

# Emerging Reprocessable and Recyclable Biobased Cross-Linked Polyurethanes Through Diels–Alder Chemistry

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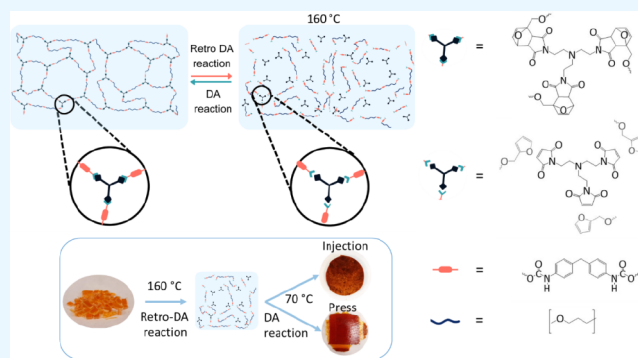
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**ABSTRACT:** Cross-linked polyurethanes (PUs) present outstanding properties and high versatility, making them ideal for use in many different applications. Nevertheless, the intersection of environmental and socioeconomic concerns regarding the recyclability of cross-linked materials presents alternative opportunities for advancing the field of cross-linked polyurethane chemistry. In this context, emerging reprocessable and recyclable biobased cross-linked PUs were synthesized within this work through Diels–Alder (DA) chemistry. Thus, a trifunctional partially biobased low-molecular-weight polyol containing the furan–maleimide Diels–Alder adduct (DA-triol) was developed to be used as a thermoreversible cross-linker in PU synthesis. First, the thermoreversibility of the cross-linker was demonstrated at temperatures as high as 160 °C (retro-DA reaction). Afterward, the DA-triol was used together with a commercial biobased macrodiol and polymeric methylene diphenyl diisocyanate (pMDI) to synthesize different formulations of PUs that ended up with properties ranging from flexible to rigid. Then, the recyclability and reprocessability of the synthesized PUs were also evaluated by compression, injection, and extrusion. Finally, the mechanical properties of the original and recycled polyurethanes were tested, obtaining recycling efficiencies higher than 80%. Thereby, these materials offer a solution to the long-standing issue of recycling of cross-linked polyurethanes, overcoming many sustainability challenges.

**KEYWORDS:** cross-linked polyurethane, biobased, Diels–Alder chemistry, thermal reversibility, reprocessing



## INTRODUCTION

Polyurethanes (PUs) can be synthesized as porous or compact materials, including flexible and rigid foams and coatings, adhesives, sealants, and elastomers (CASE),<sup>1</sup> and thereby are used in a variety of industries and applications. They are one of the most widely used polymers: in 2021, PUs were the fifth most used polymer in Europe, and their global production in 2022 was 25.78 million metric tons.<sup>2–4</sup> This is due in no small measure to their high versatility, resulting from their adjustable chemical architecture, thus obtaining PUs with different properties, from flexible materials to materials of high stiffness.<sup>5–8</sup>

As polyurethanes are so widely used, they also generate a large amount of waste, from which 23% was landfilled and 42% was used for energy recovery in 2020,<sup>3</sup> creating an environmental issue due to its low biodegradability. As a solution, scientists have been looking for better methods of final disposal, some of which include physical and chemical recycling. Besides, during the last years, the incorporation of reversible covalent bonds into their structure has been presented as a promising alternative to make polyurethanes more recyclable and reprocessable.<sup>9,10</sup>

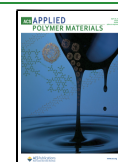
One of the most studied reversible covalent bonds is based on Diels–Alder (DA) chemistry, which consists of a chemical coupling reaction between a conjugated diene and a substituted alkene, commonly termed the dienophile, to form a substituted cyclic derivative.<sup>11</sup> For instance, the Diels–Alder reaction between furan and maleimide is thermally reversible, and takes place at low temperatures, while its reversal (retro-DA) occurs at higher temperatures.<sup>12,13</sup> The use of this type of thermally reversible bonds is becoming popular in polymer chemistry because at room temperature, the DA bonds are coupled, allowing polymerization, yet above the switching temperature, the material depolymerizes, facilitating material reprocessing. When this principle is used with cross-linkers, i.e., small multifunctional chemical structures with DA bonds, the mechanical properties of the final cross-linked polymer

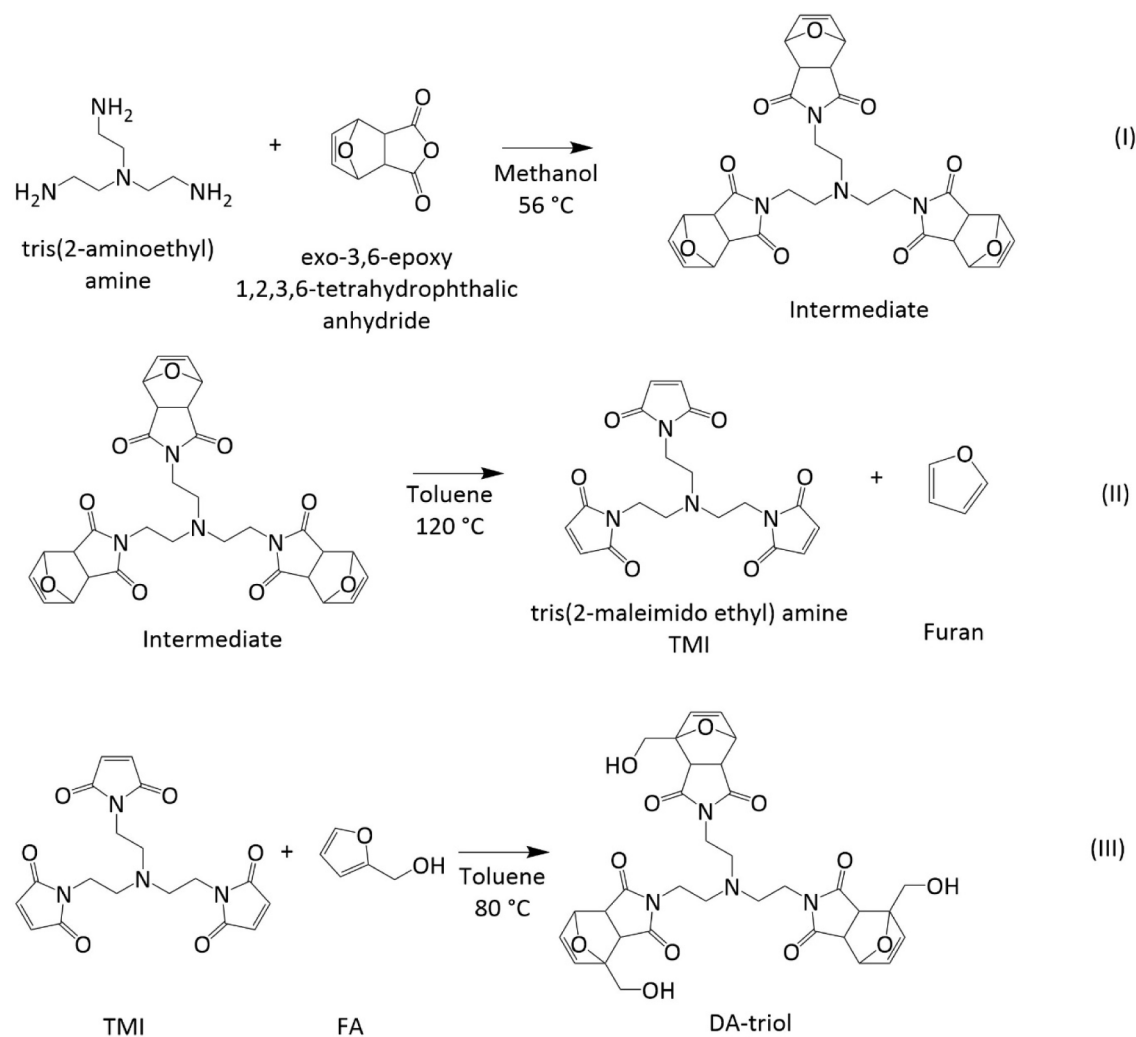
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**Figure 1.** Sequential synthesis reactions (I, II, and III) of DA-triol.

increase; nonetheless, above the switching temperature, the bonds are uncoupled and the polymer network can be uncross-linked, giving plasticity so that the material can be reshaped and subsequently recycled.<sup>14–17</sup> This phenomenon has been studied and proven to work even when the pieces are cut in half, damaged, and several healing cycles are performed.<sup>18–21</sup> Some authors synthesize polyurethanes through this furan-maleimide reaction of prepolymers (polyurethane and cross-linkers) functionalized with furan and maleimide, yet the coupling reaction turns to be slow and may not be suitable for many high-volume or industrial applications.<sup>22,23</sup>

The aim of this work is to synthesize partially biobased cross-linked polyurethanes that also contain dynamic covalent bonds in its chemical structure based on the DA thermo-reversible reaction. Thus, a biobased trifunctional polyol containing a DA adduct in its structure (DA-triol) was synthesized from a trismaleimide (TMI) and furfuryl alcohol, a component that can be obtained from polysaccharides or sugars from renewable plant sources.<sup>14,24</sup> Various formulations of cross-linked and partially biobased PUs were then synthesized using the DA-triol as cross-linker, a commercially available fully biobased polyether diol (macrodiol), and a polymeric methylene dimethyl isocyanate (pMDI). Thus, cross-linked polyurethanes containing the DA-triol were synthesized by the well-studied polyaddition reaction between

isocyanate and hydroxyl groups. In this way, the cross-linked PUs synthesized within this work present mechanical properties and behaviors of cross-linked polymers below the retro-DA reaction temperature, but due to the DA adduct, they are reprocessible. Hence, recycling tests were conducted by breaking down the PUs into pellets and reprocessing them above the retro-DA reaction temperature through compression, injection, and extrusion. Subsequently, the material was cooled to the DA reaction temperature to facilitate coupling, followed by final cooling to room temperature. The efficiency of the reaction reversibility was evaluated by mechanical tests.

## MATERIALS AND METHODS

**Materials.** Tris(2-aminoethyl) amine (96%), furfuryl alcohol (FA) (98%), and exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (98%), purchased from Sigma-Aldrich, and HPLC grade methanol (99.9%), toluene (99.8%), and *n*-hexane (95%) from Panreac were used in the synthesis of DA-triol. For the synthesis of the PUs, Velvetol H500 from WeylChem International GmbH (made with 100% biobased propanediol,  $M_w = 557$  g/mol and hydroxyl number 201 mg KOH/g) and Desmondur 44 V20L (31.71% NCO content) from Covestro were used as the macrodiol and as the polymeric isocyanate based on 4,4'-pMDI, respectively. All the products were used as received except the macrodiol and the pMDI, which were dried under vacuum for 4 h prior to use.

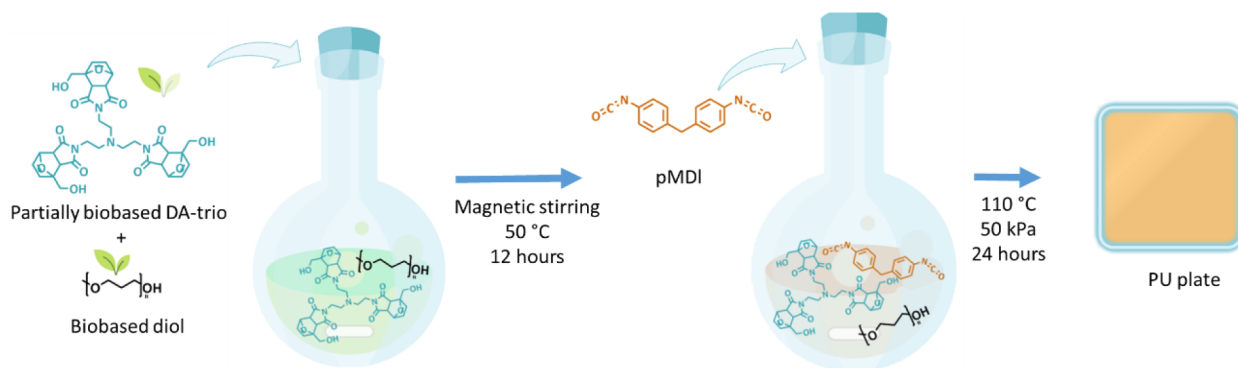


Figure 2. General scheme of the synthesis of cross-linked polyurethanes.

Table 1. Designation and Composition of Synthesized Cross-Linked Polyurethanes

sample name	OH <sub>DA-Triol</sub> /OH <sub>macrodiol</sub> (equivalent fraction)	isocyanate index	final formulation (% weight)			biobased content (% weight)
			DA-triol	macrodiol	pMDI	
PU0.0	0.0/1.0	1	0	68	32	67.8
PU0.3	0.3/0.7	1	17	49	34	56.8
PU0.5	0.5/0.5	1	29	37	34	49.0
PU0.7	0.7/0.3	1	43	22	35	40.8

**Synthesis of the DA-Triol.** The synthesis of the DA-triol was adapted from Gandini et al. and Cioc et al.<sup>24,25</sup> It consists of a sequence of three consecutive reactions (Figure 1) that were carried out in a round-bottom Pyrex reaction flask, under constant stirring and reflux, and heated using a heating mantle and a feedback temperature controller.

First, an intermediate was formed by reacting tris(2-aminoethyl) amine (4.66 g, 0.03 mol) and exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (15.56 g, 0.09 mol) in HPLC grade methanol (250 mL), at 56 °C for 3 days. The precipitate was collected, washed with methanol, and dried. A white powder was obtained as an intermediate.<sup>24</sup>

Then, the intermediate (4.00 g) was diluted in toluene (250 mL) and stirred continuously at 120 °C to subject it to the retro-DA reaction, gradually releasing furan over 24 h of reflux. The resulting mixture was rapidly cooled and then filtered, discarding the residue and drying the filtrate by vacuum evaporation of the toluene, in order to yield a yellow solid (tris(2-maleimidoethyl) amine, TMI). The obtained TMI was finally washed with hexane and dried again (2.02 g).

In the third reaction, TMI (3.00 g, 0.008 mol) and furfuryl alcohol (2.440 g, 0.02 mol, 5% excess) were mixed along with toluene (15.5 mL) to form the DA-triol. The mixture was heated to 80 °C and allowed to react for 16 h. After the reaction time, the precipitated triol was collected as a solid, washed with toluene, and then dried in a vacuum oven at 70 °C.

**Synthesis of Biobased Cross-Linked Polyurethanes.** The PUs were synthesized by a one-step bulk polymerization process without catalyst in a 25 mL round-bottom flask. First, a fraction containing the hydroxylated components was prepared. To this end, the previously dried macrodiol and the DA-triol were mixed at 50 °C for 12 h under a nitrogen atmosphere.

Then, the previously dried pMDI was added to the fraction that contains the hydroxylated components, keeping the isocyanate index equal to 1 for all of the systems. The system was then magnetically stirred in a nitrogen atmosphere for 5 min. Later, the mixture was transferred to a mold consisting of two plates, 1.5 mm apart, placed in a hot plate press, and cured at 110 °C, for 24 h and 50 kPa. After the curing process, samples of 100 × 100 × 1.5 mm<sup>3</sup> were obtained.

Different cross-linked PU formulations were synthesized varying the molar fractions of the macrodiol and DA-triol, using in all cases stoichiometric NCO:OH ratio of 1. Figure 2 illustrates the polyurethane synthesis procedure, while Table 1 summarizes the

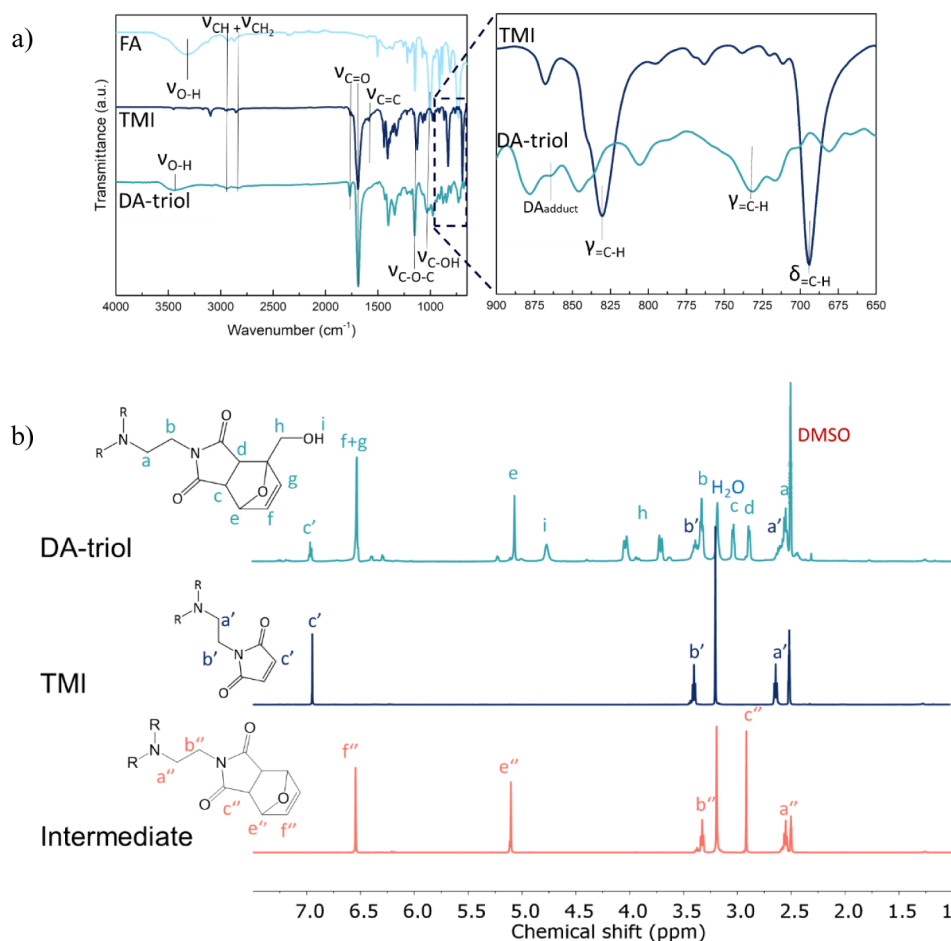
equivalent fractions, weight percentages, and biobased contents of the synthesized PU formulations and the designation of samples, named as PUXX, where XX denotes the fraction of OH equivalents of DA-triol related to the total OH equivalents. For instance, sample PU0.3 contains 1 NCO equivalent from pMDI, 0.3 OH equivalents from the DA-triol and 0.7 OH equivalents from the macrodiol. A final plate containing only DA-triol and pMDI was attempted to synthesize. However, there were difficulties achieving a proper mixing, so it was not considered for further analysis.

**Characterization.** The chemical structure of the synthesized DA-triol, intermediate, and TMI was analyzed by proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) using a Bruker Avance Neo 500 NMR spectrometer at a resonance frequency of 500 MHz. The sample temperature was set at 55 °C. The samples were dissolved in deuterated DMSO, which presented a peak at δ = 2.50 ppm as a reference. The characteristic functional groups of the synthesized materials were also analyzed by Fourier transform infrared (FTIR) spectroscopy using a PerkinElmer Spectrum Two spectrometer equipped with an ATR golden gate accessory (UATR Two). The spectra were recorded between 4000 and 650 cm<sup>-1</sup>, with 32 scans and a resolution of 4 cm<sup>-1</sup>. The progress of the retro-DA reaction versus time was also analyzed by FTIR spectroscopy.

The Diels–Alder reaction reversibility of the synthesized DA-triol and PUs, as well as the thermal behavior of the synthesized PUs, were analyzed by differential scanning calorimetry (DSC). The analyses were performed in Mettler Toledo DSC 3+ equipment, equipped with a robotic arm and an electric intercooler as a cooling unit. Between 5 and 10 mg of sample was encapsulated in aluminum pans. All heating and cooling scans were performed at a constant rate of 10 °C min<sup>-1</sup> and under a nitrogen atmosphere. Depending on the study, samples were subjected to various heating and cooling scans and isothermal steps.

The thermal stability of the samples was analyzed in a Mettler Toledo TGA/SDTA851 thermogravimetric analyzer. The samples were scanned from room temperature to 800 °C at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere.

Rectangular-shaped specimens of dimensions 3 × 30 × 1.5 mm<sup>3</sup> were punched from polyurethane samples for its posterior use in dynamic mechanical analyses and tensile tests. Dynamic mechanical analyses (DMA) were carried out to study the thermomechanical behavior, using an Eplexor 100 N analyzer Gabo equipment. Measurements were carried out in tensile mode in a temperature range from -100 to 230 °C at a scanning rate of 2 °C min<sup>-1</sup>. The



**Figure 3.** (a) FTIR spectra of furfuryl alcohol, TMI, and DA-triol (left) and amplified 900 to 650  $\text{cm}^{-1}$  interval (right). (b)  $^1\text{H}$  NMR spectra of DA-triol, TMI, and intermediate.

initial strain was established as 0.05% (linear viscoelastic range), and the operating frequency was fixed at 1 Hz.

The mechanical behavior of the synthesized biobased cross-linked PUs was evaluated using an Instron 5967 testing machine provided with a 500 N load cell and 1 kN pneumatic grips. Specimens were gripped between two clamps, maintaining a distance of 10 mm, and then, tensile tests were performed at a speed of 10  $\text{mm min}^{-1}$ , getting the corresponding stress–strain curves, from which the Young's modulus, tensile strength, and strain at break values were derived.

An AR-G2 rheometer with an environmental test chamber (ETC) oven setup (TA Instruments) and parallel plate geometry was used for rheological characterization. A constant range of normal force of  $1 \pm 0.5$  N was applied by automatically adjusting the gap to ensure proper contact between the sample and the plates. Stress relaxation analyses were performed using 8 mm diameter parallel plates and 0.1% strain to elucidate the correlation between the stress relaxation dynamics and retro-DA reaction thermochemistry. The curing process of the synthesized PUs was also studied using 20 mm diameter parallel plates in an oscillatory analysis with a frequency of 1 Hz, strain of 1% and a temperature ramp from 25 to 200  $^{\circ}\text{C}$  at a heating rate of 2  $^{\circ}\text{C min}^{-1}$ .

#### Recycling and Reprocessing of Biobased Cross-Linked PUs.

In order to design and set the conditions (temperature and time) for the recycling and reprocessing steps, DSC, rheology, and FTIR studies were performed. Thereby, based on the obtained results, the DA and retro-DA temperature, as well as the reprocessing/recycling time, were fixed. Once the parameters were set, recycling was performed. To this end, PU samples were cut into 3 mm pieces, and they were placed in a mold and pressed using a hydraulic hot plate press (maximum pressure 50 kPa) at the retro-DA reaction

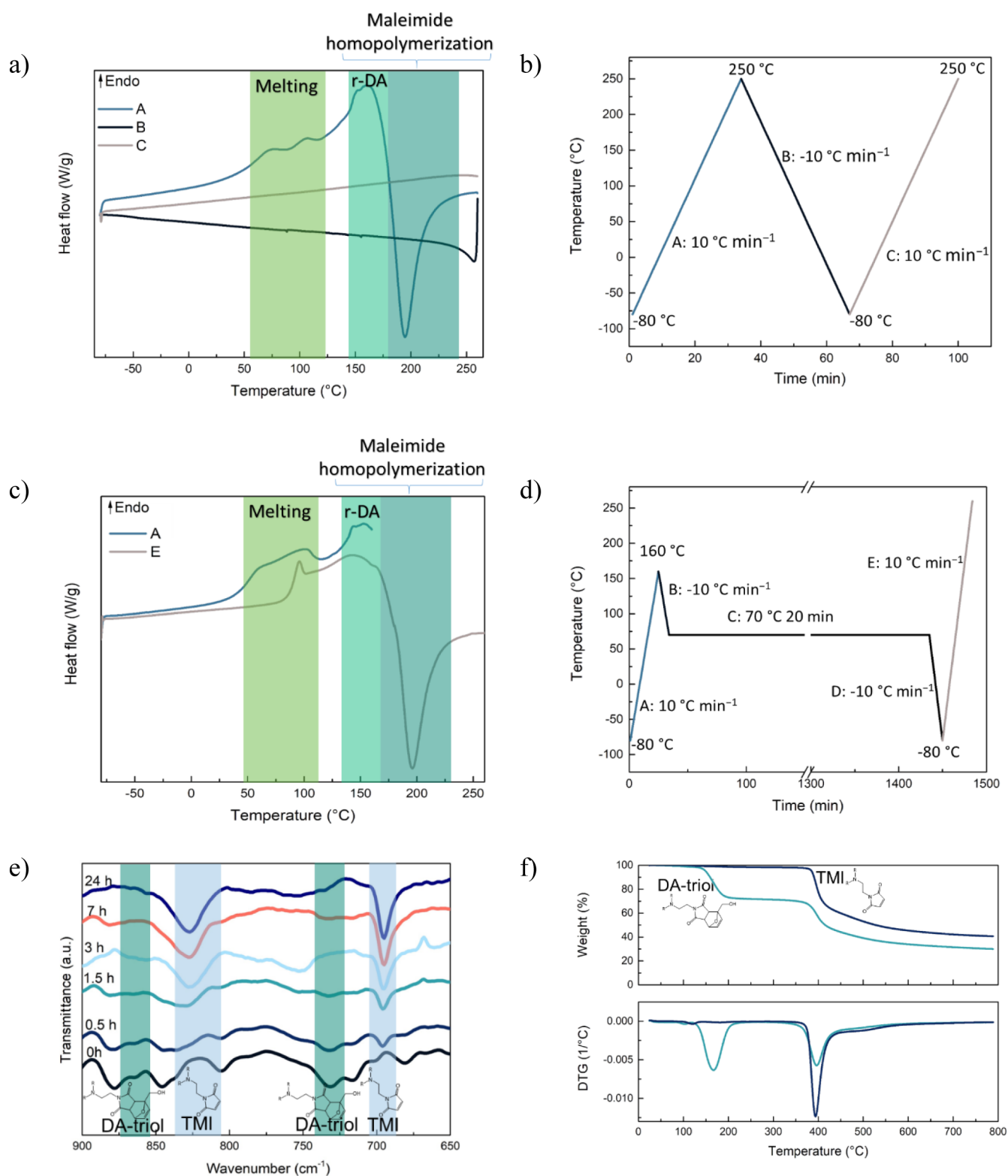
temperature and left until the reaction ends. Afterward, the temperature was lowered to the DA reaction temperature and samples were maintained at this temperature until the DA reaction completion, according to the literature.<sup>26–30</sup> In order to assess the efficiency of the recyclability, tensile properties of the original and recycled polyurethane samples were analyzed and compared. Finally, PUs were also reprocessed by extrusion and injection under the determined conditions. Extrusion was carried out at 5 rpm in a HAAKE MiniLab twin screw extruder at 160  $^{\circ}\text{C}$ , feeding 2.5  $\text{g min}^{-1}$  (3 h residence time), and using a nozzle with a diameter of 1.75 mm. A Haake MiniJet II was used to carry out the injection. The pellets were heated to 160  $^{\circ}\text{C}$  for 3 h in the injection barrel and then injected (with a 5 min injection period and a 5 min holding time at 850 bar) into the mold, which was maintained at the same temperature, resulting in the production of 20 mm round plates. The injected/extruded samples were then placed in an oven at the DA reaction temperature (70  $^{\circ}\text{C}$ ) to assess their recyclability on a semi-industrial scale.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of DA-Triol.** The DA-triol was synthesized following the three aforementioned reactions (Figure 1), obtaining yields of 53.46%, 84.39%, and 60% for the first, second, and third reactions, respectively.

The FTIR spectra of the intermediate (Figure S1) and of the DA-triol and TMI (Figure 3) confirmed the presence of the characteristic functional groups of each molecule. Figure 3 shows the spectra of TMI and DA-triol together with FA for comparative purposes. The characteristic broad band around

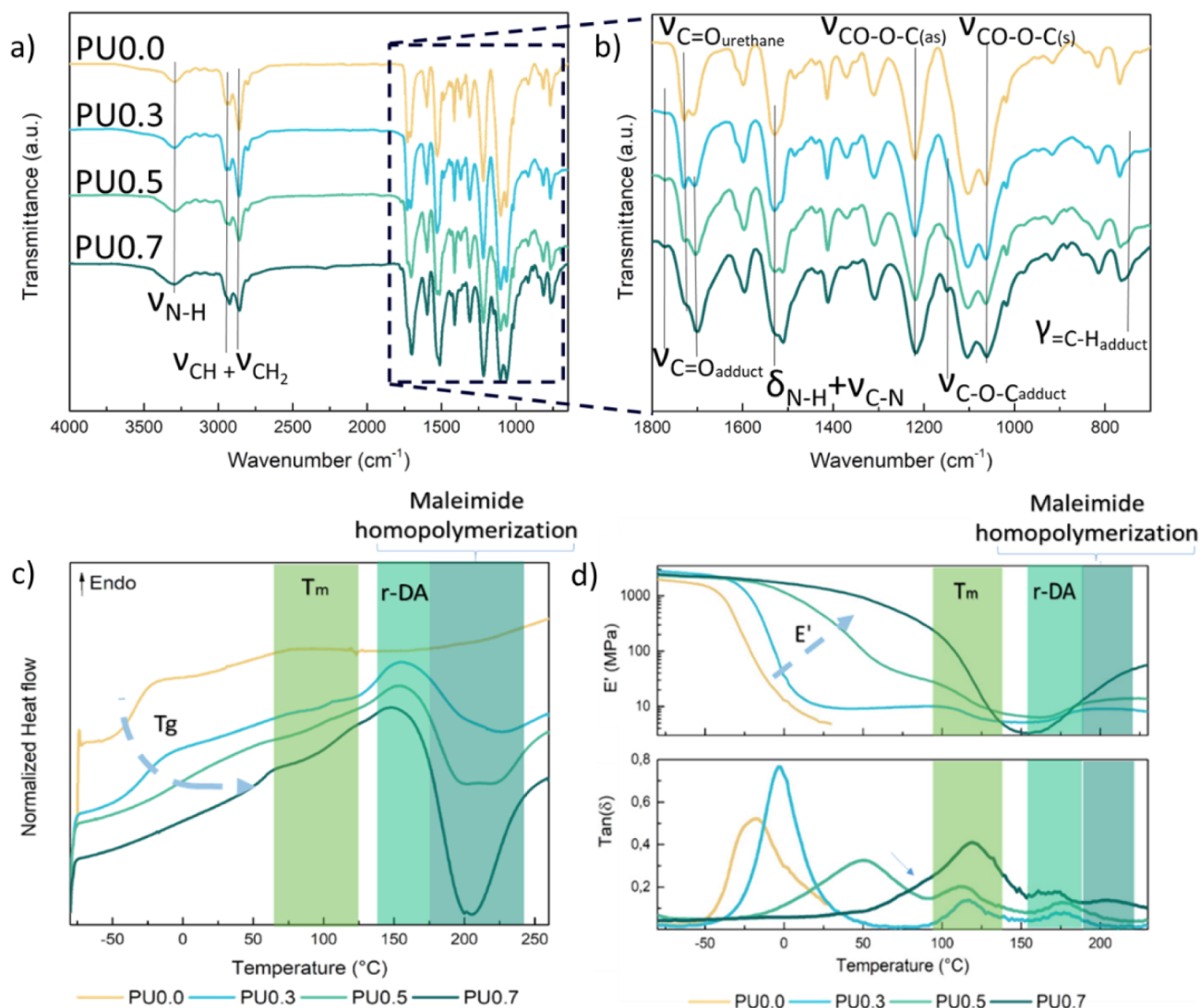




**Figure 4.** (a, c) DSC thermograms obtained from different thermal cycles (b, d) applied to DA-triol, (e) FTIR spectra of DA-triol monitored at 160 °C and at different times, and (f) evolution of weight loss as a function of temperature and its derivative for DA-triol and TMI.

3400  $\text{cm}^{-1}$  that can be seen in the DA-triol and in the furfuryl alcohol corresponds to the stretching vibration of hydroxyl groups. The bands between 3000 and 2800  $\text{cm}^{-1}$  are ascribed to the CH and  $\text{CH}_2$  stretching vibrations (asymmetric and symmetric stretching) in DA-triol, TMI, and FA. The signal located at 1688  $\text{cm}^{-1}$  presented in the TMI is related to the

$\text{C}=\text{O}$  stretching vibration of the imide group;<sup>31</sup> the double band between 1770 and 1688  $\text{cm}^{-1}$  shown in the DA-triol is specific to the DA-adduct, which indicates the DA bond formation between furan and maleimide groups.<sup>19,31,32</sup> The band located at 1147  $\text{cm}^{-1}$  is related to the stretching vibration of C–O–C bonds inside the maleimide ring, and the band



**Figure 5.** (a) FTIR spectra of the synthesized polyurethanes and (b) magnification of the 1800–650  $\text{cm}^{-1}$  interval. (c) DSC thermograms ( $10^{\circ}\text{C min}^{-1}$ ) and (d) storage modulus and  $\tan \delta$  values ( $2^{\circ}\text{C min}^{-1}$ ) as a function of temperature of synthesized PUs.

located at 1030  $\text{cm}^{-1}$  is associated with the C–O stretching vibration in the primary alcohol, confirming the presence of the primary alcohol in the DA-triol. Figure 3 also shows a magnification of the 900–650  $\text{cm}^{-1}$  interval (right panel), where the specific band of furan–maleimide adducts and the band assigned to the =C–H out-of-plane bending in the DA-triol can be seen at 863 and 730  $\text{cm}^{-1}$ , respectively.<sup>18,33</sup> In the same interval, TMI shows two typical absorption bands at 833 and 696  $\text{cm}^{-1}$  related to the =C–H out-of-plane bending and =C–H in-plane bending of maleimide group, which are not present in the DA-triol spectra.<sup>15,34–36</sup>

$^1\text{H}$  NMR spectra was used to verify the formation of the typical bonds in the intermediate, TMI, and DA-triol, showing that the expected structures were obtained (Figure 3). Intermediate:  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  6.55 (m, 2H, CH=CH-ring,  $H_f$ ), 5.10 (m, 2H, (HC=)(CH)CH–O–CH(HC=)(CH),  $H_e$ ), 3.33 (t, 2H, CH<sub>2</sub>–CH<sub>2</sub>–N(C=O)(C=O),  $H_b$ ,  $J = 6.7$  Hz), 2.92 (d, 2H, (CH)(C=O)CH–CH(C=O)(CH),  $H_c$ ) and 2.55 (t, 2H, CH<sub>2</sub>–CH<sub>2</sub>–NR<sub>2</sub>,  $H_a$ ,  $J = 6.7$  Hz). TMI:  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  6.97 (s, 2H, CH=CH-ring,  $H_c$ ), 3.37 (t, 2H, CH<sub>2</sub>–CH<sub>2</sub>–N(C=O)(C=O),  $H_b$ ,  $J = 6.6$  Hz) and 2.60 (t, 2H, CH<sub>2</sub>–

CH<sub>2</sub>–NR<sub>2</sub>,  $H_a$ ,  $J = 6.6$  Hz). DA-Triol:  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  6.53 (m, 2H, CH=CH-ring,  $H_f$  and  $H_g$ ), 5.06 (t, 1H, (HC=)(CH)CH–O–C,  $H_e$ ), 4.76 (s, 1H, –OH,  $H_i$ ), 4.03 and 3.71 (dd, 2H, C–CH<sub>2</sub>(OH),  $H_b$ ,  $J = 12.7$  Hz and  $H_b$ ,  $J = 12.7$  Hz, with  $J$  values of a typical geminal coupling), 3.33 (t, 2H, CH<sub>2</sub>–CH<sub>2</sub>–N(C=O)(C=O),  $H_b$ ,  $J = 6.6$  Hz) same as in the intermediate, 3.03 (m, 1H, CH(C=O)(CH)(CH),  $H_c$ ) displaced in relation to the intermediate, 2.88 (d, 1H, CH(C=O)(CH)(C),  $H_d$ ), 2.55 (t, 2H, CH<sub>2</sub>–CH<sub>2</sub>–NR<sub>2</sub>,  $H_a$ ,  $J = 6.7$  Hz).<sup>31,37,38</sup> The  $^1\text{H}$  NMR spectrum of the DA-triol shows small signals of the TMI ( $\delta$  6.97, 3.37, and 2.60 ppm), and polymerized FA ( $\delta$  6.41 and 6.28 ppm)<sup>39–41</sup> indicating a conversion to DA-triol of 82%.

The thermal behavior of DA-triol was analyzed by DSC (Figure 4). Two different cycles were applied to study the Diels–Alder reaction reversibility of the synthesized DA-triol. Figure 4a shows the DSC thermograms obtained from one of the cycles applied (Figure 4b), which consists of a first heating scan from  $-80$  to  $250^{\circ}\text{C}$  (ramp A), a subsequent cooling scan up to  $-80^{\circ}\text{C}$  (ramp B), and a second heating scan up to  $250^{\circ}\text{C}$  (ramp C), all of them at  $10^{\circ}\text{C min}^{-1}$ . In the ramp denoted as A, two endothermic peaks are visible at 71 and 105  $^{\circ}\text{C}$ , both

attributed to the DA-triol melting point of the endo and exo isomers, respectively.<sup>12,17,37</sup> The peaks observed at higher temperatures, with two maxima at 149 and 160 °C, are related to the retro-Diels–Alder reaction of the two stereoisomers.<sup>14,37</sup> An exothermic peak, attributed to the maleimide homopolymerization, is also observed at 195 °C.<sup>12,29</sup> In the subsequent cooling thermogram (ramp B), no evidence of DA formation was observed, which could be due to the consumption of maleimide during the first scan or the applied cooling rate. Therefore, in the second heating (ramp C), no evidence of the retro-DA reaction is observed.

In the second cycle (Figure 4d), sample was subjected to a heating scan at 10 °C min<sup>-1</sup> from -80 to 160 °C, followed by a cooling scan at 10 °C min<sup>-1</sup> up to 70 °C and a subsequent isothermal stage at 70 °C for 20 h. Finally, the sample was cooled to -80 °C and heated to 250 °C, both at 10 °C min<sup>-1</sup>. Figure 4c shows the DSC thermograms of the second cycle, in which the first heating thermogram (curve A) shows the same behavior as in the first cycle (Figure 4a, ramp A). Then, after the cooling, an isothermal step was added to allow the DA reaction to occur; as a consequence, the second heating thermogram (Figure 4b, curve E) shows two endothermic peaks at 98 and 143 °C attributed to the DA-triol melting and the retro-DA reaction, respectively. Moreover, at higher temperatures, an exothermic peak was observed at 195 °C, attributed to the formed maleimide homopolymerization, indicating that controlled heating and cooling processes can induce the retro-DA and DA reactions so that the synthesized DA-triol is viable to impart reworking properties to cross-linked polymers. Unlike what was observed in ramp A of both cycles, the single melting and retro-DA peaks observed in Figure 4b (ramp E) are probably due to the formation of only one of the isomers in the applied conditions.<sup>37,42–44</sup>

The occurrence of the retro-DA reaction in the DA-triol at 160 °C was also analyzed by FTIR spectroscopy, subjecting the sample at that temperature for 24 h. Figure 4e shows how some bands specific to the DA-adduct disappear with time at this temperature, such as the band observed at 730 cm<sup>-1</sup> that vanishes after 3 h, and some bands already observed in the TMI, such as the bands at 833 and 696 cm<sup>-1</sup>, grow, indicating its formation and confirming the occurrence of the retro-DA reaction.<sup>45</sup> Therefore, these conditions are taken into account in the recycling process.

Finally, the thermal stability of the synthesized DA-triol was analyzed by TGA and compared with its precursor, the TMI (Figure 4f). The DA-triol shows a first weight loss at 171 °C, attributed to the furfuryl alcohol released after the retro-DA reaction, as it has a boiling point of 170 °C. The observed furfuryl alcohol weight loss is about 26% and agrees quite well with its content in the DA-triol molecule, which is around 35% considering the 82% conversion previously determined by <sup>1</sup>H NMR. Finally, a second weight loss, attributed to the degradation of the TMI, is observed at 398 °C. The proven thermal stability shows how plausible the DA-triol is for heating and curing, with the warning of not exceeding 171 °C.

**Polyurethane Synthesis.** First, the polyurethane curing reaction was studied by means of the storage and loss moduli evolution with temperature. Figure S2 shows *G'* and *G''* profiles of the PU0.5 sample, where a crossover point at 103 °C could be observed, attributed to the gel point. Therefore, the curing of the PU systems was carried out at 110 °C to ensure the reaction, as well as to avoid the retro-DA reaction.

FTIR analysis was also carried out to verify that the retro-DA does not take place under these conditions (Figure S3).

Thus, the polyurethanes synthesized within this work were characterized by FTIR spectra (Figure 5a) to ensure that the urethane groups were formed appropriately and that the DA adduct was appropriately introduced in the PU chain. A band centered at 3317 cm<sup>-1</sup> is observed in the spectra of PUs, which is attributed to the stretching vibration of the urethane N–H bond. The characteristic band associated with the O–H bond observed in DA-triol (Figure 3) disappears in the spectra of PUs, indicating the complete conversion of the hydroxyl groups. The absence of an absorption band at 2270 cm<sup>-1</sup> confirms that there is no residual isocyanate group in the PUs. The bands between 3000 and 2800 cm<sup>-1</sup> ascribed to the CH and CH<sub>2</sub> stretching vibrations, which appear in DA-triol, are also preserved in the PUs. Furthermore, these groups are also present in the macrodiol. PU0.3, PU0.5, and PU0.7 samples show the characteristic double band specific for the DA adduct at 1770 and 1688 cm<sup>-1</sup>, which decreases according to the reduction of the DA-triol content in the PU formulation.<sup>32,46</sup> All samples show a band at 1702 cm<sup>-1</sup> that is related to the carbonyl stretching vibration of the urethane functional group. Furthermore, PU samples show an absorption band in the amide II region (1600–1500 cm<sup>-1</sup>) at 1529 cm<sup>-1</sup>, which is related to the bending vibration of N–H combined with the stretching vibration of C–N, characteristic band of the urethane group.<sup>47,48</sup> The bands located at 1218 and 1062 cm<sup>-1</sup> are related to the asymmetric and symmetric stretching vibrations of CO–O–C, respectively, characteristic of the urethane group. The band related to the stretching of C–O–C group of maleimide is observed at 1147 cm<sup>-1</sup>, and it is overlapped with the stretching of C–O–C group of the macrodiol, so its intensity varies depending on the amount of macrodiol or DA-triol.<sup>49,50</sup> The PUs containing the DA-triol do not show the typical maleimide absorption band located at 829 and 696 cm<sup>-1</sup>, corroborating that the retro-DA reaction did not occur during curing.<sup>18</sup> Moreover, the intensity of the band attributed to =C–H out-of-plane bending of the DA adduct at 730 cm<sup>-1</sup> increases with the DA-triol content in the PU.

DSC and DMA helped understand the thermal and thermomechanical behavior of the synthesized polyurethanes. It should be remarked that the analysis in each technique was performed at different heating rates, giving slight differences in the resulting transition temperatures. First, it is worth mentioning that the macrodiol used to synthesize the PUs presents a glass transition temperature (*T<sub>g</sub>*) at -39 °C in the DSC thermogram, not shown here deliberately. Regarding the DSC thermograms of PU0.0, PU0.3, PU0.5, and PU0.7 samples, they show a *T<sub>g</sub>* at -35, -30, -5, and 50 °C, respectively (Figure 5c), which increases in temperature as the DA-triol content increases, due to the higher cross-linking of the samples. Regarding DMA (Figure 5d), those samples present a drop in storage modulus (*E'*) values, together with a maximum in tan  $\delta$  at -18, -6, and 50 °C for PU0.0, PU0.3, and PU0.5, respectively, and a shoulder around 75 °C (depicted by an arrow) for PU0.7. As observed for DSC results, in this case also, the *T<sub>g</sub>* appears at lower temperatures in polyurethanes with low DA-triol contents (and high macrodiol fraction) and increases when increasing the cross-linking. Afterward, a melting temperature that increases with the same tendency is observed (from 70 to 107 °C in DSC,

and from 113 to 118 °C in DMA, for PU0.3, PU0.5, and PU0.7).

The retro-DA reaction is visible in all PU containing DA-triol around 150 °C, as an endothermic peak in the DSC thermogram and as a decrease in storage modulus values and the corresponding maximum in  $\tan \delta$  in DMA, indicating that the thermoreversibility of the DA-triol is preserved after curing of the polyurethane (Figure 5c,d). Finally, an exothermic peak associated with maleimide homopolymerization is visible in the DSC thermograms above 170 °C accompanied by an increase of the storage modulus values in DMA around the same temperature, which are more remarkable for the PUs synthesized with higher DA-triol contents. Table 2 summarizes

**Table 2. Summary of the Thermal Properties of the Synthesised Polyurethanes Obtained from DSC and DMA and DA-Triol Obtained from DSC**

sample name	DSC			DMA		
	$T_g$ (°C)	$T_m$ (°C)	r-DA (°C)	$T_g$ (°C)	$T_m$ (°C)	r-DA (°C)
PU0.0	-35	-	-	-18	-	-
PU0.3	-30	72; 105	155	-6	113	161
PU0.5	-5	105	154	50	115	161
PU0.7	50	107	148	75	118	155
DA-triol	--	71; 105	149; 160	-	-	-

the thermal properties of the synthesized polyurethanes obtained from DSC and DMA results. Thermal properties of DA-triol obtained from DSC (Figure 4c) are also displayed.

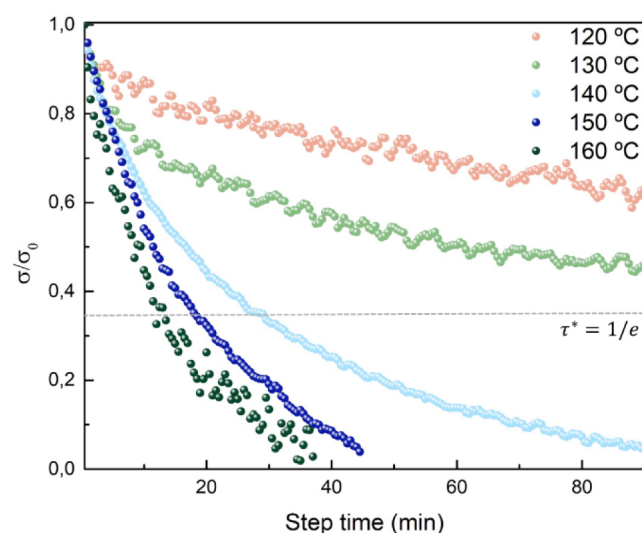
The mechanical properties of the PUs were evaluated by tensile tests, obtaining the corresponding stress–strain curves (Figure 6a), and from these curves, the Young's modulus, tensile strength, and strain at break values (Table 3). It can be seen that as the amount of DA-triol increases, the Young's modulus and tensile strength values increase, showing more resistance to deformation. However, the strain at break values decrease considerably. Figure 6b shows a picture of the samples gripped between clamps. As can be seen, PU0.0 is completely flexible and failed quickly at very low stress values as it has no cross-linking, nor crystallinity, and presents just a  $T_g$  below room temperature. Nevertheless, as the DA-triol content increases, the samples become more rigid up to PU0.7,

**Table 3. Summary of the Mechanical Properties of the Synthesised Polyurethanes**

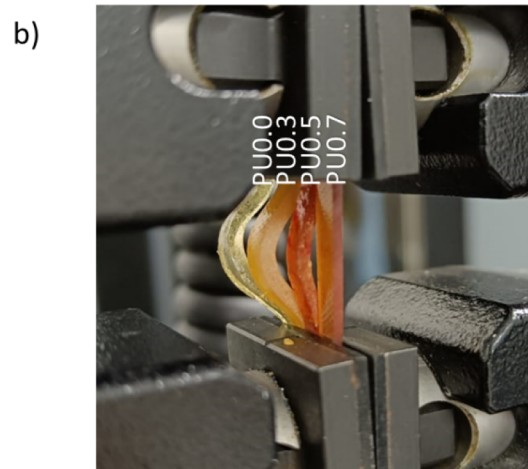
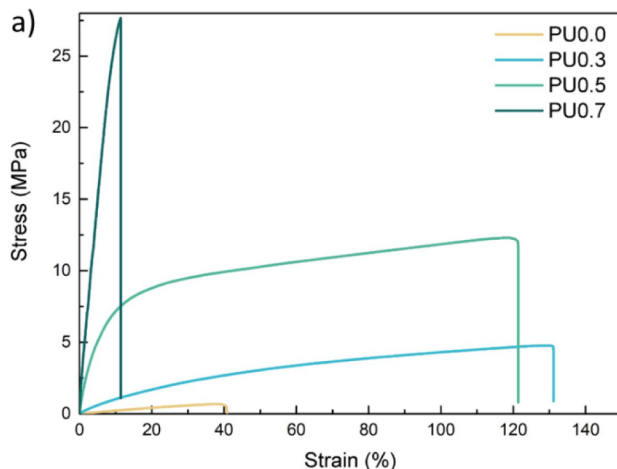
sample	Young's modulus (MPa)	tensile strength (MPa)	strain at break (%)
PU0.0	3.1 ± 0.2	0.6 ± 0.1	31.7 ± 15.3
PU0.3	16.7 ± 1.1	4.4 ± 0.1	131.6 ± 10.8
PU0.5	95.4 ± 11.1	12.4 ± 0.9	115.4 ± 13.9
PU0.7	476.5 ± 81.9	26.7 ± 1.9	10.8 ± 0.7

which shows a high Young's modulus and tensile strength values.

**Recyclability.** The most interesting characteristic of the synthesized cross-linked PUs is their malleability at high temperatures, since this characteristic benefits their reprocessing and recycling. This behavior was studied by means of stress-relaxation experiments, where the relaxation time ( $\tau^*$ ) was set as the time taken to reduce the modulus to 37% ( $1/e$ ) of its initial value.<sup>16,27,51</sup> Figure 7 shows the normalized stress–

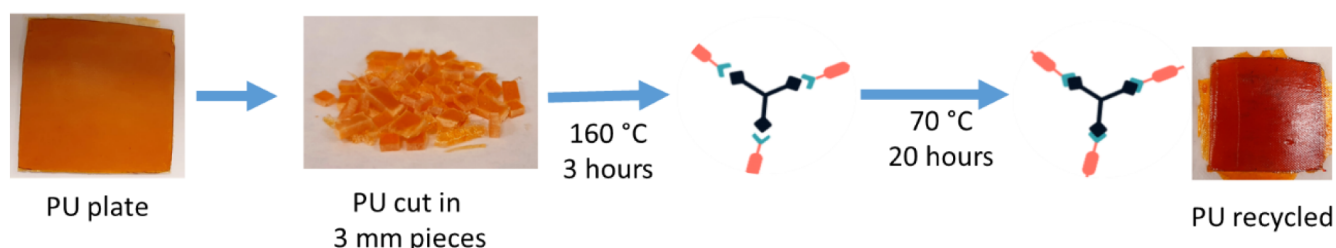


**Figure 7.** Normalized stress–relaxation curves of PU0.5 at different temperatures.

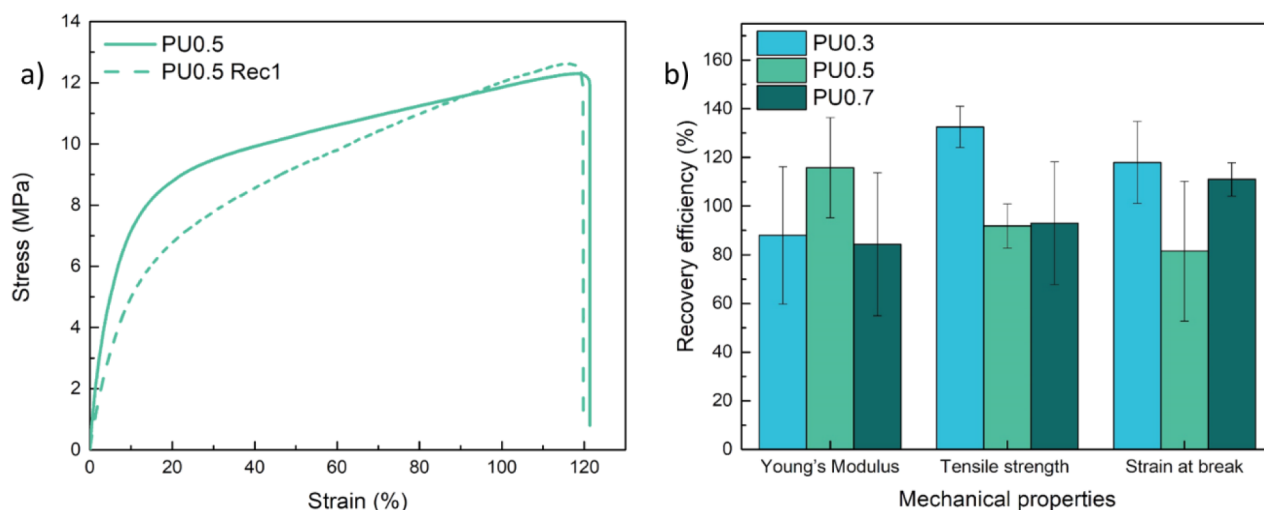


**Figure 6.** Stress–strain curves of synthesized PU materials (a) and digital image of the PUs between clamps (b).





**Figure 8.** Scheme of the performed recycling process and pictures of the original and recycled PU0.5 samples.



**Figure 9.** (a) Stress–strain curves of original and recycled PU0.5 and (b) recovery efficiencies obtained from the mechanical properties after recycling.

relaxation curves of PU0.5 at different temperatures, both below and above the temperature of retro-DA reaction observed in DSC and DMA. The material will reach its relaxation time after 18 min at 150 °C and after 12 min at 160 °C and will not relax at lower temperatures. Therefore, the recycling process should be above 150 °C, which is consistent with the retro-DA temperature found in the DSC thermograms (Figure 5). In this work, a temperature of 160 °C was selected for the recycling of PUs.

As is well known, in order to recycle the PUs, the retro-Diels–Alder reaction must be accomplished to decouple the DA adduct and make the polymer flow. According to previous results, this happens between 150 and 160 °C. Then, the Diels–Alder reaction must take place to re-cross-link the material, a reaction that can be done at lower temperatures and can take up to 48 h as observed in the literature. Most authors use temperatures between 70 and 80 °C and an average of 20–24 h.<sup>26–30,52</sup> Therefore, some cycles combining dynamic heating and cooling steps as well as isothermal steps were carried out to verify the feasibility of these reactions, and the final recycling parameters are shown in Figure 8.

The mechanical properties of the synthesized and recycled samples were compared in order to validate the recycling process. Figure 9a presents the stress–strain curves obtained for the PU0.5 sample, whereas the curves for the rest of the samples and Young's modulus, tensile strength, and strain at break values before and after recycling are presented in Figures S4 and S5, respectively. Figure 9b shows the recovery efficiencies of all the samples, regarding Young's modulus, tensile strength, and strain at break values. As can be seen, the mechanical properties remain almost similar after the recycling

process, denoting that bonds are largely restored after recycling. Thus, in general, efficiency values around 80–100% were observed. FTIR spectroscopy and DMA of the original and recycled PU were also compared, and the differences were negligible (see Figure S6). To ensure the repeatability of the DA/r-DA process, three consecutive recycling cycles were done through compression molding at the previously mentioned conditions. The recycled samples were characterized by DSC and stress relaxation experiments (Figure S7). After all the cycles, both r-DA and homopolymerization of maleimide, on the one hand, and stress relaxation, on the other hand, confirmed that thermoreversibility is still present in the sample.

Finally, preliminary semi-industrial reprocessing tests were also performed by extrusion and injection molding. To this end, PU0.5 was reprocessed by injection and extrusion at 160 °C with 3 h preheating in the injection barrel of the injection equipment and a residence time of 3 h in the case of extruder, to allow the occurrence of the retro-DA reaction. Then, the samples were placed in an oven at 70 °C for 20 h in order for the DA reaction to occur. Figures S8 and S9 show photographs of the filament and the cylindrical piece obtained by extrusion and injection, respectively, corroborating that DA-triol allows different types of reprocessing.

## CONCLUSIONS

In this work, a trifunctional polyol with dynamic covalent bonds was successfully synthesized and characterized by FTIR and <sup>1</sup>H NMR, and used then as a cross-linker in the synthesis of biobased cross-linked polyurethanes. Various formulations of polyurethanes have been prepared, demonstrating that the

presence of the cross-linker improves the mechanical properties of the PUs, and that, depending on its content, PUs ranging from flexible to rigid could be synthesized. The thermal properties of the final cross-linked polyurethanes were analyzed by DSC, finding an endothermic peak around 150 °C, which allows the decoupling of furan and maleimide adduct inserted through the cross-linker in the polymer structure, and giving thereby thermal reversibility to the system. Thus, this thermal reversibility allows PU recycling and reprocessing, which has been demonstrated by comparing the mechanical properties of both initial and recycled samples, obtaining recovery values higher than 80% and suggesting the achievement of high bond recovery reaction reversibility. Finally, preliminary semi-industrial scale reprocessability tests were performed through injection and extrusion, proving the possibility to manufacture pieces and filaments from cross-linked PUs, respectively. As a result, a pioneering strategy to incorporate recyclability into cross-linked polyurethanes is presented as a tool to overcome environmental issues related to the final disposition of this type of materials.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.3c03070>.

Additional experimental results, including photographs of experimental setup for recycling and obtained materials; Figure S1, FTIR spectra of the intermediate; Figure S2,  $G'$  and  $G''$  evolution with temperature during the curing process of PU0.5; Figure S3, FTIR spectra of the DA-triol before and after being exposed to 110 °C for 24 h; Figure S4, Young's modulus, tensile strength, and elongation at break values of the original and recycled PUs; Figure S5, stress-strain curves of PU0.3 and PU0.7; Figure S6, FTIR spectra and storage modulus and  $\tan \delta$  profiles of original and once recycled PU0.5; Figure S7, DSC thermograms and normalized stress-relaxation curves of original and recycled samples; Figure S8, digital images of the extrusion process of PU0.5; Figure S9, digital images of a cylindrical piece (20 mm diameter and height of 1.5 mm) manufactured by injection of PU0.5 (PDF)

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A.C.R.-M. contributed to methodology, investigation, writing, visualization, and formal analysis. I.L. contributed to methodology and investigation. O.E.-A. contributed to methodology and investigation. I.H. contributed to methodology and investigation. A.S. contributed to conceptualization, methodology, investigation, supervision, writing, visualization, formal analysis, and funding acquisition. A.E. contributed to conceptualization, methodology, investigation, supervision, writing, visualization, formal analysis, and funding acquisition. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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