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Influence of biobased polyol type on the properties of polyurethane hotmelt adhesives for footwear joints

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Abstract

Polyurethanes, one of the most used polymers worldwide, are strongly dependent of non-renewable fossil resources. Thus, boosting the production of new polyurethanes based on more sustainable raw materials is crucial to move towards the footwear industry decarbonisation. The aim of this study is to synthesise and characterise reactive hotmelt polyurethanes from biomass and CO₂-based polyols as bioadhesives for the footwear industry. The influence of biobased polyols on the polyurethane structure, and therefore, on their final properties was analysed by different experimental techniques such as Fourier transform infrared spectroscopy (FTIR), Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), Melting viscosity, Softening temperature and T-peel strength test, in order to assess their viability for the upper to sole bonding process. The results obtained indicated that the incorporation of different amounts of the biobased polyols produces changes in the structure and final performance of the polyurethanes. Therefore, adhesion test carried out by the T-peel test 72 h after the upper-to-sole bonding of the sustainable adhesives show high final adhesion values. These sustainable raw materials provide polyurethane adhesives with additional beneficial non-toxicity and sustainable characteristics, without harming their properties during their useful life.

Keywords: Sustainability, Footwear, Adhesives, Bio-based polyurethanes, Biobased polyol, CO₂-based polyol

Introduction

The sustainable use of resources in the production, use and disposal of a product is one of the current challenges that the European industry faces, which demands innovative developments in materials and joining technologies implementing the circular economy model [1, 2]. Due to the continuous development of raw materials, adhesives and adhesive bonding products, adhesive bonded technologies have gained a high level of acceptance in recent decades. In view of the steadily increasing regulatory requirements, a wide range of innovative solutions are already being successfully implemented through more environmentally friendly adhesive developments [3].

In several industrial sectors, the use of polyurethanes is key to the development of innovative and sustainable products. At present, the raw materials used to produce these polyurethanes come mainly from non-renewable fossil resources, which means that they need to be replaced by other low-carbon materials of renewable origin. Therefore, in the polymer industry, and specifically, in the polyurethanes sector, there is a movement towards sustainable products that minimise the use of petroleum resources, without worsening their performance [4].

There are various alternatives for obtaining polyurethane from renewable raw materials such as vegetable oils (soya, sunflower, etc.). In recent years, they are one of the main alternatives to end the use of petroleum-derived materials in the production of polyols, these being the basic raw material for the development of polyurethane [5]. The recent alternatives use as a reagent for the synthesis of polymers represents numerous advantages, for instance their biodegradability, low toxicity, sustainability, industrial viability, cost competitiveness and design of final polymer properties. Over the last few years, many studies have been carried out which have allowed the substitution of fuel oil as a raw material base, such as, soybean, sunflower, rapeseed, linseed and castor oils are the most commonly used in polymer synthesis through chemical modification [6–8].

The major components of vegetable oils are triglycerides, which are esters of glycerol with three long-chain fatty acids [9]. Fatty acids can be obtained from these vegetable oils by hydrolysis and subsequently transformed into polyols through different production routes (epoxidation, ozonolysis...) [10–12].

Another alternative to produce polyurethane is the use of carbon dioxide (CO₂) as a reagent base for polymer synthesis. CO₂ is one of the greenhouse gases that contributes more than 60% to global warming due to its large number of emissions into the atmosphere, which are uncontrolled emissions that could be a source of raw materials [13, 14].

Although it is true that the uncontrolled increase of this gas poses a threat to our planet, CO₂ is part of our life, for example, through the breathing process of living beings. At industrial scale, it is also used as an additive in food preservation and in the carbonation of beverages such as sparkling water, soft drinks, beer, etc. [15, 16].

This greenhouse gas is an interesting alternative to oil, as CO₂ is a useful, versatile, non-flammable product and is abundant in the atmosphere. In particular, carbon dioxide can be used for the production of polyols, as in the case of vegetable oils. This is a significant innovation, as this greenhouse gas leads to a future sustainable raw material for the chemical industry [17, 18].

Polyurethanes, whose history is relatively short at just over 80 years, constitute the most versatile family of polymers currently in existence, due to their properties being suitable for a wide range of applications, such as foams, elastomers, thermoplastics, thermosets, adhesives, coatings, sealants, fibres, paints, etc. [19, 20].

Specifically, in the footwear sector, polyurethanes (PU) are one of the most used materials, in insoles, coatings, elastomers, adhesives, etc., thanks to their great versatility [21]. Indeed, Thermoplastic polyurethanes (TPUs) are a relevant class of thermoplastic elastomers with a wide variety of compositions and properties. Similarly, Polyurethane adhesives are of great importance in the footwear sector, fulfilling technical requirements across the wide range of materials used in footwear manufacturing [22].

Polyurethane adhesives are highly versatile and can be designed with tailor-made and improved properties, including sustainable ones, through the selection of their reagents [23, 24]. The substitution of reagents from fossil resources with those from biological sources or CO₂ as a reagent base for polymer synthesis provides them with additional beneficial non-toxic and ecological characteristics, without detriment to their performance for application in the footwear industry [25–30].

In this work, INESCOP (Footwear Technology center) focuses on the synthesis and characterisation of polyurethane reactive hotmelt bioadhesives based on polyols from renewable sources or from CO₂ captured in industrial environments, allowing the reduction or removing fossil-based raw materials, and opting for eco-friendly ones. These sustainable raw materials provide polyurethane adhesives with additional beneficial non-toxicity and sustainable characteristics, without harming their properties during their useful life.

Experimental

Synthesis of polyurethanes for reactive hotmelt adhesive (HMPUR)

Reactive polyurethane hotmelt adhesives were synthesised from several macroglycol mixtures of polyadipate of 1,4-butanediol (Hoopol F-580, Synthesia Technology, Barcelona, Spain) [31] with an average molecular weight (Mw) of 2826 g mol⁻¹ polypropylene glycol (PPG, Quimidroga SA, Barcelona, Spain, Mw=425 g mol⁻¹) and a biobased polyol (BIO HOOPOL, Synthesia Technology, Spain) [32]. According to its technical datasheet, this macroglycol is based on a saturated crystalline polyester polyol synthesised using 100% renewable monomers from biomass. The CO₂-based polyol (Cardyon, Covestro, Leverkusen, Deutschland) [33] has an average molecular weight of Mw = 2000 g mol⁻¹ and is based on polyether carbonate diol synthesised using 15% CO₂. Besides, mdi, 4-4' methylene diphenyl diisocyanate (Sigma-Aldrich, Barcelona, Spain) was used as a diisocyanate as it is solid, and it is the best performing to produce polyurethane adhesives with the appropriate characteristics for their final application at present.

The prepolymer mixing method was used for the synthesis of reactive polyurethane hotmelt adhesives, using an optimal NCO/OH index of 1.5. And they were synthesised under a nitrogen atmosphere at 90 °C in a glass vessel placed in an oil bath and equipped with a mechanical stirrer, according to previous research carried out by the authors [15, 18, 34].

The referenced reactive polyurethane hotmelt adhesive (PUREF) was obtained by equal mixing of polyadipate of 1,4-butanediol and propylene glycol. For the incorporation of biobased polyol (BH) or CO₂-based polyol (C), the propylene glycol (PPG) was partially replaced in the formula according to Table 1.

The percentage of free NCO was calculate applying the n-dibutylamine titration method. Once the desired index is reached, the reaction was stopped [35]. Then, the HMPUR adhesive obtained was stored in hermetic disposable cartridges to be applied later by a manual hot melt applicator.

Experimental techniques

Softening temperature

The determination of the softening temperature of the HMPUR was assessed according to EN1238 [36]. The softening temperature indicates the temperature above which the viscous properties of the adhesive become dominant. The standard test defines the

Table 1 Reactive polyurethane hotmelt adhesives nomenclature obtained by partial substitution of polypropylene glycol (PPG) by biobased polyol (BH) or CO₂-based polyol (C)

HMPUR nomenclature	Biobased or CO ₂ based polyol (wt%)	Polypropylene glycol (wt%)	Diisocyanate
PUREF	0	100	4-4'methylene diphenyl diisocyanate
PUR 25BH	25	75	
PUR 50BH	50	50	
PUR 75BH	75	25	
PUR 25 C	25	75	
PUR 50 C	50	50	
PUR 75 C	75	25	

softening temperature as the temperature at which a steel ball passes through a ring filled with adhesive while immersed in a water, glycerol or mineral oil bath (depending on the softening temperature).

Melting viscosity

The apparent viscosity of the reactive polyurethane hotmelt adhesive was evaluated using a Brookfield Thermosel viscometer equipped with an SC4-27 spindle according to the test procedure described in the ASTM D3236-15 standard [37]. This consists of thermostatised camera which melts the adhesive, allowing the viscosity to be measured at a controlled temperature. This value determines the ease or difficulty of the application of the adhesive to the substrate, the working temperature, the open time, etc.

Fourier Transform Infrared Spectroscopy (FTIR)

The chemical properties of the HMPUR adhesive were determined using a Varian 660-IR infrared spectrophotometer (Varian Australia PTY LTD; Mulgrave, Australia). Attenuated total reflection (ATR) technology was used to perform 16 scans at a resolution of 4 cm⁻¹.

Thermogravimetric analysis (TGA)

The thermal stability of HMPUR was performed using a TGA 2 STARe System thermal balance equipped with STARe software (Mettler-Toledo, Switzerland). Approximately 7 to 10 mg of adhesive sample is placed in an alumina crucible. The sample was heated from 30 to 600 °C at 10 °C min⁻¹ in an inert nitrogen atmosphere (flow rate = 30 mL min⁻¹).

Differential Scanning Calorimetry (DSC)

The thermal properties of polyurethane adhesives were studied using a DSC3 + STARe Systems calorimeter (Mettler-Toledo AG, Schwerzenbach, Switzerland). Samples of approximately 9–12 mg in an aluminium pan was employed. The experiments were conducted in an inert nitrogen atmosphere (flow rate = 30 mL min⁻¹) at a heating or cooling rate of 10 °C min⁻¹. Two consecutive runs were completed: (i) heating from –15 to 110 °C, then isothermally heating at 110 °C for 3 min to eliminate the thermal history of the sample; (ii) the second heating from –65 °C to 100 °C, followed by isothermal

cooling at 25 °C for 45 min. The optimal conditions for DSC experiments were previously optimised by the author in a previous work [38].

T-peel strength test

Adhesion properties were evaluated according to the procedure described in the standard EN 1392:2007 [39]. Standard materials were used as a soling and upper material as adherent: vulcanised rubber SBR-2 and a chrome-tanned split leather, respectively. The split leather was provided by the Spanish company “Palomares Piel, S.L” (Elda, Spain). In this way, the bondability of HMPURs was evaluated in split leather/SBR rubber joints.

Before joint formation, each adherent was duly treated. Split leather test samples were roughened at 2800 rpm with a P100 aluminium oxide abrasive cloth (Due Emme Abrasivi, Pavia, Italy) using a roughing machine (Superlema S.A., Zaragoza, Spain). The SBR-2 rubber was roughened and halogenated with 2 wt% trichloroisocyanuric acid solutions in ethyl acetate. Both are typical treatment in the footwear industry today. The following procedure was used to prepare adhesive bonded joints of 150 × 30 mm (SBR rubber/HMPUR/leather).

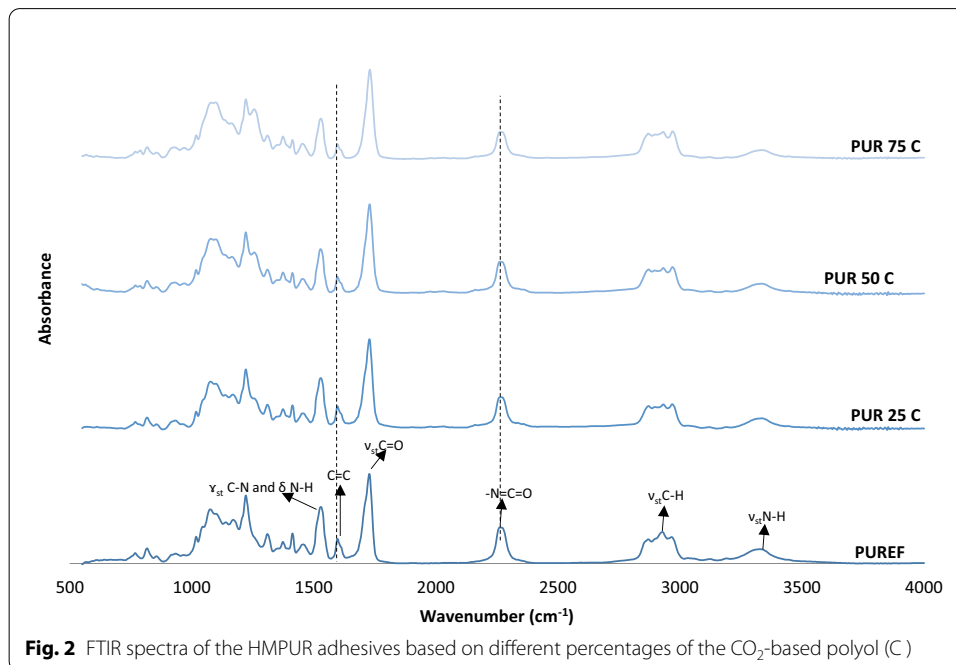
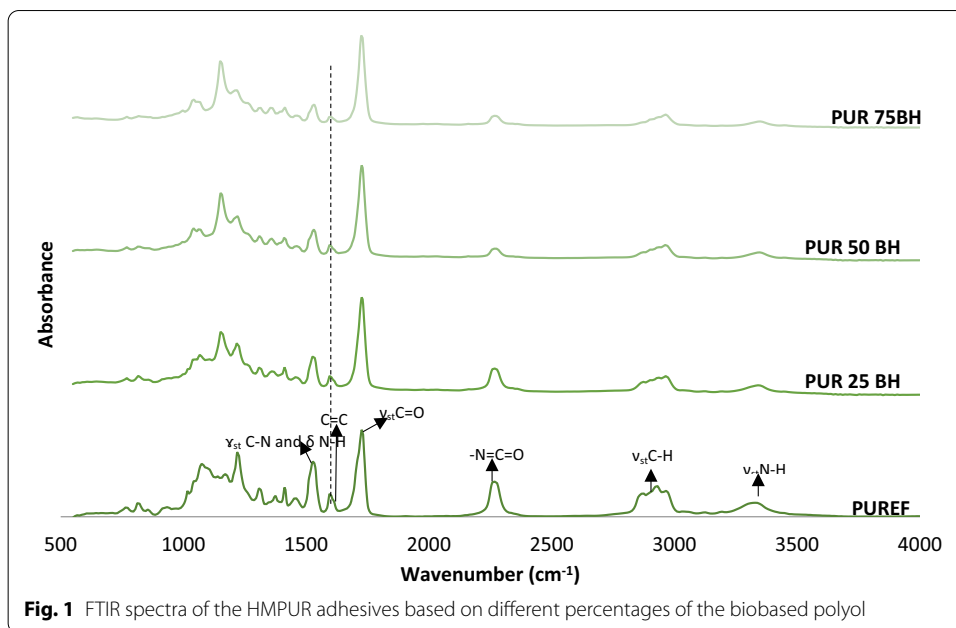
Joint formation was carried out after 30 min since the adhesive application. To enhance contact between both adhesive films, the substrates were activated by infrared radiation at 80 °C in a CAN 02/01 temperature-controlled heater provided by AC&N (Elda, Spain). The strips were immediately placed in contact with each other and a pressure of 1.8 bar was applied for 10 s to achieve a suitable joint. Then, adhesive joints were stored at 23 °C and 50% relative humidity for 72 h. Finally, T-peel strength measurement was performed in an Instron 1011 universal testing machine (Instron Ltd, Buckinghamshire, UK) at a crosshead speed of 100 mm/min. The bond strength values were then calculated as a function of the piece width, strength value and scale obtained with the testing machine, thus obtained an average and typical deviation of the five values for each sample.

Results and discussion

The chemical composition of the synthesised HMPUR adhesives contains different percentage of biobased polyester polyol and CO₂-based polyol, which are analysed by FTIR are show in Figs. 1 and 2.

FTIR spectra show the characteristic bands of a polyurethane prepolymer adhesives and the band corresponding to free reactive isocyanate groups ($-N=C=O$) [40]. The reactive polyurethane adhesives obtained require an excess of isocyanate to react with moisture and subsequent polymerisation or chemical curing to occur. In addition, it is worth noting some of the following bands that appear on all HMPUR adhesives: the N–H stretching band at 3324 cm⁻¹, the C–H stretching band at 2840–3000 cm⁻¹, *st* C=O of ester and urethane groups at 1729 cm⁻¹, stretching C=C band of aromatic groups at 1600 cm⁻¹, the stretching CN and δ NH band at 1527 cm⁻¹, and the reactive isocyanate group at 2270 cm⁻¹.

Specifically, when the biobased polyol was used, the intensity of the C=C band (characteristic aromatic group) at 1600 cm⁻¹ is also reduced, which indicates that the isocyanate content in the polyurethane formulation is lower, thus confirming the lower urethane content in the polyurethane using biobased polyester polyol. In the



case of CO₂-based polyols this reduction occurs more slightly in the HMPUR adhesives. The FTIR spectra also show the characteristic C-O stretching bands of macro-molecular diols at 1220, 1162, 1075 and 965 cm⁻¹. The relative intensity of the NCO band decreases as the content of biobased polyol increases, which is in line with the theoretical values in both news polyols.

The HMPUR adhesives obtained with biobased and CO₂-based polyols were evaluated by DSC experiments to understand their thermal behaviour.

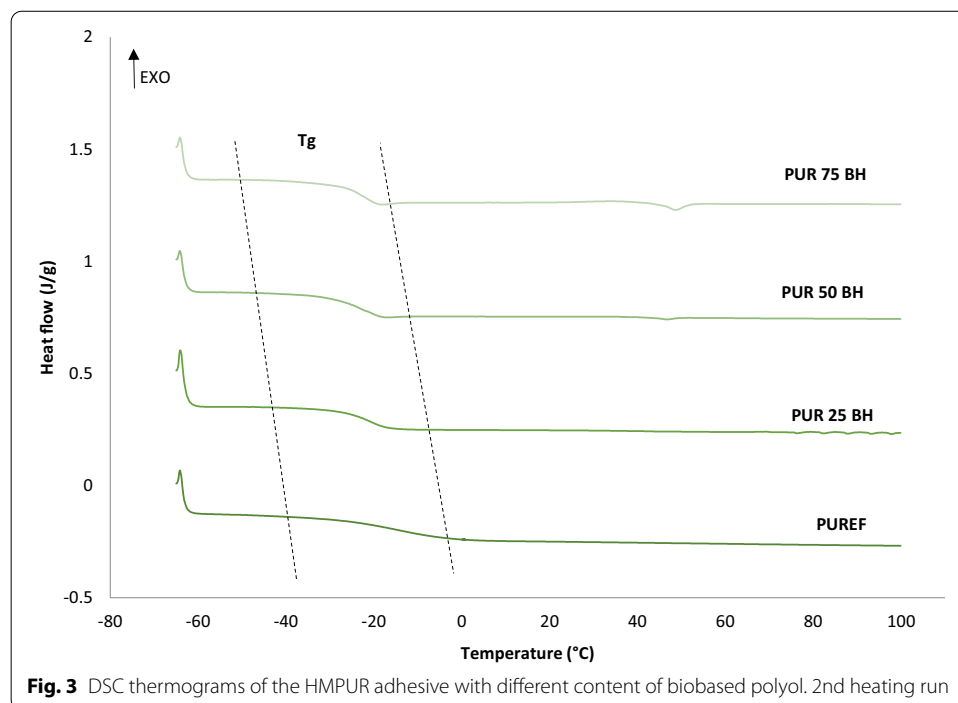
The DSC curves of the HMPUR adhesives corresponding to the second heating run, after thermal annealing are shown in Figs. 3 and 4. DSC thermograms of the reactive hotmelt adhesives show the glass transition temperature (T_g) at low temperature, decreasing slowly from -14.2 to -23 °C when the percentage of biobased polyol and CO₂-based polyol increase respectively. This change may be due to lower mobility due to the increased degree of phase separation in the polyurethane [41].

The conventional urethane prepolymer (PUREF) did not show the crystallisation and melting process of the soft segments. In the case of the HMPUR adhesive with 50 and 75% of the biobased polyol show the melting process of the soft segments, due to the crystalline nature of the biobased polyol, therefore the incorporation of biobased polyol changes the structure of HMPUR adhesives (Table 2).

By contrast, when used as a CO₂-based polyol, the HMPUR adhesives based on this polyol only show glass transition temperature (T_g) according to the similarity of the CO₂ based polyol with the conventional polyol.

The thermal stability of the synthesised bio-based or CO₂-based HMPUR adhesives was studied by thermogravimetric analysis (TGA). Figures 5 and 6 show the thermograms of the HMPUR adhesives obtained by the substitution of different percentages of the polypropylene glycol with a biobased polyol and CO₂-based polyol, respectively. The thermograms show, the decomposition of all HMPUR adhesives occurs in two stages, occurring around 300 and 400 °C, respectively, calculated at the maximum of the first derivate in DTA thermograms (Figs. 5 and 6).

The partial substitution of the propylene glycol by the biobased polyol produces an increase in thermal stability evidence by an increase in the decomposition temperature,



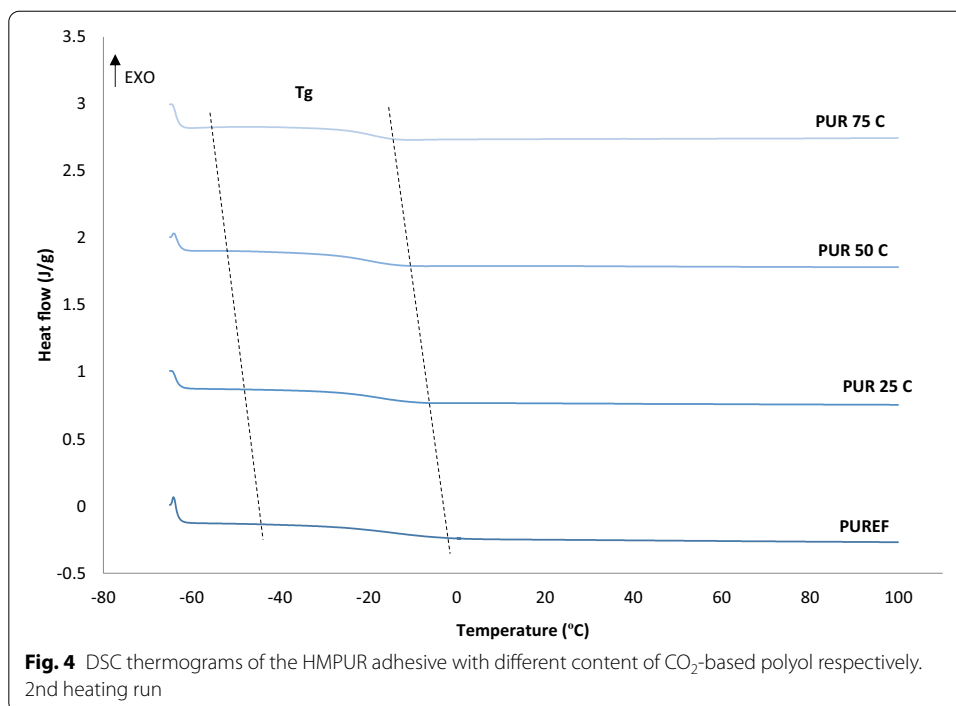
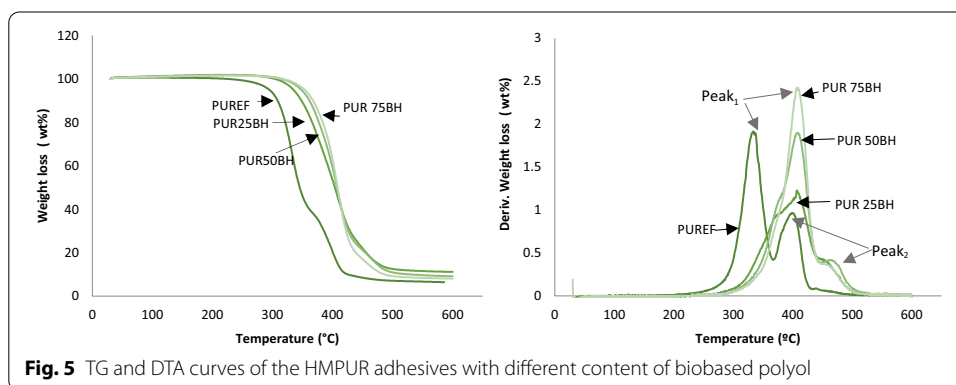
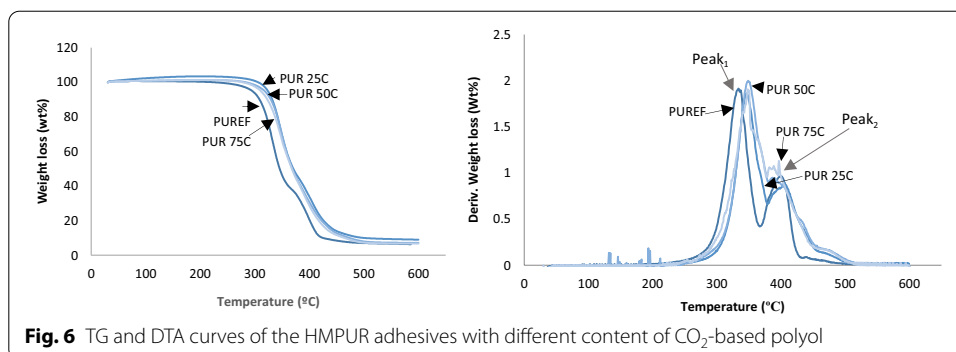


Table 2 DSC results of the HMPUR adhesives calculated from 2nd heating run

HMPUR adhesives	T_g (°C)	T_m (°C)	ΔH_m (J/g)
PUREF	-14.2	-	-
PUR 25BH	-20.9	-	-
PUR 50BH	-23.0	46.8	-0.3
PUR 75BH	-23.0	48.7	-1.1
PUR 25 C	-17.2	-	-
PUR 50 C	-21.2	-	-
PUR 75 C	-18.9	-	-



this starts at a higher temperature than the conventional HMPUR adhesive 25, 42, produced in the first decomposition process (Fig. 5). Being more pronounced the higher the



amount of the biobased polyol in the HMPUR adhesives. When the CO₂-based polyol is incorporated the increase in thermal stability is less marked than when the bio-based polyol is used, this is due to the different nature of the CO₂-based polyol (Fig. 6, Table 3).

The melting viscosity and the soft temperature of the HMPUR synthesised are included in Table 4.

The viscosity of the HMPUR adhesives is increased by the incorporation of the of biobased polyol or the CO₂-based polyol, the more propylene glycol replaced by biobased or CO₂-based polyols, the higher the viscosity of the HMPUR adhesives. These changes could be attributed to an increase of the molecular weight of the polyurethane. The final application of these adhesives is not affected by the increase in viscosity, so all adhesives flow properly.

Moreover, the biobased HMPUR adhesives have a softening point similar to the conventional HMPUR adhesive around 60°C. In the case of the biobased HMPUR adhesives present a content of 75% biobased polyol or CO₂-based polyol have the same softening point as conventional HMPUR adhesive.

The adhesion properties of HMPUR adhesives with different amounts of biobased and CO₂ polyols was studied by T-peel testing in leather/rubber joints, as described in Sect. 2. Figures 7 and 8 show T-peel strength after 72 h of joint formation as a function of the different amounts of biobased and CO₂ polyols in the HMPUR adhesives, respectively.

There is a decrease in the adhesion values of the adhesives with a partial substitution of the propylene glycol polyol by biobased and CO₂-based polyols adhesive failure of SBR2 rubber regards to the reference adhesive (PUREF). In addition, there is a shift in the failures since the reference adhesive has a rubber cohesive failure and all biobased and CO₂-based HMPUR adhesives have adhesive failure of SBR2 rubber. All biobased HMPUR adhesives meet the minimum quality requirements demanded for footwear applications according to standard test [43].

Conclusions

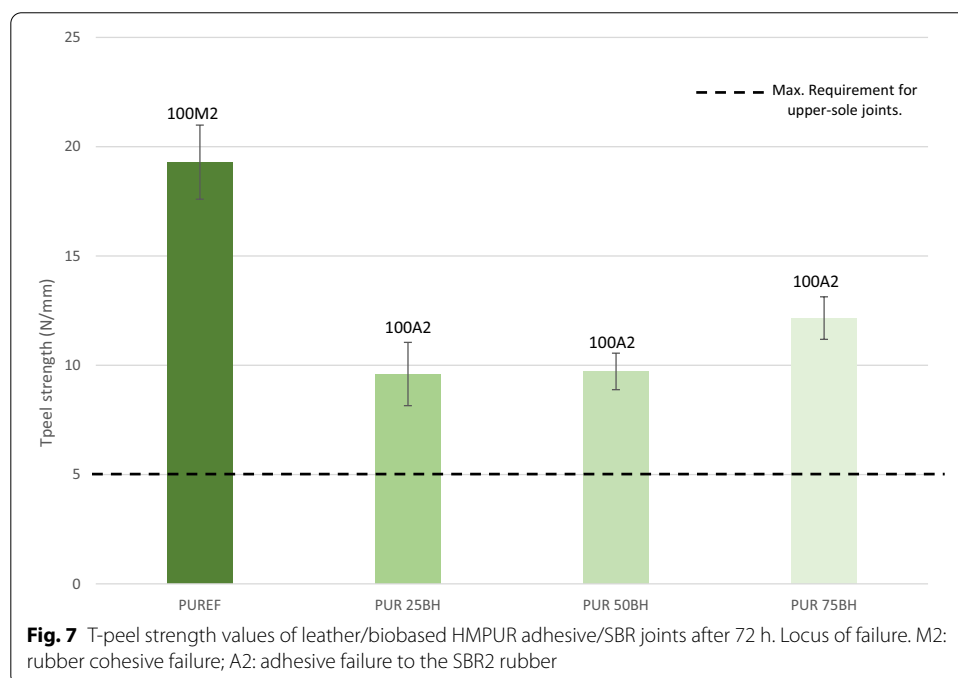
The biobased and CO₂-based reactive hotmelt polyurethane adhesives obtained are a new and sustainable solution that can reduce the use of fossil resources without detriment to their performance for footwear applications.

Table 3 Results obtained from the DTG thermograms of the HMPUR adhesives as a function of biobased and CO₂-based polyol, respectively

HMPUR adhesives	First stage		Second stage	
	Tpeak ₁ (°C)	Weight-loss (%)	Tpeak ₂ (°C)	Weight-loss (%)
PUREF	333.5	61.3	398.9	29.2
PUR 25BH	406.8	74.1	439.6	13.5
PUR 50BH	406.8	76.6	423.2	22.4
PUR 75BH	408.5	79.4	437.1	11.8
PUR 25 C	346.9	56.8	405.2	32.5
PUR 50 C	348.8	59.8	387.2	25.0
PUR 75 C	348.5	58.3	397.0	31.0

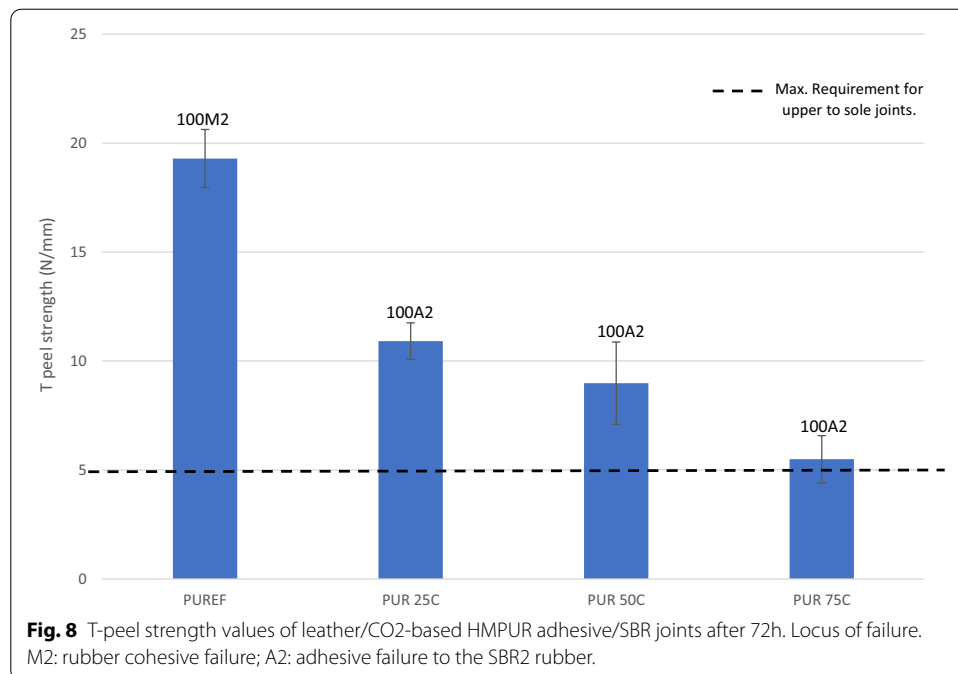
Table 4 Melting viscosity and softening point of the bio and CO₂ based HMPUR adhesives

HMPUR adhesives	Viscosity (mPa s)	Softening point (°C)
PUREF	10,000	58
PUR 25BH	13,000	56
PUR 50BH	27,000	56
PUR 75BH	32,500	58
PUR 25 C	18,000	51
PUR 50 C	22,000	51
PUR 75 C	20,500	58



The characterisation of the HMPUR adhesives obtained shows that the incorporation of different amounts of the considered polyols produces changes in the structure and final performance of the polyurethanes. The results show that the polyurethane adhesives with different thermal stability, softening point, viscosity, molecular weight have been obtained. In addition, adhesion test carried out by the T-peel test 72 h after the upper-to-sole bonding of the sustainable adhesives show high final adhesion values. Thus, the new biobased and CO₂-based adhesives meet the highest quality requirements in the footwear industry for upper-to-sole joints. Hence, the development of more sustainable adhesives from partial substitution of oil-based polyols by biobased or CO₂-based polyols with a similar performance to the conventional adhesives is now a reality.

In conclusion, this development allows biobased reactive hotmelt polyurethane adhesives to contribute to the climate neutrality of the products where they are applied, particularly in the upper-to-sole joints in the footwear. They also contribute to the sustainable development of European footwear industry. Thereby contributing to the



achievement of sustainable development goals (SDGs), in particular SDG 12 and 13, responsible consumption and production, and climate action. And finally with the SDG 17, because without technological cooperation all the other objectives cannot be achieved.

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Author's contributions

MPC, MAP performed the experiments; MPC analysed the data with the support of MAP; MPC and FA wrote the paper and all authors reviewed and revised the manuscript to its final form. EO and FA supervised the entire study. All authors have read and agreed to the published version of the approved the final manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The data presented in this study are available upon request from corresponding author.

Declarations

Ethics approval and consent to participate

Not applicable in this section.

Consent for publication

Not applicable in this section.

Competing interests

The authors declare no conflict of interest.

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