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# Oxidative biodegradation of a solid-solid polyether-urethane phase change material by *Penicillium* and *Aspergillus*

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1           **OXIDATIVE BIODEGRADATION OF A SOLID-SOLID POLYETHER-**  
2           **URETHANE PHASE CHANGE MATERIAL BY PENICILLIUM AND**  
3           **ASPERGILLUS**

4  
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14  
15           **Abstract**

16 Polyurethane-based polymers are widely used in modern materials and as Phase Change  
17 Materials (PCMs) to improve the energy efficiency of buildings. The fungal development in  
18 buildings is favoured by the degradation of polymeric materials that act as nutritional substrates.  
19 In the present study, the fungal biodegradation of a polyether-urethane PCM (PUX1520) was  
20 investigated. Two methods of biodegradation by fungal growth on agar and in liquid media  
21 were used. Fungal growth on agar plates was monitored by measuring the surface area of each  
22 mycelium over a period of 11 days. The degradation products of PUX1520 were analysed by  
23 FT-IR and MALDI-TOF. The PUX1520 polymer had no impact on the growth of *Aspergillus*  
24 *niger*, while the growth of *Penicillium* sp. was increased in the presence of PUX1520. MALDI-  
25 TOF analysis revealed the existence of different soluble forms of the polymer whose  
26 concentration decreased after exposure to the fungal strains. From FT-IR analysis on the  
27 residual polymer material, an oxidation process is proposed to describe the dissociation of the  
28 urethane functions.

29           *Keywords:* Phase change material, Polyurethane, Polymer biodegradation, *Aspergillus*,  
30           *Penicillium*

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36 **Highlights**

37 - *Penicillium* sp. is able to use PUX1520 as the sole carbon source.

38 - Biodegradation of the PUX1520 polymer occurs after the growth of *Penicillium* sp. and *A.*  
39 *niger* in a liquid medium.

40 - IR analysis of PUX1520 after mould growth reveals an oxidative degradation process.

41

## 43 1. Introduction

44 Phase change materials (PCMs) are technologies able to reduce the energy required for  
45 heating and cooling indoor environments [1]. Reversible phase changes are  
46 endothermic/exothermic transitions that can be used to store and release thermal energy.  
47 This capacity of heating storage has been investigated for several decades because of its  
48 potential to passively contribute to the temperature regulation in housing. PUX1520 is a  
49 solid-solid PCM that has been developed for this purpose [2]. This material is a semi-  
50 crystalline, cross-linked polyether-urethane. The cross-linked structure allows (i) to  
51 maintain it in a solid-state during phase changes at temperatures below 80°C, and (ii) limit  
52 the solubility of the material in water. This PCM has been designed to be incorporated into  
53 hydraulic based building materials such as plaster boards, concretes or mortars. The  
54 durability of those composites must be the same as that of the building. Microorganisms,  
55 which are present in the indoor environment, can damage building materials. Moulds, for  
56 example, have the ability to grow onto and/or within building materials and it is common  
57 to observe fungal growth on damp walls and roofs [3,4]. Mould colonisation represents a  
58 major issue in buildings facing moisture problems. They are unesthetic and unhealthy for  
59 inhabitants [5–9]. Fungal development depends on three main parameters: temperature,  
60 humidity and the presence of organic nutrients. In nature, biopolymers containing carbon,  
61 nitrogen or phosphorus are transformed into more user-friendly raw materials by  
62 microorganisms [10]. Thus, microorganisms biodegrade natural organic materials  
63 (cellulose starch, lignin) found in wood, paper or certain textile fibres. The degradation  
64 processes involve the secretion of microbial extracellular enzymes such as lipases,  
65 esterases, cellulases [11]. The degradation products of the polymers can then serve as a  
66 nutritional substrate for microbial growth [12–15]. Biodegradation can also occur with  
67 synthetic polymers (polyglycolic acid, polylactic acid, and polyurethanes in particular), and  
68 their blends. Unlike polyethylene and polystyrene, which have little or no biodegradability,  
69 polyurethanes can be vulnerable to microbial attack [16,17]. According to their chemical  
70 structure, polyurethanes are more or less sensitive to biodegradation. For example,  
71 polyester-urethanes are more susceptible to microbial biodegradation than polyether-  
72 urethanes [16], and many examples of polyester-urethane attacked by bacteria or fungi are  
73 described in the literature [13,14,18–24]. Biodegradation of polyester-urethanes has been  
74 reported for various fungi such as *Chaetomium globosum*, members of the *Cladosporium*  
75 *cladosporioides* complex, *Alternaria* sp., *Aspergillus flavus*, *Aspergillus fumigatus*,  
76 *Aspergillus tubingensis*, *Penicillium chrysogenum*, *Curvularia senegalensis*, or  
77 *Pestalotiopsis microspore* [13,14,18–24]. The mechanism proposed for the degradation of  
78 polyester-urethanes involves hydrolysis of the ester bond and/or the urethane group by the  
79 action of an esterase enzyme [13,23,25]. The current literature on the biodegradation of  
80 polyether-urethanes is more scarce, especially for moulds [13,18,26].

81 The objectives of this study were to evaluate and characterise the biodegradation of the  
82 polyether-urethane PUX1520 by ubiquitous moulds that are commonly found in housing.  
83 The growth of moulds on agar media incorporating PCM was measured. By separating the  
84 biomass from the polymer using a microfiltration membrane, we performed an FT-IR  
85 analysis of the polymer without biomass contamination. FT-IR analysis revealed which  
86 functions of the polymer have undergone degradation, providing a better understanding of  
87 the biodegradation process. In addition, MALDI-TOF analysis of the soluble fraction of the

88 polymer revealed its structure and confirmed its degradation during mould growth in liquid  
89 media.

## 90 **2. Materials and methods**

### 91 2.1. *Materials*

#### 92 2.1.1. *PUX1520 synthesis*

93 The PUX1520 polymer was synthesized according to Harlé *et al.* 2019 [2] from Polyethylene  
94 glycol (PEG, Mn = 1500g/mol) and glycerol (purity  $\geq$  99%) provided by Carl Roth GmbH +  
95 Co<sup>TM</sup> and hexamethylene diisocyanate (HMDI) provided by VWR<sup>TM</sup> (purity  $\geq$  99%). Briefly,  
96 after PEG melting, HMDI and glycerol were added at 60 °C under argon atmosphere. The  
97 reaction, which lasted 45 min, was followed by post-curing for 4 hours at 100 °C. After cooling  
98 down, the hardened material was crushed into 300 to 600  $\mu$ m size powder using a knife mill in  
99 order to be incorporated and scattered in agar media.

100

#### 101 2.1.2. *Growth media*

102 The different media used for mould growth contained water, a nutritional base in the form of  
103 malt extract (ME) at a low concentration (one tenth of the usual concentration), and/or  
104 polyether-urethane PUX1520. Agar was added at 1.5% for cultures on petri dishes. Agar and  
105 ME were supplied by Difco<sup>TM</sup>. PUX1520 powder was scattered into supercooled agar at 55°C  
106 and the mixture was poured and solidified at room temperature in 9 cm diameter petri dishes.  
107 Four types of agar media with the following compositions were prepared and used for growth  
108 tests: (i) 1.5 wt% agar in distilled water (nutrient-free medium named “Agar”); (ii) Agar + 5  
109 wt% PUX1520 (medium with PUX1520 as sole nutrient source); (iii) Agar + 0.5 wt% ME  
110 (medium with ME as sole nutrient source); (iv) Agar + 0.5 wt% ME + 5 wt% PUX1520  
111 (medium with ME and PUX1520 as nutrient sources). The broth culture medium for  
112 biodegradation tests contained 0.5 wt% ME + 5 wt% PUX1520 (medium with ME and  
113 PUX1520 as nutrient sources). The growth medium used to obtain precultures of moulds was  
114 Agar + 5 wt% ME.

#### 115 2.1.3. *Mould strains*

116 The *Aspergillus niger* and *Penicillium* sp. strains, previously isolated from a contaminated  
117 building, were stored in cryotubes at -20 °C. The moulds were collected from cryogenic tubes,  
118 spread on agar media and incubated for 5 days at 24 °C. Samples of mycelium from these pre-  
119 cultures were collected, spread again on the same new medium and incubated for 5 days at 24  
120 °C. Finally, calibrated fragments of mycelium were sampled with a circular punch and  
121 inoculated into the centre of each of the 4 types of culture media for growth tests. The culture  
122 media were then incubated for at least 11 days at 24°C. 9 replicas were realized for each culture  
123 medium and each mould strain. Statistical differences in the results were determined by an  
124 unpaired t-test. Results were considered statistically significant when  $P < 5\%$ .

125 For FT-IR analysis, a 0.45  $\mu$ m Durapore<sup>®</sup> membrane filter, the same diameter as the petri  
126 dishes, was added to the surface of each culture medium before inoculation. This membrane  
127 prevents the fungal biomass to blend with the growth medium. After inoculation, mycelia were  
128 removed by taking off the membrane and the growth media were dried at 60°C for 48 h before  
129 IR analysis.

130 For MALDI-TOF analysis, suspensions of fungal spores were prepared in a sterile 0.9% NaCl  
131 solution by scraping the surface of *Penicillium* sp. or *A. niger* precultures incubated for 20 days  
132 at 24°C. After spore collection by centrifugation, the suspensions were calibrated at a  
133 concentration of 10<sup>3</sup> spores per ml in broth containing ME and PUX1520 at concentrations  
134 indicated above and incubated for 4 weeks at 24°C. After growth, the culture supernatant was  
135 harvested by centrifugation and sterilised by filtration at 0.45 µm before MALDI-TOF analysis.

#### 136 2.1.4. Growth measurement and FT-IR analysis

137 The surface area of each mycelium was measured with the Imagej software from images taken  
138 at different times during incubation at 24°C. Each growth experiment was repeated three times  
139 for each mould and culture medium. Infrared analyses were performed from spectra obtained  
140 using a Tensor 27 IR spectrophotometer with a resolution of 2 cm<sup>-1</sup> (Bruker Optics, Marne la  
141 Vallée, France). The spectra were normalized to the C-O-C peak at 1100 cm<sup>-1</sup>.

#### 142 2.1.5. MALDI-TOF analysis

143 MALDI-TOF analyses were performed with a Bruker Biflex III equipped with a nitrogen laser  
144 ( $\lambda = 337$  nm). Mass spectra were recorded in reflection mode with an accelerating voltage of  
145 20 kV. Dithranol was used as matrix and sodium trifluoroacetate was used as dopant. The  
146 irradiation targets were prepared from dichloromethane + trifluoro acetic acid solutions.

147

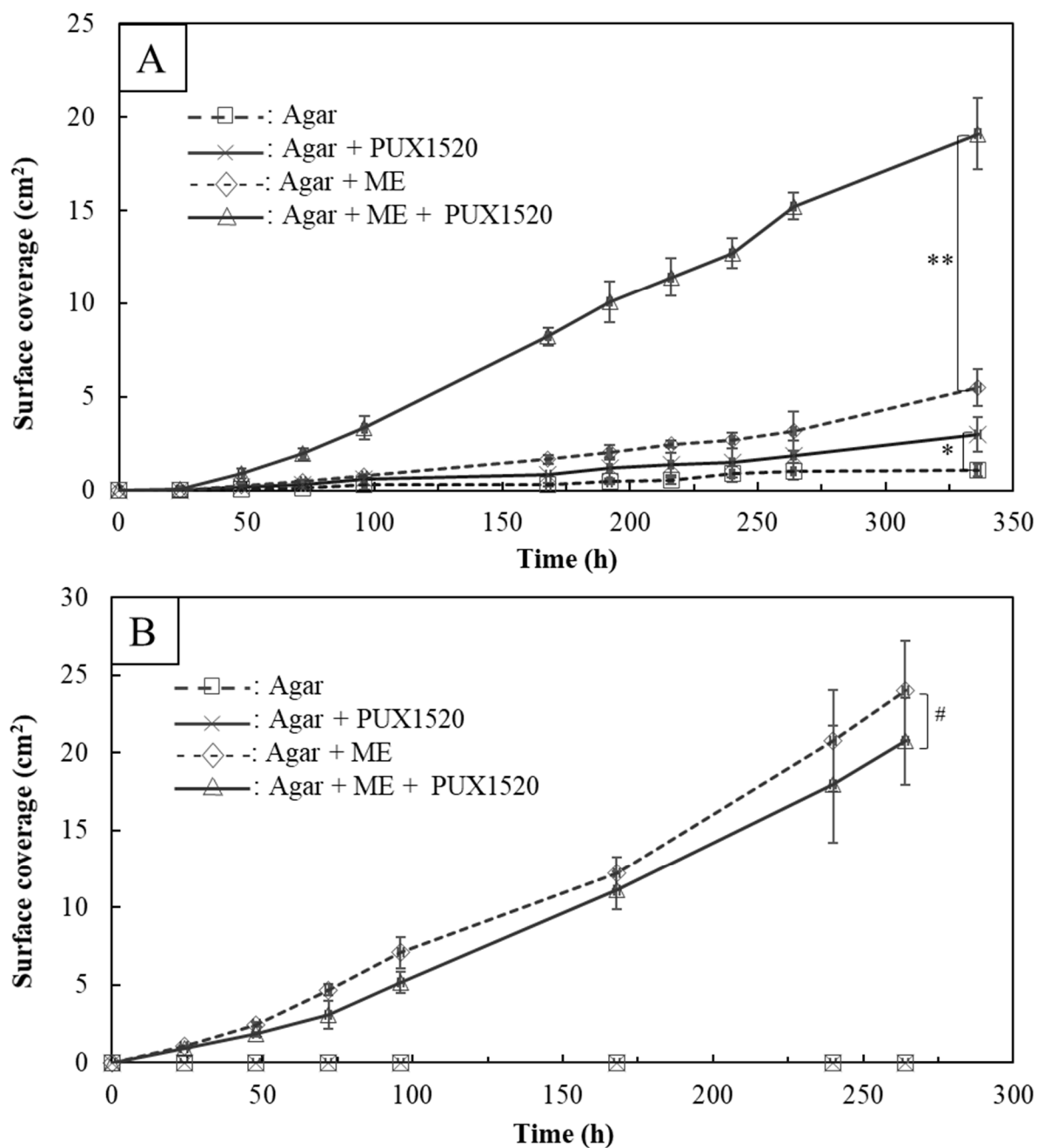
### 148 3. Results and discussion

#### 149 3.1. Fungal growth on agar media

150 The aim of this study was to determine the sensitivity of the polyether-urethane PUX1520, a  
151 phase change material developed for thermal regulation in buildings, to the fungal degradation  
152 by strains of *Penicillium* sp. and *Aspergillus niger*. To test the effect of PUX1520 on fungal  
153 growth, we incorporated it into agar culture media. The evolution of the growth of *Penicillium*  
154 sp. and *A. niger* over time on different growth media with and without the PUX1520 is shown  
155 in Fig. 1. The shape of the growth curves varied according to the nutrient medium used and the  
156 moulds tested. *A. niger* grew only on media containing malt extract (ME) whether PUX1520  
157 was present or not (Fig. 1B). This behaviour indicates that *A. niger* was not able to use  
158 PUX1520 as a nutrient. *Penicillium* sp. grew to a greater or lesser extent on all culture media  
159 (Fig. 1A). A lag phase was systematically observed for *Penicillium* sp., varying from 24 hours  
160 on the richest medium containing agar, ME and PUX1520 to 168 hours on the poorest medium  
161 containing only agar. On the growth medium containing only agar, the growth of *Penicillium*  
162 sp. was limited as it was observed just around the inoculum. A linear regression of growth  
163 curves was used to evaluate the growth rate. The growth rate of *Penicillium* sp. was 0.003 cm<sup>2</sup>/h,  
164 0.007 cm<sup>2</sup>/h, 0.013 cm<sup>2</sup>/h, and 0.054 cm<sup>2</sup>/h, in agar medium, agar medium containing  
165 PUX1520, agar medium containing ME, agar medium containing ME and PUX1520,  
166 respectively. The presence of PUX1520 resulted in faster and greater growth of *Penicillium* sp.  
167 in the presence or absence of ME, indicating that *Penicillium* sp. was able to use PUX1520 as  
168 the sole nutrient source. The growth rate of *A. niger* was 0.084 cm<sup>2</sup>/h, and 0.072 cm<sup>2</sup>/h on agar  
169 medium containing ME, and agar medium containing ME and PUX1520, respectively. On the  
170 other hand, the presence of PUX1520 did not show any effect on the growth of *A. niger*.

171

172



173

174 **Fig. 1.** Growth of *Penicillium sp.* (A) and *Aspergillus niger* (B) on agar plates of different  
 175 culture media over time. ME, malt extract. PUX1520, polyether-urethane phase change  
 176 polymer. Statistical differences were determined by an unpaired t-test. \* P < 0.05; \*\* P <  
 177 0.00002; # P > 0.18.

178

### 179 3.2. FT-IR analysis

#### 180 3.2.1. FT-IR spectra of Agar and PUX1520

181 The FT-IR spectrum of the agar molecule has been extensively reported in the literature [27–  
 182 33]. Agar is a polysaccharide chain extracted from the class of algae Rhodophyceae. This  
 183 molecule is composed of repeating units of galactose and has mainly carbon, hydrogen and  
 184 oxygen atoms in its chemical structure. However, sulphur and nitrogen can be detected as

185 residual elements. The sulphur is known to be present in the form of a monoester sulphate  
186 substituted for the C-6, C-4 or C-2 carbons of galactose. The presence of sulphur depends on  
187 the species of algae and the extraction method. The reference FT-IR spectrum of the agar used  
188 in this study is shown in Fig. 2A and the assignments of the agar signals in the spectrum are  
189 listed in Table 1. The signal at  $890\text{ cm}^{-1}$  was attributed to the presence of sulphate-ester bonds.  
190 The characteristic peaks present at  $1040$  and  $930\text{ cm}^{-1}$  came from the 3,6 anhydro-galactose  
191 bridges. The bands at  $1370$  and  $1150\text{ cm}^{-1}$  were also linked to the presence of sulphate-ester  
192 bonds. The band around  $1630\text{ cm}^{-1}$  corresponded to a stretching vibration of a peptide bond  
193 formed by amine (NH) and acetone (CO) groups. The amine functions were present because of  
194 residual proteins. Finally, the signal around  $2880\text{ cm}^{-1}$  was due to the stretching vibration of  
195  $\text{CH}_2$ .

196 PUX1520 is a polyether-urethane composed of polyethylene glycol chains polymerized and  
197 cross-linked through urethane bonds. Its reference FT-IR spectrum did not show any peak  
198 related to the NCO isocyanate functions at  $2300\text{ cm}^{-1}$  (Fig. 2A). The absence of remaining NCO  
199 suggested it was completely consumed during the synthesis of the PCM, which means that the  
200 reaction was complete. The signal at  $1710\text{ cm}^{-1}$  indicated the presence of a carbonyl group  $\text{C}=\text{O}$   
201 coming from a urethane bond. The band at  $1615\text{ cm}^{-1}$  came from the N-H deformation of  
202 urethanes. The bands at  $1570$  and  $1530\text{ cm}^{-1}$  were induced by urethane N-H bending or urethane  
203 CN stretching vibrations. In addition to the bands showing the presence of urethane links, other  
204 major peaks were identified. The bands present at  $2870$ ,  $1465$  and  $1330\text{ cm}^{-1}$  were related to  
205  $\text{CH}_2$  stretching, bending and wagging vibrations, respectively. The signals at  $1275$  and  $1240$   
206  $\text{cm}^{-1}$  were due to a combination of C-O-C asymmetrical stretching, CN stretching and  $\text{CH}_2$   
207 twisting. The major band at  $1100\text{ cm}^{-1}$  was related to the C-O-C stretching and at  $1080\text{ cm}^{-1}$  to  
208 the C-O stretching in C-O-C=O of urethane. Finally, the bands at  $960$  and  $840\text{ cm}^{-1}$   
209 corresponded to the aliphatic chains (C-C) vibrations. The transmission bands of PUX1520  
210 interfered very little or not at all with those of the agar and came from different functions.

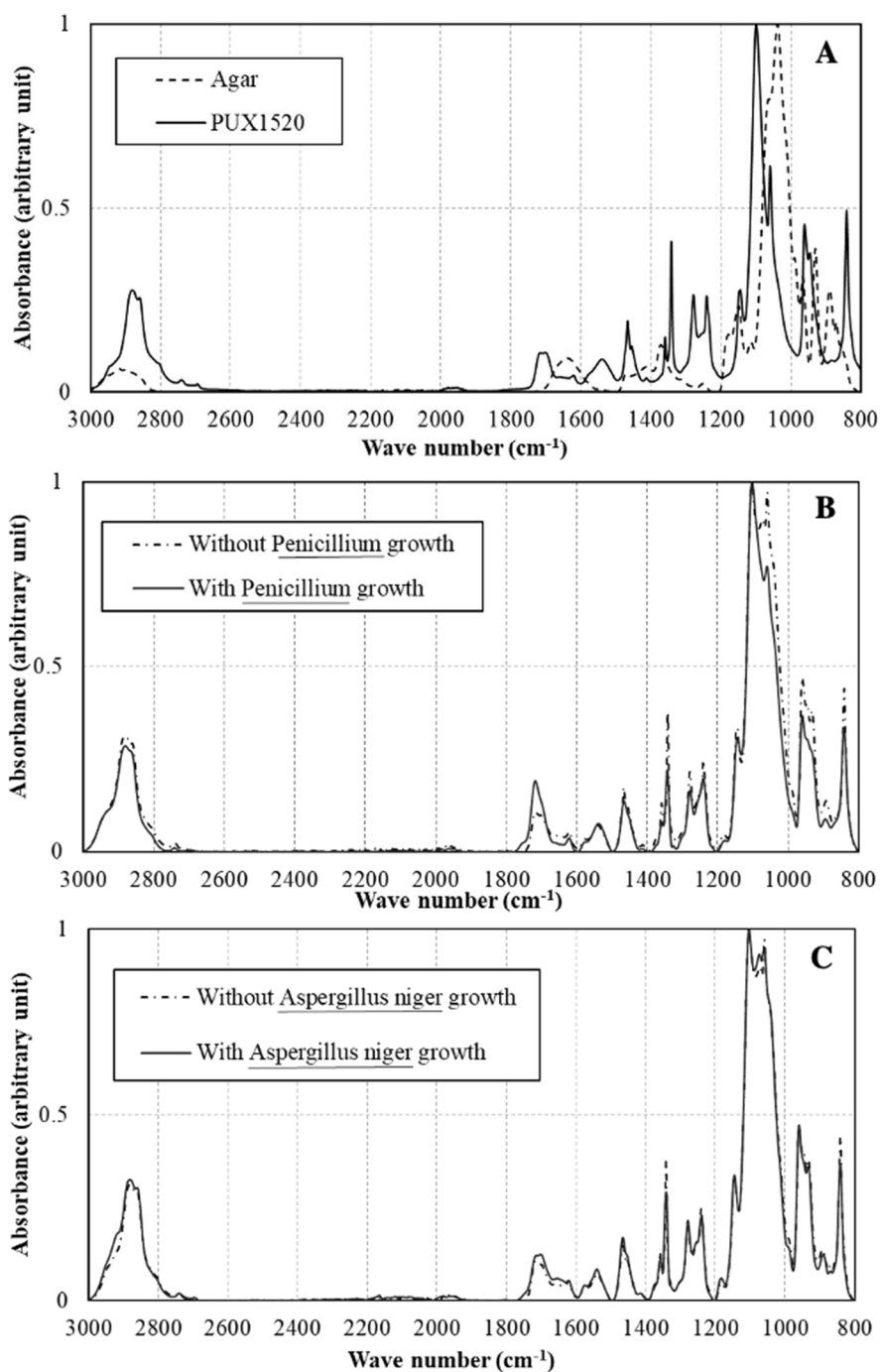
211

### 212 3.2.2. FT-IR spectra of agar medium incorporating PUX1520

213 The FT-IR spectra of the growth medium containing agar and PUX1520 with and without  
214 fungal growth are shown in Fig. 2B and 2C. Most of the absorption bands were the same as  
215 PUX1520 alone ( $2870$ ,  $1465$  and  $1330\text{ cm}^{-1}$  bands related to  $\text{CH}_2$  vibrations,  $1710\text{ cm}^{-1}$  from  
216 urethane  $\text{C}=\text{O}$  vibration,  $1570$  and  $1530\text{ cm}^{-1}$  from urethane nitrogen vibrations and bands at  
217  $1275$ ,  $1240$  and  $960\text{ cm}^{-1}$ ). Two differences were observed at  $1080$  and  $960\text{ cm}^{-1}$  where bands  
218 were larger due to the presence of signals at  $1040$  and  $930\text{ cm}^{-1}$  related to 3,6- anhydro-galactose  
219 vibrations from agar. Thus, in the mixture of agar and PUX1520, agar signals did not mask the  
220 FT-IR bands of PUX1520 and did not disrupt analysis of changes in the PUX1520 spectrum  
221 due to biodegradation. For the FT-IR analysis of agar media after fungal growth, microfiltration  
222 membranes were used to separate the biomass from the media during growth. This allowed to  
223 analyse the chemical composition of the growth media without interfering with the IR signals  
224 of the biomass. However, fungal metabolites and in particular enzymes are able to pass through  
225 the pores of the membrane and diffuse into the growth medium. The presence of fungal enzymes  
226 could lead to an increase in the NH bending vibration and the CN stretching vibration at around  
227  $1500 - 1600\text{ cm}^{-1}$ , which constitutes in the amide II signal of proteins. The decrease of both  
228 signals at  $1570$  and  $1615\text{ cm}^{-1}$  after *Penicillium* sp. growth showed that this was not the case.  
229 Significant differences in the intensities of the  $890$ ,  $960$ ,  $1080$ ,  $1240$ ,  $1275$ ,  $1330$ ,  $1465$ , and



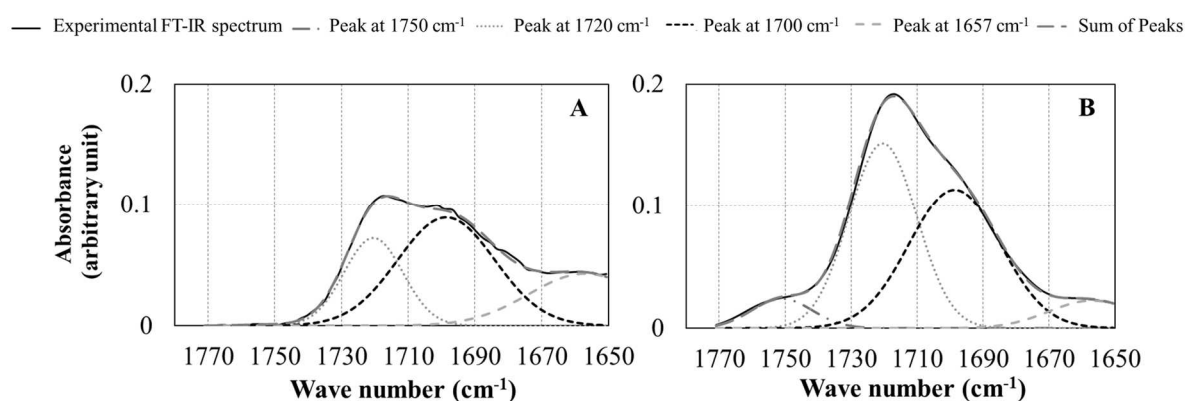
230 1710  $\text{cm}^{-1}$  bands were also observed after *Penicillium* sp. growth. All these bands were  
231 decreased except for the signal at 1710  $\text{cm}^{-1}$  that increased in intensity. The absorption band at  
232 1530  $\text{cm}^{-1}$  showed no variation in intensity. For this reason, the 1530  $\text{cm}^{-1}$  IR signal was used  
233 as the internal standard to calculate the ratio corresponding to the relative IR signals of  
234 PUX1520 (Table 1). The main modified function of the PUX1520 is the carbonyl group which  
235 IR signal was strongly increased. Several other functions of the polymer showed a significant  
236 decrease in the relative intensity of their IR band, such as C-C, C-O-C,  $\text{CH}_2$ , CN, and NH.



237

238 **Fig. 2.** FT-IR spectra of agar and PUX1520 alone (A), FT-IR Analysis of the agar + PUX1520  
239 medium with and without fungal growth (B and C).

240 A more detailed spectrum of the absorption band between 1650 and 1770  $\text{cm}^{-1}$  corresponding  
 241 to the carbonyl group is presented in Fig. 3. The deconvolution of this spectrum highlighted the  
 242 presence of a band at 1720  $\text{cm}^{-1}$  corresponding to the non-hydrogen-bonded C=O in urethane  
 243 function and of two bands at 1700  $\text{cm}^{-1}$  and 1660  $\text{cm}^{-1}$  related to the hydrogen-bonded C=O in  
 244 urethane function. After *Penicillium* sp. growth, the signal at 1720  $\text{cm}^{-1}$  increased and became  
 245 dominant, and a new signal at 1750  $\text{cm}^{-1}$  corresponding to additional non-hydrogen-bonded  
 246 C=O carbonyl functions appeared. The chemical changes of the PUX1520 after *Penicillium* sp.  
 247 growth indicated an oxidative degradation of the polymer [34–37]. This oxidation reaction led  
 248 to an increase in carbonyl groups, especially those non bonded to hydrogen, and a decrease in  
 249 the  $\text{CH}_2$  band and C-O band in the urethane C-O-C=O (Fig. 2B). The increase in the C=O  
 250 absorption band has been observed previously during the biodegradation process of Tecoflex<sup>®</sup>  
 251 commercial polyether-urethane by *Bacillus subtilis*, *Pseudomonas fluorescens*, *Pseudomonas*  
 252 *denitrificans*, and *Yarrowia lipolytica* [34]. This increase in carbonyl band was associated with  
 253 a decrease in the intensity of the NH signals indicating urethane-bond hydrolysis. We also  
 254 observed such a decrease in NH signal and CN bond during the biodegradation process of  
 255 PUX1520 by *Penicillium* sp. (Fig. 2B, Table 1). Biodegradation of PEG/castor oil-based  
 256 polyether-urethane polymers by *Chaetomium globosum* has also been reported to conduct to  
 257 increase of carbonyl functions [38]. In this case, the formation of hydrogen bonds occurred after  
 258 the molecular chain of the urethane bonds was broken. The ether linkage was not degraded  
 259 unlike the urethane bond upon *C. globosum* growth. The dissociation of the ether linkage in  
 260 polyether-urethanes occurs mainly through the formation of vinylic double bond (C=C) and  
 261 vinylic ether [35]. We did not observe any increase of vinylic functions around 1620  $\text{cm}^{-1}$  in  
 262 the IR spectrum of the degraded PUX1520, which suggested that ether bonds were not  
 263 degraded. Ether bonds are the main components of the crystalline domains of PUX1520. The  
 264 lack of dissociation of ether bonds in PUX1520 is consistent with previously published data  
 265 showing that crystalline parts of a polyurethane polymer are less prone to biodegradation [39].  
 266



267  
 268 **Fig. 3.** Deconvolution of the FT-IR spectra of agar + PUX1520 without (A) and with (B)  
 269 *Penicillium* sp. growth.

270 The FT-IR spectra of agar media incorporating PUX1520 before and after *Aspergillus niger*  
 271 growth are shown in Fig. 2C. Only slight differences in the intensities of the 890, 1330, 1530,  
 272 1570, and 1710  $\text{cm}^{-1}$  bands were observed between the two conditions. Again, the IR signal of  
 273 the carbonyl group was increased, and the IR signal of C-C and  $\text{CH}_2$  wagging were decreased.

274

275 **Table 1.** Assignments of the agar and PUX1520 signals in the corresponding FT-IR spectra  
 276 and quantitative evolution of the different signals with *Penicillium* sp. growth.

Wave number (cm <sup>-1</sup> )	Agar	PUX1520	Evolution with growth of <i>Penicillium</i> sp. (%) *
2880	CH <sub>2</sub> stretching	-	
2870	-	CH <sub>2</sub> stretching	-9
1710	-	C=O urethane H-Bounded	+72
1615	-	Hydrogen bound from NH	-31
1570	-	CN stretching / NH bending from urethane	-24
1530	-	CN stretching / NH bending from urethane	0
1465	-	CH <sub>2</sub> bending	-21
1330	-	CH <sub>2</sub> wagging	-42
1275	-	C-O-C asymmetrical stretching/ CN stretching/ CH <sub>2</sub> twisting	-20
1240	-	C-O-C asymmetrical stretching/ CN stretching/ CH <sub>2</sub> twisting	-20
1100	-	C-O-C asymmetrical and symmetrical vibrations	0
1080	-	C-O stretch in C-O-C=O from urethane	-21
1040	3,6- anhydro-galactose	-	
960	-	C-C stretching	-22
930	3,6- anhydro-galactose	-	
890	-	C-C stretching	-24

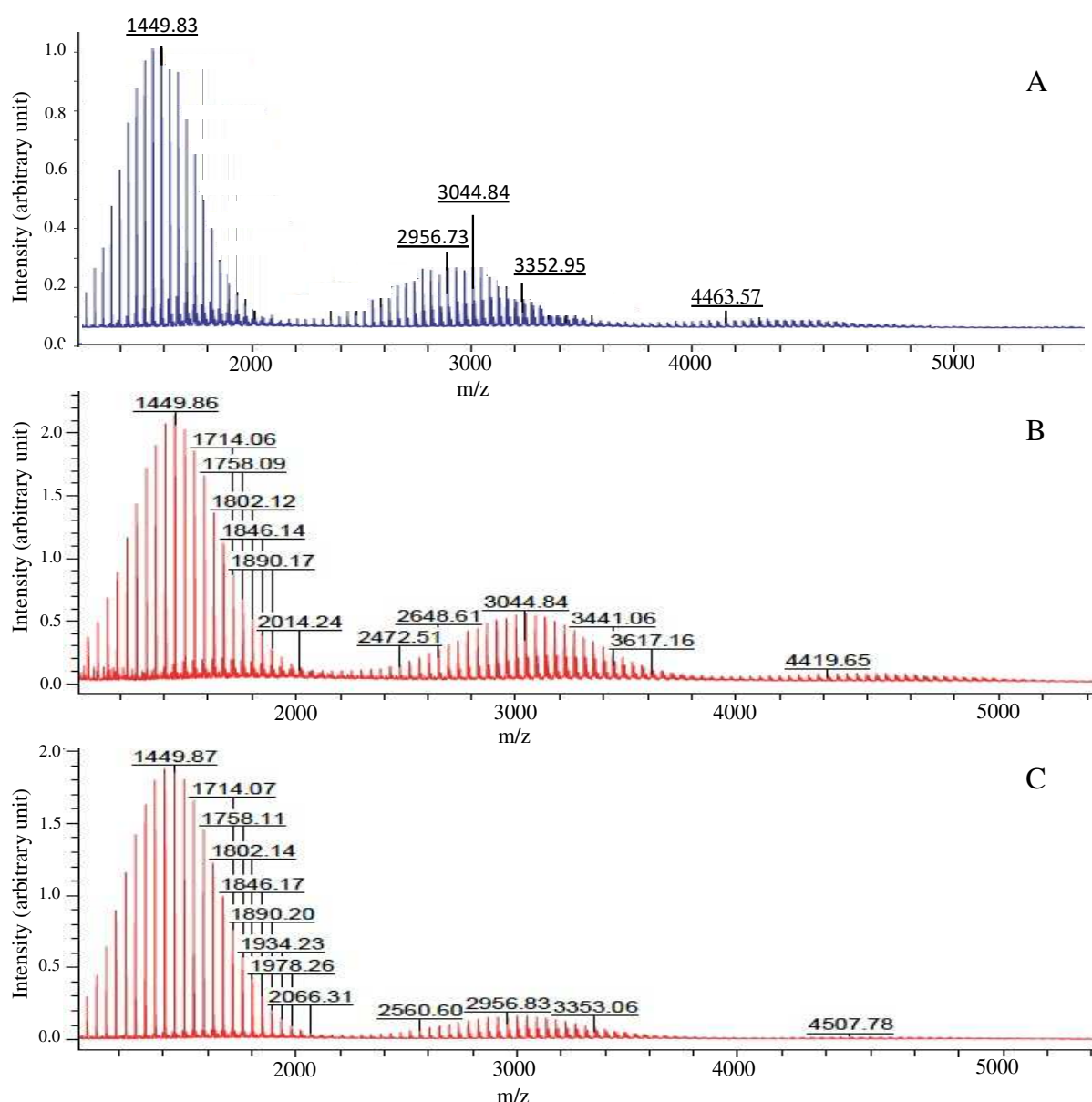
277 \* Evolution of the relative intensity of IR signals after *Penicillium* sp. growth compared to their  
 278 intensity before fungal growth.

### 279 3.3. MALDI-TOF analysis

280 In addition to unreacted PEG (signal around 1449, corresponding to the weight of PEG + Na<sup>+</sup>),  
 281 the MALDI-TOF mass spectrum revealed the presence of different polymer structures of  
 282 PUX1520 in the soluble fraction (Fig. 4 and Fig. 5). The expected structure was present and  
 283 showed a major signal around 3089. The formation of some complex polymer structures could

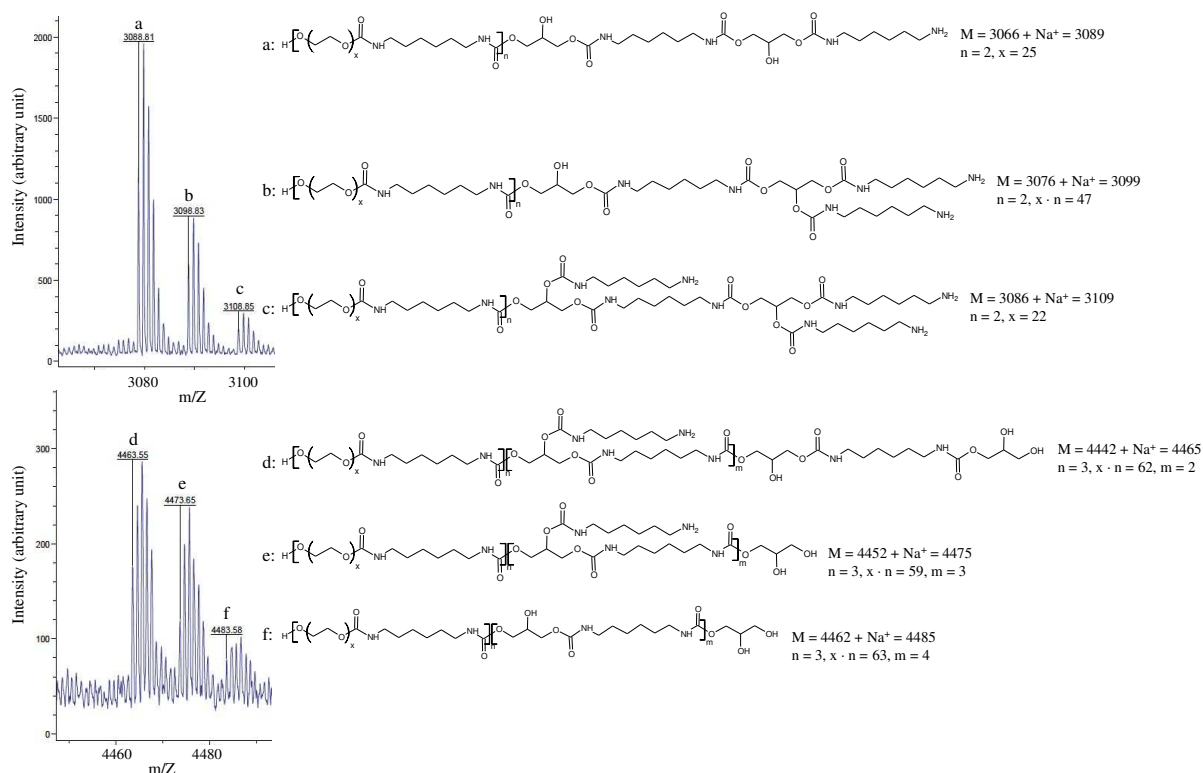
284 be related to a partial hydrolysis of HMDI during synthesis due to residual moisture. The PEG  
 285 signal at 1449 was used as a reference to calculate the relative signals of the polymer structures  
 286 (Table 2). Thus, the relative intensity of the polymer form with an m/z of 3089 decreased by  
 287 17% after exposure to *Penicillium* and by 49% after exposure to *A. niger*. The relative intensity  
 288 of the polymer form with an m/z of 4463 decreased by 30% after exposure to *Penicillium* and  
 289 by 23% after exposure to *A. niger*. No new structures were detected in the MALDI-TOF  
 290 spectrum after fungal exposure for these molecular weight ranges. This suggests that the  
 291 degraded soluble molecules were completely degraded, and that the degraded molecules of the  
 292 insoluble phase remained associated with the polymer particles.

293



294

295 **Fig. 4.** MALDI-TOF mass spectrum of sodium cationized species  $(M + Na)^+$  for polyurethane  
 296 PUX1520 incubated alone (A), with *Penicillium* sp. (B), or with *Aspergillus niger* (C) for 4  
 297 weeks at 24°C.



299

300 **Fig. 5.** Zooms of the MALDI-TOF mass spectrum of sodium ionized species  $(M + Na)^+$  for  
 301 PUX1520 and the different corresponding polymer structures.

302 **Table 2.** Relative intensity of PUX1520 with and without exposition to moulds in liquid  
 303 medium containing malt extract (ME). The PEG signal at 1449 was used to calculate ratio  
 304 corresponding to the relative signals of polymer structures.

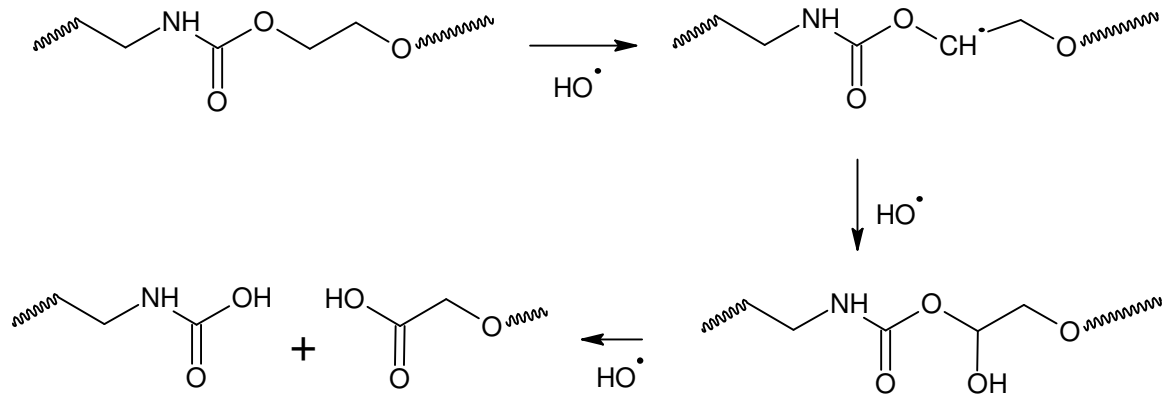
	Ratio	Ratio
	$I_{3089}/I_{1449}$	$I_{4465}/I_{1449}$
PUX1520 + ME	0.361	0.038
PUX1520 + ME + <i>Penicillium</i> sp.	0.300	0.026
PUX1520 + ME + <i>Aspergillus niger</i>	0.184	0.029

305

### 306 3.4. Proposed mechanism for the biodegradation of PUX1520

307 The mechanism for the biodegradation of PUX1520 by *Penicillium* sp. is proposed in Figure 6.  
 308 The degradation of urethane functions during fungal attack should be linked to the production  
 309 of a hydroxyl radical by the microorganism, causing the loss of a hydrogen atom at the  $\alpha$ -  
 310 methylene of the chain extender of the urethane bond as described previously [40, 41]. Then  
 311 another additional hydroxyl radical can combine with the chain radical to form a carbonyl-

312 hemiacetal. Subsequently, the chain scission and formation of a carbamic acid and carboxylic  
313 acid end groups occurs.



315 **Fig. 6.** Mechanism of the oxidative degradation of the urethane bond of PUX1520.

316

#### 317 **4. Conclusions**

318

319 Two biodegradation susceptibility tests in solid and liquid media were used to assess the  
320 durability of the solid-solid phase change material PUX1520 in the presence of moulds. For  
321 this purpose, PUX1520 powder was dispersed in different growth media which were inoculated  
322 with moulds. Using these protocols, it was possible to demonstrate that (i) PUX1520 can be  
323 used as the sole nutrient for the growth of *Penicillium* sp. but not for the growth of *A. niger*; (ii)  
324 biodegradation of the PUX1520 polymer occurs after the growth of *Penicillium* sp. and *A. niger*  
325 in a liquid medium; (iii) biodegradation of the polymer after the growth of the moulds occurs  
326 through oxidation and loss of urethane bonds.

327 For housing applications, it would be relevant to perform this biodegradability test on composite  
328 materials consisting of a mineral matrix of cement or plaster and PUX1520. Chemical  
329 modifications of the PUX1520 polymer such as grafting of antioxidants could be designed to  
330 reduce oxidative degradation by moulds.

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332

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