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# Upcycling biobased polyurethane foams into thermosets: toward the closing of the loop

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## Abstract

With the growing environmental concerns that society is nowadays facing, the development of biobased materials intensified and biobased polyisocyanates have emerged in the market. Their commercialization enabled to synthesize the first four biobased polyurethanes foams (PUFs) from biobased isocyanates, containing up to 93 % of renewable carbons. Their mechanical and thermomechanical properties were compared. In particular, one of the four PUF formulations was very promising: it foamed at room temperature and produced a low density foam  $78 \text{ kg/m}^3$  comparable to conventional fossil-based PUFs. To consider the full life cycle of such materials, these PUFs were upcycled and reshaped to bulk PUs by transcarbamoylation reaction up to 5 cycles. Moreover, a unique material (mixPU) composed of the four PUFs was prepared and reshaped, by compression molding at  $160 \text{ }^\circ\text{C}$  for 30 min, thus demonstrating the potential of this recycling pathway for PUFs from different origins. Finally, stress-relaxation experiments were carried out to evaluate the dynamic properties of the mixPU material which was shown to behave as a CAN.

## Keywords

Polyurethane foams; biobased polymers; covalent adaptable network; reshaping; transcarbamoylation; upcycling, recycling

## Introduction

The development of renewable materials is a current major concern to reduce the impact of human activities on the environment and on the climate, and to ensure sustainable consumption and production.<sup>1</sup> In 2019, 368 million tons of plastics were produced in the world representing 10 % of the global fossil feedstocks and only less than 1 % were biobased.<sup>2,3</sup> Regardless of the feedstock, this production translates directly into plastic wastes that need to be recycled. Nevertheless, infrastructures are still not able to manage this massive inflow, and 79 % of plastic wastes end up in landfills or are discarded in natural environments in which they affect ecosystems for hundreds to thousands of years.<sup>4,5</sup> Henceforth, it is crucial that plastic production, which is constantly growing, become a sustainable and circular framework.<sup>6,7</sup>

To initiate this transition, the production of biobased monomers has been widely developed to achieve sustainable polymers such as polyamides, polyurethanes, epoxy-resins and polyesters.<sup>8-12</sup> Polyurethanes (PUs), produced *via* step growth polymerization of polyisocyanates and polyols, are the 6<sup>th</sup> most produced polymer in the world with almost 20 Mt per year and their demand is constantly growing due to their excellent properties and their high versatility. They are present in a wide range of applications such as coatings, elastomers and sealants for example, but two third of their production is devoted to foams.<sup>13-18</sup> PU foam (PUF) production represents around 12 Mt per year, mostly from fossil-based resources and leads to accumulation of foam wastes.

Many biobased polyols derived from vegetables oils, carbohydrates, proteins or lignin are nowadays available in the market.<sup>14,19-23</sup> Partially biobased PUs are produced from such biobased polyols and fossil-based polyisocyanates.<sup>24</sup> In the same way as biobased PUs, biobased PUFs reported so far are only partially biobased and often prepared using fossil-based polymeric 4,4'-methylene bis(phenyl isocyanate) (pMDI).<sup>25</sup> The reaction of isocyanates and water that releases CO<sub>2</sub> provides a good foaming strategy, even if many other blowing agents are commercialized too.<sup>26</sup> A wide variety of biobased polyols were used to synthesize rigid foams, for example, crude glycerol, obtained as a byproduct in the production of biodiesel, and raw citric acid fermentation waste.<sup>27,28</sup> Sorbitol-based polyols also allowed the elaboration of PUFs with anisotropic behavior.<sup>29</sup> Biobased PUFs were also synthesized with new polyol architectures obtained from microalgae oil.<sup>30</sup>

In order to achieve more sustainable PUs, non-isocyanates PUs (NIPUs) synthesized through the aminolysis of cyclic carbonates are still in development.<sup>31-34</sup> A few NIPUs foams (NIPUFs) have been

described but their synthesis is not as optimal as PUs foams (PUF) because of the lower reactivity of cyclic carbonates making difficult to synchronize both, blowing and crosslinking reactions.<sup>35–38</sup> Our team was the first to describe NIPUFs using the H<sub>2</sub> released by the reaction of amines with poly(methylhydroxysiloxane) as a blowing agent.<sup>39</sup> Lately, Monie *et al.* described the first self-blowing NIPUFs by controlling the chemo- and regioselectivity of the nucleophilic additions of thiols to cyclic carbonates that allowed the release of CO<sub>2</sub>.<sup>40</sup> However, the foaming reaction and the lower reactivity of the cyclic carbonate-amine reaction required heat.

Recently, a few biobased polyisocyanates have emerged in the market, leading our team to report the first highly biobased PUs (until 95% renewable carbon).<sup>41</sup> These biobased polyisocyanates are less reactive than aromatic isocyanates such as the widely used pMDI. Therefore, specific formulations are needed to reach the fast reaction rates required for the production of highly biobased PUFs.

Recycling PUF is thus a major challenge. Hence, we propose in the present study a recycling process that can be applied to commercial PU foams in order to give them new life in new applications and reduce environmental impacts. The present approach is based on biosourced polyurethanes from biosourced isocyanates with reduced toxicological profiles. Hence, it proposes a more sustainable approach to PUF recycling which has recently been extended to NIPU foams.<sup>42</sup>

The development of new biobased monomers and polymer materials is an essential pathway to increase the sustainability of plastic industries. However, not only the first synthesis step needs to be improved, but the whole life cycle of polymers and especially their end-of-life have also to be considered. Therefore, the degradability of PUs and PUFs by enzymatic degradation was studied.<sup>43–45</sup> Besides, increased attention is currently drawn to the recyclability of thermosets, especially since the discovery of vitrimers in 2011.<sup>46</sup>

As early as 1956, Offenbach and Tobolsky reported polyurethane elastomers able to relax mechanical stresses, and attributed this behavior to a chemical exchange of the urea and urethane bonds.<sup>47</sup> Much later, in 2015, Fortman *et al.* took advantage of this feature to design a PHU vitrimer, namely a thermosetting 3D structure endowed with exchangeable covalent bonds. The dynamic nature of the hydroxyurethane bonds able to exchange by transcarbamoylation enabled the material to be reshaped upon heating.<sup>48</sup> Such behavior was also observed in PUs when dibutyltindilaurate (DBTDL) was added as a transcarbamoylation catalyst,<sup>49,50</sup> or even without a catalyst provided that an aromatic isocyanate was used.<sup>51</sup> Urea bonds were proved to exchange more readily and to ease the reprocessing of such materials.<sup>52</sup> Sheppard *et al.* recently managed to recycle used PUFs by twin-screw extrusion of postconsumer foams with DBTDL to incorporate the transcarbamoylation catalyst in the finished material.<sup>53</sup> These recent discoveries, along with the pursuit of a greener and more

circular consumption model, triggered the idea to prepare highly biobased PUFs that could be recycled after the foam end-of-life.

In this study, PUFs from biobased polyols and polyisocyanates have been synthesized. To the best of our knowledge, they are the first highly biobased PUFs reported so far from biobased isocyanates. Pripol® 2033, a diol obtained via the dimerization of fatty acids was used in combination with diglycerol as crosslinker. Those polyols were formulated with two different biobased diisocyanates, Tolonate™ X FLO 100 and the L-Lysine ethyl ester diisocyanate (LDI) derived from the corresponding amino acid. Four biobased PUFs were prepared by varying the nature of the diisocyanate used and the molar ratio of the two polyols. Thermomechanical and physical properties of the PUFs were studied by DSC, TGA and DMA. The use of dibutyltin dilaurate (DBTDL) as catalyst allowed on one hand the foaming process at room temperature and on the other hand the recycling PUFs and PUFs mixtures by compression molding.

## Materials & Methods

### Materials

L-Lysine ethyl ester diisocyanate (purity 97 %) was purchased from Alfa Aesar (Kandel, Germany). Tolonate™ X FLO 100 (NCO equivalent: 341 g/eq) was kindly supplied by Vencorex® Chemicals (Saint Priest, France). Laponite-S 482 was kindly supplied by BYK-Chemie GmbH (Wesel, Germany). Pripol® 2033 (OH value: 207 mgKOH/g, purity 98 %) was kindly supplied by Croda (East Cowick, United Kingdom). Dibutyltin dilaurate (DBTDL, purity 95 %) and diglycerol (purity 80 %, mixture of isomers) were purchased from TCI EUROPE N.V (Zwijndrecht, Belgium). All materials were used as received.

### Characterizations

#### Fourier Transform Infrared Spectroscopy

Infrared (IR) spectra were recorded on a Nicolet 210 Fourier transform infrared (FTIR) spectrometer. The characteristic IR absorptions mentioned in the text are reported in  $\text{cm}^{-1}$ . Materials analyses were recorded using an ATR accessory.

#### Thermogravimetric Analyses

Thermogravimetric Analyses (TGA) were carried out using a TG 209F1 apparatus (Netzsch). Approximately 10 mg of sample were placed in an aluminum crucible and heated from room temperature to 580 °C at a heating rate of 20 °C/min under nitrogen atmosphere (60 mL/min).

#### Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter, which was calibrated using adamantane, biphenyl, indium, tin, bismuth and zinc

standards. Nitrogen was used as purge gas. Approximately 10 mg of sample were placed in a perforated aluminum pan and the thermal properties were recorded between -100 °C and 150 °C at 20 °C/min to observe the glass transition temperature. The  $T_g$  values were measured on the second heating ramp to erase the thermal history of the polymer. All the reported temperatures are average values.

#### Dynamic mechanical analyses

Dynamic mechanical analyses (DMA) were carried out on a Metravib DMA 25 with Dynatest 6.8 software. Foam samples (10 x 15 x 12 mm<sup>3</sup>) and bulk material samples (1 x 30 x 5 mm<sup>3</sup>) were tested in the uniaxial tension mode at a frequency of 1 Hz with a fixed strain of  $10^{-5}$  m, while applying a temperature ramp at a rate of 3 °C/min from -60 °C to +150 °C. The  $T_\alpha$  was determined as the maximum of the loss modulus  $E''$ .

#### Compression experiments

Compression experiments were performed on 17 x 7 x 12 mm<sup>3</sup> samples with a ThermoScientific Haake Mars 60 rheometer equipped with a 60-mm plane-plane geometry as compression holders, at room temperature. The samples were compressed following the axis of the largest dimension of the samples (17 mm). A 20 N axial force was applied to the samples. Reported compression strength values were determined at 30 % of strain.

#### Stress-relaxation experiments

Stress relaxation experiments were performed on a ThermoScientific Haake Mars 60 rheometer equipped with a lower electrical temperature module and an active upper heating system, with a textured 8-mm plane-plane geometry. A 1 N axial force was applied to ensure proper contact between the plates and the samples. A 1 % torsional strain was applied on 8 mm diameter and 2 mm thickness circular samples, and the rubbery modulus evolution with time was monitored at different isotherms.

#### Swelling index

Three samples from the same material, of around 30 mg each, were separately immersed in 5 mL THF for 24 h. The swelling index (SI) was calculated using Equation 1, where  $m_2$  is the mass of the swollen material and  $m_1$  is the initial mass. Reported swelling index are average values of the three samples.

Equation 1 
$$SI = \frac{m_2 - m_1}{m_1} \times 100$$

## Gel Content

Three samples from the same material, of around 30 mg each, were separately immersed in 30 mL of THF for 24 h. The samples were then dried in a ventilated oven at 70 °C for 24 h. The gel content (GC) was calculated using Equation 2, where  $m_2$  is the mass of the dried material and  $m_1$  is the initial mass. Reported gel content are average values of the three samples.

$$\text{Equation 2} \quad GC = \frac{m_2}{m_1} \times 100$$

## Density

Parallelepipedic foam samples were measured with a caliper and weighed to determine the apparent foam density.

## Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) analyses were conducted using a Hitachi S-4500 (Tokyo, Japan) instrument operating at spatial resolution of 1.50 nm at 15 kV energy. The samples were dried and coated with an ultrathin layer of electrically conducting platinum deposited by high-vacuum evaporation.

## Optical microscopy

Optical microscopy analyses were conducted using a ZEISS Stemi 508 instrument. Cell size was determined with optical microscope pictures, reported values are average values of 100 cells.

## General procedure of PUFs synthesis

Materials were synthesized with a NCO/OH molar ratio of 1.1/1.0. As an example, PUF1 was prepared as follows. Pripol® 2033 (3.941 g, 0.7 eq.), diglycerol (0.259 g, 0.3 eq.), DBTDL (0.098 g, 0.0075eq.), Laponite-S 482 (0.150 g, 1 wt%) and water (0.074 g, 0.4 eq.) were mixed using a SpeedMixer™ for 1 min at 2,500 rpm. Then, Tolonate™ X FLO 100 (10.626 g, 1.5eq.) was added to the mixture and stirred once again 1 min at 2,500 rpm. The resulting homogeneous mixture started to foam at room temperature for PUF3 and PUF4. The same procedure was applied for PUF2, PUF3 and PUF4 by varying the monomer nature and molar ratios. The resulting PUF1 mixture and the PUF3 foam were then cured for 30 min at 150 °C, while PUF2 mixture and PUF4 foam were cured for 1 h at 100 °C.

## Reshaping procedure

The material was manually cut into flakes ( $\approx 1 \text{ mm}^3$ ) and then pressed in a PTFE mold for 30 min at 160 °C under a 6 tons load using a Carver 3960 manual heating press. For the foams mix, the same

mass of flakes from each foam was weighed and the flakes were then mixed together, prior to compression-molding.

## Results & Discussion

### PUFs Synthesis and Formulation

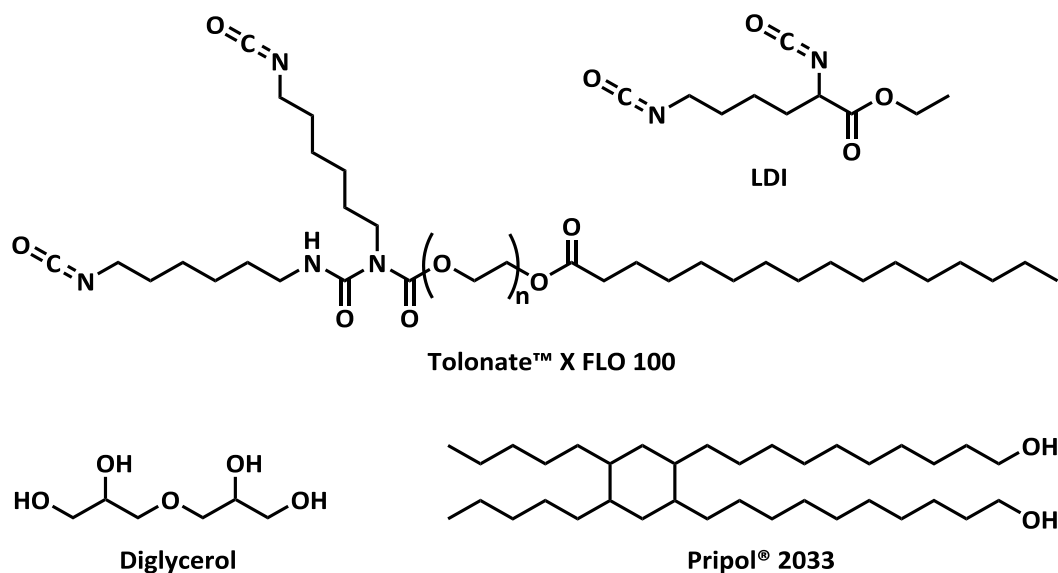


Figure 1: Diisocyanate and polyol monomers used for PUFs synthesis.

In order to obtain highly biobased PUFs, monomers were chosen with care. Indeed, commercially available biobased polyols are very common nowadays. However, only very few biobased isocyanates are available in the market. The first biobased diisocyanate chosen was Tolonate™ X FLO 100. Derived from hexamethylene diisocyanate (HDI), it contains a poly(ethylene glycol) backbone and an aliphatic part derived from palmitic acid, with an overall 32 % biobased carbons content. On the other hand, L-Lysine ethyl ester diisocyanate (LDI) is obtained from the essential L-Lysine amino acid and contains 80 % of biobased carbons. According to MSDS of supplier, LDI is not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008. Tolonate™ X FLO 100 allows us to study regular HDI-based PUF with a lower toxicological profile. It is classified as GHS07 irritating, whereas HDI is classified GHS06 and GHS08 toxic. To synthesize flexible PUFs, the fully biobased Pripol® 2033 derived from fatty acids was chosen for its long aliphatic chains which give flexibility. Diglycerol, obtained from glycerol and therefore fully biobased, was used as a crosslinking agent to bring rigidity to the polymer network (Figure 1).

To obtain flexible PUFs with different mechanical properties, two Pripol® 2033 / diglycerol molar ratios (0.7/0.3 and 0.3/0.7) were studied. (Table 1) Water was added to the formulation as foaming agent. The reaction of water with isocyanates leads to urea linkages and the formation of CO<sub>2</sub> allows the foaming process. Laponite-S 482 was added for rheological control of the foam, and DBTDL was



used to increase the reactivity of isocyanates toward water and polyols. DBTDL allowed the PUF3 and PUF4 formulations to fully foam at room temperature, without any external heating but thanks to the exotherm of the reaction (Supporting Video), while Tolonate-based PUF1 and PUF2 were only in the nucleation phase, nevertheless, the four PUFs were then cured at 100 or 150 °C depending of their diglycerol content. LDI is smaller compared to Tolonate™ X FLO 100, enabling a higher density of reactive species in the mixture leading to a higher exotherm able to trigger the complete foaming of PUF3 and PUF4. As Tolonate™ X FLO 100 is only partially biobased, PUF1 and PUF2 presented the lowest biobased carbon contents with 41 % and 47 % respectively. LDI-based foams, PUF3 and PUF4, had higher biobased carbon contents of 90 % and 93 % respectively. PUF2 and PUF4 formulations, containing more diglycerol, were cured at 100°C for 1 h. PUF1 and PUF3 were cured 30 min at 150°C, the curing temperature was increased to prevent the collapse of the foam. Indeed, as these formulations contained less crosslinking agent, the gel point was reached at longer reaction times at lower curing temperature and the fragile foam structure tended to collapse when the polymer network was not crosslinked quickly enough. The full conversion of isocyanates was confirmed by FTIR analyses (Figure S1) with the disappearance of the isocyanate band at  $2\,275\text{ cm}^{-1}$  and the appearance of the urethane carbonyl elongation band at  $1\,715\text{ cm}^{-1}$ . Moreover, the complete crosslinking of the materials was confirmed by the high gel content values, 93 % and 97 % for PUF1 and PUF2 respectively and 99 % for both PUF3 and PUF4 (Table 2). PUF1 and PUF3 with lower diglycerol contents were dense foams with densities of  $266\text{ kg/m}^3$  and  $390\text{ kg/m}^3$  respectively. Conversely, PUF2 and PUF4 with high diglycerol contents displayed lower densities of  $147\text{ kg/m}^3$  and  $78\text{ kg/m}^3$  respectively, PUF4 even exhibits a low density similar to conventional PUFs usually between 20 to  $100\text{ kg/m}^3$ .<sup>25,29,30</sup> PUFs were observed with optical and scanning electron microscopes (SEM) (Figure 2). PUF1 and PUF3 composed of lower diglycerol content have smaller opened cells of  $396\text{ }\mu\text{m}$  and  $228\text{ }\mu\text{m}$  respectively, whereas PUF2 and PUF4 have larger opened cells of  $667\text{ }\mu\text{m}$  and  $636\text{ }\mu\text{m}$  respectively (Table 1). Nevertheless, the four PUFs have a high cell size distribution, since no surfactant was used for their synthesis.

Table 1 : Formulations of PUFs and their biobased carbon content.

Foam <sup>a</sup>	Diisocyanate		Polyols		Biobased Carbon Content (%)
	LDI (eq.)	Tolonate™ X FLO 100 (eq.)	Pripol® 2033 (eq.)	Diglycerol (eq.)	
PUF1 <sup>b</sup>	-	1.5	0.7	0.3	47
PUF2 <sup>b</sup>	-	1.5	0.3	0.7	41
PUF3 <sup>c</sup>	1.5	-	0.7	0.3	90
PUF4 <sup>c</sup>	1.5	-	0.3	0.7	93

<sup>a</sup> Foams were synthesized with 0.0075 eq. of DBTDL, 0.4 eq. of water and 1 wt% of Laponite-S 482.

<sup>b</sup> Cured at 150 °C for 30 min

<sup>c</sup> Cured at 100 °C for 1 h.

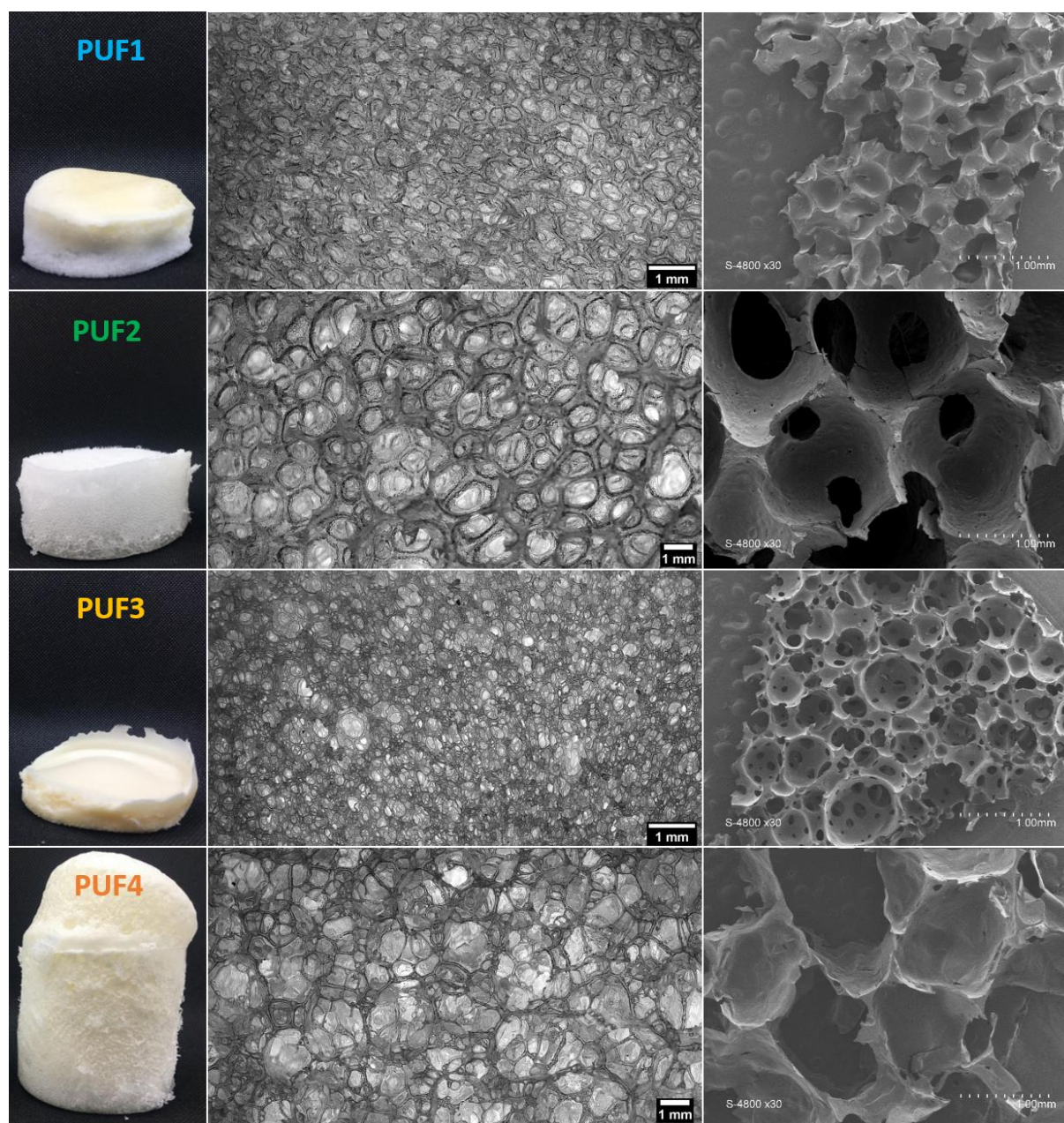


Figure 2 : Photographs of PUFs, optical microscopic and SEM pictures from left to right.

## Thermomechanical properties

The four formulations allowed to synthesize four PUFs able to cover a wide range of properties. The four PUFs exhibited  $T_g$  values ranging from -29 °C to 46 °C for PUF1 and PUF4 respectively (Table 2 and Figure S3). The structure of the diisocyanate used had a significant influence on the  $T_g$  values of the final foams. Indeed, Tolonate™ X FLO 100 possesses long alkyl chains and has a much higher molar mass than LDI, therefore, Tolonate-based foams presented the lowest  $T_g$  as it reduces the foam crosslinking densities. Moreover, the increase of diglycerol contents from 0.3 eq. to 0.7 eq. in PUF2 and PUF4 led to higher  $T_g$  values, from 12 °C to 46 °C for PUF3 and PUF4 respectively. Indeed, this can be ascribed to diglycerol content which strongly increased the crosslinking density with its high OH functionality and its small molar mass compared to Pripol 2033®. The low  $T_g$  foams PUF1, PUF2 and PUF3 were soft at room temperature whereas the higher  $T_g$  PUF4 was rigid.

Furthermore, the thermal stability of PUFs were studied by TGA (Figure S2) by comparing the temperatures at 5 % of degradation. Tolonate-based foams PUF1 and PUF2, which degraded at 270 °C and 273 °C respectively, were more thermally stable than the LDI-based foams PUF3 and PUF4 which degraded at 257 °C and 242 °C respectively. The higher Pripol® 2033 content increased the thermal stability of PUF3 compared to PUF4 from 242 °C to 257 °C whereas, it did not exhibit particular effect for PUF1 and PUF2. Indeed, PUF1 and PUF2 networks were mainly composed of Tolonate™ X FLO 100 with 70 wt% and 80 wt% respectively, because of its high molar mass (Table S1). Therefore, the effect of the polyol contents was lower.

Table 2 : PUFs properties.

Foam	$T_g$ (°C)	$T_\alpha$ (°C)	Compression strength (kPa)	$T_{d5\%}$ (°C)	Gel content (%)	Density (kg/m <sup>3</sup> )	Cell size ( $\mu$ m)
PUF1	-29	-21	53	270	93 ± 1	266 ± 35	396 ± 94
PUF2	-26	-30	10	273	97 ± 1	147 ± 16	667 ± 191
PUF3	12	22	127	257	99 ± 1	390 ± 61	228 ± 106
PUF4	46	49	106	242	99 ± 1	78 ± 9	636 ± 302

## Mechanical properties

Mechanical properties of the four PUFs were analyzed by an uniaxial compression experiment (Figure 3) using parallelepipedic foam samples. Three characteristic regimes were observed from the stress/strain curves. The first region, at low strain, corresponds to the linear elasticity due to the bending of the edge of the foam. This first region was observed for strain values ranging from 0 to around 5 % for PUF1 and PUF4 and from 0 to around 20 % for PUF2 and PUF3. Above these strain values, a plateau was observed where the stress was stable even if the strain increased. This second region corresponds to the collapse of the foam due to the compression of the cells. Above 40 - 50 %

of strain, cells were completely compressed. Therefore, the stress increased drastically. This phenomenon corresponds to the densification region (Figure S4). The compression strength (which represents the force needed to compress the foam) was determined at 30 % strain for each PUF. This strength varied with the cells characteristics and foam density but also with the composition of the PUF network. PUF1 and PUF2 ( $T_g = -29\text{ }^\circ\text{C}$  and  $-26\text{ }^\circ\text{C}$  respectively) were very soft at room temperature and did not require a high compression strength (53 kPa and 10 kPa respectively) to achieve 30 % strain. In contrast, PUF3 and PUF4 based on LDI and which have higher  $T_g$  due to their higher crosslinking density exhibited compression strength values of 127 kPa and 106 kPa respectively. In addition, the compression strength also depended on the foam density. Indeed, PUF1 which was denser than PUF2, also displayed higher compression strength. For the same reasons PUF3 had a higher compression strength than PUF4.

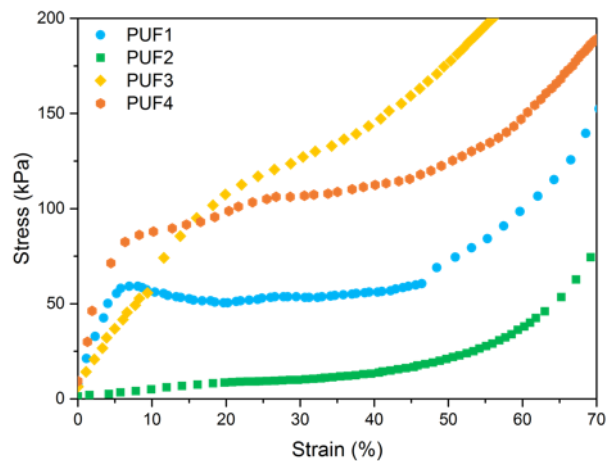


Figure 3: Stress-strain curve of PUFs obtained by a static 20 N uniaxial compression.

## Upcycling and recycling of PUFs

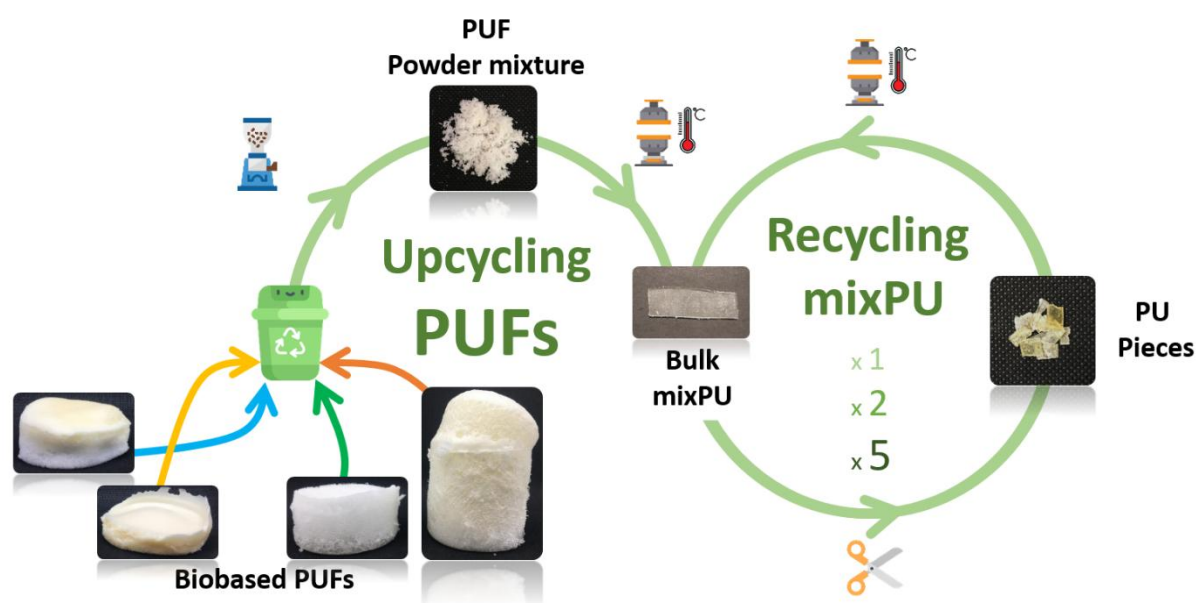


Figure 4: Reshaping strategy. Powdered foams were reshaped by compression molding for 30 min at 160 °C under a 6 tons load.

PUFs foaming required DBTDL as a catalyst, which was reported to also activate covalent bond exchange by transcarbamylation in cured PUs. With the discovery of vitrimers in 2011,<sup>46</sup> the recycling of thermosets has never been so closer to reality. To assess the potential recycling of the PUFs, reprocessing trials were performed by compression molding. The foams were first powdered, then placed in a PTFE mold and pressed at 160 °C for 30 min under a 6-ton load. Flexible transparent materials were obtained out of PUF1, PUF2, PUF3 and a stiff transparent material was obtained out of PUF4 as expected given the  $T_g$  of the corresponding pristine PUFs (Table 2, Figure S5). These four materials were obtained thanks to the transcarbamylation reaction catalyzed with DBTDL already contained in the PUFs network since their synthesis, with a content between 0.65 wt% and 1.6 wt%. Several reshaping cycles were performed. The swelling indexes and gel contents were measured after each cycle for the four PUFs to assess the degradation of the polymer network, a trend was observed (Figure 5). Gel contents decreased with the number of cycles indicating some degradation of the polymer network and a decrease of the crosslinking density leading to an increase of the soluble fraction. PUF1 bulk material ended up being fully soluble after the 5<sup>th</sup> cycle whereas PUF2, PUF3 and PUF4 bulk materials were less affected. This trend was attributed to a higher crosslinking density, either because of a higher diglycerol content (PUF2), or because of the use of LDI which is shorter than Tolonate® X FLO 100 (PUF 3), or because of both reasons (PUF 4). This difference in crosslinking density is also reflected in the Swelling Index values, as PUF 1 has the highest swelling index, whereas PUF 2 and PUF 3 have similar values and PUF 4 exhibits the lowest swelling index. Indeed, the gel contents of PUF4 bulk materials remained above 79 % after five reshaping cycles.



Even if PUF3, as PUF1, was composed of 0.3 eq. of diglycerol, its gel content remained to 60 % after five cycles thanks to the higher crosslinking density provided by LDI. Swelling indexes of PUF2 and PUF3 increased with cycles confirming a slight decrease of their crosslinking density. In contrast the swelling index of PUF4 remained stable. Consequently, PUF4 appears to be a very promising foam because of its thermomechanical and mechanical properties, its low density and its ability to be reshaped with relatively low degradation over successive cycles.

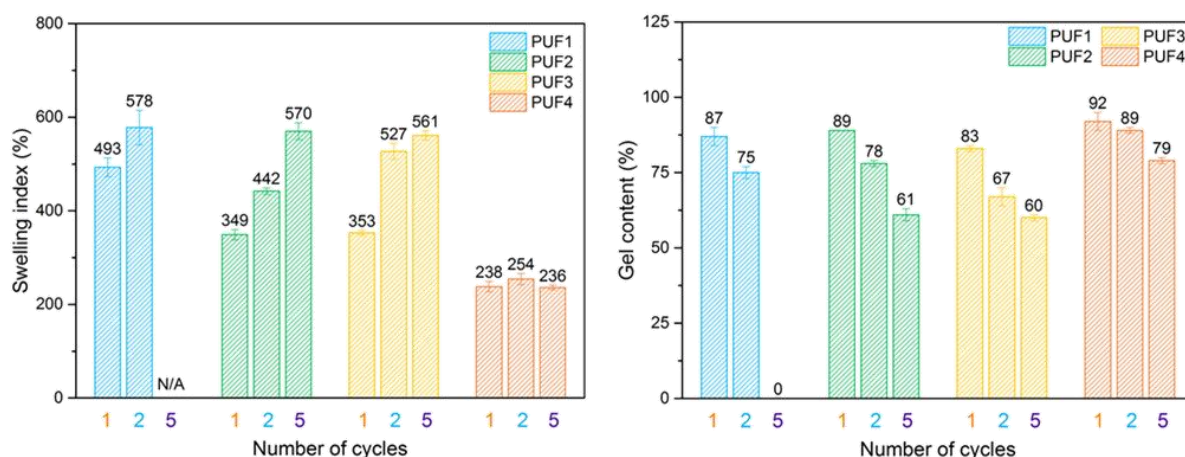


Figure 5: Evolutions of swelling indexes (left) and gel contents (right) of PUFs over 5 reshaping cycles

One of the major limitation of recycling, is the massive influx of wastes of different origins. Very selective time-consuming and labor-intensive sorting steps are necessary in order to give a second life to limited wastes. Limiting these sorting steps would be an important progress towards more cost-effective and productive recycling. One step in the right direction would be to enable wastes of different origins to be recycled together as demonstrated lately Swartz *et al.* by blending rigid and soft PU thermosets through transcaramoylation.<sup>54</sup> This possibility was assessed with the biobased PUFs described here. An equimassic mixture of the four powdered PUFs was prepared and reprocessed as described above. This reshaping procedure led to a flexible macroscopically homogeneous transparent material (mixPU). As for individual PUF up to 5 consecutive reprocessing cycles were achieved with this mixPU (Figure 4). The recycling of the four PUFs together demonstrates that a straightforward upcycling is possible for PUFs from different origins at the end of their life, if a specific collecting and recycling channel exists.

The properties of the materials obtained from mixPU reshaping steps after the first, the second and the fifth cycle were assessed by DMA (Table 3), storage modulus  $E'$  and  $\tan(\delta)$  were plotted against temperature (Figure 6). After the first cycle, two regimes are visible, with local  $\tan(\delta)$  maxima at 0 °C and 44 °C. On the DSC thermogram (Figure S6), two  $T_g$  are visible at -27 °C and 44 °C on the first

heating ramp (Table 4), but the second  $T_g$  cannot be observed on the second ramp. This behaviour can be attributed to local heterogeneity in the material likely caused by the fact that it results from the mixing of powders from different foams. The low  $T_g$  (-29 and -26 °C) PUF1 and PUF2 are responsible for the lower temperatures regime, while the higher  $T_g$  (12 and 46 °C) PUF3 and PUF4 are responsible for the upper temperatures behaviour. After the second cycle both regimes were still visible on the DMA thermogram (Figure 6) but the curve was smoothed. On the DSC thermogram (Figure S7) only one  $T_g$  was observed at -27 °C, though a local minimum of the derivative at 41 °C remained as an indicator of the local heterogeneity (Table 4). After the fifth cycle a broad single mode was observed by DMA, and the  $T_g$  observed by DSC was -18 °C (Figure S8 and Table 4). This evolution is likely caused by the successive grinding-reshaping cycles which gradually increased the homogeneity of the material. The broadness of the mode remains a manifestation of the different  $T_\alpha$  values of the pristine PUFs. Therefore, we also could consider that five cycles are needed to obtain a new homogeneous material.

Table 3 : Properties of mixPU bulk materials after several reprocessing cycles.

Reprocessing Cycle	$T_{g1}$ (°C) <sup>a</sup>	$T_{g2}$ (°C) <sup>a</sup>	$T_\alpha$ (°C)	$E'_{glassy}$ (GPa) <sup>b</sup>	$E'_{rubbery}$ (MPa) <sup>c</sup>	Swelling index (%)	Gel content (%)
1	-27	44	-15	3.8	19.3	440±16	71±1
2	-27	-	-18	3.4	15.7	453±13	64±1
5	-18	-	-17	3.7	6.5	410±22	50±2

<sup>a</sup> values for the first heating ramp <sup>b</sup> at  $T_\alpha$  -50 °C <sup>c</sup> at  $T_\alpha$  +50 °C

On the other hand, the storage modulus on the glassy plateau  $E'_{glassy}$  remained stable, at 3.8, 3.4 and 3.7 GPa respectively, whereas the values on the rubbery plateau decreased from 19.3 to 15.7 and 6.5 MPa respectively (Figure 6). In addition, the gel content dropped to 64 % after the second reshaping and to 50 % after the fifth cycle, which is probably due to partial degradation of the polymer. Surprisingly, the swelling index was stable over the five cycles and the  $T_\alpha$  did not change significantly either. Moreover, the  $T_g$  increased from -27 °C to -18 °C whereas a drop of the  $T_g$  is usually expected with the polymer degradation, as previously observed during the recycling of the four set apart PUFs. Nevertheless, a theoretical final  $T_g$  of -3 °C (average of the four PUF  $T_g$ ) was expected for mixPU with respect to the Fox Equation. There is a significant different with the experimental value at -18 °C indicating that some degradation happened. In addition, the swelling index was supposed to increase with degradation since the crosslinking density of polymer network is usually reduced, but SI remained almost stable over the recycling cycles. Finally, in contrast with the individual PUFs, the decrease of  $T_g$  and the rise of the swelling index were not observed with the degradation of mixPU. We hypothesize that this phenomenon might be due to the homogenization of the network induced

by the successive cycles applied to the mixture, and that 5 cycles are needed to homogenize the recycled material.

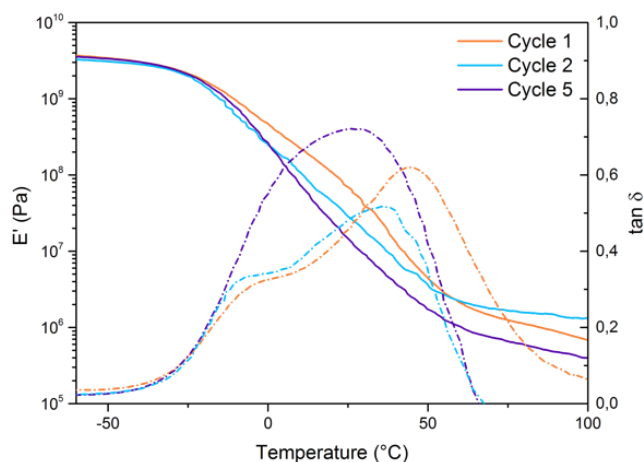


Figure 6: Storage modulus (full lines) and  $\tan(\delta)$  (dashed lines) of mixPU during DMA experiments after several reprocessing cycles.

#### Dynamic properties of PUFs with DBTDL

Covalent adaptable networks (CANs) using DBTDL as transcarbamoylation catalyst in PUs have already been described.<sup>49,50</sup> Moreover, urea bonds are known to enhance the reprocessing of these materials.<sup>52</sup> In the present study, DBTDL was used as a catalyst to obtain the biobased PUFs, moreover, the foaming reaction of isocyanates with water led to urea bonds in the thermoset structure. To highlight the dynamic behavior of the reprocessable PUFs, mixPU was characterized by stress relaxation experiments from 160 °C to 200 °C (Figure S9). Classical non-reshapable thermosets exhibit a constant stress as their networks are fixed. On the contrary, at 200 °C the stress applied to mixPU was fully relaxed in 300 s, a feature associated with an evolving network topology. The modulus at the beginning of the relaxation  $G_0$  decreased gradually with increasing temperature isotherms, from 0.7 MPa at 160 °C to 0.4 MPa at 200 °C, which suggests a dissociative CANs is at stakes. The relaxation was faster as the temperature increased from 160 to 200 °C (Figure 7a). The curves were fitted with a Kohlrausch-Williams-Watt equation (Table S3) and the relaxation times obtained were plotted in an Arrhenius diagram (Figure 7b). This plot fitted perfectly with a linear model ( $R^2 = 0.99647$ ). Hence, the material flow dependence with temperature follows an Arrhenius law, a feature of vitrimer-like dissociative CANs. The activation energy ( $E_a$ ) of mixPU was determined to be 140 kJ.mol<sup>-1</sup>, in the same order of magnitude as PU CANs previously reported.<sup>51-53</sup>



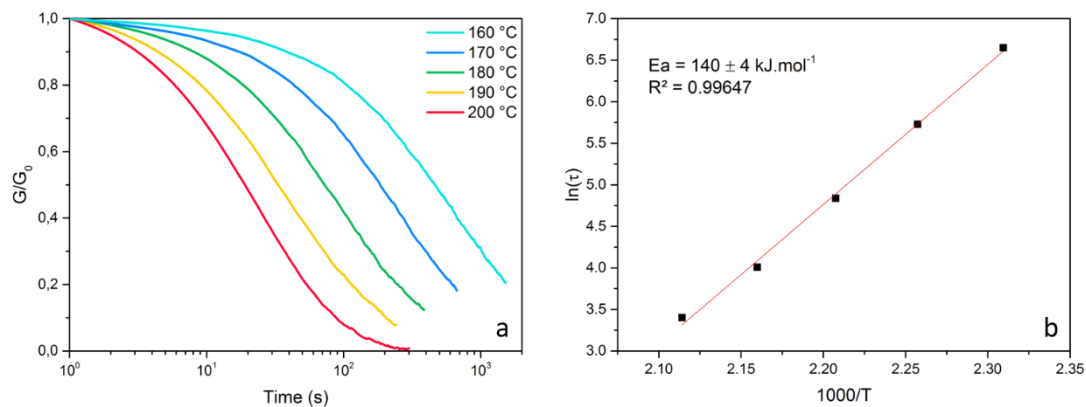


Figure 7: (a) Normalized stress-relaxation measurements of mixPU and (b) Arrhenius diagram and linear fit of  $\tau_{KWW}$  values from 160 to 200 °C.

## Conclusion

The development of more eco-friendly materials is a major stake to ensure sustainable production and consumption. Foams are found in everyday life applications and are mainly based on polyurethanes. The recent emergence of biobased polyisocyanates in the market have made the synthesis of highly biobased polyurethanes possible (until 95% renewable carbon). Here, four highly biobased PUFs, PUF1 and PUF2 based on Tolonate™ X FLO 100 and PUF3 and PUF4 based on LDI were synthesized with a renewable carbon content ranging from 41 % to 93 %. The LDI-based formulations fully foamed at room temperature, while the heating of Tolonate-based PUFs was necessary to complete their foaming. Foams with  $T_g$  ranging from -29 °C to 46 °C after curing at 100 or 150 °C were obtained. PUF1, PUF2 and PUF3 were dense foams while the PUF4 density of 78 kg/m<sup>3</sup> was comparable to conventional PUFs making PUF4 very promising. The DBTDL used to catalyze the foaming and the crosslinking reactions also served as transcarbamoylation catalyst to upcycle the foams to bulk PUs. The four PUFs were reshaped up to 5 times by compression molding. Moreover, a new PU material (mixPU) was obtained from a mixture of the four PUFs using the same recycling process. The dynamic properties of the mixPU were characterized by stress relaxation experiments, demonstrating the exchanges occurring in the PUFs CANs synthesized that enable their reshaping. The upcycling and the reshaping steps applied to this mixPU highlighted the potential to recycle foams from different origins, a key parameter to achieve foam recycling on an industrial scale. This study was performed on biobased isocyanates with lower toxicological profiles. It could be extended to regular commercial PUF in order to propose a promising recycling approach that allows them new life in new applications and reduce environmental impacts. These results correspond to a transitory approach proposing to manage the present situation regarding PU wastes.

## Associated content

### Supporting Information

The Supporting Information is available free of charge at

Detailed PUF formulations, FTIR spectra, TGA and DSC thermograms, compression experiments, photographs and  $T_g$  of recycled PUF, fitting parameters of Kohlrausch-Williams-Watts model.

### Supporting video

Foaming of PUF4 at room temperature.

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B.Q. and F.C. contributed equally to this article. Conceptualization, B.Q., F.C. and S.C.; methodology, B.Q. and F.C.; investigation, D.C., M.S., B.Q. and F.C.; resources, J.P., V.L. and S.C.; writing—original draft preparation, B.Q. and F.C.; writing—review and editing, B.Q., F.C., J.P., V.L. and S.C.; supervision, J.P., V.L. and S.C. All authors have read and agreed to the published version of the manuscript.

### Notes

The authors declare no competing financial interest.

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Reprocessable biobased polyurethane foams have been synthesized and recycled highlighting that a more sustainable approach is possible.