Water-Induced Self-Blown Non-Isocyanate Polyurethane Foams

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Abstract

For 80 years, polyisocyanates and polyols were central building blocks for the industrial fabrication of polyurethane (PU) foams. By their partial hydrolysis, isocyanates release CO_2 that expands the PU network. Substituting this toxic isocyanate-based chemistry by a more sustainable variant – that *in-situ* forms CO_2 by hydrolysis of a comonomer - is urgently needed for producing greener cellular materials. Herein, we report a facile, up-scalable process, potentially compatible to existing infrastructures, to rapidly prepare water-induced self-blown non-isocyanate polyurethane (NIPU) foams. We show that formulations composed of poly(cyclic carbonate)s and polyamines furnish rigid or flexible NIPU foams by partial hydrolysis of cyclic carbonates in the presence of a catalyst. By utilizing readily available low cost starting materials, this simple but robust process gives access to greener PU foams, expectedly responding to the sustainability demands of many sectors.

Introduction

Following 80 years of innovation, polyurethane (PU) is leading the market of synthetic foams by entering in multiple flexible to rigid materials such as thermal/acoustic insulators, structural parts in the transportation and building sectors, packaging and core parts of comfort items (e.g. cushions, pillows, mattresses,…), etc.[1] Many of these PU foams are fabricated from reactive polyols/polyisocyanates formulations, added by some water. The blowing agent, carbon dioxide (CO_2), is in-situ generated by partial hydrolysis of isocyanates during the PU matrix construction, ultimately leading to self-blown PU foams (**Scheme 1A**).[2] The amines produced during hydrolysis also react with isocyanates, introducing urea linkages within the foam structure. Although extremely versatile and facile, this chemistry is now facing severe regulation changes that restrict the utilization of toxic isocyanates. Besides, the PU foam production sector was recently deeply impacted

by raw isocyanates supply problems, and the decarbonization of the plastic sector has become a priority to safeguard this industry's future. These incentives are providing a fresh impetus for rethinking the fabrication of PU foams by an isocyanate-free approach, ideally by exploiting raw chemicals issued from bio-renewables and/or gaseous waste effluents such as CO_2. In this context, poly(hydroxyurethane)s (PHU) belong to a family of non-isocyanate polyurethanes (NIPU) and are emerging as some of the most promising greener substitutes to PUs.[3] They are produced by the copolymerization of polyamines with polycyclic carbonates, some of them finding a biobased[4] and/or CO_2 origin.[5] PHUs have already found multiple utilizations[6] as coatings,[7] elastomers,[8] hydrogels[9] or adhesives/glues.[7a, 10] The fabrication of PHU foams was also achieved by utilizing physical blowing agents (e.g. Solkane,[11] supercritical CO_2[12]) or chemical compounds that generate in-situ the blowing agent (e.g. CO_2 from K_2CO_3/citric acid[13] or H_2 from Momentive[14]). However, some of these blowing agents contribute to global warming (e.g. Solkane), are highly flammable materials (e.g. H_2) or the foaming technology is difficult to transfer to an industrial environment for large scale productions. Recently, we pioneered the preparation of self-blown PHU foams from reactive formulations by exploiting the ambivalent reactivity of cyclic carbonates.[15] In the presence of an appropriate (organo)catalyst, we promoted the divergent ring-opening of the cyclic carbonate via carbonyl attack by the amines (thus delivering the urethane linkages) and via methylene attack by (masked) thiols added to the formulation (affording S-alkylated bonds and releasing the blowing agent (CO_2)). Although flexible and rigid PHU foams were easily fabricated, the process required a careful adjustment of the formulation viscosity prior foaming, long reaction times (several hours), and used mercaptans with often unpleasant smell or some expensive masked thiols.[16]

Despite these developments, producing self-blown PHU foams by a process that mimics the versatile and cost effective water-induced self-blowing PU technology remains a distant dream that needs to be addressed for a more sustainable future to PU foams and its business. To address this issue, we envisioned to induce the partial hydrolysis of the cyclic carbonate comonomer in PHU formulations that will release CO_2 as the blowing agent during the PHU network construction. Nevertheless, the hydrolysis of five-membered cyclic carbonates (e.g. ethylene carbonate into ethylene glycol and CO_2) is not so facile than the one of isocyanates, and generally requires (large) excess of water, a high temperature and a strong alkaline environment.[17] These operative conditions are not directly applicable to prepare self-blown PHU foams.

We recently discovered that PHU hydrogels could be fabricated in water with very short gel times at room temperature under catalyst-free conditions using hydrosoluble poly(cyclic carbonate)s and polyamines. This was possible by adjusting the initial pH of the reaction medium at a value that minimized the consumption of the reactive groups by

hydrolysis of the cyclic carbonates (dominant at pH >12) and by protonation of the primary amines (dominant at pH < 9, depending on the amine pK_a).[9a,b] Capitalizing on these findings, one postulated that the undesirable cyclic carbonate hydrolysis observed in the PHU hydrogel synthesis could be exploited and favored in PHU formulations to construct water-induced self-blown PHU foams (**Scheme 1B**). In contrast to self-blown PUs, the vicinal diols formed by hydrolysis of cyclic carbonates will not be involved in further crosslinking reaction and will be present in the polymer matrix as pending groups. Herein, we describe this new methodology that opens the road to a versatile, cheap and universal up scalable foaming method for PHU foams, applicable to either open and closed molds, that is compatible to most of the production processes for PU foams.
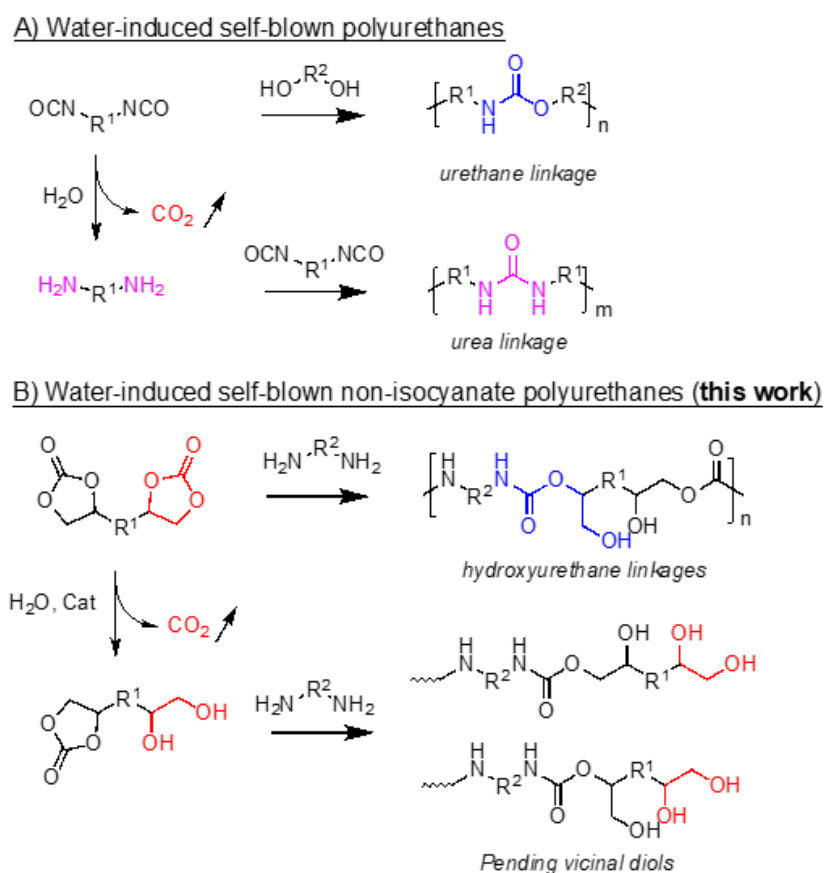
Scheme 1: Comparison of the main reactions involved in the formation of self-blown polyurethanes and non-isocyanate polyurethanes.

Results and Discussion

Hydrolysis of a Model 5-Membered Cyclic Carbonate

To validate the concept and define operative conditions adaptable to the fabrication of PHU foams, we first studied the hydrolysis of a model cyclic carbonate (ethylene carbonate, EC) under solvent-free conditions at different temperatures (25, 60, 80 and 100 °C), in the presence of various base catalysts (triethylamine, DBU or KOH) and water contents (from 0 to 1 eq vs EC) (**Figure 1A**).

All experiments were monitored by 1H-NMR spectroscopy by quantifying the conversion of EC into ethylene glycol (**Figures S2-10**) and the main relevant results are depicted in **Figures 1B-D**. The influence of the temperature on the hydrolysis of EC ([EC]/[water] = 1/1) was first evaluated at various temperatures, yet selecting a nitrogen base, i.e. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst (0.05 eq vs EC). **Figure 1B** highlights the importance of the temperature on the hydrolysis efficiency with a very low amount of hydrolyzed product at r.T (< 5 mol%). Such result differs from a previous work that showed that a high hydrolysis level of EC was obtained at r.T when a large excess of water (> 60 eq.) was utilized in a strong alkaline medium.[9a] The hydrolysis degree increased to 17% within 3 h at 60 °C, and reached 59% and 87% at 80 and 100 °C, respectively. It was controlled by the content of water from 25% with 0.25 eq water (vs EC) to 87% with 1 eq water at 100 °C in the presence of 0.05 eq of DBU (vs EC) (**Figure 1C**). To potentially tune the on-time release of CO_2 during the foaming process, other catalysts such as KOH or NEt_3 were tested at 100 °C (0.05 eq vs EC, EC/water = 1, **Figure 1D**). DBU was found to be the most efficient catalyst, followed by KOH and NEt_3 as attested by EC conversions that dropped from 87 to 46% and 9%, respectively, after 3h at 100 °C. No reaction was noted in the absence of a base. Based on our previous works describing the synthesis of PHU coatings in water, the hydrolysis of cyclic carbonates strongly depended on the pH of the reaction medium, and thus on the pK_aH of the amine used in the formulation.[9a-c] Therefore, the higher catalytic activity of DBU compared to NEt_3 was in line with their pK_aH and thus basicity (DBU; pK_aH = 24.33 in acetonitrile vs NEt_3; pK_aH = 18.46).[18] Although KOH is a strong base, its activity was significantly lower than the one of DBU. However, the possible lack of complete solubility of this inorganic base in the solvent-free organic medium might account for this difference.
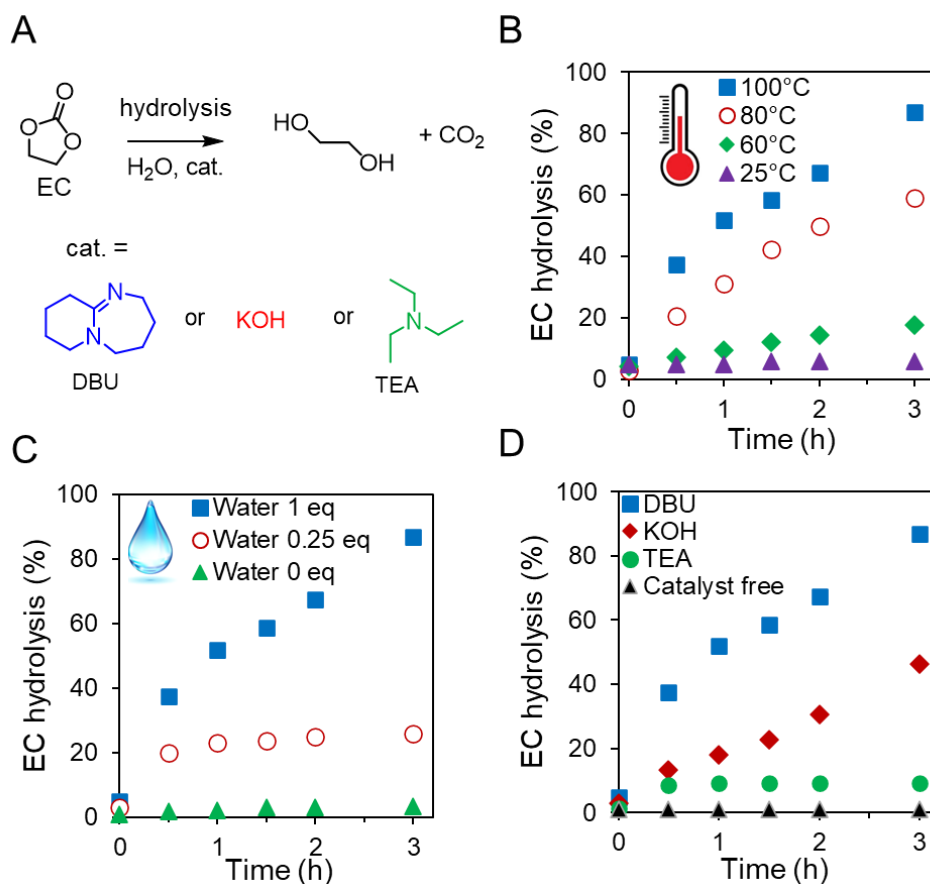
Figure 1: A) Hydrolysis of ethylene carbonate (EC) into ethylene glycol and CO_2. B) Temperature dependence of the hydrolysis of EC using DBU as a catalyst (conditions: EC/water = 1, 0.05 eq of DBU vs EC, 3 h); C) Influence of the water content on the EC hydrolysis over time (conditions : 100 °C, 0.05 eq of DBU vs EC); D) EC hydrolysis with different catalysts (conditions : 0.05 eq of cat. vs EC, EC/water = 1, 100 °C).

Based on these results, it was assumed that the cyclic carbonate hydrolysis could be exploited to produce self-blown PHU foams from solvent-free formulations composed of poly(cyclic carbonate)s and polyamines, added by water and a suitable catalyst (e.g. DBU). However, the foaming is a complex process that requires simultaneous PHU network formation and the gas generation right on-time. The imbalance between both phenomena leads either to the formation of a highly cross-linked material before gas generation or to premature gas release, both leading to poorly foamed materials. Indeed, in the first case, the crosslinked matrix cannot expand when CO_2 is generated while in the second case, the formulation is not viscous enough to trap the blowing agent. Therefore, the aminolysis of the cyclic carbonate has to be slightly faster than the hydrolysis such

that the PHU under construction (and thus not too densely crosslinked) can easily expand and trap the CO_2 bubbles.

Prior testing the foaming, the concomitant rates of aminolysis and hydrolysis were thus studied on tricomponent model reactions to identify the best operating conditions. This was carried out on a mixture of EC with water (for the hydrolysis) and m-xylylene diamine (XDA) (for the aminolysis). A primary amine group to cyclic carbonate molar ratio ([NH$_2$]/[EC]) of 0.75 was used, leaving 0.25 eq of free EC for the production of CO_2. This ratio was already presented as the optimal one for preparing self-blown PHU foams when using (masked) thiols as decarboxylation precursors.[15,16a]

The first set of reactions was performed with or without DBU using 0.25 eq of water (vs EC) at 80 (**Figure 2B**) or 100 °C (**Figure 2C**). The aminolysis did not significantly depend on the presence of DBU with an aminolysis yield higher than 90% after 30 min at both 80 and 100 °C that did not evolve further. This is in sharp contrast to the hydrolysis that was slow without DBU with a hydrolysis yield of 13% after 30 min and 16% after 3h at 100 °C, compared to 42% after 30 min and 71% after 3h in the presence of the organobase. The same trend was noted at 80 °C, however with a lower hydrolysis yield. Unlike the catalyst-free hydrolysis experiments highlighting no decomposition of EC (**Figure 1D**), a slow hydrolysis of EC was observed under DBU-free conditions (**Figures 2B-2C**), that is due to the presence of XDA, a weak base, that catalyzed the reaction.

In the second set of reactions, we modulated the content of water for the DBU catalyzed reactions (0.05 eq. vs EC) performed at 80 and 100 °C. **Figures 2D** and **2E** illustrate that, while the aminolysis yield remained high and unaffected by the content of water, the hydrolysis yield was easily tuned by the amount of water, from 36 to 69% by increasing the water content from 0.25 eq (vs EC) to 2 eq at 80 °C or from 71 to 97% for 0.25 eq and 1 eq. water, respectively, at 100 °C after 3 h of reaction. This indicates that the formation of CO_2 can be easily controlled by adjusting the water content while not affecting the aminolysis rate that is fast in any case. As discussed above, controlling the formation rate and content of blowing agent is particularly relevant when PHU foaming is considered.
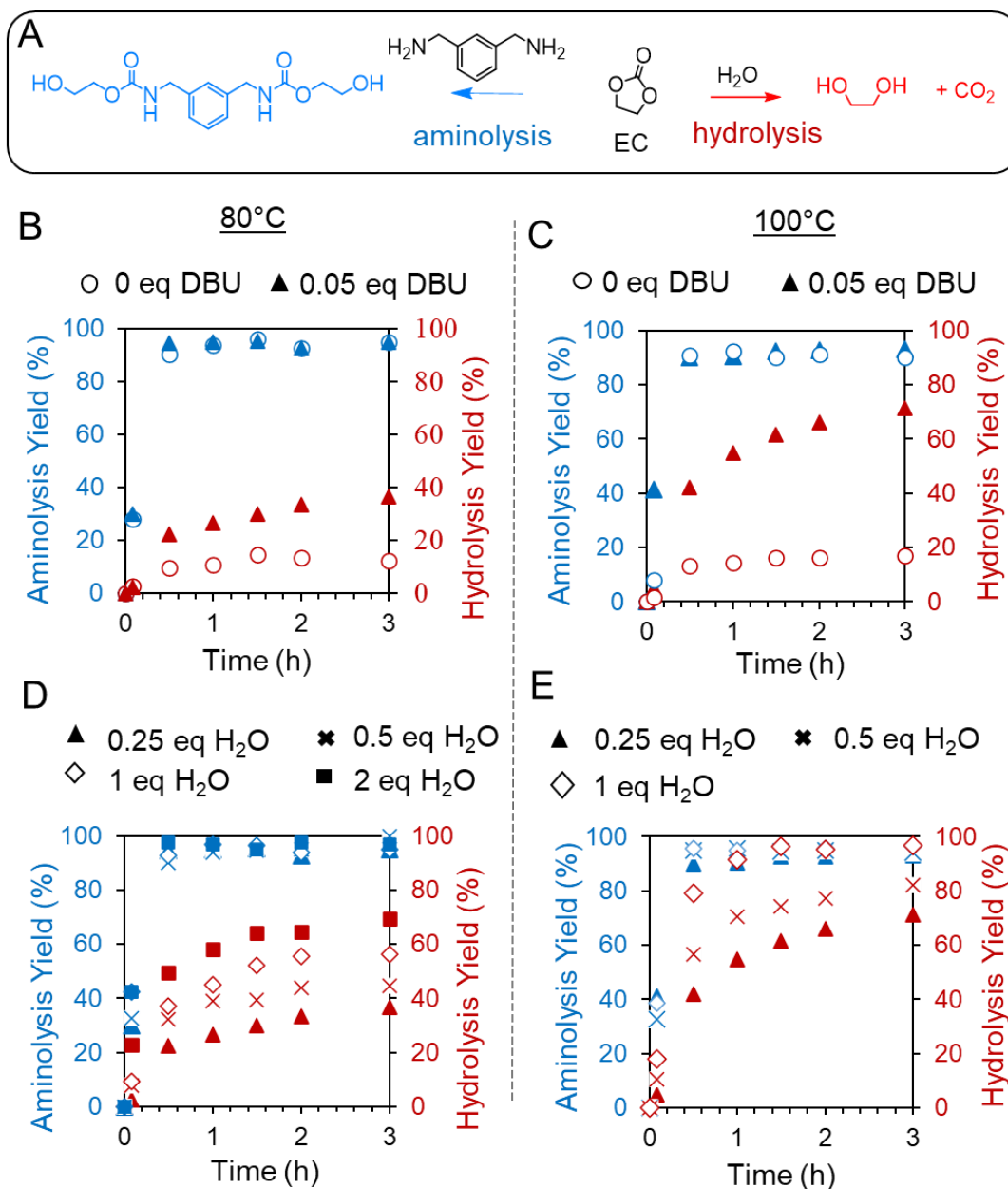
Figure 2: Concomitant hydrolysis and aminolysis of ethylene carbonate (EC) in the presence of water and XDA. A) Scheme of the reactions, B) Yield of the reactions at 80 °C with and without DBU, in the presence of 0.25 eq of water (vs EC), C) Yield of the reactions at 100 °C with and without DBU, in the presence of 0.25 eq of water (vs EC), D) Yield of the reactions at 80 °C for different water contents in the presence of DBU (0.05 eq), E) Yield of the reactions at 100 °C for different water contents in the presence of DBU (0.05 eq). (Kinetics of reactions followed by 1H-NMR are provided in supporting information in **Figures S11** to **S19**)

Preparation of Water-Induced Self-blown PHU Foams.

PHU foams were prepared from solvent-free PHU formulations composed of a tris(cyclic carbonate) (trimethylolpropane triscarbonate, TMPTC) and a diamine (aromatic: m-xylylene diamine, XDA; or aliphatic: 1,2-bis(2-aminoethoxy)ethane, EDR 148); or hexamethylene diamine, HMDA) (**Figure 3**). A fixed [amine]/[cyclic carbonate] ($[NH_2]/[5CC]$) ratio of 0.75 was used to leave 25 mol% of the initial 5CC available for the hydrolysis, and thus for the production of the blowing agent. Different contents of water were then added to the formulations, together with DBU as catalyst (0.05 eq. vs 5CC). The main formulations, reaction conditions and foams characteristics are summarized in **Table 1**, and representative images of the foams are depicted in **Figure 4**.
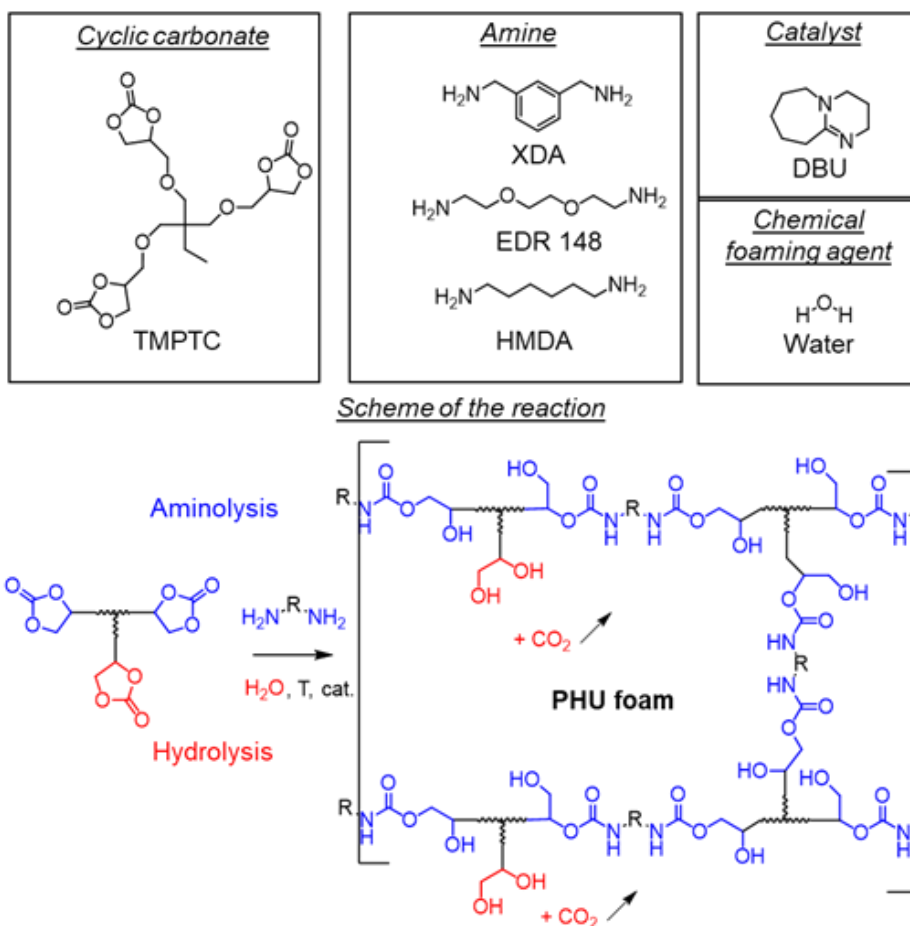

Figure 3: Components of the solvent-free PHU formulation and scheme for producing water-induced self-blown PHU foams.

We first investigated the foaming of the solvent-free formulation containing XDA at 100 °C, the temperature that provided the fastest cyclic carbonate hydrolysis at low water content (0.25 eq vs 5CC) for the model reaction (**Figure 2C**). Under these conditions, a foam with an open cell morphology was obtained with a density of 153 kg.m^{-3} and an average cell diameter of 2.3 ± 1.1 mm (**Table 1**, **entry D**; **Figure 4D**). The ratio to opened and closed cells was evaluated by SEM analysis using the Fitzgerald procedure,[19] by assessing the areas of holes (Ah) and cell faces (Ac). Higher is the Ah/Ac ratio and higher is the open porosity of the foams. For sample D, an open-cell porosity with holes-on-cell area ratio Ah/Ac of 21.3% is calculated by SEM (**Figure 4D**). Importantly, no foaming was noted under identical experimental conditions without water (**Table 1**, **entry A**). In the absence of DBU, some foaming was noted, however a high density foam of 597 kg.m^{-3} was collected (**Table 1**, **entry C**). This was the result of some hydrolysis of the cyclic carbonate catalyzed by XDA, in line with the previous model reactions. As the foaming was performed at the boiling point temperature of water, we might argue that a physical foaming occurred by water evaporation. We thus realized the same procedure by substituting water by a physical foaming agent that could not hydrolyze the cyclic carbonates while presenting a similar boiling point than water, i.e. heptane (bp = 97°C). No foaming was observed in that case (**Table 1**, **entry B**). An additional proof of a foaming process mainly governed by the decarboxylation of the cyclic carbonates rather than by water evaporation lied on the formation of a calcium carbonate precipitate when the gas emitted during the foaming was trapped in a calcium hydroxide solution (see **Figure S20** in ESI for details).

We then added a commercially available synthetic clay (hydrotalcite, 12 wt% vs TMPTC) to the formulations as clay fillers are known to act as a nucleating agents,[15,20] thus increasing the cell density, decreasing the cell size and generally improving the foam homogeneity. They are also expecting to increase the formulation viscosity, which should facilitate trapping the blowing agent in the polymer matrix. By adding hydrotalcite to the formulation of foam D (**Table 1**) and foaming following an identical procedure, the cell size was indeed strongly decreased from 2.3 ± 1.1 mm (without clay) to 0.39 ± 0.19 mm (with clay) without affecting the foam density (154 kg.m^{-3}) nor significantly the porosity (Ah/Ac = 26.5 %) (**Table 1**, **entry E**; **Figure 4E**).

We then studied the foaming of formulation D at lower temperature, i.e. 80 °C. The foaming time had to be extended from 3 to 5 h in order to avoid the foam collapse during cooling. Decreasing the foaming temperature from 100 to 80 °C resulted in twice denser foams (327 vs 153 kg.m^{-3}) of smaller cell size (1.08 ± 0.17 vs 2.3 ± 0.11 mm) (**Table 1**, **entry F**; **Figure 4F**). As previously observed, adding hydrotalcite (12 wt% vs TMPTC) decreased the cell size (0.38 ± 0.19) with limited effect on the foam density (366 kg.m^{-3}; **Table 1**, **entry G**). The foam density was decreased by increasing the amount of water

from 0.25 to 1 eq in the presence (214 kg.m^{-3}; **Table 1**, **entry H**) or not of hydrotalcite (179 kg.m^{-3}; **Table 1**, **entry I**) as the result of more generated CO_2.

Aliphatic diamines were also considered for producing PHU foams. In contrast to foams prepared from XDA under similar operating conditions at 80 °C, an heterogeneous and rather dense foam (429 kg.m^{-3}) with an open cell morphology was obtained with EDR 148. Importantly, the addition of hydrotalcite strongly improved the foam quality, i.e. it is homogeneous and of lower density (335 kg.m^{-3}) with a smaller cell size (comparison **Table 1**, **entries J** and **K**; **Figures 4J** and **4K**). The lower reactivity of EDR 148 in comparison to XDA[9b] rendered the polymerization slower, thus the blowing agent released at the early stage of the process could not be efficiency trapped by the matrix leading to a low quality foam. When hydrotalcite was added, the increase of viscosity (as attested by rheological measurements in **Figure S64**) combined to the nucleating effect of the filler facilitated the expansion of the matrix as well as the cell size reduction (1 vs 0.38 mm) in accordance with PU literature.[20] By substituting EDR 148 for the more reactive HMDA,[21] foams of density around 250 kg.m^{-3} were collected with or without hydrotalcite (**Table 1**, **entries L** and **M**). Although similar densities were obtained in the two cases, hydrotalcite strongly decreased the cell size as illustrated by comparison of **Figures 4L** and **4M**. As illustrated in **Figure 4**, the addition of hydrotalcite was thus beneficial to the foaming in all cases by improving the foam homogeneity as well as by decreasing the cell size.

The gel content (GC) as well as the thermo-mechanical properties of some relevant foams were then evaluated and results are presented in **Figure 5** (full data are summarized in **Table S2**). **Figure 5A** shows that the gel content of the foams prepared with XDA and 0.25 eq water were high (≥ 95%) when prepared at both 80 and 100 °C, confirming the crosslinked nature of the polymer matrix. This gel content decreased to 86% for a higher content of water of 1 eq at 80 °C. This was explained by a higher content of hydrolyzed cyclic carbonate groups, that were therefore not available for crosslinking with the amines. The same trend was noted when hydrotalcite was added to the formulation (foams E, G, I; **Figure 5A**). To further get insight on the effect of the water content on the foam density and gel content, we prepared additional foams based on similar formulations at 100 °C in the presence of hydrotalcite by varying the water content over a large extent (from 0 to 8 eq vs 5CC). Results are shown in **Figure 5B**. The lowest density (100-150 kg.m^{-3}) was reached between 0.25 and 2 eq of water and rapidly increased for lower and higher contents. Moreover, the gel content slightly decreased from 95% to about 85% when water was added up to 2 eq. This gel content further decreased to 80 and 30 % when 4 and 8 eq water were added to the formulation, respectively. This impressive gel content drop at higher water content was the result of extensive hydrolysis of cyclic carbonate groups of TMPTC that were no more available for crosslinking with the amine. It also explained the

higher foam density observed when using 8 eq water. Indeed, the low crosslinking degree of the PHU matrix did not prevent the foam to collapse.

Table 1: Properties and morphological characterization of water-induced self-blown PHU foams in opened mold.

Entr.	Amine	T/ time [a]	Catalyst (eq *vs* 5CC)	Foaming agent (eq *vs* 5CC)	Hydrotal. (*vs* TMPTC)	Density (kg.m^{-3})	Cell size (mm)	A_h/A_c (%)[b]
A	XDA	100 °C	DBU (0.05 eq)	-	-	963	NA[c]	NA[c]
B		/3h	DBU (0.05 eq)	Heptane	-	1075	NA[c]	NA[c]
C			/	H$_2$O (0.25 eq)	-	597	NA[c]	NA[c]
D			DBU (0.05 eq)	H$_2$O (0.25 eq)	-	153 ± 5	2.3 ± 1.1	21.3
E			DBU (0.05 eq)	H$_2$O (0.25 eq)	12 wt%	154 ± 1	0.39 ± 0.19	26.5
F		80 °C	DBU (0.05 eq)	H$_2$O (0.25 eq)	-	327 ± 3	1.08 ± 0.17	< 1
G		/5h	DBU (0.05 eq)	H$_2$O (0.25 eq)	12 wt%	366 ± 12	0.38 ± 0.19	13.2
H			DBU (0.05 eq)	H$_2$O (1 eq)	-	214 ± 55	>2	NA
I			DBU (0.05 eq)	H$_2$O (1 eq)	12 wt%	179 ± 34	0.54 ± 0.13	14.1
J	EDR 148	80 °C	DBU (0.05 eq)	H$_2$O (1 eq)		429 ± 40	1.00 ± 0.27	19.9
K		/5h	DBU (0.05 eq)	H$_2$O (1 eq)	12 wt%	335 ± 35	0.38 ± 0.15	18.6
L	HMDA	80 °C	DBU (0.05 eq)	H$_2$O (1 eq)		269 ± 32	>5	NA[c]
M		/5h	DBU (0.05 eq)	H$_2$O (1 eq)	12 wt%	255 ± 15	<5	NA[c]

[a] T/time is for temperature and time of foaming. [b] Ah/Ac states for the ratio between the areas of holes (Ah) and cell faces (Ac), [c] NA refer to incapacity to measure the parameter due to sample morphology.
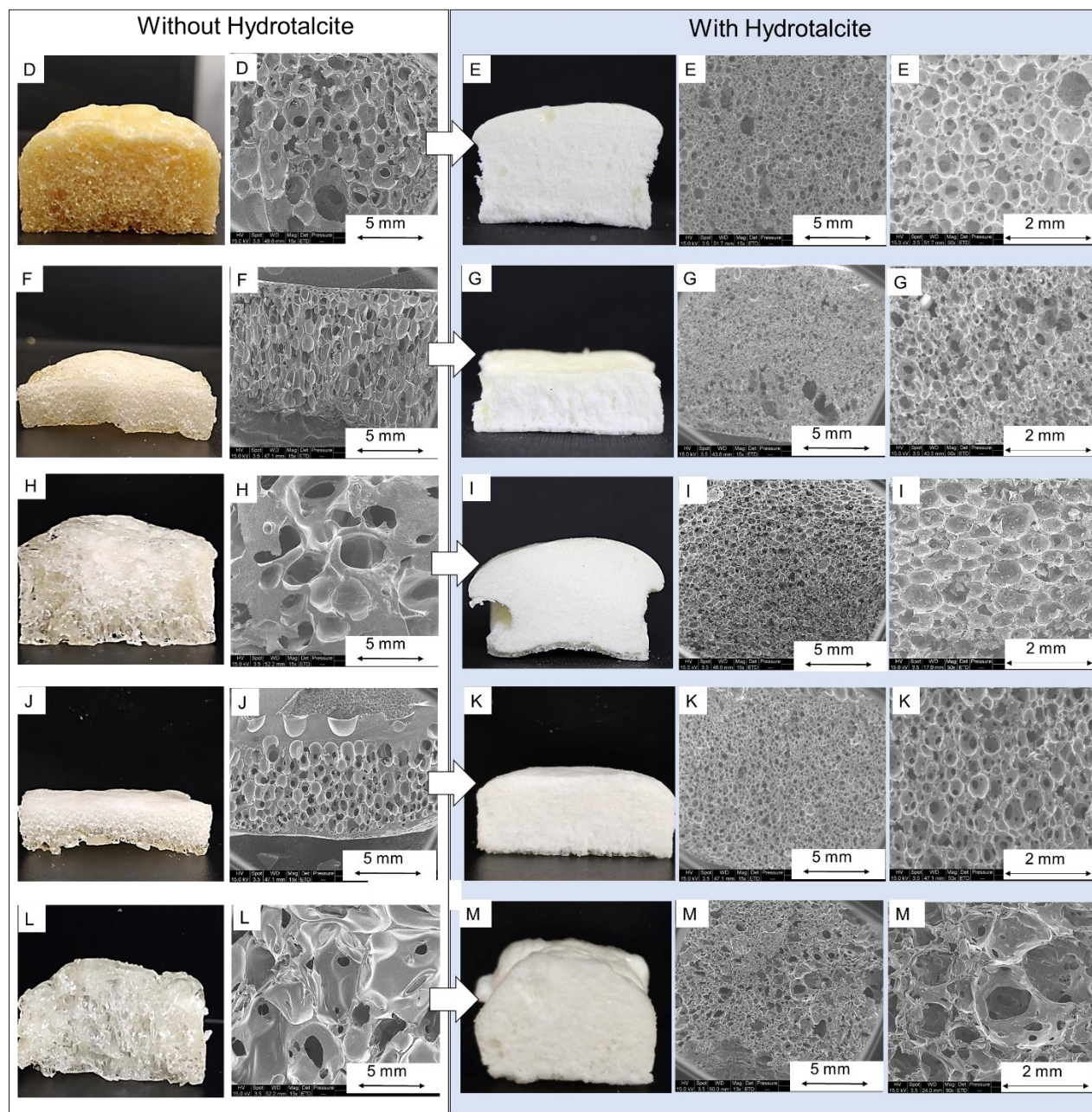
Figure 4: Pictures and SEM characterizations of self-blown PHU foams presented in **Table 1**. Photography of the inert part for each foam is associated with the SEM image. On the same line are compared foams prepared with the same formulation without hydrotalcite (on the left) and with hydrotalcite (on the right).
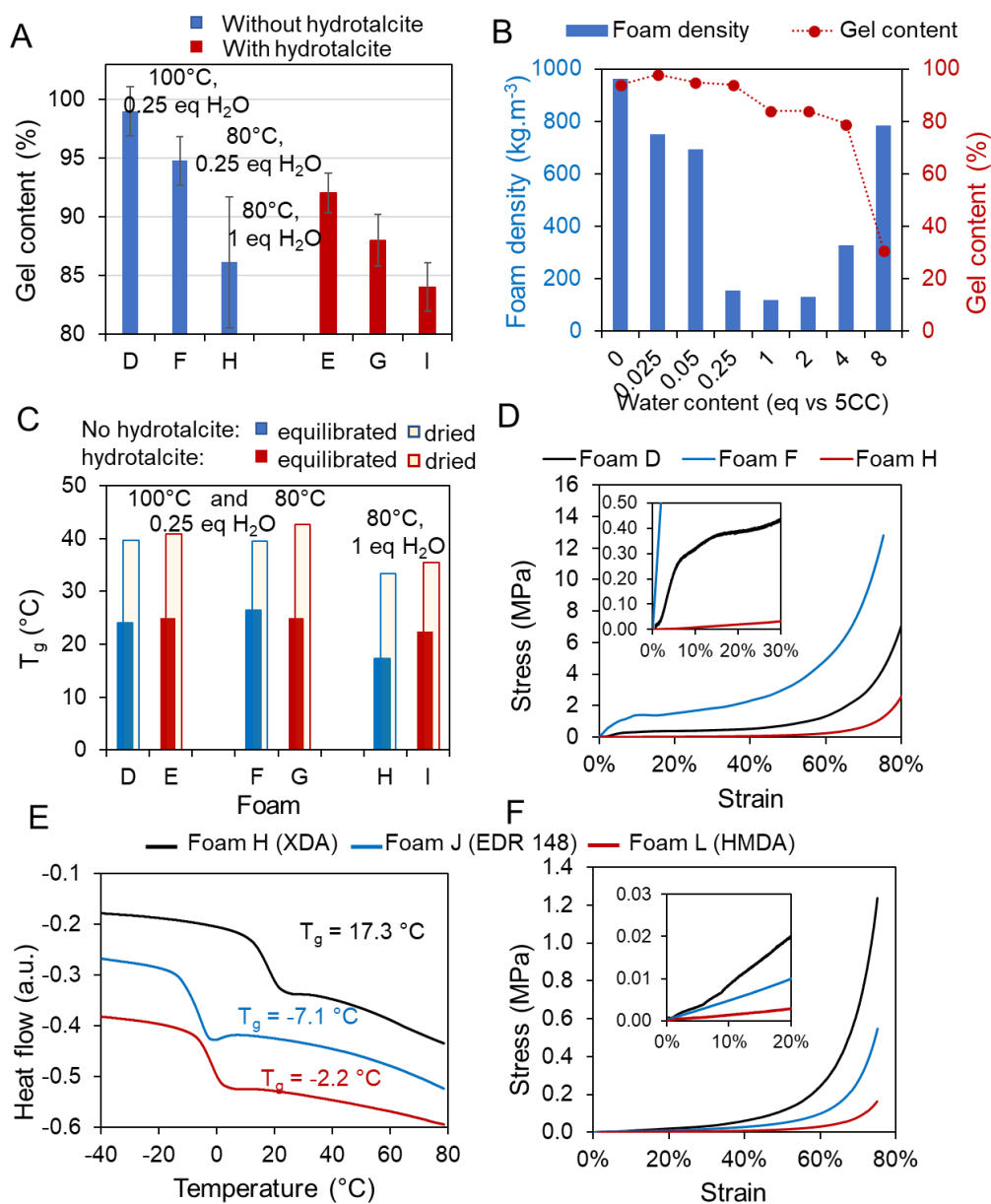
Figure 5: Gel contents, foam densities and thermo-mechanical properties of PHU foams. A) Influence of the foaming temperature and water amount on the gel content. B). Influence of the water content on the foam density and gel content for foams prepared with TMPTC, XDA ($NH_2 = 0.75$ eq vs 5CC), DBU (0.05 eq vs 5CC) and hydrotalcite at 100 °C for 3h. C) Influence of the foaming temperature and water content on the glass transition temperature (T_g) of dried or equilibrated foams. D) Compressive curve of equilibrated foams synthesized at 100 (foam D) and 80 °C with different water amounts (foams F and H). E) Effect of the diamine on the glass transition temperature of the equilibrated foams. F) Compressive curve of equilibrated foams synthesized with different diamines.

The glass transition temperature (T_g) of the equilibrated foams (thus stored under ambient atmosphere for 48 h) were determined by differential scanning calorimetry (DSC) and the results are summarized in **Figure 5C** (all DSC thermograms are shown in section 5.3 of the supporting information). Hydrotalcite had no significant effect on the T_g of XDA-based foams prepared with 0.25 eq water at 100 or 80 °C (T_g around 25 °C in both cases). For a higher content of water (1 eq vs 5CC), T_g of the unloaded foam was decreased to 17°C as the result of a lower cross-linking degree and a higher content of soft vicinal diol chain ends (resulting from 5CC hydrolysis) that increased chain segment motion. As previously observed for other PHU foams,[16a] but also coatings,[22] PHU are more hydrophilic than conventional PUs (due to the presence of the pending hydroxyl groups) and absorbed a low content of air moisture (between 2 and 3 wt% as determined by thermogravimetric analysis) that induced a strong hydroplasticization of the polymer matrix. In agreement with these reports, when the foams were fully dried and rapidly analyzed by DSC, T_g's were strongly raised from about 25 to 40°C.

The mechanical resistance of the three equilibrated foams D, F and H was assessed by compression tests (**Figure 5D**). It is worth noting that the three foams presented different densities and therefore, their mechanical properties could not be fairly compared. However, foam D that was characterized by the lowest density (153 kg.m^{-3}) presented the highest compression modulus with a value of 6.66 MPa compared to 0.149 MPa for H. This is fully in line with the highly crosslinked nature of this matrix as verified by the gel content (> 98%, **Figure 5A**).

As expected, more flexible aliphatic diamines (i.e. EDR 148 and HMDA) strongly affected the thermo-mechanical properties of the foams. By comparing foams synthesized under similar conditions (80 °C with 1 eq of water vs 5CC) with XDA (foam H), EDR 148 (foam J) or HMDA (foam L), we found a decrease in T_g from XDA (17.3 °C) to HMDA (-2.2 °C) and EDR 148 (-7.1 °C) for similar gel contents (> 86%) (**Figure 5E**). The more rigid XDA-based foam presented the highest compression modulus, i.e. 0.149 MPa vs 0.05 MPa for foam J and 0.03 MPa for foam L; **Figure 5F**, **Table S2**).

The importance of the pending OH groups on the hydrophilic character of the foams was further highlighted by calculating the equilibrium water content (EWC) of some selected foams prepared under identical conditions by using different amines (i.e. foams E (issued from XDA), K (from EDR 148) and M (from HMDA)). Samples were equilibrated under humid atmosphere (100% humidity) or by immersing the samples in water, both for 24 h at room temperature. Results are depicted in **Figure S65A**. In brief, in the first case (humid atmosphere), EWC reached about 10 % compared to 100-160 % in the second case (immersion in water). Importantly, a T_g difference as high as 40 °C was noted between the dried foams and the humid ones (**Figure S65B**), which consequently strongly affected

the compression modulus of the samples (**Figure S65C**). The water effect was particularly impressive for foam K with a compression modulus of 5.2 MPa (T_g = 40 °C) at the dried state against 0.04 MPa (T_g = 0 °C) for the humid one (equilibrated under 100% humidity). This hydroplasticization was reversible as, when again dried, the initial properties of the dried foams were recovered. When stored on the bench for 6 months, the foams presented similar gel contents as those directly measured after their preparation, suggesting that they did not degrade over this period of time (**Figure S65D**).

Although some works report on the presence of some urea linkages within PHU backbone,[23] our foams did not seem to present these linkages as the polymerization/foaming process was shorter and generally performed at lower temperature, not prone to urea formation (see ESI, section 8 for details).

Importantly, the pending hydroxyl groups of the foams were exploited to repurpose the foams into polymer films by compression at 160 °C (2 ton pressure, 2h) as illustrated for foams D and J (**Figure S67**). Similarly to other PHU materials,[16a,24] transcarbamoylation reactions were expected to occur upon thermal activation, which enabled reprocessing the crosslinked PHU. This product repurposing offers a perspective to recycle our foams, although further investigations (out of scope of this paper) are needed to fully characterize the process.

To illustrate the versatility of the foaming process, we also evaluated some formulations containing a dicyclic carbonate (instead of a tricyclic one) and a triamine (instead of a diamine) for the formation of foams. We tested two liquid linear dicyclic carbonates, i.e. neopentyl dicyclic carbonate (5CC1) and a polyethylene glycol dicyclic carbonate (5CC2; Mn = 628 g/mol) with tris(2-aminoethyl)amine (TAE) in the presence of water (25 mol%), DBU (0.05 mol%) and hydrotalcite (12 wt% vs dicyclic carbonate) at 100 °C for 3h (**Figure S68A**). Although these formulations were not optimized, **Figures S68B-C** illustrate that foams were obtained in the two cases with a density of 226 kg.m^{-3} (with 5CC1) and 480 kg.m^{-3} (with 5CC2), both characterized with a low T_g. The gel contents were however lower compared to foams obtained from the tricyclic carbonate and diamine (72-76% vs 85-95%), in line with a lower crosslinking degree as expected. This illustrates that easily accessible dicyclic carbonates can also be used for preparing the foams.

Foaming in Closed Molds, Scaling-Up and Acceleration of the Process – a Step Towards the RIM Process.

The reaction injection molding (RIM) process[25] in closed molds is largely used in industrial environment to produce PU foamed materials of pre-determined (complex) shape, density and size such as flexible foams for automotive seat cushion. In this process, the monomers, stored in separate tanks, are pumped to an internal high pressure mixer and the mixture is then delivered into a pre-heated mold at approximately atmospheric pressure. The foaming then occurs inside the mold cavity. We thus decided to evaluate the potential of our technology to fit with this industrially important RIM process by foaming some of our previous formulations (**Table 1**, **entries E** and **G**) in a homemade circular stainless steel closed mold (**Figure 6A**). Since the expansion of the foam is limited by the mold volume, the theoretical density was calculated by dividing the weight of the formulation by the volume of the mold. A density of 230 kg.m^{-3} was here targeted. After preheating the mold at 80 or 100 °C for 30 min, the formulation prepared in a syringe at room temperature was directly injected into the hot mold. After 3h at 100 °C, a rigid and homogeneous foam of open cell morphology with a density close to the theoretical value completely filled the mold (Foam Ec, **Figure 6A-B**; **Table 2**). At 80 °C, some collapse of the foam was observed after 5h of foaming, probably due to uncomplete crosslinking. We therefore arbitrary extended the foaming time to 24 h, which furnished a rigid foam without any collapse and with a density close to 230 kg.m^{-3} (**Figure 6C**; **Table 2**, Sample Gc). Compared to the free foaming process in open molds (**Table 1**, **entries E** and **G**), the foams produced in closed molds were characterized by a slightly smaller pore size (0.3 vs 0.4 mm). The other characteristics such as gel contents and T_g's remained unaffected (**Table 2**), and the thermal degradation temperatures at 5% mass loss (Td5%) determined by thermogravimetric analysis (TGA) were similar to those of other self-blown PHU foams (Td5% around 250 °C).[15] ATR spectroscopy of foams Ec and Gc confirmed the almost full consumption of the cyclic carbonate groups during the foaming process with the almost complete disappearance of their carbonyl elongation band at 1795 cm^{-1} (**Figures S69** and S73).
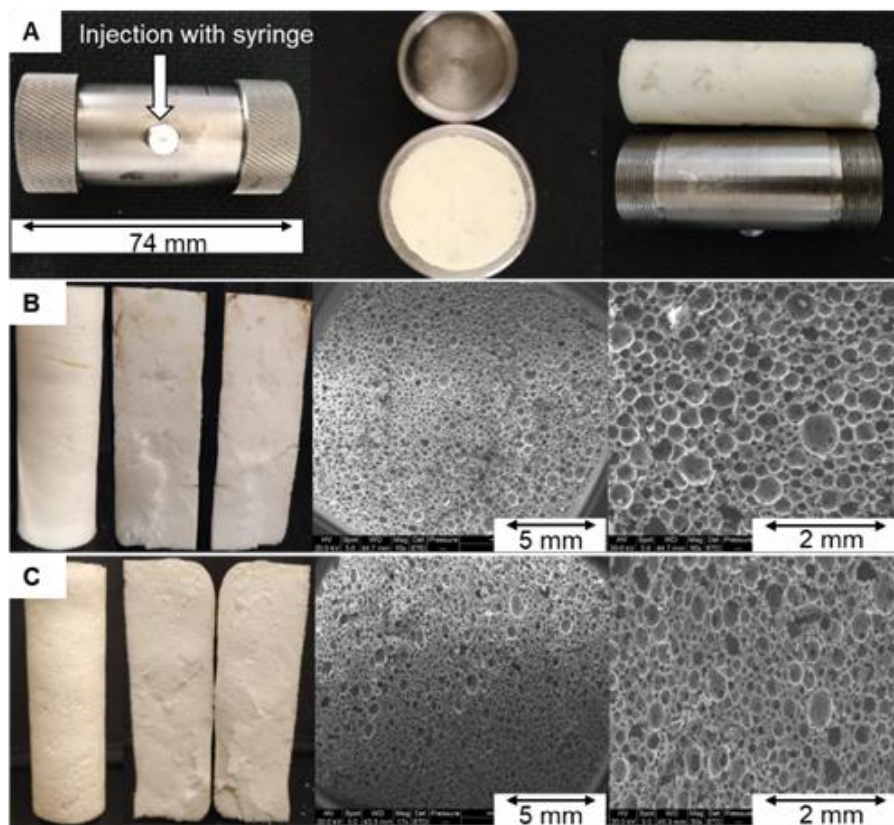
Figure 6: (A) Image of closed mold foaming with image of the metallic mold and the foam Ec that filled the mold; (B) foams Ec out of the mold and cut in two pieces, with SEM images; (C) foams Gc out of the mold and cut in two pieces, with SEM images. The properties of foam Ec and Gc are depicted in **Table 3** and formulations are described in **Table 1** (**entries E** and **G**).

The implementation of the technology to the industrial production of PHU foams would however require much shorter foaming periods. We thus investigated some ways for accelerating the foaming process. The best and reproducible procedure consisted in preheating all components of the formulation separately (to avoid initiating the reaction) for 5 minutes at 100 °C, prior to mixing them and injecting the formulation in the pre-heated mold (100 °C). As a representative example, a PHU foam based on EDR 148, TMPTC and hydrotalcite was produced in 30 min following this procedure. Compared to the foam prepared by the classical foaming process (no pre-heating of the different components, 100 °C, 3h), the foam obtained by the "fast process" presented a slightly lower density (301 vs 407 $kg.m^{-3}$) while the other characteristics (gel content, T_g) were very similar as illustrated in **Figure 7A-D**. This fast foaming process was scaled-up from 7 to 650 g in a closed aluminum mold (25 x 15 x 5 cm), furnishing a foam with very similar density, gel

content and T_g values (**Figure 7E-F**). This illustrates the ease to scale-up the fast foaming process that is now approaching the timescale needed for the RIM process.

Table 2: Reaction conditions and characteristics of the foams produced in a closed mold

	T/ time	Water (eq *vs* 5CC)	D (kg.m^{-3})	Cell size (mm)	A_h/A_c (%)[a]	GC (%)[b]	$T_g/T_{g\ dried}$ (°C) [c]	$T_{d5\%}$ (°C) [d]	Comp. Modulus (MPa) [e]
E$_c$	100 °C /3h	0.25	208 ± 32	0.29 ± 0.13	17	93	24.2/ 43.0	250	5.9 ± 0.12
G$_c$	80 °C /24h	0.25	252 ± 22	0.21 ± 0.08	18	97	25.2/ 44.3	254	2.7 ± 0.5

[a] Ah/Ac states for the ratio between the areas of holes (Ah) and cell faces (Ac). [b] GC is for gel content measured after 24h of immersion in THF. [c] T_g is the glass transition measured by DSC for foam equilibrated under ambient conditions for 48h and T_g dried states for the T_g for dried foams. [d] Td5% is for the degradation temperature at 5% mass loss determined by TGA. [e] is the compression modulus determined by compression test on equilibrated foams. Formulations are described in **Table S1** and DSC, TGA and compressive curves are presented in section 11 of the supporting information
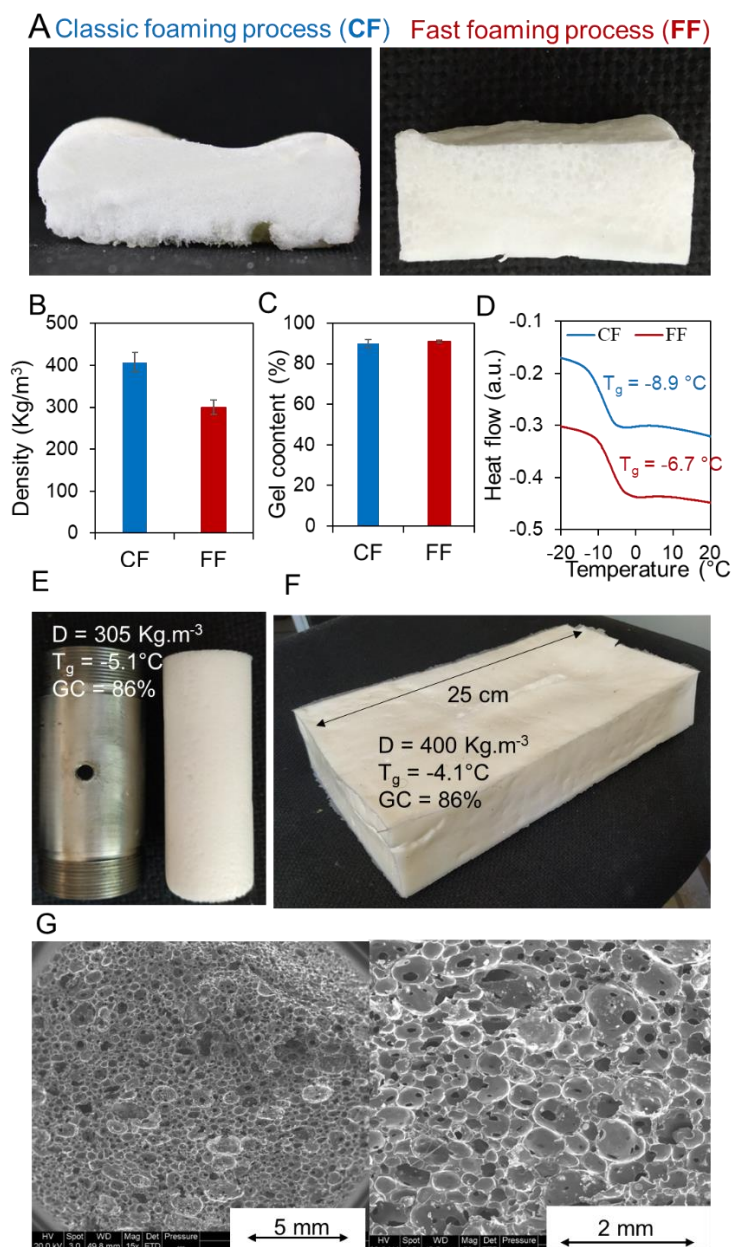
Figure 7: Comparison of the foams prepared by the classical foaming process (CF) (reagents are mixed at r.T. and foamed at 100 °C for 3h) and the fast foaming process (FF) (reagents are separately pre-heated at 100 °C for 5 min, followed by mixing and foaming in a pre-heated mold for 0.5 h at 100 °C). A) image of the two foams; B) density, C) gel content and D) DSC thermograms of the foams. Synthesis conditions: TMPTC (5CC = 1 eq), EDR 148 (NH_2 = 0.75 eq), water (0.25 eq), DBU (0.05 eq). E) Image of the foam (7g) obtained by the fast foaming process in closed mold. F) Scale-up of the foam (650 g) in closed mold obtained by the fast foaming process. G) SEM of the scale up of the foam in closed mold.

Conclusion

We have reported a facile, fast, robust and versatile process for preparing water-induced self-blown non-isocyanate polyurethane foams that mimics the conventional industrial PU foaming process.[26]   Aided by model reactions, we found that water, added by a base catalyst (e.g. DBU or KOH), efficiently hydrolyzed 5-membered cyclic carbonates in a temperature range of 80 to 100 °C. This hydrolysis released carbon dioxide that was then exploited as a blowing agent in PHU formulations composed of a tris(cyclic carbonate) and a diamine. By testing different amines (aromatic and aliphatic), temperatures and water contents, we found optimal conditions for self-blowing PHU networks by partially hydrolyzing cyclic carbonate groups. Rigid and flexible foams were accessible (depending on the nature of the amine) with a foam morphology that was easily tuned by the content of water and the addition of clay. The initial foaming technology in open mold was extended to closed molds, which offers great perspectives for further transfer to the industrial fabrication of complex foamed materials of pre-determined shape via the reactive injection molding (RIM) process. This was illustrated for the fabrication of foams in 30 minutes by separately pre-heating the various components of the formulation, prior mixing and directly injecting them in a pre-heated mold, without requiring any pre-reaction. This constitutes an important improvement compared to most of state-of-the-art self-blowing PHU technologies that require hours or even days for completion.[13-16] Scaling-up of the technology was also feasible at the 650 g scale. This work highlights that self-blown non-isocyanate polyurethane foams are now accessible by utilizing water to in-situ generate the blowing agent (CO_2) by reaction with one of the comonomers of the formulation (the poly(cyclic carbonate)). The challenge to mimic the conventional water-induced PU foaming for NIPU foams is thus no longer a distant dream. Preliminary investigations also show that the crosslinked foams can be repurposed into polymer films by compression at 160°C, offering new perspective for foam recycling. Our new process offers a greener alternative to PU network foams from very simple formulations at low cost, is potentially compatible to existing foaming infrastructures, and opens enormous potential for the next generation of recyclable foams adapted to the demands of many sectors. Extension to the RIM process is currently under investigation.

Acknowledgements

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