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# 1 Relationship between chemical and mechanical degradation of 2 aged paper: fibre versus fibre-fibre bonds

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16  
17 **Abstract** Paper is susceptible to chemical degradation through hydrolysis and oxidation, resulting in  
18 embrittlement and failure. Understanding the embrittlement process is important to ensure the preservation and  
19 longevity of historical paper-based documents. However, the complex and architected paper microstructure is a  
20 major challenge for fully understanding this process. Two papers with different microstructures were artificially  
21 aged under hydrolytic and oxidative exposure conditions, and the consequences of ageing were studied. The fibre  
22 embrittlement, the fibre-fibre bonds deterioration, and the evolution of paper microstructure upon ageing are  
23 evaluated through macroscopic and localised mechanical tests, as well as through morphological observations at  
24 the microscopic scale. It was concluded, from the different tests in the two principal orientations of the paper, that  
25 fibre embrittlement plays a more significant role in the embrittlement process than fibre-fibre bonds deterioration.

26 Specifically, the cellulose chain scissions led to fibre embrittlement, irrespective of the oxidative or hydrolytic  
27 nature of the chemical degradation mechanism. Furthermore, we identify a critical degree of polymerisation for  
28 cellulose ( $DP_c \sim 750$ ) below which the evolution of mechanical properties accelerates significantly, regardless of  
29 the type of mechanical testing performed. Fibre analysis suggests that the decline in fibre resistance results in  
30 fractures occurring under stress at weak points of the fibres, such as kinks or twists.

31 **Keywords** Hydrolysis, Oxidation, Microstructure, Morphology, Tensile testing, Fibre orientation.

## 32 **1 Introduction**

33 Paper embrittlement is a major concern for the preservation of books and documents. Among the various aspects  
34 of paper ageing, mechanical resistance is of prime importance because it can seriously impede handling and  
35 reading. To address this issue, papers can be treated via a polymer network reinforcement, or lined on a more  
36 resistant paper substrate (Piovesan et al. 2018; Ferrandin-Schoffel et al. 2023). Permanent paper, which contains  
37 an alkaline reserve to slow down its ageing, can be used for long-term preservation and archival purposes (Frase  
38 1997). However, understanding the consequences of degradation on the mechanical behaviour of paper, and more  
39 specifically the role of the fibres and fibre-fibre bonds in the embrittlement process, can help to better formulate  
40 the papers and the treatments with the aim of improving durability. The objective of this study is to provide further  
41 insight into the correlation between chemical and mechanical ageing of paper, in order to understand how the  
42 chemical degradation under different ageing conditions affects its mechanical properties. In this regard, two papers  
43 with different microstructures were studied.

44 Paper is a structured material made from plant fibres, usually from wood, bast fibres plants or cotton. During the  
45 manufacturing process, the fibres are separated from each other by chemical and mechanical treatments, suspended  
46 in water, then dried in the shape of sheets (Young and Rowell 1986; Neimo 1999). The papermaking machine  
47 induces an orientation of the fibres in the sheet, conferring to the paper an anisotropic mechanical behaviour. The  
48 fibres are entangled and adhere to each other through fibre-fibre bonds. These bonds consist on different adhesion  
49 phenomena: weak bonds such as Coulomb forces, Van der Waals forces and hydrogen bonds, and molecular  
50 interdiffusion between the swollen fibres in contact, mechanical entanglement of the fibrils on the surface of the  
51 fibres (Hirn and Schennach 2015). These fibrils are produced by the refining process in order to increase the  
52 contact surface and the mechanical entanglement, and therefore the adhesion between fibres (Sampson and Wang  
53 2020). Moreover, the manufacturing process can induce defects along the fibre, such as kinks, or twists (Aslan et  
54 al. 2011; Ali 2012; Ciesielski et al. 2019; Richely et al. 2022). The characteristics of the fibres, including their

55 nature, length and diameter, as well as the density of the sheets and the degree of refining are parameters that can  
56 vary from one paper to another, and that can have a strong impact on the mechanical properties (Iribarne and  
57 Schroeder 2000; l'Anson et al. 2006; Kontturi et al. 2021). These parameters should be monitored in order to  
58 reveal the relevant physical parameters that govern the changes in the mechanical behaviour upon chemical  
59 degradation.

60 Paper also contains other plant fibre structures, especially fibres' fragments of small size called fines, defined as  
61 the fraction of the pulp stock that will pass a round hole 76  $\mu\text{m}$  in diameter (TAPPI standard method T 261 cm-  
62 00). They will be considered in this study, as they can have an impact on the mechanical strength of paper. Printing  
63 paper also contains additives, such as fillers and surface treatment products (Henniges et al. 2016), that can also  
64 impact mechanical behaviour.

65 However, the mechanical strength of paper is mostly determined by its structure, e.g., a random network of  
66 entangled fibres. The density of the network is responsible for contacts between fibres (Sampson 2001, 2009).  
67 They adhere to each other through deformable fibre-fibre bond (Iribarne and Schroeder 2000; Barbier et al. 2009)  
68 thanks to the phenomena described hereabove. The mechanical properties of paper are thus due to the strength of  
69 individual fibres, of fibre-fibre bonds, and to the entanglement between fibres.

70 Macroscopic mechanical properties can be obtained through tests such as compression, tensile tests or fatigue tests,  
71 which give information on the visco-elastoplastic behaviour of paper with damage (Haslach, Jr. 2000). Due to the  
72 orientation of the fibres in the sheet, these properties are determined in the two principal axes of the sheet (Kurei  
73 et al. 2022). However, to have access to the strength of individual fibres and fibre-fibre bonds, specific tests can  
74 be used, as for example tensile tests on unique fibres or adhesion tests on unique fibre-fibre bonds (Schmied et al.  
75 2012; Yue et al. 2019; Maraghechi et al. 2023). Obtaining individual fibres behaviour is challenging, especially  
76 because papers include a wide range of fibres dimensions. Moreover, it may not accurately mirror the actual stress  
77 within a paper under tensile test. Therefore, *in-situ* characterisation is necessary, and localised tests can be used.  
78 For example, the zero-span tensile test consists of pulling a paper strip with no gap between the jaws. It is  
79 considered that the pulling is exerted only on the fibres without loading the network (Gurnagul and Page 1989;  
80 Wathén et al. 2005; Batchelor et al. 2006). Similarly, water-saturated tensile test involves immersing the paper in  
81 water prior to testing, which results in the weakening of fibre-fibre bonds and favours fibre slippage.

82 Another approach consists in varying the structural parameters of paper and measure their impact on macroscopic  
83 properties to determine the contributions of fibre and fibre-fibre bonds resistance on the mechanical strength of

84 paper (Marulier et al. 2015; Deogekar et al. 2019). Authors have studied the morphology of fibres by cutting them  
85 before the papermaking process, as well as the strength of bonding through refining or adjoining additives to the  
86 pulp (l'Anson et al. 2006). The impact of fibres morphology has been correlated to the mechanical properties in a  
87 semi-empirical equation introduced by Page (Page 1969) (**equation 1**). In particular, this equation links tensile  
88 and zero-span tensile strength to the length of fibres and to the bonding areas. Such microstructure parameters can  
89 be obtained through microscopic observations or X-ray microtomography (Peyrega et al. 2009; Bache-Wiig and  
90 Henden 2010; Wernersson et al. 2014; Emerson et al. 2017). However, quantification from such images can be  
91 difficult due to insufficient resolution leading to incomplete fibre identification, especially for dense papers. The  
92 wide range of available tests and their limitations highlight the need for a comprehensive study at the different  
93 length scales.

94 Cellulose being the main polymer that composes paper fibres, its degree of polymerisation (DP) is a key parameter  
95 to be monitored during the ageing of paper. The chemical degradation under archival conservation conditions is  
96 mainly due to the hydrolysis of cellulose (Gehlen 2010; SriBala and Vinu 2014). However, for permanent papers,  
97 the kinetics of the acid-catalysed hydrolysis being slowed down by an alkaline reserve, the oxidation of cellulose  
98 cannot be neglected (Nevell and Zeronian 1985; Margutti et al. 2001; Potthast et al. 2006). These two degradation  
99 mechanisms have several impacts on paper, including cellulose chain scissions and a change in cellulose  
100 crystallinity, consequently affecting paper water content (Haas et al. 1967; Gehlen 2010; Driemeier et al. 2012).

101 In the literature, the impact of chemical ageing on the mechanical strength of paper has been evaluated mostly  
102 through tensile and zero-span tensile tests (dry and wet) and folding endurance tests (Emsley et al. 1997; Zervos  
103 and Moropoulou 2005; Carrascal et al. 2018; Kurei et al. 2022). A significant reduction in folding endurance as  
104 well as an embrittlement of paper is observed in both artificially and naturally aged paper (Wilson et al. 1955;  
105 Barrow and Sproull 1959; Horst et al. 2020). Based on Page's equation, Zou concluded that acid cotton paper  
106 embrittlement under accelerated ageing was due to a decrease of fibre strength (Zou et al. 1994). Kaminska  
107 demonstrated that the relationship between the number of cellulose chain scissions and the zero-span breaking  
108 strength was linear (Bégin and Kaminska 2002). Nevertheless, these studies focused on paper that underwent  
109 hydrolytic degradation, without considering the possible effects of oxidation, and only a few instances report on  
110 the latter (Arney and Jacobs 1980; Whitmore and Bogaard 1995).

111 In this study, the impact of the two reactions, *i.e.*, hydrolysis and oxidation, will be considered. Because these  
112 reactions are slow under natural ageing conditions, artificial ageing of paper can be used to obtain degraded states

113 (Bégin and Kaminska 2002; Strlič and Kolar 2005; Jeong and Potthast 2021). Although it does not exactly replicate  
114 natural ageing, this method remains valid to degrade paper since cellulose chain scissions are promoted in all cases.  
115 The aim of the study is to determine the impact of different exposure conditions on the mechanical behaviour of  
116 paper, and more specifically on the fibre strength, the fibre-fibre bonds resistance, and the microstructure of paper.  
117 Due to the large number of structural parameters that can be involved in the embrittlement process, this multi-  
118 scale approach is applied to two papers with different microstructures. The first part focuses on the evolution of  
119 macroscopic mechanical properties of paper under artificial ageing conditions that favour either hydrolysis or  
120 oxidation reactions. Secondly, this work intends to decouple the effects on the fibres and on the fibre-fibre bonds  
121 specifically. A third part is dedicated to the evolution of the fibre resistance and the fibre-fibre bonds at the  
122 microscopic scale, allowing to relate chemical changes to macroscopic mechanical behaviour.

## 123 **2 Experimental**

### 124 **2.1 Materials**

125 Two different papers were used for this study. One is a commercially available paper from Canson®, grade  
126 *Barrière*, referred herein as paper A. It meets the standard for paper permanence ISO 9706. It is made from  
127 bleached kraft pulp with a mix of 50 % of long fibres (softwood) and 50 % of short fibres (hardwood), and was  
128 refined, according to the supplier. It contains about 3 % wt. of alkaline mineral particles ( $\text{CaCO}_3$ ) to prevent the  
129 acidification. Other components, such as alkyl ketene dimer (AKD) sizing and kaolin are present in minute  
130 quantities. This paper was chosen because of its archival quality and essential durability for long-term preservation.  
131 The second paper is a filter paper Whatman n°40 made from acid-washed cotton linters (ashless grade), referred  
132 hereafter as paper B. It therefore contains only cellulose and has no additives. As opposed to paper A, it is acidic  
133 and thus prone to faster degradation. It was chosen as a model since widely studied in the paper degradation  
134 literature.

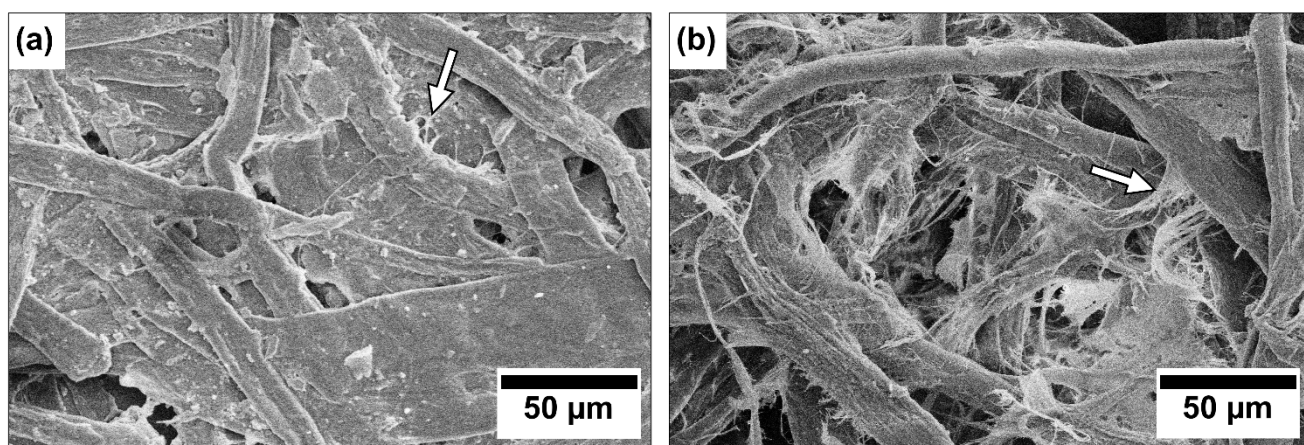
135 The main characteristics of papers A and B were measured, and their microstructures were observed, as  
136 summarised in **Table 1**. The methods used are defined hereafter, e.g., size and mass measurements to calculate  
137 thickness, grammage and density, MorFi analysis for fibre lengths, thermogravimetric analysis (TGA) for ash  
138 content and size-exclusion chromatography (SEC) for DP. There are major differences between the two papers,  
139 especially in terms of grammage and fibres length. In particular, paper A exhibits a significant difference between  
140 the mean length and the length-weighted length, indicating a wider length distribution than in paper B. The long  
141 fibres being responsible for the mechanical resistance, this could give paper A better strength, accordingly to the

142 fact that it should meet the mechanical criteria of ISO 9706 standard. **Fig. 1** shows the microstructure of the surface  
 143 of both papers. Paper B exhibits more fibrillation than paper A, indicating more mechanical treatment like refining  
 144 during papermaking process. Paper A has also flatter fibres, in coherence with his higher density.

145 **Table 1:** Main characteristics of papers A and B. Thickness and grammage were measured using a micrometric  
 146 gauge and a precision weighing scale, fibre length by MorFi analysis, ash content by thermogravimetric analysis  
 147 (TGA), number-average degree of polymerisation ( $DP_n$ ) of cellulose by size-exclusion chromatography (SEC),  
 148 and other characteristics by microscopic observations.

Characteristics	Paper A	Paper B
Thickness ( $\mu\text{m}$ )	$100 \pm 4$	$210 \pm 3$
Grammage ( $\text{g}\cdot\text{m}^{-2}$ )	$80 \pm 4$	$95 \pm 5$
Density	$0.80 \pm 0.04$	$0.45 \pm 0.02$
Fibres	softwood/hardwood	cotton linters
Fibres length ( $\mu\text{m}$ )	$508 \pm 5$	$445 \pm 5$
Length-weighted fibres length ( $\mu\text{m}$ )	$870 \pm 10$	$750 \pm 10$
Ash content (%)	$16.4 \pm 0.6$	$0.4 \pm 0.6$
$DP_n$ of cellulose	$1870 \pm 30$	$360 \pm 10$

149



150

151 **Fig. 1:** Microstructure of papers A (a) and B (b) (SEM). The arrows indicate fibrillation between fibres.

## 152 2.2 Accelerated ageing

153 Different degradation states of the paper were achieved through exposures to artificial ageing conditions. The  
 154 papers were exposed at 90 °C in closed glass tubes under different atmospheres (humid or dry, air or nitrogen) and

155 for different durations (e.g. 2, 4, 10, 25 and 50 weeks). Before exposure, the papers were prepared as follows: the  
156 sheets were cut in strips of 15 mm × 120 mm in the two directions of the sheet to enable mechanical testing in the  
157 main direction of the fibres (machine direction, referred hereafter as longitudinal direction) and in the  
158 perpendicular direction (cross direction, referred hereafter as transverse direction). About 20 to 30 strips  
159 (equivalent to 4 g of dry paper) were introduced in 15 cL Wheaton® glass tubes.

160 Two tubes per ageing duration were preconditioned under each specific atmosphere:

- 161 • 50 % RH in a climate room at 23 °C for 48 h (*humid air*)
- 162 • 0 ppm oxygen and 50 % RH in a glovebox at 23 °C for 48 h (*humid nitrogen*)
- 163 • circa 0 % RH in an oven at 105 °C for 2 h (*dry air*)
- 164 • circa 0 ppm oxygen and 0 % RH in a glovebox at 23 °C for 48 h (*dry nitrogen*)

165 The tubes were closed with a polypropylene screw cap and a PTFE septum insert (Duran Groups®, max. 140 °C).  
166 A three-layered film (PET, aluminium, polyethylene) was added on the tubes opening to improve tightness. They  
167 were then aged at 90 °C in the following conditions:

- 168 • 50 % RH in an environmental chamber (*humid air and humid nitrogen*)
- 169 • circa 0 % RH in an oven (*dry air and dry nitrogen*)

### 170 **2.3 Chemical analysis**

171 The degree of polymerisation (DP) of cellulose was measured by size-exclusion chromatography (isocratic HPLC  
172 pump Waters® 515 at 0.4 mL·min<sup>-1</sup> and 100 µL injection volume, autosampler Dionex® UliMate 3000, 4 columns  
173 Agilent® PLGel miniMIX A (20 µm and 4.6 mm × 250 mm) thermostated at 60 °C, MALS detector Wyatt  
174 Technologies® Dawn EOS at 60 °C, differential reflective index detector Waters® 2414 at 55 °C). Samples about  
175 10.4 mg of paper were prepared and analysed three times according to Dupont (Dupont 2003). Astra® 5.3.4.14,  
176 Wyatts Technologies® was used for the data acquisition and analysis.

177 The ash content in the papers was measured by thermogravimetric analysis (TGA), with a TA Instrument® TGA  
178 Q50 apparatus controlled via QSeries™ software at a scanning speed of 10 °C per minute until 800 °C, under  
179 nitrogen at a flow rate of 90 mL·min<sup>-1</sup>. The reported ash content corresponds to the relative mass remaining at  
180 800 °C.



## 181 2.4 Mechanical tests

182 Mechanical tests were carried out in a climate room at 23 °C and 50 % RH. The unaged and aged paper strips  
183 (15 mm × 120 mm) were conditioned for at least 48 hours in the climate room before the tests. Paper is an  
184 anisotropic material due to its fabrication process, leading to a mean orientation of the fibres along the machine  
185 direction. These tests were therefore performed in the two main directions of the sheet, *i.e.* the main direction of  
186 the fibres (machine direction), and the perpendicular axis (cross direction), referred herein as longitudinal and  
187 transverse directions, respectively.

188 The mechanical tests were adapted from TAPPI standards T 494 om-01 for tensile properties, T 511 om-02 for  
189 folding endurance and T 231 cm-96 for zero-span breaking strength. For tensile test, a DY20 Adamel Lhomargy  
190 dynamometer coupled with an MTS Systems® TestWorks software was used with the following setting: 5 cm of  
191 span between the jaws, speed of 1 mm·min<sup>-1</sup>, fracture detection at 50 % of the maximal stress. Folding endurance  
192 tests were realised on a Tinius Olsen® MIT folding tester at a speed of 200 folds per minute and a bending angle  
193 of 270°. The initial applied stress was equivalent to 500 g instead of 1 kg because of the low resistance of the most  
194 degraded papers. For zero-span tensile tests, a Pulmac® Z-span tester was used. The clamping pressure used was  
195 410 kPa (60 psi), as it was the maximum stable pressure authorised by the installation and is sufficient to prevent  
196 slippage (Batchelor et al. 2006).

197 Each result is the average of several repeat measurements using strips from the two ageing tubes of each exposure  
198 condition. For tensile tests, 6 strips were tested for paper A, and 4 strips for paper B, in the two directions. The  
199 tests for which strips broke within 1 cm distance to the jaws were considered as invalid. For zero-span tensile and  
200 folding endurance tests, at least 10 strips were used for each paper and exposure conditions.

201 All the  $DP_n$  and mechanical testing data used to draw the following graphs are available in a Supplementary  
202 Information file (**Table S1**).

## 203 2.5 Observations on the microstructure

204 The microstructure of the paper surface was observed by scanning electron microscopy (SEM), using a Hitachi®  
205 4800 microscope. Prior to the observation, the samples were metallised through a gold deposition process (2  
206 minutes at 1.2 kV and 5 mA). The observations were conducted at an acceleration of 5 to 10 kV and 10 mA, and  
207 detection was performed using two secondary electron (SE) detectors positioned at high and low angles.

208 Fracture surface of paper strips were observed through a Zeiss® SteREO Discovery V.20 binocular lens with a  
209  $\times 2$  objective, coupled with Archimed® software. Three images were recorded for each strip at the failure zone,  
210 resulting in 18 images for each ageing condition for paper A and 12 images for paper B. These images were treated  
211 with ImageJ® software to measure the mean extracted fibre lengths at failure surface.

212 Microstructure characteristics of the fibres were obtained with a MorFi LB01 instrument at Pagora, Grenoble INP,  
213 France. MorFi analysis consists in gathering images of fibres in suspension. Paper is first defibrated in water; the  
214 obtained pulp is continuously pumped into the system and monitored with a speed camera. Several dozens of fibres  
215 are captured for each image, and multiple images can be recorded within a few minutes. This technique is both  
216 fast and statistical.

217 The samples for MorFi analysis were prepared as follows: about 2 g of paper are weighted and placed in hot water  
218 (around 65 °C) during a few hours. The volume of water is adjusted to a concentration of 1 g·L<sup>-1</sup>. The rehydrated  
219 paper is then defibred in a blunt blades pulper for 5 minutes at 50 Hz, adding 5 minutes if the defibration was not  
220 complete. Each pulp suspension is sampled in three replicas of 300 mg and ran through the MorFi machine; a  
221 fourth sample is measured in case the repeatability criteria are not met (standard deviation below 20 µm on length  
222 and 0.2 µm on diameter). MorFi software is set to stop the analysis after 50,000 elements detected as fibres (length  
223 between 0.1 and 10 mm and diameter between 5 and 75 µm) are measured.

## 224 **3 Results and discussion**

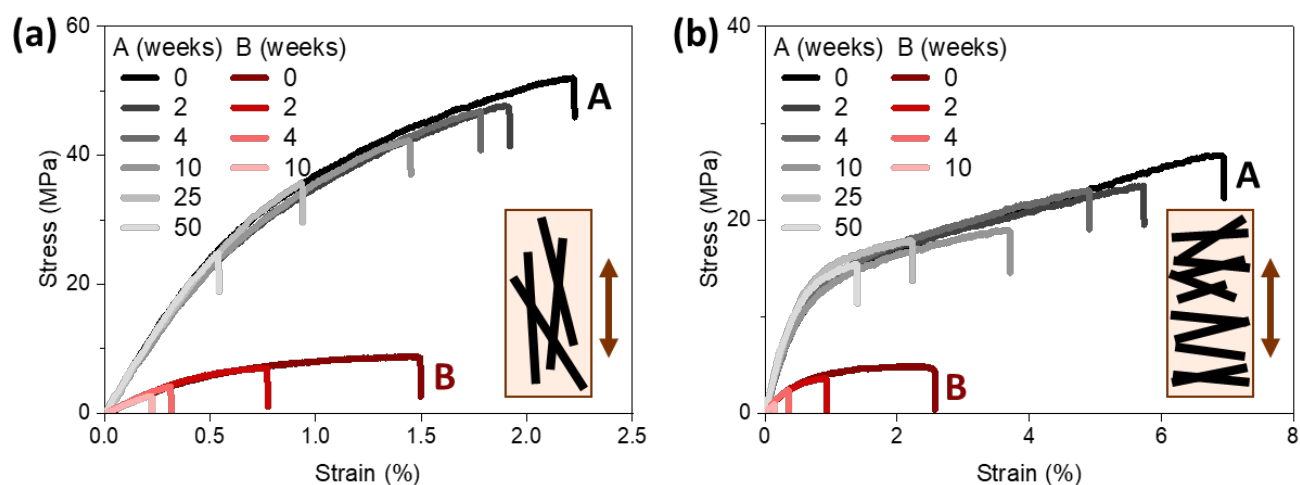
### 225 **3.1 Macroscopic scale: mechanical behaviour**

226 To follow macroscopic embrittlement, the behaviour of the two papers aged under different conditions and  
227 subjected to tensile test and folding endurance test is examined to evaluate the consequences of hydrolysis and  
228 oxidation reactions.

#### 229 **3.1.1 Embrittlement process**

230 The stress-strain curves from tensile tests in the two main orientations of the fibres are presented in **Fig. 2** for the  
231 two papers aged under humid air conditions. The shape of the curves is characteristic of the elastoplastic behaviour  
232 of paper (Hill et al. 1995; Fernández-Diego et al. 2021). First, the mechanical properties at the unaged stage are  
233 presented in order to exhibit the structure-properties relationship for the two papers (**Table 2**). Stress at break and  
234 elastic modulus are normalised by the density of the papers. Brittleness index is defined by Zou as the ratio of  
235 elastic strain energy to the total tensile energy absorption (TEA) at the time of failure (Zou et al. 1994).

236



237

238 **Fig. 2:** Stress-strain curves for papers A and B in the longitudinal direction of the fibres (a) and in the transverse  
 239 direction (b), at unaged state and after ageing for 2 to 50 weeks under humid air conditions.

240 **Table 2:** Tensile properties of unaged papers A and B in longitudinal and transverse directions: stress at break  
 241 and elastic modulus are normalised, *i.e.* divided by the density of paper. Brittleness index is the ratio of elastic  
 242 strain energy to the total tensile energy absorption at the time of failure.

	Paper A		Paper B	
	Longitudinal direction	Transverse direction	Longitudinal direction	Transverse direction
Normalised stress at break (MPa)	$58.5 \pm 1.9$	$29.9 \pm 1.6$	$19.4 \pm 0.3$	$10.4 \pm 0.7$
Strain at break (%)	$2.2 \pm 0.2$	$6.4 \pm 0.7$	$1.5 \pm 0.1$	$2.3 \pm 0.2$
Normalised elastic modulus (GPa)	$5.9 \pm 0.2$	$2.9 \pm 0.3$	$3.0 \pm 0.1$	$1.8 \pm 0.1$
Brittleness index (%)	$33.8 \pm 3.4$	$10.7 \pm 0.8$	$42.1 \pm 3.6$	$25.6 \pm 4.4$

243

244 Large discrepancies between paper A and paper B were found (**Table 2**): at unaged state, paper B has smaller  
 245 normalised stress at break, normalised elastic modulus, and strain at break than paper A in both directions. Its  
 246 brittleness index is higher, corresponding to a more fragile behaviour. To explain these observations, the initial  
 247 characteristics of the papers were measured (**Table 1**). Even if paper B exhibits higher degree of refining (**Fig. 1**),  
 248 it has a lower density, slightly shorter fibres, and a considerably lower  $DP_n$  of cellulose, all of which suggests  
 249 weaker network and weaker fibre resistance (Bronkhorst 2003; Picu 2021). Moreover, the papermaking process

250 of paper A includes the addition of strengthening agents such as the sizing. Its higher strength is coherent with its  
251 use as a printing paper, compared to paper B, which is designed for filtering and hence has no additives. Paper A  
252 is also more rigid than paper B as indicated by the much higher elastic modulus. This can be explained by its higher  
253 density that increases the probability of fibre-fibre bonding, which is responsible for more rigid networks.

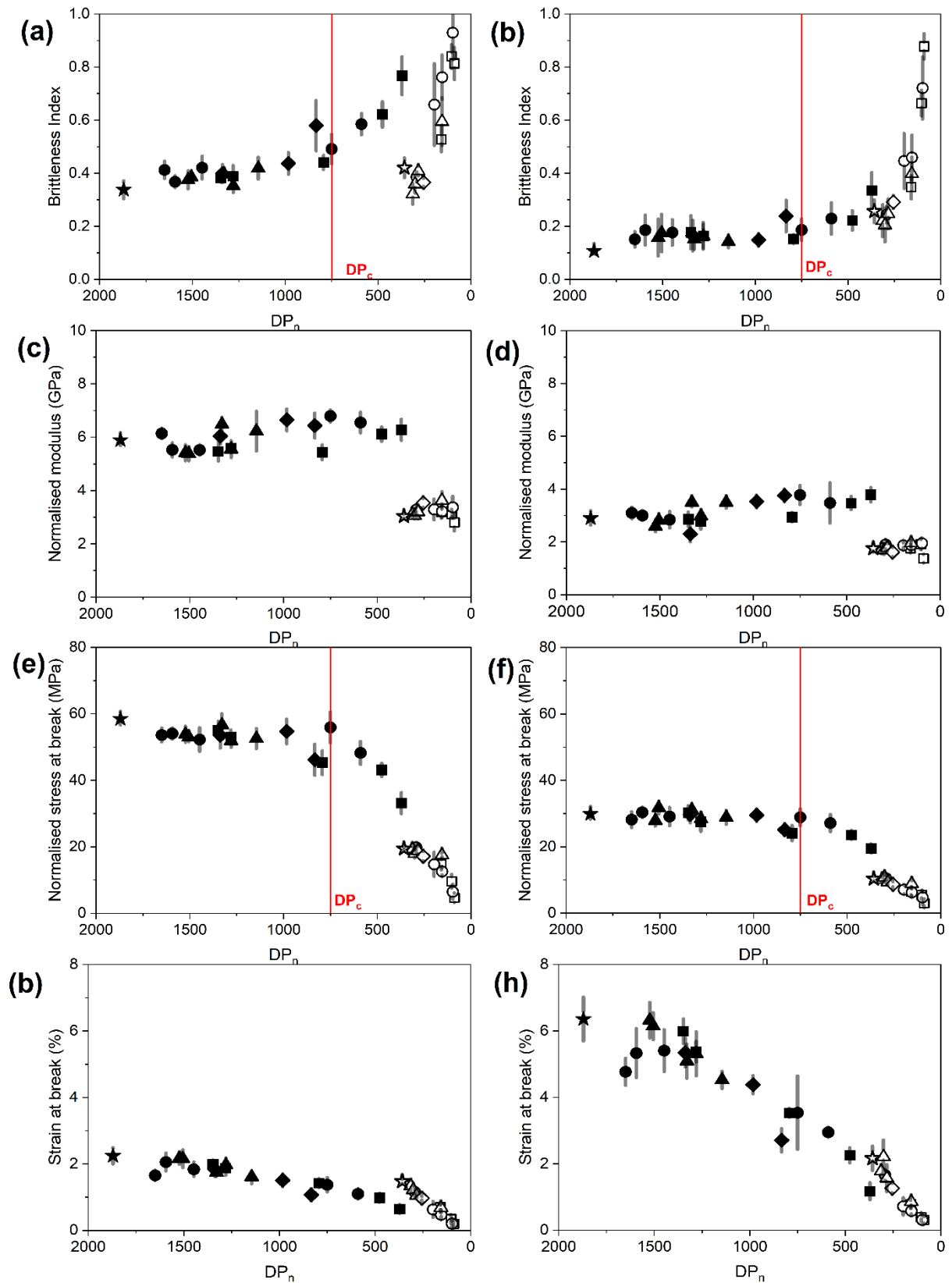
254 **Table 2** also shows the anisotropy of the papers: as expected, the transverse direction exhibited smaller normalised  
255 elastic modulus and brittleness index, leading to larger strain at break for both papers (Cox 1952; Leheny et al.  
256 2021). The anisotropy can be quantified through the ratio of elastic modulus in longitudinal to transverse direction.  
257 This ratio is 2.0 in the case of paper A, and 1.7 for paper B. The larger anisotropy of paper A can be explained by  
258 a different fabrication process. Moreover, in the inelastic zone of the strain-stress curve, the slope is smaller in the  
259 transverse direction. The difference in the inelastic behaviour is also linked to the fibre orientation. This could be  
260 explained by rearrangement processes: in the transverse direction, the fibres have more degree of freedom to align  
261 with the tensile axis than in longitudinal direction. This leads to two to three times higher strain at break.

262 As shown on **Fig. 2**, the artificial ageing leads to earlier failure: the strength and the strain at break decrease, but  
263 the elastic modulus remains stable, as confirmed by the literature (Kurei et al. 2022). The embrittlement of paper  
264 B occurs for shorter exposure times than that of paper A. After a 10-week ageing, it reaches a strength for which  
265 paper is hardly manipulable. The evolution of the mechanical properties with ageing is presented below.

### 266 **3.1.2 Correlation between mechanical properties and chemical degradation**

267 The detailed evolution of tensile test parameters is illustrated in **Fig. 3** for both papers aged under the different  
268 exposure conditions, and in the two main directions. The chemical degradation state is expressed in terms of  
269 number-average degree of polymerisation ( $DP_n$ ), value used to calculate the length of cellulose chain, knowing  
270 that both ageing mechanisms, hydrolysis and oxidation, lead to chain scissions.  $DP_n$  data for paper A and B aged  
271 under humid air, humid nitrogen, and dry air up to 10 weeks have been presented from a kinetic point of view in  
272 recent work (Vibert et al. 2023). It showed in particular that the presence of oxygen enhanced the degradation of  
273 both papers, and that the degradation of paper B was faster than that of paper A whatever the ageing condition.

274



275

276 **Fig. 3:** Evolution of mechanical properties with the decrease of degree of polymerisation, as measured by tensile  
 277 test for the two papers in the longitudinal direction (a, c, e, f) and in the transverse direction (b, d, f, h) upon all  
 278 exposure conditions for different durations between 0 and 50 weeks at 90 °C (initial values ★, humid air ■,

279 humid nitrogen ●, dry air ▲, dry nitrogen ◆, full symbols for paper A and empty symbols for paper B). The  
280 vertical red line indicates the value of critical  $DP_n$ .

281 **Fig. 3** shows that the evolution of the mechanical parameters of the two papers followed the same trend  
282 independently of the orientation of the fibres and the exposure conditions. Papers become increasingly more brittle  
283 as shown by the increase of the brittleness index, and a concomitant decrease of the stress and the strain at break,  
284 while the elastic modulus remains constant.

285 Interestingly, the data points for a given paper and direction align on a unique curve as a function of  $DP_n$ . In other  
286 words, the embrittlement process is independent of the exposure conditions. This confirms the zero-span tensile  
287 strength data of Zou for acidic paper (Zou et al. 1994). However, to our knowledge in the case of permanent paper,  
288 which is reported to be more prone to oxidation (Kolar 1997), this result had not been reported before. In particular,  
289 it demonstrates that, even when oxidation plays a role in the chemical degradation (Vibert *et al.*, 2023), this does  
290 not lead to a different mechanical behaviour of the paper. The influence of oxidation on the embrittlement process  
291 could have been expected as certain types of oxidation mechanisms could impact hydrogen bonding, as for  
292 example the oxidation of hydroxyl groups into carbonyl groups along the glucose ring (Kolar 1997). However,  
293 this has been shown to be negligible (Ahn et al. 2012). This would have reduced the number of donors of hydrogen-  
294 bonds, which are responsible for bonding in the fibres, and at fibre-fibre bonds. In this study, such behaviour was  
295 not observed, thus oxidative exposure conditions do not lead to fibre-fibre bonds degradation.

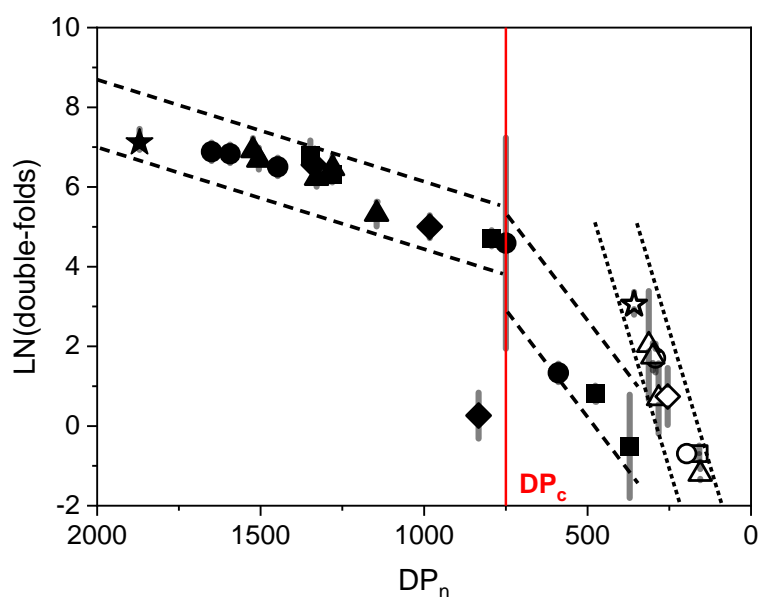
296 **Fig. 3** also exhibits the existence of a critical DP for paper A, under which the decrease of normalised stress at  
297 break accelerates. According to the brittleness index and to the normalized stress at break as a function of  $DP_n$ , the  
298 critical  $DP_n$  associated to the beginning of the embrittlement process lies between 500 and 1000. The existence of  
299 a critical DP ( $DP_c$ ) was notably shown in the literature in relation with the zero-span tensile tests (Zou et al. 1993);  
300 this point will be discussed below. It was not observed for paper B, for which the initial  $DP_n$  value is already below  
301 500 due to the acidic manufacturing process, which decreases the DP.

302 A slight decrease in the slopes of the curves on **Fig. 3** prior to reaching the  $DP_c$ , after which a more significant  
303 decrease of the mechanical property occurs, was observed for both stress at break and brittleness index of paper  
304 A. Conversely, the strain at break exhibited an almost linear decrease, and again no evolution was observed for  
305 the elastic modulus. This latter observation is consistent with the literature (Zou et al. 1994; Kurei et al. 2022).  
306 Since the elastic modulus is partly related to the elasticity of fibre-fibre bonds, the authors suggested that its  
307 constancy may be explained by the absence of degradation of the bonds.



### 327 3.1.3 Fatigue properties: folding endurance

328 The papers were also tested for mechanical fatigue in the longitudinal direction. Folding endurance is a localised  
 329 bending fatigue test. The results for all the ageing conditions are shown in **Fig. 5**. Again, the decrease in the folding  
 330 endurance does not depend on the ageing condition. It appears to be linear with the  $DP_n$  for paper B, as well as for  
 331 paper A up to approaching degradation levels corresponding to the  $DP_c$ . This critical  $DP_n$ , identified by the slope  
 332 break, is again around 750. The slope is also stiffer than for tensile properties as a function of  $DP_n$ , similarly to  
 333 tensile fatigue tests that highlight the effect of chemical degradation (Yue et al. 2019).



334

335 **Fig. 5:** Evolution of the folding resistance in longitudinal direction with the degradation, as expressed as the  
 336 logarithm of the mean number of double-folds at break (initial values ★, humid air ■, humid nitrogen ●, dry air  
 337 ▲, dry nitrogen ◆, full symbols for paper A and empty symbols for paper B). The vertical red line indicates the  
 338 value of critical  $DP_n$ .

339 It is interesting to note that the critical  $DP_n$  for folding endurance to start showing a faster decay is the same as for  
 340 stress at break. This suggests that the damage mechanisms in the folding and tensile tests are bound to similar  
 341 chemical degradation mechanisms. For both tests, stress is applied on both fibres and fibre-fibre bonds. However,  
 342 during folding, bending applies more on the fibres than on the bonds because the strain is localised on a precise  
 343 section of the paper. During tensile tests, the stress is distributed in all the sample, and applies to both fibres and  
 344 fibre-fibre bonds. Therefore, the stress applied on the fibre-fibre bonds is different for tensile and folding test. This  
 345 would suggest that the  $DP_c$  mechanism relates more specifically to the fibre and not to the fibre-fibre bonds.

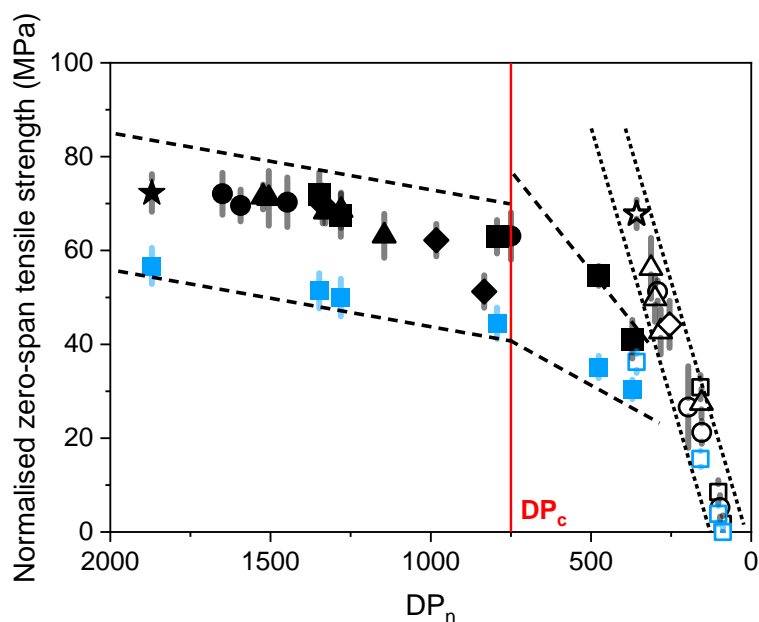


### 346 3.2 Mesoscopic scale: decoupling the mechanical behaviour of fibre and fibre-fibre bonds

347 The decrease in paper strength relates to the location of the embrittlement mechanism, predominantly at fibre-  
 348 fibre bonds or within the fibres. To decouple the effects, the zero-span tensile test was used as a fibre-specific  
 349 test, providing information on the intrinsic degradation of the fibres.

#### 350 3.2.1 Zero-span tensile tests

351 **Fig. 6** shows the normalised zero-span tensile strength of the two papers aged in the different conditions.  
 352 Confirming the earlier results on the tensile properties, for a given paper and in a specific direction all the data  
 353 points aligned on the same curve, showing no individual effect of the oxidation or the hydrolysis on the mechanical  
 354 degradation of fibres. As with the other mechanical tests, differences between the papers and dependency on the  
 355 fibre's direction are visible.



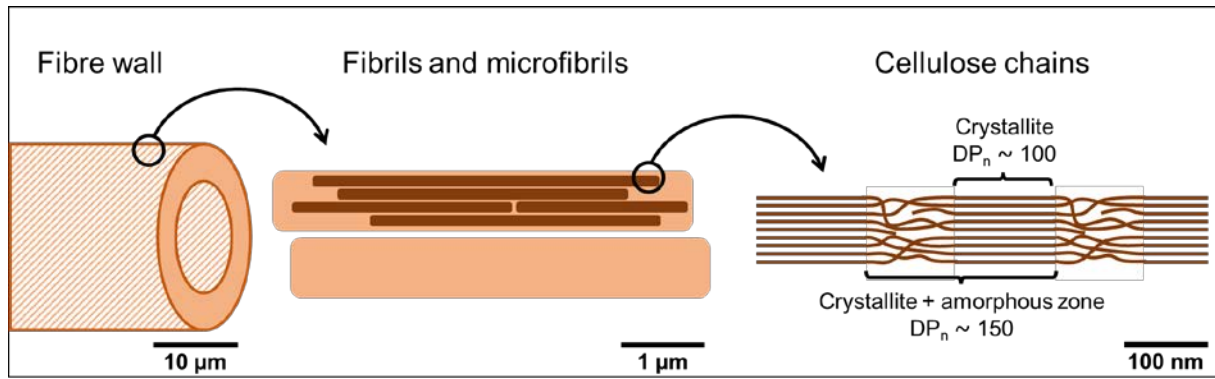
356 **Fig. 6:** Zero-span tensile strength normalised by the density of paper in the two principal directions vs  $DP_n$   
 357 (initial values ★, humid air ■, humid nitrogen ●, dry air ▲, dry nitrogen ◆, full symbols for paper A and empty  
 358 symbols for paper B, black for longitudinal direction and light blue for transverse direction). The vertical red line  
 359 indicates the value of critical  $DP_n$ .

361 The value of zero-span tensile strength of the unaged samples in the transverse direction is higher than that for the  
 362 stress at break in the normal tensile test, being 72.3 and 58.5 MPa for paper A and 67.8 and 19.4 MPa for paper B,  
 363 respectively. This can be due to the fact that zero-span tensile test is localised (Wathén et al. 2005), *i.e.* the stress

364 is applied on both sides of a section of the sheet. The resulting strength is the average strength of a randomly  
365 selected section in the paper sheet, whereas during tensile test, the paper sheet breaks at the weakest section.

366 As for tensile test, in the transverse direction, the zero-span resistance is lower than in the longitudinal direction  
367 at all equivalent degradation states and conditions. By volume conservation, the surface of fibres in a longitudinal  
368 as in a transverse section is the same. However, due to the alignment of cellulose chains in the crystallites almost  
369 parallelly with the direction of the fibre (Young and Rowell 1986), fibres should be more resistant under  
370 longitudinal tensile, where cellulose chains are stressed, than under transverse tensile, where hydrogen bonds  
371 between cellulose chains are. The higher zero-span tensile strength in the longitudinal direction of the paper can  
372 simply be explained by the much larger number of fibres passing through a given section if the latter is  
373 perpendicular to the direction of fibres than if it is parallel to the direction of fibres.

374 As observed for other tests, paper A exhibited a shallow decrease in the high  $DP_n$  ranges, and a steeper decrease  
375 after the  $DP_c = 750$ . This would indicate that the embrittlement mechanism is more related to the fibre than to the  
376 fibre-fibre bond. Again, no slope break, and hence no critical  $DP_n$ , was observed for paper B for which the initial  
377  $DP_n$  is already below 750. This is consistent with the literature, where a critical  $DP$  in zero-span tensile test was  
378 observed between 500 and 1000 (Zou et al. 1994; Tétreault et al. 2019). However, to our knowledge, no  
379 explanation for the existence of a critical value has been proposed. Such degree of polymerisation threshold has  
380 been observed for conventional semi-crystalline polymers (Fayolle et al. 2008). It is associated with the critical  
381 molar mass to ensure a minimum thickness of amorphous phase, which is responsible for plastic deformation  
382 mechanisms. However, the specific fibrillar and microfibrillar structure of cellulose adds a level of complexity.  
383 Given the fibre morphology, schematised in **Fig. 7**, a  $DP$  of 750 corresponds to 4 or 5 units of crystalline plus  
384 amorphous zones, considering that the crystallinity of paper is 70 % and that the LODP of 100 corresponds to the  
385 average length of a crystallite (Young and Rowell 1986). It also corresponds to an average of 1.5 scissions per  
386 cellulose chain for paper A. This might be the average degradation level under which transfer of applied stress  
387 along the fibres and through fibre-fibre bonds becomes less efficient.



388

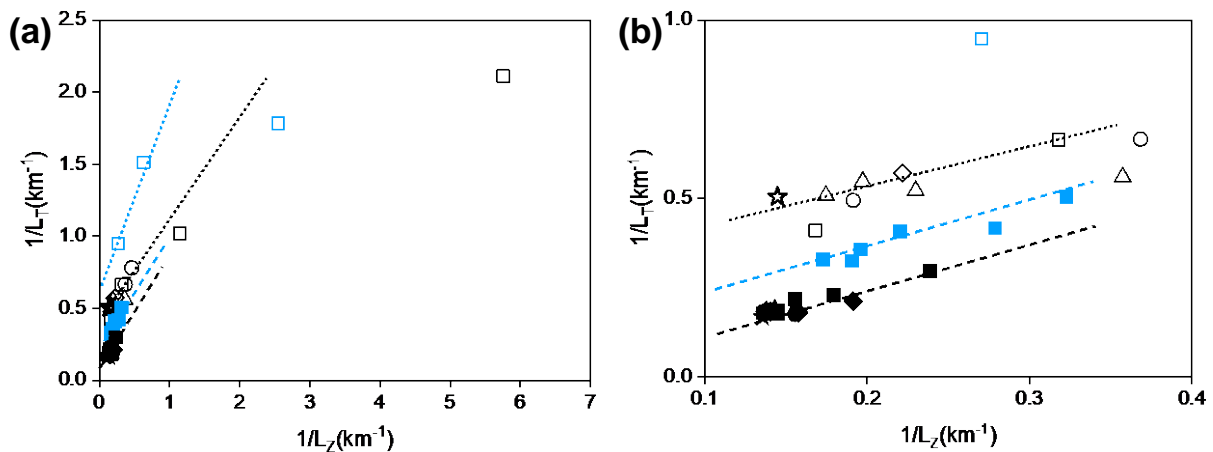
389 **Fig. 7.** Schematic representation of the microstructure of a cellulose fibre at the scale of the fibre, the fibrils, and  
 390 the cellulose chains according to (Kortschot 1997) and (Young and Rowell 1986).

### 391 3.2.2 Page equation

392 The results of the zero-span tensile tests and of the tensile strength tests showed the evolution of the paper strength.  
 393 The comparison between these values can be used to assess the contribution of fibre-fibre bonds to the paper  
 394 strength, and how it evolves with ageing. In this regard, the semi-empirical Page equation relates the two tests as  
 395 follows (Page 1969):

$$396 \quad 1/L_T = 9/8 * 1/L_Z + 12g/bL\alpha \quad (2)$$

397 with  $L_T$  and  $L_Z$  being respectively the breaking length in tensile and in zero-span tensile test (in km), *i.e.*, the  
 398 equivalent length of paper for which the strip breaks under its own weight,  $g$  the standard acceleration due to  
 399 gravity,  $b$  the surface shear bonding strength (in  $\text{kg} \cdot \text{m} \cdot \text{s}^{-2}$ ),  $L$  the mean fibre length (in m), and  $\alpha$  the contact area  
 400 relative to the mass of paper (in  $\text{m}^2 \cdot \text{g}^{-1}$ ).  $bL\alpha$  represents the shearing bonding of the paper. This equation expresses  
 401 the fact that tensile resistance arises both from fibre resistance and fibre-fibre bonding.



402

403 **Fig. 8:** (a) Graphical representation of the Page equation for papers A and B, with  $L_T$  the tensile breaking length  
 404 and  $L_Z$  the zero-span breaking length. The data points in the lower inverse length area being aggregated, (b) zoom  
 405 of (a) (initial values ★, humid air ■, humid nitrogen ●, dry air ▲, dry nitrogen ◆, full symbols for paper A and  
 406 empty symbols for paper B, black for longitudinal direction and light blue for transverse direction).

407 **Table 3:** Parameters of the Page equation for papers A and B:  $1/L_T = a/L_Z + 12g/bLa$ , with the correlation  
 408 coefficient  $r^2$  for papers aged under humid air.

Paper	Direction	Exposure condition	$a$	$r^2$	$bLa$ ( $km^2 \cdot s^{-2}$ )
A	Longitudinal	humid air	1.18	0.97	6.8
		all conditions	1.08	0.85	4.3
	Transverse	humid air	1.11	0.91	0.9
B	Longitudinal	humid air *	1.20	0.77	0.4
		all conditions *	0.80	0.78	0.3
	Transverse	humid air *	1.57	/	0.2

409 \* For paper B, the data for 4 and 10 weeks under humid air conditions were not included because of excessive damage.

410 To assess the validity of Page model in the case of artificial ageing of paper due to hydrolysis and oxidation, tensile  
 411 and zero-span breaking lengths were plotted in **Fig. 8**. The curve was not linear for high values of  $1/L_T$ . However,  
 412 most data set points of a same paper and orientation were aligned. The four data points that exhibited non-linear  
 413 behaviour correspond to the highest degradation states of paper B, *i.e.* aged for 4 and 10 weeks in humid air  
 414 conditions. In terms of  $DP$ , these samples have reached the levelling-off degree of polymerisation (LODP), e.g.  
 415 the  $DP$  for which where the kinetics of cellulose hydrolysis slows down tremendously (Battista et al. 1956;  
 416 Stephens et al. 2008). At this advanced stage of degradation, Page model is no longer valid. However, it is  
 417 interesting to note that Page equation is valid before reaching the LODP, even for  $DP$  values lower than the  $DP_c$   
 418 of 750 defined previously.

419 The parameters in the Page equation were assessed in the linear regime of the slopes. **Table 3** presents the results  
 420 of the linear regressions. The slope, named  $a$ , between zero-span and tensile breaking lengths is found to be close  
 421 to 9/8 for both papers. In Page's equation, this value of 9/8 accounts for the Poisson ratio of the paper being of 1/3.  
 422 As a comparison, Zou found a slope around 1.25 for the same paper as paper B aged in humid air, which is slightly  
 423 above that of Page (Zou et al. 1994). It is not surprising that the slopes that were found here are not exactly those

424 of Page or Zou, according to the fact that the Poisson ratio of the paper depends on the fibre orientation (Cox  
425 1952), and may depend on the nature and processing of the fibres.

426 Furthermore, **Table 3** shows that the linear regression is less accurate when all the data points are included. Since  
427 the ageing conditions were found to have no differentiated impact on the mechanical embrittlement, this  
428 observation can be explained by the fact that, except for the humid air condition, the embrittlement level is low,  
429 and the data points are therefore clustered.

430 Page equation also gives an estimate of the shear bonding  $bLa$ . This parameter is reported in **Table 3**. It is higher  
431 for paper A than for paper B. This can be explained by a difference in bonding strength, in fibre length, or in  
432 contact area. As shown in **Table 1**, the fibres in paper A are in average longer by 15 % than in paper B and the  
433 density of paper A about two times higher. Assuming that density is almost linear with contact area (Sampson  
434 2003) , the  $\alpha$  parameter of paper A is also twice that of paper B. Taking into account these ratios, the surface shear  
435 bond  $b$  in paper A would be around 8 times higher than that in paper B.

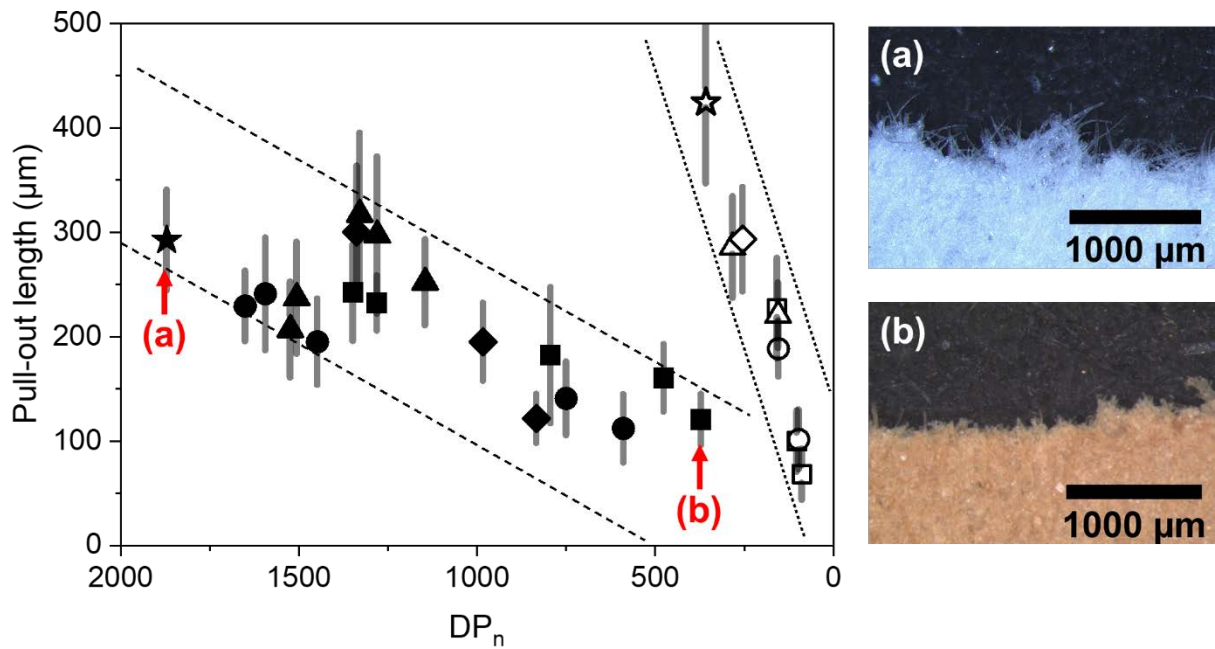
436 **Table 3** shows an unexpected difference between the longitudinal and transverse directions, even more pronounced  
437 for paper A. Indeed, according to the definition provided by Page, none of the  $b$ ,  $L$  and  $\alpha$  parameters are defined  
438 as dependent on the direction of the fibres. However, it can be presumed that  $b$  is in fact dependent on the  
439 orientation, as it can account for the projection of bonding shear along the considered axis. This explanation is  
440 consistent with the fact that fibre-fibre bonds are not submitted to the same stress depending on the orientation.

### 441 **3.3 Microscopic scale: Morphology of the fibres**

442 The microstructure of paper was evaluated using two different and complementary techniques: localised  
443 observations of the fracture surfaces to obtain *in situ* information, and MorFi analysis that enables a statistical  
444 evaluation of the morphology of fibres.

#### 445 **3.3.1 Fracture surfaces**

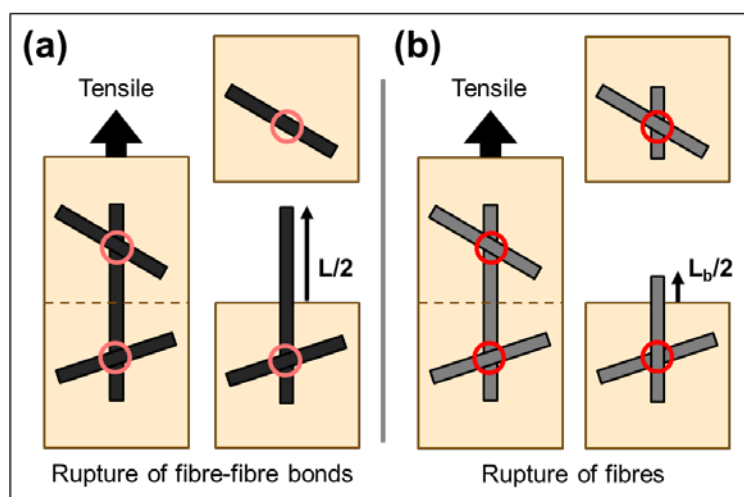
446 To evaluate the impact of ageing on the rupture mechanism of the papers, the fracture surfaces after tensile tests  
447 were observed and the length of pulled-out fibres was measured. The results, reported in **Fig. 9**, show that the pull-  
448 out length decreased for both papers as function of  $DP_n$ . Furthermore, this evolution seems almost linear with  $DP$ ,  
449 with a steeper slope for paper B than for paper A.



450

451 **Fig. 9:** Evolution of the mean length of the pulled-out fibres in the fracture zone for longitudinal direction tensile  
 452 tests ( $\Delta = 50 \mu\text{m}$ ) as a function of  $DP_n$  (initial values  $\star$ , humid air  $\blacksquare$ , humid nitrogen  $\bullet$ , dry air  $\blacktriangle$ , dry nitrogen  
 453  $\blacklozenge$ , full symbols for paper A, and empty symbols for paper B). Microscopy images of fracture surfaces for paper  
 454 A at initial state (a) and after 50-week in humid air (b).

455 The pull-out length depends on the slippage of fibres at the fracture surface (Wathén et al. 2005). If the fracture is  
 456 due to the rupture of the fibre-fibre bonds (**Fig. 10a**), the fibre at fracture surface would entirely slip out the  
 457 network, and the pull-out length would be in average equal to half the fibre length (as half of the fibre would stay  
 458 in each part of the broken strip, in average). On the contrary, if the fracture is due to rupture of the fibres while the  
 459 fibre-fibre bonds remain constant (**Fig. 10b**), only the length equivalent between two bonds would slip, and the  
 460 pull-out length would be equal to half of the average bond-to-bond length.



461

462 **Fig. 10:** Scheme of the pull-out length at fracture surface for embrittlement of either fibre-fibre bonds (red circles)  
463 (a) or fibres (b), with  $L$  the fibre length and  $L_b$  the bond-to-bond length.

464 The initial pull-out length of paper A and B are about 300  $\mu\text{m}$  and 550  $\mu\text{m}$ , respectively. Compared to the fibre  
465 length of both papers (508 and 445  $\mu\text{m}$ , respectively (**Table 1**)), these values are significantly higher than expected,  
466 *i.e.* 254 and 223  $\mu\text{m}$  maximum, respectively. This can be explained by a measurement bias. Indeed, the longer  
467 pulled-out fibres are better detected in the binocular lens images, and the smaller fibres might not be measured  
468 using ImageJ® software. The measured pull-out length is therefore higher than the actual pull-out length.  
469 However, since measurements and image treatments were done in the same manner for all the images, the  
470 comparison upon ageing is still relevant.

471 It can also be stressed out that, at the initial stage, paper B exhibited longer extracted fibres than paper A, even if  
472 its fibres are in average shorter. This can be justified by the differences in the average number of contacts and  
473 fibre-fibre bonding strength. The lower density of paper B could explain less contact between the fibres, and  
474 therefore longer bond-to-bond length. On the other hand, the absence of additives, such as AKD sizing or fillers,  
475 induces weaker bonding between fibres. These two factors lead to longer pull-out. Moreover, the presence of fine  
476 elements and strengthening additives can reinforce the bounding, and thus a lower pulled-out length. This can also  
477 explain the stiffer slope (**Fig. 9**), as fibre strength becomes all the more predominant in pull-out lengths in the case  
478 of paper B.

479 The general decrease of pull-out length can be interpreted as a decrease of the fibre strength. Indeed, if the fibre  
480 strength remained constant, the fibre-fibre bonds should be responsible for the diminution. To achieve such  
481 diminution, it would require a decrease of bond-to-bond length, *i.e.* an increase of the number of fibre-fibre bonds,  
482 or an increase of bonding strength. None of these hypotheses have been reported in the literature, nor do they seem  
483 consistent with chemical degradation or paper morphology. Fracture surfaces provide therefore further evidence  
484 of the embrittlement being due a decrease in the fibre strength.

### 485 **3.3.2 Fibres length and shape**

486 The morphology features of fibres were measured using a MorFi analyser. This technique is based on image  
487 analysis of paper pulp, e.g., fibres in suspension in water. It has to be noted that the repulping process induces  
488 mechanical stress on the fibres during their separation, which can lead to earlier fibre break. The length measured  
489 by MorFi is therefore referred hereafter as repulped fibre length, as opposed to *in situ* fibre length. Moreover, the

490 image analysis can induce a bias since only elements with sizes included between 0.1 and 10 mm length and  
 491 between 5 and 75  $\mu\text{m}$  thick are considered as fibres by the software, smaller elements being considered as fines.

492 **Table 4:** Morphological parameters of the fibres and pulps as measured with MorFi: arithmetical mean length of  
 493 fibres (standard deviation:  $\Delta = 5 \mu\text{m}$ ), length of fine elements over the total length of detected objects ( $\Delta = 2 \%$ ),  
 494 percentage of kinked fibres ( $\Delta = 0.4 \%$ ), for unaged paper and paper aged under humid air conditions.

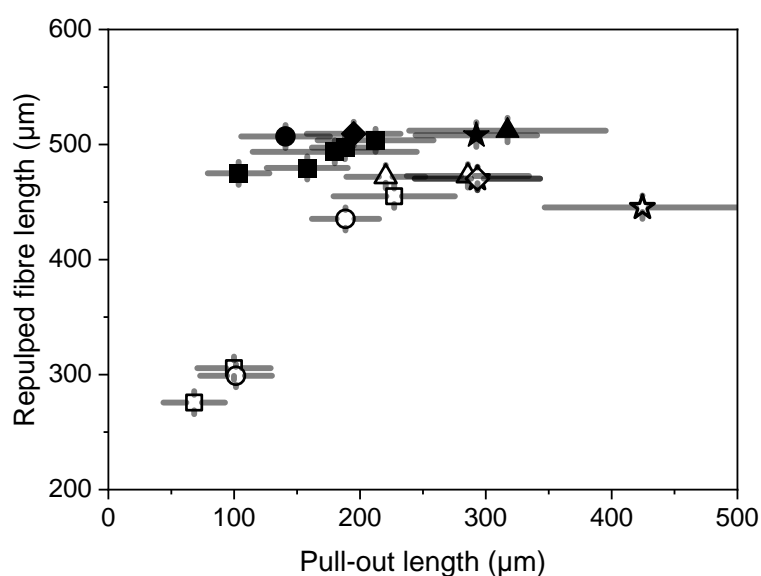
Paper	Ageing (weeks)	$DP_n$	Length ( $\mu\text{m}$ )	Fine elements (%)	Kinked fibres (%)
Paper A	0	1870	508	37	14.8
	2	1348	504	41	15.0
	4	1281	497	41	14.5
	10	793	494	42	15.0
	25	476	480	41	14.2
	50	371	475	39	14.2
Paper B	0	358	445	29	16.1
	1	326	451	27	16.3
	2	159	455	25	17.0
	4	103	306	48	6.1
	10	88	276	61	3.8

495  
 496 The evolution of the repulped fibre length upon ageing is presented **Table 4**. The ageing leads to a decrease of the  
 497 fibre length in both papers. It is interesting to note that this diminution is significant for paper B after 4 weeks of  
 498 ageing, considering the standard deviation of 5  $\mu\text{m}$ , with the length decreasing by 38 % for 75 % decrease of  $DP_n$ ,  
 499 compared to 6 % for paper A for 80 % decrease of  $DP_n$ . This degradation state corresponds to the reach of LODP,  
 500 i.e., the chemical degradation state for which cellulose becomes less accessible, as observed in the case of the  
 501 graphical representation of Page equation where a plateau is reached (section 3.2.2). A faster weakening of the  
 502 fibres after LODP can explain the abrupt decrease of repulped fibre length between 2 and 4 weeks of ageing. The  
 503 non-linearity observed after LODP implies that  $bLa$  parameter of Page equation can no longer be considered  
 504 constant. It is also noteworthy that no specific behaviour related to the repulped fibre length can be observed at  
 505 the  $DP_c$  of 750.



506 The abrupt change in average length in the case of paper B was related to other morphological parameters. **Table**  
 507 **4** shows that this phenomenon is accompanied by an increase in the proportion of fine elements, and a drastic  
 508 reduction of the percentage of kinked fibres. This evidences the fact that fibres break more easily, and the smaller  
 509 parts of broken fibres no longer account as fibres but as fines. Moreover, the rupture of fibres most probably occurs  
 510 at fibre kinks, explaining why the number of kinked fibres decrease. The production of fines from fibre breaks  
 511 would only happen for a fraction of the broken fibres, justifying why the increase of the proportion of fines is  
 512 lower than the decrease of kinked fibres. This seems to happen for  $DP_n$  lower than 100, and was thus not observed  
 513 in the case of paper A.

514 Two phenomena can be put forward to explain specific breakage at kinks. On the one hand, if a kinked fibre is  
 515 stressed at its extremities, the kink will be bent due to a localised concentration of stress (Aslan et al. 2011; Richely  
 516 et al. 2022). This would lead to breaking at kinks. A homogenous chemical degradation along the fibre could  
 517 thereupon lower the breaking criteria of kinks, allowing increasingly more fibre rupture during MorFi sample  
 518 preparation, and thus a decrease of repulping fibre length. On the other hand, kinks are defects created in the fibres  
 519 during the papermaking process. It can induce failures in both amorphous and crystalline zones (Ciesielski et al.  
 520 2019), leading to less ordered cellulose. Chemically reactive sites could be more accessible to reactants, and thus  
 521 more prone to degradation. More degradation in these areas would lead to less resistance of the fibres. This would  
 522 mean that cellulose chains break at specific locations, leading to low and heterogenous chemical degradation. Even  
 523 though possible, this was not observed for the papers tested (Vibert et al. 2023). Breakage at kinks is thus  
 524 principally due to stress concentration, and the second phenomenon might happen to a lesser extent.



525

526 **Fig. 11:** Length of fibres measured in MorFi compared to the length of pulled-out fibres measured by  
527 microscopy at fracture surface (initial values ★, humid air ■, humid nitrogen ●, dry air ▲, dry nitrogen ◆, full  
528 symbols for paper A and empty symbols for paper B).

529 The fibre length obtained with MorFi analysis was compared to the length of the fibres at the fracture surface. The  
530 results are presented on **Fig. 11**. For paper A, it shows that extracted lengths decrease more rapidly than repulped  
531 fibre lengths. For paper B, the slope is constant only at low degradation levels after which it shows a linear  
532 correlation for samples with  $DP$  below 250.

533 As already mentioned (section 3.3.1), the relationship between extracted length and fibre length could give insight  
534 in the breaking mechanisms. On **Fig. 11**, the slope for paper A is 0.1, while the slope for paper B is close to zero  
535 for low degradation levels and is 1.4 for higher degraded states. If we assume that the extraction length depends  
536 on the fibre length, the correlation would be linear with a slope of 2. Indeed, for fibres that in average break in the  
537 middle, when the fibre shortens by 1, the extracted length shortens by 0.5. Therefore, it can be concluded that the  
538 evolution of the extracted length is not due to fibre shortening, but to a diminution of the fibre strength.

#### 539 **4 Conclusions**

540 In conclusion, the results indicated that the embrittlement mechanism of paper was not affected by the exposure  
541 conditions, since oxidative and hydrolytic exposure conditions lead to similar effects. The embrittlement process  
542 is essentially driven by the reduction of degree of polymerisation by cellulose chain scissions.

543 The evolution of paper mechanical behaviour with ageing is primarily attributed to the embrittlement of the fibres  
544 rather than to the fibre-fibre bonds modifications, as evidenced by the validity of Page equation. Testing the paper  
545 in the transverse direction of the fibres allowed for the characterisation of the network by varying the ratio of fibres  
546 to fibre-fibre bonds, which helped to confirm the first hypothesis.

547 A critical degree of polymerisation was identified around  $DP_n$  of 750 in the case of paper A, below which the  
548 embrittlement occurs more significantly. The existence of this critical  $DP$  was confirmed by zero-span tensile tests,  
549 indicating that the damage mechanism is localised in the fibre.

550 The fracture preferentially occurs at morphological defects along the fibres, as highlighted by MorFi measurements  
551 for different states of paper degradation. This is not necessarily a symptom of heterogeneous degradation, but more  
552 likely a concentration of stress at the kinks leading to early breakage in the conditions of the MorFi analysis.

## 553 **5 Statements & Declarations**

### 554 **Ethics approval and consent to participate**

555 Not applicable.

### 556 **Consent for publication**

557 All the authors give their consent for the publication of this manuscript.

### 558 **Availability of data and materials**

559 Data will be available upon reasonable request.

### 560 **Competing interests**

561 The authors have no relevant financial or non-financial interests to disclose.

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563 Not applicable.

### 564 **Authors' contribution**

565 Caroline Vibert: Conceptualization, Methodology, Investigation, Writing - Original Draft, Visualization; Anne-

566 Laurence Dupont: Resources, Writing - Review & Editing, Supervision, Project administration, Funding

567 acquisition; Justin Dirrenberger: Supervision, Funding acquisition; Raphael Passas: Resources, Data Curation,

568 Writing - Review & Editing; Denise Ricard: Resources, Funding acquisition; Bruno Fayolle: Writing - Review &

569 Editing, Supervision, Project administration, Funding acquisition.

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574

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## 738 **Supplementary Information**

739 The online version contains supplementary material: <https://doi.org/10.1007/s10570-023-05683-x>.