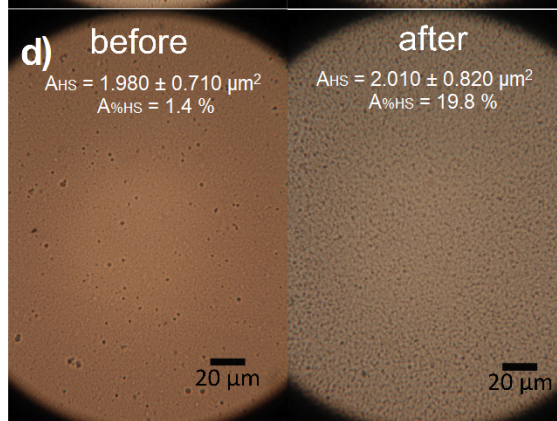
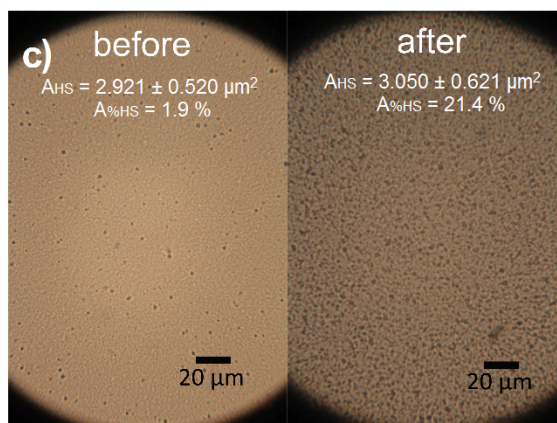
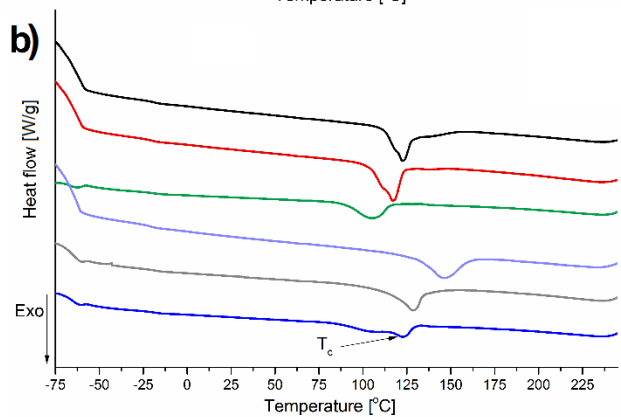
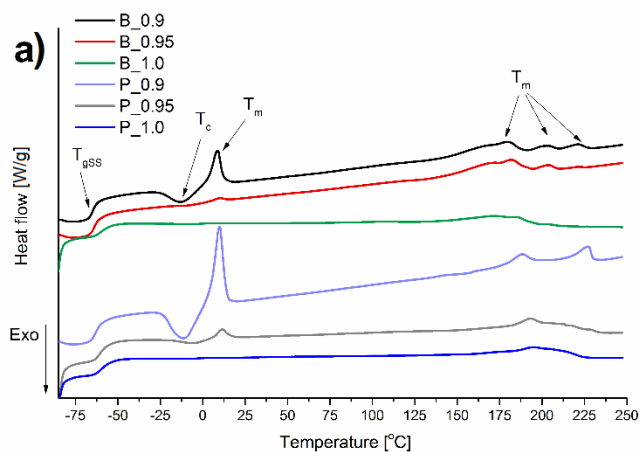
a) extension of the prepolymer chains with using bio-BDO

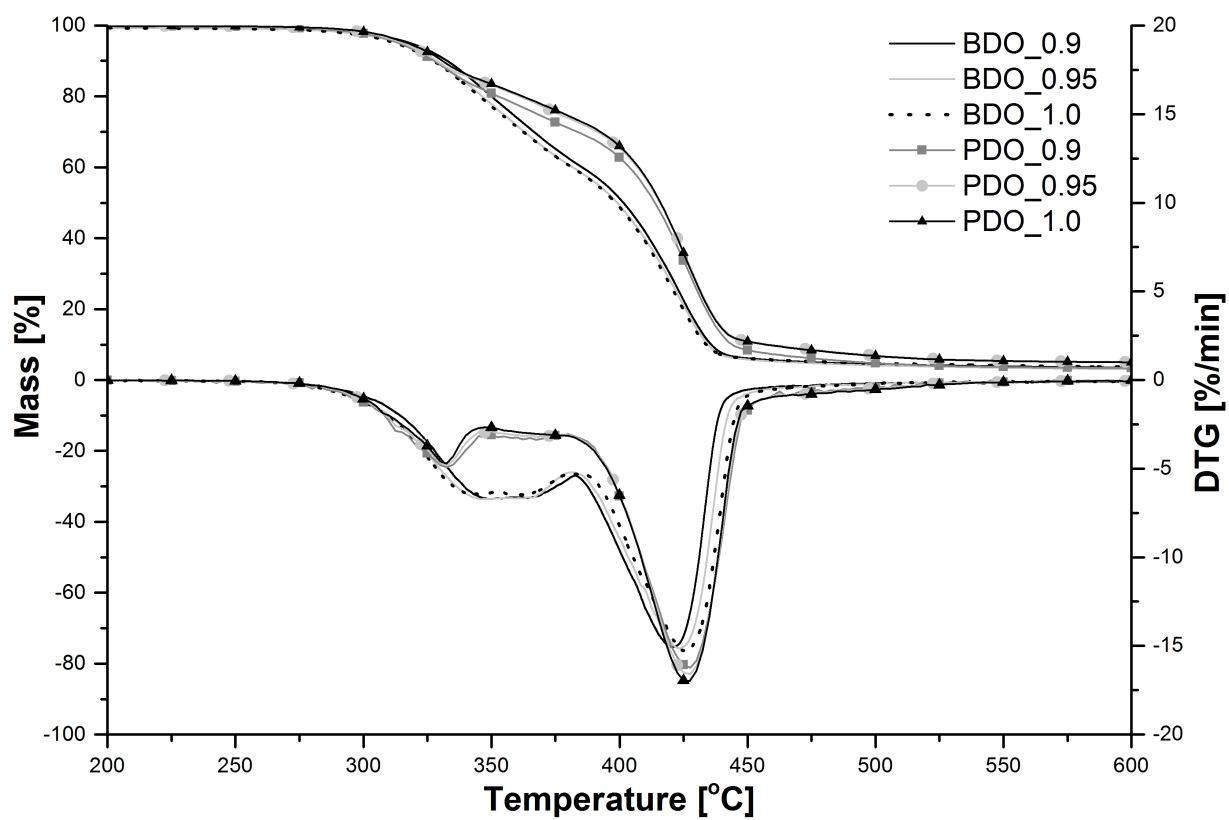


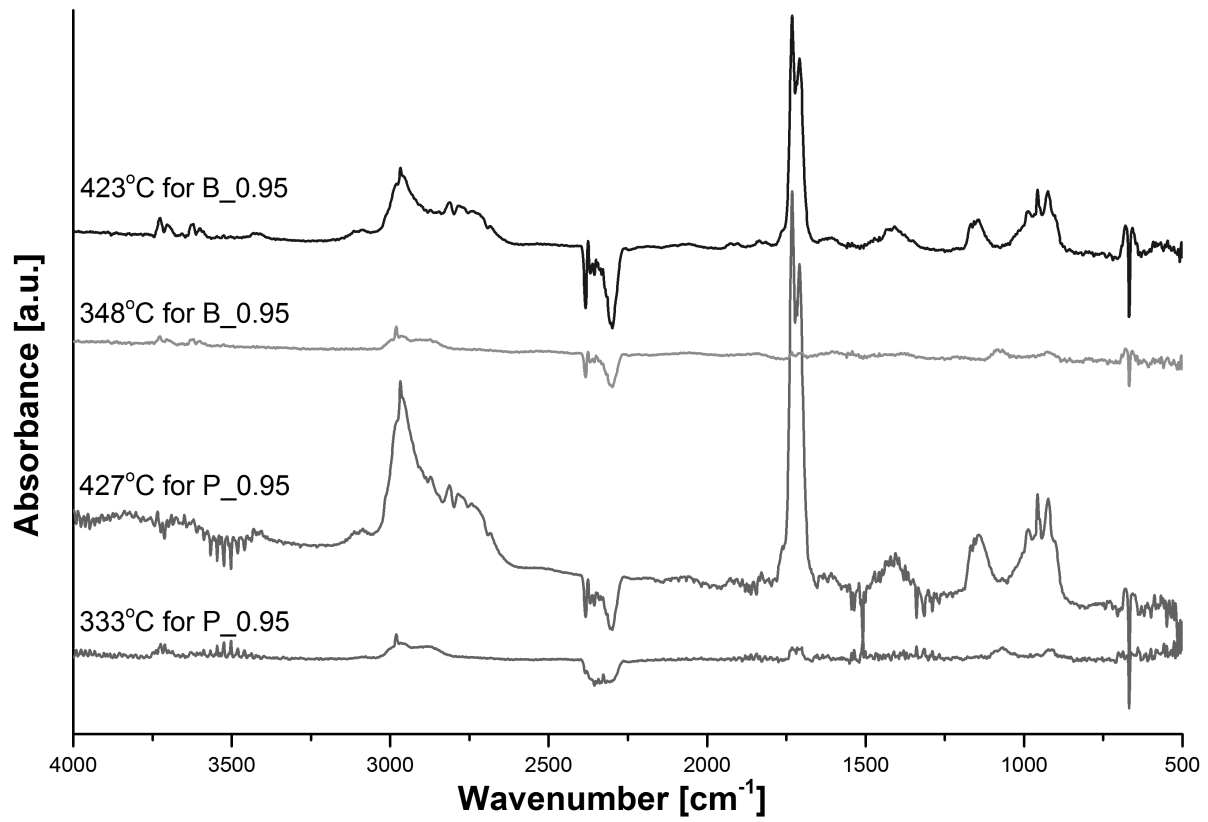
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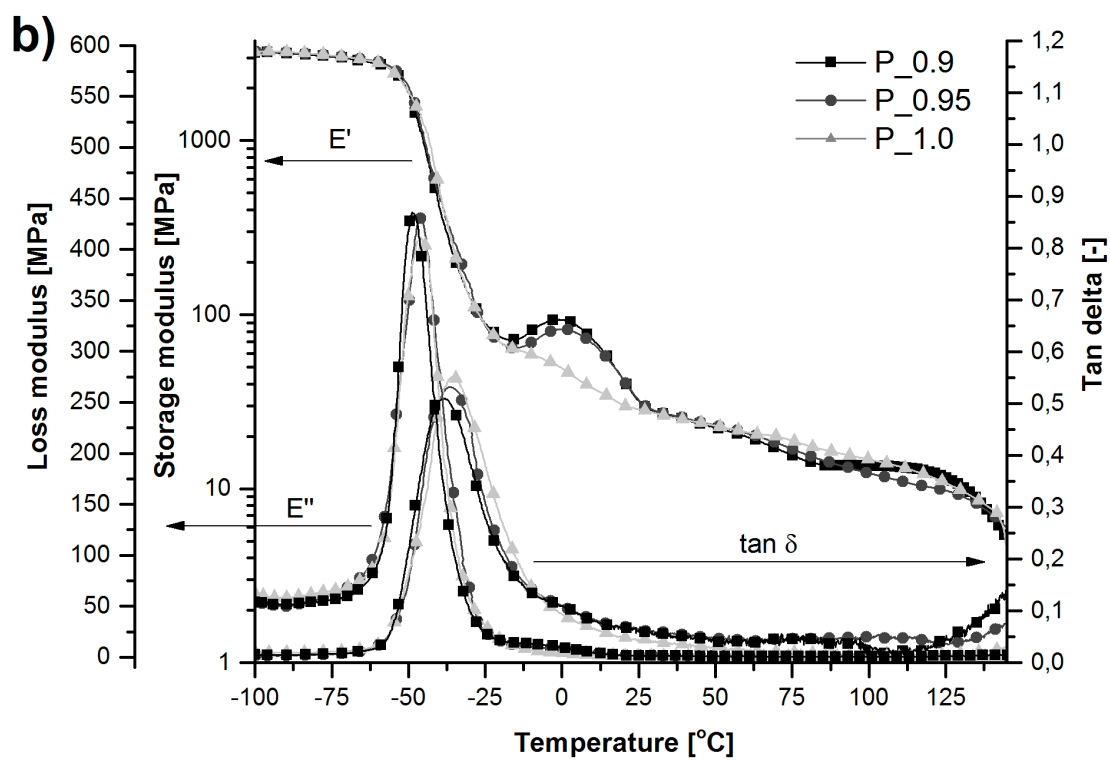
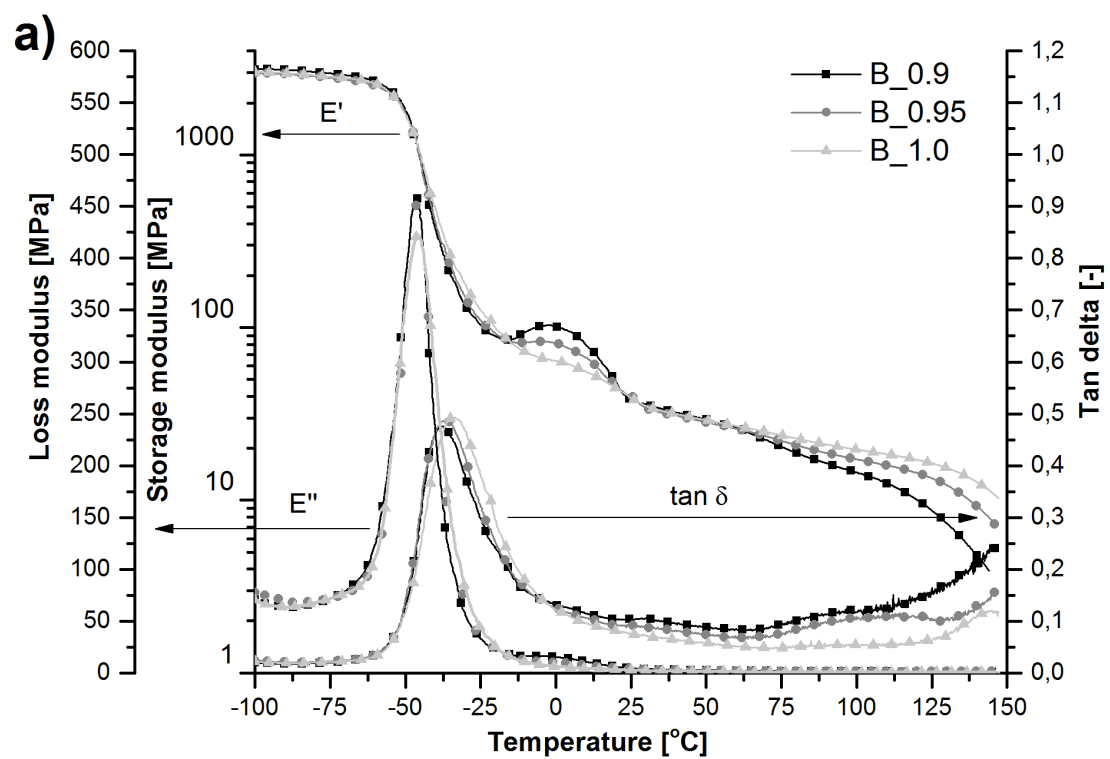


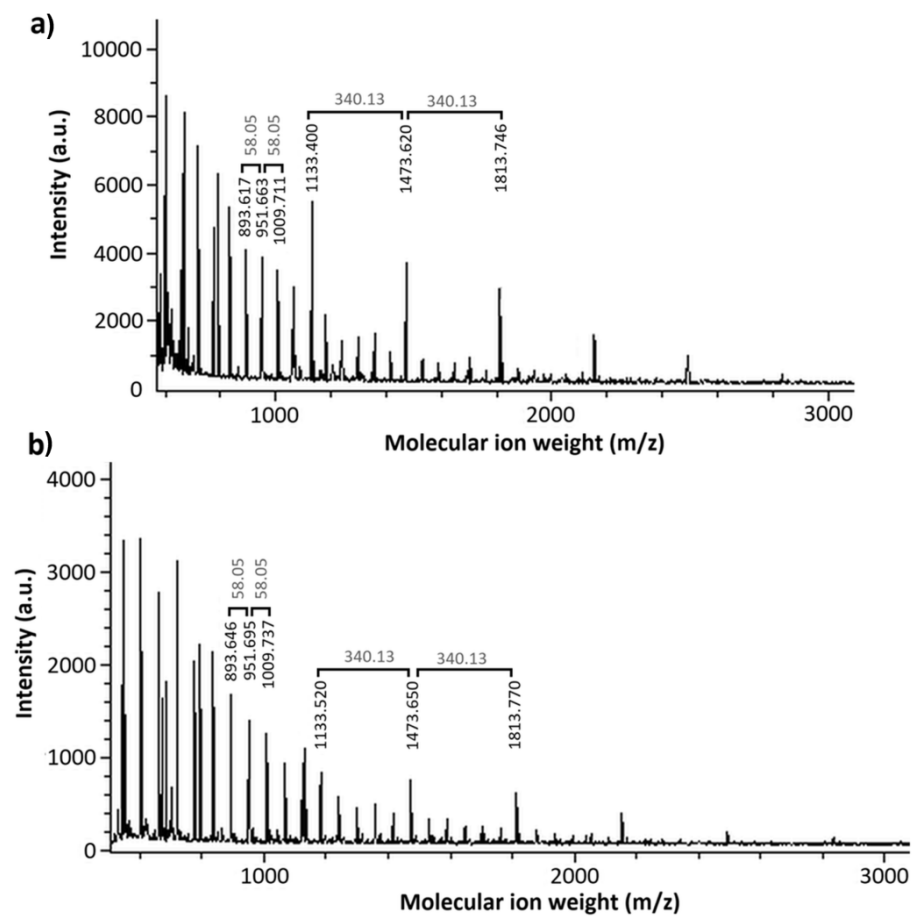






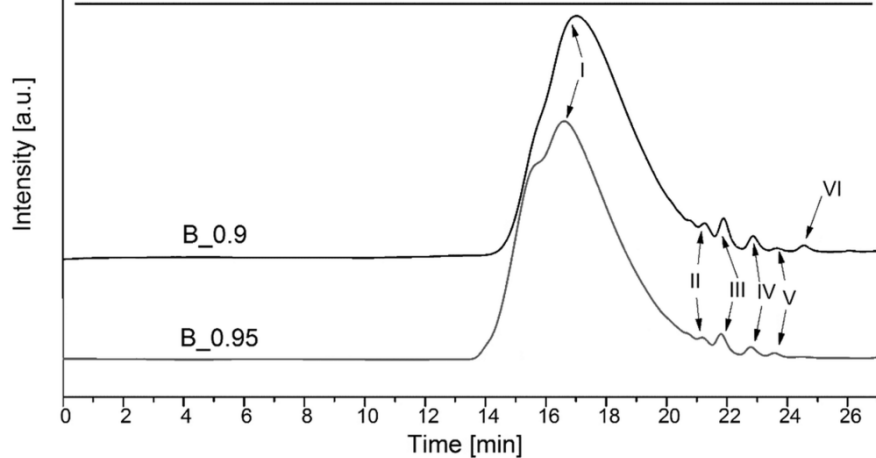






**c)**

Sample	$M_{pI}$	$M_{pII}$	$M_{pIII}$	$M_{pIV}$	$M_{pV}$	$M_{pVI}$
B_0.9	42153 (95.9%)	2353 (1.4%)	1528 (1.9%)	786 (0.7%)	450 (0.1%)	225 (0.003%)
B_0.95	53239 (96.9%)	2384 (0.9%)	1541 (1.3%)	750 (0.6%)	442 (0.3%)	-



**Figure captions**

**Figure 1.** The synthesis of bio-based thermoplastic TPUs.

**Figure 2.** a) FTIR-ATR spectra of bio-based TPU systems, b) Gauss model fitting of sample B\_0.95. The solid line represents the sum of the overlapped peak-components (I – III), and the dashed lines represent the deconvoluted distributions.

**Figure 3.** DSC thermal transition curves of the second heating (a) and first cooling (b) ramps of the bio-based TPUs. POM microphotographs of samples B\_0.9 (c), and B\_0.95 (d), before (left) and after (right) a thermal treatment at 250 °C (under vacuum) followed by a controlled cooling at 2 °C/min. AHS is the area and A%HS is the area fraction (and an estimation of the volume fraction) of HS aggregates.

**Figure 4.** TGA and DTG curves of the bio-based TPUs.

**Figure 5.** FTIR spectra recorded during the 1st and 2nd mass loss step for the bio-TPU systems B\_0.95 and P\_0.95.

**Figure 6.** DMTA curves of the TPUs based on (a) bio-BDO and (b) bio-PDO as a function of the temperature.

**Figure 7.** MALDI-TOF spectra of systems a) B\_0.9 and b) B\_0.95 highlighting the repetitive low molecular mass units representing monomeric/oligomeric species in the final TPUs, and c) SEC results of systems B\_0.9 and B\_0.95, where  $M_{pn}$  represents  $M_n$  (g/mol) of the nth peak.

### Highlights

- Available H-bond donor groups improve interphase bonding.
- Tunability between hard and soft TPU segments based on the [NCO]/[OH] molar ratio.
- Broad processability range, including in ideal range for FDM additive manufacturing.

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