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1 Breakthrough in polyurethane bio-recycling: an efficient laccase-mediated system for the  
2 degradation of different types of polyurethanes.

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7

8 **Abstract**

9 Development of green, efficient and profitable recycling processes for plastic material will  
10 contribute to reduce the expanding plastic pollution and microplastics accumulation in the  
11 environment. Polyurethanes (PU) are versatile polymers with a large range of chemical  
12 compositions and structures. This variability increases the complexity of PU waste management.  
13 Biological recycling researchers have recently demonstrated great interest in polyethylene  
14 terephthalate. The adaptation of this route towards producing polyurethanes requires the  
15 discovery of enzymes that are able to depolymerize a large variety of PU. A laccase mediated  
16 system (LMS) was tested on four representative PU models, with different structures (foams  
17 and thermoplastics), and chemical compositions (polyester- and polyether-based PU). Size  
18 exclusion chromatography was performed on the thermoplastics and this revealed a significant  
19 reduction in the molar masses after 18 days of incubation at 37°C. Degradation of foams under  
20 the same conditions was demonstrated by microscopy and compression assay for both  
21 polyester- and polyether-based PU. This study represents a major breakthrough in PU

22 degradation, as it is the first time that enzymatic degradation has been clearly demonstrated on  
23 a polyether-based PU foam. This work is a step forward in the development of a sustainable  
24 recycling pathway, adapted to a large variety of PU materials.

25

26 [Keywords](#)

27 Polyurethanes, Laccase, Biocatalysis, Polymer degradation, Recycling, PU foam

28

## 29 Introduction

30 Increasing plastic production and the failure of plastic waste management have resulted in  
31 negative effects on our environment such as pollution and the accumulation of persistent  
32 microplastics. The battle against plastic pollution is one of the largest challenges of the coming  
33 decades (Lau et al., 2020). The implementation of a circular economy aims at reducing energy  
34 and raw material consumption, as well as limiting waste generation. This concept emerges in  
35 the plastic industry by promoting the development of sustainable recycling processes (Blank et  
36 al., 2019). Plastic waste can be seen as a new feedstock for a greener production of value-added  
37 materials (Johnston et al., 2017). Nowadays, plastic materials are mainly recycled by  
38 thermomechanical processes (Ignatyev et al., 2014). However, these processes are only suitable  
39 for thermoplastic materials. Thermoset materials cannot be easily reprocessed because of their  
40 cross-linked macromolecular architectures.

41 Polyurethanes are generally obtained by polyaddition between polyisocyanates and polyols,  
42 mainly polyesters or polyethers, to produce different structures such as PU foams, which are  
43 highly resistant thermoset materials (Figure 1). Flexible and rigid foams represent 32 and 36% of  
44 the global PU production, respectively (Magnin et al., 2019b). Flexible foams are mainly used for  
45 automotive seats, furniture or bedding while rigid PU foams are essentially insulation material  
46 for the construction industry (Furtwengler and Avérous, 2018). PU are also produced for  
47 coatings, adhesives, sealants and elastomers, making this family of polymers highly versatile.  
48 End-of-life PU foams, which represent the main source of PU waste, are ground and used as  
49 fillers for low added-value products (Zia et al., 2007). Research is thus underway to develop a  
50 green recycling pathway common to different types of PU. For example, the chemical recycling

51 of PU foam by glycolysis is drawing attention. An efficient process was developed on poly(ether  
52 urethane) foams at high temperature, 190°C (Simón et al., 2016).

53 Recently, the biological recycling of polyethylene terephthalate (PET) plastic bottles was  
54 developed (Tournier et al., 2020). This biological recycling consists of the depolymerization of  
55 polymer chains, under mild and green conditions (at a temperature lower than 90°C, in aqueous  
56 media), with enzymes. The degradation products recovered are then used as the building blocks  
57 for the synthesis of second-generation polymers. Contrary to PET, the biological recycling of PU  
58 is much more challenging, due to the large variety of compositions and structures (Cregut et al.,  
59 2014) and to the inherent robustness of the urethane bond and the fact that polyurethanes are  
60 designed for long term applications (Lucas et al., 2008).

61 Until now, enzymatic depolymerization of PU has only been demonstrated on thermoplastic  
62 poly(ester urethanes). Lipases that hydrolyze ester segments of poly(ester urethanes) are now  
63 well documented in the literature (Biffinger et al., 2015; Gautam et al., 2007a; Schöne et al.,  
64 2016) showing that this pathway is limited to a type of polymer structure that is not  
65 representative of PU diversity and market. Urethane bond hydrolysis appeared possible with  
66 amidase on model molecules (Akutsu-Shigeno et al., 2006; Gamerith et al., 2016; Magnin et al.,  
67 2019a). Nevertheless, the efficient hydrolysis of urethane linkages from high molar mass PU has  
68 not been fully demonstrated yet. PU based on polyether polyols (poly(ether urethanes)) are  
69 much more difficult to degrade than PU made from polyester polyols (poly(ester urethanes))  
70 (Christenson et al., 2006; Ferris et al., 2010). Besides, even if foams represent the major source  
71 of PU waste, their enzymatic degradation has almost never been studied. As far as we know,

72 only one publication deals with the degradation of a poly(ester urethane) foam using a porcine  
73 pancreatic lipase (Ng et al., 2017).

74 Where hydrolytic enzymes (such as lipases) fail to be competent, oxidoreductases might bring a  
75 solution. Laccase is a multicopper oxidase with a wide range of biotechnological applications  
76 such as biomass valorization, xenobiotics bioremediation or paper bleaching (Keum and Li,  
77 2004; Riva, 2006). Laccases are widely used for the degradation of biopolymers such as lignins.  
78 Only few publications deal with the use of laccase for the degradation of synthetic polymers.  
79 Laccases have already been involved in the degradation of thermoplastic poly(ester urethane)  
80 and polyethylene films (Ignat et al., 2011; Santo et al., 2013). To increase the oxidative potential  
81 of laccase, a mediator can be added to the enzymatic solution. A laccase-mediated system  
82 (LMS) consisting of a laccase from *Trametes versicolor* and 1-hydroxybenzotriazole (HBT) as a  
83 mediator, has successfully degraded polyethylene and nylon 6,6 (Fujisawa et al., 2001).  
84 Recently, Inderthal et al., suggested that LMS could be a proper alternative for the degradation  
85 of non-hydrolyzable polymers (Inderthal et al., 2020).

86 In this paper, we investigate the application of LMS to the degradation of tailor-made model PU.  
87 Four representative model PU were synthesized: polyester- and polyether-based PU produced  
88 as thermoplastics and foams, to evaluate their respective degradations, to develop a global  
89 biological recycling process. Degradation was performed with the laccase from *Trametes*  
90 *versicolor* with HBT as mediator. HBT was chosen because of its high redox potential of 1.08 V  
91 (Munk et al., 2017). The enzymatic degradation of foams has been rarely studied in the  
92 literature and the corresponding analytical part is almost inexistent. An analytical set was thus  
93 developed to evaluate the enzymatic degradation of PU foams. We also decided to mimic the

94 LMS degradation with an abiotic degradation process, by using UV treatment. Both LMS and UV  
95 are radical oxidation processes.

## 96 [Material and methods](#)

### 97 [Chemicals, reagents and enzymes](#)

98 Niax L537XF and DABCO BLV, used for foams synthesis were provided by Momentive (USA) and  
99 Evonik (Germany), respectively. Common reagents and solvents were purchased from Sigma  
100 (France) and used as received.

101 Degradation enzyme is the laccase from *Trametes versicolor* from Sigma (Reference 38429,  
102 Batch number BCCB8880, activity on catechol: 0.84 U/mg). Enzymatic activity is measured using  
103 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) 0.04 mM in an acetate buffer (0.1  
104 M, pH4.5) (Llevot et al., 2016). One unit of activity corresponds to the mass of enzymes required  
105 to oxidize one mole of substrate per minute (Llevot et al., 2016). Activity measured is  
106 0.01 U/mg.

### 107 [Polymer synthesis](#)

108 Four model polymers were synthesized (details are given in SI) with an aromatic di-isocyanate,  
109 toluene diisocyanate (TDI) (Figure 1). Two are based on a polyester polyol (Polycaprolactone Mn  
110 = 2000) and two on a polyether (Polytetrahydrofuran Mn = 2000). For each system, a  
111 thermoplastic polyurethane (TPU) and a PU foam (cross-linked structure) were produced. Foams  
112 were obtained by adding glycerol to the formulation. Details of the synthesis are available in the  
113 Supplementary Information. PU foams were cut into cubes of 1.2 x 1.2 x 1.2 cm. The synthesized

114 TPU were then obtained as coatings prepared in glass vials of 4 mL by solvent casting with a  
115 solution of 20 mg of TPU in 1 mL of THF. The coating thickness was in the range of micrometers.

#### 116 Enzymatic degradation

117 Foam cubes were incubated in 12 mL glass vials. Coatings of thermoplastics were prepared in 4-  
118 mL glass vials as described above. Final volumes were 5mL for the foam and 1mL for the PU  
119 coatings. The liquid fraction was composed of a sodium acetate buffer (0.1 M, pH4.5), HBT at  
120 0.2 mM and laccase at an activity of 9 mU (equivalent ABTS). A negative control without laccase  
121 was carried out for each condition. Experiments were performed in triplicate. Every two or  
122 three days, the liquid fraction of each reaction was removed, and fresh enzymatic solutions  
123 were added to PU foams and coatings. After 18 days of incubation, foam cubes and TPU  
124 coatings were rinsed with distilled water, dried over night at 40°C under vacuum and weighted.  
125 Particular attention was given to the foams to avoid pressing them during rinsing, to maintain  
126 their mechanical properties. As the controls and the samples incubated with enzymes were  
127 treated the same way, the potential effect of drying on the weight was neglected.

#### 128 Procedure for UV treatment

129 Foams were irradiated at room temperature in a Luzchem Photoreactor with LZC4-14 lamp at  
130 350 nm with a light intensity of 5.04 W.cm<sup>-2</sup>. Foams were disposed in such a way that the same  
131 side was exposed (Newman2001). UV irradiation lasted 9 days.



132 Polymer analysis

### 133 *Size Exclusion Chromatography*

134 TPU were dried under vacuum at 40°C for 24 hours. Samples were then solubilized in 2 mL of  
135 THF and filtered with PTFE filter 0.2 µm directly in the HPLC glass vial. 10 µL of dissolved  
136 polymer solution were then injected in an Acquity-APC (Waters) in THF at 40 °C. Three columns  
137 (Acquity APC XT 450 Å 2.5 µm 4.6x150 mm, 200 and 45) were connected. Detection was  
138 performed with a photodiode array detector at 254 nm. Run of 11 minutes with a THF flow of  
139 0.6 mL/min were applied. A calibration using polystyrene (PS) standards was established for  
140 molar mass and dispersity determination.

### 141 *Scanning electron microscopy*

142 Scanning electronic microscopy (SEM) was used to study the evolution of the surface  
143 morphology of the degraded systems. Vega-3 (Tescan, Brno, Czech Republic) apparatus in high  
144 vacuum mode with working distances in the range of 13–22 mm and an acceleration voltage of  
145 3 kV was used. Before examination, samples were coated with a thin layer of gold with a gold  
146 coater (Quorum Q 150 RS; Quorum Technologies, Lewes, UK).

### 147 *Compression test*

148 Compression tests were performed on foams before and after degradation. The apparatus used  
149 was a Discovery Hybrid Rheometer 3 (TA Instruments), equipped with parallel plates of 25 mm  
150 diameter. The data were collected with the software Trios. Two type of compression test were  
151 performed. The procedure applied to rigid foam consisted in the compression of 1.2 x 1.2 x 1.2  
152 cm foam cubes to 90% of their heights at a speed of 20 µm/s. For flexible foams, the  
153 compression was performed to 50% of cubes height at a speed of 40 µm/s. For data treatment,

154 the axial force expressed in Newtons was divided by the initial foam surface (mm<sup>2</sup>), to obtain  
155 the stress in MPa.

#### 156 *Infrared-spectroscopy*

157 A Fourier transformed infrared spectrometer Nicolet 380 from Thermo Scientific (US) was used  
158 in reflection mode equipped with an ATR diamond module (FTIR-ATR). An atmospheric  
159 background was collected before each sample analysis (32 scans, resolution 4 cm<sup>-1</sup>).

#### 160 *Statistical analysis*

161 The student's t-test with  $p < 0.05$  as the minimal level of significance was performed on weight  
162 loss, molar masses, compression test and FT-IR analysis. Statistical comparisons were made  
163 using two-sided Student's unpaired t-test.

#### 164 *Results and discussion*

165 The two thermoplastics PU (TPU) present close molar masses ( $M_w$  in the range of 70 000 –80  
166 000 g/mol and  $M_n$  of about 20 000 g/mol) so that their degradation could be directly compared.  
167 These values are also comparable to those conventionally found on commercial TPU.  
168 Concerning the two foams, the PCL-based PU foam is rigid while the PTHF-based PU foam is  
169 much more flexible. Long building blocks based on polyethers bring a high mobility to the  
170 corresponding macromolecular architectures due to the flexible ether linkages(Barikani and  
171 Barmar, 1996). Thus, the comparison of the degradation of the two foams not only relies on the  
172 difference of chemical structures, polyester versus polyether, but also on the difference of  
173 mechanical behavior.

174 TPU coatings and PU foams were incubated 18 days at 37°C with buffer containing HBT  
175 (Negative control) and with buffer containing laccase and HBT (Lac HBT). After incubation,  
176 changes in the visual aspects are noticed. Polymers were weighted before and after the  
177 degradation to evaluate the weight loss. Yellowing is observed for both PCL- and PTHF-based  
178 TPU coatings (Figure 2a). The color change is more noticeable for the PCL-based TPU. Weight  
179 losses of 7.2 and 17.2% were measured for the negative control and the Lac HBT of the PCL-  
180 based PU, respectively. Weight loss is in the range of 1% for the PTHF-based TPU incubated with  
181 both buffer and Lac HBT (Figure 2b).

182 For the PCL-based PU foam, an erosion of the cube corners with the buffer and with the  
183 enzymes can be noticed. There is no observable difference between the negative control and  
184 the foam incubated with Lac HBT. Weight losses are 8.6 and 12.1% for the negative control and  
185 the Lac HBT, respectively. A brown color appears on the PTHF-based foam incubated with Lac  
186 HBT in comparison to the foam incubated with the buffer that remained white. Weight losses  
187 are 1.7 and 2.3% for the negative control and the Lac HBT, respectively.

188 Important weight losses measured for the PCL-based PU negative control for both coating and  
189 foam, may be the result of slight hydrolysis in the buffer at 37°C. For the foam, this  
190 phenomenon is obviously combined with the release of micro pieces due to the fragmentation  
191 of the cube mainly coming from physical stress. This foam is rigid and a little bit crumbly  
192 resulting in mechanical erosion of the cube corners. Despite the bias of the negative controls,  
193 differences of weight losses with PCL-based foams incubated with Lac HBT are significant.  
194 Consequently, LMS increases the degradation of the PCL-based PU foam and might induce the  
195 release of water-soluble degradation products.

196 Degradation of the PTHF-based PU coatings is not detected through weight loss measurement.  
197 However, the yellow color might suggest the occurrence of degradation, but still too low to  
198 induce a significant weight loss. In a previous study, we already noticed a yellow color after the  
199 attested enzymatic degradation of a polyurethane (Magnin et al., 2019a). For the PTHF-based  
200 PU foam, a significant weight loss seems to indicate a degradation of the corresponding PU.

201 The weight loss measurement suggests a significant degradation for the foams and not for the  
202 TPU. Complementary analyses must be performed to validate these observations. However,  
203 there is no other common analytical technique for TPU coatings and PU foams. As PU coatings  
204 can be solubilized in organic solvents, SEC was performed to appraise the evolution of the molar  
205 mass after degradation with Lac HBT. We first compared the elution profiles of one  
206 representative replicate of each sample. All the chromatograms are presented in Figure S1 in  
207 the Supplementary Information (SI). Oligomers of a molar mass around 300 g/mol appear in  
208 both TPU coatings degraded with Lac HBT. Zooming in on the main peak of the molar mass  
209 distribution reveals a slight shift towards lower molar mass for the PU incubated with Lac HBT in  
210 comparison to the negative control (Figure 3). For the PCL-based coatings, a decrease in the  
211 population of chains with masses between 1000 and 10000 g/mol can also be noticed.

212 To assess the significance of these observations, the number average molar mass ( $M_n$ ), the  
213 mass average molar mass ( $M_w$ ) and dispersity ( $\mathcal{D}$ ) were compared. Increase of  $M_n$ , no change of  
214  $M_w$  and decrease of  $\mathcal{D}$  are measured for the PCL-based PU coating. Decrease of both  $M_n$  and  
215  $M_w$  and increase of  $\mathcal{D}$  are noticed for the PTHF-based PU coating.

216 Oligomers detected at 300 g/mol may be degradation products. It has already been shown that  
217 oligomers remain entrapped on polymer surface after degradation leading to the appearance of  
218 a new peak in SEC (Magnin et al., 2019a). Slight but significant differences between the negative  
219 control and the Lac HBT for both polymers demonstrate that the PU was degraded by the LMS.  
220 However, mechanisms of degradation seem to differ. LMS appears to act on the low molar mass  
221 polymer chains of the PCL-based PU coating. These oligomers are reduced into soluble  
222 degradation products that are removed and contribute to the weight loss previously described.  
223 Removal of the oligomers induces an increase of the  $M_n$ , since it is more sensitive to low molar  
224 mass polymer chains, and a decrease of  $\bar{M}_w$ . Degradation of the poly(ether urethane) is shown by  
225 a decrease of both average molar masses,  $M_n$  and  $M_w$ . The weight loss and the molar mass  
226 measurement seem to indicate a more efficient degradation on the PCL-based TPU than on the  
227 PTHF-based TPU.

228 Hydrolytic enzymes have already shown efficient degradation on PCL-based TPU. A weight loss  
229 of 35% has been reported after 50 days of incubation with an esterase (Magnin et al., 2019a). In  
230 the present study, the degradation measured after 18 days of incubation is slight and seems to  
231 be lower than degradation with hydrolases. However, even if the degradation of poly(ester  
232 urethane) is limited in the studied conditions, this is a very promising result in the objective of  
233 having a recycling route common to different types of PU materials. Enzymatic degradation of a  
234 thermoplastic poly(ether urethane) with hydrolases has also been described (Campinez et al.,  
235 2013; Christenson et al., 2006; Ferris et al., 2010). Yet, in these studies, isocyanates are aliphatic  
236 and linear to make the polymers more prone to hydrolysis. The model described in the present  
237 study is synthesized with aromatic isocyanate and is then closer to real PU waste.

238 As foams are cross-linked polymers, they cannot be solubilized in solvents and analyzed by SEC.  
239 Other techniques must be developed to complete the weight loss and aspect evaluation.  
240 Scanning Electron Microscopy, compression test and FT-IR were performed on foams degraded  
241 with LMS. The same analyses were carried out on foams degraded with UV to mimic LMS  
242 degradation.

243 A qualitative evaluation of the degradation was performed with microscopic observation. To  
244 avoid analyzing surfaces simply eroded by the shaking, a slice was cut in the core of the foam for  
245 microscope observation. Even if efforts were made to observe samples that are representative  
246 of the enzymatic degradation, SEM images can easily be biased as only a small piece of material  
247 can be observed. For the PCL-based PU foam, few holes are observed at the surface of the cells  
248 walls. These holes are absent in the negative control. Holes observed in the PTHF-based PU  
249 foam incubated with the laccase HBT are larger and more widespread, even leading to the  
250 opening of the cells. Comparison can be performed with UV-degraded foams (Figures S2 and S3  
251 from SI). Similar holes are observed in the middle of cells for both polymers. As for the  
252 enzymatic degradation, holes on the PTHF-based PU foam are larger and more widespread than  
253 those on the PCL-based PU foam. This observation is not consistent with the higher weight loss  
254 measured for the PCL-based PU foam. As SEM observations are performed on a slice cut in the  
255 middle of the foam cube, it is possible that the diffusion of enzymes was better in the PTHF-  
256 based PU foam than for the PCL-based PU foam leading to widespread holes even in the middle  
257 of the cube. The PCL-based PU foam may have a greater degradation on the surface.

258 Thanks to SEM observations, we can notice that both foams initially have closed cells. This  
259 morphology (desired for insulation foams) probably limits the enzyme diffusion to the core of

260 the foam pieces, especially for the PCL-based PU foam. Open-cell foams might be more prone to  
261 enzymatic degradation because of better access of enzymes to the polymer surface.

262 Due to the alteration of the integrity of the 3D structures of the foams, we can hypothesize  
263 that mechanical properties of the foams will be affected. To test this hypothesis and to evaluate  
264 the evolution of these mechanical properties, compression tests were performed in the foam  
265 rise direction, before and after incubation. To consider the difference of behavior and rigidity,  
266 the more rigid PCL-based PU and softer PTHF-based PU foams were compressed at 10 and 50%,  
267 respectively. Figure 5a shows hysteresis of compression for one replicate of each sample. All the  
268 compression curves are available in Figure S4 and S5 (in SI). For the PCL-based PU foam, a  
269 decrease of the stress is measured after incubation with the buffer and with the Lac HBT. This  
270 decrease is higher for the sample incubated with the Lac HBT. After a comparable slope at the  
271 beginning of the compression test, a decrease of stress when reaching the plateau is observed  
272 after incubation for the negative control and the Lac HBT. As for the PCL-based PU, the decrease  
273 is higher for the Lac HBT. To quantify the change in mechanical properties, the parameter that  
274 has been chosen is the value of the maximum stress (after 18 days) expressed as a % of the  
275 initial value (Figure 5b). For the PCL-based PU, the mean maximal stress is reduced to 95% of  
276 the initial value for the negative control. A higher evolution (89% of the initial value) is obtained  
277 with the Lac HBT. For the softer PTHF-based foam, the maximum stress is reduced to 87% and  
278 77 % of the initial value with the negative control and the Lac HBT, respectively. Compression  
279 tests were also performed on UV-degraded foams. The poly(ester urethane) foam presents a  
280 higher maximal stress (at 10% strain) after degradation while the poly(ether urethane) foam  
281 shows a lower maximal stress (at 50% strain) after 9 days of UV treatment (Figure S6 from SI).

282 The increase in maximal stress for the PCL-based PU may be the result of crosslinking induced  
283 by UV (Yang et al., 2010). Mechanisms seems then to differ between LMS and UV treatment of  
284 poly(ester urethane). The significant decreases in maximum stress after enzymatic incubation  
285 for both PU foams validate the initial hypothesis saying that alteration of the structure shown by  
286 SEM is the result of enzymatic degradation and can be measured by compression assay.

287 FT-IR analysis was also performed on the PU foams to detect specific chemical functions that  
288 may help us elucidate the degradation mechanisms. To compare the intensities of signals,  
289 curves were normalized according to the peaks at  $1595\text{ cm}^{-1}$  corresponding to the stretching  
290 vibration of the aromatic (C=C) which is assumed not to be altered during degradation  
291 (Yarahmadi et al., 2017). All the spectra are available in Figure S7 (from SI). No difference is  
292 observed between the negative control and the sample incubated with laccase HBT for the PCL-  
293 based PU foam. For the PTHF-based PU foam, several peaks at specific wavelengths display  
294 slight variations between the negative control and the foam incubated with Lac HBT. Peaks at  
295  $1655$  and  $1530\text{ cm}^{-1}$  tend to increase for the foam incubated with Lac HBT in comparison to the  
296 negative control while signals at  $1410\text{ cm}^{-1}$  and  $1365\text{ cm}^{-1}$  tend to decrease for the Lac HBT  
297 (Figure 6a). However, these observations may seem inconsistent and raise the question of the  
298 significance of the variations. To confirm these trends, mean of the intensities of the three  
299 replicates (three different samples treated or not with LMS) was calculated for the Lac HBT and  
300 the negative control (Figure 6b). Changes in the intensities are small but significant between  
301 samples incubated with the buffer and with the Lac HBT.

302 Similar analysis was performed on the PU foam submitted to UV radiation degradation for 9  
303 days (Figure S8 in SI). Interpretation of the UV treatment appears more straightforward. The



304 signal at  $1530\text{ cm}^{-1}$  accounts for the N-H deformation and C-N stretching vibration of the  
305 urethane group (Bruckmoser and Resch, 2014) and the signal at  $1100\text{ cm}^{-1}$  is attributed to the C-  
306 O-C elongation (Scholz et al., 2019). Both decrease after UV alteration tending to show that  
307 ether and urethane linkages are altered. In parallel, the signals at  $1650\text{-}1750\text{ cm}^{-1}$  and  $3300\text{ cm}^{-1}$   
308 increase. They correspond respectively to carbonyl groups (C=O) and -NH/-OH. New moieties of  
309 carboxylic acids, aldehydes or ketones, alcohol and amines seem to appear during degradation.  
310 The only common variation between enzymatic and UV treatment is the increase of the signal at  
311  $1655\text{ cm}^{-1}$ . Carbonyl groups may also be released in the case of enzymatic degradation. The  
312 band at  $1365\text{ cm}^{-1}$  corresponds to the (CH<sub>2</sub>) bending vibration of the methylene groups next to  
313 the oxygen atom of ether function (Wilhelm and Gardette, 1998). The decrease of this signal for  
314 samples incubated with Lac HBT could be explained by the degradation of polyether segment.  
315 However, no change is measured for the band at  $1100\text{ cm}^{-1}$  assigned to the C-O-C elongation.  
316 The differences and conflicting observations made on FT-IR analyses between enzymatic and UV  
317 treatment highlight the need for a more pronounced enzymatic degradation to obtain clearer  
318 variations in IR spectra. The only hypothesis that can be formulated is that the polyether  
319 segment is more impacted by enzymes than the urethane parts of the polymer.

320 Till now, the biological degradation of PU foams has been mainly described with  
321 microorganisms such as bacteria, fungi or microbial communities (Álvarez-Barragán et al., 2016;  
322 Cregut et al., 2014; Gautam et al., 2007b). Poly(ester urethane) foams have been submitted  
323 once to enzymatic degradation (Ng et al., 2017) and our paper describes for the first time the  
324 enzymatic degradation of a poly(ether urethane) foam. The advantage of the enzymatic  
325 degradation compared to microbial one is the availability of valuable degradation products after

326 enzymatic depolymerization. Indeed, microbial degradation leads to a consumption of  
327 degradation products for microbial growth making this process suitable for bioremediation but  
328 not for biological recycling/upcycling. Moreover, enzymatic degradation is easier to control and  
329 is more reproducible than microbial degradation. Enzymes such as laccases are already  
330 produced at an industrial level and commercially available.

### 331 **Conclusion**

332 Four PU were successfully synthesized and submitted during 18 days to a degradation step with  
333 laccase and HBT as a mediator. For the TPU, SEC analysis revealed a decrease in molar masses  
334 for all the PU. For the foams, weight loss, compression test and microscope observations  
335 revealed that both polyester- and polyether-based PU foams were altered by the enzymatic  
336 degradation.

337 Degradation conditions (pH, temperature, -agitation rate...) used in this experiment were mainly  
338 based on a study which describes the efficient laccase degradation of synthetic polymers  
339 (Fujisawa et al., 2001). As the results presented in this paper shows slight degradation, these  
340 conditions must be optimized to obtain a better degradation of PU materials. Moreover, some  
341 pathways -could be investigated to improve the degradation. For instance, combination of  
342 degrading enzymes such as amidases and esterases with the present laccase could lead to a  
343 more complete depolymerization of PU material. Combination of this biological process with  
344 physical process (grinding into powder) or chemical degradation (glycolysis) can be explored as  
345 well.

346 Consequently, this study describes the enzymatic degradation of four model PU representative  
347 of actual PU waste. Enzymatic degradation of polyurethanes with laccase-mediated system  
348 could be a powerful tool for the deconstruction of a large variety of PU materials. After  
349 improving degradation efficiency, the recovery of building blocks after LMS treatment will be  
350 the next step in the development of a global PU biorecycling pathway. Such a green process will  
351 hopefully contribute to the reduction of PU pollution, which is particularly critical in the oceans.  
352 Moreover, economical value can be generated for PU foam and building industries which has  
353 currently no proper way for PU waste disposal.

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358 Koenig for providing polymer materials.

#### 359 [Supporting information](#)

360 Procedure for polymer synthesis, full data of SEC chromatograms/FT-IR spectra/Compression  
361 test of PU degraded with enzymes and analysis of UV degraded polymers are available in  
362 Supporting Information (SI).

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365 Notes: The authors declare no competing financial interest.

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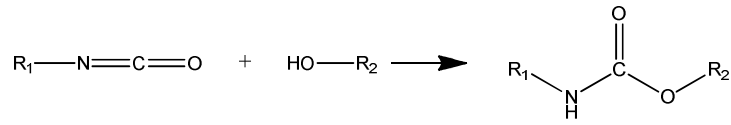
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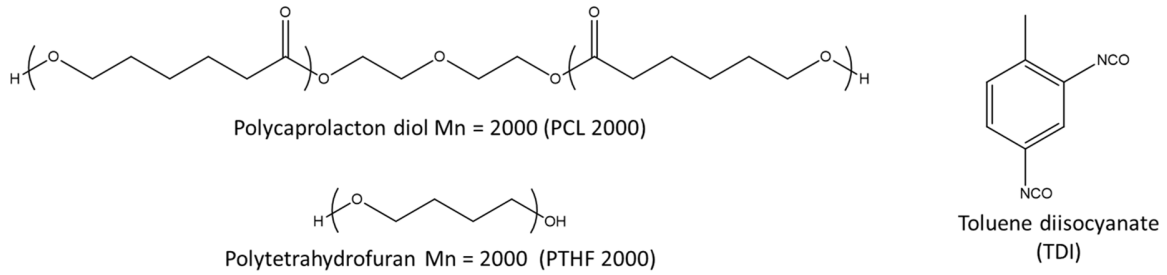
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Figure 1 – Synthesis of the urethane linkage from an alcohol and an isocyanate

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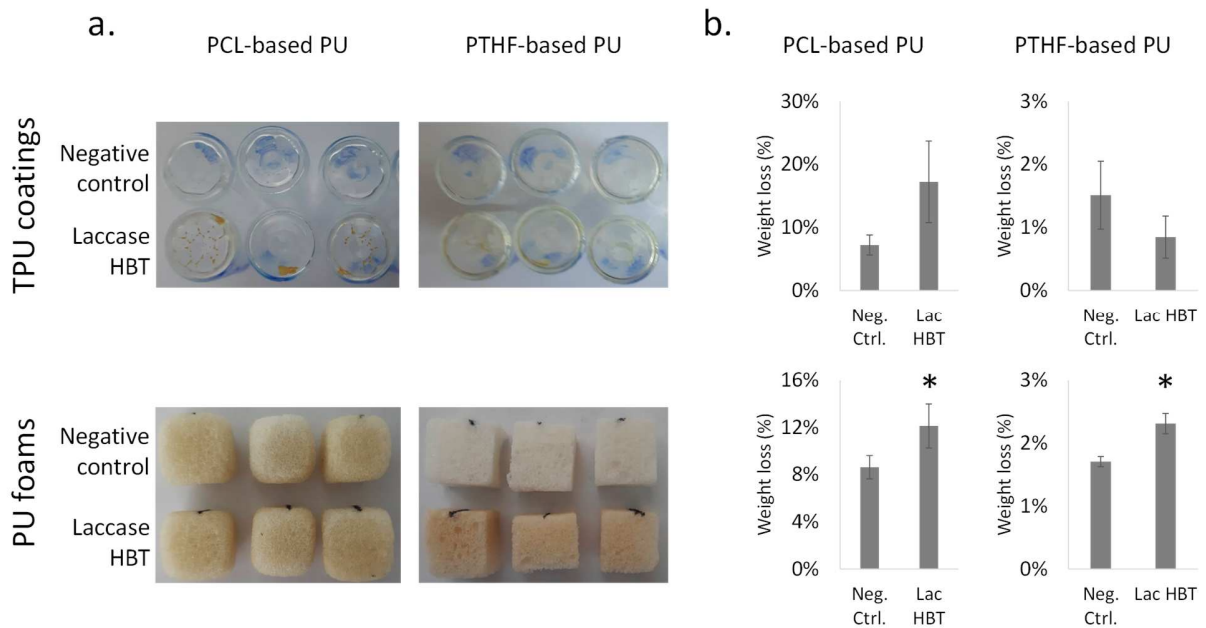


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Figure 2 – Molecular structure of PU building blocks

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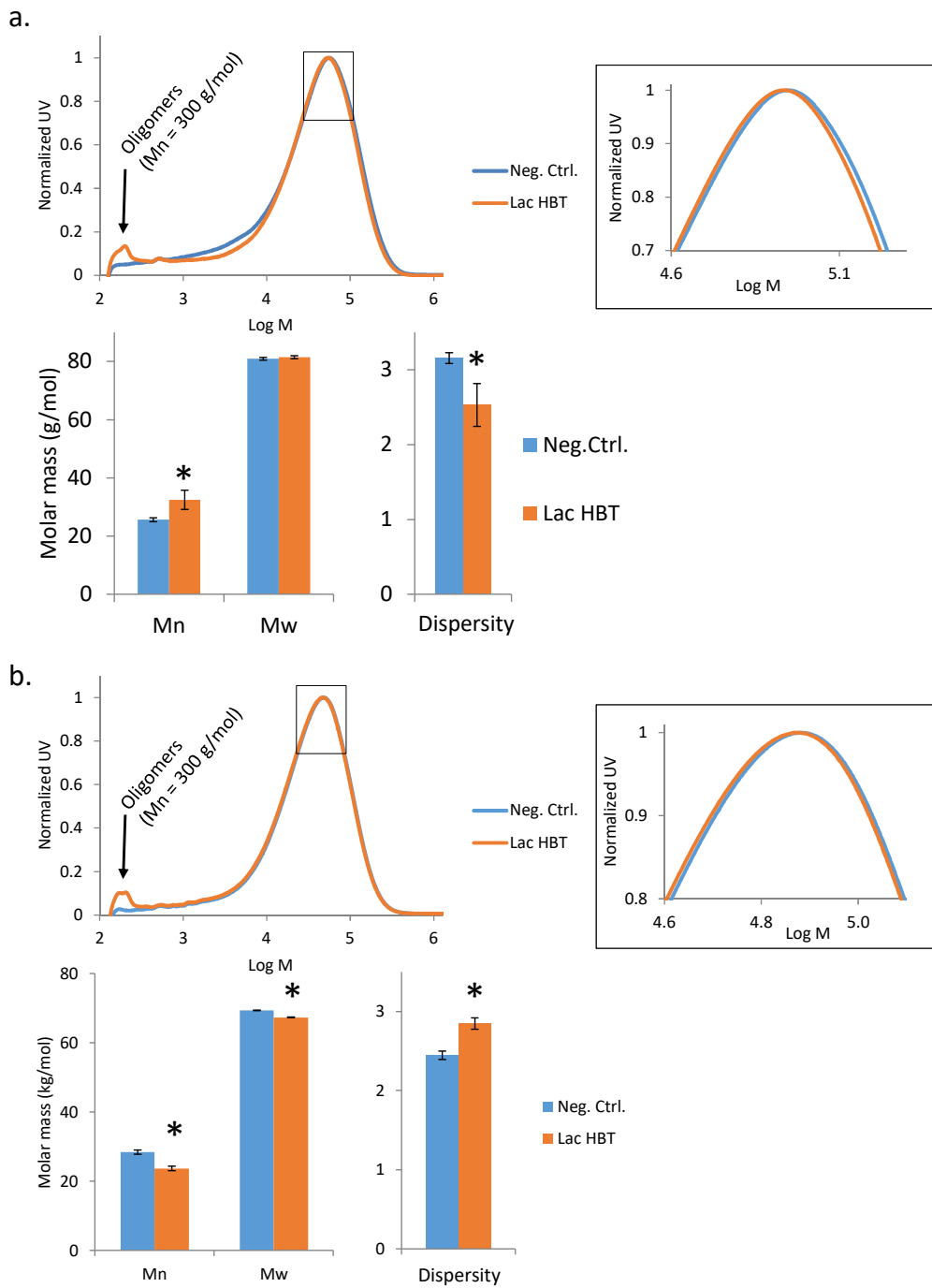
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Figure 3 – (a) Visual aspect of the polyurethanes and (b) weight loss after 18 days of incubation with LMS in comparison with a buffer without enzymes for the TPU coatings (top) and PU foams (bottom) (n=3)

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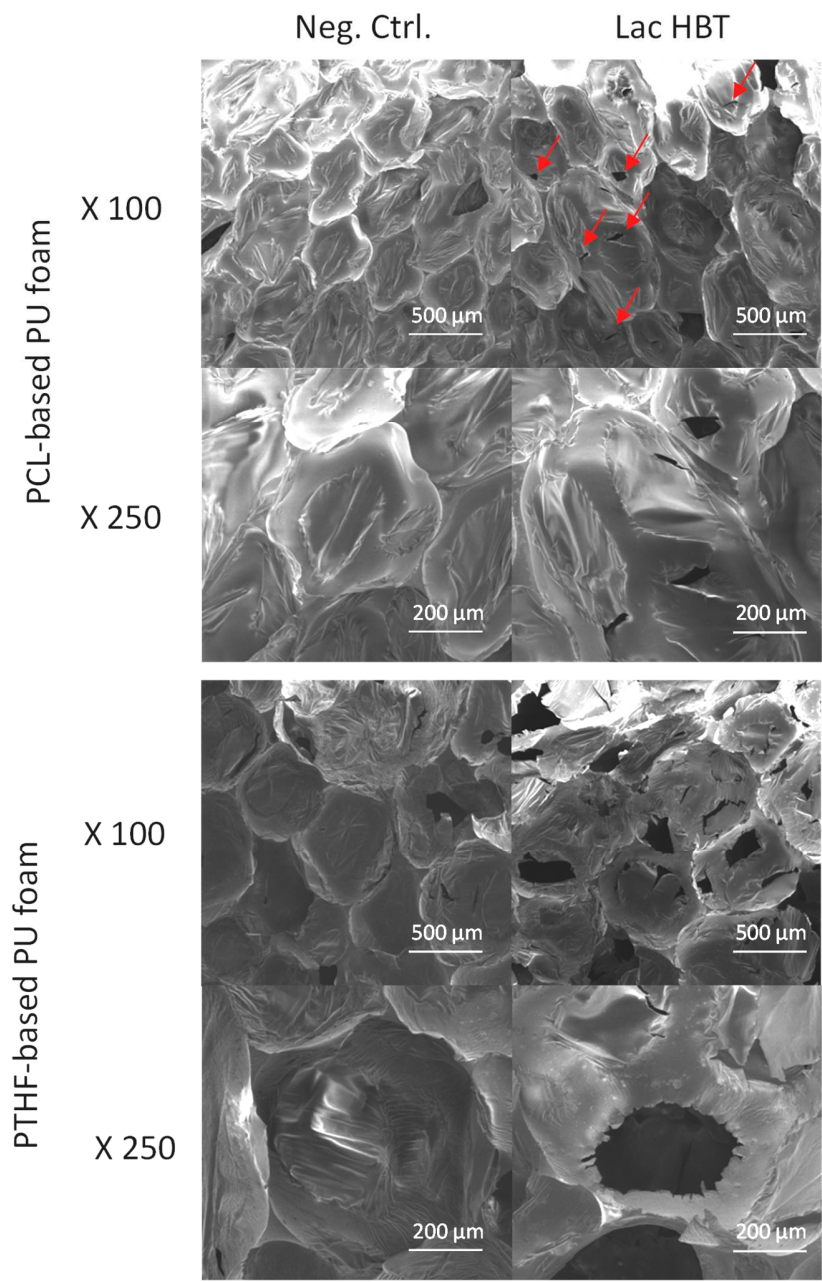


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475 *Figure 4 – Size Exclusion Chromatography analysis of (a) PCL-based TPU and (b) PTHF-based TPU*

476 ( $n=3$ )





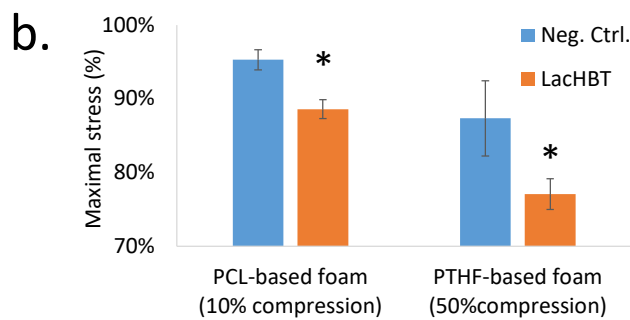
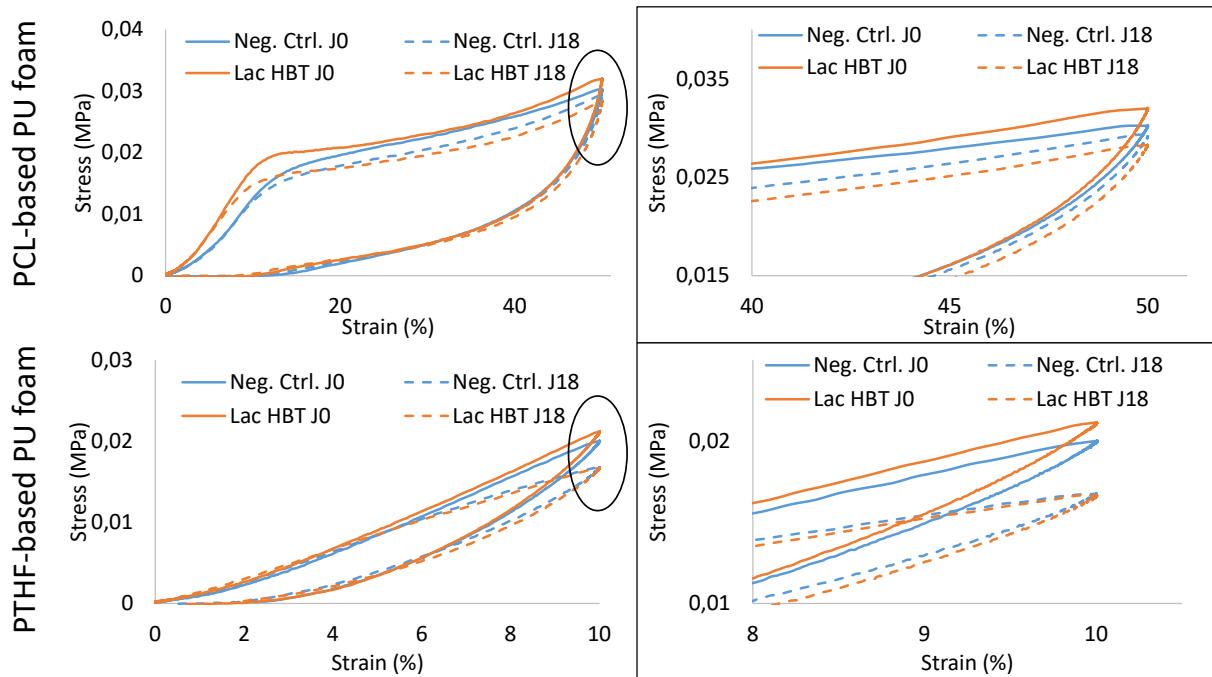
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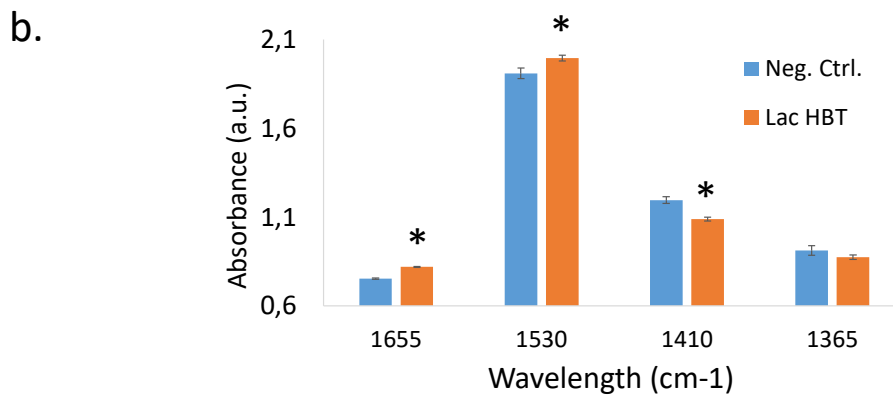
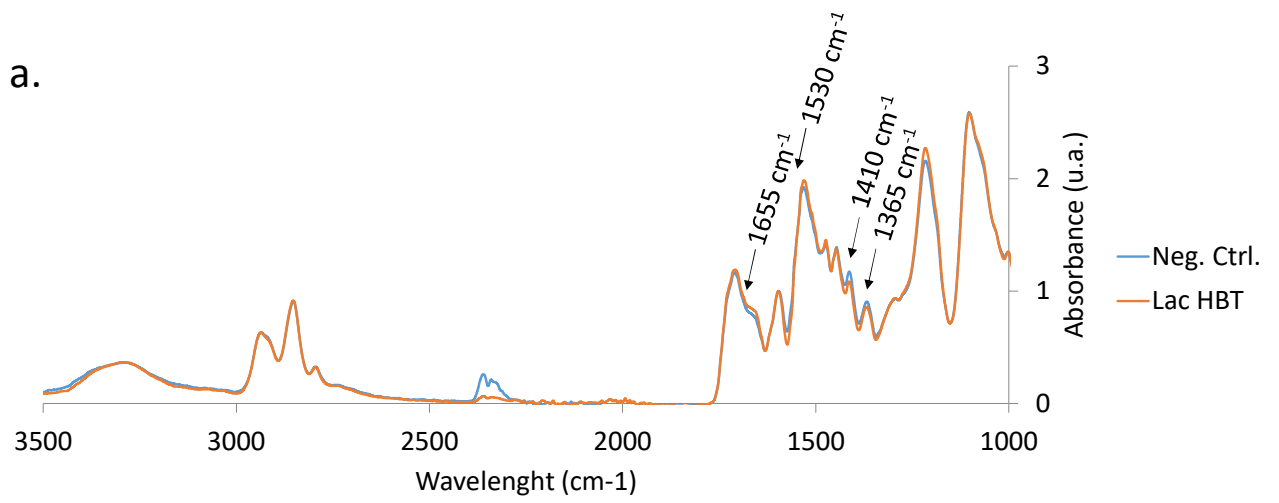
*Figure 5 – Scanning Electron Microscopy observation of the PU foams*



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482 *Figure 6 – (a) Compression tests performed on PU foams before and after degradation (left),*  
 483 *focus on the maximal stress at 50% and 10% (right) and (b) evaluation of the maximal stress at*  
 484 *10% for the PCL-based PU foam and 50% for the PTHF-based PU foam (n=3)*

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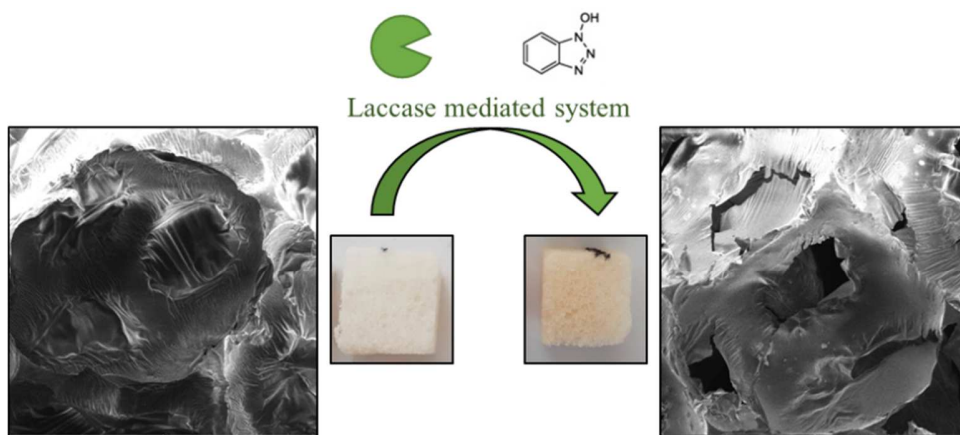


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487 *Figure 7 – (a) FT-IR analysis of the PTHF-based PU foam and (b) IR intensities of specific*  
 488 *wavelengths (n=3)*

489

490 **Graphical Abstract:**



Enzymatic depolymerization of poly(ether urethane) foam

491

492 Text: Enzymatic depolymerization of poly(ether-urethane foams