Synthesis of Oligo(butylene succinate)-based Polyurethanes: Influence of the Chemical Structure on Thermal and Mechanical Properties

L. Poussard*[,1], A. Mecheri[1], J. Mariage[1], I. Barakat[1], L. Bonnaud[1], J.-M. Raquez[1,2] and P. Dubois[1,2]

[1]*Materia Nova Research Center, Laboratory of Polymeric and Composite Materials (SMPC), Avenue N. Copernic 1, 7000 Mons, Belgium*
[2]*Center of Innovation and Research in Materials & Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials (SMPC), University of Mons (UMons), Place du Parc 23, 7000 Mons, Belgium*

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ABSTRACT: Biobased oligo(butylene succinate)-based thermoplastic polyurethanes (TPUs) were prepared following a two-step polymerization process: condensation of succinic acid and butanediol and the chain extension of resulting hydroxyl-terminated butylene succinate oligomers (OBS) in the presence of butanediol as chain extender and isophorone diisocyanate (IPDI) as coupling agent. Mechanical and thermal properties of the elaborated TPUs were evaluated in terms of hard segment and compared with those of commercial polybutylene succinate (PBS), Bionolle 1001. Whatever the compositions, the ultimate tensile properties of OBS-based TPUs and Bionolle 1001 were found to exhibit similar values ($\varepsilon_r \approx 400\%$, $\sigma_r \approx 40$ MPa), which can be explained by their close molecular weight (60000 g.mol^{-1} equiv. PS). Interestingly, a higher content of hard segments within OBS-based TPUs leads to materials exhibiting higher rigidity, smaller degree of crystallization, lower melting temperature and weaker stability of the materials with temperature. Such a trend was attributed to the presence of urethane functions and their ability to set up strong H-bonding interchain interactions.

KEYWORDS: Polybutylene succinate, biobased polyurethanes, thermal and mechanical properties

1 INTRODUCTION

Due to increasing concerns about sustainable development, many renewable materials have been extensively studied over the past decades. The use of biobased polymers represents an environmentally-friendly alternative to conventional petroleum-based polymers. Among these biobased polymers, polybutylene succinate (PBS) as synthesized from biobased succinic acid and butanediol is of growing interest because its thermal and mechanical properties can compete with the family of polyolefins for packaging applications [1–4]. Although PBS has been known since the works of Carothers [5], there have been recent efforts pushing towards the synthesis of high-molecular-weight PBS for commercial purposes by Showa Denko (Bionolle) [6] during the nineties, and more recently by BioAmber [7], Reverdia [8] or Purac [9]. These last three companies focus namely on the production of biobased succinic acid by the bacterial strain fermentation process of sugars on a large scale (production of several kilotons per year). Interestingly, succinic acid is viewed as one of the most important renewable building blocks paving the way to a large variety of polymers [10, 11].

Polybutylene succinate is classically synthesized in a two-step process: a first esterification step of succinic acid and butanediol, leading to oligobutylene succinate OBS, and a second condensation step of these as-formed oligomers under vacuum to achieve PBS with weight-average molar mass, e.g., higher than 180,000 g/mol [4]. Different ways were evaluated to reach such high-molecular weight PBS, including several esterification catalysts such as distannoxane [12] or organometallic (Ti, Zr, Sn, Hf, and Bi) and metal oxide-based (Ge and Sb) systems [13] during the second stage synthesis of PBS. To span the range of PBS applications, the synthesis of PBS-based copolymers was also attempted from this two-step condensation process

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**Corresponding author*: loic.poussard@materianova.be

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with other saturated monomers like dimethyl adipate [14, 15], dimethylazelate [16], or unsaturated and functionalizable monomers like dimethyl fumarate [17], 7-octene-1,2-diol [18] or 2,5-furandicarboxylic acid [19]. However, these two-stage processes proved to be relatively long, requiring the use of high temperature.

Recently chain-extension reaction of butylene succinate oligomers has received particular attention as a more flexible synthetic pathway by comparison with the two-step condensation process, as well as a better way to control the polybutylene succinate processability. Most of the chain-extension reactions are carried out from a,w-dihydroxy-functionalized OBS as soft segments and butanediol as hard segment precursor in the presence of diisocyanate agents as coupling agents including aromatic toluene diisocyanate [20], 4,4'-methylene diphenyl diisocyanate [21], aliphatic hexamethylene diisocyanate [22] or 4,4'-methylenebis(cyclohexylisocyanate) H_{12}MDI [23, 24]. The role of these hard segments within polyester urethanes is to act as physical crosslinkers through hydrogen bonding between urethane functions [25, 26].

Interestingly, the properties of resulting PBS copolymers may be designed by means of structure (choice of diisocyanate) and compositions depending on the desired applications [20]. However it is worth noting that the content in urethane reported in literature is relatively high (min. 30 weight %), thus reducing the ability of PBS to be biodegradable [21].

The present study aims at developing a fast process to prepare OBS-based thermoplastic polyurethanes (TPUs) exhibiting good mechanical properties. These OBS-based polyurethanes were obtained by chain-extension reactions of a,w-dihydroxy-functionalized butylene succinate oligomers with low content in hard segment (less than 20 weight %). As a model we have used aliphatic isophorone diisocyanate (IPDI) as coupling agent. To boost up the process, two different approaches were investigated: i) a variation of isocyanate index equal to 105 and 150 respectively for TPU 1 and TPU 3, ii) a two-stage process starting from OBS and diisocyanate to first obtain an isocyanate-terminated prepolymer, followed by the subsequent addition of butanediol as chain extenders (TPU 2). The effect of isocyanate content on the mechanical and thermal properties of resulting OBS-based TPUs was investigated and compared with a commercial Bionolle 1001 PBS produced by Showa Denko [6] and a tailor-made PBS.

2 EXPERIMENTAL

2.1 Chemicals

Butanediol (99% purity), succinic acid (99% purity) and isophorone diisocyanate (99% purity) were obtained from Merck and used without further purification. Tin(II)-ethylhexanoate ($SnOct_2$) (96% purity) was supplied by Alfa Aesar. Chloroform grade HPLC (99.5% purity) and deuterated chloroform ($CDCl_3$, 99.8% d) were used as received from VWR and Euriso-Top respectively.

2.2 Preparation of Polymers

Synthesis of oligobutylene succinate (OBS)

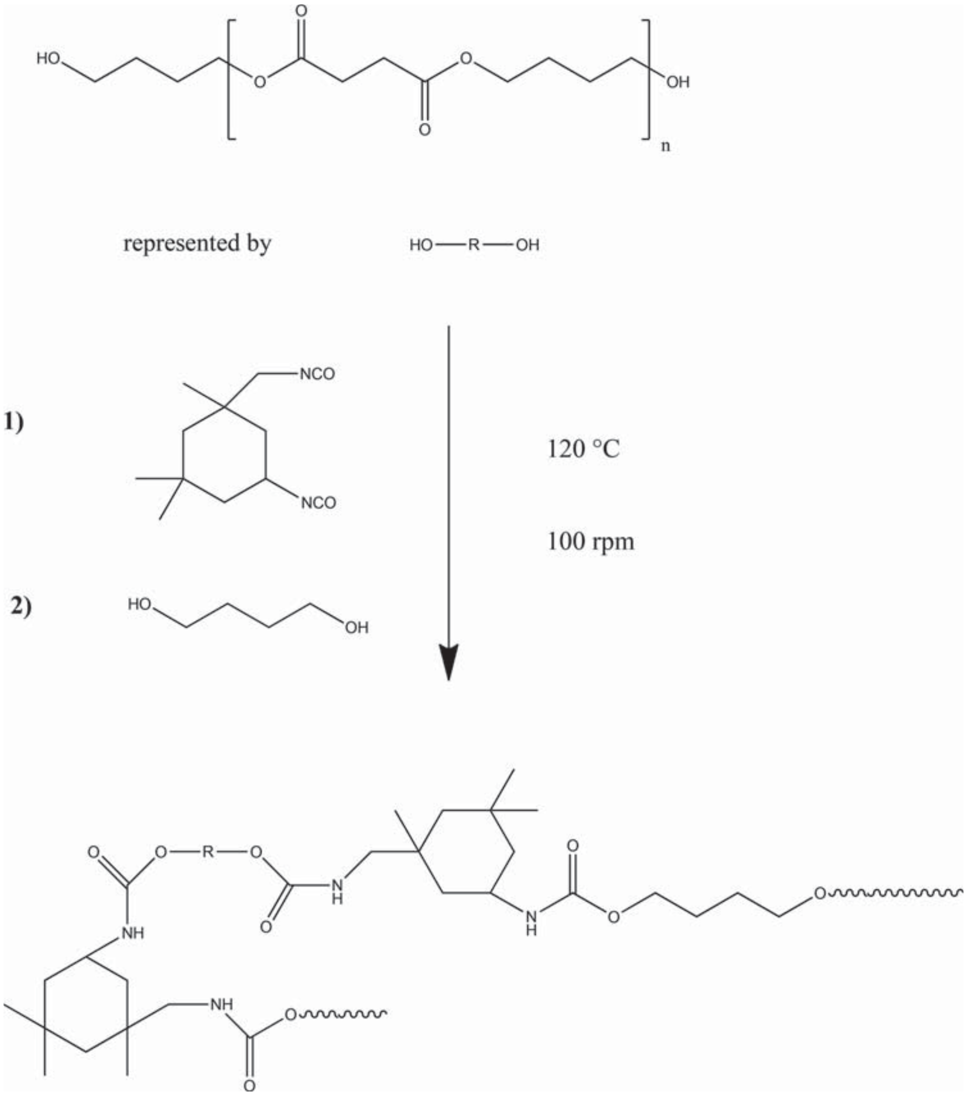
In a 2 L four-necked reactor equipped with mechanical stirrer, condenser and inlet for nitrogen or vacuum, butanediol (916 g, 10.16 mol) and succinic acid (800 g, 6.77 mol) were molten together with a [OH] to [CO_2H] molar ratio of 1.5 at 180°C. After one hour, the reaction temperature was slowly increased to 240°C. When the temperature reached 240°C, $SnOct_2$ was added ($5.10^{-4} \times CO_2H$, 0.15% reactants weight, 440 ppm Sn) and vacuum was applied to set the reaction for 3 hours. Hydroxyl-terminated oligobutylene succinate was characterized by hydroxyl value titration method using the ASTM D 1957–86 standard. Assuming the end groups are hydroxyl functions, the number-average molecular weight was estimated to be 2500 $g.mol^{-1}$. Synthesized OBS was kept at 60°C under vacuum before use.

Synthesis of polybutylene succinate (PBS home)

High-molecular-weight PBS was synthesized by condensation of OBS using a stainless 50 mL Autoclave-France reactor. 20 g of OBS were molten at 140°C under nitrogen for 30 minutes with a second addition of catalyst $Sn(Oct)_2$ (0.1 weight %) to get the optimized amount of catalyst required for high-molecular-weight PBS. Then, condensation was carried out at 240°C for 3 hours under vacuum. The resulting PBS (PBS home) was retrieved then molded by hot press method at 150°C.

Synthesis of thermoplastic polyurethanes (TPUs)

The synthetic route to make OBS-based TPUs materials is shown in Scheme 1. It consists either in a one-step (for TPU 1 and 3 without chain extender) or a two-step bulk polymerization process (using butanediol as chain extender for TPU 2). The typical experimental procedure was described for TPU 2: OBS (7.11 g, 16 mmol) was molten at 120°C in a 250 mL four-necked reactor equipped with mechanical stirrer and inlet for nitrogen or vacuum. After melting, an extra amount of catalyst $SnOct_2$ (130 mg, 0.032 mmol) and isophorone diisocyanate (7.11 g, 32 mmol) were added for one hour at 100 rpm under nitrogen atmosphere. After one hour, butanediol (1.30 g, 14.4 mmol) was added. For all OBS-based TPUs, a huge increase



Scheme 1 Synthesis of oligo(butylene succinate)-based thermoplastic polyurethanes by two-step chain extension reaction.

of viscosity was observed in less than 2 minutes. The resulting polymer was recovered and then molded by hot press method at 150°C to obtain film specimens (80 x 120 x 1 mm) for DMA and tensile testing experiments. The compositions of all TPUs are listed in Table 1.

2.3 Measurements

Analytical methods

Fourier transform infrared spectra were obtained by using Perkin-Elmer Spectrum 2000 spectrometer, equipped with a monoreflexion system MIRacle ATR (Pike Technologies). Spectra were recorded in transmission mode in the range of 4000–500 cm^{-1} with a nominal resolution of 4 cm^{-1}. Both PBS- and OBS-based TPUs dissolved in deuterated chloroform $CDCl_3$ were analyzed by ^{1}H NMR on a Bruker Advance 500 MHz spectrometer at 295 K.

Size-exclusion chromatography (SEC) was performed in $CHCl_3$ at 30°C using an Agilent liquid

Table 1 Formulation of OBS-based TPUs.

Ref	Functions molar ratio OBS / BD / IPDI	I_{NCO}	Hard segment (%w)
TPU 1	1 / 0 / 1.05	105	8.5
TPU 2	1 / 0.90 / 2	105	17.4
TPU 3	1 / 0 / 1.5	150	11.8

chromatograph equipped with an Agilent degasser, an isocratic HPLC pump (flow rate = 1 mL/min), an Agilent autosampler (loop volume = 200 µL, solution concentration = 1 mg/mL), an Agilent-DRI refractive index detector and three columns: one PL gel 10 µm guard column and two PL gel Mixed-D 10 µm columns (linear columns for separation of narrow polystyrene standard ranging from 500 to 10^6 g/mol).

Thermal analysis

Differential scanning calorimetry (DSC) measurements were carried out with a DSC Q1000 apparatus (T.A. Instruments) under nitrogen flow (50 mL/min). A heating/cooling/heating procedure from −80 to 150°C at a rate of 10°C min^{-1} was applied. The thermal transitions were acquired from the cooling and second heating runs. For some polymer samples, the glass transition temperature (T_g) proved to be characterized by low C_p variations and could not be readily observed on the DSC thermograms. Accordingly, these T_g values were directly detected owing to the DSC Q1000 computer program.

Thermogravimetric analysis

The thermal decomposition behavior was investigated under a nitrogen atmosphere through thermogravimetric analysis (TGA) using a TA Instrument Q500 (Waters). A 20 mg weight sample was heated from 30 to 550°C at a heating rate of 10°C min^{-1}.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) was performed using a TA Instrument DMA Q800 (Waters) in tension mode on rectangular samples of 1 mm thickness to determine the storage modulus E′ and the loss factor tan δ. All the samples were strained at 0.01% at 1 Hz frequency with a 125% ratio of static force to dynamic force. They were scanned at a constant heating rate of 3°C.min^{-1} over a temperature range of −100 to 150°C.

Mechanical properties

Stress-strain measurements were performed on dumbbell-shaped samples cut from the PBS and TPU sheets according to the ASTM D638 standard. Experiments were carried out at 20°C using a Hounsfield H10KT apparatus equipped with 1000 N load cell. The crosshead speed was chosen at 10 mm.min^{-1}. For each formulation, at least 5 samples were tested to determine the Young modulus E, the stress at break (σ_R) and the strain at break (ε_R).

3 RESULTS AND DISCUSSION

Biobased thermoplastic polyurethanes were prepared upon a one-stage or a two-stage melt-process by first mixing hydroxyl-terminated butylene succinate oligomers (OBS) and isophorone diisocyanate (IPDI) upon various molar isocyanate-to-hydroxyl molar ratios. If required by the formulation in a second step, adding butanediol was further carried out as a chain extender into the reaction medium. The SnOct_2 (0.15% reactants weight) was employed as both esterification and chain-extension catalyst. When the isocyanate index – I_{NCO} – is equal to 105 (i.e., 5% excess of NCO) for TPU 1 and TPU 2, the reaction proved faster in the presence of the chain extender for TPU 2, with a strong increase of viscosity after addition of butanediol. Moreover, in the case of higher NCO excess (I_{NCO} equal to 150 for TPU 3), the process took place very fast even without any addition of butanediol as shown with the experiment TPU 3 for which the reaction medium turned into a solid within a few minutes.

For sake of comparison a homo-PBS was synthesized using a conventional two-stage condensation process (see Experimental Section). The synthesis of this model homo-PBS (coined as “PBS home”) had almost a three-fold longer reaction time, but was practiced with a finer viscosity control.

The synthesized TPUs have been characterized by FTIR and ^{1}H NMR and compared with the commercial PBS Bionolle 1001 and the herewith synthesized PBS home. The FTIR spectra of the OBS-based TPUs are shown in Figure 1. As expected, the NCO stretching band at 2270 cm^{-1} was not visible due to the complete conversion of NCO into urethane moieties in the presence of SnOct_2 as catalyst. Two specific peaks revealed the difference between both PBS- and OBS-based TPUs:

i. N-H stretching vibration at around 3400 cm^{-1}. It is assumed that the shoulder of both symmetrical and asymmetrical stretching bands indicates that most of the N-H functions make hydrogen bonding with carbonyl functions from urethane and ester groups [27].
ii. N-H bending and NH-CO stretching bands of urethane group at around 1540 cm^{-1}. The higher the hard segment content, the higher the absorbance at this wavenumber.

From FTIR, it is hardly possible to distinguish the functions of the ester and urethane carbonyl functions as both C=O stretching bands are at around 1715 cm^{-1}. The ^{1}H NMR analysis of OBS-based TPUs and PBS gives additional information as shown in Figure 2. In addition to the main peaks characteristic

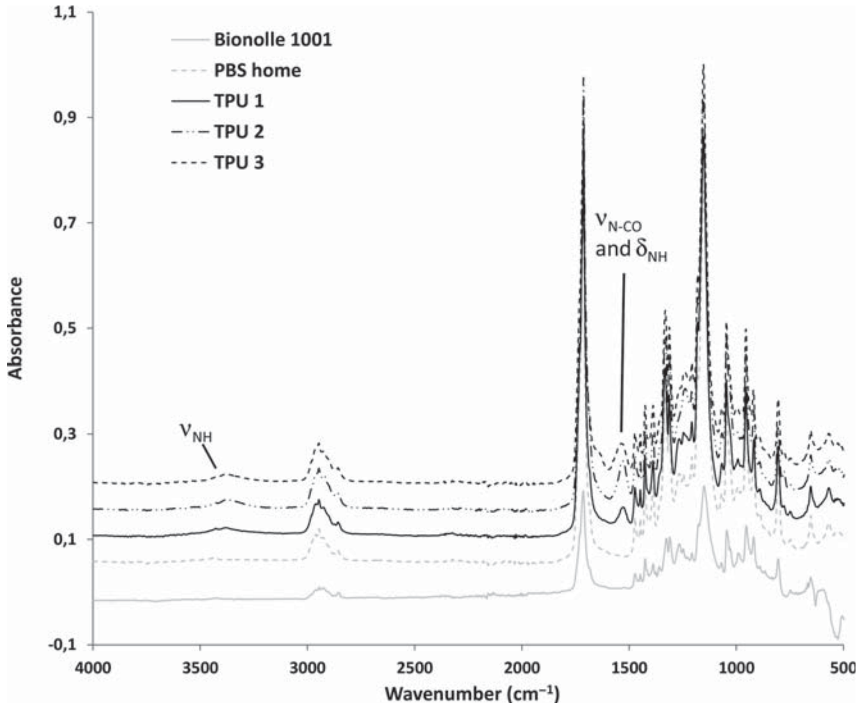


Figure 1 FTIR spectra of OBS-based TPUs compared to PBS.

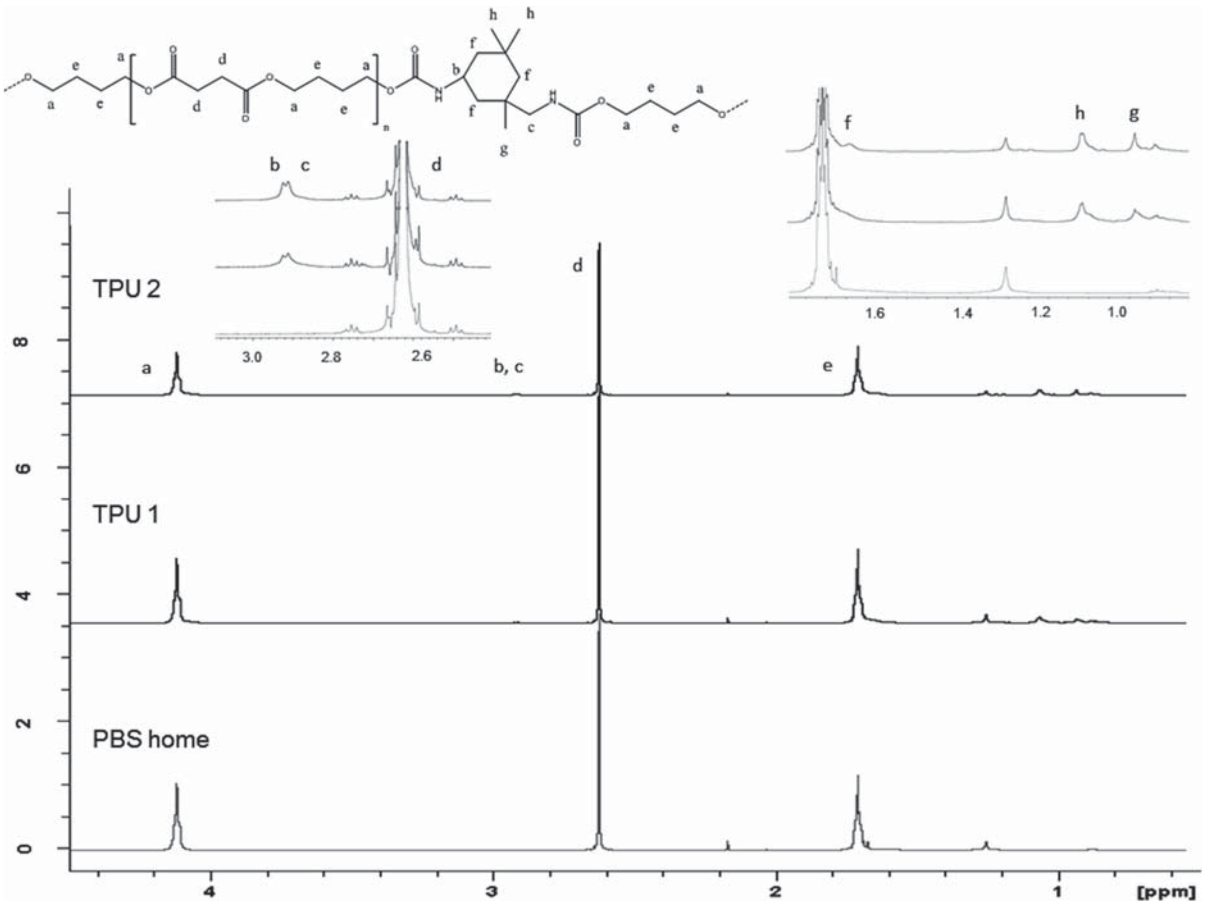


Figure 2 ^{1}H NMR spectra of OBS-based TPUs compared to PBS.

of as-synthesized PBS (CH_2 in succinic unit, and in butanediol unit, mid-CH_2 and CH_2 in α position of the ester group appearing respectively at d) 2.63, e) 1.72 and a) 4.12 ppm), other peaks are assigned to urethane moieties and IPDI-based derivatives. The methylene groups (g, h) from the IPDI derivatives show up at 1.08 and 0.91 ppm and the protons from cyclohexyl group at 1.63 ppm. The urethane moieties are identified from the resonance peaks at 2.91 ppm, corresponding to CH and CH_2 in α position of N-H function (**b** and **c**). As expected, although these signals are of weak intensity, it can be seen that the height of these peaks increases with the hard segment content. It is noteworthy that TPU 3 was not analyzed by ^1H NMR technique as it is not being fully soluble in $CDCl_3$.

Although we cannot exclude any fractionation, it seems that from SEC results, TPUs exhibit high molecular weights (between 37,700 and 67,400) and dispersities similar to those of as-synthesized PBS (as expressed in polystyrene calibration) (Table 2). As shown in Figure 3, the mechanical properties of PBS-based TPUs were determined by tensile testing experiments and compared with those of Bionolle 1001 ($\varepsilon_r \approx$ 429%, $\sigma_r \approx$ 48 MPa) and as-synthesized PBS home ($\varepsilon_r \approx$ 175%, $\sigma_r \approx$ 32 MPa). It may be pointed out that the as-synthesized PBS reaches a lower strain at break more likely due to the relatively low molecular-weight of the polyester chains (M_n around 37,700 in PS equivalent). Higher strain at break for TPU 1 with similar molecular weight can be achieved and may be explained by the presence of hydrogen bonding from the urethane functions present within OBS-based TPUs, not present for homo-PBS.

Both PBS- and OBS-based TPUs have similar Young Moduli (around 400 MPa) comparable with those reported in literature depending on the stress experiment procedure. This proves that when the hard segment content in TPUs is relatively low (maximum at 17.4%), there is no real impact of urethane hydrogen interactions. To demonstrate this, when a higher excess of isocyanate (I_{NCO} equal to 150) was used, TPU 3 with further H-bonds was obtained as well as the presence of allophanate linkages. As a result, TPU 3 exhibits a higher Young Modulus (+ 45%) compared to other TPUs, without limiting the strain at break.

From Figure 4 the dynamical mechanical curve of OBS-based TPUs are compared to those of homo-PBS. Tan δ curves (Figure 4b) provide some evidence about the presence of urethane linkage content and, consequently, H-bonding from OBS-based TPUs. Indeed, when compared to PBS, a shift towards higher

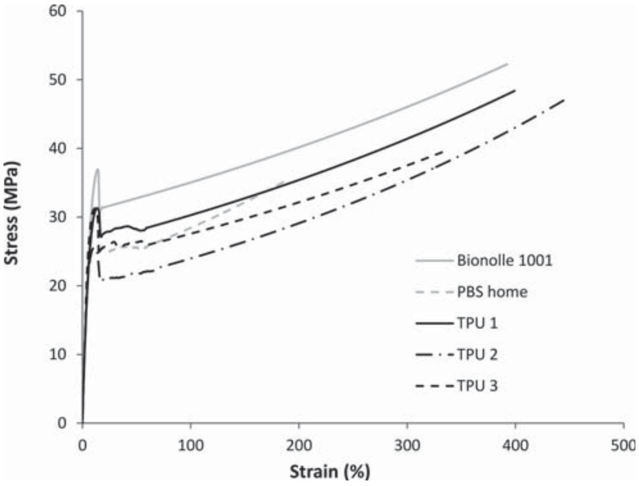


Figure 3 Stress-strain curves of OBS-based TPUs compared to commercial and as-synthesized PBS.

Table 2 Mean molecular-weight and mechanical properties of OBS-based TPUs with various hard segment content compared with PBS.

	Size exclusion chromatography		Stress – strain experiments			DMA
References	**$\overline{M}_n$ (g/mol)**	**Đ**	**E (MPa)**	**σ_r (MPa)**	**ε_r (%)**	**T_α tan δ (°C)**
PBS home	37700	2.20	398 ± 58	32 ± 4	175 ± 7	-24.9
Bionolle	67400	3.71	438 ± 90	48 ± 7	429 ± 97	-28.4
TPU 1	43700	4.00	421 ± 60	39 ± 9	371 ± 30	-19.1
TPU 2	64100	3.34	396 ± 70	45 ± 6	442 ± 72	11.0
TPU 3	Not determined		598 ± 68	36 ± 6	308 ± 30	-9.0

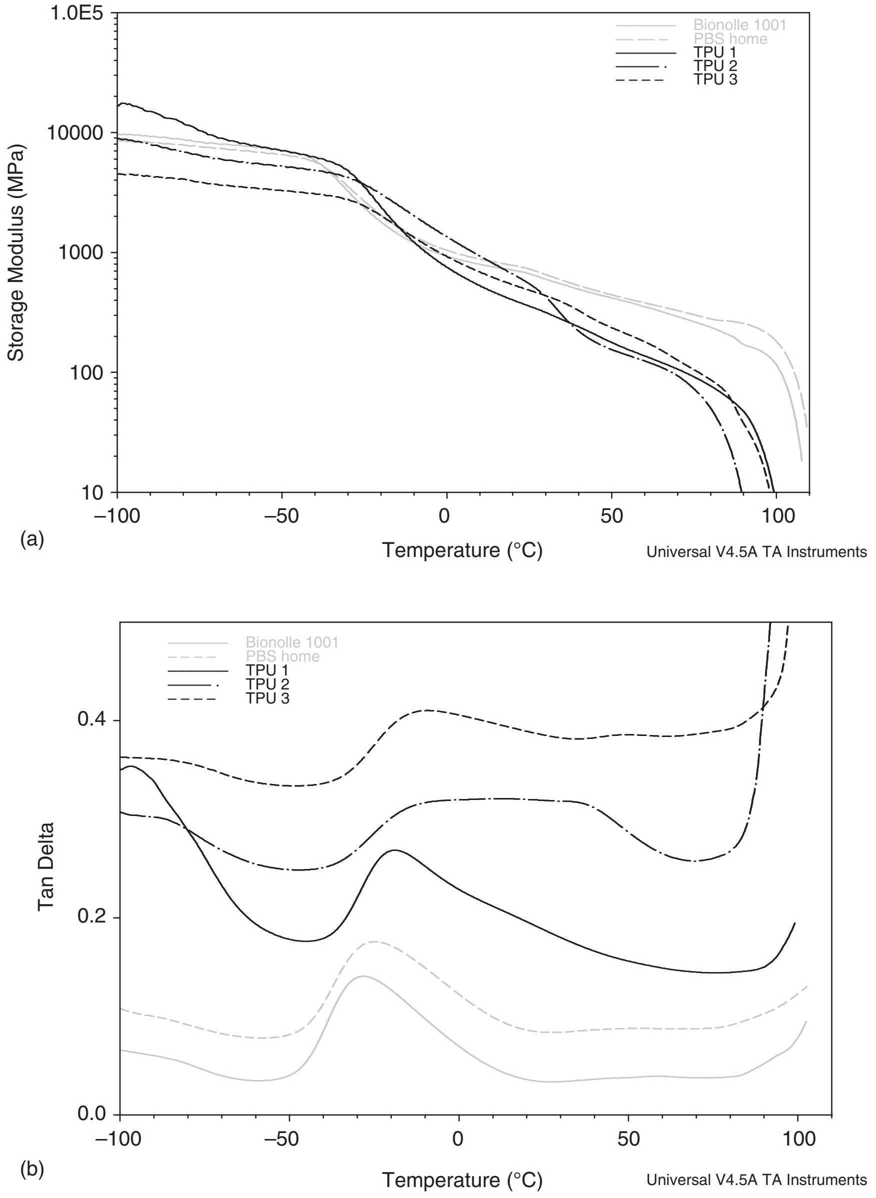


Figure 4 DMA Analysis of OBS-based TPUs compared to commercial and synthesized PBS. **a**) Storage modulus, **b**) tan δ (curves offset for an easier reading)

temperature and a peak broadening are observed. In the case of Bionolle 1001 and as-synthesized PBS, they contain some soft segments with a α transition at −28.4 and −24.9°C, respectively. This small difference in temperature highlights the softer character of Bionolle 1001, which is in good agreement with the molecular weight and tensile property differences mentioned previously for these PBS. Concerning the TPUs, when the hard segment content increases from 8.5 to 17.4%, the T_α shifts from −19 to 11°C (T_α from tan δ reported in Table 2), together with a broadening of T_α peak. This is attributed to the increase of hard segment content and likely by the increase of H-bonds from the urethane moieties. However, the storage modulus curves depicted in Figure 4(a) show that in most cases TPUs have lower storage modulus than those of PBS over the investigated range of temperatures. This can be explained by the slight reduction of degree of crystallization of resulting TPUs compared with the studied PBS samples.

The DSC thermograms of both PBS- and OBS-based TPUs are shown in Figure 5 and the thermal transition data are summarized in Table 3. Even if T_gs are hard to distinguish, as shown in Figure 5 (see Experimental Section), all the materials are soft as revealed by similar glass transitions temperatures between −40 and

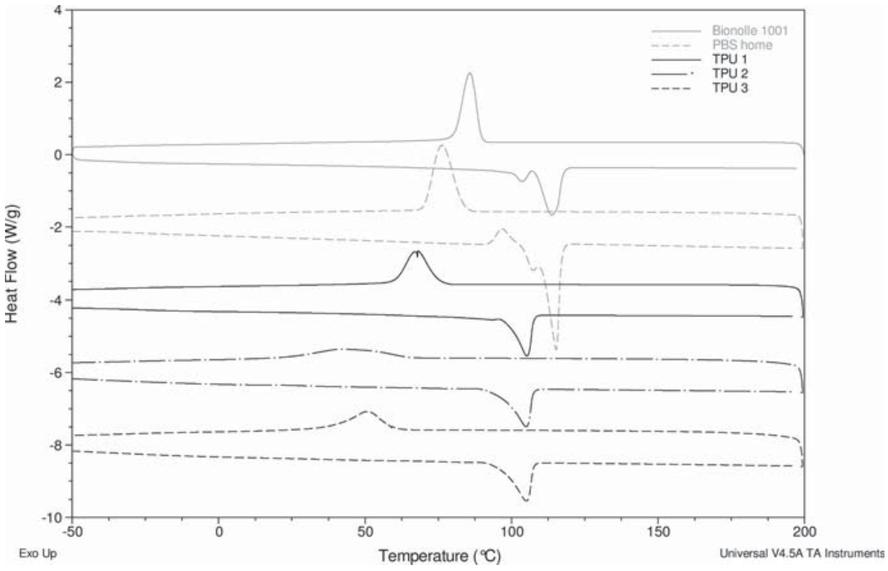


Figure 5 DSC thermograms of OBS-based TPUs compared to PBS: crystallization peak during cooling and melting peaks during the second heating.

Table 3 Thermal properties of OBS-based TPUs compared with PBS.

		DSC Cooling		DSC 2nd heating			TGA	
References		T_c (°C)	ΔH_c (J.g^{-1})	T_g (°C)	T_f (°C)	ΔH_f (J.g^{-1})	$T_{5\%}$ (°C)	$T_{d\,max}$ (°C)
OBS	/	74.0	83.4	-34.8	112.8	90.1	299.7	389.3
PBS	***PBS home***	77.6	65.4	-35.1	115.0	68.2	328.1	394.4
	Bionolle	86.2	55.9	-34.4	115.3	44.1	328.4	398.9
PBS-PU	***TPU 1***	68.0	47.3	-28.1	105.2	35.0	294.9	384.0
	TPU 2	42.1	36.8	-40.1	105.0	43.3	293.0	375.8
	TPU 3	50.6	43.0	-29.3	105.1	44.8	285.7	355.9

−30°C, actually in agreement with T_α values from DMA analysis. Regarding the melting behavior of resulting materials, the melting point for TPUs (105°C) is clearly shifted to lower temperatures compared to PBS (115°C). In addition, a broadening of the melting peak with a weaker ΔH_m value is observed with the hard segment content.

The crystallization ability of OBS-based TPUs is largely depressed with respect to both PBS and OBS (Table 3), since ΔH_c of TPUs are at least 30% inferior to these of PBS. The typical temperature transitions of both PBS are indeed similar to those of initial oligomer butylene succinate. In contrast, it is seen that the irregularities induced by the hard segments in TPUs, generate T_c and T_f decreases of 10°C with respect to the initial OBS.

The presence of hard segments within OBS-based TPUs may act as defects, preventing the crystallization of PBS-based materials from occurring, but also inducing a decrease of crystallization temperature (T_c) on cooling: T_c for TPUs in the range 42–68°C against 77–86°C for PBS. Similar results were observed by Michell *et al*. about PLLA-based polyurethanes [25]. T_c is also affected by the hard segments content: the higher the urethane linkage content, the lower T_c.

The thermal stability of polymers is an important factor to know since it can limit their application range. Figure 6 shows the thermal degradation behavior of PBS- and OBS-based TPUs. As indicated by the temperature loss of 5% of the original weight ($T_{5\%}$ in Table 3), TPUs degradation starts at around 290°C whatever the hard segment content. In contrast, the degradation of pure OBS and PBS starts at a higher temperature, at 300°C and around 328°C respectively for the two investigated PBS samples

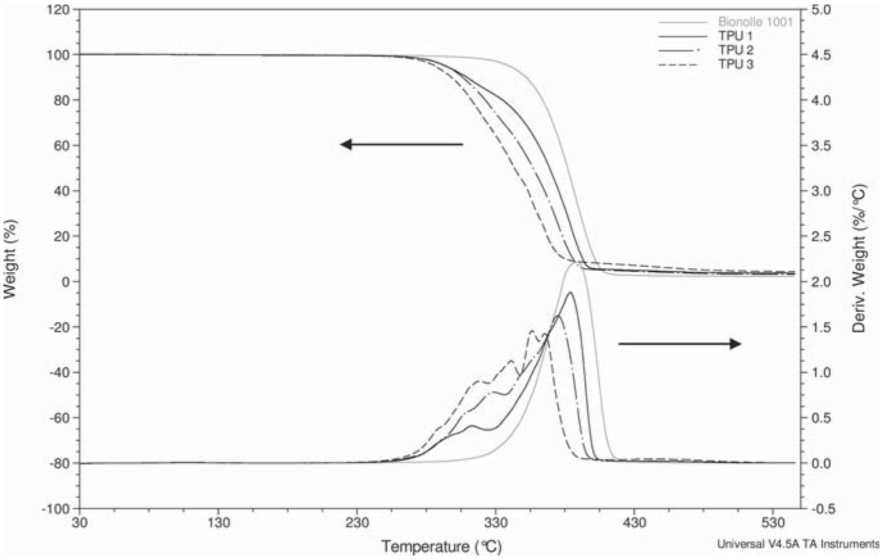


Figure 6 Thermogravimetric analyses of OBS-based TPUs compared to PBS.

(tailor-made and commercial Bionolle). The higher thermal stability of PBS compared to OBS is relevant with their increased molecular weight. About OBS-TPUs, the presence of hard segments is shown between 250 and 330°C where the area is proportional to their relative content. This range of temperatures corresponds to the degradation of the urethane functions. These results indicate that OBS-based TPUs have less thermal stability compared to homo-PBS, even if the maximum rate of decomposition ($T_{d\,max}$ in Table 3) is lower for TPUs, due to the broader range of thermal degradation. The TGA analysis is relevant with DMA results concerning influence of isocyanate index. The thermal stability appears reduced for TPU 3 (I_{NCO} = 150) compared to TPUs 1 and 2 (I_{NCO} = 105). It seems that in the case of low hard segment content, the allophanate functions exhibited lower thermal stability compared to urethane functions. These results may be in agreement with those reported in literature with polyurethanes and allophanate-based on polybutadienes [28].

4 CONCLUSION

The OBS-based TPUs were synthesized with various hard segment contents composed of butanediol and IPDI, between 8.5 and 17.4%. As mentioned in the literature, with PBS or other renewable polyesters [21, 26], a higher hard segment content, a greater density of H-bonds between ester C=O acceptor and hydrogen bonds between urethane N-H donor increased hard segment–soft segment interactions. Hard segment content seems to be the key factor affecting the behavior of OBS-based TPUs:

- higher rigidity of TPUs compared to pure PBS as revealed by dynamical mechanical analysis (T_α increased from –19 up to 11°C),
- smaller crystallization ability and reduced melting temperatures due to defaults attributed to urethane functions versus highly crystallizable OBS soft segment,
- reduced stability at temperature due to the thermal degradation or urethane groups close to 290°C.

However, such OBS-based TPUs synthesized with IPDI exhibit a reproducible ductile behavior as observed from tensile experiments ($\varepsilon_r \approx 400\%$) in the whole range of studied hard segment content, which is not easier to reach with conventional pure PBS. Among other applications, the tunability of such OBS-based TPUs' formulations may pave the way as potential candidates for impact modifiers.

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