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# 1 Ultrasonic welding of poly(vinyl alcohol) 2 coated-papers hydrophobized by 3 chromatogeny grafting

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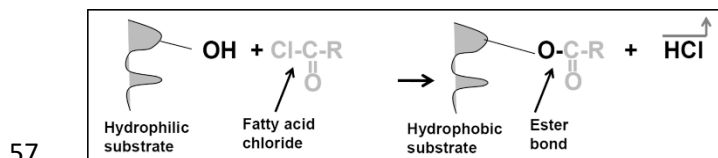
11 **Abstract** Chromatogeny grafting is an efficient method to hydrophobize lignocellulosic materials.  
12 Grafted papers are good candidates to replace plastic products in several applications requiring  
13 water barrier properties such as food packaging. However, chromatogeny grafting tends to  
14 reduce the sealability which is currently limiting the development of these materials. In this  
15 context, this study aims to investigate on the ultrasonic welding as a processing method to  
16 assemble papers coated with poly(vinyl alcohol) and grafted by chromatogeny. To reach such a  
17 goal, grafted and non-grafted papers, presenting different poly(vinyl alcohol) coating weight,  
18 have been welded under controlled conditions and peeled to evaluate the strength of welded  
19 joints. Results indicate that grafted-papers can be assembled by ultrasonic welding. However, it  
20 requires more severe processing conditions and the resulting peeling strength is lower than for  
21 non-grafted papers. Nevertheless, mechanical performances are quite satisfying in regard of the  
22 requirements of most packaging applications. Chromatogeny grafting modifies the adhesion  
23 mechanisms involved in the formation of the welded joints. Joint strength also increases with the  
24 poly(vinyl alcohol) coating weight which can be used as an adjusting parameter to optimize the  
25 adhesion. Overall, ultrasonic welding has proven its efficiency to assemble chromatogeny  
26 grafted-papers which is promising regarding the development of paper-based water barrier  
27 packaging solutions.

28 **Keywords** *Ultrasonic welding, chromatogeny grafting, hydrophobic papers, flexible*  
29 *packaging, adhesion, poly(vinyl alcohol)*

## 30 1 Introduction

31 Papers, boards, and lignocellulosic materials in general have regained interest for  
32 the last ten years. Today, many industrial sectors are trying to limit the use of non-  
33 degradable and non-recyclable materials in order to reduce their environmental  
34 impact and to adapt to the changes in legislation. In this context, the substitution  
35 of plastics by papers or lignocellulosic materials is a promising way, especially  
36 for packaging applications or single-use devices. However, lignocellulosic  
37 materials are highly hydrophilic, which makes them not suitable for applications

38 where contact with water is considered (liquid containers, food packaging). To  
39 solve this problem, research works have been focused recently on the  
40 hydrophobization of lignocellulosic materials. One of the technologies that have  
41 emerged is chromatogeny grafting. It consists in chemically grafting alkane  
42 oligomers by esterification onto a substrate using fatty acid chlorides (**Fig. 1**)  
43 (Samain 2002). Its application to cellulose-based products has been studied for  
44 several years in order to improve the hydrophobicity of these water-friendly  
45 materials (Stinga 2008; Berlioz et al. 2008). Used on poly(vinyl alcohol) (PVOH)  
46 layers (which are naturally barrier materials against fat, gases, and aromas), it  
47 increases the water repellency and decreases the water vapor transmission rate  
48 (Stinga et al. 2009; Schmid et al. 2012, 2014). Thus, grafted PVOH-papers  
49 present good barrier properties against water, fat, and oxygen and can also be  
50 water repellent. They are good candidates to replace plastic products in cosmetic  
51 or food packaging applications (wrapping paper/box, liquid containers, and so  
52 on...). However, one of the current limitations to the development of these  
53 materials comes from the difficulty to assemble PVOH-papers modified by  
54 chromatogeny grafting. Conventional methods such as heat-sealing or gluing are  
55 generally ineffective which is prohibitive for a large number of packaging  
56 applications.



58 **Fig. 1:** Principle of the chromatogeny reaction

59 In this context, the main concern of the present study is to investigate on the  
60 ultrasonic (US) welding as a potential processing method to assemble papers  
61 coated with PVOH and grafted by chromatogeny. US welding has recently  
62 emerged as a possible solution to manufacture bio-based materials (Regazzi et al.  
63 2019a; Teil et al. 2021) and to assemble papers and paperboards (Regazzi et al.  
64 2019b; Monot et al. 2021; Charlier et al. 2021). US welding is a processing  
65 method which consist in applying high-frequency acoustic vibrations (20 to 40  
66 kHz) under pressure (Tolunay et al. 1983; Benatar et al. 1989). US welding and its  
67 derivative are already used at the industrial scale to weld metals and thermoplastic  
68 (TP) polymers (Bhudolia et al. 2020; Li et al. 2022). Today, it is considered as a

69 possible alternative to heat-sealing or hot-melt gluing which are the most  
70 commonly used processes to assemble films, plastic bags, papers, or boards.  
71 Compared to these methods, US welding presents a lot of advantages: processing  
72 speed is quite high, heat generation is localized at the welding interface, and there  
73 is no need for additional substances. Vibrations also tend to remove liquids and  
74 powders from the welding zone which increase the success rate when sealing  
75 containers in industrial conditions.

76 However, the use of US welding to assemble lignocellulosic materials has not  
77 been much reported so far. 15 years ago, Stamm and Gfeller and al. used  
78 vibrational welding to assemble wood pieces, but at a much lower frequency (100  
79 Hz) (Gfeller et al. 2003; Stamm 2005). More recently, Teil et al. and Regazzi et  
80 al. manufactured and characterized biocomposites made of native starch granules  
81 and wood fibers and obtained by ultrasonic compression molding (Regazzi et al.  
82 2019a; Teil et al. 2021). Only a few recent studies, done by the same team of  
83 authors, discuss the use US welding to assemble paper-like materials (Regazzi et  
84 al. 2019b; Monot et al. 2021; Charlier et al. 2021). While working with 100%  
85 lignocellulosic papers, Regazzi et al. showed that papers can be welded only for  
86 high lignin and hemicelluloses contents in the paper pulp (Regazzi et al. 2019b).  
87 Structural analyses have suggested that the establishment of adhesion originates  
88 from a thermoplastic mechanism. When reaching high temperatures, the  
89 amorphous parts of papers (lignins and hemicelluloses) flow to form a matrix  
90 surrounding fibers which results in the formation of a new composite structure at  
91 the welding interface. More recently, Charlier et al. worked on the influence of  
92 process parameters in the US welding of polyvinyl alcohol (PVOH) coated papers  
93 using an instrumented welding machine designed to assemble papers and  
94 paperboards (Charlier et al. 2021). It was found out that the successful US  
95 welding of papers is associated to a two-step condition: finding the optimized  
96 process parameters to efficiently convert acoustic vibration into interfacial heat,  
97 and finding the optimized coating properties to develop strong welded joints.  
98 Thus, it seems that the coating layer is the main component involved in the  
99 development of adhesion at the welding interface. Based on these findings, Monot  
100 et al. also investigated on the US welding of folding boxboards (FBB) (Monot et  
101 al. 2021). The authors studied the influence of the composition of the coating  
102 formulation (deposited for printability purposes) on the weldability. Results

103 indicate that FBB can be assembled for high coating weight and binder content in  
104 the coating formulation.

105 Thus, the objective of this study is to evaluate the effect of surface properties  
106 when welding PVOH-coated papers grafted by chromatogeny. The main goals  
107 are:

- 108 • to check if it is possible to assemble grafted PVOH-papers using US  
109 welding,
- 110 • to evaluate the loss of weldability resulting from the grafting reaction,
- 111 • to assess how much the weldability is affected by the PVOH coating  
112 weight.

113 To reach such a goal, an instrumented US welding device (developed in 3SR  
114 laboratory in the frame of previous research works (Charlier et al. 2021)) was  
115 used to weld papers under controlled conditions. Grafted and non-grafted PVOH-  
116 papers, presenting different PVOH coating weight, have been welded and peeled  
117 to evaluate the strength of welded joints. The influence of material properties on  
118 the mechanical performances of welded papers is finally discussed and put in  
119 relation with the adhesion mechanisms identified by structural observations.

## 120 **2 Materials and methods**

### 121 **2.1 Materials**

122 The reference paper is a Machine-Glazed kraft paper of 80 g/m<sup>2</sup> (Terrana from  
123 Gascogne Papier). It is a dense (1.21 g/cm<sup>3</sup>) and high mechanical strength paper  
124 (tensile strength 8.26 kN/m and 4.00 kN/m in the machine and cross directions,  
125 respectively) suitable for food contact and presenting a clean and smooth surface.  
126 Poly vinyl alcohol (PVOH) layers were deposited using a two-step procedure in  
127 order to obtain controlled amount of PVOH onto the surface of the reference  
128 paper. First, paper reels were coated by CTP with PVOH F17 (from  
129 Thaiprochemical) using TKP's coating machine at 40 m/min in a processing way  
130 close to soft tip blade coating. PVOH was cooked at 11.2% and 35°C to fit the  
131 process viscosity requirements (330 mPa.s). The amount of deposited PVOH is  
132 initially 2,7 g/m<sup>2</sup> on the topside and 0,5 g/m<sup>2</sup> on the backside. Then, additional  
133 amounts of PVOH F17 were deposited by CTP using the same cooking conditions

134 in one to three additional steps to obtain a full set of samples with different  
 135 coating weights using a dedicated bar coating device (Elcometer Instruments,  
 136 Aalen, Germany). Additional depositions were performed on the topside of the  
 137 reference paper, except for the 1.9 g/m<sup>2</sup> coating which was performed on the  
 138 backside, using Mayer rods with different wire diameters. The thickness of the  
 139 coated papers is close to 100 μm and can slightly change depending on the  
 140 amount of PVOH deposited. Standard properties of the PVOH used in the frame  
 141 of this study are reported in Table 1.

<b>PVOH properties</b>		
<b>Molar mass</b>	(kg/mol)	90
<b>Density</b>	(g/cm <sup>3</sup> )	1,1
<b>Glass transition temperature</b>	(°C)	85
<b>Melting temperature</b>	(°C)	200

142 Table 1: PVOH standard properties (from supplier).

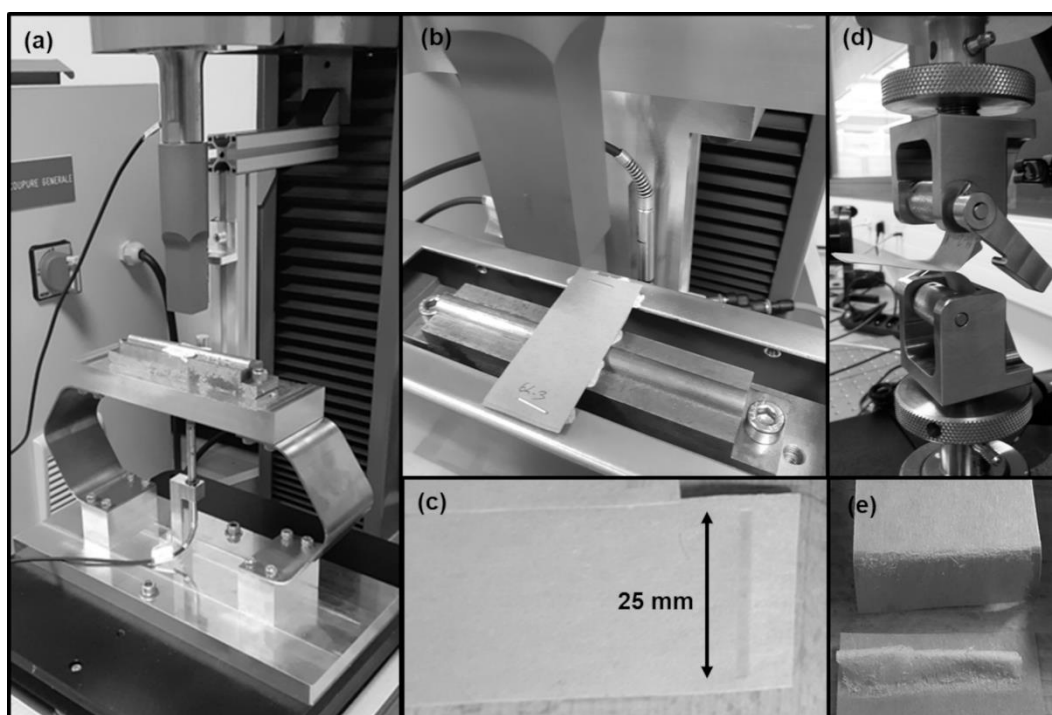
143 PVOH coated papers were grafted with fatty acids by CTP using CTP's  
 144 chromatogeny pilot at 70 m/min. PVOH grafting was performed by applying  
 145 around 0.4 g/m<sup>2</sup> of palmitoyl chloride at the surface of papers. Papers were then  
 146 heated at 190°C onto a heating cylinder (diameter 1.5 m) during about 3 s while  
 147 advancing into the pilot to enable the chromatogeny reaction. Finally, air flushing  
 148 was used to wash the by-products (HCl and fatty acids) and the unreacted reagent.  
 149 PVOH-papers grafted in these conditions present a total content of fatty acids of  
 150 about 150 mg/m<sup>2</sup>. Grafting efficiency was controlled by determining the water  
 151 absorption of grafted papers using Cobb method (ISO 535:2014) at 23±2°C and  
 152 45±5% of relative humidity. Papers were exposed to distilled water during 1800 s.  
 153 The surface characteristics of all paper samples prepared in the frame of this study  
 154 are summarized in Table 2.

<b>PVOH coating weight</b>	(g/m <sup>2</sup> )	<b>0.5</b>	<b>1.9</b>	<b>2.7</b>	<b>4.2</b>	<b>5.7</b>	<b>7.2</b>	<b>8.7</b>	<b>11.7</b>
<b>Paper side</b>		Back	Back	Top	Top	Top	Top	Top	Top

<b>Cobb<sub>1 800</sub> of grafted papers</b>	(g/m <sup>2</sup> )	-	28.7 ± 2.2	23.5 ± 0.1	19.4 ± 2.2	23.3 ± 2.2	14.9 ± 2.6	15.9 ± 0.1	16.7 3.2
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155 Table 2: Summary of PVOH coating weights deposited on the paper samples used in the present  
156 study and the associated Cobb<sub>1 800</sub> values of grafted layers.

## 157 2.2 Ultrasonic Welding



158

159 **Fig. 2:** Instrumented US welding device (a), setting up of a paper sample onto the US welder (b),  
160 welded paper (c), peeling set-up to evaluate the performances of welded papers (d), and peeled  
161 sample showing a cohesive failure propagation (failure criterion = 5) (e).

162 An ESW ultrasonic welder, supplied by Sonimat and instrumented by 3SR  
163 laboratory (Charlier et al. 2021), was used to assemble papers (**Fig. 2(a)**). The  
164 welding machine is an electromechanical press equipped with a 2000 N force  
165 sensor and an acoustic apparatus connected to a 20 kHz high frequency generator.  
166 The acoustic apparatus is mounted on the mobile crosshead whereas the anvil and  
167 its support are mounted on the base of the machine. A controller, located on the  
168 column of the press, allows the operator to set-up the welding parameters. The  
169 acoustic apparatus is composed of a sonotrode/horn (surface 20x25 mm<sup>2</sup>), a  
170 booster (gain 2.0), and a piezoelectric converter (CR 20). The peak-to-peak  
171 amplitude of the acoustic vibration is 92 μm and it can be adjusted on the  
172 controller from 60 to 100% of its value. The anvil support is mounted on springs,

173 the compliance of which provides to the anvil freedom to move in the crosshead  
174 (vertical) direction. Such a configuration is appropriate to weld thin materials such  
175 as papers. The anvil presents a cylindrical surface of radius 5 mm on which the  
176 paper sample is laid. Such a tooling creates a welded joint with the shape of a line  
177 of 25 mm-length and approximately 1 mm- width (**Fig. 2(c)**). The spring tooling  
178 is composed of two V-shaped leaf springs fixed on the base of the machine. The  
179 anvil is mounted on the top of the springs (measured stiffness of the apparatus =  
180 450 N/mm).

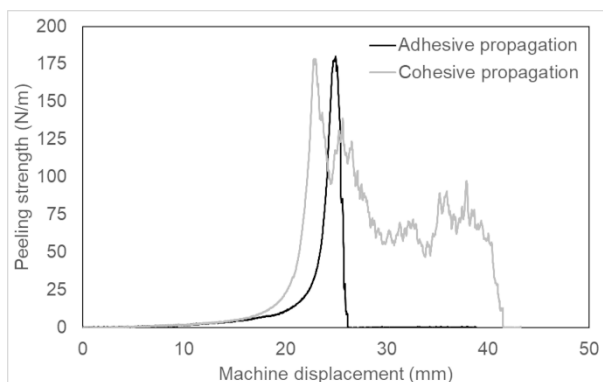
181 To perform the welding, paper samples are stapled, placed on the anvil, and  
182 maintained with adhesive paste (**Fig. 2(b)**). This is necessary to avoid paper  
183 slipping leading to inefficient weldings. The machine is calibrated by assigning a  
184 “mechanical” zero displacement corresponding to a force of 20 daN. US weldings  
185 are carried out at a temperature of  $23\pm 2^{\circ}\text{C}$  and a relative humidity of  $40\pm 10\%$   
186 using a displacement-controlled procedure and a force setpoint at which the  
187 motion is stopped. When reaching the set force, the spring ensures the steadiness  
188 of the force while the horn keeps vibrating until reaching the end condition of the  
189 welding (an energy threshold). The set force is varied between 25 and 85 daN.  
190 Welding velocity is set to 2.0 mm/s and amplitude to 60%. US vibrations are  
191 triggered 1.5 mm above the mechanical zero where there is still no contact  
192 between horn and anvil. Post-welding loads corresponding to the set force are  
193 applied at the end of the welding during 1 s. Attention was also paid to the  
194 anisotropy of papers. The orientation of papers was kept the same for all samples:  
195 the welding line is parallel to the machine direction. Unless it is specifically  
196 indicated otherwise in the result section, a studied paper is welded on itself,  
197 coated side on coated side. The resulting joint is referred according to the  
198 characteristics of the coating (PVOH weight, grafting occurrences). Thus, the  
199 actual amount of PVOH present at the welding interface is twice the coating  
200 weight of the studied paper. Additional details are reported when needed in  
201 section 3.

### 202 **2.3 Measuring the adhesion of welded joints**

203 T-peeling tests were performed to evaluate the mechanical performances of  
204 welded papers using an Instron 5944 testing machine equipped with a 2 kN sensor  
205 (**Fig. 2(d)**). Paper samples, of approximate dimensions  $6\times 3\text{ cm}^2$  (**Fig.2(c)**), were



206 peeled along the width of the welded joint with a displacement rate of 1 mm/s and  
207 peeling efforts were reported in N/m (**Fig. 3**). Regarding paper anisotropy, the  
208 peeling direction is perpendicular to the machine direction. The force required to  
209 bend the studied papers is negligible compared to the peeling forces. Values used  
210 in section 3 to discuss mechanical performances refer to the peak force per unit  
211 width which corresponds to the failure of the welded joint. A criterion based on  
212 visual observation was used to describe the behavior of failure propagation during  
213 peeling. A numerical value is attributed to the tested samples, 1 being fully  
214 adhesive, and 5 being fully cohesive failure propagation (**Fig. 2(e)**). Values in  
215 between correspond to mixed behavior evaluated in proportion to the amount  
216 surface concerned. Mean strengths, standard deviations, and failure criteria were  
217 calculated on 3 samples. Peeling tests were carried out at  $23\pm 2^{\circ}\text{C}$  and  $45\pm 5\%$  of  
218 relative humidity.



219

220 **Fig. 3:** Typical peeling curves of welded papers showing an adhesive (failure criterion = 1) and a  
221 cohesive failure propagation (failure criterion = 5).

## 222 **2.4 Assessment of welding performances**

223 In a previous work, power supplied by the high frequency generator was  
224 identified as a key parameter reflecting the severity of welding conditions (i.e. the  
225 amount of power per volume unit received by the welding interface) (Charlier et  
226 al. 2021). The peeling strength of welded papers changes with the power response  
227 of the machine. In this study, power was adjusted solely by changing the welding  
228 force (25, 45, 65, and 85 daN). In these conditions, it is considered that the  
229 “processing conditions” can be described, at first order, by one single parameter,  
230 the maximal power ( $P_m$ ) supplied by the US generator (also referred as the  
231 welding power).

232 To discuss the performances of welded papers, the peeling strengths will be  
233 presented in the results section as a function of the maximal power ( $P_m$ ) supplied  
234 by the welder (weldability curves). During the analysis, the focus will be made on  
235 the maximal level of adhesion showed by the welded papers (referred in section 3  
236 and 4 as “weldability potential”), and on the processing conditions, described by  
237  $P_m$ , required to reach the weldability potential (referred in section 3 and 4 as  
238 “welding easiness”). Both criteria need to be taken into account when discussing  
239 how well a material responds to US welding. In these conditions, it is assumed  
240 that the changes in welding performances from one sample to another are only  
241 resulting from the differences in surface properties.

242 The presented testing method and data analysis, developed and validated during a  
243 previous study led by the same team (Charlier et al. 2021), do not correspond to  
244 any existing standard. The US welding of papers being still an emerging topic,  
245 there seem to be no appropriate standard to evaluate the adhesion in welded joints  
246 **yet**. But it is inspired from standardized methods used in flexible packaging.

## 247 **2.5 Structural analyses**

248 The morphology of paper welded joints was analyzed using SEM. Cross-section  
249 SEM observations were performed using a JSM-IT500HR LV microscope (from  
250 Jeol) in secondary electron mode operating at 10 kV. Sample were previously  
251 metallized using a coating device to deposit layers of carbon of a few nanometers.

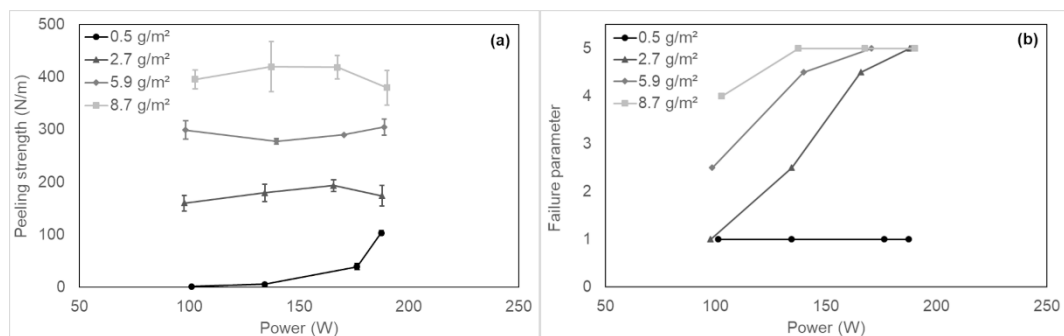
# 252 **3 Results**

## 253 **3.1 Influence of PVOH coating weight on the welding performances of non-** 254 **grafted papers**

255 The mechanical performances of non-grafted welded joints are strongly  
256 influenced by the amount of deposited PVOH (**Fig. 4**). The peeling strength  
257 required to separate welded papers improves when the quantity of coated PVOH  
258 increases (about 150 N/m for 2.7 g/m<sup>2</sup> of PVOH, and 400 N/m for 8.7 g/m<sup>2</sup> of  
259 PVOH). The welding power (in the investigated range) does not affect the  
260 performances of welded papers as the peeling strength remains the same whatever  
261 the maximal power supplied by the frequency generator ( $P_m$ ). Only the 0.5 g/m<sup>2</sup>  
262 PVOH-papers seems to show a dependency between adhesion levels and welding

263 power. 0.5 g/m<sup>2</sup> PVOH-papers cannot be welded at P<sub>m</sub> lower than 140 W but it is  
 264 possible to reach about 100 N/m for P<sub>m</sub> close to 180 W. Overall, the mechanical  
 265 performances of welded PVOH-papers are quite good. A minimum level of 160  
 266 N/m is generally expected for flexible packaging applications. It can be reached  
 267 only by depositing about 3 g/m<sup>2</sup> of PVOH on the reference paper.

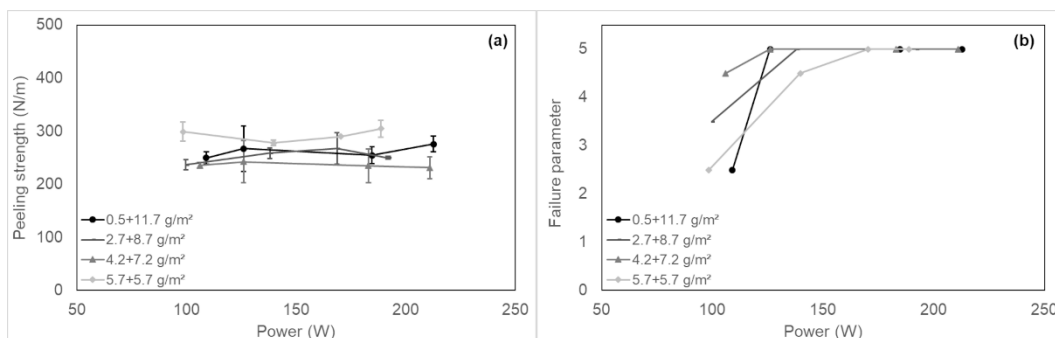
268 Failure propagation in welded PVOH-papers is influenced by both the processing  
 269 conditions and the amount of coated PVOH (**Fig. 4**). It is mostly adhesive at low  
 270 P<sub>m</sub>. As P<sub>m</sub> increases, it progressively switches to cohesive. A mixed adhesive-  
 271 cohesive behavior is observed for intermediate P<sub>m</sub> values (140-160 W). At last, all  
 272 failure propagations are cohesive at 180 W. For a given P<sub>m</sub>, the propagation  
 273 behavior also tends to be more cohesive for larger amounts of deposited PVOH.  
 274 Thus, 8.7 g/m<sup>2</sup> PVOH-papers show a full cohesive propagation at 140 W whereas  
 275 it is mostly adhesive for 2.7 g/m<sup>2</sup> PVOH-papers. Once again, the 0.5 g/m<sup>2</sup> PVOH-  
 276 paper is an exception as no cohesive failure propagation was observed at all.



277

278 **Fig. 4:** Peeling strengths (a) and failure criteria (b) vs P<sub>m</sub> for non-grafted PVOH-papers presenting  
 279 various coating weights and welded at different welding forces.

280 There is no influence of the distribution of PVOH coating weight on each of the  
 281 two welded surfaces on the mechanical performances of welded papers (**Fig. 5**).  
 282 The peeling strength of welded joints remains the same for a given total amount of  
 283 PVOH at the welding interface whether the PVOH is one-sided or equally  
 284 distributed on both papers. The failure propagation mode is also not affected by  
 285 the PVOH distribution.

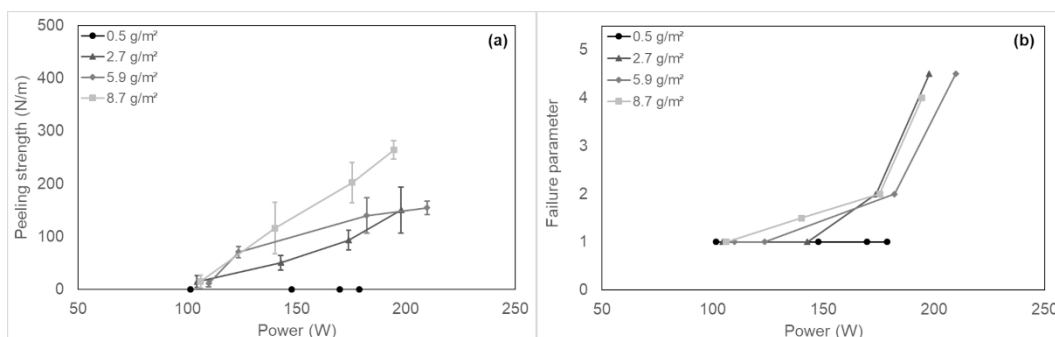


286

287 **Fig. 5:** Peeling strengths (a) and failure criteria (b) vs  $P_m$  for non-grafted PVOH-papers welded at  
 288 different welding forces and presenting an asymmetrical repartition of the PVOH coating weight.  
 289 Total coating weight is close to 12 g/m<sup>2</sup>.

### 290 3.2 Influence of chromatogeny grafting

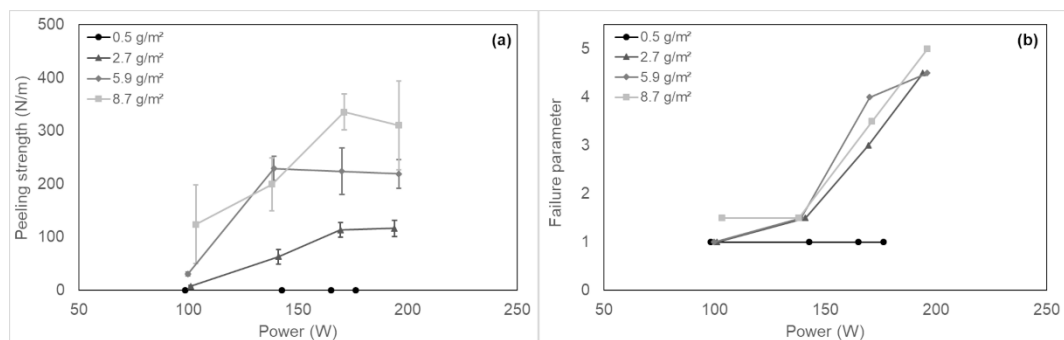
291 The mechanical performances of welded joints obtained from the welding of  
 292 grafted papers are also influenced by the amount of deposited PVOH (**Fig. 6**). The  
 293 peeling strength increases with the quantity of coated PVOH. At 200 W, a peeling  
 294 strength of 125 N/m and 250 N/m are obtained for 2.7 g/m<sup>2</sup> and 8,7 g/m<sup>2</sup> of  
 295 PVOH, respectively. Unlike non-grafted papers, the welding power affects the  
 296 performances of welded papers. The peeling strength increases with  $P_m$  and the  
 297 best mechanical performances are observed at the highest powers. The 0.5 g/m<sup>2</sup>  
 298 PVOH-papers show no adhesion at all, whatever the processing conditions. The  
 299 failure propagation mode when separating grafted joints is mainly influenced by  
 300 the welding power (**Fig. 6**). It is mostly adhesive but switches to cohesive when  
 301 reaching large  $P_m$  values (180-200 W). There is no mixed behavior in between.  
 302 Unlike non-grafted welded papers, the failure propagation mode is not much  
 303 influenced by the amount of deposited PVOH.



304

305 **Fig. 6:** Peeling strengths (a) and failure criteria (b) vs  $P_m$  for grafted PVOH-papers presenting  
 306 various coating weights and welded at different welding forces.

307 Intermediate behaviors are observed when welding non-grafted onto grafted  
 308 papers. The mechanical performances of welded joints are influenced both by the  
 309 amount of deposited PVOH and, to some extent, the welding power (**Fig. 7**). The  
 310 peeling strength increases with the quantity of coated PVOH. At 200 W, peeling  
 311 strengths of 125 N/m and 300 N/m are obtained for 2.7 g/m<sup>2</sup> and 8,7 g/m<sup>2</sup> of  
 312 PVOH, respectively. The welding power partially affects the performances of  
 313 welded papers: the peeling strength increases with P<sub>m</sub> until it reaches a plateau  
 314 starting at approximately 160 W. Above 160 W, the mechanical performances  
 315 remain constant which means that they are not influenced any more by the  
 316 welding power. The failure propagation mode when separating grafted from non-  
 317 grafted papers is similar to the one of grafted papers (**Fig. 7**). It is adhesive for  
 318 most of the studied P<sub>m</sub>. It switches to cohesive only when reaching high P<sub>m</sub> (180-  
 319 200 W) and there is no mixed behavior in between.

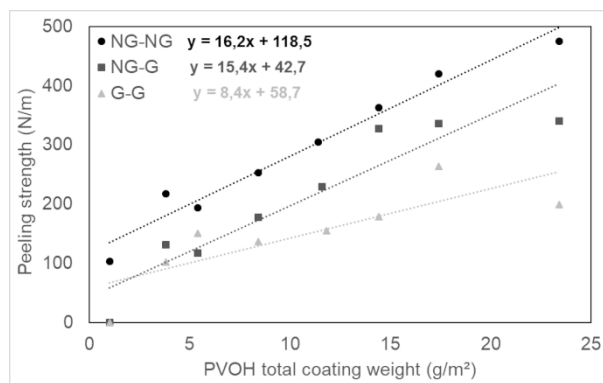


320

321 **Fig. 7:** Peeling strengths (a) and failure criteria (b) vs P<sub>m</sub> when welding a non-grafted PVOH-paper  
 322 onto a grafted PVOH-paper at different welding forces. The PVOH coating weights are the same  
 323 on both grafted and non-grafted papers.

324 The influence of PVOH coating weight on the mechanical performances of  
 325 welded joints for grafted and non-grafted papers is detailed in **Fig. 8**. This  
 326 representation includes all tested PVOH-papers and considers only the maximal  
 327 strength measured while testing the samples welded at different set forces. As for  
 328 non-grafted papers, there is no effect of the distribution of PVOH coating weight  
 329 when welding grafted papers. It seems that the peeling strength of grafted and  
 330 non-grafted joints increases linearly with the PVOH weight present at the welding  
 331 interface. It is also true when welding non-grafted onto grafted PVOH-papers.  
 332 The linear fittings presented in **Fig. 8** give an estimation of the level of adhesion  
 333 that can be obtained depending on the total amount of PVOH at the welding  
 334 interface. Overall, chromatogeny grafting tends to reduce the weldability of  
 335 PVOH-papers: the strength of grafted joints is lower than the strength of non-

336 grafted joints for identical processing conditions. The level of adhesion obtained  
 337 when welding grafted onto non-grafted papers is located in between. Overall, the  
 338 mechanical performances obtained when welding grafted PVOH-papers are  
 339 satisfying. It is possible to reach 100 N/m<sup>2</sup> when welding two grafted papers even  
 340 at low PVOH contents. However, reaching 160 N/m<sup>2</sup> requires the addition of  
 341 larger amounts of PVOH. Indeed, the coefficients obtained from the linear  
 342 regressions indicate that increasing the amount of PVOH to improve the  
 343 performances of welding joints is about half as efficient for grafted papers  
 344 compared to non-grafted. When welding grafted onto non-grafted papers, it is  
 345 possible to reach 160 N/m<sup>2</sup> for a total PVOH coating weight of 4 g/m<sup>2</sup>.



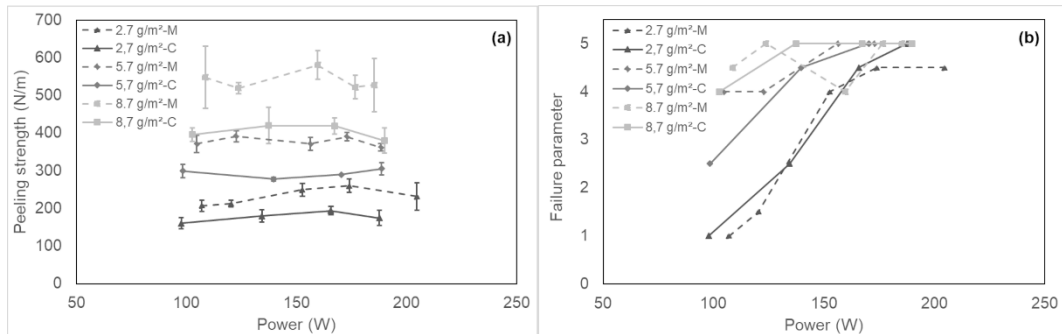
346

347 **Fig. 8:** Peeling strengths of welded joints vs total coating weight at the welding interface for  
 348 grafted and non-grafted PVOH-papers. NG-NG corresponds to the welding of two non-grafted  
 349 (NG) PVOH-papers. G-G corresponds to the welding of two grafted (G) PVOH-papers. NG-G  
 350 corresponds to the welding of a grafted PVOH-paper onto a non-grafted PVOH-paper. Each data  
 351 point corresponds to the maximal peeling strengths measured for the studied samples.

### 352 3.3 Influence of welding direction

353 Because the reference material was manufactured using a paper machine, its  
 354 mechanical response is anisotropic (see Material section). All experiments  
 355 presented so far were conducted in order to obtain welded joints parallel to the  
 356 machine direction (except for **Fig. 9**). It means that the peeling direction is  
 357 perpendicular to fiber orientation. When welding non-grafted papers  
 358 perpendicularly to the machine direction, the peeling strength increases up to 30%  
 359 while keeping an identical failure propagation behavior (**Fig. 9**). This represents a  
 360 clear interest for practical application. It means that by anticipating the welding  
 361 direction when designing a packaging product, it is possible to reduce the  
 362 thickness of the PVOH layer while keeping the same peeling properties. This  
 363 effect was also observed in grafted papers, but to a smaller extent. Grafted PVOH-

364 papers welded in the cross direction display mechanical performances 10% higher  
365 than those grafted in the machine direction.



366

367 **Fig. 9:** Peeling strengths (a) and failure criteria (b) vs  $P_m$  for non-grafted PVOH-papers presenting  
368 various coating weights and welded at different welding forces in two different directions. M  
369 means that the peeling direction is the machine direction. C means that the peeling direction is  
370 the cross direction (default configuration).

## 371 4 Discussion

### 372 4.1 Consequences of chromatogeny grafting on the weldability potential 373 and the welding easiness of PVOH-papers

374 As mentioned in section 3.2, the mechanical performances of grafted and non-  
375 grafted welded joints do not show the same evolution regarding the welding  
376 power. While the peeling strength of non-grafted welded papers remains constant  
377 whatever the power delivered by the welding machine, the grafted ones require a  
378 certain  $P_m$  to be able to develop adhesion. Thus, the US welding machine needs to  
379 provide more power to be able to weld grafted papers. It means that it is easier to  
380 weld non-grafted papers compared to grafted ones. Moreover, for an equivalent  
381 amount of deposited PVOH, the performances of non-grafted joints are superior to  
382 the grafted ones. A maximal peeling strength of 420 N/m was measured in non-  
383 grafted joints for a PVOH deposition of 8,7 g/m<sup>2</sup>, whereas it was only 264 N/m  
384 for grafted joints (**Fig. 4, 6, 8**). Thus, results obtained in the frame of this study  
385 indicate that chromatogeny grafting decreases both the weldability potential and  
386 the welding easiness of PVOH-papers.

387 However, it is possible to assume that both grafted and non-grafted papers  
388 actually exhibit a similar peeling strength vs. welding power behavior, made of an  
389 ascending step followed by a plateau. In such an assumption, the present results  
390 only show the plateau for the non-grafted papers since the ascending part would

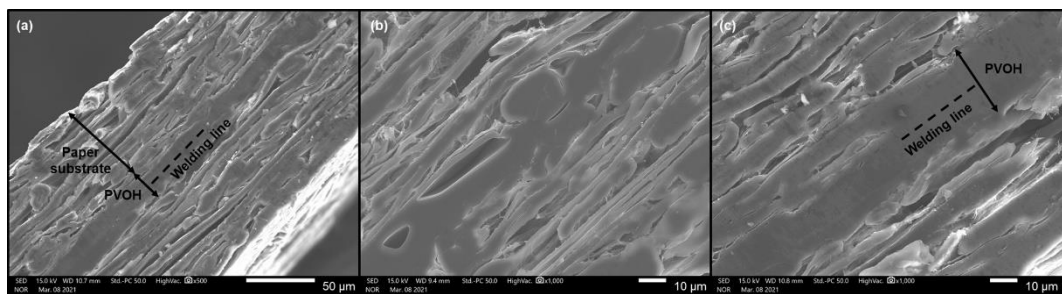
391 have required smaller welding powers to be evidenced. Considering that no  
392 peeling strength plateaus were observed for grafted papers, it is possible that the  
393 weldability potential of these materials was not reached with the processing  
394 conditions selected in this study. Thus, it can only be concluded with certainty  
395 that the welding easiness is affected by chromatogeny grafting. Further  
396 investigation would be required to ascertain if chromatogeny grafting also affects  
397 the weldability potential of PVOH-papers. In this study, it was not possible to  
398 weld the reference paper at larger welding powers using the presented set-up.

#### 399 **4.2 Adhesion phenomena involved in the US welding of PVOH-papers**

400 A structural characterization of welded joints was done to understand the  
401 differences in mechanical properties resulting from chromatogeny grafting. Cross-  
402 sections of non-grafted welded joints displaying total PVOH coating weights of  
403 12.4 and 17.4 g/m<sup>2</sup> are reported in **Fig. 10**. Micrograph (a) shows the whole cross-  
404 section of a welded joint (**Fig. 10(a)**). The welding line runs diagonally from  
405 bottom-left to top-right. The fibrous structure of the reference paper can be  
406 observed on each side of the welding line. Fibrous structures are quite dense for a  
407 paper-like material as the pictures do not show much porosity. The low porosity  
408 can be partially explained by the characteristics of the reference paper (high  
409 density, machine glazed). Also, the US welding of fibrous materials tends to make  
410 the structure denser, especially near the interface (Leban et al. 2004; Regazzi et al.  
411 2019b; Charlier et al. 2021). The establishment of adhesion at the welding  
412 interface seems quite straightforward. Focusing on the welded zone, it seems that  
413 the two PVOH layers have melded and merged into a single one, thus bonding the  
414 two papers. It is not possible to identify an interface between the two welded  
415 papers. It means that it is not possible to distinguish which part of the PVOH layer  
416 belonged to one sheet of paper or the other. The US welding of non-grafted  
417 PVOH-papers is quite similar to the US welding of thermoplastic polymers, the  
418 difference being that the welding concerns thin thermoplastic layers deposited  
419 onto fibrous substrates instead of bulk parts. Moreover, the PVOH layers seem to  
420 have impregnated deeper inside the fibrous structure. Some paper fibers are  
421 completely embedded in the PVOH layer (**Fig. 10(b) and (c)**). It results in the  
422 creation of a new interfacial composite material constituted of paper fibers  
423 embedded in a PVOH matrix which is relatively homogenous alongside the



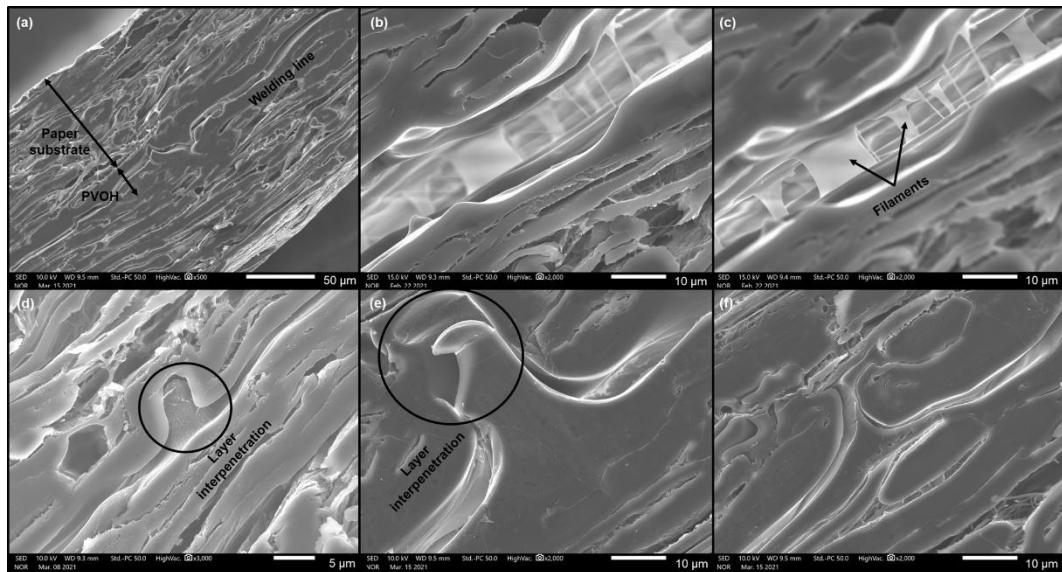
424 welding line. Such kind of structure is expected to locally reinforced the material  
425 (fiber-matrix reinforcement mechanisms). The thickness of the newly-formed  
426 layer depends on the initial PVOH content: the higher is the coating weight, the  
427 thicker is the composite layer. It probably explains why the peeling strength of  
428 non-grafted joints increases with the PVOH coating weight (**Fig. 4, 8**). As the  
429 composite layer probably presents better mechanical properties than its  
430 surroundings, it could also explain why cohesive failure propagation is mainly  
431 observed when peeling non-grafted joints (**Fig. 4**).



432

433 **Fig. 10:** SEM cross-sections of welded joints obtained from non-grafted PVOH papers: sample  
434 overview (a), and fibers embedded in the PVOH layer (b), (c). Total PVOH coating weight is 17.4  
435 g/m<sup>2</sup> in pictures (a) and (b) and 12.4 g/m<sup>2</sup> in picture (c).

436 The general aspect of the cross-sections of welded joints obtained from grafted  
437 PVOH-papers looks alike what is observed in non-grafted joints, except near the  
438 interphase region (**Fig. 11**). The main difference is that the interface between the  
439 two welded papers can be seen all along the welding line. The two PVOH layers  
440 have not merged to form a new material. Moreover, the welding interface is not  
441 homogeneous. Instead, three specific patterns alternating along the welding line  
442 can be identified. These patterns seem to be related to different types of adhesion  
443 mechanisms. The related zones will be referred in the following as non-welded,  
444 filamentous, and interpenetrating layer zones. Non-welded zones correspond to  
445 locations where the two paper sheets are not in contact at all. Filamentous zones  
446 refer to places where the surfaces are only bonded together by PVOH filaments  
447 which can stretch up to 10 μm (**Fig. 11(b), (c)**). At last, interpenetrating layer  
448 zones correspond to locations where the grafted PVOH layer of a paper has crept  
449 and penetrated inside the structure of the other paper (**Fig. 11(d), (e), (f)**).



450

451 **Fig. 11:** SEM cross-sections of welded joints obtained from grafted PVOH papers: sample  
 452 overview (a), filaments bonding PVOH layers (b), (c), and interpenetration of PVOH layers (d), (e),  
 453 (f). Total PVOH coating weight is 17.4 g/m<sup>2</sup> in pictures (a), (b), (c), (e), and (f), and 5.4 g/m<sup>2</sup> in  
 454 picture (d).

455 Chromatogeny grafting is used to turn the PVOH layer, initially hydrophilic, into  
 456 a water repellent surface. The grafting reaction actually modifies the chemical  
 457 composition of the PVOH layer in about a 1μm-depth. Near surface molecules  
 458 transform into poly(vinyl stearate) (PVS) displaying different molar mass,  
 459 crystallinity, and thermodynamic properties compared to the PVOH coating. In  
 460 layer interpenetration zones, it seems like the grafted layers have flowed and  
 461 shaped themselves around the fibrous structure (**Fig. 11(d), (e), (f)**). But the two  
 462 layers have not merged. This means that the PVS part has flowed but not melted.  
 463 It is as if a very thin envelop, behaving like a ductile thermoset material, was on  
 464 top of the PVOH layer, preventing it to merge with the other one (not unlike  
 465 standard core-shell structures). Based on these hypotheses, it is possible to  
 466 elaborate on the adhesion mechanisms related to the identified patterns:

- 467 • *Interpenetrating layer zones:* It seems that the coating layers flow into the  
 468 fibrous networks, but do not merge because of the properties of the PVS  
 469 envelop. It creates strong and local mechanical anchoring between the two  
 470 papers (**Fig. 11(d), (e), (f)**). For large welding power ( $P_m > 150$  W), the  
 471 flowing of the coating layer is favored and the occurrences of layer  
 472 interpenetration are increased. It is consistent with the mechanical  
 473 performances of grafted joints which increase for higher welding forces  
 474 (**Fig. 6**).

475 • *Filamentous zones*: it probably corresponds to zones where the grafting  
476 reaction did not totally succeed. It is possible that the PVS envelop could,  
477 in some places, present holes, i.e. non-grafted zones, through which  
478 PVOH could flow. Thus, filaments should correspond to zones where  
479 PVOH has melted and merged (PVOH-filaments, **Fig. 11(b), (c)**). In term  
480 of occurrences, filamentous zones were observed more frequently when  
481 welding non-grafted with grafted PVOH-papers, which is consistent with  
482 the discussed hypothesis.

483 The adhesion in welded joints obtained from grafted PVOH-papers is expected to  
484 be a “sum” of the two identified phenomena. It also explains why more adhesive  
485 failure propagation were observed when peeling grafted joints compared to non-  
486 grafted PVOH-papers. At last, it is possible to assume that by increasing the  
487 welding power, it might become possible to break the PVS envelop to merge the  
488 grafted layers. As suggested in the previous section, it could be possible to obtain  
489 in this case equivalent joint structure and mechanical properties for grafted and  
490 non-grafted PVOH-papers. However, such phenomenon was not observed for the  
491 studied welding conditions, and it remains highly speculative that such a result  
492 could be obtained without damaging the paper itself.

493 So far, the authors have not been able to explain the causes responsible for this  
494 envelop effect that prevents the merging of the two grafted layers. The molar mass  
495 near surface is expected to increase harshly considering that each time the grafting  
496 reaction succeed, a OH-group (17 g/mol) is replaced by a 16-C alkane chain (225  
497 g/mol). This could affect thermal properties given the dependency between molar  
498 mass and characteristic temperatures such as melting and glass transition  
499 temperatures ( $T_m$  and  $T_g$ ). However, PVS commonly displays a  $T_m$  close to 40-  
500 50°C (Nzé et al. 2012; Wang et al. 2018). Consequently, the  $T_m$  of the grafted  
501 layer is expected to be lower than the one of PVOH ( $T_m$  close to 200°C). Thus, it  
502 is unlikely than thermal properties are causing this envelop effect. Further  
503 investigations are required to progress on this subject.

## 504 **5 Conclusion**

505 US welding is an efficient method to assemble PVOH-papers grafted by  
506 chromatogeny. The mechanical performances of welded joints are mainly

507 influenced by the PVOH coating weight and whether papers are grafted or not.  
508 The weldability of grafted-papers is indeed reduced as it requires more severe  
509 processing conditions and the resulting peeling strength is lower than in non-  
510 grafted papers. Chromatogeny grafting actually modifies the adhesion  
511 mechanisms involved in the formation of the welded joints. Nevertheless,  
512 mechanical performances are quite satisfying in regard of the requirements of  
513 most packaging applications (usually 160 N/m). PVOH coating weight could also  
514 be used as an adjusting parameter to optimize the adhesion, as the performances  
515 of welding joints increase approximately linearly with the coating weight. Results  
516 are promising regarding the development of paper-based solutions for packaging  
517 applications requiring oxygen, fat, and water barrier properties.

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577

## 578 **Statements and Declarations**

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