

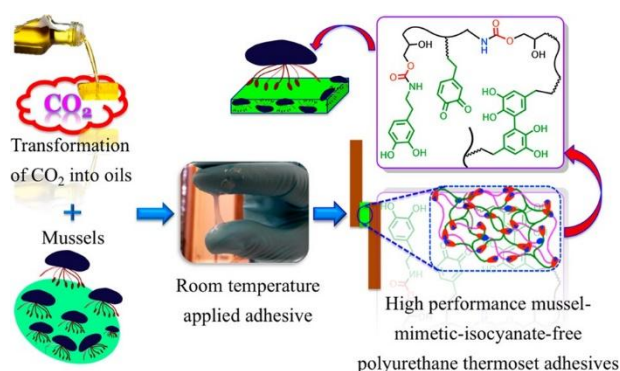
# CATECHOL CONTAINING POLYHYDROXYURETHANES AS HIGH-PERFORMANCE COATINGS AND ADHESIVES

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## Abstract

Green routes for the synthesis of high-performance isocyanate-free polyurethane coatings and adhesives are intensively searched for. In this article, we report a solvent- and isocyanate-free formulation for novel poly(hydroxyurethane) glues bearing strongly adherent catechol groups. These adhesives are prepared by the polyaddition of a CO<sub>2</sub>-sourced tricyclic carbonate, hexamethylene diamine, and a catecholamine (dopamine). The role of the catechol functions on the PHU curing and on the final PHU properties are investigated. Although the dopamine slows down the curing of the formulation, this catecholamine added at only 3.9 mol % impressively improves the mechanical and adhesion performances of PHU. The lap shear adhesion of our product surpasses those of PHU that do not contain the catechols. We also demonstrate that the catechol-bearing PHU glues are competing with the adhesion performances of commercial PU glues, at least when a thermal curing is implemented to overcome the low reactivity of cyclic carbonate with amines. The use of renewable feedstocks, the solvent-free process, the atom economy polyaddition reaction, and the absence of any toxic reagent benefit the sustainability of the final product.



## Keywords

Polyhydroxyurethane, Non-isocyanate polyurethane, Adhesives, Coatings, Carbon dioxide chemistry, Solvent-free synthesis

## Introduction

Due to their tunable bonding strength, design flexibility, durability, and cost effectiveness, polymer-based adhesives are broadly diversified in our daily life with applications ranging from post-it notes to the

aerospace industry.<sup>1-8</sup> A large palette of adhesives are found on the market place, such as those made of cyanoacrylate (Super Glue), epoxy resins, and polyurethane, to cite only a few. The main common drawback of many commercial adhesives is that they are produced from some toxic compounds. The production of high-performance adhesives by greener routes and eventually from renewable resources is gaining increased interest.

Polyurethane (PU)-based adhesives are largely used for bonding metal substrates due to their high adhesion strength.<sup>9-14</sup> However, the classical method for their production uses isocyanates that are toxic and so have associated health concerns.<sup>15-18</sup> PU adhesives prepared by greener alternatives are thus searched for, but their adhesive performances have to compete with those of conventional PUs. The polyaddition of di(poly)cyclic carbonates with di(poly)amines is an attractive strategy for producing poly-(hydroxyurethane)s (PHUs), a green variant for conventional PUs.<sup>19-30</sup> The presence of an hydroxyl group in the  $\beta$ -position of the urethane contributes to the improvement of the adhesion with various substrates, the chemical resistance, and mechanical properties of the polymer due to multiple hydrogen bondings.<sup>31-33</sup> Only a few recent reports are describing the potential of PHUs as adhesives. PU/PHU hybrid adhesives produced from cyclic carbonates and functional  $\alpha,\omega$ -telechelic isocyanate-based PU prepolymers with polyamines achieved good adhesion onto some polymers (polyimide and poly(vinyl chloride)) but also on aluminum (Al).<sup>34</sup> However, these adhesives are still using some conventional PUs in their formulations. Caillol et al.<sup>35</sup> recently reported the preparation of all PHU glues with high adhesion strength ( $\approx 15$  MPa) on wood (W) and glass, but their adhesion on painted Al was moderate ( $\approx 3$  MPa). Hybrid poly(dimethylsiloxane) (PDMS)-hydroxyurethane formulations achieved 7 MPa on glass and 0.9–1.7 MPa on metal (stainless steel, titanium, and Al).<sup>36,37</sup> Our group recently reported on the solvent-free preparation of PHU thermosets reinforced by ZnO nanoparticles that presented a high shear adhesion strength (up to 16.3 MPa) on Al.<sup>32</sup> We highlighted that the reinforcement of PHU with ZnO particles strongly improved the adhesion of PHU by 270%, leading to PHU adhesives with competitive adhesion strength compared to commercial PU-adhesives. Cyclocarbonated vegetable oils combined to amines and reinforced with ZnO particles also provided more sustainable adhesives.<sup>33</sup> Although high-adhesion performances were achieved for these PHUs, the lap-shear strength of the commercial PU glues was still higher.

In order to improve adhesion in a wet environment, researchers were recently inspired by marine mussels.<sup>38-40</sup> The excellent adhesion of these organisms to any substrates was attributed to the presence of a large quantity of 3,4-dihydroxyphenylalanine in their surface proteins.<sup>41-47</sup> The catechol of 3,4-dihydroxyphenylalanine has indeed the ability to form a large diversity of chemical interactions and to self-cross-link, helping the proteins to solidify and to bind tightly to various types of surfaces.<sup>48</sup> Messersmith et al.<sup>49-51</sup> demonstrated that polydopamine (PDA) served as a universal surface-modifying agent for virtually any substrates thanks to the presence of covalent and reversible coordination bonds between catechol groups and the surface.<sup>52-55</sup> Recent studies have revealed that PDA-modified PU can be used as a catalytic support,<sup>56,57</sup> and that PDA modification can enhance the flame retardancy<sup>58</sup> and mechanical properties of the PU.<sup>59-61</sup> The dopamine-containing PU showed an adhesive strength of 5.2 MPa on iron.<sup>62</sup> The design of mussel-inspired isocyanate-free PU adhesive materials may generate a new class of high-performance materials competing with conventional PUs. To the best of our knowledge, the development of high-performance adhesives by incorporating pendent catechol groups into the backbone of PHUs has never been reported.

### Scheme 1. Design and Synthesis of Mussel-Mimetic-Polyhydroxyurethane Solvent-free Adhesives



**Table 1.** Formulation Composition and Characteristic Properties of Mussel-Mimetic PHU Thermosets

sample code	TMPTC/HMDA(mol)/DOP (mol %) <sup>a</sup>	EWC <sup>b</sup> (%)	water	THF	GC <sup>c</sup> (%)		T <sub>g</sub> <sup>f</sup> (°C)	T <sub>d50%</sub> <sup>g</sup> (°C)	E <sup>h</sup> (MPa)	σ <sub>u</sub> <sup>i</sup> (MPa)	σ <sub>f</sub> <sup>j</sup> (%)
					CA <sup>d</sup> (°)	CCA <sup>e</sup>					
PHU 1	1/1.5/0	38 ± 4	95.2	92.1	61 ± 2	5B	35.3	331	12.7 ± 0.1	17.4 ± 0.1	5.8 ± 0.2
PHU 2	1/1.485/1.2	40 ± 3	94.1	93.8	61 ± 3	5B	38.4	355	16.7 ± 0.2	23.8 ± 0.8	5.2 ± 0.4
PHU 3	1/1.475/2.0	41 ± 4	97.5	96.4	61 ± 3	5B	39.3	360	19.6 ± 2.1	31.1 ± 0.3	5.3 ± 0.3
PHU 4	1/1.45/3.9	41 ± 6	98.2	96.7	59 ± 2	5B	42.6	359	29.7 ± 2.6	34.2 ± 0.7	4.7 ± 0.3
PHU 5	1/1.425/5.8	42 ± 4	97.9	97.3	58 ± 3	5B	42.8	361	21.1 ± 0.6	23.2 ± 1.5	3.1 ± 0.5
PHU 6	1/1.4/7.7	42 ± 7	96.4	98.0	58 ± 3	5B	43.2	361	17.6 ± 0.7	20.1 ± 1.3	2.6 ± 0.1
PHU 7	1/1.375/9.5	43 ± 2	97.6	98.3	57 ± 4	5B	43.3	360	16.5 ± 0.6	14.6 ± 0.6	1.3 ± 0.3
PHU 8	1/1.3/14.8	44 ± 5	98.2	99.1	57 ± 3	5B	45.1	360	N.d.	N.d.	N.d.

<sup>a</sup>Optimum formulation compositions. <sup>b</sup>EWC: Equilibrium water content of self-standing films (0.125 cm<sup>3</sup>) immersed in water for 96 h, at room temperature. <sup>c</sup>GC: Gel content determined in water and THF. <sup>d</sup>CA: Contact angle measurements. <sup>e</sup>CCA: Cross-cut adhesion test (5B-0% of coating area removed within crosscuts). <sup>f</sup>DSC: glass transition temperature, at heating rate 10 °C min<sup>-1</sup>. <sup>g</sup>TGA: temperatures at 50% degradation (T<sub>d50%</sub>), at heating rate 20 °C min<sup>-1</sup>. <sup>h</sup>E: Young's modulus. <sup>i</sup>σ<sub>u</sub>: Ultimate tensile strength. <sup>j</sup>σ<sub>f</sub>: Fracture stress.

With the main purpose to develop sustainable high-performance PHU adhesives, we describe the solvent-free preparation of PHU thermosets bearing catechols by the addition of a catecholamine, dopamine (DOP), to the formulation of the multifunctional cyclic carbonate and the diamine (Scheme 1). The addition of DOP is expected to improve both the cohesive strength of the adhesive and the interaction with the substrates. In this study, we systematically study the influence of the addition of DOP on the rate of crosslinking and the thermomechanical and the adhesion properties of the cross-linked PHUs. The best adhesive formulation is then investigated on a large diversity of substrates (Al, stainless steel (SS), plexiglass (GI), W, and polyethylene (PE)) and is benchmarked to commercial PU glues and state-of-the-art PHU adhesives.

## Experimental section

### Materials and methods.

Trimethylolpropane triglycidyl ether (TMPTTE), tetrabutylammonium iodide (TBAI, purity >99%), hexamethyl diamine (HMDA), dopamine hydrochloride (DOP), pyrocatechol, and methanol were purchased from Sigma-Aldrich. Carbon dioxide (CO<sub>2</sub>) N45 was supplied by Air Liquid. 1,3-Bis(2hydroxyhexafluoroisopropyl)-benzene was purchased from Fluorochem. All chemicals were used as received without any further purification. Al-2024-T3 (thickness of 0.8 mm) substrates were received from SONACA, Belgium. Stainless steel (SS, 316-AK steel, thickness of 1 mm) and Plexiglas (GI, poly(methyl methacrylate) (PMMA), thickness of 3 mm) were kindly supplied by Testas (Belgium) and Plastiservice (Belgium), respectively. Wood (beech, thickness of 10 mm) substrates were purchased from Brico, and plastics (high density PE, HDPE (ELTEX K44-20), thickness of 3 mm) were developed in the lab.

#### Surface treatments.

The substrate surfaces [Al, SS, GI, W, and PE] were cut into desired dimensions (50 mm × 10 mm), and surfaces were cleaned to degrease the unwanted weak boundary layers, such as surface contaminants, oil, grease, oxides, etc. The scrubbing of Al-substrates was similar to our previously reported method.<sup>32,33</sup> SS, GI, W, and PE substrates were cleaned with an acetone/isopropanol (1/1, v/v) mixture followed by washing with water. The procedure was repeated 3 times, and then the substrate was wiped with tissue paper and dried at room temperature for 2 h.

#### Preparation of polymeric coatings and films.

Prior to prepare solvent free thermoset coatings and films, the required amount of DOP (Table 1) was dissolved in MeOH (3 mL), added to TMPTC (2.0 g, 4.6 mmol), and heated at 60 °C for 5 min. The reaction mixture was allowed to stir for 20 min at room temperature until an homogeneous solution was obtained, and then solvent was removed under vacuum. Subsequently, a stoichiometric amount of HMDA (compared to cyclic carbonates, see Table 1) was added into the reaction mixture that was then stirred for 1 min at 60 °C and 2 min at room temperature to obtain an homogeneous mixture. Then, the viscous mixture was deposited on bare Al (Al-2024-T3) by using a bar-coat applicator (ASTM D823) to obtain a coating thickness in the range of 50–60 μm. All coatings were repeated 6 times for evaluating the reproducibility. The coated substrates were cured at 100 °C for 18 h in an oven. These coatings were then evaluated for a crosscut adhesion test and contact angle measurements.

The freestanding films with 5 mm thickness were prepared by pouring the viscous DOP/TMPTC/HMDA mixtures into a Teflon mold (3.5 × 3.5 × 0.5 cm<sup>3</sup>) for the determination of the water content (EWC), gel content (GC), contact angle, and thermal properties. Additionally, dog-bone-shaped samples were made using Teflon molds for the evaluation of the mechanical properties. The samples were cured in an oven at 100 °C for 18 h.

#### Preparation of lap-shear joints.

The adhesive joints were prepared to determine tensile lap-shear adhesion strength of the designed thermosets. The viscous oligomeric solution (~ 10 mg) was deposited onto the cleaned substrates with an overlapped gluing area of 100 mm<sup>2</sup>, and the second substrate was placed into contact. Then, the samples

were pressed gently with fingers, without formation of defects, and/or squeezed out of the adhesive in the joints. The adhesively bonded joints were allowed to cure in an oven at 100 °C for 18 h.

## Characterization methods.

Fourier transform infrared spectra (FTIR) measurements.

FTIR measurements were carried out on a Nicolet IS5 spectrometer (Thermo Fisher Scientific) equipped with a diamond attenuated transmission reflectance (ATR) device, 32 scans were recorded for each sample over the range of 4000–500 cm<sup>-1</sup> with a normal resolution of 4 cm<sup>-1</sup>, and spectra were analyzed with ONIUM software.

Rheology measurements.

The influence of the content of dopamine on PHU solvent-free formulations (~ 0.5 g) was determined by rheology measurements carried out on ARES from Rheometric Scientific TA Instruments at 100 °C for 40 min at a frequency of 1 Hz and a strain of 1% using time sweep measurements. The cross-linking density ( $\nu_e$ ) of the networks was calculated from the rubbery plateau region by using the following formula<sup>63,64</sup>

$$\nu_e = G' / 3RT \quad (1)$$

where  $G'$  is the storage modulus of the thermoset in the rubbery plateau region at 100 °C for 40 min,  $R$  is gas constant, and  $T$  is the absolute temperature.

Thermal characterizations.

Thermogravimetric analysis (TGA) of the coatings was evaluated using a Q500 from TA Instruments at a heating rate of 20 °C min<sup>-1</sup> over the temperature range of 0–700 °C under a nitrogen atmosphere. DSC (differential scanning calorimetry) analysis was carried out on a Q100 from TA Instruments using standard Al pans, calibrated with indium, and using nitrogen as the purge gas. The samples were measured at a heating rate of 10 °C min<sup>-1</sup> over a temperature range from -80 to 200 °C under a flowing nitrogen atmosphere, using TA analysis software provided with the instrument.

Tensile properties.

The measurements were performed at room temperature using an Instron 5594 tensile machine at a speed of 10 mm min<sup>-1</sup> with a load capacity of 10 000 N applied forces perpendicular to the adhesive materials. Young's modulus ( $E$ ), ultimate tensile strength ( $\sigma_u$ ), and fracture stress ( $\sigma_f$ ) were estimated by the average values of at least 6 repeated flat dog-bone shaped samples with the following dimensions, length = 3 cm, length of narrow fraction = 1 cm, width = 0.5 cm, width of narrow fraction = 0.2 cm, and thickness = 0.05 cm.

Swelling behavior and gel content.

Equilibrium water swelling of PHU samples was evaluated by measuring water content of freestanding films at room temperature.<sup>21</sup> After the curing process, PHU samples of 0.125 cm<sup>3</sup> were immersed in 10 mL of Milli-Q water or THF at room temperature for 96 h. The amount of water or THF was measured until the weight of the swollen samples remained constant. The equilibrium water content (EWC) was measured as a function of time using eq 1. After swelling measurements, the samples were dried in oven at 70 °C for 24 h. Gel content was measured using eq 2

$$\text{EWC (\%)} = \left( \frac{W_s - W_i}{W_i} \right) \times 100 \quad (2)$$

$$\text{GC(\%)} = \left( \frac{W_f}{W_i} \right) \times 100 \quad (3)$$

where  $W_s$  is the weight of the swollen sample,  $W_i$  is the initial weight, and  $W_f$  is the final weight of the dried sample.

Crosscut adhesion tests.

Crosscut adhesion tests were carried out according to ASTM D3359 standards. A cross-hatch cut pattern, consisting of six vertical parallel lines and six horizontal lines separated by 3 mm, was created onto series of PHU-coated Al substrates with a sharp razor blade, followed by the application of a high-pressure sensitive adhesive tape (Intertape tm 51596-ASTM D3359, Gardco). The tape was then removed by rapidly pulling it off at an angle of 180°. The quality of the coating was visually estimated by comparison with the percentage (%) of area removed from the total surface. The coatings were classified as 5B: 0% of the coating was removed.

Water contact angle measurements.

Measurements were obtained on an OCA-20 apparatus (Dataphysics Instrument GmbH) in the sessile drop configuration by depositing a 5- $\mu$ L droplet of Milli-Q water. Mean contact angle values were determined from at least 5 repeated measurements realized at different locations of each Al-coated surface.

Lap-shear tests.

The adhesion properties of thermosets were evaluated at 298 K (load or force (N)) as a function of displacement (mm) using an Instron 5594 equipped with a 10 000 N load cell and applied force parallel to the adhesive bond with a displacement rate of 2 mm min<sup>-1</sup> until pulling apart the bonded joints. The substrates with dimensions of 50 mm  $\times$  10 mm were used for single lap-shear measurements, and gripping length on both sides of test specimens was 25 mm. The tests were performed on 5 repeated samples from each type of adhesive to determine the average lap-shear adhesion strength of adhesives. The lap shear strength was calculated by the formula

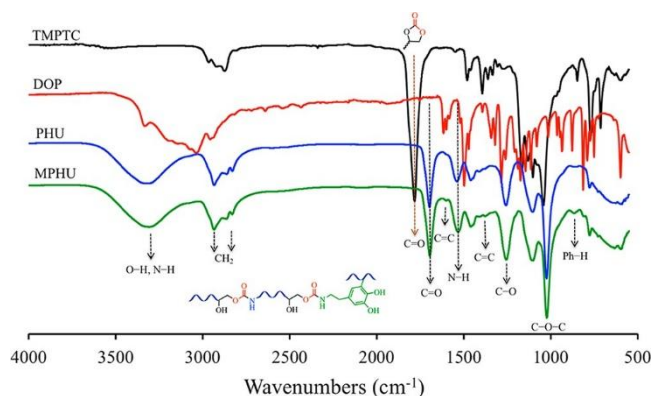
$$\tau = \frac{P}{A} \quad (4)$$

where  $\tau$  is lap-shear strength (in N mm<sup>-2</sup> or MPa),  $P$  is the maximum loading force to remove and break the adhesive (N), and  $A$  is the overlapped or gluing area of adhesive joint (100 mm<sup>2</sup>).

## Results and discussion

Modified PHU thermosets were synthesized by reaction between a trifunctional cyclic carbonate, i.e., trimethylolpropane tris-carbonate (TMPTC), HMDA, and DOP under equimolar conditions between the cyclic carbonate and the amine groups (Scheme 1). TMPTC was synthesized in kilogram scale by the solvent-free organocatalyzed coupling of carbon dioxide with TMPTE.<sup>65-69</sup> A premixing of TMPTC and DOP was carried out in methanol in order to obtain an homogeneous solution before removing the solvent under vacuum, followed by the addition of HMDA. The formulations were then cured at 100 °C. The conversion

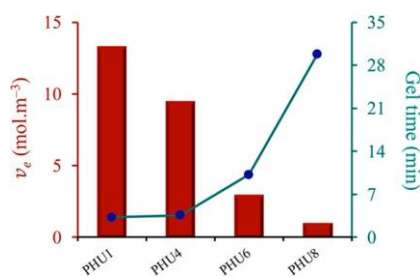
of cyclic carbonates into PHUs was monitored by FTIR spectroscopy (Figure 1) with the disappearance of a cyclic carbonate band at  $1782\text{ cm}^{-1}$  and the appearance of characteristic bands of neat and mussel-mimetic PHUs at  $\nu_{\text{max}}\text{ (cm}^{-1}\text{)}$  3316 (O–H, N–H), 1697 (C=O), 1539 ( $\delta$ (N–H) +  $\gamma$ (C–N)), 1376 (C=C, ph), 1416 (C–C, ph), 1460, 1255 (C–O), 1104, 1022 (C–O–C), and 869 (C–H, ph). The influence of the DOP content on the cross-linking, gel time, swelling, thermomechanical properties, and on the adhesive performances of the PHU thermosets was then evaluated and discussed below.



**Figure 1.** FTIR spectra of PHU, modified PHU, TMPTC, and DOP.

### Curing kinetics by rheology.

As the addition of monofunctional amines, here DOP, in thermosets formulation can adversely affect the formation of the network, the effect of the addition of DOP on the curing kinetics was systematically evaluated by rheology at  $100\text{ }^{\circ}\text{C}$  for 40 min (Figure S1). The measurements were performed on the solvent-free PHU formulations with increasing content of DOP (0, 3.9, 7.7, 14.8 mol %) compared to TMPTC/HMDA (keeping an equimolar content of amine and cyclic carbonate groups for all formulations). All rheological data are summarized in Table S1. For all formulations, the loss modulus ( $G''$ ) was initially higher than the storage modulus ( $G'$ ), confirming that PHU was not cross-linked before the measurement. Figure S1 illustrates that  $G'$  increased faster than  $G''$  with the reaction time, and a crossover point was observed that corresponds to the gel point ( $G' = G''$  and/or  $\tan \delta = 1$ ). As expected, the gelation time increased (from about 3 to 30 min, Figure 2), the storage moduli reduced (from 123.2 to 8.5 kPa, at 40 min, Table S1), and the cross-linking density reduced from  $13.2$  to  $0.9\text{ mol}\cdot\text{m}^{-3}$  with the content in DOP (0–14.8 mol %, Figure 2). These results tend to confirm that part of the DOP molecules react with the cyclocarbonate functions and are grafted on the resulting PHUs. However, at low DOP content (10 mol % and below), this effect remains marginal and good PHUs thermosets are expected to be formed in these conditions. Nevertheless, more studies are required to elucidate the complex structure of this cross-linked system.



**Figure 2.** Cross-linking density ( $\nu_e$ ) and gel time for the different PHU samples [PHU1<sub>0 mol %</sub>, PHU4<sub>3.9 mol %</sub>, PHU6<sub>7.7 mol %</sub>, and PHU8<sub>14.8 mol % of DOP</sub>].

## Swelling measurements.

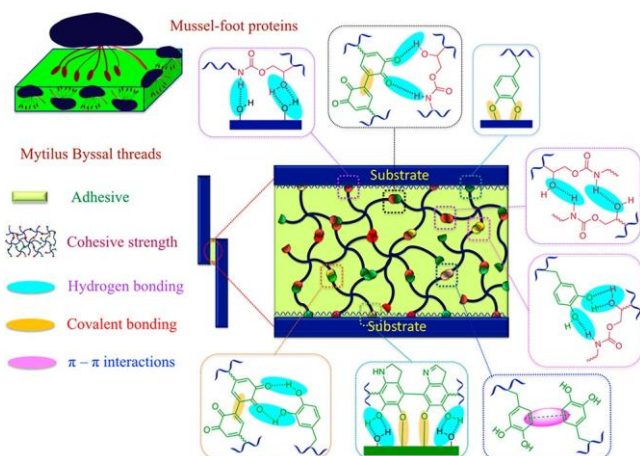
The degree of cross-linking density of PHU thermosets after curing at 100 °C for 18 h was qualitatively studied by measuring the EWC (eq 2) and GC (eq 3) with the immersion of their freestanding films (0.125 cm<sup>3</sup>) in 10 mL of Milli-Q water for 96 h at room temperature. The obtained values are reported in Table 1. EWC slightly increased from 38 ± 4 to 44 ± 5% by raising the DOP molar ratio from 0 to 14.8 mol % (PHU1 to PHU8). The increase of the EWC may be attributed to the presence of polar functional groups (catechol) within the mussel-mimetic-cross-linked PHUs. The gel content was above 94% in all cases, demonstrating the formation of highly cross-linked materials and the absence of free DOP that could be extracted from the samples. This gel content was also high in THF, confirming the absence of extractable short chains.

## Thermal properties.

The thermal properties of crosslinked PHU with incorporated DOP (0–14.8 mol %) were evaluated by TGA and DSC (Figure S2). The temperature at 50% of degradation ( $T_{d50\%}$ ) and glass transition temperature ( $T_g$ ) values are reported in Table 1. All PHUs presented a high thermal stability with a  $T_{d50\%}$  that increased from 331 °C for PHU1, that did not contain any DOP, to 360 °C for PHU3, that contained only 2 mol % of DOP. At higher DOP content, the  $T_{d50\%}$  remained constant around 360 °C. The  $T_g$  of PHU-thermosets was progressively increased with the DOP content from 35 °C (neat PHU1) to 45 °C (PHU8 containing 14.8 mol % of DOP). This  $T_g$  increase is assumed to be the result of the reduction of the chain mobility, owing to presence of dihydroxybenzene functions that form strong H-bond interactions.

## Mechanical properties.

The structure–property relationships of mussel-mimetic PHU thermosets were investigated by conventional tensile tests. A variety of network structures was obtained by varying the TMPTC/HMDA/DOP molar ratios, while the processing conditions were maintained constant (see the Experimental section for details), Figure S3. All data are also summarized in Table 1. The neat PHU<sub>0% DOP</sub> exhibited Young's modulus up to 12.7 MPa, ultimate tensile strength of 17.4 MPa, and stress at a break of 5.8%. The presence of low DOP content (3.9 mol %, PHU4) had a remarkable beneficial impact on the Young's modulus with a 233% increase, i.e., from 12.7 for PHU1 to 29.7 MPa for PHU4, and on the ultimate tensile strength with a 196% increase, i.e., from 17.4 to 34.2 MPa. These improvements in the mechanical strength associated with ductile fracture and extensive plastic deformation of thermosets are likely attributed to the development of multiple hydrogen bonding interactions between modified PHUs and DOP,  $\pi$ – $\pi$  interactions, and eventually self-polymerized catechols. All of the possible interactions in the modified PHU adhesives have been schematized in Figure 3. However, when higher DOP content (>3.9 mol %) was introduced in the formulation, a decrease of the Young's modulus and stress at break were observed, which demonstrates a transition from a ductile to a brittle fracture of adhesive materials with a lack of plastic deformation. The presence of a high amount of catechol probably restricts too much the mobility of the chains that leads to brittle fracture.



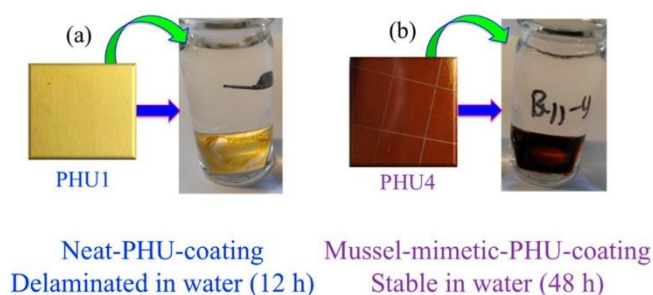
**Figure 3.** Overview of the possible interactions in the bulk mussel-mimetic PHU adhesive-substrate interface.

### Coating properties.

The solvent-free incorporated DOP containing PHUs was coated on a bare and cleaned Al with thickness of  $\sim 50\text{--}60\ \mu\text{m}$  (see the Experimental section for details). Their adhesion strength was then evaluated by performing crosscut tests according to the ASTM D3359 standards. Whatever the coating, the edges of the cuts were completely smooth, and none of the squares were removed from the coating. All tested coatings were thus all classified as 5B-0% removal of the coating, thus very adherent to the substrate, Table 1.

The binding ability of the coatings was further evaluated in a wet environment after immersing the coated substrate in water. The neat PHU coating was rapidly peeled off (Figure 4a) from the substrate after 12 h of immersion due to the high hydrophilicity of PHU1 (contact angle (CA) =  $61^\circ$ , Table 1). In contrast, the coating containing DOP (PHU4) did not peel off when immersed in water for 48 h (Figure 4b), despite the coating being hydrophilic (Table 1). This comparative study reveals that the incorporation of DOP inside the PHU formulation is beneficial for improving the water resistance of the coating.

Coatings immersed in water at room temperature



**Figure 4.** Photographic images of bare Al-2024-T3 substrates coated with (a) neat PHU (peeling off in water after 12 h) and (b) Mussel-mimetic PHU thermoset (PHU4, 3.9 mol % DOP, catechol-functionalized PHU) (no peeling off in water after 48 h).

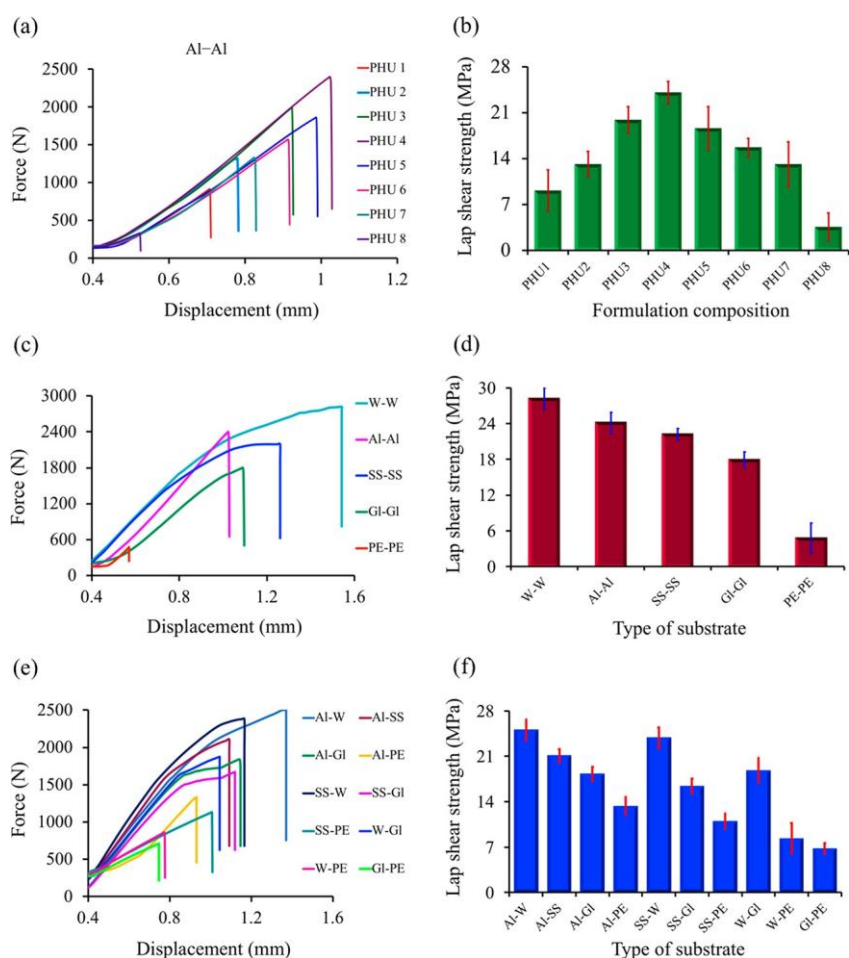
### Adhesion properties.

The influence of catechol on the adhesion performance of cross-linked PHUs was investigated by lap-shear tests (Figure 5a) on Al substrates (Al-2024-T3) that are frequently used in aerospace and aircraft applications. The lap-shear bonding strength (MPa and/or  $\text{N}\cdot\text{mm}^{-2}$ ) was calculated by dividing the maximum load or force (N) by the adhesive surface area ( $\text{mm}^2$ ), using eq 4. Figure 5b shows that neat PHU (PHU1) was characterized by a shear adhesion strength of  $9.1 \pm 3.1\ \text{MPa}$ . The shear strength was strongly improved

by the addition of DOP, with a maximum value of  $24.1 \pm 1.7$  MPa with only 3.9 mol % DOP (PHU4), which represents a 264% increase compared to neat PHU1 (Figure 5b). Moreover, the adhered metal-lap joints failed in a cohesive manner for all samples, with both surfaces remaining covered by the adhesive (Table S2). The improvement of the adhesive properties was therefore attributed to the improvement of the cohesive strength of the glue via covalent and noncovalent interactions, as illustrated in Figure 3. These observations are in full agreement with the mechanical properties (Table 1, Figure S3).

However, when the DOP content was further increased in the formulation, the adhesion performances progressively decreased with an adhesion strength of  $13.1 \pm 3.4$  MPa for PHU7 (9.5 mol % DOP) and  $3.6 \pm 2.1$  MPa for PHU8 (14.8 mol % DOP). This decrease might be explained by the slowing down of the curing kinetics at high DOP content, as demonstrated by rheological measurements (Figure 2), and by the transition from a ductile to a brittle material, as evidenced by mechanical measurements (Figure S4).

The development of an adhesive formulation that is able to efficiently glue a large diversity of substrates is challenging due to their diverse chemical nature, surface energy, wettability, and roughness.



**Figure 5.** Evolution of lap-shear strength of adhesively bonded joints of neat and mussel-mimetic polyhydroxyurethanes was investigated by using an Instron-5594 apparatus. (a) Force vs displacement curves of neat (PHU1, 0% DOP) and group of mussel-mimetic PHU thermosets (PHU2–8, 0–14.8 mol % DOP) evaluated for affixed Al substrates. (b) Influence of the quantity of DOP on shear adhesion strength of PHU adhesives on Al substrates. (c) Force vs displacement curves of PHU4 (3.9 mol %-DOP) evaluated for similar attachment of substrates (Al, SS, W, GI, and PE). (d) The shear adhesion strength of PHU4 as a function of adherently bonded similar substrates. (e) Force vs displacement curves for PHU4 (3.9 mol % DOP) for dissimilar attachment of substrates. (f) Shear adhesion strength of PHU4 on dissimilar substrates.

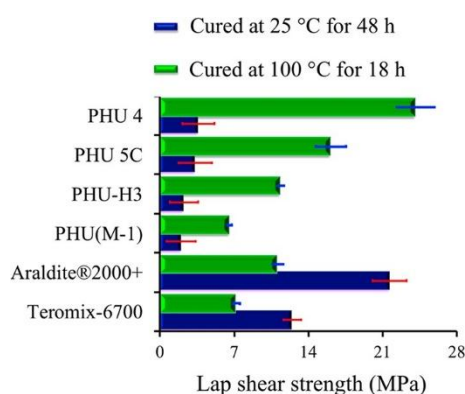
In this study, the highest performing mussel-inspired glue for Al (PHU4, 24.1 MPa, Al–Al) was then tested for gluing similar/dissimilar substrates, such as SS, W, Gl, and PE (Figure 5c–f). Interestingly, the highest shear adhesion strength of 28.2 MPa was measured for wood (W–W). It remained high for SS, with a value of 22.1 MPa, and slightly decreased to 17.9 MPa for Gl. Although lower, the shear adhesion strength for PE remained satisfactory with a value of 4.76 MPa (Figure 5c,d, Table S3). This lower value for PE is the result of the low surface roughness and hydrophobic character of the substrate that do not favor the interaction between catechol-hydroxyurethane groups and the substrate. In most cases, we noticed a mixture of failure modes (cohesive-C.F.–/adhesive-A.F.–failure modes) in adhered joints. For PE, an adhesive failure is always noted, indicating a low interaction between the hydrophilic glue and the hydrophobic substrate, although the adhesive performances are more than satisfactory. Interestingly, the adhesive strength on PE obtained with the DOP-modified PHU (PHU4, 4.76 MPa) is much higher than the one of unmodified PHU (PHU1, 1.18 MPa), demonstrating that the presence of DOP improves the interaction between the adhesive and the substrate. The failure pattern of adhesively bonded joints is summarized in Table S3 and schematically presented in Figure S4.

The highest performing formulation (PHU4) was also tested for affixing dissimilar substrates (Al–W, Al–SS, Al–PE, Al–Gl, SS–PE, etc., Figure 5e,f, Table S3). PHU4 is highly efficient to glue wood to metals (either to Al and SS) with a remarkable adhesion strength of 25 MPa for Al–W and of 23.8 MPa for SS–W. High-adhesive performances are also noted for Al–SS (21.1 MPa). Although slightly lower, the lap-shear strengths remained high when PHU4 was used to assemble Gl to W (18.2 MPa), to Al (18.2 MPa), or to SS (16.3 MPa).

Importantly, this glue is also efficient to glue the hydrophobic plastic (PE) to the different substrates with lap-shear strengths of 13.3 MPa for Al, 10.9 MPa for SS, 8.3 MPa for W, and 6.7 MPa for Gl.

## Benchmarking.

Finally, the high shear bonding strength of catechol-bearing PHU thermoset adhesive (PHU4) was benchmarked against commercial (Teromix-6700 and Araldite2000), petrochemically based (PHU(M-1),<sup>35</sup> PHU-5C),<sup>32</sup> and biobased (PHU-H3)<sup>33</sup> polyurethane adhesives (Figure 6). The processing conditions were held constant for fair comparison. The results are shown in Figure 6.



**Figure 6.** High-performance mussel-mimetic PHU thermoset adhesive (PHU4) benchmarked against commercial PU (Teromix6700 and Araldite2000+) and reported PHU adhesives (thus, TMPTC/EDR-148, PHU5C:TMPTC/HMDA/PDMS/CC-ZnO, and PHU-H3:CSBO/HMDA/CC-ZnO) evaluated for Al substrate. The curing conditions (time and temperature), amount of adhesive, and overlapping/gluing area were held constant.

When cured at 25 °C, the commercial PU adhesives present the best adhesion performance with lap-shear strength values up to 21.7 MPa for Araldite2000 and up to 12.5 MPa for Teromix-6700, whereas PHU adhesives are characterized by a low shear strength (PHU(M-1),<sup>35</sup> PHU-5C,<sup>32</sup> PHU-H3,<sup>33</sup> and PHU4:1.9, 3.3, 2.2, and 3.6 MPa, respectively). The low adhesive performance of PHUs is the result of the slow aminolysis of the cyclic carbonates at room temperature (and thus incomplete curing), compared to the fast isocyanate/ alcohol reaction observed for the conventional PUs. As expected, the adhesive performances of all PHU are strongly improved when cured at 100 °C for 18 h. At this temperature, the amine/cyclic carbonate reaction (and therefore the curing) is promoted. Impressively, the mussel-mimetic PHU adhesive (PHU4) competes with the performance of universal commercial-PUs when cured under these conditions with a remarkable lap-shear strength of 24.1 MPa. These performances surpass those of the state-of-the-art PHUs,<sup>32,33,35</sup> even those that have been reinforced by ZnO nanofillers for optimal adhesion to Al (PHU 5C). This benchmarking study clearly highlights that well-designed PHU adhesives are realistic alternatives to commercial PU adhesives, provided that hot curing is permitted.

## Conclusions

Novel mussel-mimetic PHU thermoset adhesives were prepared by the solvent-free polyaddition of a TMPTC, HMDA, and DOP. We have systematically studied the influence of DOP content on the formulation performances, such as the cross-linking, thermomechanical, and adhesion properties. We found that the incorporation of only 3.9 mol % DOP to the PHU formulation strongly increased the Young's modulus by 233% and the ultimate tensile strength by 196%, providing a PHU with unprecedented adhesion performances. Indeed, an impressive adhesion strength of 28.2 MPa was noted for wood, and remarkable shear adhesion strengths were measured for metal substrates with values as high as 24.1 MPa for Al, 22.1 MPa for SS, but also for organic glass, such as Gl (17.9 MPa). Importantly, this formulation was also able to efficiently glue substrates of varying nature, such as a hydrophobic plastic (PE) with metals (SS or Al), W, or Gl. The adhesion performances of our product surpass those of PHU that do not contain the catechol groups. A benchmarking study has demonstrated that the catechol-bearing PHU glues are competing with the adhesion performances of commercial PU glues (Teromix-6700 and Araldite 2000 plus), at least when a thermal curing is implemented to overcome the low reactivity of cyclic carbonate with amines. We have demonstrated that the catechol groups improved both the cohesion of the glue network and its adhesion to the substrate. The valorization of CO<sub>2</sub>, the solvent-free process without any release of toxic reagent, and the use of DOP (that can be produced from tyrosine<sup>70-72</sup> or phenylalanine<sup>73</sup> amino acids) benefit the environment and align with principles of Green Chemistry.<sup>74,75</sup> Current efforts are now dealing with the optimization of the formulations to enable curing at room temperature and with the use of all biosourced products.

Associated content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.8b03429](https://doi.org/10.1021/acssuschemeng.8b03429).

Rheology measurements, thermal and mechanical properties, lap-shear strength, and failure mode of adhesive joints (PDF)

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### Author Contributions:

S.P. carried out all experiments. J.-M.T. advised S.P. in rheology and thermo-mechanical measurements and contributed to the discussion of these results. B.G. advised and supervised S.P. in the formulations to be used and in the synthesis of the cyclic carbonate by the CO<sub>2</sub> chemistry. C. J. and C.D. are the supervisor and co-supervisor, respectively, of the PhD thesis of S.P., and they are at the origin of the project. C.D. suggested to use dopamine in the formulation to improve the performances of the coatings.

### Notes:

The authors declare no competing financial interest.

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