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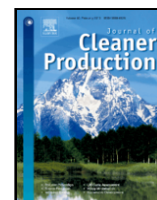
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Increasing circular and bio-based content of a thermosetting polyurethane for encapsulation of optoelectronic devices: A multivariate investigation

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ABSTRACT

Transparent thermosetting polyurethanes (PU) with increased circular and bio-based content have been developed with an effective and efficient approach based on the Design of Experiment. Starting from a commercial PU formulation for light-emitting diode encapsulation, the fossil-based polyol blend has been partially replaced with potentially recycled bis(hydroxyethyl) terephthalate (BHET) diol and bio-based polyol. BHET has been directly implemented in the polyol blend without requiring any additional solvent or treatment. The multivariate approach allowed to study formulative (BHET, bio-based and fossil-based polyols) and process factors (mixing time and temperature of polyol blend and PU blend) of the polymer preparation by using optical spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. The effect of each factor on the optical and thermal properties of the resulting polyurethane films have been observed and clearly quantified. Particularly, the implementation of BHET improved the thermal stability of PU but reduced the film transmittance as the concentration increases. Circular and bio-based content into the polyol blend has been increased up to 80%_{w/w} and the formulation has been optimized by following a property-driven analysis. Polyurethane formulated with the selected polyol blend showed transparency, thermal behaviour, long-term stability, and cost comparable to the starting commercial formulation. Market-level properties and ease of preparation highlight that circular and bio-based PUs can be rapidly developed and implemented within current polyurethane production processes, promoting the shift towards Circular Economy with solid industrial symbiosis. At last, the present approach can be easily repurposed to further improve sustainability of polyurethanes, as well as to develop other classes of polymers.

Abbreviations

BHET	Bis(2-hydroxyethyl) terephthalate
DoE	Design of experiments
DSC	Differential scanning calorimetry
GHG	Greenhouse gas emissions
IPDI	Isophorone diisocyanate
LED	Light-emitting diode
NIPU	Non-isocyanate polyurethane

OFAT	One factor at a time
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PU	Polyurethane
TGA	Thermogravimetric analysis

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1. Introduction

In the plastics sector, polyurethanes (PUs) own a market share of almost 7% with a global production exceeding 27 Mt per year (Geyer et al., 2017; Plastics Europe, 2021). Polyurethanes can be linear (thermoplastic) or networked (thermoset) polymers and they could be exploited in a plethora of applications, from adhesives to foams, from building insulations to athletic tracks (Das and Mahanwar, 2020; Janik et al., 2014; Liu et al., 2020). Among the multitude of PU uses, protective layers deserve marked interest thanks to PU durability, corrosion and weather resistance (Jones et al., 2017; Noreen et al., 2016). More in detail, thermosetting PU-based coatings and encapsulants for optoelectronic devices (e.g., optical display) and photovoltaics are receiving increasing attention due to their emerging role in our daily life (Bonomo et al., 2020; Lu et al., 2021; Wiesmeier et al., 2013; Yuwawech et al., 2018). In this perspective, the protective materials should ensure both high-performance and long lifetime along with UV light and thermal stability (Uddin et al., 2019).

As for the whole plastics sector, the conventional synthetic pathway of PUs, i.e. the polyaddition reaction between alcohols and isocyanates (Akindoyo et al., 2016), involves the use of reagents and precursors derived mainly from virgin and petroleum-based sources, dramatically undermining the sustainability of the polymers (Das and Mahanwar, 2020). Recently, the EU-promoted shift towards Circular Economy and sustainable plastics is affecting the whole PUs value-chain, pushing both industries and academic research to thoroughly innovate the whole PUs life-cycle from the raw materials selection to the end-of-life disposal (Cornille et al., 2017; Kreye et al., 2013; Sardon et al., 2015). The use of bio-based and recycled precursors, instead of virgin raw fossil-derived ones, is a promising approach to overcome the fossil-dependency and reduce negative impacts on the climate and the environment (European Commission, 2020; Helling and Russell, 2009; Parcheta and Datta, 2017).

Polyurethanes with improved sustainability have been proposed from several bio-based polyol precursors derived from e.g. soybean oil (Miao et al., 2013), canola oil (Aydoğmuş and Kamişli, 2022), castor oil (Borrero-López et al., 2020; Morales-Cerrada et al., 2021), lignin (Cassales et al., 2020), and cardanol (Vijayan et al., 2022). Besides bio-based precursors, also recycled plastics and waste-derived materials are receiving particular attention from the scientific community (Hahladakis et al., 2020; Garcia and Robertson, 2017; Muñoz Meneses et al., 2022; Payne et al., 2019). In this context, bis(2-hydroxyethyl) terephthalate (BHET, Fig. 1), a low molecular weight diol, can be obtained from the chemical glycolysis of polyethylene terephthalate (PET) (DamayantiWu, 2021; Esquer and García, 2019; Raheem et al., 2019), which is one of the most wasted polymer (Geyer et al., 2017). Thus, BHET appears to be a promising building block for the development of different circular polymers (Bhandari et al., 2023).

BHET has been already applied into polyurethane formulations by following different strategies. Some authors report the use of BHET as starting reagent for the synthesis of both OH-terminated (Hui He et al., 2022; Jamdar et al., 2017; Lusinchi et al., 1998) and NCO-terminated (Bhattacharyya et al., 2016, 2017) precursors, subsequently formulated

with isocyanates and alcohols, respectively, to obtain the final PU. However, the need of chemical treatments or additional syntheses (often characterized by multiple steps) is in contrast with the aim of circular economy in saving materials and energy, meanwhile tend to nullify the advantages in using waste-derived resources. Moreover, aiming to accelerate the creation of an effective industrial symbiosis and a well-established market for secondary raw materials, the ease of implementation for recycled materials in current processes and products appears an essential requirement (Bucknall, 2020). Hence, every additional process required for the PU formulation hinders a rapid and simple industrial scale-up of circular BHET-based PUs. In this perspective, a more interesting approach reports the use of BHET diol as the only hydroxyl source during the synthesis of polyurethane, without adding any other alcohols into the formulation (Kawkumpa et al., 2019; Lee and Jung, 2022; Li et al., 2014; Pham et al., 2021). In comparison to PUs formulated with common aliphatic diols (e.g. 1–4 butanediol, polyethylene glycol), BHET causes significant variations in PU properties. The thermal resistance and mechanical properties, like compression and tensile strength, are greatly increased, while the optical properties, like transparency, are negatively affected (Kawkumpa et al., 2019). These variations are related to the presence of the aromatic ring in the short structure of BHET, which also tends to crystallize into the polymer matrix. However, such rigid and opaque materials have little potential in coating applications for optoelectronics and photovoltaics, where transparency and/or flexibility are often required. Hence, a viable strategy to overcome these issues involves the use of BHET in addition to other diols or polyols to obtain (or tune) the proper desired properties in the polyurethane, according to the intended final application and avoiding additional treatments (Cywar et al., 2021). Polyethylene glycol (Kawkumpa et al., 2019), polycaprolactone diol (Lee and Jung, 2022; Maafi et al., 2010), castor oil (Cevher and Sürdem, 2021; Lee and Jung, 2022), and other polyols (Eider Mendiburu-Valor et al., 2023; Li et al., 2022; Zhang et al., 2022) have been recently combined with BHET to develop thermoplastic or waterborne polyurethanes with more tunable properties and higher versatility. However, to the best of our knowledge, transparent thermosetting polyurethanes formulated with BHET are not reported in the literature yet, as well as any comparison between BHET-based polyurethanes and some specific commercial PU reference.

In this scenario, the present study is focused on the development of thermosetting PUs with improved circular and sustainable content through a facile and efficient substitutional approach, while maintaining valuable optical and thermal properties comparable to the commercial PU reference. More in detail, starting from a commercial fossil-based polyol used to prepare PU coatings for light-emitting diodes (LED), Sovermol780 and BHET have been implemented into the formulation as bio-based polyol and potentially waste-derived diol, respectively. In developing new polymer formulations, many different parameters (e.g., components ratios, temperatures, time, etc.), along with their potential dependency, could influence the final polymer properties and their effects are often challenging to be analysed and predicted. To investigate such a multivariate system, a chemometric approach, like the Design of Experiments (DoE), represents a key-enabling method against the traditional one-factor-at-a-time (OFAT) process (Kennard and Stone, 1969). DoE allows the simultaneous investigation of several experimental variables (factors) affecting one or more responses with a limited number of experiments, thus saving materials, energy and time together with reducing costs and waste production during the research activity. For all these reasons, DoE shows an impressive wide range of applications, from drug delivery and synthesis optimization to solar cell development (Diem Ferreira Xavier et al., 2022; Galliano et al., 2020, 2021; Mahmoudi et al., 2019; Pontremoli et al., 2023; Roberto de Alvarenga Junior and Lajarim Carneiro, 2019; Rosso et al., 2022), and already proved to be an effective tool even in the field of polymers (Aydoğmuş and Kamişli, 2022; Debska and Dobrowolski, 2018;

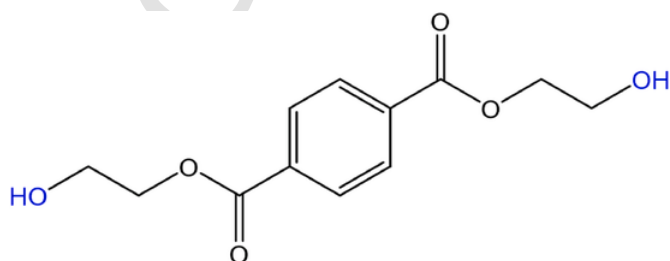


Fig. 1. Molecular structure of bis(2-hydroxyethyl) terephthalate (BHET).

Nurman et al., 2021; Wang et al., 2018). Therefore, DoE has been exploited during the present investigation to partially replace the fossil-based polyol with circular and bio-based components, without requiring additional solvents, additives, or further synthetic steps. The effect of BHET implementation on the final PU properties was investigated through UV–Vis spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), and clearly observed and quantified. The long-term stability under prolonged light exposure was also evaluated and swelling test were performed to deepen the investigation on the BHET effect inside the polymer matrix. The optimized PU formulation retains valuable properties in terms of transparency, UV light and thermal stability comparable with the starting commercial PU reference, thus leading to a more circular, sustainable, but also ready-to-market product.

2. Materials and methods

2.1. Materials

LCR540RT (Demak Polymers) is a 100% fossil-based polyol (a mixture of polypropylene glycol triols and glycerin starter, with molecular weight of 450 and 750), trifunctionalized ($f = 3$) and it contains UV light stabilizers. Sovermol780 (BASF) is a branched polyether/polyester polyol with a 65% bio-based content and a functionality equal to 3 and were supplied by Sigma-Aldrich. DK180HV (Demak Polymers) is a prepolymerized polyisocyanate with high viscosity, composed by a mixture of isophorondisocyanate (IPDI) and IPDI prepolymer/linear polyester. The mercury-based catalyst was supplied by Demak Polymers. Castor oil (CAS 8001-79-4) was supplied by Alfa Aesar. Bis(2-hydroxyethyl) terephthalate (CAS 959-26-2), ethanol ($\geq 99.8\%$, CAS 64-17-5), 2-propanol ($\geq 99.9\%$, CAS 67-63-0), petroleum ether ($> 98\%$, CAS 8032-32-4), diethyl ether (≥ 99.8 , CAS 60-29-7), tetrahydrofuran (≥ 99.9 , CAS 109-99-9) and acetone ($\geq 99\%$, CAS 67-64-1) were supplied by Sigma-Aldrich. Acetonitrile ($> 99\%$, CAS 75-05-8) was provided by J. T. Baker and dimethylformamide ($> 99\%$, CAS 68-12-2) by AnalAR NORMAPUR.

2.2. Formulation process

PU film preparation involves 4 steps (Fig. 2): (i) mixing of polyols in blend; (ii) degassing of polyol blend; (iii) polyisocyanate addition and mixing; (iv) PU blend casting and film polymerization.

6 g of polyol blend (i-a) is prepared by mixing Sovermol780 (sov), LCR540RT (lcr), BHET and catalyst. Polyols (sov, lcr) and BHET are added in different ratios as indicated in Table 2. The catalyst amount is calculated keeping constant the ratio between the catalyst percentage by weight and the active OH groups, to normalize the catalyst within the different formulations: a quantity of catalyst equal to 0.215% by weight for 321 hydroxyl groups was kept constant. The polyol blend is heated and stirred by a hotplate (i-b) at different temperature and time (tiPol e TePol in Table 2). Then, (ii) the blend is degassed under vacuum for 10 min, and (iii-a) subsequently mixed with DK180HV polyisocyanate with stoichiometric ratio (hydroxyl:isocyanate groups = 1:1), (iii-b) under heating and stirring (tiPU and TePU in Table 2) to obtain the final PU formulation (5 g). Finally, (iv) the PU formulation is deposited on a polypropylene substrate and left to polymerize at room temperature for a week. Final PU films of 0.8 mm thickness were obtained. Two replicates are made for each experimental condition.

2.3. Methods

The UV–Vis spectrophotometric characterization was performed with an Agilent Cary 300 Bio spectrophotometer. The wavelengths range from 800 nm to 200 nm, with a scanning speed of 5 nm per second. The measurements were realized in solid-state mode.

Thermogravimetric analysis was performed on a TGA Q600 (TA Instrument). The measurements were carried out under nitrogen flow with heating ramp of 5 °C/min up to 600 °C. The balance plug and sample purge flows, in nitrogen flux, were 40 ml/min and 100 ml/min, respectively. The measurements were carried out in an alumina pan.

Differential Scanning Calorimetry (DSC) analysis was performed with a TA Instruments Q200 equipped with the RCS90 cooling system. Three measurement cycles (heating, cooling and heating) were carried out under nitrogen with an isotherm of 5 min between each step. The heating ramps were set at 20 °C/min, up to 180 °C. The cooling ramp was set at 10 °C/min, up to -80 °C. The measurements were carried out in an aluminium pan.

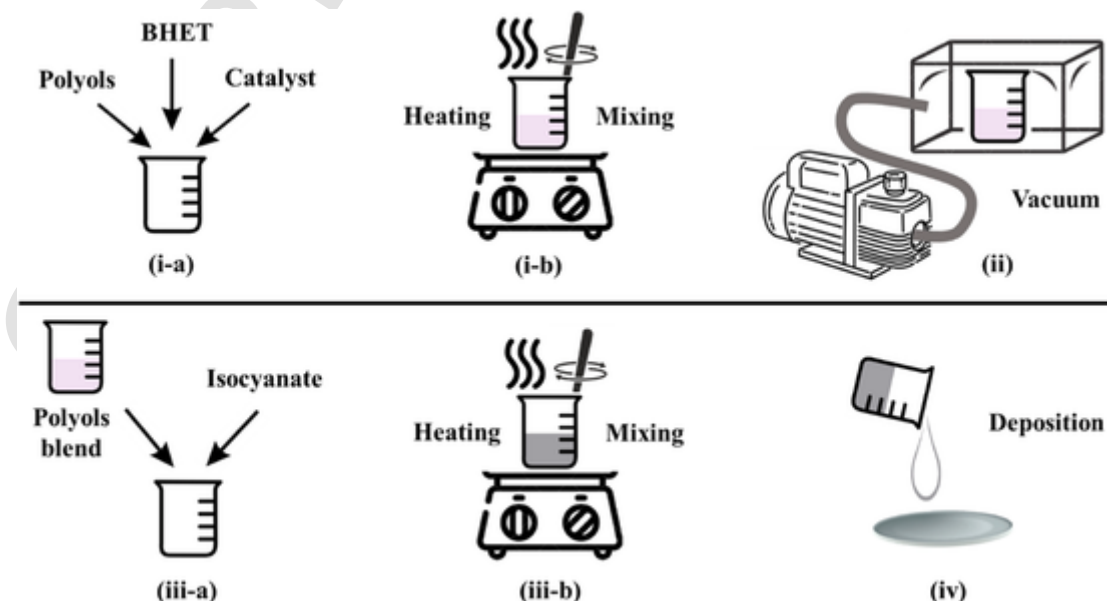


Fig. 2. Schematic formulation process of thermosetting PU-based film.

Two different aging methods were used to assess PU film stability. UV irradiation was performed by a QUV accelerated weathering tester (Model QUV/se, Q-panel lab products). The cycle operating conditions was: 8 h at 70 °C under UV light + 4 h at 50 °C in dark with 100% air humidity, for 20 days. Thermal aging test was performed by heating samples in an oven at 80 °C for 50 days.

Polymer swelling was studied by monitoring the weight variation of PU film when immersed in water. PU films (~2 g) were placed in a closed vial with distilled water (100 ml) at 20 °C. The measurements were carried out periodically for 7 h by removing the sample from water and fast drying the excess of solvent with towel paper. The swelling percentage (S%) was calculated using Eq. (1) (Cassales et al., 2020):

$$S\% = \frac{W - W_0}{W_0} \cdot 100 \quad (1)$$

where W_0 is the sample weight at $t = 0$ and W is the sample weights at different swelling time.

Wattmeter measurements were assessed to monitor the energy consumption of the mixing processes and to find the best formulative conditions for energy saving. The measurements were carried out with a Brennenstuhl wattmeter for different times and temperatures and the results were recorded in the order of kW/h.

3. Results and discussion

3.1. Investigation of circular precursors and operative conditions

Bio-based and waste derived components have been selected and exploited for a progressive reduction of fossil-based LCR540RT polyol. Aiming at having a polymer to be exploited as film coatings for optoelectronics, transparency and thermal stability of the developed PUs have been monitored during the substitution of LCR540RT polyol in all the different proposed formulations.

Due to the physical state of the BHET (solid powder), multi-step process is mandatory for its implementation to PU formulation, comprising at least the BHET dissolution into a liquid component and the subsequent formulation of the PU blend. The first attempt involved the implementation of BHET into the polyol blend through a three-step solvent-assisted procedure: BHET was initially solubilized into the solvent, subsequently mixed with LCR540RT polyol, and finally the solvent was completely removed under vacuum evaporation. Although the BHET diol showed complete solubilization in different solvents (Table S1), it was prone to re-precipitate during the solvent removal. In addition, the use of solvents was undesired as it is contrary with the criteria of sustainability. For these reasons, the solvent-assisted procedure for BHET implementation was considered unsuitable for our purpose and, hence, not furtherly investigated.

A second approach involved the direct dissolution of the BHET into the polyol blend, without adding any solvent. Two different bio-based polyols were tested: castor oil and Sovermol780. The former has been chosen for its widespread presence in the literature for PU development (Borrero-López et al., 2020; Morales-Cerrada et al., 2021), while the latter is a commercial bio-based polyol used in the coating field. The integration of a solid powder also entailed the inevitable consideration of additional process parameters, such as mixing times and temperatures. Dissolution tests were performed with 10%, 15% and 20% w/w of BHET, stirring at different temperatures (from r.t. to 85 °C), up to 90 min. At r.t., BHET could be only partially solubilized in both polyols. At higher temperatures ($T > 65$ °C), Sovermol780 led to a total BHET dissolution, while undissolved BHET was still present in castor oil. Such a behaviour could be ascribed to the higher hydroxyl number (i.e. hydroxyl group per mass) of Sovermol780 (510 mgKOH/g), compared to castor oil (160 mgKOH/g) (Hartman et al., 1987). The total dissolution of 20% BHET was achieved only with Sovermol780 at 85 °C. However, the mixture was difficult to handle as BHET immediately precipitated

once the system cooled down. Hence, BHET concentrations higher than 20% were not further examined. In general, Sovermol780 showed better dissolution ability compared to castor oil and thus it was selected for further investigations. Another interesting consideration derives from the effect of LCR540RT polyol on the BHET dissolution. At 50 °C, Sovermol780 was not able to dissolve 10% BHET, but the combination with LCR540RT leads to higher BHET dissolution. For this reason, a percentage of LCR540RT (from 20% to 46% w/w) was kept within the polyol blend. The BHET implementation into the polyurethane formulation involves only a slight modification in the conventional process.

After BHET dissolution test, different PU formulations have been tested for qualitative evaluations. It was observed that the replacement of LCR540RT with Sovermol780 lowered the flexibility of the final PU limiting the application versatility. For this reason, the complete substitution of LCR540RT was avoided. It should be stressed that flexibility can be further modulated by the selection of a specific isocyanate precursor (Akindoyo et al., 2016); however, this falls outside the aim of this work.

Furthermore, the final PUs transparency resulted to be greatly affected by the mixing temperature of DK180HV isocyanate with the polyol blend: low transparency was achieved when mixing at r.t., whereas high temperatures lead to more transparent PUs.

From these screening analyses, many parameters and their interactions could affect the whole formulation process sizeably impacting on the final PU properties. For this reason, to simultaneously evaluate the influence of several parameters, a multivariate statistical approach (i.e., Design of Experiment, MODDE Pro software, v. 12.1) was preferred over an OFAT one.

Seven parameters have been investigated as factors: three were formulative and four were process-related factors (Table 1).

The influence of these factors on the final properties of polyurethane film has been evaluated by measuring four different responses: (i) BHET dissolution in the polyol blend, (ii) film transmittance (% T_{555nm}), (iii) degradation temperature ($T_{5\%}$) and (iv) glass transition temperature (T_g). BHET dissolution was evaluated using a progressive and qualitative scale: 0 = no dissolution; 1 = partial dissolution; 2 = almost complete dissolution; 3 = complete dissolution, considered the goal of the study in order to work with a homogeneous and optimal polyol blend. The BHET dissolution have been evaluated before the formulation between polyols and isocyanate, therefore the influences of factors TePU and tiPU were not considered for this response. Optical transmittance, fundamental parameter LED coating applications, have been evaluated at 555 nm and compared to the commercial formulation (% $T_{555nm} = 88\%$). Degradation temperatures and glass transition temperatures are related to the PU thermal stability: the former was estimated at 5% weight loss, the latter at the characteristic point of inflection.

Finally, after the factors and responses selection, a screening analysis method with linear D-optimal model has been selected for DoE investigation (Fang and Perera, 2011; Pal et al., 2021; Zareanshahraki and Mannari, 2021). Table 2 shows the 18 experiments resulted from selected DoE along with the corresponding measured responses.

Table 1
Formulative and process factors with ranges selected for the DoE investigation.

	Factors	Abbreviation	Ranges	Units
Formulative	BHET ratio	BHET	0.08–0.2	a
	Sovermol780 ratio	sov	0.4–0.72	a
	LCR540RT ratio	lcr	0.2–0.46	a
Process	Polyols stirring time	tiPol	30–90	min
	Polyols stirring temperature	TePol	50–70	°C
	Polyurethanes mixing time	tiPU	2–6	min
	Polyurethanes mixing temperature	TePU	40–70	°C

^a Ratio is referred to the total polyol blend (equal to 1).

Table 2

DoE plan for the investigation of circular and bio-based PU formulations. Run Std is related to standard commercial PU. Data were collected 7 days after the deposition (except for BHET dissolution obtained during the process).

Factors								Responses			
Run	tiPol [min]	TePol [°C]	tiPU [min]	TePU [°C]	BHET	sov	lcr	BHET dissolution	%T _{555nm} [%]	T _{5%} [°C]	T _g [°C]
1	90	50	2	40	0.200	0.400	0.400	1	75.2	277	48.5
2	60	60	4	55	0.140	0.516	0.344	2	83.5	273	49.2
3	90	70	6	40	0.200	0.600	0.200	2	19.5	283	51.8
4	90	70	2	40	0.080	0.460	0.460	3	81.4	285	45.5
5	30	50	6	70	0.080	0.720	0.200	2	84.4	276	55.3
6	30	50	2	40	0.200	0.600	0.200	1	57.7	274	54.0
7	90	70	6	70	0.080	0.460	0.460	3	82.9	280	46.8
8	90	70	2	70	0.200	0.600	0.200	2	84.4	281	54.9
9	60	60	4	55	0.140	0.516	0.344	2	80.7	270	49.0
10	90	50	2	40	0.08	0.720	0.200	2	87.5	267	53.3
11	30	70	2	40	0.20	0.400	0.400	2	2.3	276	49.5
12	30	70	6	40	0.08	0.720	0.200	3	85.8	267	52.0
13	30	70	2	70	0.08	0.720	0.200	3	91.2	270	55.0
14	30	70	6	70	0.20	0.400	0.400	2	79.2	277	49.8
15	90	50	6	70	0.20	0.600	0.200	1	67.8	270	52.6
16	30	50	6	40	0.08	0.460	0.460	2	85.0	271	45.1
17	30	50	2	70	0.08	0.460	0.460	2	90.1	276	41.8
18	60	60	4	55	0.14	0.516	0.344	2	84.2	274	48.7
Std	/	/	1	20	0.00	0.0	1.0	/	88.0	270	35.0

3.2. Study of the experimental conditions influence on the final PU

The influence of the experimental conditions on the responses (last four columns in Table 2) needs to be carefully evaluated. The responses (y) were represented as a function of the seven factors using a first order linear model. In this perspective, Fig. 3 shows the coefficient plot, a graphical representation of how each factor affects a given response. The green bars indicate the coefficient of each factor in the model equation, whereas the error bars (black segments) are the confidence interval at 95%.

The best BHET dissolution in the polyol blend was obtained with higher mixing temperature (TePol), as expected. None of the 18 experiments showed completely no BHET dissolution (0). No other process factors appeared to significantly influence the dissolution of BHET (Fig. 3-a), but only the amount of the diol itself, as largely expected. As shown in Fig. 3-a, both Sovermol780 and LCR540RT improved the BHET solubility similarly.

The transmittance of the final polymer was mostly influenced by two different factors: TePU (process factor) and BHET amounts (formulative factor). The highest transmittance values were obtained for low BHET amounts and high TePU (Fig. 3-b). The most significant negative effects on %T_{555nm} were found in samples where BHET was not completely dissolved, due to unavoidable scattering phenomena, while the transmittance did not seem particularly influenced by the BHET amount if completely dissolved into the PUs. Both the BHET dissolution in the polyol blend and the transparency were negatively affected by BHET ratio (Fig. 3-a, 3-b), while only the transparency were not influenced by TePol. This observation highlighted that the formulation step between polyols and isocyanate, performed under different conditions (tiPU and TePU), plays a significant role in achieving the dissolution of BHET into the final PUs, as well as higher transmittance values.

The T_g values ranged between 41.8 °C and 55.3 °C, and T_g variation could depend on various factors, like e.g. the intrinsic packing density of the polymer (Privalko and Lipatov, 1974). The lowest T_g values were

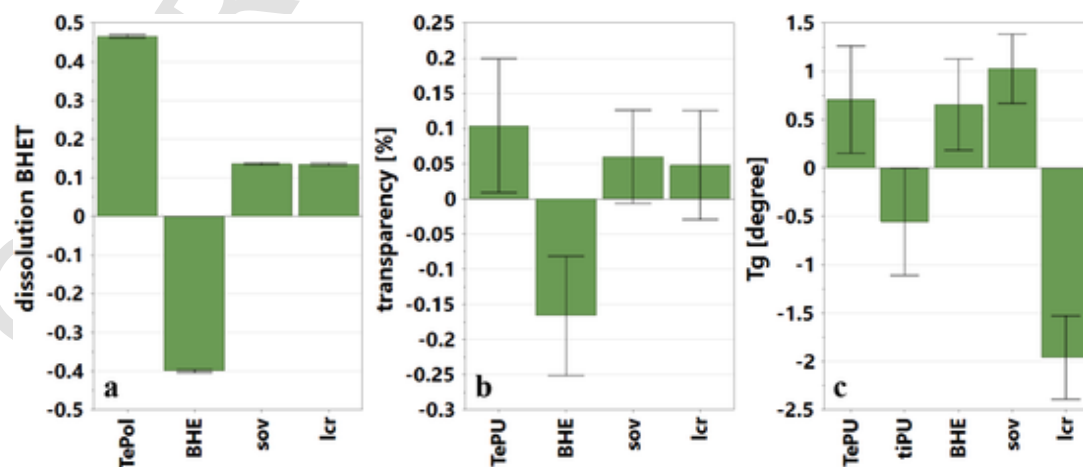


Fig. 3. Coefficient plots with the influential formulative and process factors for a) BHET dissolution, b) transparency, c) T_g. Not significant process factors were excluded from the model and not reported. Error bars reported in plot a) have no statistical meaning being related to qualitative observation. Model equations: a) $y = 2.05882 + 0.466329 * TePol - 0.399681 * BHET + 0.135858 * sov + 0.135133 * lcr$; b) $y = -1.31657 + 0.104043 * TePU - 0.166384 * BHET + 0.0599349 * sov + 0.0481366 * lcr$; c) $y = 50.6471 + 0.708644 * TePU - 0.556211 * tiPU + 0.656711 * BHET + 1.02856 * sov - 1.96011 * lcr$.

obtained with high LCR540RT concentrations and low quantities of Sovermol780, confirming the effect on flexibility highlighted during the preliminary experiments. On the contrary, higher BHET concentration resulted in higher T_g , probably due to the aromatic short structure of BHET (Wei et al., 2005). Concerning process factors, lower PU mixing temperature and longer PU mixing time lead to lower T_g values (as shown in Fig. 3-c), but the influence of these factors resulted lower than the formulative ones.

The influence of the factors on $T_{5\%}$ response was difficult to be determined given the high uncertainty associated with the confidence intervals (Fig. S1). $T_{5\%}$ values did not show substantial variations and all values of DoE plan ranged from 267 °C to 285 °C, which are comparable or slightly superior to the commercial PU formulation ($T_{5\%} = 270$ °C). Despite the low significance of multivariate analysis, the increase in $T_{5\%}$ can be ascribed to the addition of BHET (Lee and Jung, 2022; Li et al., 2022; Pham et al., 2021), ensuring an optimal thermal stability of the PU film.

3.3. Optimal formulation determination

In light of this promising results, an attempt was made to find a formulation able to maximize both the bio-derived and recycled components and simultaneously minimize energy costs, maintaining (or even improving) the properties of the commercial PU. The Sweet Spot plot (Fig. 4) was used to find the optimal formulation, able to respect the desired responses and to optimize operative and formulative conditions: selecting desired responses ranges (i.e. ranges within the responses must fall), the software generates the plot, in which the different areas, where the responses are within the user specified ranges, are highlighted. Regarding the desired responses, BHET dissolution ≥ 2.7 (value evaluated within the Sweet Spot area to be understood as a value close to total dissolution) and $\%T_{555nm} \geq 88\%$ have been set as target range in the Sweet Spot plot. The previous study of the experimental condition did not exclude a total BHET dissolution in the final PUs. Nevertheless, a value close to 3 for BHET dissolution in the polyol blend has been considered more appropriate in order to obtain the highest possible transmittance values ($\%T_{555nm} \geq 88\%$). On the other hand, T_g and $T_{5\%}$ were not limited, being all the obtained values acceptable for application in optoelectronics.

Within the whole Sweet Spot area, process factors have been chosen considering time requirements, amount of circular precursor and energy consumption. The shortest mixing times ($t_{iPol} = 30$ min and $t_{iPU} = 2$ min) have been selected to guarantee a rapid process. The highest temperatures ($T_{ePol} = 70$ °C and $T_{ePU} = 70$ °C) allowed to increase as much as possible the BHET concentration in PU formulation.

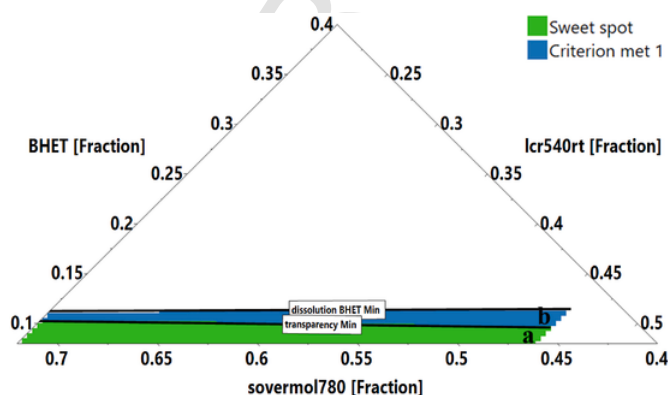


Fig. 4. Sweet Spot plot with formulative factors (BHET, LCR540RT, and Sovermol780). Green area (a): Sweet Spot where criterion met both BHET dissolution and transparency; Blue area (b): Criterion met only the BHET dissolution. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Albeit higher temperatures usually increase the energy consumption, their combination with shorter treatment time leads to a minimization in energy consumption: indeed, as confirmed by wattmeter measurements, 6 g of polyol under stirring and heating at 50 °C for 90 min required 0.14 kW/h (32.3 g CO₂-eq, EU-27 GHG intensity 2020), while stirring at 70 °C for 30 min required 0.09 kW/h (20.8 g CO₂-eq, EU-27 GHG intensity 2020), resulting in 36% decrease in CO₂-eq emissions. (European Environmental Agency).

The Sweet Spot plot presents two different areas which define formulative combinations to achieve the required BHET dissolution and/or transparency criteria. The blue area in Fig. 4-b define the formulative conditions to achieve a complete BHET dissolution (≥ 2.7) but not the desired transparency ($\%T_{555nm} < 88\%$). The green area (Fig. 4-a) represents the Sweet Spot where both the selected criteria are met. To verify the model reliability a validation procedure was followed. Two PU was formulated following two different conditions extrapolated from the Sweet Spot plot. The obtained responses fall within the confidence intervals provided by the software, hence the model was considered valid (Table S3).

All the possible formulations in the Sweet Spot allow to achieve the desired properties. In our case, the polyol blend with the highest circular content was selected as the optimized one, resulting in 10% BHET, 70% Sovermol780, and 20% LCR540RT (w/w). The PU obtained with the optimized polyol blend will be referred as PU_{opt}.

The total percentage of bio-based and recycled components within the polyol blend was 55.5% w/w which corresponds to 24.4% w/w within the final polyurethane film (Fig. 5). For sake of truth, it should be recalled that PUs with higher bio-based content have been already reported in the literature (Borrero-López et al., 2020; Cassales et al., 2020). However, these studies do not show the different physical and mechanical properties between bio-based and commercial fossil-based polymers, therefore it is not possible to evaluate whether it is actually possible to replace the existing product on the market with any formulated samples. On the contrary, our study presents the implementation of bio-based and circular components leading to a ready-to-market polyurethane.

PU_{opt} has been compared to the commercial standard PU (Table S2). The measured $\%T_{555nm}$ and $T_{5\%}$ were 87.6% and 270.0 °C, respectively, and matched with the standard's requirements of 88.0% and 270.3 °C. However, the transmittance profiles are slightly different in the UV part: Fig. 6 shows a drop at 360 nm for the PU_{opt} and at 375 nm for the commercial PU. This difference is due to the UV stabilizer already presents into LCR540RT polyol, therefore a lower amount is present into the optimized PU formulation (Fig. S2). Coatings with transparency at shorter wavelengths is generally desired to widen the field of applications, allowing a greater portion of radiation to cross the polymer film. However, the potential harmful effect of UV radiation on the coating material must be considered, and the amount of UV stabilizer should be properly tuned to achieve the desired compromise in terms of transparency and stability to UV light.

The thermal stability of commercial and optimized PUs was also measured by TGA analysis and different decomposition profiles were observed above 330 °C (Fig. 6). To understand which component affects the thermal stability, PUs with different amounts of BHET and Sovermol780 were compared: samples with the same BHET amounts and different quantity of Sovermol780 showed similar TGA profiles (Figs. S3-b). On the contrary, samples with different BHET amount showed different TGA profiles (Figs. S3-a), indicating higher stability with increase BHET amount. This evidence was also corroborated by the previous DoE analysis on the degradation temperature where BHET shows a beneficial effect, although the whole model for $T_{5\%}$ was considered inadequate. The improved thermal stability of polyurethanes due to BHET implementation are even in accordance with several published works (Lee and Jung, 2022; Li et al., 2022; Pham et al., 2021), and it

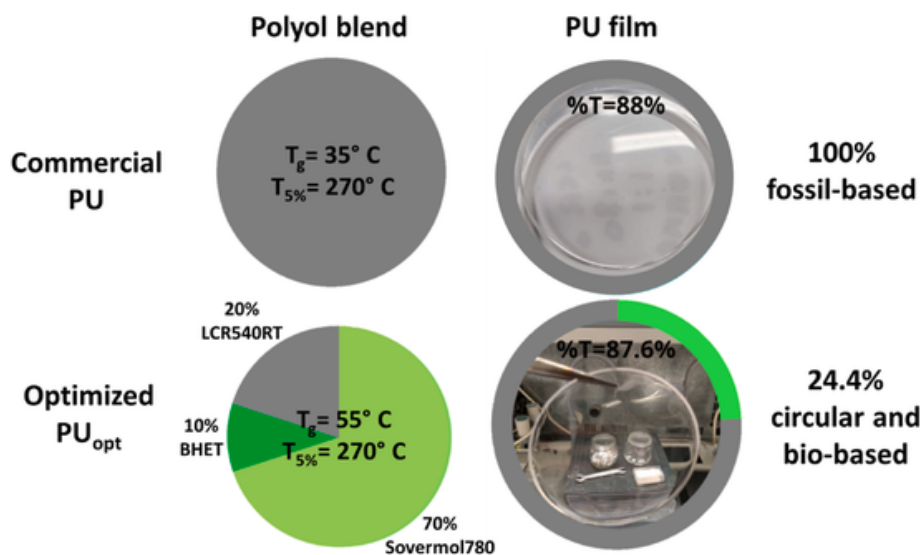


Fig. 5. Summary of the formulation and properties of circular bio-based PU_{opt} compared to the starting commercial PU.

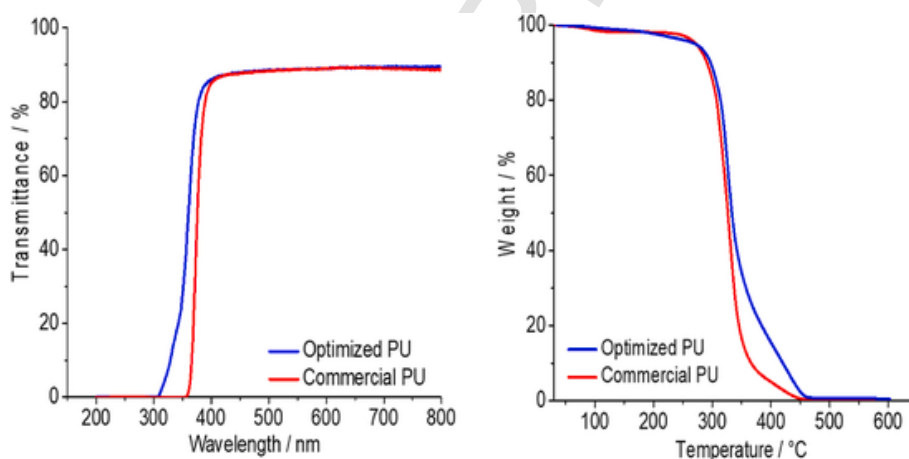


Fig. 6. Transmittance (left) and TGA analysis (right) of commercial and optimized PU films.

was attributed to short aromatic structure of BHET diol. (Tsuchiya et al., 2019; Conrad and Shoichet, 2007; Wei et al., 2005).

The glass transition temperature of the optimized PU (55 °C) is the only parameter not in line with the standard PU formulation (35 °C), however it is still suitable for the application in optoelectronics. In fact, PU coatings and encapsulants should be as thermally stable as possible during their application and the glass transition should not fall within the operating temperatures. Hence, higher T_g values guarantee thermal stability for a wider range of working conditions and applications.

Although the substitution of fossil-based materials with bio and circular ones is a meaningful step in the reduction of environmental impacts, dedicated Life Cycle Assessment should be conducted to quantitatively assess the sustainability of the obtained PUs. Unfortunately, LCA data related to raw materials employed in our formulations are not provided from the suppliers.

At last, a preliminary and basic cost analysis of the circular and bio-based PU_{opt} formulation has been compared with the commercial PU to elucidate the marketability of the final product. The calculation indicated 5.5 €/Kg for the commercial PU and 12.5 €/Kg for the PU_{opt} formulation with virgin BHET (Fig. S4). The use of BHET leads to a greener process, but economically disadvantageous. An economical and circular solution could be represented by using recycled BHET: its use would not only ensure a reduction in the production costs (from 12.5 €/Kg to 6.0

€/Kg) but would also represent a better alternative to virgin BHET in reducing resource consumption.

3.4. Rationalization of the influences of BHET

The possible influences of BHET on PU film properties has been evaluated by comparing two BHET-free polyurethanes with the commercial reference and the PU_{opt} formulation. These PUs (PU1: Sovermol780 + DK180HV; PU2: Sovermol780 (80% w/w of the polyol) + LCR540RT (20% w/w of the polyol) + DK180HV) respect the 1:1 ratio between OH:NCO functional groups and the amount of catalyst was evaluated according to the OH groups. The same characterizations done on previous films was carried out on PU1 and PU2 and the obtained results are reported in Table 3.

PU1 showed the higher overall percentage of green components (27% against 24.4% of PU_{opt}) but without recycled component, whereas PU2 has the lowest percentage of green components (22.5%).

The presence of BHET in PU_{opt} did not result in significant changes in the transmittance values, and no deterioration has been noted in this regard. The addition of a small amount (10% w/w) of waste-derived material led to circular PUs comparable to the commercial reference (100% fossil-based) in terms of transparency. On the other hand, sizable differences in the T_g values were observed: PU_{opt} shows lower T_g temperature (55 °C) compared to PU2 (68 °C), as expected by the in-

Table 3
Comparison between commercial and more sustainable PU formulations.

Sample	%T _{555nm} [%]	T _{5%} [°C]	T _g [°C]	Bio-based Component ^a [%]	Recycled Component ^{a,b} [%]	Pol:Isoc Ratio ^a
Commercial PU	88	270	35	0	0	100: 100
PU _{opt}	88	270	55	20	4.4	100: 129.1
PU1	91	274	70	26.9	0	100: 141.4
PU2	89	275	68	22.5	0	100: 130.9

^a Calculated by weight.

^b Considering recycled BHET.

creased amount of Sovermol780 within PU2. This is also confirmed by PU1 (Sovermol780 is the only polyol here) which showed the highest T_g (70 °C). The higher impact of Sovermol780 agreed with the DoE analysis (see Fig. 3), while the introduction of BHET led to a better thermal stability (Figs. S3 and S5), as previously discussed.

The effect of BHET on the PU properties was further investigated through swelling tests. As well known, a good encapsulating material must guarantee both low water absorptivity and moisture permeability, depending on the final application (Uddin et al., 2019). The evaluation of barrier properties of polymer films is usually measured in terms of water vapor transmission rate and oxygen transmission rate. However, these analyses require high costs and extremely long measurement time to obtain reliable results (Bonomo et al., 2020). To overcome this obstacle, the swelling behaviour of PUs in distilled water were taken into consideration as a first approximation of the barrier properties of the BHET-based films. All circular and bio-based PUs exhibited maximum S% values between 0.6% and 1.35% (Fig. 7), reaching a plateau after 7 h of immersion in water. These values were comparable with the commercial fossil-based reference from Demak® (0.95%), showing the implementation of BHET and Sovermol780 has no significant detrimental effect on the barrier properties of PU film.

In addition, the swelling test allowed to investigate the crosslinking level into the polymer matrix, being S% inversely proportional to the degree of crosslinking (Chen et al., 2002; Javni et al., 2013; Yarmohammadi and Shahidzadeh, 2018). In this perspective, PUs based on Sovermol780 (PU1 and PU2) showed the lowest S% values, suggesting a higher crosslinking degree than commercial LCR540RT-

based PU. The difference in crosslinking was attributed to the higher hydroxyl number of Sovermol780 (510 mgKOH/g) compared to LCR540RT (321 mgKOH/g), which leads to the formation of a greater number of urethane links into the polymer matrix. This conclusion was also corroborated by higher glass transition (T_g) and degradation (T_{5%}) temperatures observed with Sovermol-based PUs. Similarly, BHET diol with hydroxyl value of 440 mgKOH/g (Kojima et al., 2001) and short rigid structure is expected to increase the crosslinking of PU, as often reported (Bhattacharyya et al., 2016; Jamdar et al., 2017; Li et al., 2022). However, the partial substitution of LCR540RT and Sovermol780 polyols with BHET diol led to slightly greater water uptake, and the higher the BHET amount (8%, 10% and 20%), the higher the swelling percentage (~0.95%, ~1.05%, ~1.30%). This behaviour was attributed to the lower functionalization of BHET (f = 2), compared to LCR540RT and Sovermol780 (f = 3), which leads to more linear and less linked polymer chains, thus decreasing the crosslinking degree into the PU matrix (Yarmohammadi and Shahidzadeh, 2018).

Nevertheless, the measured water uptake for the optimized PU formulation is comparable with other fossil-based PU coatings proposed in literature and on the market, (Electrolube technical bulletin UR5640, 2022; SCS, 2016; Jamdar et al., 2017) demonstrating suitable barrier properties for developing new bio-based and circular coatings and encapsulants.

3.5. Aging tests

Encapsulants for optoelectronics must demonstrate good resistance to UV irradiation and thermal degradation (Uddin et al., 2019). To evaluate the long-term stability of PU samples, long-term aging tests were performed and the variation in optical transparency ($\Delta\%T_{555nm}$) have been measured. The PU_{opt} showed excellent resistance ($\Delta\%T_{555nm} = 12.8\%$) compared to the commercial formulation ($\Delta\%T_{555nm} = 21.7\%$) after 50 days at 80 °C. A possible explanation of this phenomenon could be due to the different components in the polyol blend. The reference uses only LCR540RT (polyether), while for PU_{opt} a polyethers-polyesters polyol mixture. It is widely proven that polyesters polyurethanes withstand longer at high temperatures and are more resistant to thermal aging than polyether polyurethanes (Xie et al., 2019).

The optimized PU also showed good results from the QUV aging point of view: 500 h under UV irradiation produced a 3.7% loss in $\Delta\%T_{555nm}$, while the commercial PU showed <1% loss. The UV light stability showed by the commercial PU is due to the larger amount of LCR540RT polyol which contains the UV stabilizer. Hence the resistance of PU_{opt} film to UV light can be easily tuned by adding the proper quantity of stabilizer into the polyol blend.

4. Conclusions

Starting from a commercial thermosetting polyurethane for LED encapsulation, the fossil-based polyol blend has been replaced by circular and bio-based components up to 80%. The implementation of BHET diol and Sovermol780 polyol into the PU formulation has been obtained without additional solvent or treatment. The DoE analysis allowed to observe and quantify the effect of several formulative and process factors on the developed PUs. Particularly, the implementation of BHET improved the thermal stability of PU film thanks to its rigid short structure owning aromatic unit, while reduced the optical transparency due to its tendency to recrystallize in the polymer matrix. This drawback can be limited by increasing the mixing temperature during the PU formulation up to 70 °C. The optimized polyol blend is composed by 10% BHET (potentially waste-derived), 70% Sovermol780 (bio-based), and 20% LCR540RT (fossil-based).

PU film prepared with the optimized polyol blend showed transmittance ($\%T_{555nm} = 88\%$), decomposition temperature (T_{5%} = 270 °C),

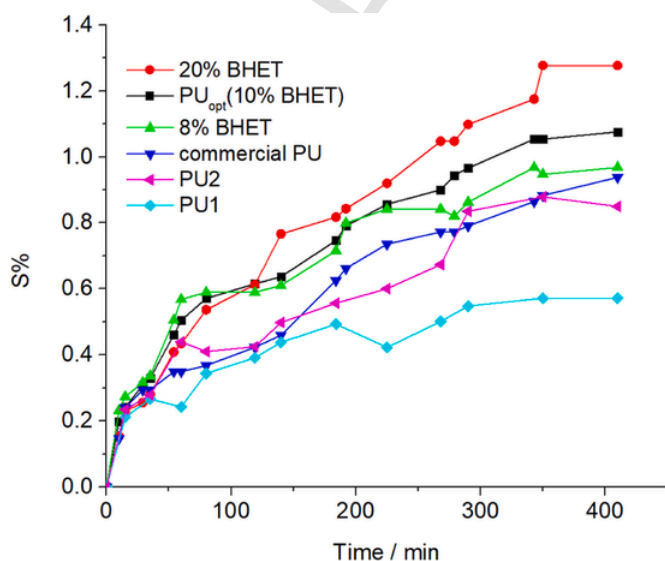


Fig. 7. Swelling test in distilled water of selected PUs.

UV light resistance ($\Delta T_{555nm} < 4\%$ after 500 h), thermal stability ($\Delta T_{555nm} < 13\%$ after 50 days at 50 °C), and water uptake ($S\% \approx 1\%$) comparable with the starting commercial formulation. Only the glass transition temperature ($T_g = 55\text{ °C}$) resulted significantly higher than the commercial PU reference, therefore ensuring thermal stability for a wider range of working conditions. Furthermore, a preliminary and basic cost analysis showed the optimized polyurethane with recycled BHET could be produced with a price similar to the commercial PU reference.

Market-level properties and ease of preparation highlight that circular and bio-based PUs can be rapidly developed and implemented within current polyurethane production processes, promoting the shift towards Circular Economy with solid industrial symbiosis.

In conclusion, the present approach can be easily repurposed to further improve sustainability of polyurethanes with alternative components, as well as to develop other classes of polymers.

Uncited References

Li et al., 2019

CRedit authorship contribution statement

Nicole Mariotti : Data curation, Formal analysis, Investigation, Visualization, Validation, Writing – original draft. **Gabriele Viada** : Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft. **Simone Galliano** : Conceptualization, Methodology, Software, Writing – original draft, Writing – review & editing. **Alberto Menozzi** : Funding acquisition, Resources, Supervision, Writing – review & editing. **Federica Tammaro** : Investigation, Writing – review & editing. **Walter Gianelli** : Writing – review & editing. **Matteo Bonomo** : Supervision, Writing – original draft. **Claudia Barolo** : Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2023.137161>.

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