SUPPORTING INFORMATION

Valorization of Waste Biomass for the Fabrication of Isocyanate-Free Polyurethane Foams

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Contents

1. Precursor preparation

TMPTC synthesis

Trimethylolpropane triglycidyl carbonate (TMPTC) was synthesized from CO_2 and trimethylolpropane triglycidyl ether as reported elsewhere.[1] Briefly, in a typical experiment, trimethylolpropane triglycidyl ether (TMPTE, 1 L, 1.157 kg) was transferred into a 2 L high pressure reactor. Then, 35.29 g of tetrabutylammonium iodide (TBAI, 2.5 mol% *vs* TMPTE) was added prior closing the cell. The cell was then equilibrated at 110 °C for 24 h, keeping the CO_2 pressure constant to 90 bar and the stirring rate to 200 rpm. The complete conversion of TMPTE into TMPTC was confirmed by ^{1}H-NMR spectroscopy (> 98%, collected crude product > 1,4 kg). TMPTC was used without any purification after degassing for 30 minutes at 50 °C under reduced pressure to remove adsorbed CO_2.

GTC synthesis from bio-based glycerol triglycidyl ether (IPOX CL 12). GTC (1.25 kg) was quantitatively produced by coupling CO_2 to IPOX at 90 bar, 110 °C for 24 h in the presence of tetrabutyl ammonium iodide as catalyst (2.5 mol% vs IPOX) under solvent-free conditions following a detailed protocol described in our previous work (*J. Am. Chem. Soc.* **2024**, *146*, 988−1000; https://doi.org/10.1021/jacs.3c11637). Before use, the product was degassed by thermal treatment at 80 °C for 16 h and then by vacuum treatment at 60 °C for 16 h to remove dissolved CO_2.

Keratin preparation

Keratin was prepared using the sulfitolysis approach, as reported in previous work.[2] Briefly, the wool fibers were first immersed in a 1:1 solution of methanol and acetone overnight and then thoroughly rinsed with Milli-Q water three times. The cleaned fibers were allowed to dry overnight in an oven at 30 °C. Each gram of pretreated wool was immersed in 20 mL of an aqueous solution containing the following reagents: 0.2 M sodium metabisulfite, 0.5 g SDS per 1 g of wool, and 8 M urea. The extraction was performed under continuous stirring at 70 °C for 24 h. Then, the solution was filtered through a 40-mesh stainless steel grid. The filtrate was subsequently dialyzed against Milli-Q water using a dialysis tubing (molecular weight cut-off, MWCO, 6000−8000 Da) for 3 days with six water changes. The resulting solution was centrifuged (two times, at 9000 rpm and 4°C for 20 min) to remove fiber residues and freeze-dried to obtain keratin powder.

2. Evaluation of keratin thiol function content

At first, we estimated the amount of free thiol groups present in the extracted keratin, as reported previously.[2] Indeed, we hypothesized that similar to the previous systems, these would promote the decarboxylation of 5CC, then leading to the foaming of the formulation.

Table S1. Summary of the PHU foams properties prepared with different contents of keratin.

Sample	Keratin content (wt%)	Thiol equivalent (eq.)	Density (kg.m^{-3})	Gel content (%)
A	1	0.001	252 ± 19	87.8 ± 2.3
B	5	0.007	229 ± 10	91.5 ± 0.5
C	10	0.016	244 ± 12	91 ± 1.5
D	20	0.035	188 ± 9	92.5 ± 0.8

E	30	0.061	318 ± 1	92.4 ± 0.9

The amount of thiol functions (in mmol) were estimated using the following equation:

$$\frac{m_{Keratin}}{MM_{a.a.}} \times CMCys \times 1000$$

Where $m_{protein}$ is the weight of keratin, $MM_{a.a.}$ is the average mass of one residue and CMCys is the content of thiol-bearing residues (in mol%) in the extracted keratin (see Table S1 of the reference work).[2]

The number of thiol equivalents was then obtained by respect to the cyclic-carbonate groups for each formulation.

NB: It is worth mentioning that we can also estimate the amount of thiol functions per gram of protein, given the amount of thiol equivalent in the table and that 10 wt% of filler corresponds to 0.71g of keratin in our formulation. Thiol content is then estimated to 0.78mmol/g of keratin.

3. Optimization of the NH_2/5CC ratio of the liquid formulations

The optimal NH_2/5CC ratio was searched for the liquid formulations containing two different families of biofillers, i.e a protein (keratin) and a lignin derivative (sodium lignosulfonate), at 5 wt% loading. For that purpose, the NH_2/5CC ratio was tuned from 0.5 to 0.65. While the functional groups are far to stoechiometry, such a ratio is theoretically enough to obtain a gelled network according to the Flory-Stockmayer theory (see development below). For both fillers, when working at a ratio close to 0.5, the formulations cured at 100 °C for 5 h (optimal curing time previously established[3]) provided foams of poor mechanical strength that deformed plastically when handled, with important error bars on the measured density (Figure S1). The foaming was way more reproducible for a NH_2/5CC ratio between 0.6 and 0.65, with densities around 250 kg.m^{-3} with keratin and 300 kg.m^{-3} for lignosulfonate. For higher ratios, the density drastically increased (e.g. with sodium lignosulfonate, ratio of 0.75 led to a density higher than 500 kg.m^{-3}). The optimized ratio was thus set to 0.6 for the study. Similar conclusions could be drawn from foaming at 90°C, although giving slightly denser samples.

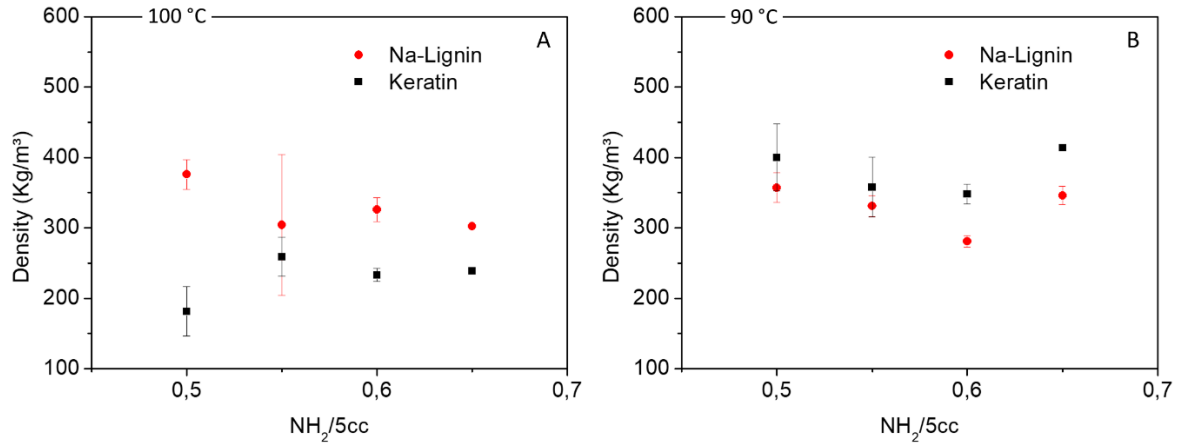
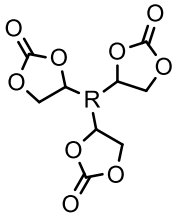
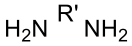


Figure S1. Densities of PHU foams prepared with varying NH_2/5CC ratios with 5 wt% keratin (*black squares*) and sodium lignosulfonate (*red circles*) at 100 °C (A) and 90 °C (B) for 5 h.

Definitions extracted from Flory and Stockmayer theory:

In a system, composed of a branching unit (i.e. monomer with more than 2 functionalities "A") and a difunctional monomer with 2 functionalities "B", present in a non-stoichiometric A to B ratio, A being used to define a cyclic carbonate moiety and B an amine moiety (system schematized below),





Stating that:

- The branching monomer has a functionality *f* equal to 3
- There is no difunctional monomer with functionalities A, then ρ the fraction of A groups in the branched unit on the total number of A groups is equal to 1

And given:

- r is the ratio of A to B groups
- α (P_A) is the branching probability presented as a function of P_A, the conversion in A groups, $\alpha(P_A) = \frac{r.P_A^2.\rho}{1-r.P_A^2(1-\rho)} = \frac{r.P_A^2}{1}$
- α_c is the critical branching probability, defined as the strictly minimal value of α for the gelation to occur, $\alpha_c = \frac{1}{f-1}$

We can obtain an expression of P_c, the conversion in A groups at the gel point (i.e. P_A when, $\alpha = \alpha_c$) as follow,

$$P_c = \frac{1}{\sqrt{r + r.\rho.(f-2)}} = \frac{1}{\sqrt{2r}}$$

Then, for our system where A and B groups are not present in a stoichiometric amount, we can provide the following tables of P_c for various values of r (directly linked to the $[NH_2]/[5cc]$ ratio X via the relation r=1/X) given α_c=0.5 . Values of r must remain <u>higher or equal to P_c</u>, as we cannot expect more 5CC group to be converted by aminolysis than the initial amount of amine functions provided to the system.

$[NH_2]/[5cc]$	**r**	**P_c**
0.5	2	0.5
0.55	1.82	0.524
0.6	1.67	0.548
0.65	1.54	0.57

Estimated theoretical conversion in cyclic carbonate (P_c) at the gel point for various starting NH_2/5CC ratios (i.e. r values).

We can then expect to obtain well-formed gels for conversion in cyclic carbonate functions by aminolysis higher than 50 to 60 % for ratios between 0.5 and 0.65, which is qualitatively observed by FTIR by comparison between the 5CC and the urethane C=O bands (see next section).

4. Study of the keratin-based foaming system

To evaluate the compatibility between the used keratin extract and our formulation (TMPC, *m*-XDA, DBU), the latter was mixed similarly to the foaming procedure, but kept at room temperature and analysed by SEM giving the following images.

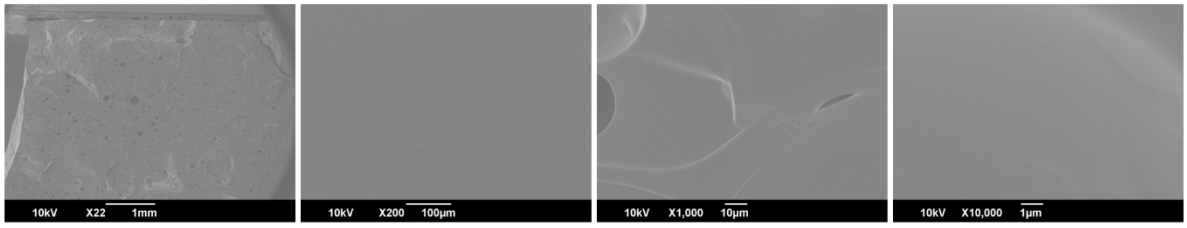


Figure S2. SEM micrographs of unfoamed formulation containing 10 wt% keratin after stirring and left at room temperature.

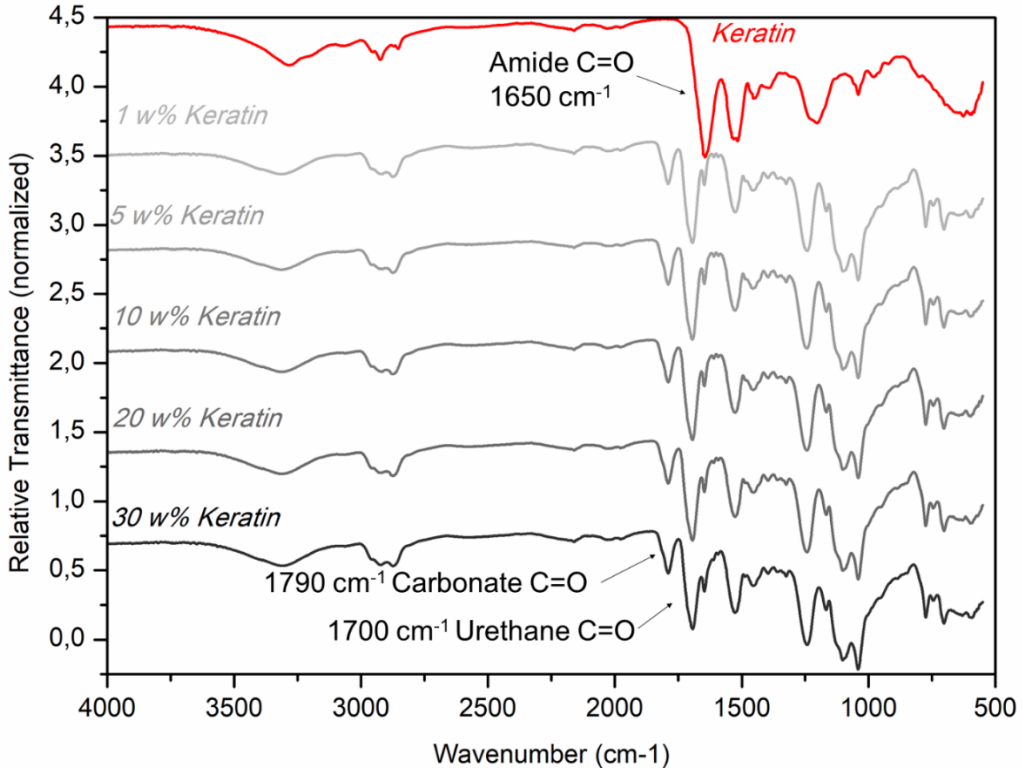


Figure S3. FTIR analysis of PHU foams produced with different contents of keratin. Conditions of foaming: NH_2/5CC = 0.6, 1 to 30 wt% keratin, 5 mol% DBU (by respect to 5CC moieties), 5 h, 100 °C.

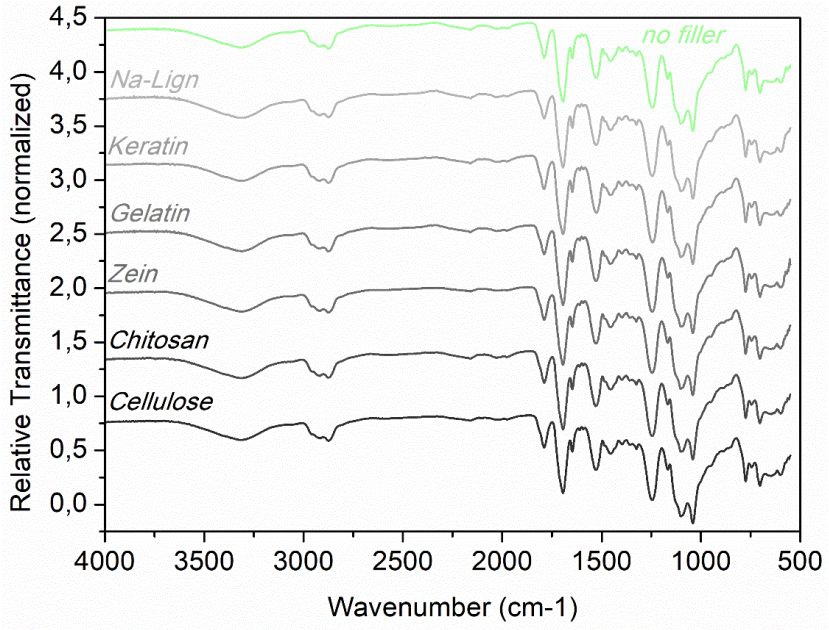


Figure S4. FTIR analysis of PHU without biofiller and PHU foams with 10 wt% of biofiller. Conditions of foaming: NH_2/5CC = 0.6, 10 wt% biofiller, 5 mol% DBU (by respect to 5CC moieties), 5 h, 100 °C.

5. Evaluation of the water content of the biofillers and assessment of the theoretical foam density based on this water content.

In this section, we evaluated the theoretical foam density of the various PHU foams based on the theoretical amount of CO_2 generated by hydrolysis of the cyclic carbonate groups. The content of water necessary for this hydrolysis was brought by the biofillers and determined by isothermal TGA (Figure S5). This theoretical foam density was also based on the assumption that all generated CO_2 was trapped within the PHU matrix, which could never be the case. As only part of generated CO_2 could in practice be trapped by the polymer matrix, this theoretical density represented the lowest value that could be obtained. The aim of this study was to compare this theoretical density to the experimental one. When the theoretical one was higher than the experimental one, this clearly indicated that the hydrolysis level was not high enough to generate the foams with the noted experimental density. As shown in Table S2, all foams containing 1 wt% biofillers presented a much lower experimental foam density than the theoretical one, indicating that another source of CO_2 should be responsible for the blowing.

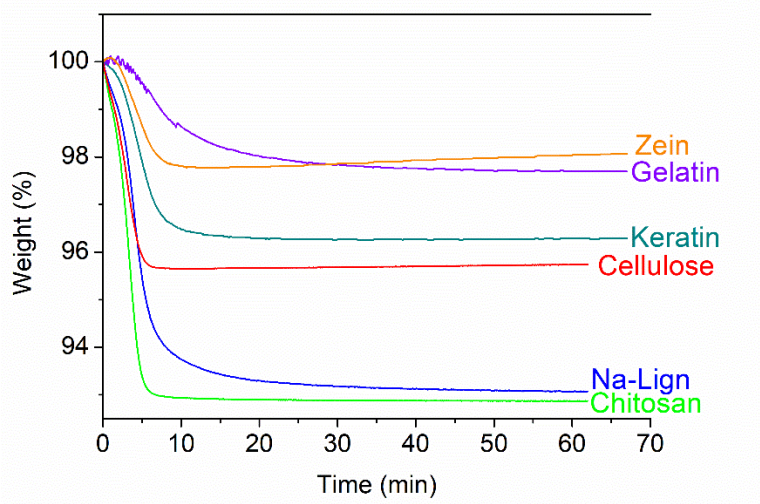


Figure S5. Isothermal TGA (100 °C, 1 h under N_2 flow) analysis of the various biofillers. Water content of the biofiller was obtained from the weight lost at the end of the analysis.

Table S2. Water content in the biofillers, CO_2 volume generated by hydrolysis, and theoretical and experimental foam density of the PHU foams.

Biofiller	Biofiller water content (wt%)[a]	Biofiller content (wt%)	Water equivalent (eq. *vs* 5CC)[b]	CO_2 volume (mL)[c]	Theoretical foam density ($kg.m^{-3}$)[d]	Exp. foam density ($kg.m^{-3}$)
Keratin	3.7	1	0.004	4.1	623	252+-19
		10	0.042	44.8	141	244+-12
Gelatin	2.3	1	0.002	2.5	727	264+-18
		10	0.026	27.9	210	258+-23
Zein	2.0	1	0.002	2.2	754	277+-24
		10	0.023	24.2	234	318+-10
Sodium lignosulfonate	7	1	0.007	7.7	466	239+-0.8
		10	0.011	84.8	80	319+-23
Cellulose	4.3	10	0.049	52.1	124	270+-16
Chitosan	7.1	10	0.081	86	79	276+-15

[a]Calculated by isothermal TGA (100 °C for 1 h). [b]Number of equivalent of water determined from biofiller estimated from isothermal TGA. [c]CO_2 volume determined from the water content obtained by isothermal TGA of the biofillers. [d]Theoretical foam density based on the theoretical amount of CO_2 generated by hydrolysis of the cyclic carbonate groups and assuming that all generated CO_2 was trapped within the PHU matrix.

To obtain the data in this table, the CO_2 volume and theoretical density was calculated based on the following formulation composition: 5 g (11.5 mmol) of TMPTC (i.e. 34.5 mmol of 5CC functions, assumed functionality of 3 cyclic carbonate functions per TMPTC molecule), 1.41 g (10.36 mmol) of m-

XDA (i.e. 20.7 mmol of NH_2 functions) and 0.26 g (1.7 mmol) of DBU loaded with 0.065 g (i.e. 1 wt%) or 0.71 g (i.e. 10 wt%) of biofiller.

The volume of CO_2 was assumed to be identical to the amount of water brought by the filler and that hydrolyzed the same amount of cyclic carbonate groups. It was obtained by applying the ideal gas law at atmospheric pressure (101300 Pa) and foaming temperature (100°C or 373 K).

The theoretical foam density was then obtained from the following formula:

$$Density_{th} = \frac{m_{formulation}}{V_{formulation} + V_{CO2}}$$

Where $m_{formulation}$ is the total mass of the formulation (comonomers, DBU and biofiller), $V_{formulation}$ is the volume of the formulation assuming a density of 1 and V_{CO2} is the volume of generated CO_2.

Karl-Fischer Titrations:

The water content was determined from duplicates in methanol for (i) sodium lignosulfonate (ARBON18) and (ii) the formulation that did not contain the diamine (to avoid crosslinking) (i.e. ARBON18 (10 wt%) + TMPTC + DBU following the procedure described below:

(i) 5 mL methanol + 100 mg sodium lignosulfonate

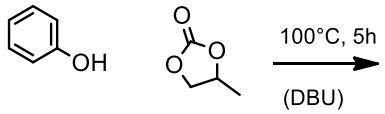
(ii) TMPTC (0.45 g, 5CC = 3.1 mmol), DBU (0.023 g, 1.51 mmol) and 0.053 g of lignosulfonate (10 wt.% of the total mass of the foam) were introduced in a small glass flask (SEC flask) and mechanically stirred at room temperature for 2 minutes to obtain a homogeneous viscous paste. Methanol was added (5 mL) and the mixture stirred until homogeneous. Then, 1 mL was picked out and titrated.

For (i), we obtained between 6 mg and 6.5 mg H_2O per 100 mg of lignosulfonate, which is close to the value obtained by TGA (7 %).
For (ii), a water content between 0.963 – 0.927 mg H_2O/100 mg of formulation was calculated, thus close to 2 wt% (i.e. 20% of hydrolyzed 5CC) of water in the formulation as determined by ^{1}H-NMR analysis (Figure 4, Table1 and connected text). We did not perform additional titrations by Karl-Fischer because the electrode was rapidly damaged with these formulations.

6. Model reactions between nucleophiles and propylene carbonate

In this section, we investigated possible reactions of specific chemical groups (phenol, alcohol, carboxylic acid, sulfonate) present in some biofillers with the cyclic carbonate groups to deliver CO_2 (the blowing agent) by methylene attack. For that purpose, dried model molecules (phenol, propionic acid, sodium 1-dodecanesulfonate, 1-butanol) were separately reacted with dried propylene carbonate (as model cyclic carbonate) in the presence of DBU under similar conditions than for the foaming (100 °C, 5 h), and ^{1}H-NMR was recorded before and after reaction to identify any addition product.

6.1. Reaction between phenol and propylene carbonate



Propylene carbonate (1 equivalent; 1 g, 9.7 mmol) and DBU (0.05 equivalent; 0.074 g, 0.49 mmol) (both dried on molecular sieves 3Å) were mixed with phenol (1 equivalent; 0.91 g, 9.7 mmol) in a Schlenk tube with a magnetic stirrer and placed in an oil bath at 100 °C for 5h. Before reaction and after 5 h, 1

drop of crude product was removed, diluted with 0.5 µL of DMSO-d_6 and analyzed by ^{1}H-NMR. The overlay is shown in Figure S6. No significant reaction was noted.

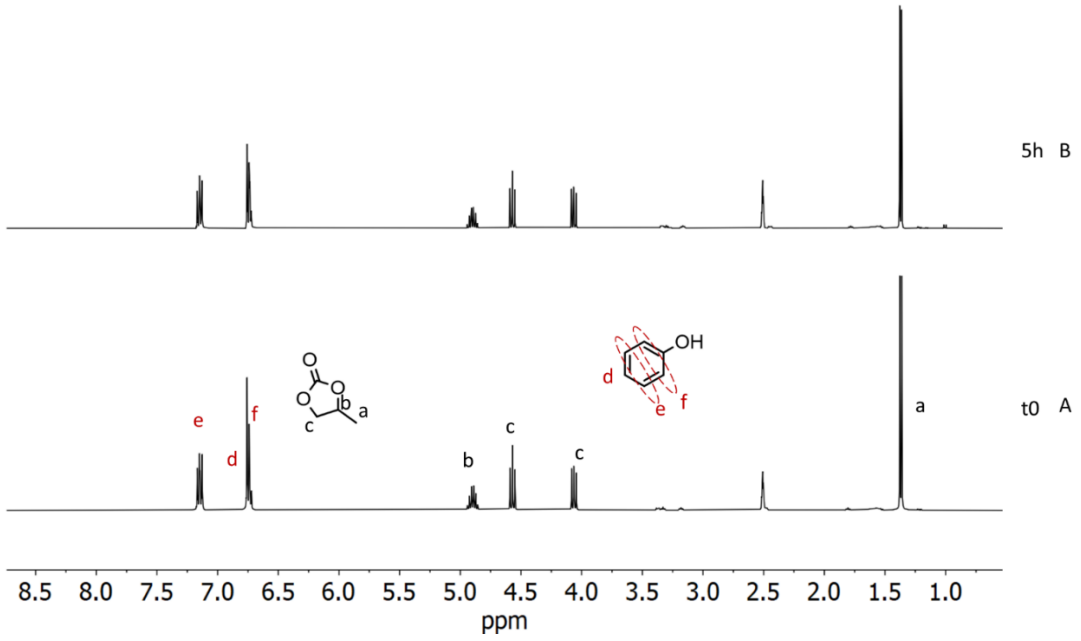
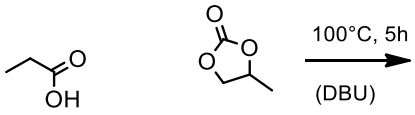


Figure S6. ^{1}H-NMR spectra for the reaction of propylene carbonate with phenol (A) before and (B) after 5 h at 100 °C.

6.2. Reaction between propionic acid and propylene carbonate



Propylene carbonate (1 equivalent; 1 g, 9.7 mmol) and DBU (0.05 equivalent; 0.074 g, 0.49 mmol) (both dried on molecular sieves 3Å) were mixed with 1-propionic acid (1 equivalent; 0.72 g, 9.7 mmol) in a Schlenk tube with a magnetic stirrer and placed in an oil bath at 100 °C for 5h. Before reaction and after 5h, 1 drop of crude product was removed, diluted with 0.5 µL of DMSO-d_6 and analyzed by ^{1}H-NMR. The overlay is shown in Figure S7. No significant reaction was noted.

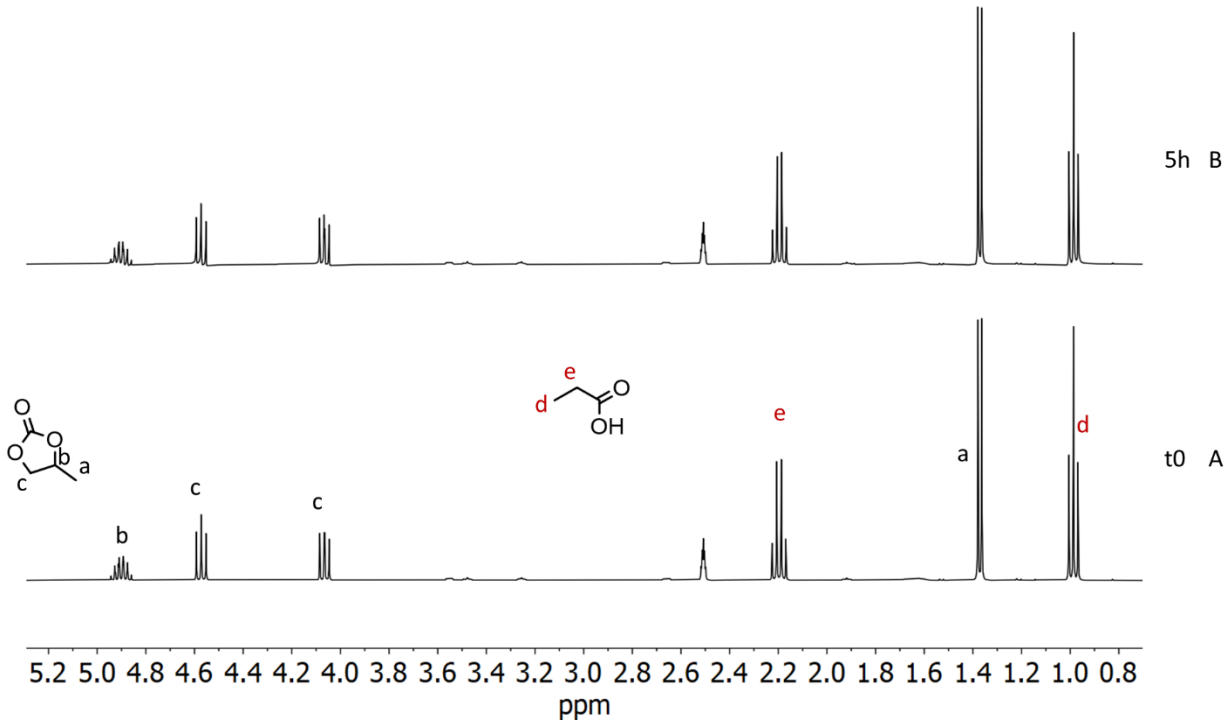
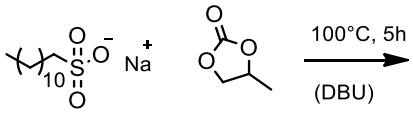


Figure S7. ^{1}H-NMR spectra for the reaction of propylene carbonate with 1-propionic acid (A) before and (B) after 5 h at 100 °C.

6.3. Reaction between sodium 1-dodecanesulfonate and propylene carbonate



Propylene carbonate (1 equivalent; 0.187 g, 1.835 mmol) and DBU (0.05 equivalent; 0.014 g, 0.092 mmol) (both dried on molecular sieves 3Å) were mixed with sodium 1-dodecanesulfonate (1 equivalent; 0.5 g, 1.835 mmol) in a Schlenk tube with a magnetic stirrer and placed in an oil bath at 100 °C for 5h. Deuterated DMSO (1 mL) was added to ensure good homogenization. Before reaction and after 5 h, 2 drops of crude product were removed, diluted with 0.5 µL of DMSO-d_6 and analyzed by ^{1}H-NMR. The overlay is shown in Figure S8. No significant reaction was noted.

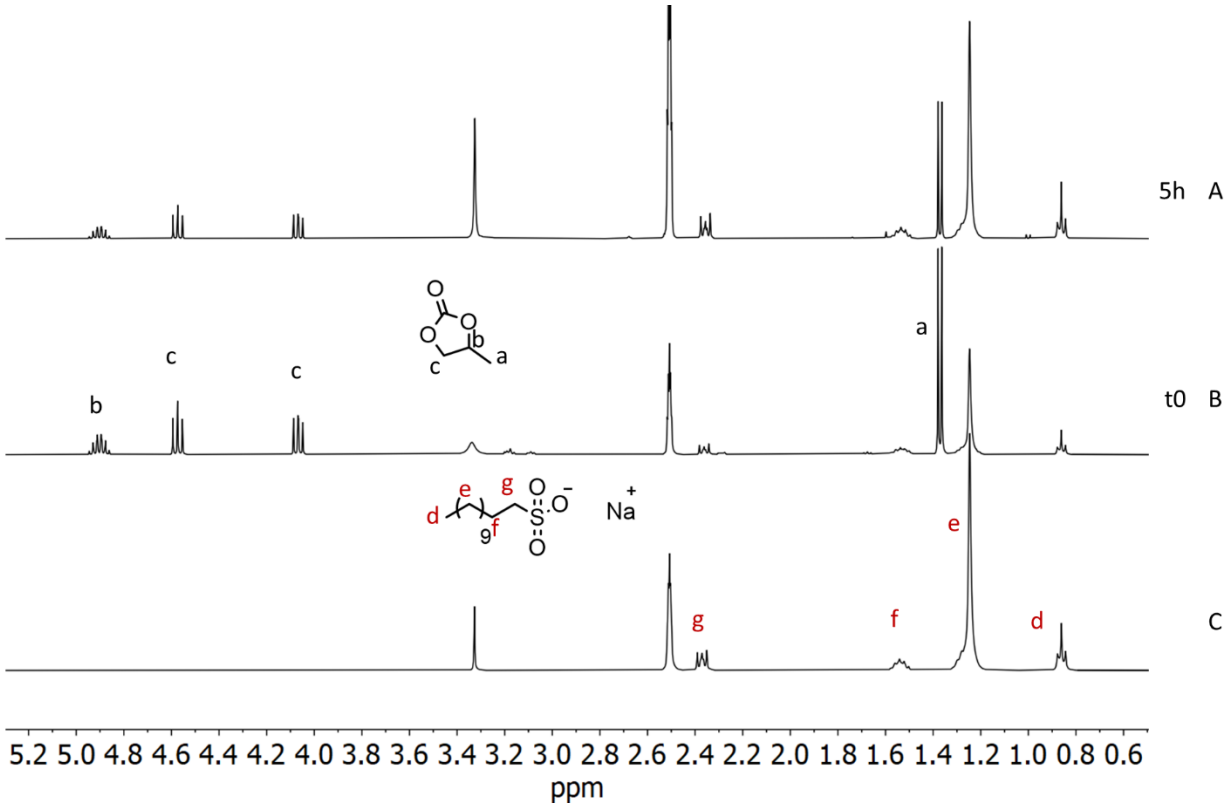
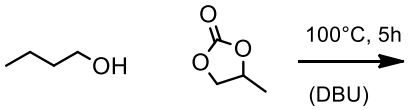


Figure S8. ^{1}H-NMR spectra for the reaction of propylene carbonate with sodium 1-dodecanesulfonate. (C) sodium 1-dodecanesulfonate, (B) reaction mixture prior and (A) after 5 h at 100 °C.

6.4. Reaction between 1-butanol and propylene carbonate



Propylene carbonate (1 equivalent; 1 g, 9.7 mmol) and DBU (0.05 equivalent; 0.074 g, 0.49 mmol) (both dried on molecular sieves 3Å) were mixed with 1-butanol (1 equivalent; 0.72 g, 9.7 mmol) in a Schlenk tube with a magnetic stirrer and placed in an oil bath at 100 °C for 5 h. Before reaction and after 5 h, 1 drop of crude product was removed, diluted with 0.5 µL of DMSO-d_6 and analyzed by ^{1}H-NMR. The overlay is shown in Figure S9. No significant reaction was noted.

After 5 h of reaction, despite low conversion of the propylene carbonate (PC), we observed the appearance of a doublet at 1 ppm, typical of propylene glycol. With respect to the methyl group of butanol and butylcarbonate used as references (0.87ppm), a yield of around 25% was measured for propylene glycol. The only known pathways leading to the formation of this product are either (a) the propylene carbonate hydrolysis, or (b) the 2 steps alcoholysis of propylene carbonate. It is worth mentioning that another decarboxylation reaction might occur from PC alcoholysis by methylene attack. However, we could not highlight the ether product in our analyses.

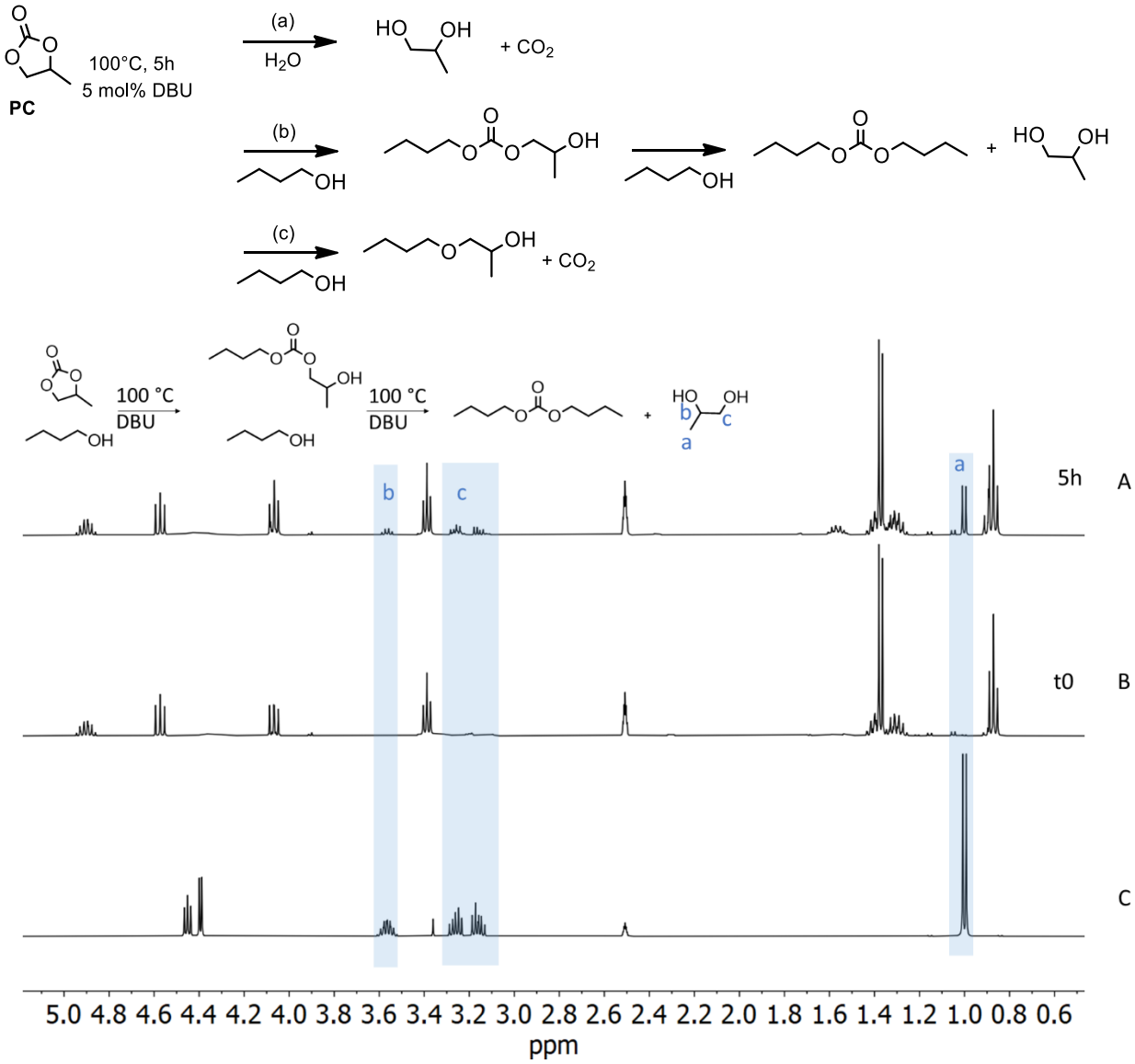


Figure S9. ^{1}H-NMR spectra for the reaction of propylene carbonate with 1-butanol in presence of DBU (B) before and (A) after 5 h at 100 °C. Propylene glycol is formed as attested by the spectrum of the pure compound (C).

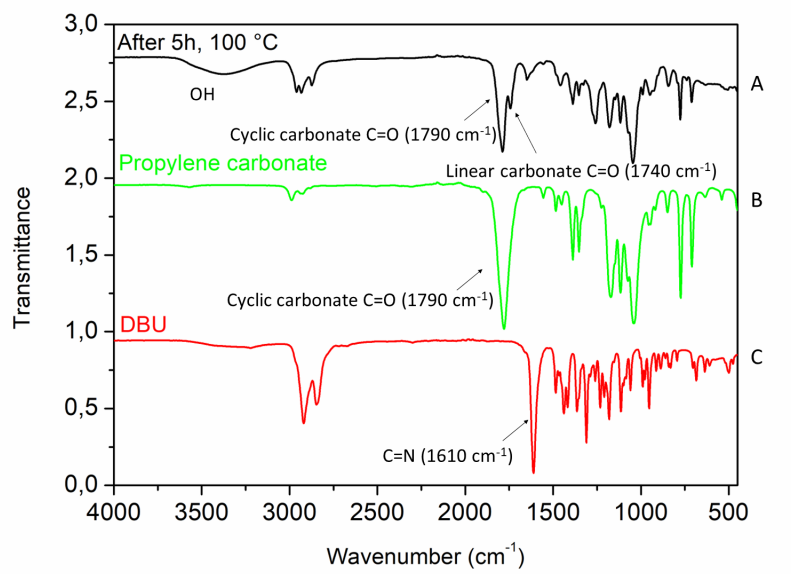


Figure S10. ATR-FTIR spectrum of the mixture between 1-butanol, propylene carbonate and DBU after 5 h at 100 °C (A). Propylene carbonate (B) and DBU (C) spectra for comparison.

Performing the experiment under drier conditions (i.e. also drying butanol on molecular sieves like the other reactants, flame and vacuum drying the Schlenk tube before weighting the reactant directly inside through a septum and ensuring a constant argon flow during the whole reaction time) did not lead to different results. Moreover, an infrared analysis performed on the crude highlighted the presence of a linear carbonate product as confirmed by a signal at 1740 cm^{-1} corresponding to the C=O stretching band.[4]

It is worth mentioning that the signal typical of the linear carbonate product has not been observed in any of the spectra recorded on the foam formulations.

Additional NMR experiments were performed, including ^{13}C-NMR of the reactants and the reactive mixture. The additional peaks were identified as belonging to the linear carbonate product. It also

confirmed the presence of propylene glycol. The fully interpreted HSQC experiment is also provided and no additional product could be identified in this experiment.

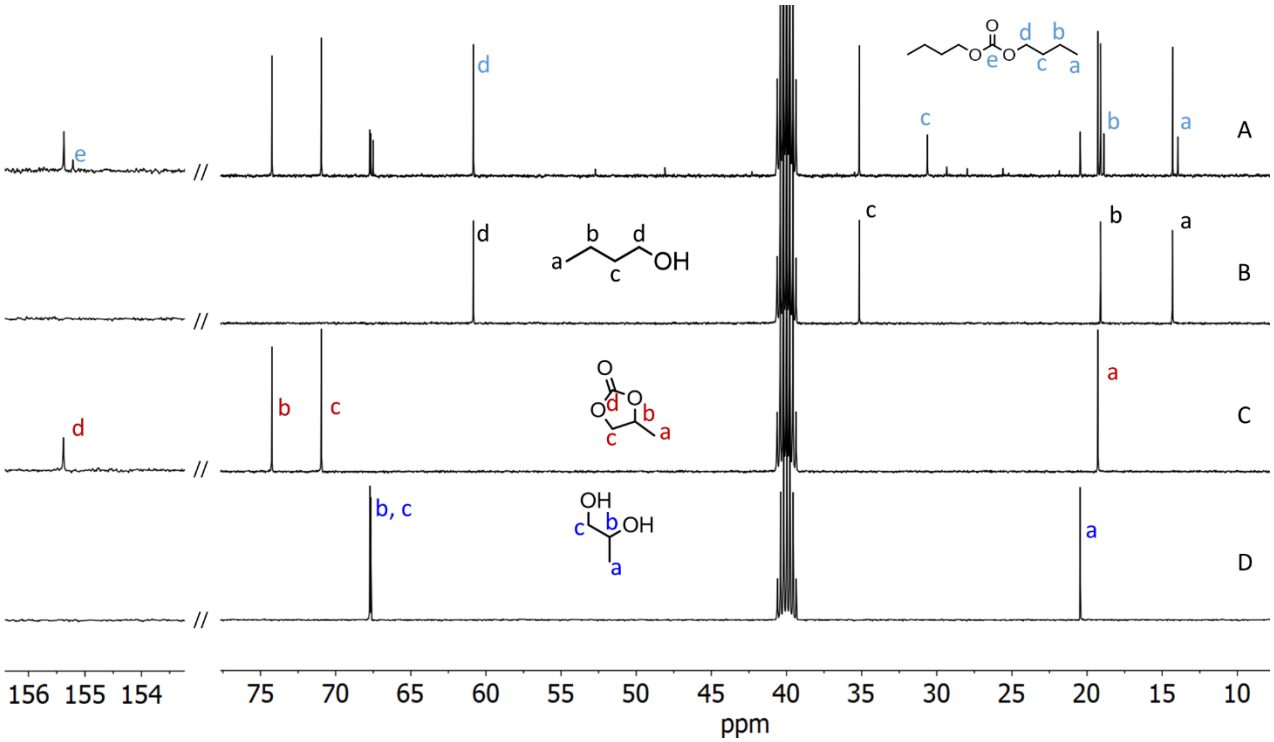


Figure S11. ^{13}C-NMR spectra for the reaction of propylene carbonate with 1-butanol (A) after 5 h at 100 °C, and (B) of pure 1-butanol, (C) propylene carbonate and (D) propylene glycol.

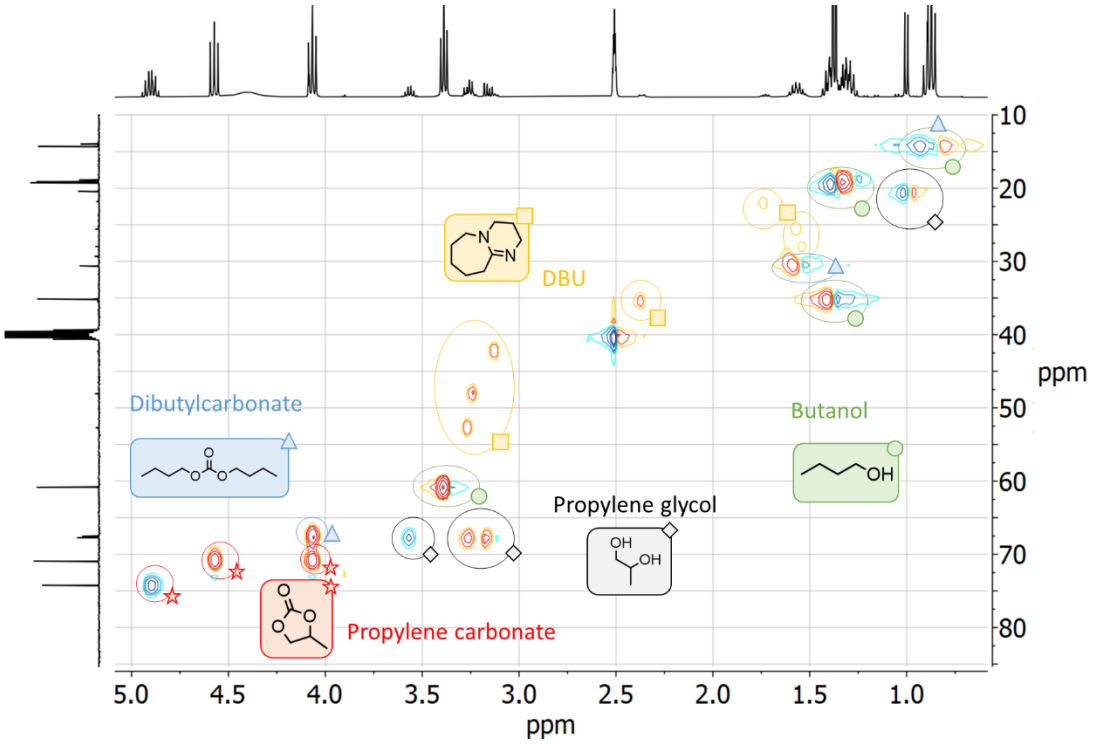


Figure S12. HSQC spectrum for the reaction of propylene carbonate with 1-butanol after 5 h at 100 °C.

In conclusion, most of the investigated reactive groups (phenol, lignosulfonate) do not exhibit significant reactivity towards cyclic carbonate to deliver CO_2.
In the particular case of 1-butanol, we could highlight a noticeable reaction with cyclic carbonate leading to the release of propylene glycol beside a bis-butylcarbonate as the main product. However, in the case of the foam formulations containing a reactive diamine, the higher reactivity of the amino function is expected to make the aminolysis strongly favored compared to the reported alcoholysis. This is confirmed by the absence of any linear carbonate signal in the infrared spectra of the prepared foams using any of the investigated fillers (Figures S3, S4). Moreover, most hydroxyl groups that can be present or appear during the course of the foaming (i.e. from the biofillers, hydroxyurethane pending OH's, pending diols resulting from the hydrolysis of TMPTC) would likely not be as sterically available as the small molecules we used in this section, again supporting the idea that alcoholysis is not playing a significant role in the generation of the blowing agent in our process.

7. TMPTC hydrolysis experiments

In a representative experiment, TMPTC (0.45 g, 5CC = 3.1 mmol), DBU (0.023 g, 1.51 mmol) and 0.053 g of sodium lignosulfonate (10 wt.% of the total mass of the foam) were introduced in a small glass flask (SEC flask) and mechanically stirred at room temperature for 2 minutes to obtain a homogeneous viscous paste. The formulation was placed in an oven at 100 °C. After 5 minutes at 100 °C, additional manual mixing of the formulation was realized to guarantee the perfect homogenization of the mixture. The sample was then left to react at 100 °C for 5 h, and then cooled at room temperature. Bubbles are observed during the experiment except when no biofiller was added. ^{1}H-NMR spectra obtained after the reaction are shown in Figure 3 and compared to the ^{1}H-NMR spectrum of TMPTC.

The hydrolysis of TMPTC was estimated as follow:

$$Hydrolyzed\ TMPTC\ (\%) = \left(1 - \frac{\left(\frac{\int b_{mixture}}{\int a_{mixture}} \times nH_b\right)}{\left(\frac{\int b_{TMPTC}}{\int a_{TMPTC}} \times nH_a\right)}\right) \times 100 = \left(1 - \frac{\left(\frac{\int b_{mixture}}{\int a_{mixture}}\right)}{\left(\frac{\int b_{TMPTC}}{\int a_{TMPTC}}\right)}\right) \times 100$$

Where $a_{mixture}$ and $b_{mixture}$ are the signals corresponding to the signal associated to the CH_3 group of both the TMPTC and its hydrolyzed product at 0.8 ppm, and the CH group of the cyclic carbonate groups of TMPTC at 4.9 ppm, respectively, in the mixture reacted for 5 h at 100°C. The number of H protons corresponding to each signal are noted nH_a and nH_b. a_{TMPTC} and b_{TMPTC} are the corresponding signals on the TMPTC analysed alone (bottom spectrum on Figure 3). Hydrolysis levels are summarized in Table 1.

Alternatively, assuming the normalization has been performed on the integral of the signal at 0.8 ppm on all spectra, the following formula can also be used and provide the same result:

$$Hydrolyzed\ TMPTC\ (\%) = \frac{\int b_{TMPTC} - \int b_{mixture}}{\int b_{TMPTC}} \times 100$$

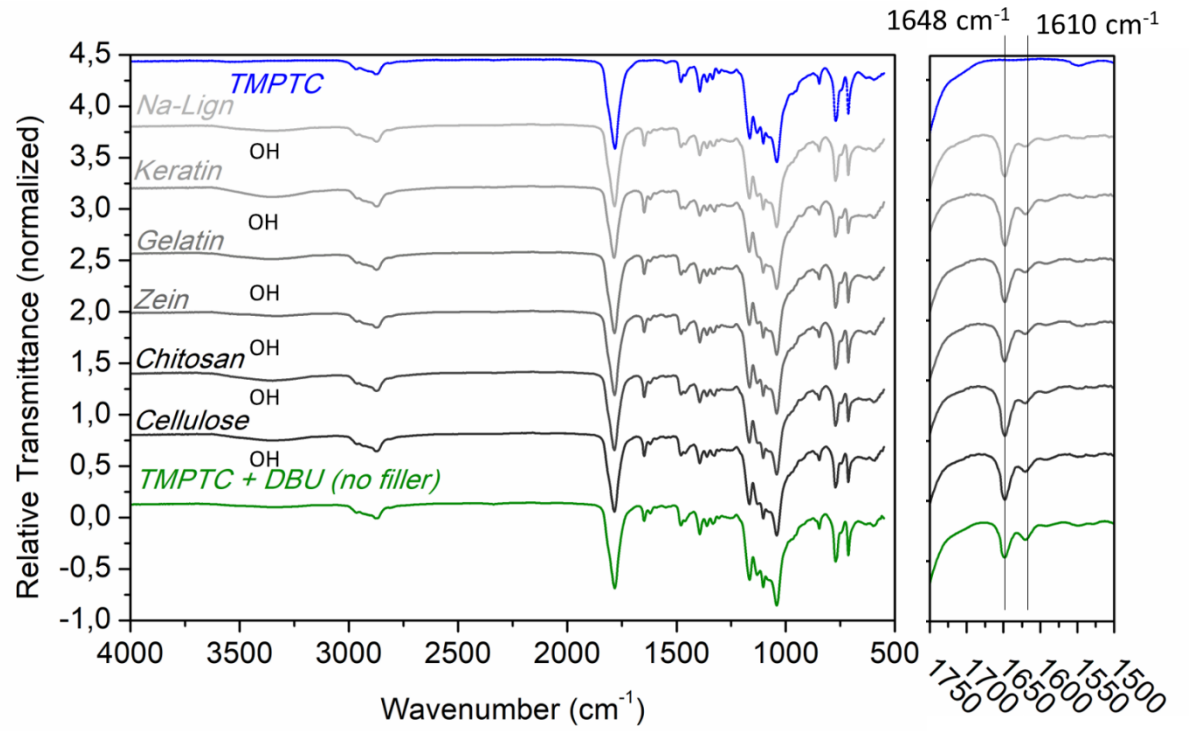


Figure S13. FTIR spectra of TMPTC (blue), the media resulting from the reaction of TMPTC with the biofillers (10 wt%) in the presence of DBU after 5 h at 100 °C (grey scale), and the media resulting from the reaction of TMPTC in the presence of DBU without biofiller (green). The right part of the figure is a zoom on the C=N stretching modes at 1610 cm^{-1} of DBU and at 1648 cm^{-1} for the $DBUH^+/HCO_3^-$ adduct.

8. SEM characterization of the foams pore-size distributions

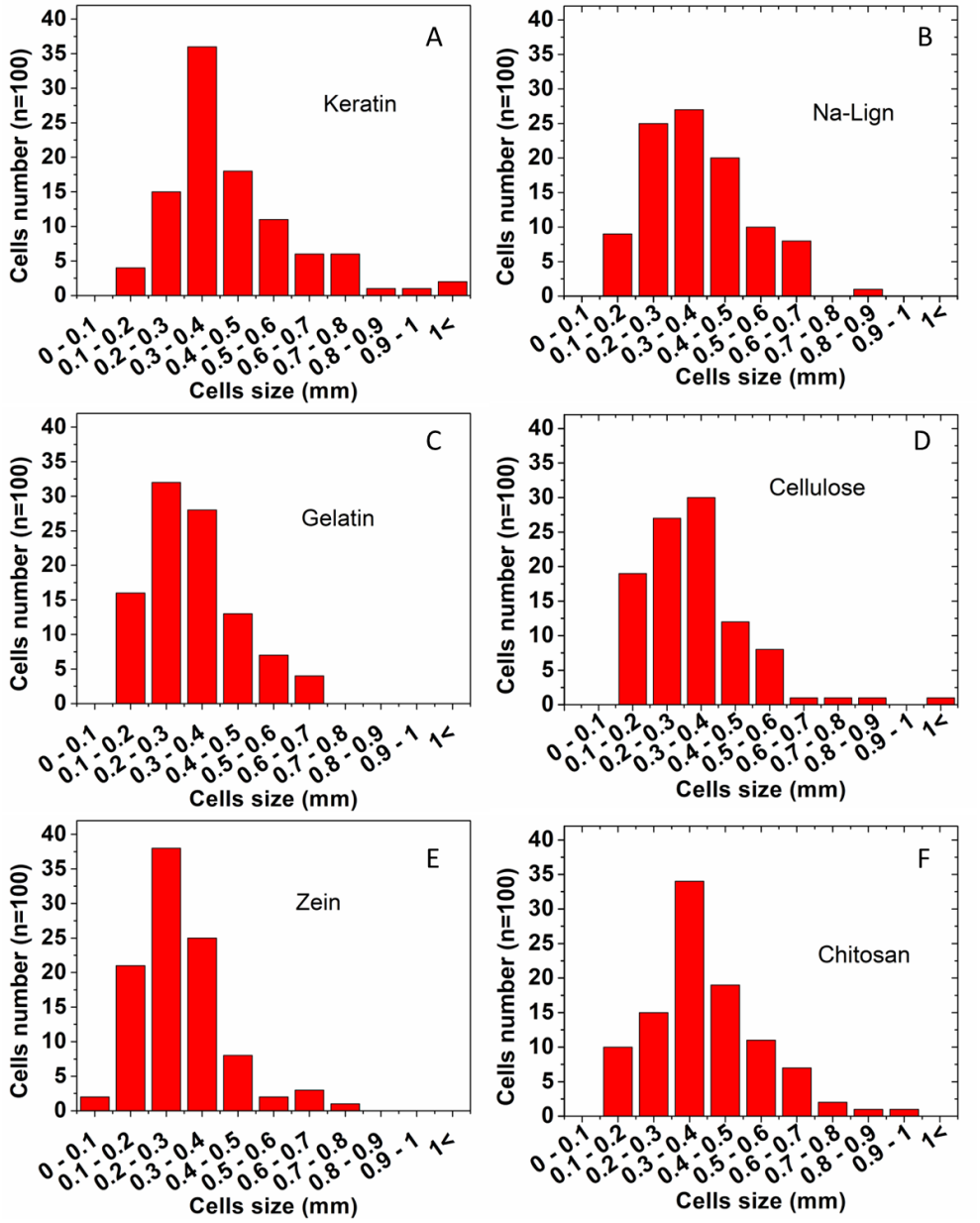


Figure S14. Pore-size distributions of the foams prepared with 10 wt% of the various fillers. (A) Keratin, (B) Na-Lign, (C) gelatin, (D) cellulose, (E) zein, (F) chitosan.

9. Thermo-mechanical properties of the foams.

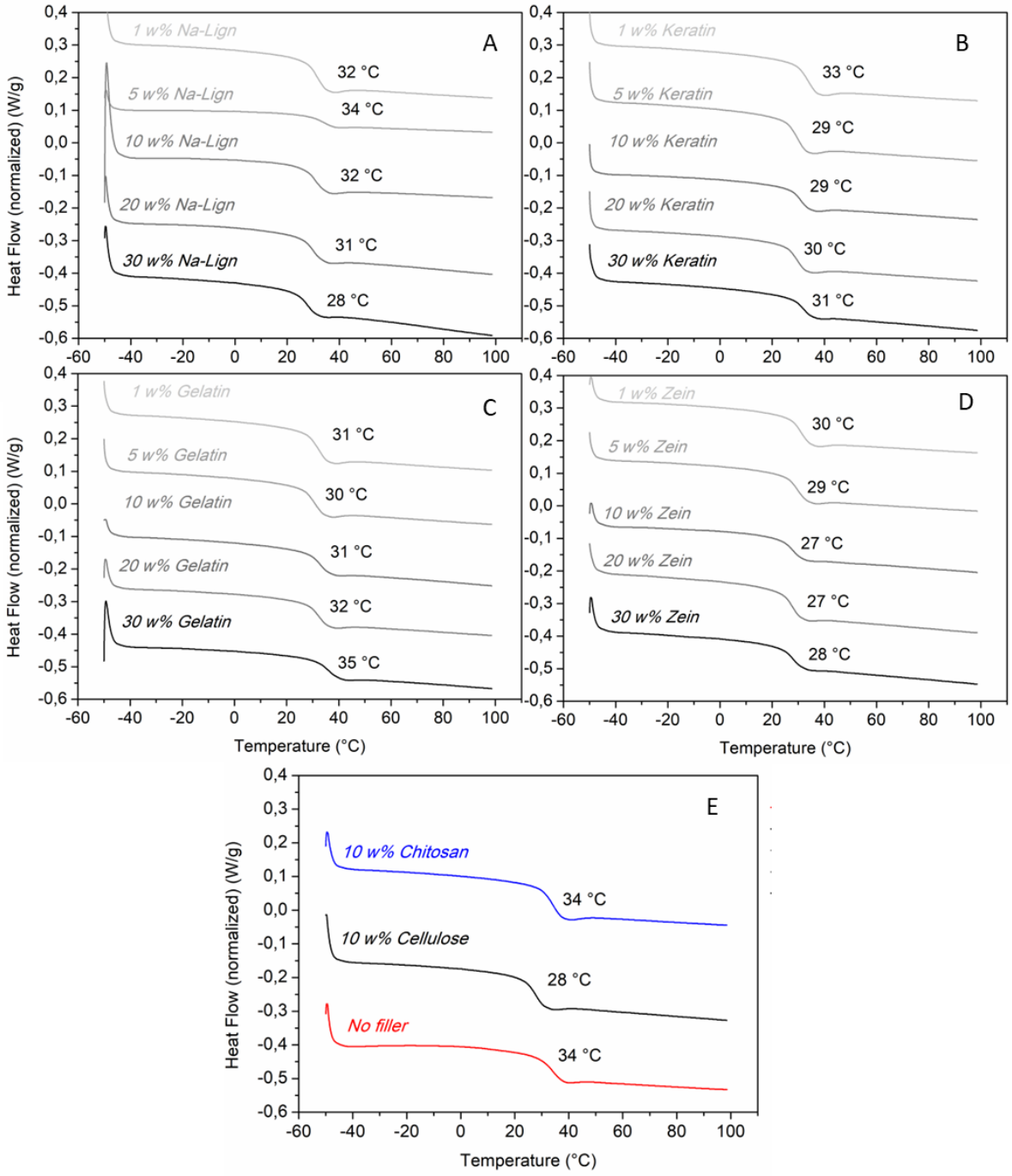


Figure S15. 2nd DSC heating cycles of foams prepared with the various biofillers at 10 wt% loading: Na-Lign (A), keratin (B), gelatin (C), zein (D), chitosan, cellulose and without filler (E). Biofillers dried at 50 °C under vacuum for 24 h prior DSC analysis.

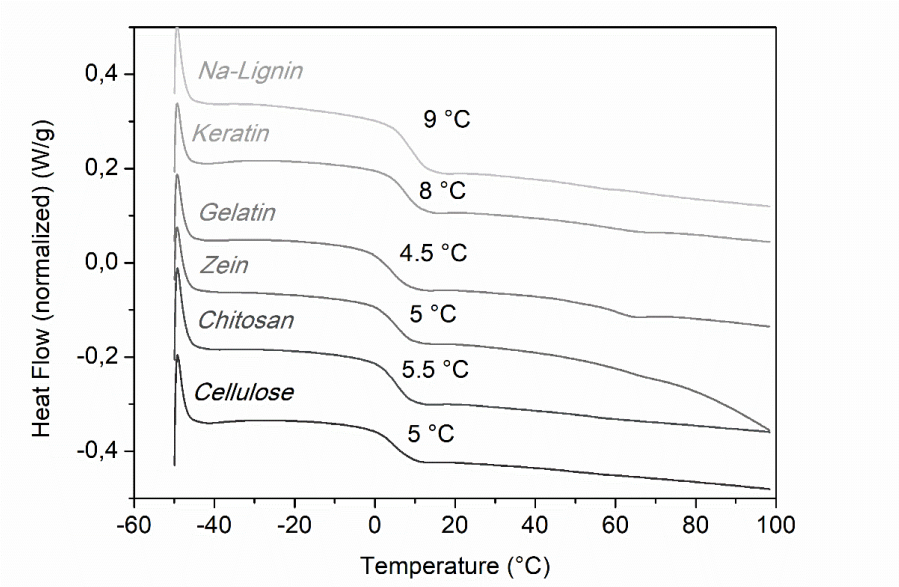


Figure S16. 1st DSC heating cycles of foams prepared with various fillers at 10 wt% content: Na-Lign, keratin, gelatin, zein, chitosan and cellulose, preliminarily conditioned under ambient atmosphere.

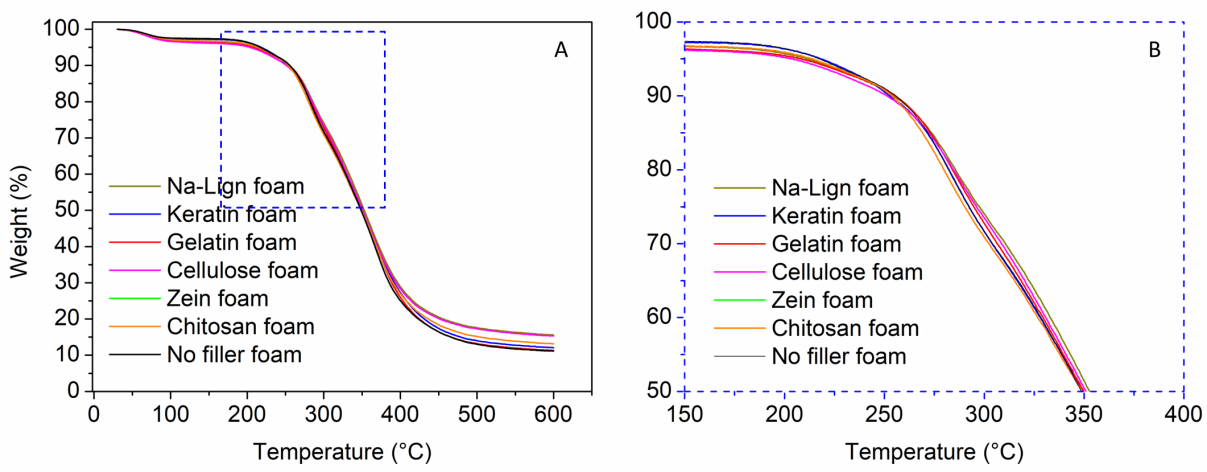


Figure S17. TGA curves of the foams with 10 wt% of the various fillers. The right graph is a zoom on the part of the curve used to estimate $T_{d5\%}$ (i.e. from the water evaporation plateau around 160 °C).

10. Aging study of PHU foams

Studied foam samples were prepared according to the previously described procedure. The samples (in triplicates) were placed in a climatic chamber for 1 week at 25 °C and 80 % relative humidity (RH), and the sample weight and their glass transition temperatures were monitored over time after 1, 4, 8, 24 h and 1 week. Moisture uptake and T_g values are depicted in Figure 6.

11. Characterization of reprocessed PHU foams

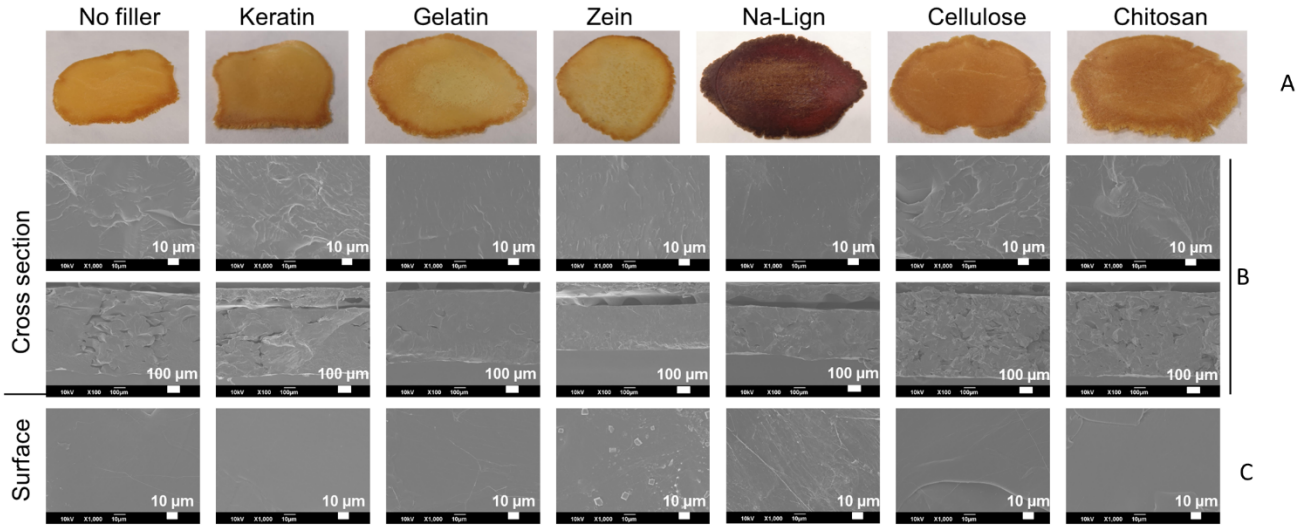


Figure S18. (A) Photography, SEM of the (B) cross section and (C) surface of the PHU films obtained by reprocessing the foams containing 10 wt % of the biofillers. SEM micrographs show the homogeneous and pore-free structure of the obtained films.

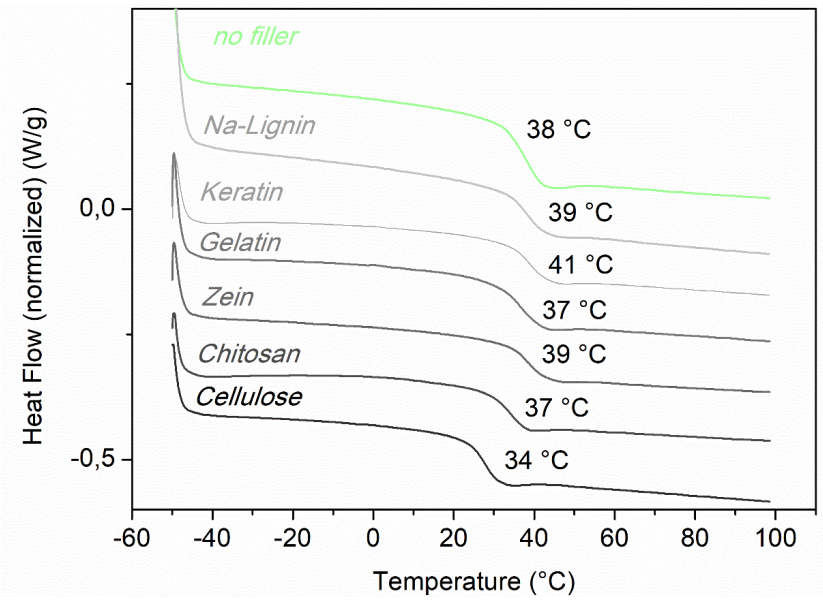


Figure S19. 2nd DSC heating cycles of films resulting from reprocessing (160 °C, 1 h, 1T) of the foam formulations containing 10 wt% of biofiller. Samples were first dried at 50 °C under vacuum for 24h before analysis.

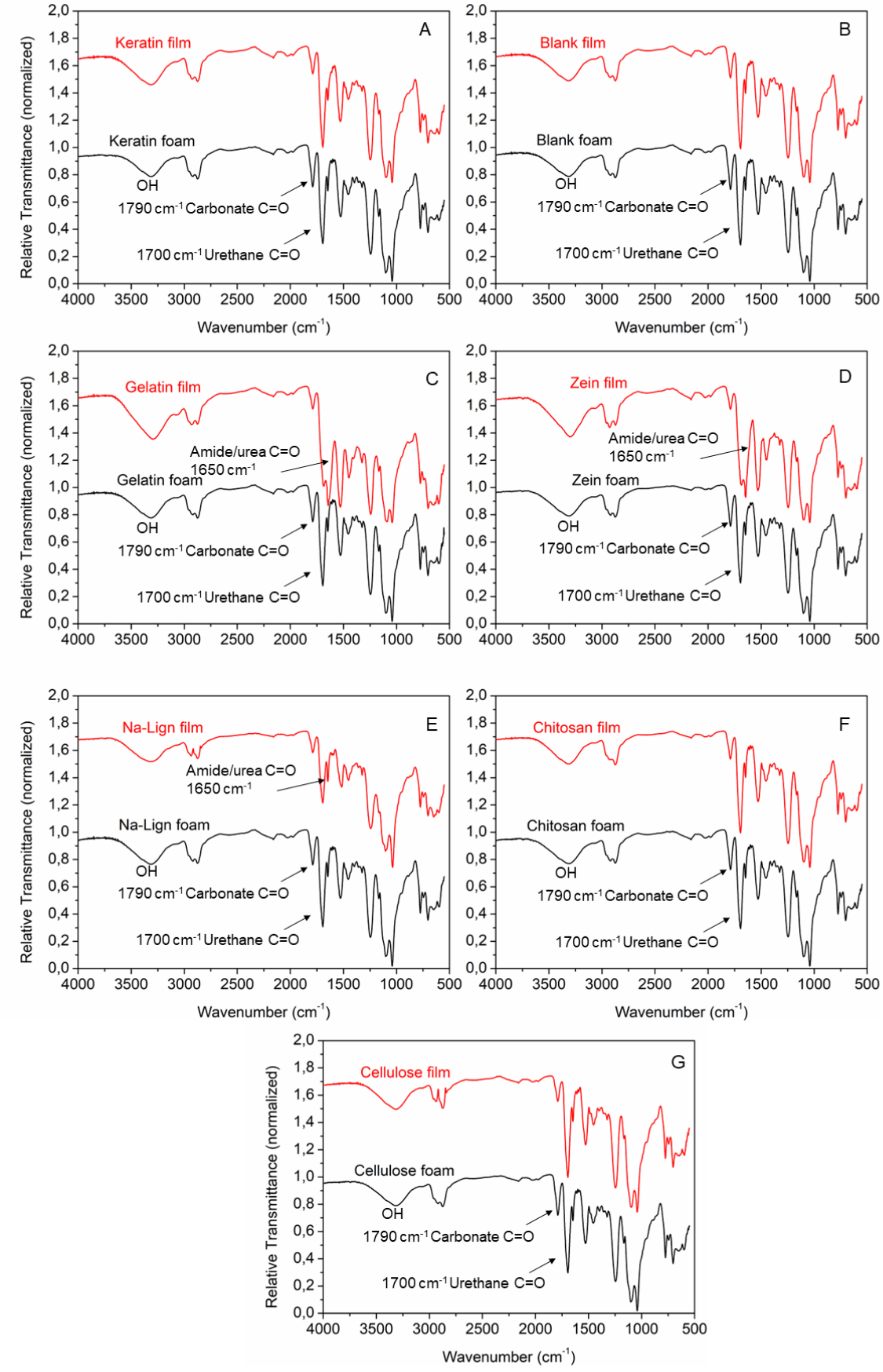


Figure S20. IR spectra of the PHUs foams with the different biofillers (10 wt%) (black) and their reprocessed films (red).

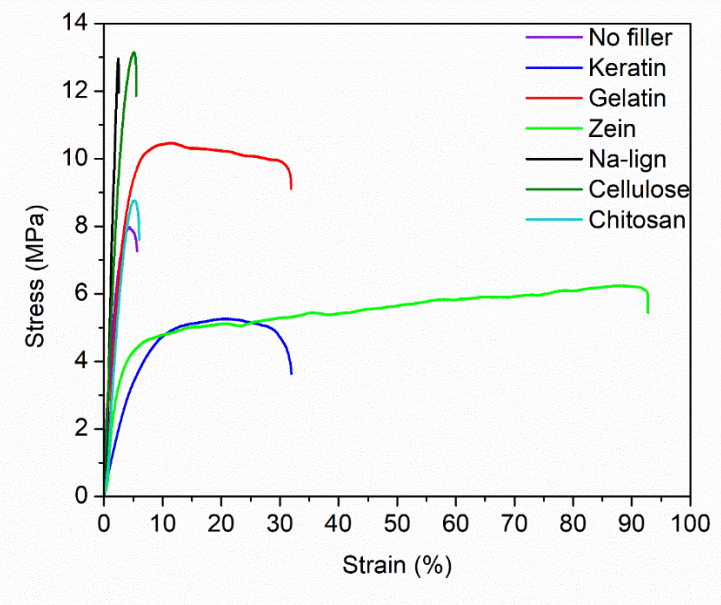


Figure S21. Representative stress-strain curves resulting from the tensile testing of PHU films obtained by reprocessing the PHU foams loaded by 10 wt% of biofillers.

12. Benchmarking of PHU foams and selected conventional polyurethane foams containing biofillers.

Table S3. Comparison of PHU foams produced by the water-induced self-blowing process with and without biofillers, and selected conventional polyurethane foams containing biofillers.

Type of foam	Conditions	Density ($kg.m^{-3}$)	Reference
NIPUF-Blank[a]	m-XDA/TMPTC (NH_2/5CC=0.6) 5 mol% DBU 5h, 100 °C	477±44	This work
NIPUF-10 wt% biofiller	m-XDA/TMPTC (NH_2/5CC=0.6) 5 mol% DBU 5h, 100 °C 10 wt% biofiller	146 to 370	This work
NIPUF-Water foaming	m-XDA/TMPTC (NH_2/5CC=0.6) 5 mol% DBU 5h, 100 °C H_2O/5CC=0.25	120±5	This work*
NIPUF-Water foaming	m-XDA/TMPTC (NH_2/5cc=0.75) 5 mol% DBU 3h, 100 °C H_2O/5CC=0.25	153±5	3

PUF benchmark-water foaming	PMDI/PEPO[b] Amine catalyst Surfactant H_2O=0 to 3 phr[c]	40 to 120	5, 6
PUF benchmark-water foaming 10 wt% lignin	PMDI/PEG-PPGtriol-glycerol DABCO catalyst Surfactant 10wt% lignin	87.1	7, 6
PUF benchmark-water foaming 1.5 wt% CF[d]	PMDI/Polyester polyol Catalyst Flame retardant SBO-PO[e] 1.5 wt% CF	35±3	8
PUF benchmark-water foaming Microcrystalline cellulose	MDI/Polyether polyol Surfactant Catalyst 120min, 80°C 1 wt% cellulose	62 to 72	9

Comparison of various types of PU and NIPU (PUF/NIPUF) foams. All NIPU foams were prepared with MXDA as diamine hardener.

[a] NIPU foam prepared without extra water or biofiller addition. [b] Polymeric methane diphenyl diisocyanate (PMDI)-polyether polyol. [c] Parts per hundred of polyols by weight. [d] Keratin-rich chicken feathers. [e] Soybean-oil based polyol. *Prepared solely for comparative purposes.

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