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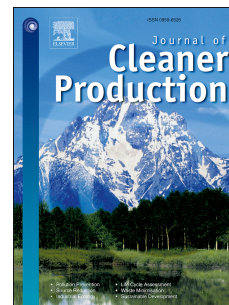
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Article title: The role of hydrogen bonding on tuning hard-soft segments in bio-based thermoplastic poly(ether-urethane)s

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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 CO₂ 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 cm^{-1} at 4
126 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 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 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 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_α).

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 ml/min . The sample weight was
151 approximately 6 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 kV and 30 mA and monochromatized with Ni foil (β filter). The measurements were
158 performed in Bragg-Brentano geometry in the range of $2\theta = 5 - 70^\circ$ with a step 0.1° . The exposure
159 time at each step was 15 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 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 (NaCF₃COO; 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_0.9	0.9	34.6	20	44 300	2.21	10365
B_0.95	0.95	34.3	24	59 900	2.45	19374
B_1.0	1.0	34.1	31	84 500	2.66	86648
P_0.9	0.9	34.1	18	38 300	2.06	10182
P_0.95	0.95	33.8	23	50 500	2.14	18928
P_1.0	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 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 cm^{-1} , with the
 204 maxima at 3320 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 cm^{-1} was generally more intense for the materials based on bio-
 207 BDO. The bimodal band with the maxima at 2857 cm^{-1} and 2960 cm^{-1} was assigned to the CH
 208 asymmetric and symmetric stretching in the CH_2 groups, respectively, while the deformation vibrations
 209 of the C-H groups were observed at 1410 cm^{-1} . The carbonyl groups (C=O) stretching vibrations were
 210 observed in the range between 1660 and 1740 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 cm^{-1}) of SS (Niemczyk et al.,
 214 2017). Moreover, bands associated with the urethane groups' N-H out-of-plane bending (1599 cm^{-1})
 215 and C–N stretching vibration (1520 cm^{-1}), and with the polyether polyol's free ether bond (strong, 1100
 216 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 cm^{-1}); II) H-bonding
 218 between N-H and C-O-C groups (1062 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 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 cm^{-1} ,
 242 occurring in the prepared TPUs.

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



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

243 * ν - 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 (ΔH_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 ΔH_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 μm (areas ~ 0.502 - 7.080 μm^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 ΔH_c and ΔH_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)	ΔH_c (J/g)	Total ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	Total ΔH_m (J/g)
B_0.9	-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_0.95	-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_1.0	-59.6	104.6	7.0	7.0	2.0	0.03	5.5
					173.2	5.4	
					204.8	0.1	
P_0.9	-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	
P_0.95	-61.6	-5.4	0.8	8.5	11.5	1.0	8.6
		128.2	8.5		193.4	7.6	
P_1.0	-60.1	129.1	6.5	6.5	1.0	0.1	6.1
					195.4	6.0	

290 * ΔH_m – melting enthalpy; ΔH_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 _{5%} [°C]	T _{10%} [°C]	T _{50%} [°C]	T _{90%} [°C]	Char (wt.% at 650°C)	I step degradation		II step degradation	
						T _{max} [°C]	DTG _{max} [%/min]	T _{max} [°C]	DTG _{max} [%/min]
B_0.9	325.8	338.1	403.0	437.4	3.13	349.5	-6.72	422.2	-15.07
B_0.95	326.1	339.0	403.9	437.6	2.77	348.4	-6.70	423.4	-15.13
B_1.0	327.3	339.5	407.5	441.9	3.21	348.1	-6.39	423.2	-15.29
P_0.9	315.9	327.6	413.8	444.1	3.29	332.4	-4.95	427.2	-16.24
P_0.95	316.5	328.7	415.8	458.1	4.97	333.3	-4.82	427.4	-16.61
P_1.0	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 cm^{-1}), with carbonyl groups (1720 cm^{-1}), and with C-O-C vibrations (1070 cm^{-1}). The bands within the
332 range 4000 – 3500 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 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 cm^{-1} , 2670 – 2960 cm^{-1} , 1730 cm^{-1} , 1510 – 1340 cm^{-1} , 1100 cm^{-1} and 911 – 995 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 cm^{-1} were connected with C-H stretching vibrations, the multiple peaks in the range
339 1660 – 1760 cm^{-1} with C=O stretching vibrations, and the band at 954 cm^{-1} with C-H bending vibrations
340 of aldehyde groups. The band at 1100 cm^{-1} was attributed to C-O stretching vibrations, and the bands
341 at 2960 – 2860 cm^{-1} to C-H stretching vibrations of the ether groups. The multiple peaks with several
342 maxima at 1479, 1429, 1335 cm^{-1} originated from the CH_2 and CH_3 groups from polyols. Finally, the
343 band in the range 3573 – 3768 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 1st and 2nd 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° . 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°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_α of the SS, herein also denoted as T_{gSS} (Table 5). Additionally,
 365 above the T_{gSS} the E' decreased steadily up to -20°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°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°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°C	100°C		
B_0.9	-37.8	0.42	3020	420	42	14	-46.2	458
B_0.95	-36.4	0.47	2989	389	41	18	-46.1	449
B_1.0	-35.7	0.50	3010	370	40	20	-45.4	418
P_0.9	-38.2	0.49	3214	405	40	13	-46.6	434
P_0.95	-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 (ϵ) 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 ϵ 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 ϵ), hardness, and density of the bio-TPUs.

Sample	TS_b [MPa]	ϵ [%]	E [MPa]	H [°ShD]	d [g/cm ³]
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B_0.9	7.7 ± 0.2	200 ± 21	38.5 ± 0.2	80.1 ± 0.4	1.138 ± 0.012
B_0.95	20.0 ± 1.5	621 ± 18	37.0 ± 0.9	82.6 ± 0.1	1.135 ± 0.003
B_1.0	28.2 ± 1.3	768 ± 23	33.4 ± 1.1	83.3 ± 0.2	1.131 ± 0.011
P_0.9	7.2 ± 1.2	189 ± 14	33.2 ± 1.1	80.6 ± 0.3	1.162 ± 0.010
P_0.95	18.4 ± 1.0	589 ± 31	30.7 ± 0.2	82.0 ± 0.2	1.160 ± 0.009
P_1.0	24.6 ± 2.1	680 ± 20	29.9 ± 0.8	84.1 ± 0.2	1.157 ± 0.009

404 ***TS_b**– 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_0.9	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_0.95	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_1.0	7.2 ± 0.2	7.4 ± 0.5	10.6 ± 0.3	10.9 ± 0.4	21.2 ± 0.1	21.5 ± 0.1
P_0.9	37.3 ± 0.4	37.5 ± 0.3	56.1 ± 0.1	56.4 ± 0.4	89.1 ± 0.9	90.2 ± 1.0
P_0.95	25.6 ± 0.3	25.4 ± 0.8	32.5 ± 0.5	33.0 ± 0.1	61.3 ± 0.7	61.5 ± 0.6
P_1.0	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 ϵ (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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482 **Conflict of interest**

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

484 **Founding**

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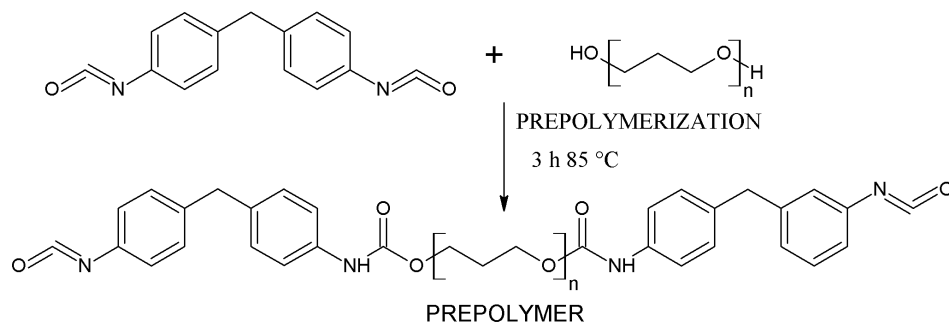
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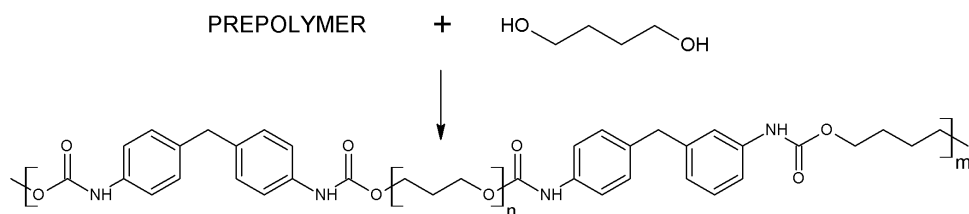
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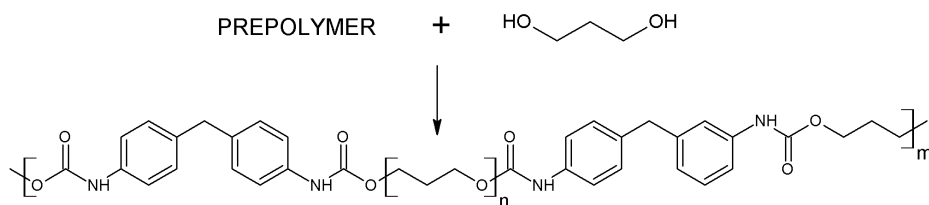


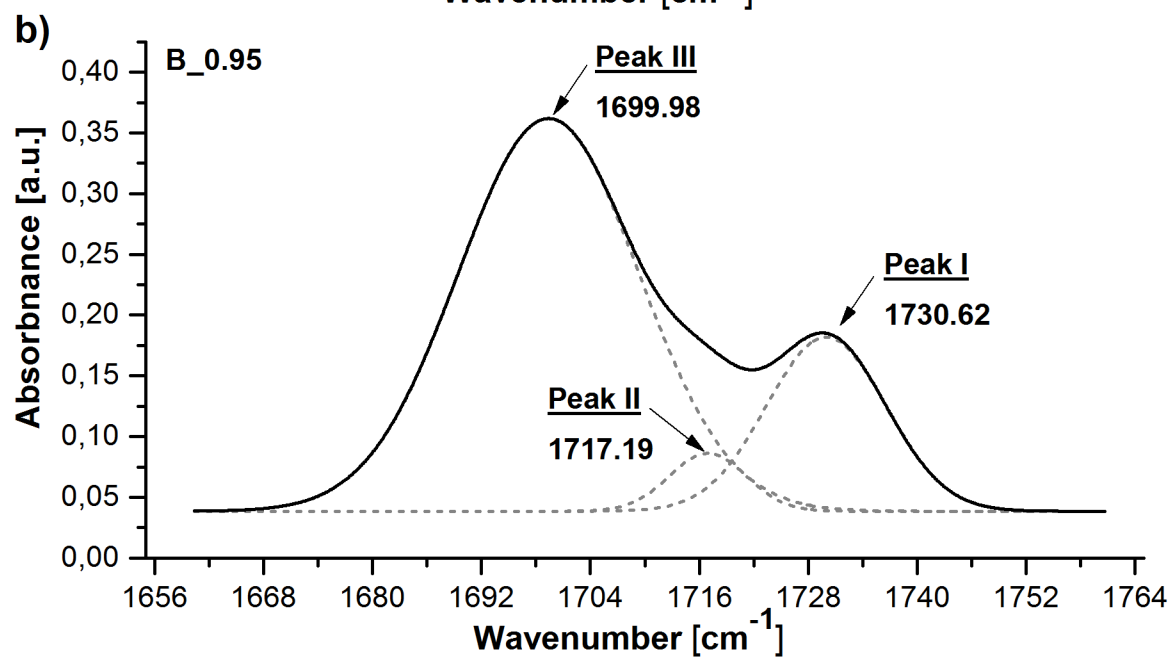
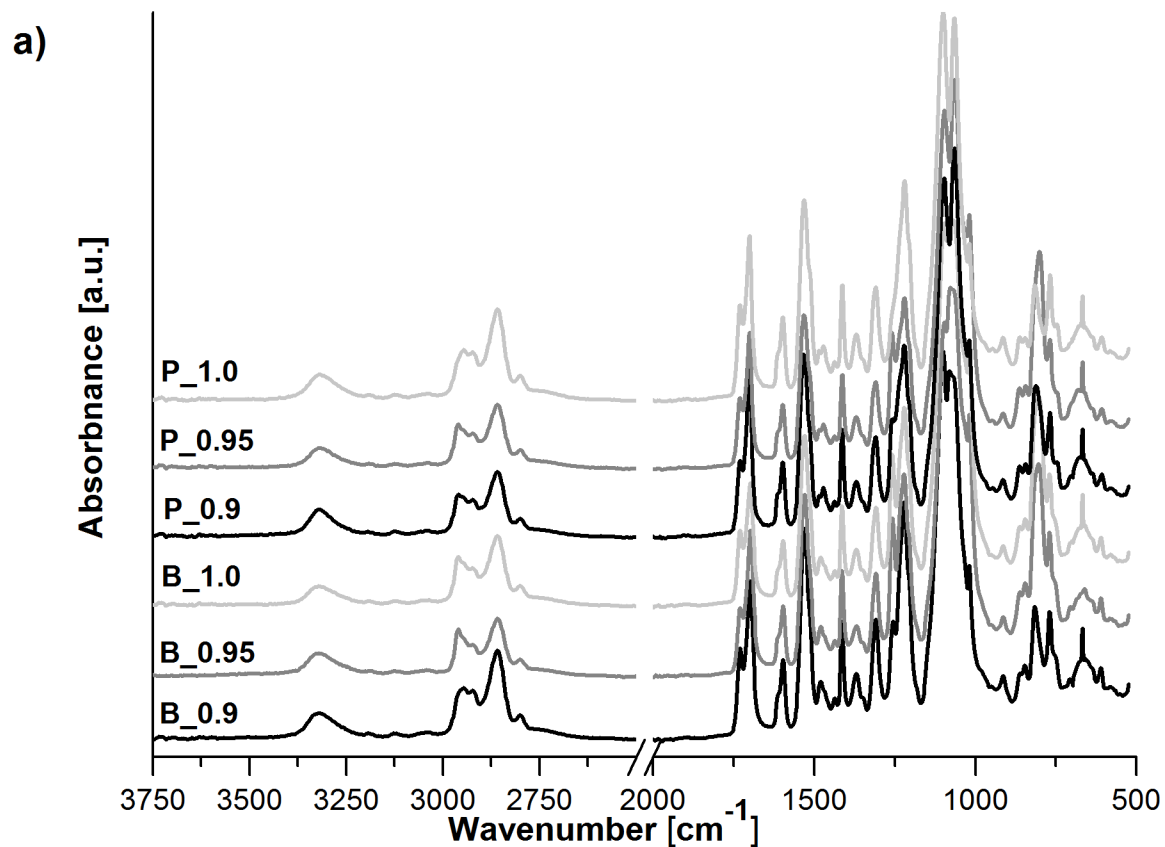
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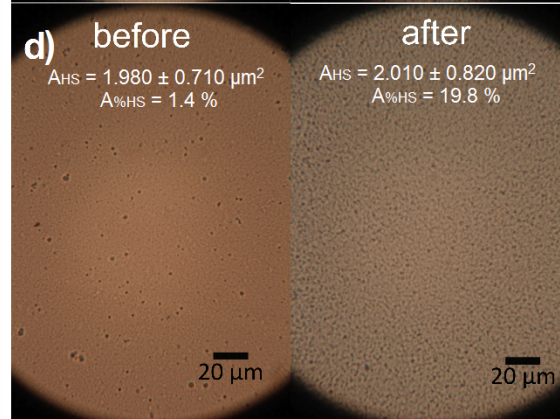
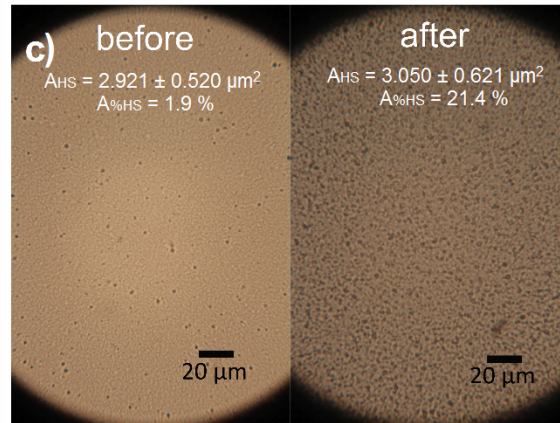
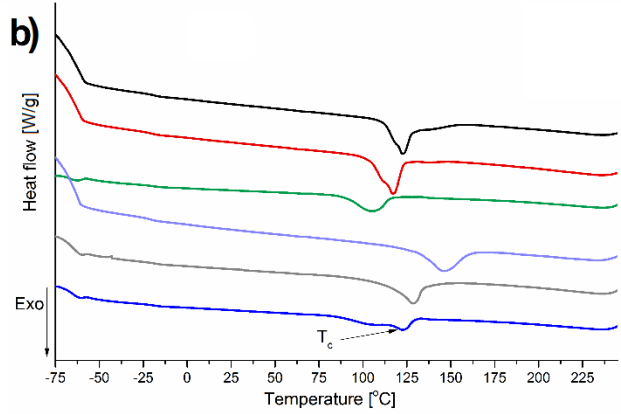
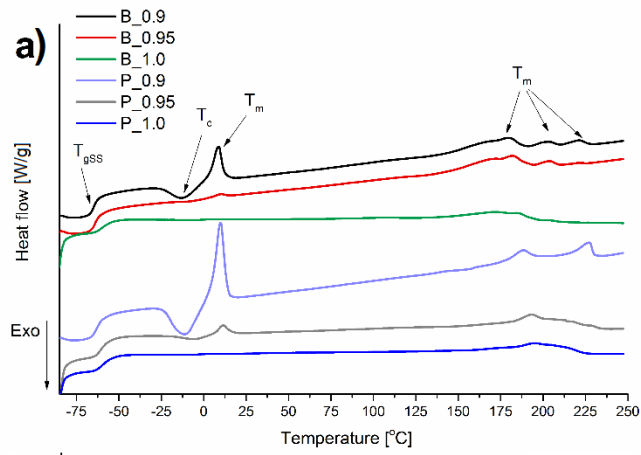
a) extension of the prepolymer chains with using bio-BDO



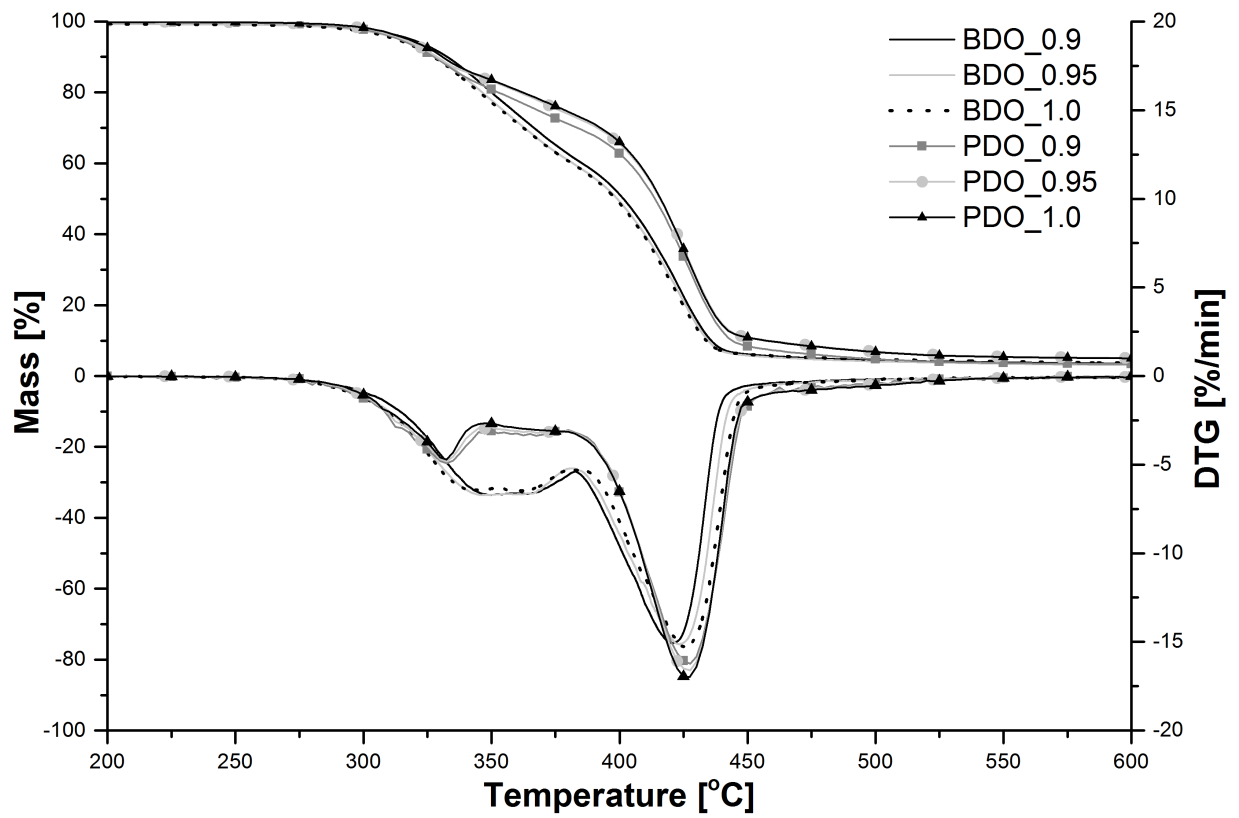
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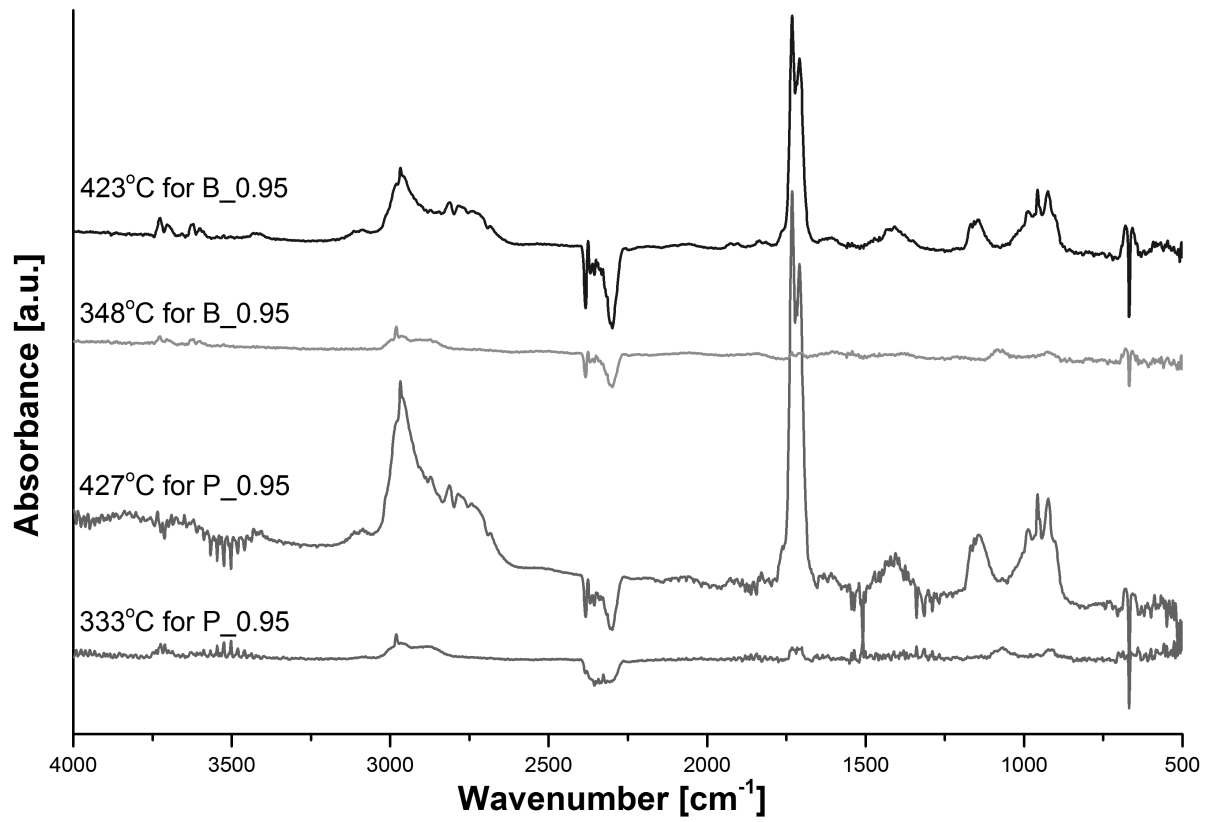


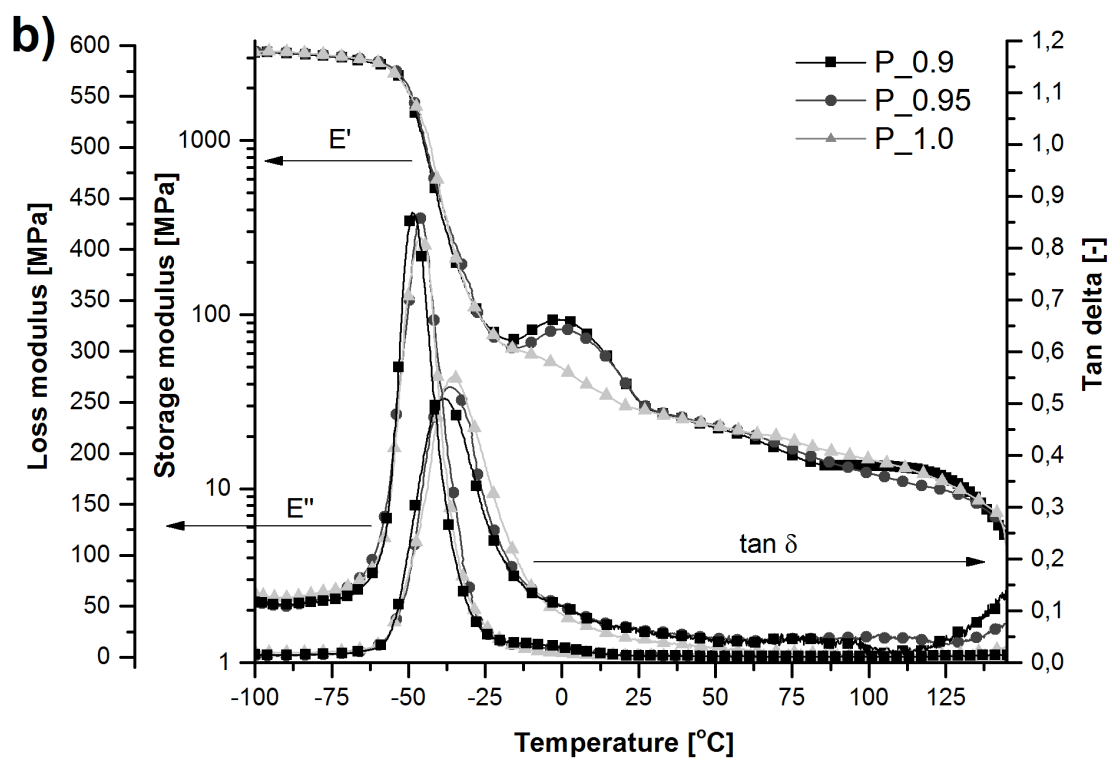
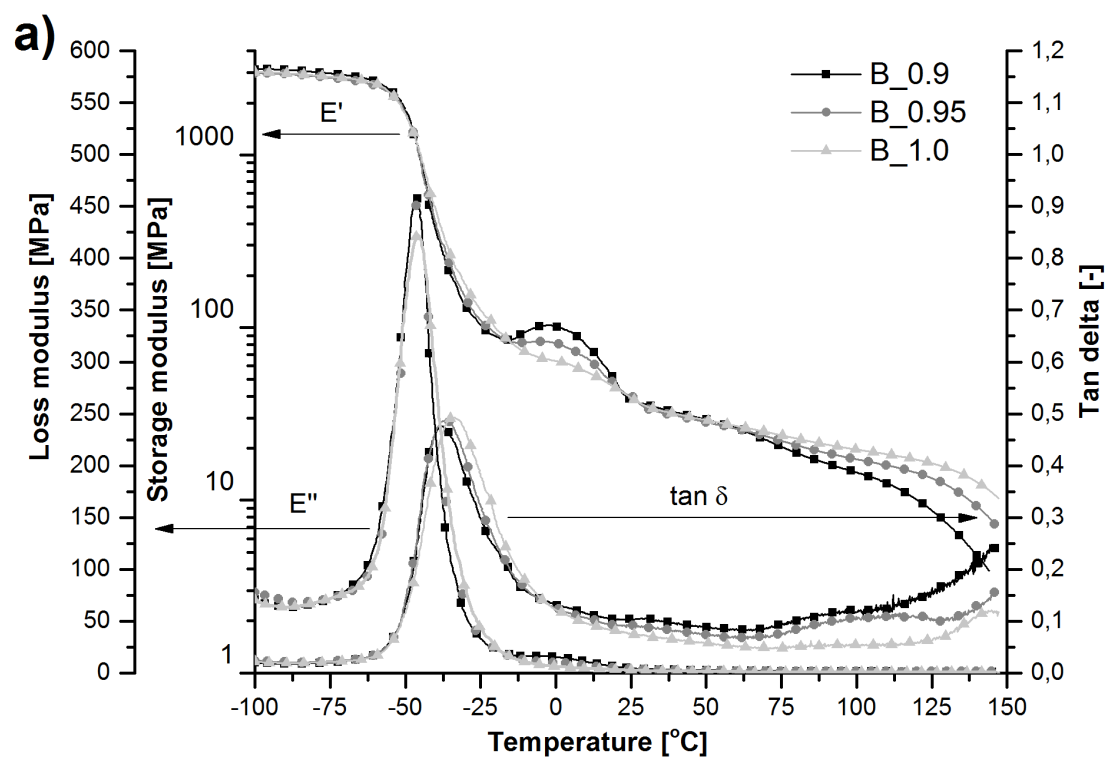


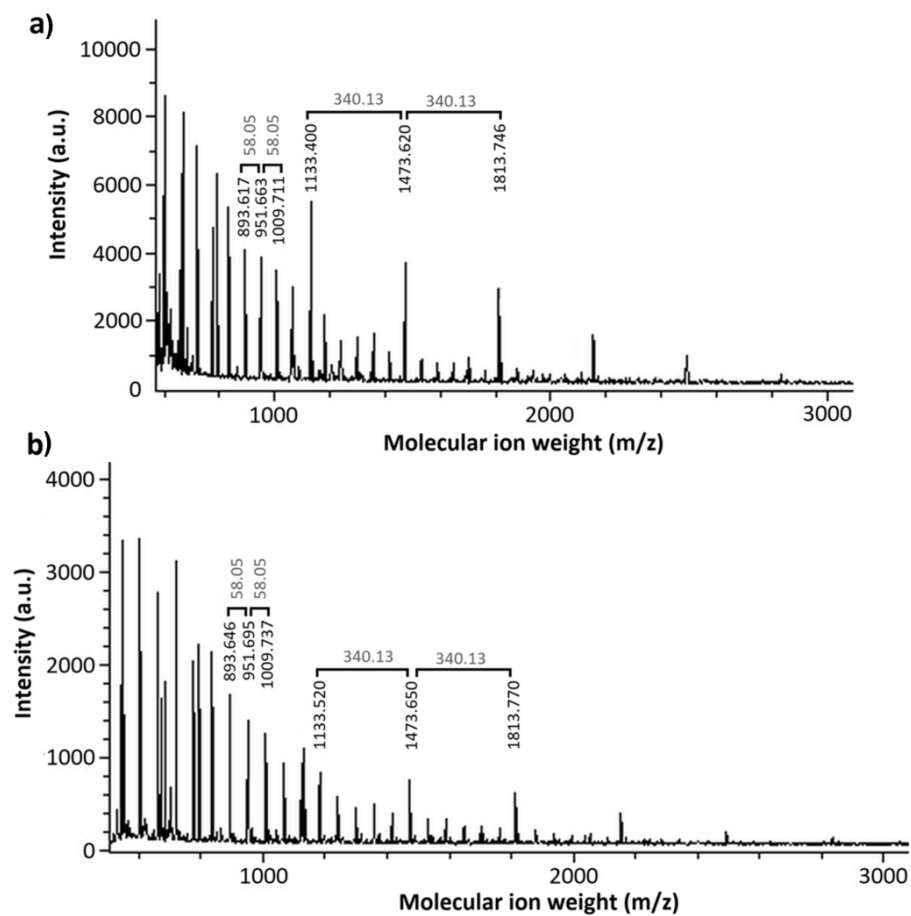


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c)

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%)	-

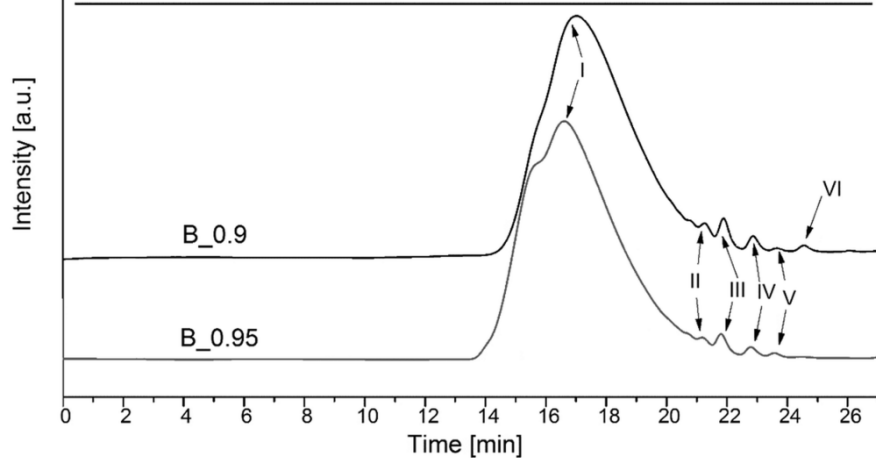


Figure captions

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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