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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.

Keywords Ultrasonic welding, chromatogeny grafting, hydrophobic papers, flexible
 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
- 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

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



57

58 Fig. 1: Principle of the chromatogeny reaction

In this context, the main concern of the present study is to investigate on the 59 ultrasonic (US) welding as a potential processing method to assemble papers 60 coated with PVOH and grafted by chromatogeny. US welding has recently 61 emerged as a possible solution to manufacture bio-based materials (Regazzi et al. 62 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 method which consist in applying high-frequency acoustic vibrations (20 to 40 65 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

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

However, the use of US welding to assemble lignocellulosic materials has not 76 77 been much reported so far. 15 years ago, Stamm and Gfeller and al. used vibrational welding to assemble wood pieces, but at a much lower frequency (100 78 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 and wood fibers and obtained by ultrasonic compression molding (Regazzi et al. 81 2019a; Teil et al. 2021). Only a few recent studies, done by the same team of 82 83 authors, discuss the use US welding to assemble paper-like materials (Regazzi et al. 2019b; Monot et al. 2021; Charlier et al. 2021). While working with 100% 84 lignocellulosic papers, Regazzi et al. showed that papers can be welded only for 85 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 surrounding fibers which results in the formation of a new composite structure at 90 the welding interface. More recently, Charlier et al. worked on the influence of 91 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 development of adhesion at the welding interface. Based on these findings, Monot 99 100 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

indicate that FBB can be assembled for high coating weight and binder content inthe coating formulation.

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

to check if it is possible to assemble grafted PVOH-papers using US
 welding,

- to evaluate the loss of weldability resulting from the grafting reaction,
- to assess how much the weldability is affected by the PVOH coating
 weight.

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

120 2 Materials and methods

121 2.1 Materials

110

122 The reference paper is a Machine-Glazed kraft paper of 80 g/m² (Terrana from Gascogne Papier). It is a dense (1.21 g/cm^3) and high mechanical strength paper 123 (tensile strength 8.26 kN/m and 4.00 kN/m in the machine and cross directions, 124 respectively) suitable for food contact and presenting a clean and smooth surface. 125 Poly vinyl alcohol (PVOH) layers were deposited using a two-step procedure in 126 order to obtain controlled amount of PVOH onto the surface of the reference 127 128 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 close to soft tip blade coating. PVOH was cooked at 11.2% and 35°C to fit the 130 131 process viscosity requirements (330 mPa.s). The amount of deposited PVOH is 132 initially 2,7 g/m² on the topside and 0,5 g/m² on the backside. Then, additional amounts of PVOH F17 were deposited by CTP using the same cooking conditions 133

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

PVOH properties				
Molar mass	(kg/mol)	90		
Density	(g/cm^3)	1,1		
Glass transition temperature	(°C)	85		
Melting temperature	(°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

around 0.4 g/m² of palmitoyl chloride at the surface of papers. Papers were then

heated at 190°C onto a heating cylinder (diameter 1.5 m) during about 3 s while

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

about 150 mg/m². Grafting efficiency was controlled by determining the water

absorption of grafted papers using Cobb method (ISO 535:2014) at $23\pm2^{\circ}$ C and

 $45\pm5\%$ 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

are summarized in Table 2.

PVOH									
coating	(g/m²)	0.5	1.9	2.7	4.2	5.7	7.2	8.7	11.'
weight									
Paper		Back	Back	Top	Ton	Ton	Ton	Ton	То
side		Dack	Dack	төр	Top	Top	Top	Top	10

Cobb1 800	(g/m²)	(g/m²) -	29.7	22.5	10.4	22.2	14.0 +	15.0	167
of grafted			$28.7 \pm$	$23.3 \pm$	19.4 ±	$23.3 \pm$	14.9 ± 2.6	$13.9 \pm$	10.7
papers			2.2	0.1	2.2	2.2	2.0	0.1	5.2

155 Table 2: Summary of PVOH coating weights deposited on the paper samples used in the present

156 study and the associated Cobb_{1 800} values of grafted layers.

157 2.2 Ultrasonic Welding



158

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

- 162 An ESW ultrasonic welder, supplied by Sonimat and instrumented by 3SR
- laboratory (Charlier et al. 2021), was used to assemble papers (**Fig. 2**(**a**)). The
- welding machine is an electromechanical press equipped with a 2000 N force
- 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
- acoustic apparatus is composed of a sonotrode/horn (surface 20x25 mm²), a
- booster (gain 2.0), and a piezoelectric converter (CR 20). The peak-to-peak
- amplitude of the acoustic vibration is $92 \,\mu m$ and it can be adjusted on the
- 172 controller from 60 to 100% of its value. The anvil support is mounted on springs,

the compliance of which provides to the anvil freedom to move in the crosshead 173 174 (vertical) direction. Such a configuration is appropriate to weld thin materials such as papers. The anvil presents a cylindrical surface of radius 5 mm on which the 175 176 paper sample is laid. Such a tooling creates a welded joint with the shape of a line of 25 mm-length and approximately 1 mm- width (Fig. 2(c)). The spring tooling 177 is composed of two V-shaped leaf springs fixed on the base of the machine. The 178 179 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 are carried out at a temperature of 23±2°C and a relative humidity of 40±10% 185 using a displacement-controlled procedure and a force setpoint at which the 186 187 motion is stopped. When reaching the set force, the spring ensures the steadiness of the force while the horn keeps vibrating until reaching the end condition of the 188 welding (an energy threshold). The set force is varied between 25 and 85 daN. 189 190 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 anisotropy of papers. The orientation of papers was kept the same for all samples: 194 the welding line is parallel to the machine direction. Unless it is specifically 195 196 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

T-peeling tests were performed to evaluate the mechanical performances of
welded papers using an Instron 5944 testing machine equipped with a 2 kN sensor
(Fig. 2(d)). Paper samples, of approximate dimensions 6x3 cm² (Fig.2(c)), were

peeled along the width of the welded joint with a displacement rate of 1 mm/s and 206 207 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 in section 3 to discuss mechanical performances refer to the peak force per unit 210 211 width which corresponds to the failure of the welded joint. A criterion based on visual observation was used to describe the behavior of failure propagation during 212 213 peeling. A numerical value is attributed to the tested samples, 1 being fully adhesive, and 5 being fully cohesive failure propagation (Fig. 2(e)). Values in 214 between correspond to mixed behavior evaluated in proportion to the amount 215 216 surface concerned. Mean strengths, standard deviations, and failure criteria were calculated on 3 samples. Peeling tests were carried out at $23\pm2^{\circ}$ C and $45\pm5\%$ of 217 218 relative humidity.



Fig. 3: Typical peeling curves of welded papers showing an adhesive (failure criterion = 1) and acohesive failure propagation (failure criterion = 5).

222 2.4 Assessment of welding performances

In a previous work, power supplied by the high frequency generator was
identified as a key parameter reflecting the severity of welding conditions (i.e. the
amount of power per volume unit received by the welding interface) (Charlier et

- al. 2021). The peeling strength of welded papers changes with the power response
- of the machine. In this study, power was adjusted solely by changing the welding
- 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).

To discuss the performances of welded papers, the peeling strengths will be 232 233 presented in the results section as a function of the maximal power (P_m) supplied by the welder (weldability curves). During the analysis, the focus will be made on 234 235 the maximal level of adhesion showed by the welded papers (referred in section 3 and 4 as "weldability potential"), and on the processing conditions, described by 236 237 P_m, required to reach the weldability potential (referred in section 3 and 4 as "welding easiness"). Both criteria need to be taken into account when discussing 238 239 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.

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

247 2.5 Structural analyses

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

252 **3 Results**

3.1 Influence of PVOH coating weight on the welding performances of non grafted papers

255 The mechanical performances of non-grafted welded joints are strongly

influenced by the amount of deposited PVOH (**Fig. 4**). The peeling strength

- required to separate welded papers improves when the quantity of coated PVOH
- increases (about 150 N/m for 2.7 g/m² of PVOH, and 400 N/m for 8.7 g/m² 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
- the maximal power supplied by the frequency generator (P_m). Only the 0.5 g/m²
- 262 PVOH-papers seems to show a dependency between adhesion levels and welding

power. 0.5 g/m² PVOH-papers cannot be welded at P_m lower than 140 W but it is 263 possible to reach about 100 N/m for P_m close to 180 W. Overall, the mechanical 264 performances of welded PVOH-papers are quite good. A minimum level of 160 265 266 N/m is generally expected for flexible packaging applications. It can be reached only by depositing about 3 g/m^2 of PVOH on the reference paper. 267 Failure propagation in welded PVOH-papers is influenced by both the processing 268 conditions and the amount of coated PVOH (Fig. 4). It is mostly adhesive at low 269 Pm. As Pm increases, it progressively switches to cohesive. A mixed adhesive-270 cohesive behavior is observed for intermediate P_m values (140-160 W). At last, all 271 272 failure propagations are cohesive at 180 W. For a given P_m, the propagation 273 behavior also tends to be more cohesive for larger amounts of deposited PVOH.

274 Thus, 8.7 g/m² PVOH-papers show a full cohesive propagation at 140 W whereas

it is mostly adhesive for 2.7 g/m² PVOH-papers. Once again, the 0.5 g/m² PVOH-

276 paper is an exception as no cohesive failure propagation was observed at all.



277

Fig. 4: Peeling strengths (a) and failure criteria (b) vs P_m for non-grafted PVOH-papers presenting
 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

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

distributed on both papers. The failure propagation mode is also not affected by

the PVOH distribution.



Fig. 5: Peeling strengths (a) and failure criteria (b) vs P_m for non-grafted PVOH-papers welded at
 different welding forces and presenting an asymmetrical repartition of the PVOH coating weight.
 Total coating weight is close to 12 g/m².

290 3.2 Influence of chromatogeny grafting

The mechanical performances of welded joints obtained from the welding of 291 292 grafted papers are also influenced by the amount of deposited PVOH (Fig. 6). The peeling strength increases with the quantity of coated PVOH. At 200 W, a peeling 293 294 strength of 125 N/m and 250 N/m are obtained for 2.7 g/m² and 8,7 g/m² 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^2 PVOH-papers show no adhesion at all, whatever the processing conditions. The 298 failure propagation mode when separating grafted joints is mainly influenced by 299 the welding power (Fig. 6). It is mostly adhesive but switches to cohesive when 300 301 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

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

Intermediate behaviors are observed when welding non-grafted onto grafted 307 308 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 peeling strength increases with the quantity of coated PVOH. At 200 W, peeling 310 strengths of 125 N/m and 300 N/m are obtained for 2.7 g/m² and 8,7 g/m² of 311 PVOH, respectively. The welding power partially affects the performances of 312 welded papers: the peeling strength increases with P_m until it reaches a plateau 313 starting at approximately 160 W. Above 160 W, the mechanical performances 314 remain constant which means that they are not influenced any more by the 315 welding power. The failure propagation mode when separating grafted from non-316 317 grafted papers is similar to the one of grafted papers (Fig. 7). It is adhesive for most of the studied P_m . It switches to cohesive only when reaching high P_m (180-318 319 200 W) and there is no mixed behavior in between.



Fig. 7: Peeling strengths (a) and failure criteria (b) vs P_m when welding a non-grafted PVOH-paper
 onto a grafted PVOH-paper at different welding forces. The PVOH coating weights are the same
 on both grafted and non-grafted papers.

324 The influence of PVOH coating weight on the mechanical performances of welded joints for grafted and non-grafted papers is detailed in Fig. 8. This 325 representation includes all tested PVOH-papers and considers only the maximal 326 327 strength measured while testing the samples welded at different set forces. As for non-grafted papers, there is no effect of the distribution of PVOH coating weight 328 329 when welding grafted papers. It seems that the peeling strength of grafted and non-grafted joints increases linearly with the PVOH weight present at the welding 330 331 interface. It is also true when welding non-grafted onto grafted PVOH-papers. The linear fittings presented in **Fig. 8** give an estimation of the level of adhesion 332 333 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 mechanical performances obtained when welding grafted PVOH-papers are 338 satisfying. It is possible to reach 100 N/m² when welding two grafted papers even 339 340 at low PVOH contents. However, reaching 160 N/m² requires the addition of larger amounts of PVOH. Indeed, the coefficients obtained from the linear 341 342 regressions indicate that increasing the amount of PVOH to improve the 343 performances of welding joints is about half as efficient for grafted papers compared to non-grafted. When welding grafted onto non-grafted papers, it is 344 possible to reach 160 N/m² for a total PVOH coating weight of 4 g/m². 345



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

352 3.3 Influence of welding direction

346

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%
- 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
- 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-

papers welded in the cross direction display mechanical performances 10% higherthan those grafted in the machine direction.



366

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

371 **4 Discussion**

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

As mentioned in section 3.2, the mechanical performances of grafted and non-374 grafted welded joints do not show the same evolution regarding the welding 375 power. While the peeling strength of non-grafted welded papers remains constant 376 whatever the power delivered by the welding machine, the grafted ones require a 377 378 certain P_m to be able to develop adhesion. Thus, the US welding machine needs to provide more power to be able to weld grafted papers. It means that it is easier to 379 380 weld non-grafted papers compared to grafted ones. Moreover, for an equivalent amount of deposited PVOH, the performances of non-grafted joints are superior to 381 382 the grafted ones. A maximal peeling strength of 420 N/m was measured in nongrafted joints for a PVOH deposition of 8,7 g/m², whereas it was only 264 N/m 383 384 for grafted joints (Fig. 4, 6, 8). Thus, results obtained in the frame of this study indicate that chromatogeny grafting decreases both the weldability potential and 385 386 the welding easiness of PVOH-papers. However, it is possible to assume that both grafted and non-grafted papers 387 actually exhibit a similar peeling strength vs. welding power behavior, made of an 388

- ascending step followed by a plateau. In such an assumption, the present results
- only show the plateau for the non-grafted papers since the ascending part would

have required smaller welding powers to be evidenced. Considering that no 391 392 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 that the welding easiness is affected by chromatogeny grafting. Further 395 investigation would be required to ascertain if chromatogeny grafting also affects 396 397 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.

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

A structural characterization of welded joints was done to understand the 400 401 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/m² are reported in Fig. 10. Micrograph (a) shows the whole crosssection of a welded joint (Fig. 10(a)). The welding line runs diagonally from 404 405 bottom-left to top-right. The fibrous structure of the reference paper can be observed on each side of the welding line. Fibrous structures are quite dense for a 406 407 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. 2019b; Charlier et al. 2021). The establishment of adhesion at the welding 411 interface seems quite straightforward. Focusing on the welded zone, it seems that 412 413 the two PVOH layers have melded and merged into a single one, thus bonding the two papers. It is not possible to identify an interface between the two welded 414 papers. It means that it is not possible to distinguish which part of the PVOH layer 415 belonged to one sheet of paper or the other. The US welding of non-grafted 416 417 PVOH-papers is quite similar to the US welding of thermoplastic polymers, the difference being that the welding concerns thin thermoplastic layers deposited 418 419 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 creation of a new interfacial composite material constituted of paper fibers 422 423 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 non-grafted joints increases with the PVOH coating weight (Fig. 4, 8). As the 428 429 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

Fig. 10: SEM cross-sections of welded joints obtained from non-grafted PVOH papers: sample
overview (a), and fibers embedded in the PVOH layer (b), (c). Total PVOH coating weight is 17.4
g/m² in pictures (a) and (b) and 12.4 g/m² 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 interphase region (Fig. 11). The main difference is that the interface between the 438 439 two welded papers can be seen all along the welding line. The two PVOH layers have not merged to form a new material. Moreover, the welding interface is not 440 441 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, filamentous, and interpenetrating layer zones. Non-welded zones correspond to 444 445 locations where the two paper sheets are not in contact at all. Filamentous zones refer to places were the surfaces are only bonded together by PVOH filaments 446 447 which can stretch up to $10 \,\mu m$ (Fig. 11(b), (c)). At last, interpenetrating layer 448 zones correspond to locations were the grafted PVOH layer of a paper has creeped 449 and penetrated inside the structure of the other paper (Fig. 11(d), (e), (f)).





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/m² in pictures (a), (b), (c), (e), and (f), and 5.4 g/m² in
454 picture (d).

Chromatogeny grafting is used to turn the PVOH layer, initially hydrophilic, into 455 a water repellant surface. The grafting reaction actually modifies the chemical 456 457 composition of the PVOH layer in about a 1µm-depth. Near surface molecules transform into poly(vinyl stearate) (PVS) displaying different molar mass, 458 459 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 layers have not merged. This means that the PVS part has flowed but not melted. 462 463 It is as if a very thin envelop, behaving like a ductile thermoset material, was on top of the PVOH layer, preventing it to merge with the other one (not unlike 464 465 standard core-shell structures). Based on these hypotheses, it is possible to 466 elaborate on the adhesion mechanisms related to the identified patterns:



475 Filamentous zones: it probably corresponds to zones where the grafting reaction did not totally succeed. It is possible that the PVS envelop could, 476 in some places, present holes, i.e. non-grafted zones, through which 477 PVOH could flow. Thus, filaments should correspond to zones where 478 479 PVOH has melted and merged (PVOH-filaments, Fig. 11(b), (c)). In term 480 of occurrences, filamentous zones were observed more frequently when welding non-grafted with grafted PVOH-papers, which is consistent with 481 482 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 studied welding conditions, and it remains highly speculative that such a result 491 492 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 reaction succeed, a OH-group (17 g/mol) is replaced by a 16-C alkane chain (225 496 497 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 40-50°C (Nzé et al. 2012; Wang et al. 2018). Consequently, the T_m of the grafted 500 501 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

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

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