

## Effects of Radio Frequency and Heat on Wood Bonding with a Poly(vinyl acetate) Dispersion Adhesive

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**ABSTRACT:** Water-based poly(vinyl acetate) dispersions are widely used as wood adhesives with dielectric heating systems. However, little is known about the effects of radio frequency (RF) exposure or heat on the adhesive characteristics and on the performances of bonded joints. In this study, the properties of bonded joints exposed to RF were compared with hot pressing and with standard drying, and the observed behavior was explained. Joint characteristics were evaluated by means of both conventional (e.g., shear strength in both dry and wet conditions, etc.) and unconventional (e.g., bondline temperature, moisture content at interface, etc.) procedures, and also selected properties of polymeric film were measured (e.g., water absorption, analysis of the fraction dissolved in water, glass transition temperature [ $T_g$ ], etc.) to explicate the observed differences. Results evidenced that the effect of both RF and heating was to appreciably speed up the drying process. However, when high values of energetic impulse (owing to both hot pressing and RF) were given to the assemblies, permanent changes were induced into the polymeric glue line. This occurrence was a time-driven process and reflected mainly on the mechanical performance in wet conditions, which improved appreciably in comparison to the standard reference series. The reason of such behavior was connected to the poly(vinyl alcohol) phase present inside the polymer, and a role was also assigned to  $AlCl_3$ , used as complexing agent of the polymeric protective colloid. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1157–1169, 2013

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### INTRODUCTION

The field of application of radio frequency (RF) intended for wood adhesives is based on the dielectric heating induced by electromagnetic waves, which are able to warm materials that are poor conductors of heat.<sup>1–3</sup> The first patents relating to applications in bonding can be found already at the beginnings of the 1940s.<sup>4,5</sup> However, they did not mention the adhesive performance relating to operating conditions.

Although a large body of work relates to the health effects of RF radiation,<sup>6,7</sup> the literature on the impact of applying RF to poly(vinyl acetate) (PVAc) bondlines on bond performance of wood-to-wood assemblies is limited to the study of the substrate grain orientation (radial–radial, radial–tangential, and tangential–tangential) and of the wood moisture content (WMC),<sup>8</sup> or to energetic issues.<sup>9</sup> Instead, a comprehensive set of measurements able to determine and possibly explain the structural changes that RF induces on the wood–adhesive performances as related to the polymeric film structure has never been studied.

The very wide variety of applications of polymer latexes (adhesives, binders, paper coatings, textile finishes, floor polishes, printing inks, etc.) makes their film-formation process an important area of research. The film-formation process consists of transforming a stable dispersion of colloidal polymer particles into a continuous solid film; this process is complex because it is affected by many factors such as presence and type of coalescing aid, chemistry of the crosslinking agent, in particular either if it is used during the polymerization phase or if it is post-added as curing agent, and so on.<sup>10</sup>

Generally, the coalescing aid is a low-molecular-weight compound chosen to decrease the polymer glass transition temperature and thus favor the coalescence of particles through their deformation.<sup>11</sup> Also, important is the role played by poly(vinyl alcohol) (PVOH), which mainly acts as a protective of polymer particles during the polymerization phase. However, after the film-formation process, PVOH uniformly distributes at the boundaries of PVAc particles. This reduces the film performances in wet conditions because of two main reasons<sup>12</sup>:

**Table I.** Typical Analytical and Technical Characteristics of the Used Adhesive

Analytical characteristics	Method	Value
Polymer base	-	PVAc
Dispersing system	-	PVOH
Solid content	ISO 3251:2005 <sup>20</sup>	52%
Viscosity	ISO 2555:2002 <sup>21</sup>	15,000 MPa·s
pH	ISO 976:1996 <sup>22</sup>	3
Minimum film-forming temperature	ISO 2115:1996 <sup>23</sup>	3°C
Shear strength in normal conditions	EN 204:2001 <sup>24</sup> D1	16.0 (±0.8) MPa
Shear strength in wet conditions	EN 204:2001 <sup>24</sup> D3-3	3.0 (±0.6) MPa
Shear strength at 80°C	EN 14257:2006 <sup>25</sup>	7.5 (±0.3) MPa

1. The introduction of hydrophilic OH groups into the latex.
2. Its water solubility and the presence of many microscopic pores which allow water to penetrate easily into the adhesive film.

Within this picture, the use of a protective colloid complexing agent allows interacting with PVOH molecules to reduce availability of hydrophilic groups.  $\text{AlCl}_3$  is often used as the complexing agent. It is commonly believed that the addition of  $\text{AlCl}_3$  has a dual effect: (a) it increases acidity, and thus promoting the crosslinking reaction with the specific comonomer usually added to the dispersion and (b) it interacts with the electron-donating groups of the polymer, such as the PVOH chains and the PVAc chains containing grafted PVOH, with the formation of structures similar to chelates.<sup>13</sup> Both occurrences appreciably improve the adhesive performances in wet conditions.<sup>10,11</sup> On the other hand, it is known how the strength of bonded wood joints is strongly dependent on an appropriate combination of polymer properties and wood characteristics.<sup>14–17</sup>

The effect of heat on the film-formation process has not been fully investigated still now, at least for commercial-type dispersions. A phase rearrangement owing to annealing at temperatures higher than the PVOH glass transition temperature provoked coalescence of the unconnected PVOH clusters initially contained in the film obtained from PVAc/PVOH dispersions.<sup>18</sup> According to the same author, this fact improved the adhesion between PVOH and PVAc particles. However, those dispersions did not include neither  $\text{AlCl}_3$  nor crosslinking agent.

Moreover, it was previously suggested that aluminum chloride could undergo thermal decomposition and hydrolysis under heating, thus producing free acid, which in turn promotes a self-crosslinking reaction involving the crosslinking agent.<sup>19</sup>

The aim of this study was to analyze how different process parameters affected the characteristics of bonded joint exposed to RF, in comparison to hot pressing and to the standard drying procedure at room temperature. Joint characteristics were evaluated by means of both conventional (e.g., shear strength in both dry and wet conditions, etc.) and unconventional (e.g., bondline temperature, moisture content at interface [MCI], etc.) procedures, and also selected properties of polymeric film were measured (e.g., water absorption, analysis of the fraction

dissolved in water, glass transition temperature [ $T_g$ ], etc.) to explain the observed differences.

## MATERIALS AND METHODS

A PVAc water-based dispersion adhesive with the characteristics reported in Table I was used for all the tests. It was a water-resistant adhesive belonging to the D3 class as defined by EN 204:2001.<sup>24</sup> The formulated commercial product is formed essentially by a base (a crosslinked PVAc dispersion stabilized by PVOH), a coalescing aid, and  $\text{AlCl}_3$  as the complexing agent of the polymeric protective colloid. For the majority of evaluations, the product was used as such. However, depending on the experimental needs, only the base plus the coalescing agent or the base plus  $\text{AlCl}_3$  were used.

### Preparation of Wood Assemblies

Wood assemblies were prepared by gluing beech thin boards of 640 mm × 125 mm × 5 mm. Each thin board was divided in two parts and, after spreading the adhesive on both sides, they were overlapped and put under the press to prepare the assembly. In such a way, the natural variability of wood was kept to a minimum. Beech (*Fagus sylvatica* L.) with a density of 695 ± 15 kg/m<sup>3</sup> and regular grain as specified in EN 205:2003<sup>26</sup> was used for the preparation of the various specimens.

All tests were performed in parallel on:

1. Specimens prepared by gluing assemblies at room temperature with the standard gluing conditions (23°C, 50% RH) as specified in the product technical data sheet (pressure 0.8 N/mm<sup>2</sup>, open time <1 min, closed time 4 min, pressing time 2 h, adhesive quantity 150 g/m<sup>2</sup> by spreading the glue on each side of the assembly). This condition represented the reference one for evaluating the adhesive's performances.
2. Specimens prepared by hot pressing the assemblies in a laboratory electrohydraulic press (HP series). This latter had a 2 N/mm<sup>2</sup> maximum potential pressure, with heated plates allowing working in the temperature range between 23 and 250°C.
3. Specimens prepared by exposing the assemblies to the high-frequency value of 7 MHz (RF series). This was accomplished on the same press used for hot pressing, which was equipped with a RF generator (produced by Cavallo, supplied power in the range between 4 and

10 kW with a variable frequency between 3 and 10 MHz, equipped with an amperometer able to continuously measure the anodic current). The press device metal plates were replaced by wood ones when the RF unit power was combined with the press. Anode and cathode of the RF generator were connected through an aluminum band (width 70 mm and thickness 0.3 mm) to two electrodes set on the wood plates of the press device. In such a way, the plane of bonding was parallel to electrodes and orthogonal to the electric field direction. An aluminum frame was used to ensure an additional connection between the press and the RF generator to keep the same potential and avoid electrostatic discharge. RF energy was applied for the selected exposure time (variable from 30 to 120 s, depending on the considered condition); then, the RF generator was turned off and the glued assemblies were kept under pressure for a total pressing time of 6 min, constant for the various evaluations. During RF exposure, the anodic current was manually kept constant at the selected level by acting on the related potentiometer.

For each one of the three series (standard, HP, and RF), only selected gluing parameters were varied: pressing and exposure times, amount of adhesive, moisture content into the adherends, anodic current (only for the RF series), and conditioning time. This latter was the time elapsed from the release of the pressure till the submission to external stresses (either of mechanical or of physical type). Conversely, the other process parameters (pressure, open and closed times) were the same as for the standard reference samples.

### Mechanical Evaluations

Mechanical tests were carried out to evaluate the performances of bonded joints. More specifically, shear strengths according to class D1 (preliminary conditioning phase for the standard series: 7 days at  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  RH) and D3-3 (preliminary conditioning phases for the standard series: 7 days at  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  RH, followed by complete immersion of specimens in water for 4 days, samples tested wet) of EN 204:2001 were evaluated. However, some modifications to the conditions provided into these standards were adopted when eventually considered necessary (as specified into the specific parts of the text). Ten specimens from same assembly were used for each series, unless expressly specified.

A series of mechanical tests were also carried out after exposing samples to the higher temperatures of 40 and  $80^\circ\text{C}$ . In this latter case, after the selected conditioning time (e.g., 7 days at  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  RH for the standard series), specimens were kept in an oven at  $80^\circ\text{C}$  for 1 h before testing, as provided in EN 14257:2006 (WATT 91)],<sup>25</sup> and a similar procedure (except for the exposure temperature) was also followed for the series at  $40^\circ\text{C}$ . Tests were carried out on 20 specimens per series, taken from two different assemblies, unless differently specified.

In addition to tests on glued joints, a series of tensile tests on the polymeric film alone were also carried out. Films were prepared by spreading dispersions on a polyethylene sheet by means of an automatic film applicator, run at a speed of 12.5 mm/s and set to a thickness of 500  $\mu\text{m}$ . Once spread, they were put in a climatic chamber set at  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  RH. In the case of stand-

ard series, films were kept in these conditions for 7 days. Instead, in the case of RF and HP series, after 24 h films were exposed to 0.7 A for 90 s and to  $120^\circ\text{C}$  for 30 min, respectively. After, specimens were conditioned for 7 days in a climatic chamber set to the same conditions as reported above. Force and elongation were continuously measured during tests. Specimens were loaded at a head rate of 20 mm/min.

### Measurement of the Bondline Temperature

In hot-pressed samples, the temperature was continuously measured during the pressing time by means of a thermocouple (mod. Ebro EBI-2T-311) directly inserted in a 3-mm diameter hole drilled across the bondline just after the overlapping of the wood thin boards. In the case of RF specimens, an online measurement of the temperature was prevented by the metallic nature of the thermocouple, which reflected the radiation. Therefore, temperature was measured by using an IR thermometer (mod. OPTRIS LS-PLUS), pointing on a spot of  $\geq 1$  mm on the external edge of assembled thin boards. This value was compared with the one obtained by inserting the same thermocouple used for HP specimens in a hole made before spreading the adhesive. In this case, measurements were run within 5 s from the end of the exposure to RF. The comparison between the two techniques evidenced a very rapid decrease of bondline temperature after the RF generator was switched off: the maximum observed drop in BLT was  $15^\circ\text{C}$  (from  $115^\circ\text{C}$ , measured by the IR thermometer, to  $100^\circ\text{C}$ , measured by the thermocouple) for joints exposed at 0.8 A for 80 s. This occurrence suggested thermally insulating (by means of rock-wool strips inserted between the press plates) the boards during the 6-min pressing time with the RF generator turned off. Additionally, the outermost 8–10 mm of boards were discarded and not used for specimen preparation.

### Measurement of Moisture Contents

Moisture content of wood adherends was measured when appropriate by using an electrical moisture meter (mod. Holzmeister LG9NG), with resolution of 0.1 units. In addition to WMC, the MCI was also measured by means of the same instrument. In this latter case, the moisture-meter tips were placed just into the bondline. However, considering the limited thickness of the bondline and the different resistivities of glue compared to that of wood, a series of measurements were carried out on specimens with 2-cm thick adherends to verify the reliability of the obtained data. More specifically, measurements were compared when the tips were inserted: (a) into the bondline, as in the usual case; (b) into the same wood adherend,  $< 5$  mm far from the bondline; and (c) into the two different wood adherends, across the bondline,  $< 5$  mm far from it. Measurements were carried out at several moisture contents (range, 7–12%), and a maximum difference of 1% between (a) and either (b) or (c) was observed, thus confirming that measurements were not practically affected by the precise insertion of tips.

### Release of PVOH After Immersion Tests

Polymer films were prepared as for tensile tests (see **Mechanical Evaluations** section). Samples were obtained by punching disks with diameter of 60 mm. They were weighed and then immersed in 100-mL deionized water without stirring for 7 days at  $23^\circ\text{C}$ . After this period, water was collected and the amount of PVOH assessed by means of a spectrophotometer UV-visible (Hach Lange DR/5000), after mixing the same solution with boric acid and iodine solutions. In fact, PVOH forms a green colored

complex with boric acid and iodine. Mixtures for calibration were prepared by adding weighed quantities of PVOH (in our case, from 0.2 to 2 mg) to water, and then adding a 40 g/L solution of boric acid and a 0.1N solution of iodine. Such mixtures were kept at 25°C for 15 min; then measurements were carried out at the wavelength of 690 nm.

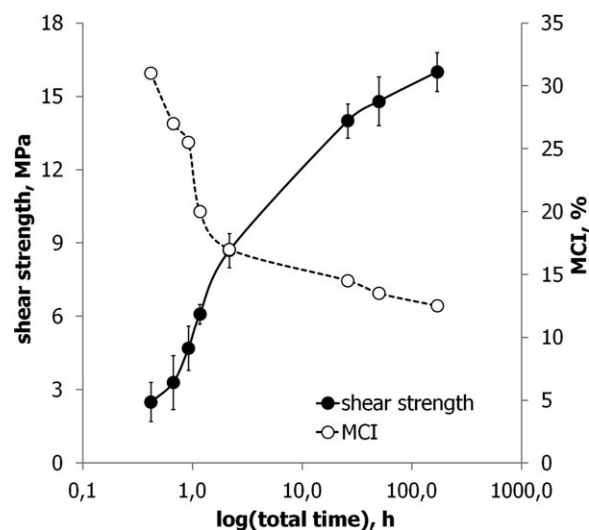
Furthermore, dissolution-in-water tests were carried out on commercial solutions of liquid PVOH (purchased by Kuraray, 12 ± 1% dry content) to which 3% w/w of a 27.6% w/w AlCl<sub>3</sub>·6H<sub>2</sub>O solution was added. In this case, films were prepared as for tensile tests (see **Mechanical Evaluations** section) but with a 1500 μm thickness applicator. Some samples were kept in standard conditions for 7 days after preparation. Moreover, some other samples were exposed at 120°C for 30 min, and still others at 0.7 A for 90 s before a conditioning phase of at least 7 days in a climate chamber (23°C and 50% RH). All tests were performed in duplicate. Also in this case, 60-mm diameter disks were prepared by punching films before exposure or before the conditioning in the climatic chamber, depending on the considered series. Disks were weighed before their immersion in 100 mL deionized water, where they were kept at 23°C for 7 days without stirring. Then, residual films were collected and put in an oven at 110°C for at least 1 h and, however, until a constant weight was reached. Finally, samples were weighed at this nominally anhydrous state. The mass variation in percentage was calculated in relation to the initial weight.

#### Measurement of Glass Transition Temperature

$T_g$  was measured by making use of a differential scanning calorimeter (DSC). In our case, a Netzsch DSC 204 FI was used. Polymeric films were dried for at least 1 week at 23 ± 1°C and 50 ± 2% RH after spreading and/or exposure to energetic impulse (according to the considered series). Moreover, samples were kept for 3 h in an oven at 25°C under vacuum to remove the residual humidity. Tests were carried out on 10 mg portions encapsulated in 40 μL aluminum pan with the following thermal program: from 25 to -60°C at 20°C/min; isothermal at -60°C for 10 min; from -60 to 60°C at 10°C/min.  $T_g$  was determined by the half-height method, as the midpoint temperature of the heat capacity step change.

#### Attenuated Total Reflectance–Fourier Transform Infrared Analysis

Attenuated total reflectance–fourier transform infrared (ATR–FTIR) spectra were recorded on PVOH films with a Bruker Alpha FTIR spectrometer with the following settings: 40 scans for sample; spectral resolution: 4 cm<sup>-1</sup>, wave number range: 4000–400 cm<sup>-1</sup>, using a diamond single reflection ATR device. At least three measurements per sample were acquired directly on solid films, after they were kept under vacuum for 24 h at 25°C. No additional preliminary treatment was executed. Spectra were processed by using the software OPUS 6.5 (Bruker Optics, Ettlingen, Germany). Postspectroscopic manipulation was kept to a minimum: spectra were normalized according to the Min–Max normalization procedure, carried out between 1800 and 800 cm<sup>-1</sup>. By this procedure, the absorbance unit is automatically set to 0 in correspondence of the minimum (in our case at 1800 cm<sup>-1</sup>), whereas it is automatically set to 2 for the maximum (in our case, at the band at 1092 cm<sup>-1</sup>).



**Figure 1.** Behavior of the shear strength and of MCI versus total process time (the sum of pressing time and conditioning time). For process times until 130 min, the conditioning time was set to 10 min. In the case of longer process times, the pressing time was set to 120 min. Joints were assembled in normal conditions (23°C and 50% RH). Vertical bars in the shear strength values represent standard deviations.

## RESULTS AND DISCUSSION

### Shear Strength of Joints in Normal Conditions (According to class D1 of EN 204)

As expectable, the shear strength of a reference joint assembled in standard conditions increased by increasing the total process time. The increase was quantified and the results evidenced a clear enhancement of performance up to 1 day process time; then, the increase was much more limited (Figure 1). It is interesting to notice how MCI diminished from 31 to 12.5%, whereas WMC remained almost unchanged (8.5–9.5%). This shear strength increase was mostly owing to the advancing of the film-formation process, which raises the mechanical cohesive characteristics of bondline. Graph in Figure 1 shows very well how the parameter MCI was directly connected to the mechanical performance of joints glued with PVAc adhesives when tested in normal conditions.

The effect of direct heating on the shear strength of the assemblies was evaluated in the HP samples. Results evidenced that for the 40-min conditioning time, when temperature increased from 80 to 100°C the shear strength values measured at 5, 15, and 30 min pressing times increased and MCI decreased (Table II). The observed differences of values among the various times for a same temperature were statistically significant: ANOVA tests evidenced how  $F$ -values were higher than 64, 30, and 13 at the temperatures of 80, 100, and 120°C, respectively, whereas  $F$ -crit was slightly higher than 3 in all cases. Also, considering only the series at 15 and 30 min (in principle, this elevated difference could be only imputable to the low values observed after 5-min pressing time), the behavior was analogous:  $F$ -values were higher than 10, 6, and 8 at the temperatures of 80, 100, and 120°C, respectively, whereas  $F$ -crit was slightly higher than 4 (again for all temperatures). Interestingly, BLT values varied



**Table II.** Shear Strength in Normal Conditions and MCI for Samples Hot Pressed During Gluing (HP Series)<sup>a</sup>

		Pressing time (min)			
		5	15	30	
Conditioning time: 40 min	Shear strength (MPa)	80°C	7.4 (±0.7) (F)	11.0 (±0.6) (E)	12.5 (±1.1) (C)
		100°C	12.0 (±1.2) (CD)	14.5 (±0.9) (B)	15.6 (±1.1) (A)
		120°C	11.5 (±1.1) (DE)	12.6 (±1.0) (C)	14.2 (±1.4) (B)
	MCI (%)	80°C	20.0 (±1.5)	18.0 (±1.5)	16.0 (±1.0)
		100°C	17.0 (±2.0)	15.0 (±1.0)	13.0 (±0.5)
		120°C	14.5 (±1.5)	12.5 (±1.0)	11.0 (±1.0)
Conditioning time: 7 days	Shear strength (MPa)	80°C	14.0 (±1.1) (E)	13.5 (±0.7) (E)	13.8 (±1.0) (E)
		100°C	14.0 (±0.9) (E)	14.8 (±0.7) (DE)	16.0 (±0.9) (C)
		120°C	15.2 (±0.9) (CD)	18.9 (±1.2) (B)	21.7 (±1.2) (A)
	MCI (%)	80°C	13.0 (±0.5)	13.0 (±1.0)	13.0 (±0.5)
		100°C	13.5 (±1.0)	13.0 (±1.0)	12.5 (±1.0)
		120°C	12.5 (±0.5)	12.0 (±1.0)	12.0 (±1.0)

<sup>a</sup>Standard deviation are given in brackets. Letters in each series refer to the statistical groups (from A to F) identified after Student's *t*-test analysis at a 5% probability level. Groups are different between 40 min and 7 days conditioning times.

accordingly: at 5-min pressing time BLTs were 65 and 85°C for the HP/80 and HP/100°C series, respectively, whereas at 15- and 30-min pressing time BLTs were 73, 92, and 90/92°C for the HP/80, HP/100, and HP/120°C series, respectively. Therefore, an increase of BLT was always observed when passing from 80 to 100/120°C, thus meaning that the energy transferred from the heated plates to the assemblies caused the effective speed up in the water evaporation process which is associated to the contemporary coalescence of polymer particles within the dispersion (film-formation process).

In the case of 7 days conditioning time, two classes could be detected. To the first class belonged the series with the lowest initial energy supplied to joints, namely HP/80°C/5-30 min and HP/100°C/5-15 min. For this class, the ANOVA test provided a *P*-value of 0.08, thus evidencing that differences among series were not significant (the null hypothesis could not be rejected at 5% confidence level). In contrast, all differences obtained in the series belonging to second class (constituted by HP/120°C/5-30 min and HP/100°C/30 min) were significant (except for the series HP/100°C/30 min plus HP/120°C/5 min, whose

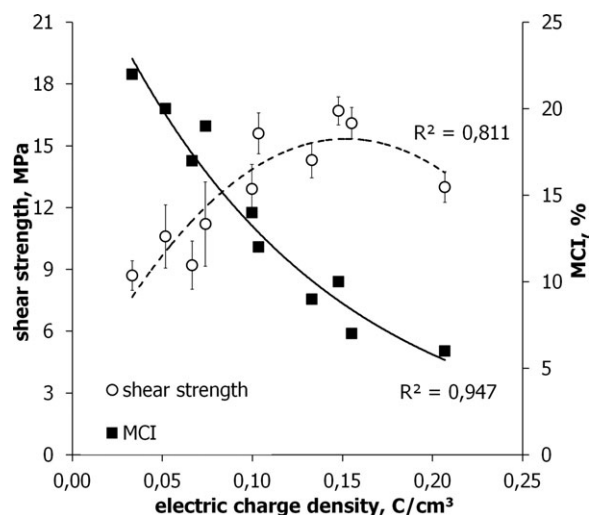
difference was not significant): in all the comparisons carried out, the highest *P*-value was of the order of 10<sup>-8</sup> (for the series HP/100°C/30 min plus HP/120°C/5-15 min), whereas it was even lower in the other cases (10<sup>-14</sup> for all series of second class, and 10<sup>-10</sup> for the series HP/120°C/5-30 min). These observations were also confirmed by Student's *t*-test analysis, which allowed grouping each series in definite statistical groups (Table II). Therefore, it appeared how the higher was the energy supplied to joints, the higher was the shear strength in normal conditions. This occurrence was mainly evident for the series HP/120°C/5-30 min. It is worth noticing that the observed values were also higher than the reference one, obtained for joints glued in standard conditions (Table I).

RF exposure caused a rapid increase of shear strength and the contemporary decrease of MCI, at least in the case of the 40-min conditioning time (Table III). Differently from what observed in the case of the HP series (where results did not increase when passing from 100 to 120°C at each pressing time), shear strength values increased uniformly up to 120 s. This behavior was attributable to the corresponding increase of

**Table III.** Shear Strength in Normal Conditions and MCI for the RF Series<sup>a</sup>

		Time of exposure to RF (s)			
		30	60	90	120
Conditioning time: 40 min	Shear strength (MPa)	8.4 (±1.8)	9.6 (±2.1)	13.3 (±1.4)	15.6 (±2.5)
	MCI (%)	20.0 (±2.0)	17.0 (±1.5)	13.0 (±1.5)	10.0 (±1.0)
Conditioning time: 7 days	Shear strength (MPa)	15.5 (±2.1)	16.0 (±1.5)	16.0 (±1.4)	16.0 (±0.9)
	MCI (%)	14.0 (±1.0)	13.5 (±0.5)	13.5 (±0.5)	10.5 (±0.5)

<sup>a</sup>The anodic current of the RF generator was set to 0.45 A. Samples were pressed during and after exposure, until a final pressing time of 6 min (constant for all the considered cases). In all, 20 specimens from two separate assemblies were tested for the series at 40-min conditioning time, 10 specimens from a same assembly for the series tested after 7 days. Standard deviation are given in brackets.



**Figure 2.** Behavior of shear strength and of MCI versus total unit energy (expressed in terms of electric charge) supplied by RF. Values were obtained after a conditioning time of 40 min. The combination of RF operative parameters related to each unit energy value was the same of that reported in Table IV. Coloration of glueline after RF exposure was also the same as reported in Table IV. Interpolation curve for shear strength is:  $-545.3x^2 + 165.6x + 2.8$ . Vertical bars represent the 95% confidence interval. Interpolation curve for MCI is:  $30.1 \cdot \exp(-8.2x)$ .

BLT with exposure time: BLT was 50°C at 30 s, 65°C at 60 s, 99°C at 90 s, and 105°C at 120 s. Interestingly, MCI after the exposure time of 120 s was very low (10%, lower than the equilibrium values reached during both hot pressing and standard gluing, also for longer conditioning times). Both BLT and MCI data implied that RF exposure conferred an elevated energy amount (in a short time) to the assembly, which dried wood substrate in addition to the glue line.

Differently from HP series, for RF samples values of both shear strength and MCI after the 7 days conditioning time levelled to an almost constant value.

An additional series of tests was carried out to determine the main factor governing the RF process. More specifically, in such tests the quantity of energy transferred to bondline through RF was changed by varying both the exposure time and the anodic current, whereas the tension,  $V$ , was kept constant at 4 kV. In such a way, the energetic level globally involved into the process was systematically modified and its effect evaluated.

The electric charge density value, expressed in  $C \cdot cm^{-3}$ , supplied by the RF generator to the assembly was calculated according to the following expression:

$$Q = \frac{\text{Anodic current} \times \text{Exposure time}}{\text{Assembly volume}}$$

This quantity is proportional to the unit energy supplied to joints, which is  $QV$ .

Results evidenced how, for the conditioning time of 40 min, the higher was the unit energy supplied to the assembly the lower was MCI and the higher was the shear strength value (Figure 2). However, while MCI uniformly decreased with energy (the decreasing curve fitted well with an exponential curve,  $R^2 = 0.947$ ), the shear strength first increased by increasing unit energy, reached a maximum at 0.10–0.15  $C \cdot cm^{-3}$  and then decreased for higher energies. It has to be noted that also an increasing discoloration of the bondline was observed starting from 0.13 until 0.20  $C \cdot cm^{-3}$ , where the joint began appreciably brown-colored. In principle, this observed decrease in mechanical strength could be imputable both to thermal degradation in wood and to some kind of structural modification into glue. However, the measured BLT values were limited: 105°C after both 120 s at 0.45 A (corresponding to 0.13  $C \cdot cm^{-3}$ ) and 90 s at 0.7 A (0.16  $C \cdot cm^{-3}$ ), and 109°C after 120 s at 0.7 A (0.21  $C \cdot cm^{-3}$ ). Therefore, the hypothesis of glue modification seemed to be more realistic.

After 7 days of conditioning time, the results of assemblies exposed to lower levels of unit energy (electric charge, 0.03–0.05  $C \cdot cm^{-3}$ ) evidenced values comparable to those obtained after standard gluing (Table IV), whereas joints to which higher

**Table IV.** Shear Strength in Normal Conditions and MCI for Various Values of Electric Charge Density Supplied by Means of RF<sup>a</sup>

Combination of RF operative parameters (exposure time at anodic current)	Electric charge density ( $C \cdot cm^{-3}$ )	Shear strength (MPa)	MCI (%)	Notes
30 s at 0.45 A	0.033	15.5 ( $\pm 2.1$ )	14.0 ( $\pm 1.5$ )	
30 s at 0.7 A	0.052	16.4 ( $\pm 0.9$ )	14.0 ( $\pm 1.0$ )	
60 s at 0.45 A	0.067	16.0 ( $\pm 1.5$ )	14.0 ( $\pm 1.0$ )	
30 s at 1 A	0.074	19.0 ( $\pm 1.1$ )	14.0 ( $\pm 0.5$ )	
90 s at 0.45 A	0.100	16.0 ( $\pm 1.4$ )	14.0 ( $\pm 1.5$ )	
60 s at 0.7 A	0.103	18.7 ( $\pm 1.1$ )	13.0 ( $\pm 0.5$ )	
120 s at 0.45 A	0.133	16.0 ( $\pm 0.9$ )	11.0 ( $\pm 1.0$ )	Glueline brown colored
60 s at 1 A	0.148	18.8 ( $\pm 1.7$ )	12.0 ( $\pm 1.0$ )	Glueline brown colored
90 s at 0.7 A	0.155	18.1 ( $\pm 1.1$ )	12.0 ( $\pm 1.0$ )	Glueline brown colored
120 s at 0.7 A	0.207	14.6 ( $\pm 0.7$ )	11 ( $\pm 1.0$ )	Glueline brown colored

<sup>a</sup>Data are referred to a conditioning time of 7 days. Samples were pressed during and after exposure to RF, until a final pressing time of 6 min. Standard deviation are given in brackets.

**Table V.** Shear Strength in Normal Conditions and MCI for the RF Series when the Adhesive Quantity Spread onto Wood Surfaces was Varied<sup>a</sup>

		Adhesive quantity spread onto wood surfaces (g/m <sup>2</sup> )					
		100		150		200	
		Shear strength (MPa)	MCI (%)	Shear strength (MPa)	MCI (%)	Shear strength (MPa)	MCI (%)
Exposure time (s)	30	9.2 (±1.8) (DE)	21.0 (±1.5)	8.5 (±1.1) (E)	21.0 (±2.0)	8.5 (±1.4) (E)	24.0 (±2.0)
	60	10.9 (±3.0) (D)	17.0 (±1.0)	10.1 (±1.8) (DE)	17.0 (±1.5)	9.8 (±1.5) (DE)	22.0 (±2.0)
	90	14.4 (±2.5) (BC)	10.0 (±1.0)	13.7 (±1.6) (C)	12.0 (±0.5)	14.7 (±3.4) (BC)	14.0 (±1.5)
	120	15.7 (±2.7) (AB)	7.5(±0.5)	16.7 (±1.7) (A)	10.0 (±0.5)	16.6 (±1.6) (A)	11.0 (±1.0)

<sup>a</sup>The anodic current of the RF generator was set to 0.45 A. Data are referred to a conditioning time of 40 min. Samples were pressed during and after exposure, until a final pressing time of 6 min. In total, 20 specimens from two separate assemblies were tested for the series at 100 g/m<sup>2</sup>, 10 specimens from a same assembly for the series at 150 and 200 g/m<sup>2</sup>. Standard deviations are given in brackets. Letters in each series refer to the statistical groups (A-E) identified after Student's t-test analysis at a probability level of 5%.

energies were supplied during pressing presented higher values of shear strength (18–19 MPa), more similar to those observed for the series HP/120°C/15–30 min. Finally, at the unit energy corresponding to electric charge of 0.20 C·cm<sup>-3</sup> a decrease in mechanical performance was measured, which confirmed the analogous decrease observed after 40-min conditioning time.

For both the two considered conditioning times, data evidenced that the amount of unit energy supplied to the assembly played the most important role in determining the mechanical characteristics of joints in normal conditions. However, both wood and dispersion contained water (although in a very different amount between them), and therefore they were able to absorb energy from the electric field provided by the RF generator. Therefore, two additional series of tests were carried out to separately evaluate the effect of these two factors.

#### Effect of the Adhesive Quantity Spread onto the Wood Surfaces on Shear Strength of Irradiated Joints

This series was prepared to evaluate the effect of energy supplied by the RF generator when the glue was spread in different amounts onto the two wood surfaces of each assembly. In the case of 7-day conditioning time, as already observed for the other conditions reported above, both shear strength and MCI levelled to the statistically equivalent values of 13.3 (±1.1) MPa and 12.9 (±1.2)%, respectively. Instead, for the 40-min conditioning time, results confirmed that for a same amount of glue the higher was the RF exposure time (and hence the energy supplied to the assembly), the higher was the shear strength of joints and the lower was MCI (Table V). Conversely, for a same exposure time the glue amount did not play an appreciable role in determining the mechanical performances of samples, at least in the considered range. In fact, the observed differences were not statistically significant: the *P*-values obtained after ANOVA tests carried out for each exposure time were higher than 0.4 for the 30 s series, higher than 0.5 for the 60 s series, 0.7 for the 90 s series, and finally higher than 0.4 for the 120 s series. These results indicated that the null hypothesis could not be rejected at 5% confidence level. This occurrence was imputable to the limited amount of water into the bondline as compared to moisture content in wood adherends. In fact, considering the

glue solid content (Table I) and the dimensions of the used thin boards (**Preparation of Wood Assemblies** section), a water amount of 6.9–13.8 g (depending on the glue quantity spread onto the wood surfaces) was present into the bondline, which was appreciably lower than the total moisture content calculated for the two wood thin boards (50 g, see next section for the estimation procedures).

#### Effect of Moisture Content of Adherends on Shear Strength of Irradiated Joints

This series was prepared to evaluate the effect of energy supplied by the RF generator when the wood adherends had different moisture contents. To such purpose, adherends were kept in a climatic chamber, set at different temperatures and humidity conditions, up to constant weight and, however, for not <2 weeks. At the end of this conditioning period, WMC was measured by the electrical moisture meter. Then, the adherends were glued and exposed to RF within 15 min from their removal from the climatic chamber.

Considering that all previous tests evidenced that values levelled after 7 days of conditioning time, in this case data were only measured after the 40-min conditioning. Results evidenced that performances of joints appreciably diminished by increasing WMC (Table VI), thus evidencing the effect of energy depletion owing to the presence of moisture into wood adherends. The amount of water in wood adherends can be calculated on the basis: of wood density (**Preparation of Wood Assemblies** section) at the nominal moisture content of 10% (this latter was the equilibrium value for wood kept at 23°C and 50% RH), of volume of adherends (**Preparation of Wood Assemblies** section), and of the various moisture levels. The calculated total water amount in assemblies was approximately 30 g for the lowest humidity levels (5–7%), approx. 50 g for the intermediate levels (9–10%), and 60 g for the highest levels (12–13%). The extent of performance decrease owing to these water contents, from the driest to the most humid joints, was relevant: more specifically, it was of the order of 40% (referred to the value in normal conditions, i.e. at 9–10% moisture content) in the cases of the lowest energies (exposure times of 30 and 60 s) and of 20% after 90-s exposure time. Analogously, the higher fraction

**Table VI.** Shear Strength in Normal Conditions and MCI for the RF Series When the Moisture Content of Wood Adherends Was Varied<sup>a</sup>

Exposure time (s)	Wood moisture content (%)					
	5-7		9-10		12-13	
	Shear strength (MPa)	MCI (%)	Shear strength (MPa)	MCI (%)	Shear strength (MPa)	MCI (%)
30	9.0 (±1.8)	20.5 (±2.0)	8.5 (±1.1)	21.0 (±2.0)	5.4 (±2.5)	25.0 (±3.0)
60	12.0 (±1.4)	17.0 (±2.0)	10.1(±1.8)	17.0 (±1.5)	7.5 (±2.2)	22.0 (±2.0)
90	15.5 (±2.2)	12.5 (±0.5)	13.7 (±1.6)	12.0 (±0.5)	12.8 (±1.9)	18.0 (±2.5)
120	16.0 (±2.0)	9.5 (±1.0)	16.7 (±1.7)	10.0 (±0.5)	-	-

<sup>a</sup>The anodic current of the RF generator was set to 0.45 A. Data are referred to a conditioning time of 40 min. Samples were pressed during and after exposure, until a final pressing time of 6 min. The symbol '-' means that values were not measured in those cases. Standard deviations are given in brackets.

of energy dissipated into wood adherends also reflected on higher values of MCI after the considered exposure time: at 30-s MCI passed from 20.5% for the driest adherends to 25% for the most humid ones, and similar increases of approximately 5% (in absolute terms) were also observed for the other exposure times (Table VI). It is worth to note that in some cases (for the condition 120 s/12–13%, and for all exposure times at more elevated moisture contents) measurements were not possible because an electric arc developed during exposure to RF.

#### Shear Strength of Joints in Wet Conditions (According to Class D3-3 of EN 204)

Reference samples glued in standard conditions showed wet shear strength of 3.0 (±0.6) MPa. When samples were hot pressed during gluing, it was observed that, while the pressing time of 15 min was only just sufficient to reach the performance of the standard series (except for the combination at lowest energy, 80°C/1-day-conditioning-time, which was insufficient), for the longer pressing time of 30 min this value was always reached and also exceeded (Table VII). A positive effect on the wet shear strength was not only related to temperature, as expected, but also to conditioning time. More specifically, at 80°C the joint performances appreciably increased for both pressing times of 15 and 30 min when passing from 1 day of conditioning time to 7 days (Table VII), thus evidencing some kind of film modification during time. However, this latter time-dependent phenomenon was also related to temperature, and in fact at 120°C it was no more evident. Interestingly, for the highest pressing temperature of 120°C the measured wet shear strength was appreciably higher than the reference value of 3.0 MPa obtained in standard conditions.

Also in the case of RF series, a behavior analogous to that observed for the HP samples was evidenced: the more was the exposure time the higher were the obtained shear strengths for the wet assemblies (Table VIII). Moreover, for the lowest electric charge densities (up to 0.07 C·cm<sup>-3</sup>) the threshold level of 3.0 MPa (standard joints) was not reached after the conditioning time of 40 min. In contrast, when the unit energy corresponding to 0.10 C·cm<sup>-3</sup> or larger was supplied to the assembly, the 3.0 MPa threshold value was always reached and also appreciably exceeded (Table VIII). However, differently from what observed for the shear strengths values in normal (dry) conditions (Table IV), in this case the joints performances did not decrease for the higher values of unit energy, but they remained unchanged also at the electric charge of 0.20 C·cm<sup>-3</sup>. Moreover, also these measurements confirmed that, for the lowest unit energies corresponding to electric charge of 0.05 and 0.06 C·cm<sup>-3</sup>, a longer conditioning time had a positive effect on the wet mechanical characteristics of joints, whereas this effect was no more observed in the case of values of 0.07 C·cm<sup>-3</sup> or higher.

#### Shear Strength of Joints Tested at High Temperature

Testing bonds at higher temperatures (40 or 80°C) uniformly reduced strength (Table IX). Those bonded assemblies tested after 40 min of conditioning all had lower strength than conventionally bonded specimens (strength 7.5 ± 0.3 MPa; Table I). More specifically, while samples of HP series never reached this threshold, independently on both pressing time and temperature (except for the combination 80°C/30 min, whose value was statistically equivalent to the reference,  $P = 0.13$  after ANOVA), RF samples reached the reference value only for the highest anodic current and exposure time ( $P = 0.21$  after ANOVA for the comparison between standard and RF/0.7A/90–

**Table VII.** Shear Strength in Wet Conditions for Samples Hot Pressed During Gluing<sup>a</sup>

Pressing time (min)		Conditioning time: 1 day		Conditioning time: 7 days	
		80°C	120°C	80°C	120°C
		15	2.2 (±0.2)	3.1 (±0.3)	2.9 (±0.2)
30	3.0 (±0.1)	4.6 (±0.5)	4.0 (±0.3)	4.2 (±0.3)	

<sup>a</sup>20 specimens from two separate assemblies were tested for the various series at 120°C, 10 specimens from a same assembly for those at 100°C. Standard deviations are given in brackets. The reference (standard) value is listed in Table I.



**Table VIII.** Shear Strength in Wet Conditions for Various Values of Electric Charge Density Supplied by Means of RF<sup>a</sup>

Combination of RF operative parameters (exposure time at anodic current)	Electric charge density (C·cm <sup>-3</sup> )	Conditioning time: 40 min	Conditioning time: 7 days
30 s at 0.7A	0.052	1.2 (±0.4)	2.5 (±0.2)
60 s at 0.45A	0.066	2.3 (±0.7)	2.8 (±0.5)
30 s at 1A	0.074	2.2 (±0.4)	1.9 (±0.3)
90 s at 0.45A	0.100	3.9 (±0.8)	4.1 (±0.7)
60 s at 0.7A	0.103	3.5 (±0.7)	3.7 (±0.6)
120 s at 0.45A	0.133	4.7 (±0.7)	4.7 (±0.5)
60 s at 1A	0.148	4.5 (±0.7)	3.8 (±0.5)
90 s at 0.7A	0.155	4.1 (±0.4)	4.0 (±0.5)
120 s at 0.7A	0.207	4.0 (±0.6)	3.9 (±0.6)

<sup>a</sup>Samples were pressed during and after exposure to RF, until a final pressing time of 6 min. In total, 20 specimens from two separate assemblies were tested for each series. Standard deviations are given in brackets. The reference (standard) value is listed in Table I.

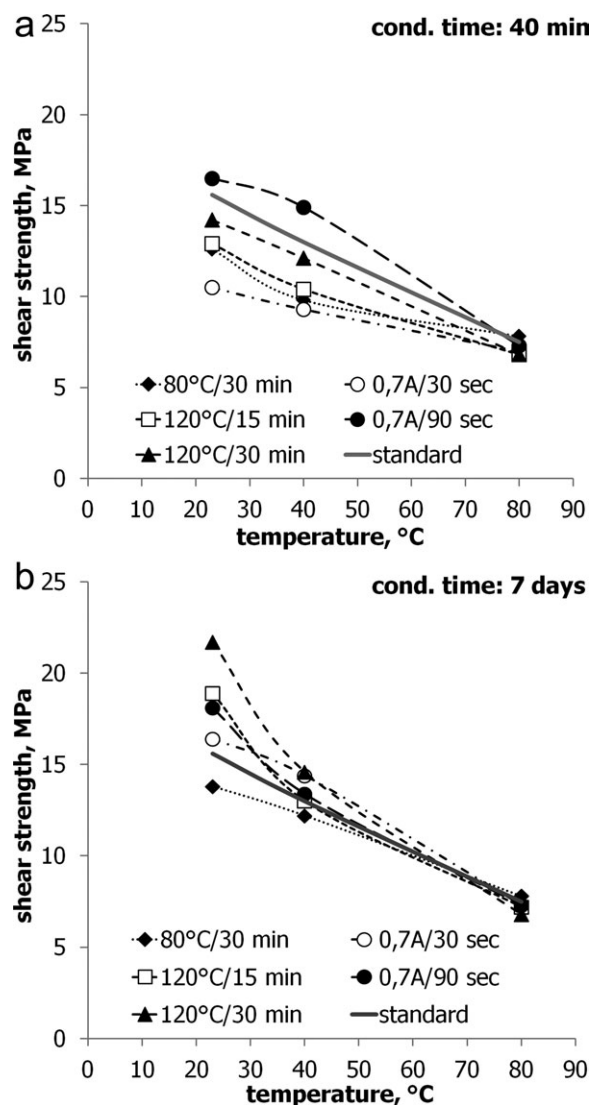
120 s series) (Table IX). However, the conditioning time had a positive effect on the joint performances, and both HP and RF series reached the value of the standard one, although in HP samples an apparently unfavorable effect of temperature was observed (at 120°C values decreased for both 15 and 30 min series). As expected, the MCI values measured just after each conditioning time were very similar to those values obtained when the mechanical characteristics in normal conditions were evaluated. More specifically, they varied from 18–22% (after 30 s exposure time and 40 min conditioning time) down to 8.5–10.5% (after 120 s exposure time and again 40-min conditioning time); these values were similar to those reported in Tables II and IV and Figure 1. After 1-h exposure at 80°C, all MCIs decreased owing to wood drying (and consequently interphase

drying), with values from 8.5 to 5.5%. However, differently from what observed in the case of tests at 23°C, shear strength values at 80°C were not affected by MCI. This occurrence demonstrated that at such a high temperature the wood support did not play a role in determining the mechanical characteristics of joints, whereas they were influenced only by the cohesive strength of the glue. This fact could theoretically facilitate the identification of eventual modifications into the glue structure imputable to HP or RF treatment. However, this temperature was too high and it did not allow to put in evidence the occurrence of eventual modifications by means of shear strength; in fact, a general levelling of values was observed. For this reason, although it was a not standard characterization, the lower temperature of 40°C was also tested for selected

**Table IX.** Shear Strength (MPa) Tested at 80°C in Dry Conditions<sup>a</sup>

			L	H
Conditioning time: 40 min at 23°C/50% RH+ 1 h at 80°C	HP	15 min	6.9 (±0.7) (DE)	6.9 (±0.6) (DE)
		30 min	7.8 (±0.5) (A)	6.9 (±0.5) (DE)
	RF	30 s	5.7 (±1.7) (F)	7.0 (±0.7) (CD)
		60 s	6.5 (±0.3) (E)	7.2 (±0.4) (BCD)
		90 s	7.2 (±0.5) (BCD)	7.3 (±0.6) (BC)
Conditioning time: 7 days at 23°C/50% RH+ 1 h at 80°C	HP	15 min	7.6 (±0.4) (AB)	7.1 (±0.6) (CD)
		30 min	7.8 (±0.2) (A)	6.9 (±0.7) (D)
	RF	30 s	7.3 (±0.4) (BCD)	7.3 (±0.5) (ABCD)
		60 s	7.5 (±0.5) (ABC)	7.2 (±0.5) (BCD)
		90 s	7.4 (±0.5) (ABC)	7.4 (±0.8) (ABC)
		120 s	7.7 (±0.7) (AB)	7.5 (±0.5) (ABC)

<sup>a</sup>For the HP series, samples were hot pressed during gluing. For the RF series, samples were pressed during and after exposure, until a final pressing time of 6 min. For the HP series, L = 80°C, H = 120°C. For the RF series, L = 0.45 A, H = 0.7 A. In total, 20 specimens from two separate assemblies were tested for the 40-min series, 10 specimens from same assembly for the 7-day series. Standard deviations are given in brackets. Letters in each series refer to the statistical groups (A–F) identified after Student's t-test analysis at a 5% probability level. Groups are different between 40 min and 7 days conditioning times. The reference (standard) value is listed in Table I, and it belonged to groups AB for the conditioning time of 40 min, and to groups ABC for the 7-day conditioning time.



**Figure 3.** Joint shear strength versus test temperature: (a) after a conditioning time of 40 min; (b) after a conditioning time of 7 days. In both Figures, standard series was that in which samples were kept at 23°C and 50% RH for 7 days. Values of standard deviation were avoided to improve the readability. In both figures, three statistical groups (A–C) were identified after Student's *t*-test analysis at a 5% probability level. In (a) they were 0.7A/90 s (A), 120°C/30 min (B), standard (B), 80°C/30 min (C), 120°C/15 min (C), and 0.7A/30 s (C). In (b) 120°C/30 min (A), 0.7A/30 s (A), standard (B), 0.7A/90 s (B), 120°C/15 min (B, C), and 80°C/30 min (C).

combinations, and the results are shown in Figure 3. The behavior observed at 80°C was basically confirmed also at 40°C: for the shorter conditioning time of 40 min the joints were less performing than the reference, with the relevant exceptions of the two series at the highest initial energetic impulse, namely 0.7A/90 s (whose value was significantly higher,  $P = 0.03$  after ANOVA) and 120°C/30 min (whose difference was not statistically significant,  $P = 0.07$  after ANOVA). Instead, after 7 days of conditioning time only the joints dried with the combination 80°C/30 min evidenced value lower than the reference (with a significant difference,  $P = 0.01$  after ANOVA). Moreover, MCI

values for the HP series and for the RF series to which the lowest initial energetic impulse was given were of the order of 12–15% after 1 h conditioning at 40°C, whereas they fell in the range of 5–10% for the highest energetic impulse RF series (in standard series, MCI in the same conditions was 14.5%). These tests confirmed that the energetic level initially supplied to joints during drying is very important in determining the strength value of assemblies in dry conditions, but that the same joints are not at their maximum after a brief time from exposure unless an elevated energetic level is initially supplied. Therefore, the eventual structural modifications in glue did not develop immediately but some time after exposure.

### TESTS ON POLYMERIC FILMS AND GENERAL DISCUSSION

All results for the shorter conditioning time of 40 min evidenced that the joint performances improved by increasing the energy supplied to the assembly, both for HP and RF series, owing to the contemporary advancing of both the film-formation process into the glue line and the progressive decrease of MCI. This latter parameter played a role only for shear strength in dry conditions, whereas as expected, it was not influent in wet conditions. Moreover, results also showed that in the case of low-energy values supplied to the assemblies, the conditioning time positively affected the shear strength both in dry and in wet conditions. This fact occurred for the lower temperature of 80°C and the lower pressing time of 5 min during hot pressing, and the lower anodic current of 0.45 A and unit energies corresponding to electric charge lower than  $0.05\text{--}0.06\text{ C}\cdot\text{cm}^{-3}$  after exposure to RF. Conversely, in the case of high-energy levels supplied to joints (higher temperature and pressing times for the HP series and higher unit energies in the RF series) a difference was observed. The shear strength in dry conditions increased by rising the conditioning time (from 15.2 to 18.9–21.7 MPa for the HP series, Table II, from 15.5–16.4 to 18.1–19 MPa for the RF series, Table IV), whereas this occurrence was not observed (or it was observed only limitedly) when joints were tested wet (Tables VII and VIII). Moreover, an additional difference was observed between the HP and the RF series in the case of wet shear strengths. In the former, it was not possible to carry out tests after 40-min conditioning time, as in the other cases, because joints broken after the 4 days soaking phase.

All the evidence reported above is compatible with the hypothesis that heating assemblies during pressing causes structural modification of the bondline and appreciably improve joint performance. According to this hypothesis, when low levels of energy were provided to the assemblies this modification process evolved during time, whereas if adequate levels of energy were supplied, a final stage into the structure of the adhesive layer was reached soon. Once this limit was attained, performances did not increase and rather, depending on the considered mechanical characteristic, they decreased. More specifically, in the RF samples the shear strength in normal conditions decreased when too high values of energy were supplied, thus indicating a worsening of bondline mechanical characteristics. However, glue became more hydrophobic, and in fact strength values in wet conditions were higher than the reference ones.

**Table X.** Tensile Mechanical Properties and  $T_g$  Measured by DSC of Pure Polymeric Films<sup>a</sup>

	Yield stress (MPa)	Stress at break (MPa)	Elongation at break (%)	$T_g$ (°C)
Standard	0.7 ( $\pm 0.3$ )	8.2 ( $\pm 0.9$ )	814 ( $\pm 29$ )	27.5
HP 120°C/30 min	5.6 ( $\pm 0.9$ )	8.0 ( $\pm 1.2$ )	388 ( $\pm 37$ )	28.0
RF 0.7 A/90 s	2.1 ( $\pm 1.0$ )	5.0 ( $\pm 1.3$ )	532 ( $\pm 41$ )	27.0

<sup>a</sup>Standard deviation in brackets.

In this case, the performances after overexposure to RF did not decrease, because the mechanical strength of the joint was more imputable to the weakness of the wet interphase rather than to the glue line cohesive strength.

To investigate about the structural modification into the glue owing to the initial energetic impulse supplied to the joint, a series of additional tests on the polymeric film alone were carried out. Tensile mechanical tests showed that some differences existed between films dried in standard conditions and films of both HP and RF series: these latter both evidenced higher yield stress, and similar (HP) or lower (RF) maximum stress than the standard film (Table X). The observed differences are better illustrated by looking at the stress–strain curves shown in Figure 4 for representative samples of each series: curves related to both RF and HP specimens evidenced higher yield stress values than standard series although this latter failed at higher final values of both stress and elongation, thus evidencing a more plastic behavior. This fact clearly demonstrated that structural modifications occurred into the polymeric film after the energetic impulse owing to RF or high-temperature exposure.

The fact that values of  $T_g$  as measured by DSC were practically the same among the three considered series (Table X) is not contrasting with this observation. In fact, as mentioned, the film formation in latex is a complex process in which several substances are involved, including PVOH, the coalescing aid and the protective colloid complexing agent (in our case  $AlCl_3$ ), in addition to the crosslinked PVAc. It is commonly thought that PVOH is located in shells at the surfaces of PVAc particles in the dispersion, interacting with them through entanglements. However, such entanglements are limited to the outermost layers of particles, whereas their core can be considered as constituted by almost pure PVAc. Through DSC, only the transition associated to the PVAc core of particles can be accurately determined, whereas the other transitions are more difficult to detect (also with other techniques), because of the interactions between  $AlCl_3$  and PVOH. Therefore, DSC measurements evidenced only that these structural modifications did not interest the PVAc core of particles into the polymeric film.

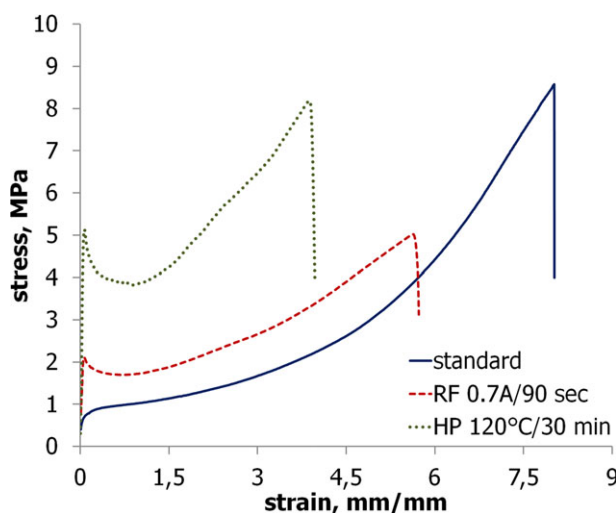
To evaluate the effect of the coalescing aid on the characteristics of joints in wet conditions, a dispersion was prepared in which the coalescing agent was absent. Values obtained were 3.1 ( $\pm 0.2$ ) and 4.4 ( $\pm 0.2$ ) MPa for the standard series and for the

HP/120°C/30 min series, respectively. These values were very similar to the results obtained for the commercial dispersion (3.0 and 4.2 MPa, respectively), and thus evidencing a minor role of the coalescing aid with reference to the energetic impulse.

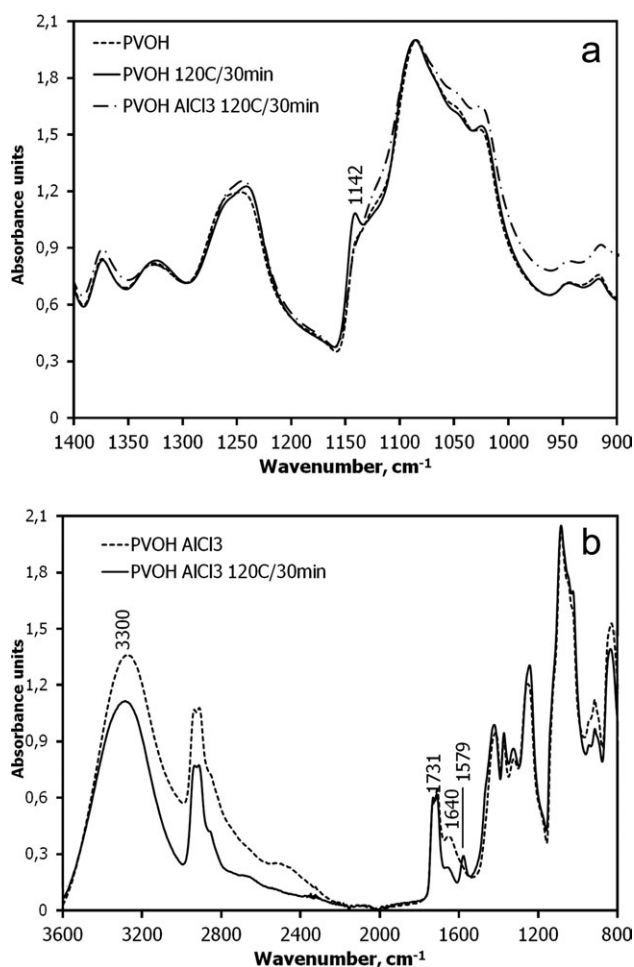
In contrast, when the dispersion was prepared without  $AlCl_3$  and dried in standard conditions, worse results were obtained: in a formulation where pH was uncontrolled, all specimens broke after the water immersion phase, as expected. Instead, in a different formulation where orthophosphoric acid was used to adjust to pH 3, the same as for commercial dispersions, the wet shear strength value of 0.4 ( $\pm 0.3$ ) MPa was obtained. This increase was because strong acids act as catalyst and induce postcuring (i.e., an enhancement of the self-condensation reaction interesting the crosslinking agent) in dispersions even at room temperature.<sup>27</sup> A similar behavior was observed when joints were dried at 120°C for 30 min. In such a case, both dispersions prepared without  $AlCl_3$  showed the same wet shear strength value of 0.5 ( $\pm 0.2$ ) MPa, and thus evidencing a limited improvement attributable to a temperature-induced partial hydrophobization process into dispersions. Therefore, these measurements confirmed the decisive effect of  $AlCl_3$  in determining the joint performances in wet conditions, and they also evidenced that the importance of acid-catalyzed postcuring was much more limited.

Moreover, a series of water absorption tests were carried out on polymeric films alone, after which water was collected and the released PVOH measured. The standard, RF, and HP series released 21.0, 7.8, and 3.2 mg of PVOH/g of film, respectively, showing that the initial heating had a strong impact on the film properties.

Therefore, modifications mainly occurred in the PVOH phase inside the film. As mentioned, it has been previously reported<sup>18</sup> of a thermally induced coalescence of PVOH clusters from PVAc/PVOH dispersions, owing to thermal annealing above



**Figure 4.** Stress–strain curves of polymeric films dried according to the considered series (standard, HP, and RF). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** ATR-FTIR spectra showing (a) the lack of the band at  $1142\text{ cm}^{-1}$ , attributable to crystalline PVOH, when heated at  $120^\circ\text{C}$  in the presence of  $\text{AlCl}_3$ ; (b) the strong reduction of bands at  $3300$  and at  $1640\text{ cm}^{-1}$ , attributable to O—H stretch of free alcohol and water hydroxyl groups, respectively, in the PVOH films heated at  $120^\circ\text{C}$  for 30 min in the presence of  $\text{AlCl}_3$ . Spectra were Min–Max normalized ( $800\text{--}1800\text{ cm}^{-1}$ ).

PVOH glass transition temperature. In our case, BLT observed in RF exposed joints was in fact as high as  $109^\circ\text{C}$  (**Shear Strength of Joints in Normal Conditions (According to class D1 of EN 204)** section). However, for our commercial-type dispersions, this PVOH phase rearrangement was not imputable to crystallization. In fact, ATR-FTIR analysis carried out on pure PVOH films with and without the presence of  $\text{AlCl}_3$  evidenced that the peak at  $1142\text{ cm}^{-1}$ , normally attributed to PVOH crystallites,<sup>28,29</sup> was not induced by temperature ( $120^\circ\text{C}/30\text{ min}$ ) in the presence of  $\text{AlCl}_3$  [Figure 5(a)]. Furthermore, dissolution-in-water tests carried out on PVOH films with the addition of  $\text{AlCl}_3$  evidenced that films dried in standard conditions completely dissolved in water. On the contrary, when the same films were exposed to  $120^\circ\text{C}$  for 30 min only  $17.7\%$  ( $\pm 0.3\%$ ) of the initial mass was lost, and this value was very similar ( $20.0 \pm 0.7\%$ ) when they were exposed to  $0.7\text{A}/90\text{ s}$  RF.

Considering that PVOH dissolution-in-water tests were carried out on films without the addition of any crosslinking agent, we

believe that the hypothesis of self-cross-linking reaction induced by thermal decomposition of  $\text{AlCl}_3$  (as suggested in Ref. 19) does not apply on our case. In contrast, the PVOH rearrangement appeared more related to the advancement and more effective interaction between PVOH and  $\text{AlCl}_3$ , which is induced by high temperature, with the consequent dramatic decrease of polymer hydrophilicity. Also, ATR-FTIR analysis confirmed this observation. Vibrations at  $3300$  and  $1640\text{ cm}^{-1}$ , assigned to O—H stretch, attributable to free alcohol and water hydroxyl groups, appreciably diminished in PVOH films heated at  $120^\circ\text{C}$  for 30 min in comparison to films not exposed to such a high temperature [Figure 5(b)]. However, the same spectra also evidenced a limited reduction of the band at  $1731\text{ cm}^{-1}$ , owing to the presence of esters as residues after hydrolysis of PVAc, in films subjected to temperature. This reduction is accompanied by the appearance of the band at  $1579\text{ cm}^{-1}$ , assigned to acetates,<sup>30</sup> which indicated the hydrolysis of ester groups. Therefore, this mechanism suggests a beginning of PVOH degradation, which apparently did not yet cause a decrease of mechanical performance of polymeric dispersions or of joints with wood.

## CONCLUSIONS

Water-based PVAc dispersions are widely used as wood adhesives with both heat and dielectric heating systems. However, little is known about the effect of RF exposure on the adhesive characteristics and on the performances of bonded joints. In this study, the properties of bonded joints exposed to RF were compared with hot pressing and with standard drying, and the observed behavior explained. All results evidenced how the application of an initial energetic impulse (owing to both RF and heating) to the joints appreciably speeds up the drying process, and that final performances of joints were practically equivalent among HP and RF series although this latter was faster.

When joints were tested dry, a week of conditioning time levelled the performance of the standard and low-energy RF and HP treatments, whereas high-energy input during film formation induced permanent changes. This implied that performances were higher than those obtained in standard series. However, when the initial energy was too high, the polymer weakened and the decrease in joint performances was observed owing to the weakening of the polymer. With reference to water resistance, HP and RF performed better than the standard series at short times and large energy inputs, whereas 1 week of conditioning levelled out the effect of mild heating during pressing. However, a minimum conditioning time of 1 day (instead of 40 min) was necessary in the case of tests on wet samples. Moreover, no performance decrease was observed after a prolonged exposure, and samples always broken at the wood–adhesive interphase, which indicated that at the wet state the wood–adhesive interphase was weaker than the glue although this latter was mechanically worsened (as evidenced in dry conditions).

Also, tests at high temperatures (both  $40$  and  $80^\circ\text{C}$ ) performed in normal (dry) conditions showed a strength increase between 40 min and 7 days of conditioning. This occurrence evidenced



how the modification into the glue structure after exposure to the initial energetic impulse was a time-driven process.

Therefore, all performed tests showed that much heating the bondline during film formation, whether through RF or conventional hot pressing, induced structural modifications into the bondline, as indeed confirmed through the various tests carried out on the pure polymeric films. More specifically, these modifications were related to a better interaction of PVOH phase with  $\text{AlCl}_3$  (used as a complexing agent of the polymeric protective colloid), which caused a hydrophobization process in PVOH. This was evidenced by means of some release-in-water tests, carried out on both polymeric dispersions and PVOH/ $\text{AlCl}_3$  films, and confirmed by IR analysis.

The observed process implies a PVOH phase rearrangement initiated at high temperature, which requires time to be completed when the initial impulse given by RF or by direct heat is not sufficiently intense or long. This occurrence is also consistent with the observation of a time-driven progression.

All the reported results confirmed the determinant influence of temperature, induced by RF exposure as well as direct heating, in considerably improving the coordination capability of  $\text{AlCl}_3$  toward PVOH molecules, which in turn appreciably improve the mechanical and water-resistance properties of glued films.

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