Metal-free organocatalysts for high hydrolytic stability single component polyurethane adhesives and their application in decorative insulation facades manufacturing

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ABSTRACT

We focused on developing polyurethane (PU) adhesives with superior ambient thermal and hydrolytic stability, a crucial factor for industrial productivity. Our approach involved creating PU prepolymers that can withstand varying temperatures in ambient conditions. These prepolymers consist of conventional isocyanate-terminated polyurethane and metal-free acid:base organic catalysts, with the stability of the adhesive relying on the organocatalyst employed. We tested a series of 11 latent organocatalysts derived from the reaction between 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and various acids. Among these, the catalyst based on 1-naphthoic acid exhibited exceptional stability, lasting at least 3 h at 60 °C and an average relative humidity of 65% under vigorous stirring. We assessed this stability using a fan-based stirrer and analyzed the curing conditions kinetically through DSC. Furthermore, our adhesive formulation is environmentally friendly as it is free of metals, specifically tin (typically present in catalysts such as dibutyltin dilaurate). This quality enhances its sustainability. To validate the practical applicability of the adhesives, we conducted tests using decorative facade models composed of siliciclastic sandstone extracted from a quarry in Vilviestre del Pinar (Burgos, Spain. Latitude: 41.951024° N, longitude: 3.078283° W) and extruded polystyrene (XPS). The results demonstrated the excellent hydrolytic and thermal stability of the adhesives, highlighting their significant potential for panel manufacturing in this context.

1. Introduction

Polyurethanes (PUs) are used in many diverse applications, ranging from aeronautics to everyday products. Due to their extreme utility and relatively low cost, these materials account for nearly 5 wt% of total worldwide polymer production and are expected to exceed 21 million tons annually by 2022. The commercial success of this polymer family is the result of several factors such as the simplicity of the polymerization process and/or the wide diversity of available monomers, which allows their industrially production in various formats such as coatings, elastomers, adhesives, etc., being one of the most widely produced polymers globally [1]. Moreover, polyurethanes can be easily prepared in the form of foam due to the self-blowing ability of the isocyanates in the presence of water [2].

The basic formulation of a PU is a polyisocyanate and a polyol, both with ≥ 2 functionalities. PU adhesives are used as two- or one-component formulations. Two-component adhesives (2 K-PU) consist of a polyisocyanate prepolymer and a single polyol or mixture thereof. On the other hand, one-component adhesives (1 K-PU) consist of a moisture-curing prepolymer containing a single or a mixture of isocyanate-terminated polyols, where moisture is supplied from the air and substrate, or it can be added during adhesive application. Depending on the application, additives such as colorants, stabilizers, flame retardants, water, and catalysts are usually added, with the catalytic system playing a key role [3]. The choice of the most suitable catalyst (and ultimately, the PU formulation) is conditioned by the adhesive

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application method (such as spray application, bead application, scraper technology, or dosing roller technology), and the curing conditions (pressure and temperature).

In many industrial applications, such as decorative insulation facades, adhesive dosing during manufacturing involves open-air systems. Therefore, the selection of the most suitable catalyst relies on the observed stability when adhesives are exposed to air during manufacturing with varying degrees of humidity and/or medium to high temperature. For instance, the use of silanized polyurethanes is not suitable due to their high reactivity with water [4].

Within the field of industrial PU-based adhesives, tin catalysts have always had great relevance, especially dibutyltin dilaurate (DBTDL) [5–7], followed by tertiary amines [8], catalysts based on metals such as Mg or Al [9], or organocatalysts [3,10]. However, tin catalysts are not environmentally friendly and have low hydrolytic stability under open-air conditions. Other non-latent catalysts (such as tertiary amines) cause very fast curing, while the lack of catalyst shows high hydrolytic stability but very long curing times. Moreover, there is no current evaluation method to ensure that the stability of the adhesives in the open-air system is achievable before they are directly applied in the dosing system. This fact also leads to loss of time and money during manufacturing due to premature curing of adhesives in dispensing systems during mould changes or unexpected production stops. As a result, open-air dosing limits the service time of the PU and conditions their industrial use due to the combination of humidity and temperature that lowers adhesive stability, leading to more costly processes and challenges. In this sense, the use of latent catalysts is being investigated with a wide variety of chemical structures ranging from cyclic guanidines [10] to acid-blocked tertiary amine catalyst [11,12], with the objective of produce adhesives with high ambient stability [10,12].

In this study, we present a novel development involving the preparation and characterization of single-component polyurethane (PU) adhesives catalyzed by 11 latent organocatalysts. These catalysts offer exceptional thermal and humidity resistance, making them highly suitable for use in metal-free PU dosing technologies that are exposed to air and varying temperatures (see Fig. 1). To achieve this, we successfully synthesized 11 robust and highly potent Brønsted acid organocatalysts specifically designed for polyurethane adhesives. These organocatalysts are derived from salts obtained from 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) and various organic acids. Furthermore, we devised a Low-Scale Stability Assessment Method to assess the feasibility of these adhesives for open-air industrial applications, closely resembling real-world processes. This method involved utilizing a fan as a stirrer and analyzing RGB parameters of photographs captured with a smartphone as a monitoring tool. We validated this method using FTIR analysis. By employing this approach, we were able to select the most optimal adhesive formulation based on its stability under open-air conditions and its curing characteristics, determined by the creaming time. To demonstrate the practical applicability of the adhesives, we conducted a proof of concept (POC) test by using them in the production of a decorative facade insulation panel model. The study concludes with promising results, showcasing the potential of these innovative adhesives in real-world manufacturing applications.

2. Experimental

2.1. Materials

All materials and solvents were commercially available and used as received unless otherwise indicated. The following materials and solvents were used: 1,8-diazabicyclo 5.4.0 undec-7-ene (DBU) (99%, Aldrich), ethyl acetate (≥99.9%, VWR), *d*imethylsulfoxide-*d*$_6$ (99.9%, VWR), dimethylformamide (99.9%, Supelco), polymeric-MDI (99%, Voranate M229, DOW, 30 %NCO), polypropylene glycol with average Mn ~2,000 (PPG-2000, ≥99.9%, Alfa Aesar), polypropylene glycol with average Mn ~1,000 (PPG-1000, ≥99.9%, Alfa Aesar), 1-naphthoic acid (≥98.0%, TCI), 2-(methylamino)benzoic acid (≥99.0%, TCI), 4-carboxyphenylboronic acid (97%, TCI), 9-anthracenecarboxylic acid (≥99.0%, TCI), 5-(*tert*-butyl)isophthalic acid (≥99.0%, TCI), 5-aminoisophthalic acid (≥98.0%, TCI), benzoic acid (≥99.0%, TCI), benzenesulfonic acid (≥98.0%, TCI), 2-chloro-5-nitrobenzoic acid (≥98.0%, TCI), 4-chlorobenzoic acid (≥99.0%, TCI), 3,5-dinitrobenzoic acid (≥98.0%, TCI), dibutyltin dilaurate (DBTDL, 95%, Sigma-Aldrich).

The proof of concept was carried out with a sandstone type siliciclastic stone (geographical origin in Sierra de Cameros, Vilviestre del Pinar, Burgos, Spain - latitude: 41.951024° N, longitude: 3.078283° W-).

2.2. Instrumentation and general methods

Viscosity data was obtained using a Brookfield viscometer (Model RVDV-II+, LR99102), at 100 RPM, spin number 04, and 30 °C.

To obtain the isocyanate index (% NCO) of the adhesives, the standard D2572 − 97 (2010) of the ASTM committee entitled "Standard Test Method for Isocyanate Groups in Urethane Materials or Prepolymers" was followed.

^{1}H and ^{13}C{^{1}H} NMR spectra (Advance III HD spectrometer, Bruker Corporation, Billerica, Massachusetts, USA) were corded at 300 MHz for ^{1}H and 75 MHz for ^{13}C using deuterated dimethylsulfoxide (DMSO-*d*$_6$) at 25 °C as solvent. Catalysts #9 and #10, exceptionally, were tested at 50 °C for avoiding signals from different the conformational isomers in ^{13}C NMR specta.

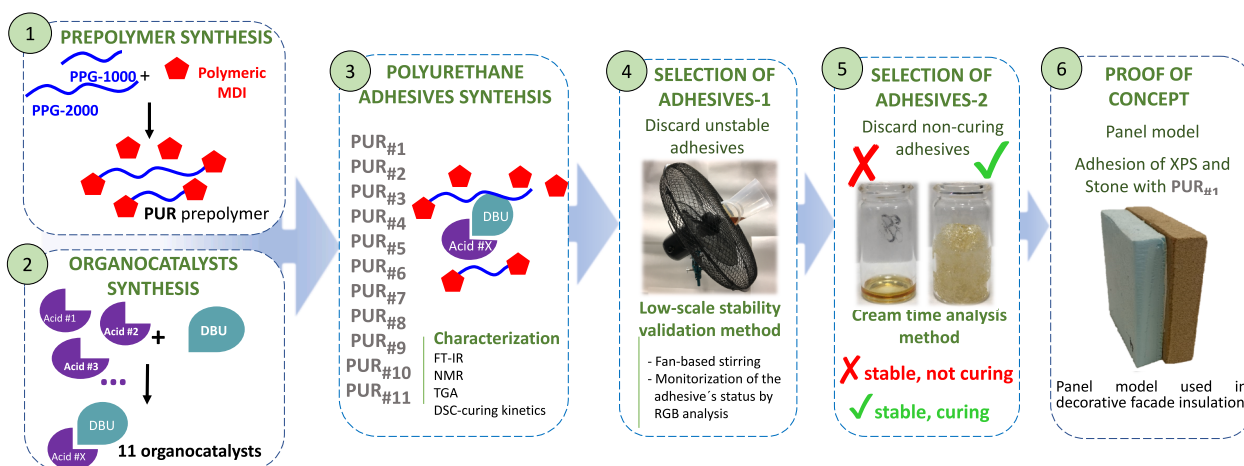The catalystś thermal characterization was performed by

Fig. 1. Table of contents.

thermogravimetric analysis (Q50 TGA analyzer, TA Instruments, New Castle, DE, USA) with 3–7 mg of sample under nitrogen atmosphere at $10\ °C·min^{-1}$.

The catalyst's and adhesive's thermal characterization was performed by differential scanning calorimetry under a nitrogen atmosphere at a heating rate of 15 and 20 $°C·min^{-1}$, respectively (Q200 DSC analyzer, TA Instruments, New Castle, DE, USA). Catalysts were previously dried in a vacuum oven at 35 °C, and the experiment was performed with 10–15 mg of sample. Regarding the PUR adhesives, 4 g of the prepolymer were weighed, and 26 mg of catalyst dissolved in 150 mL of the solvent specified in Table 1 (manuscript) were added. Finally, 80 mL of water was added, the mixture was homogenized, and the experiment was performed with 10–15 mg of sample. This experiment was used as the basis for the theoretical analysis of the curing kinetics of PUR#1, using the "TA Advantage Specialty Library" software. More information can be found in Figs. S1f-S11f.

Infrared spectra (FTIR) were recorded with an infrared spectrometer (FT/IR-4200, Jasco, Tokyo, Japan) with an ATR-PRO410-S single reflection accessory.

The adhesion test was conducted using an adhesion tester (AT-1000, Neurtek, Eibar, Spain). Square sandstone samples of 5 cm side and 2 cm thickness were bonded to a square base of extruded polystyrene (XPS) of 20 cm side and 6 cm thickness. In addition, a square steel piece of 5 cm side and 1 cm thickness was glued to the opposite side of the sandstone. This steel piece was connected to the adhesion equipment, which applied a perpendicular force to the surface until the sandstone and components were separated from the XPS, allowing the determination of strength in MPa.

Digital photographs were taken with a Huawei p30 pro (Huawei, Shenzhen, China), placing the films within a homemade lightbox to reproduce always the same lighting conditions [13]. The distance between the object and the smartphone was 13 cm. RGB parameters of digital photographs were extracted using the smartphone app "Colorimetric Titration" [14,15].

2.3. Specific methods

2.3.1. Organocatalysts' synthesis

The organic acid was dissolved in ethyl acetate or diethyl ether in a round-bottom flask, according to the amounts described in Supplementary Material (Table S1 in SM-Section 1). Only when necessary, small amounts of DMF were used to promote solubility for the more insoluble acids. Over the clear solution, the DBU dissolved in 5 mL of ethyl acetate was added, and the mixture was stirred for 5 min at RT. The formed precipitates were filtered off and washed with ether and hexane. Quantitative yields were obtained for all organocatalysts. Characterization of all organocatalyst by FT-IR, NMR, TGA, and DSC is shown in Figs. S1-S11 (SM-Section S1).

2.3.2. PUR prepolymer synthesis

The prepolymer (adhesive without catalyst) was synthesized in a jacketed glass flask. 100 g of polymeric MDI, 8 g of PPG-1000 and 8 g of PPG-2000 were added, and the mixture was magnetically stirred for 3 h at 60 °C under nitrogen atmosphere. Large magnetic stirrers were used, in this way a good homogenization of the mixture was achieved at low revolutions (150–300 RPM). The prepolymer was stored at 4 °C. Additional characterization of the prepolymer can be found in SM-Section S2.

2.3.3. PUR#1-PUR#11 adhesives' preparation

Catalyst was added to the prepolymer dissolved in propylene carbonate or DMSO, as specified in Table 1, to prepare different PUR adhesives (PUR#1 to PUR#11). In both cases, the minimum solvent amount was utilized.

Additionally, an adhesive variant with the most common tin catalyst (DBTDL) was also prepared and used to validate the Low-Scale Stability Assessment Method. PUR_DBTDL was prepared by dissolving 4 mg of

DBTDL in 4 g of adhesive.

2.3.4. Low-scale stability assessment method

The monocomponent PU adhesives dosed in open-air dosing systems often remain exposed to air, both static or spinning, in the industry, for long periods due to mold changes, part changes, unexpected stops, or production-promoting strategies. Then is when adhesives with low thermal and hydrolytic stability begin to break down, and bubbles start to appear because of the reaction of the isocyanates of the PU prepolymer with ambient humidity.

There is no standardized method for measuring adhesive's stability, which simulates stirring and realistic temperature and humidity conditions. Thus, we have designed a Low-Scale Stability Assessment Method, using homemade material available to anyone, which has proven to be a helpful tool to discard unstable adhesives. The system is based on a horizontally placed fan to stir the adhesives (8 g) in a plastic beaker, as shown in Fig. 2a, as a model for an open-air dosing system to test the hydrolytic stability of the developed adhesives. We opted for this system because standard laboratory orbital shakers neither tilt enough to adequately move a fluid with such a high dynamic viscosity (503.3 ± 1.4 CPs) nor generate a moist environment through strong air currents.

During the stirring, the adhesive's appearance can be visually controlled. Still, we decided to record this appearance with a smartphone, by taking a photo of the cups in the homemade backlight box (Fig. 2b) to reproduce the same light conditions [13].

We validated our method by testing the prepolymer (PUR, without catalyst and therefore a very stable hydrolytic mixture) and the adhesive with a tin catalyst (PUR_DBTDL, a very unstable hydrolytic mixture). Both mixtures were tested with the fan-based stirrer at room conditions (20 ± 2 °C, 65% RH), and photographs of the adhesive were taken every 5 min (Fig. 2c). In parallel, samples were also taken for analysis by FT-IR. The RGB parameters were extracted from the photos with the "Colorimetric Titration" app [14,15], and the intensity of the NCO peak was extracted from FT-IR spectra. Both variables were represented versus time, as shown in Fig. 2d.

The formation of bubbles in the adhesive (and, therefore, its deterioration, which can be seen in Fig. 2c) results in a decrease in the main color components, which are essentially numeric values associated with a color. Therefore, in order to classify an adhesive as "stable," our main requirement is that it should not exhibit any bubbles after 60 min of stirring with a fan-based stirrer.

2.3.5. Cream time

0.5 g of adhesive (PUR#1-PUR#11) were weighed in a 12 mL vial, and 50 μL of distilled water was added. The sample was manually homogenized with a Pasteur pipette, and the vial was heated at 130 °C in an oil bath. The cream time was recorded as the time until no further foam evolution was observed.

3. Results and discussion

The characterization of the organocatalysts by NMR revealed compounds of high purity without further purification. Moreover, characterization of the prepolymer revealed a %NCO of 25%, adequate as it is intended for use as a moisture-curing adhesive, where water would be added after the adhesive dosing in an industrial application. Regarding the dynamic viscosity, we obtained a mean value of 503.3 ± 1.4 CPs, i.e., within the usual range in this type of adhesive.
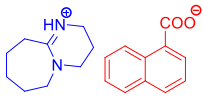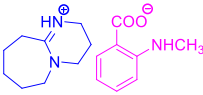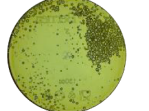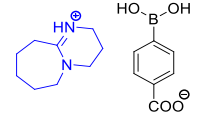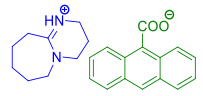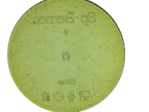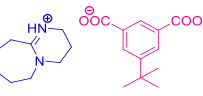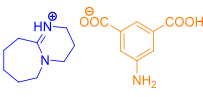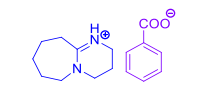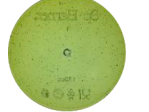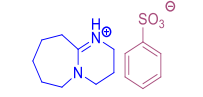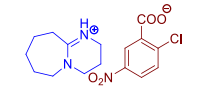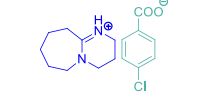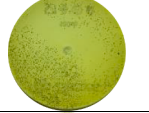
3.1. Discarding unstable and no-curing adhesives

The results obtained by the Low-Scale Stability Assessment Method (photo of the adhesive after 60 min in the fan-based stirrer), and by the cream time method are shown in Table 1.

Adhesives PUR#2, PUR#3, PUR#5, PUR#7, PUR#9, PUR#10, and PUR#11 presented low or very low hydrolytic stability, as can be seen in

Table 1

Results for all tested catalysts. The table shows the chemical structure of the catalyst, the % of catalyst, the type of solve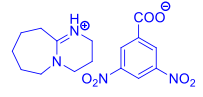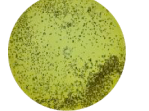nt used to dissolve each catalyst, the % of solvent, the photograph of the adhesive after 60 min in the fan-based stirring system (20 ± 2 °C, 65% RH), the cream time with the post-curing photo, and a few observations.

Adhesive	Catalyst			Solvent (%)		Photo after 60 min stirring	Curing		Comments
	Formula	%		Name	%		Photo	Cream Time (sec)	
PUR#1		0.1		Propylene carbonate	0.4			180	Good hydrolytic stability. Poor foaming. Acceptable cream time.
PUR#2		0.1		DMSO	0.4			150	Very low hydrolytic stability.
PUR#3		0.1		DMSO	0.8			116	Low hydrolytic stability.
PUR#4		0.1		Propylene carbonate	0.8			-	No curing
PUR#5		0.1		DMSO	0.8			90	Low hydrolytic stability.
PUR#6		0.1		DMSO	1.6			86	Cloudy appearance
PUR#7		0.1		Propylene carbonate	2.5			42	Low hydrolytic stability.
PUR#8		0.1		Propylene carbonate	2.5			-	No curing
PUR#9		0.1		Propylene carbonate	2.5			42	Low hydrolytic stability.
PUR#10		0.1		Propylene carbonate	2.5			100	Very low hydrolytic stability.
PUR#11		0.1		Propylene carbonate	2.5			50	Very low hydrolytic stability.
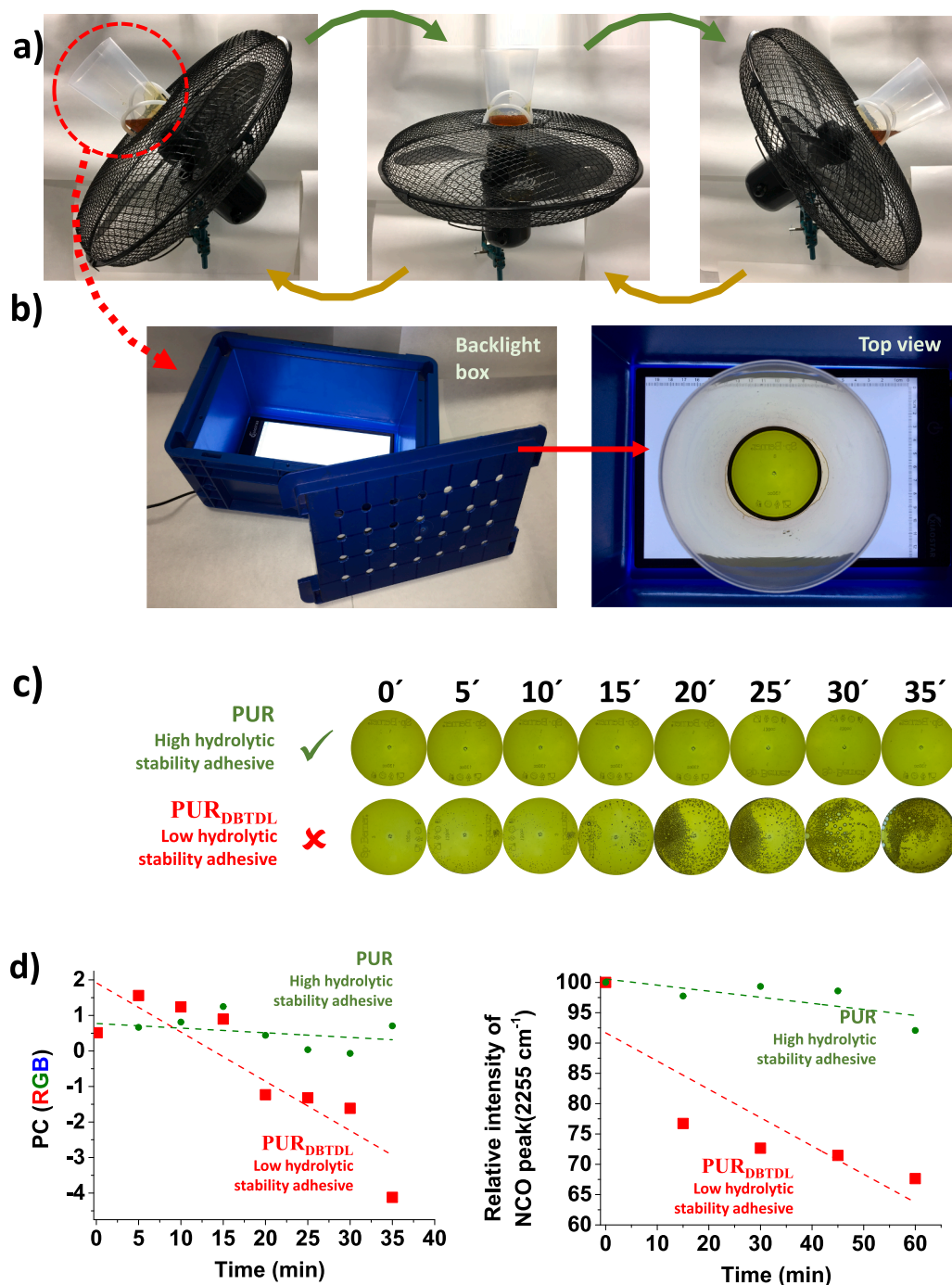
Fig. 2. a) Fan-based homemade stirrer for viscous samples. b) Backlight box for recording adhesives' appearance. c) Photos of the adhesives at different stirring times in the fan-based stirrer. d) Representation of the evolution of each photograph's RGB principal color components (left), and the evolution of the relative intensity of the NCO peak at 2243 cm^{-1} (right), showing in both cases the negative evolution of PUR$_{DBTDL}$.

the images in Table 1. This phenomenon appears to be associated with the presence of functional groups in the acid (in addition to the carboxylic group itself), which can engage in intermolecular interactions with other species, including water. This interaction leads to the breakdown of the salt, the release of DBU, and the initiation of adhesive curing, consequently compromising its latent properties.

PUR$_{#6}$ was discarded due to its cloudy appearance, related to the presence of solids in the adhesive due to its low solubility. On the other hand, adhesives PUR$_{#4}$ and PUR$_{#8}$ were very stable, but they did not cure under the temperature conditions of our test (see "Cream time" method). This is attributed to the remarkable thermal stability exhibited

by the formed salt, which remains intact even in the presence of external chemical agents (such as water, indicating good hydrolytic stability) and high temperatures (indicating good thermal stability).

From a chemical standpoint, it is worthwhile to closely analyze several cases. Firstly, adhesives PUR$_{#1}$, PUR$_{#4}$, and PUR$_{#7}$ contain the same functional group (carboxylic acid) in the catalyst structures with 1, 2, and 3 benzene rings, respectively. When the catalyst structure contains 1 ring (catalyst #7, CAT$_{#7}$), the adhesive has low hydrolytic stability but good cream time. However, when the catalyst structure contains 3 rings (CAT$_{#4}$), the adhesive has high hydrolytic stability but does not cure. This can be ascribed to the higher hydrophobicity of

molecules with higher number of condensed aromatic rings. Therefore, the catalyst with 2 rings ($CAT_{\#1}$) gives rise to an adhesive with intermediate properties, i.e., acceptable hydrolytic stability and cream time.

Another interesting comparison from a chemical perspective is considering the functional groups. For example, although both the $CAT_{\#1}$ and $CAT_{\#8}$ structures have a single aromatic ring, the sulfonic acid group in $CAT_{\#8}$ is significantly more acidic than the carboxylic acid group in $CAT_{\#1}$. Consequently, the ionic bond generated by the sulfonic acid group is much stronger and water is not able to break it. Therefore, the $PUR_{\#8}$ adhesive does not cure under the conditions of our test. Thus, the number of rings in the catalyst structure and the type of functional group present in the adhesive can greatly impact its hydrolytic stability, cream time, and curing ability. Understanding these chemical principles is crucial to developing effective adhesives with desired properties.

Additionally, the thermal analysis by thermogravimetry (TGA) of the organocatalysts revealed several remarkable data (overlayed in Fig. 3a, and individually represented in SM-Section S1). For example, the excellent thermal stability of $CAT_{\#8}$, with T_5 and T_{10} values of 339 °C and 367 °C, respectively (temperatures at which the catalyst suffers a weight loss of 5% and 10%). This catalyst did not work under our curing conditions; however, its thermal properties make it ideal to be used at industrially relevant polymerization/depolymerization reactions [12,16]. Similarly, $CAT_{\#9}$ and $CAT_{\#11}$ have very high thermal stability but low hydrolytic stability.

On the other hand, a DSC study of the curing kinetics of the most stable catalyst ($CAT_{\#1}$) confirmed that the % conversion at 40 °C was less than 2.3% after 1 h (Fig. 3b). This fact is highly noteworthy, since the tested mixture contained 2% water, which was added to $PUR_{\#1}$ just before starting the experiment. However, at 130 °C the conversion percentage is 100%, confirming that PUR#1 is an excellent latent catalyst with high hydrolytic stability.

In short, catalyst #1 is not the catalyst with the highest thermal resistance, nor does it give rise to the fastest adhesive, but it gives rise to the adhesive with the best balance of stability, curing kinetics and foaming, so we decided to improve foaming, which was quite poor in this first test.

3.2. Improving PUR#1 adhesive

Some modifications over $PUR_{\#1}$ were carried out, summarized in Table 2. Propylene carbonate was again chosen as the solvent for the catalyst, and two other solvents with high vapor pressures, such as dichloromethane and chloroform, were tested to increase the foaming.
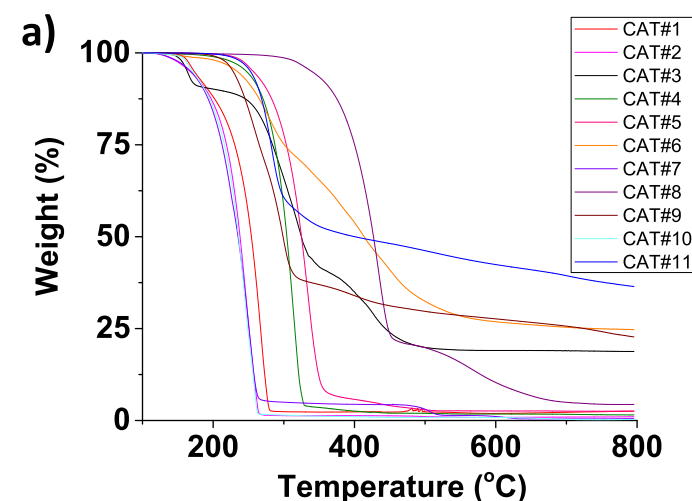
Note that all solvents were found to be inert additives by DSC experiments and the same curing curves were obtained with and without solvent. The w% of the catalyst ranged between 0.1 and 0.3%, and the w % of the solvent between 0.4 and 5%.

All the adhesives presented good hydrolytic stabilities. However, the foam generated with adhesives PUR_{1_4} and PUR_{1_5} had very low density, and they were discarded. Adhesive PUR_{1_1} was also discarded due to poor foaming. The remaining adhesives were considered suitable for the industry. Adhesive PUR_{1_7} was chosen to carry out a proof of concept (POC) since we consider it a good candidate in terms of cream time, stability, and foaming.

3.3. Proof of concept (POC). Testing PUR$_{1-7}$ for preparing a panel model used in decorative facade insulation

The POC aims to simulate open-air dosing systems in the industry, considering mold/part changes, unexpected stops, etc. So, the adhesive was stirred at 60 °C in an open beaker under 65% RH conditions. After 3 h, the adhesive did not present any bubbles, viscosity increase, or evidence of curing, so we concluded it has excellent hydrolytic and thermal stability. At this point, the adhesive was tested in a preliminary assay to bond sandstone and XPS, giving rise to a panel model used in decorative facade insulation. The adhesive was applied to the XPS using a dosing roller, and the sandstone was preheated to 90 °C before bonding the two parts (Fig. 4). This POC has shown the potential and advantage of using this kind of adhesive for industrial applications, obtaining a resistance in the adhesion test of 0.15 ± 0.02 MPa (the data is the average of 4 replicates).

4. Conclusions

Our key focus was to showcase the efficacy of acid:base organic catalysts in creating monocomponent polyurethane (PU) adhesives with superior ambient thermal and hydrolytic stability, emphasizing their advantageous application in the manufacturing of decorative insulation facades. By replacing conventional metallic catalysts with our proposed organocatalyst, we achieved PU adhesives that withstand at least 3 h of stirring at 60 °C and 65% RH, while being environmentally friendly without containing metals like tin. The selection of the organic acid for synthesizing the acid:base catalyst plays a crucial role in attaining these desired properties. We have observed that the stability of the adhesive is directly influenced by the stability of the catalyst, which, in turn, depends on the ability of the organic salt to undergo separation solely due
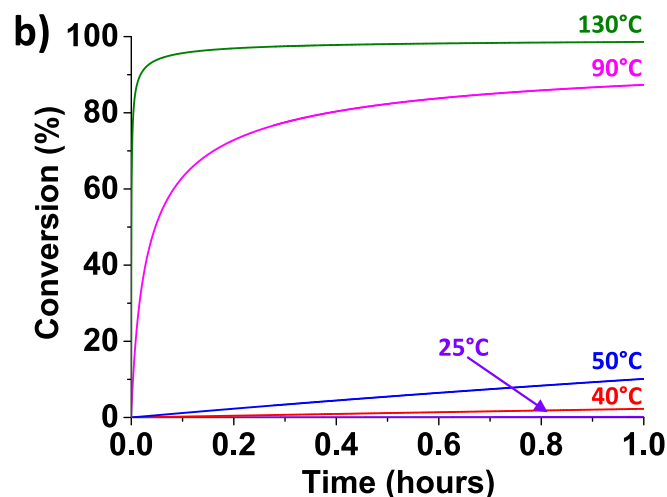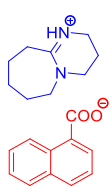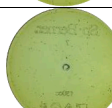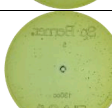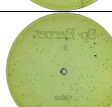

Fig. 3. a) Catalysts' thermograms. Experimental conditions: 10–15 mg; inert atmosphere (N_2); ramp at 10 °C min^{-1}. b) Curing kinetics of $PUR_{\#1}$ adhesive, showing the conversion % *vs* time at 25, 40, 50, 90 and 130 °C. Experimental conditions: 10–15 mg of sample containing PUR + 0.65% catalyst #1 + 3.75 % propylene carbonate + + 2% water; nitrogen atmosphere at a heating rate of 20 °C·min^{-1}.

Table 2
Results for organocatalyst based on DBU and naphthoic acid. The table shows the chemical structure of the catalyst, the % of catalyst, the type of solvent used, the % of solvent, the photograph of the adhesive after 60 min in the fan-based stirring system (20 ± 2 °C, 65% RH), the cream time with the post-curing photo, and a few observations.

Adhesive	Catalyst		Solvent (%)		Photo after 60 min stirring Formula	Curing		Comments
	Formula	%	Name	%		Photo	Cream Time (sec)	
PUR#1_1		0.1	Propylene carbonate	0.4			180	Poor foaming
PUR#1_2		0.2	Propylene carbonate	3.7			90	Good foaming. Improvable cream time
PUR#1_3		0.2	CHCl$_3$	5			76	Good foaming. Improvable cream time
PUR#1_4		0.1	DCM	5			144	Excessive foaming.
PUR#1_5		0.2	DCM	5			81	Excessive foaming.
PUR#1_6		0.25	DCM	5			80	Good foaming. Improvable cream time
PUR#1_7		0.3	DCM	5			63	Good foaming. Acceptable cream time
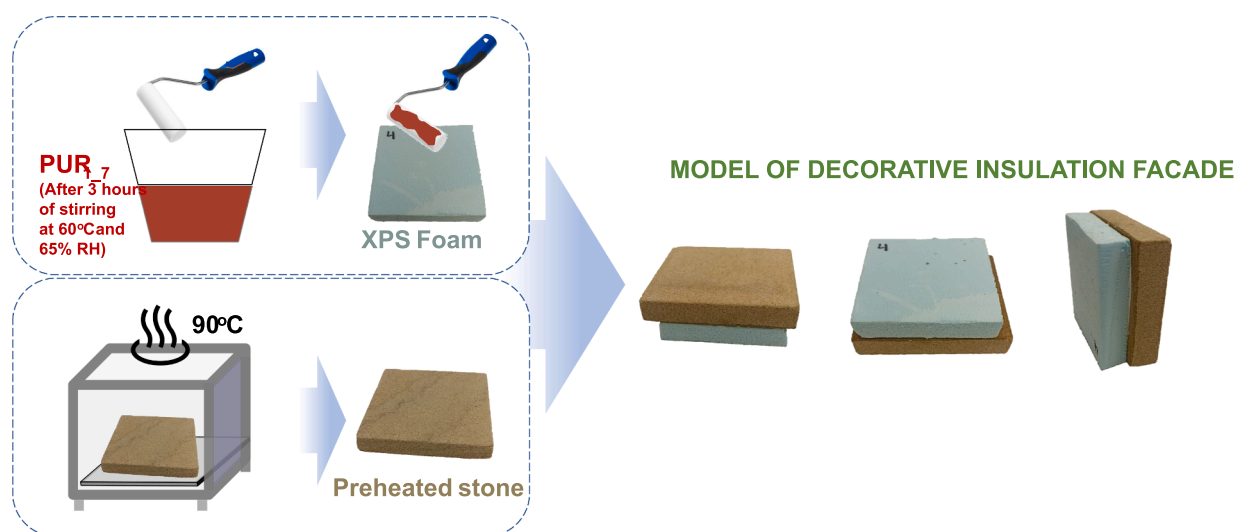
Fig. 4. Experimental procedure carried out in the proof of concept. First, the adhesive was stirred in an open beaker at 60 °C for 3 h. Afterward, the adhesive was applied with a dosing roller on a piece of XPS. Finally, the XPS piece and the sandstone (preheated at 90 °C) were bonded.

to temperature effects, rather than interactions with molecules like water. Among the tested catalysts, the organocatalyst based on 1-naphthoic acid and DBU showed the highest hydrolytic stability and was evaluated under simulated industrial conditions. Initial tests using a dosing roller to apply the adhesive for bonding sandstone and XPS in decorative insulation facades yielded promising results. On the other hand, the organocatalyst based on benzenesulfonic acid and DBU exhibited excellent thermal stability but was less effective at 130 °C.

However, we anticipate its suitability for polymerization depolymerization reactions requiring harsher conditions. We also demonstrated the use of a fan-based stirrer as a laboratory model for open industrial dosing machines, especially for monitoring hydrolytic stability. These findings open up new avenues for the application of acid:base organic catalysts in diverse adhesive formulations and industrial processes.

5. Open data

Open Data is available at https://riubu.ubu.es/handle/10259/5684 under the name "Metal-free organocatalysts for high hydrolytic stability single component polyurethane adhesives and their application in decorative insulation facades manufacturing".

CRediT authorship contribution statement

Saúl Vallejos: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – original draft, Writing – review & editing. **Miriam Trigo-López:** Formal analysis, Investigation, Methodology, Validation, Writing – review & editing. **Haritz Sardon:** Investigation, Supervision, Validation, Writing – original draft. **José Manuel González-Martín:** . **Sara González-Moreno:** Methodology, Validation, Writing – review & editing. **José M. García:** .

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

Acknowledgments

Supplementary material

Catalyst synthesis and characterization; adhesive synthesis and characterization.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.conbuildmat.2023.132643.

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