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Study of the solubility and composition of welded wood material at progressive welding times

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Abstract The solubility in water and carbohydrates/lignin composition after hydrolysis of wood welded by linear friction welding was studied. Welded beech (WB) and welded spruce (WS) were analyzed at welding times (Wt) of 1, 1.5, 2, 2.5, 3 s, and 2, 4, 6, 8, 10, 12 s, respectively. Scratched welded material was first extracted in water, dried, cryo-milled, and then hydrolyzed with sulfuric acid. Maximal percentages of solids dissolved in water were 17.7 and 10 for WB and WS and 2.2 and 1.4 for un-welded beech and spruce, respectively. Among water extracts, lignin, mono-oligosaccharides, acetic acid, vanillin, furfural, 5 hydroxymethylfurfural (5HMF), and syringaldehyde were quantified. Maximal percentages of water soluble lignin in WB and WS were 5 and 3.6, respectively; molecular weight and polydispersity were also determined. Regarding carbohydrates in the water extracts, a maximum of 1.4 % oligosaccharides in WB and 1 % monosaccharides in WS were detected. After hydrolysis, an increase in the amount of Klason lignin and a progressive diminution of some sugars take place at consecutive Wt of WB and WS. This study allows explaining to a good extent the behavior of welded joints face to liquid water. Moreover, the degradation of certain wood components is clearly presented.

1 Introduction

Linear friction welding for wood is an assembly technology that requires short process time, no glue nor special preparation of surface. Potential application fields for linear friction welding are related to interior applications (i.e. furniture) (Gfeller et al. 2003; Stamm 2006; Ganne-Chédeville 2008; Omrani 2009) with caution on high relative humidity environments (Rhême et al. 2013a, b). Hitherto, two applications at pilot scale have been developed, the wood core of snowboards and the covers for wine barrels, but no other examples realized in this field are yet available. Outdoor applications are not possible due to the lack of resistance of welded wood to water. During the last years, several authors have been working at improving the water resistance of the welded joint. Some improvements have been reported by using rosin or shortening welding time (Mansouri et al. 2009, 2011; Omrani et al. 2009a; Pizzi et al. 2011; Vaziri et al. 2011).

Linear friction welding consists in the continuous frictional movement between two wood surfaces which are pressed against each other. Friction in the interface rises temperature, softening lignin that bonds wood fibers (Gfeller et al. 2003; Stamm 2006; Ganne-Chédeville 2008; Omrani 2009). Fibers become detached, partially "ground" and welded material is formed. When friction is stopped pressure is still applied until solidification-compaction of the joint. The densification of the welded material and nearby zones goes together with chemical and anatomical changes.

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The chemical modifications produced in the welded material have also been studied with several methods. Solid state CP-MAS ^{13}C-NMR was used to show lignin demethoxylation, apparently slight increase of amorphous carbohydrates, autocondensation of lignin, deacetylation of hemicelluloses, cross-linking reactions of lignin with carbohydrate-derived furfural or self-polymerization of furfural during welding (Gfeller et al. 2003). Further, the formation of quinones by oxidation of phenols, dehydration, and mechanism of condensation of lignins by aryl–aryl and aryl-CH$_2$-aryl links have been reported by Delmotte et al. (2008) in coupled studies with FTIR. Delmotte et al. (2009) argue that at higher amounts of non-oxidized phenolic groups greater strengths of the welded joint are obtained. Ganne-Chédeville et al. (2008a) describe some possible mechanisms of the chemical reactions at welding times from 0 to 11 s. Pizzi et al. (2006) mentioned that is not possible to draw conclusions about the relative proportions of lignin and carbohydrates from CP-MAS ^{13}C-NMR spectra. Sun et al. (2010) studied high speed rotation welding by pyrolysis-GC–MS, DSC and XPS. Percentages of Guaiacyl-, Syringyl-Lignin and carbohydrates related products issued from py-GC–MS are presented; however, these percentages are based on identified products and differ from the typical composition of wood references (Wagenführ 2000; Fengel and Wegener 2003). Further, Belleville et al. (2013) studied high speed rotation welding by pyrolysis-GC–MS, XPS and ATR-FTIR. Results of XPS show an increase in the O/C ratio in welded maple, which is attributed to the formation of substances containing oxygenated functionality. Stamm et al. (2006) analyzed lignin fragments of WS by thioacidolysis-GC/MS. In this method, the reagent is able to break the arylglycerol-β-aryl ether linkage of the lignin. It provides useful information about the composition and structure of the lignin fragments. In the same study, aminolysis was used to show the increase of phenolic OH and decrease of aliphatic OH groups in WS. Stamm et al. (2005b; 2006) also performed extraction and hydrolysis of spruce welded by circular friction welding. Extraction was carried out with acetone and hydrolysis with trifluoroacetic acid (TFA). Most methods mentioned above describe possible structural changes in chemical components of wood; however they are not suitable to obtain mass balances of the welded material.

In the present work, where different welding times for beech and spruce were tested, hydrolysis with sulfuric acid allows finding clear trends in the composition of the welded material. In addition, this method is well adapted to the small available quantities of welded material, which is a thin dark line in the order of few hundreds of microns. Moreover, the previous step of water extraction separates some monomeric/oligomeric sugars, decreasing the risk of sugars degradation during hydrolysis. The combined methods of extraction with water followed by hydrolysis of the extraction residue with sulfuric acid are employed for the first time for welded wood. These methods allow for the first time a better understanding of the solubility of degradation products in water at different welding times. This information is needed in order to define the most appropriate welding parameters.

2 Materials and methods

2.1 Raw materials

Beech (*Fagus sylvatica*) and spruce (*Picea abies*) were assembled by linear friction welding for 1, 1.5, 2, 2.5, 3 s, and 2, 4, 6, 8, 10, 12 s, respectively. The frequency was 100 Hz and welding pressure 1.5 MPa for both species. Amplitude was 2.8 and 3 mm, holding time 5 and 40 s, holding pressure 2 and 1.5 MPa for beech and spruce, respectively. The process was carried out in a Branson M-DT24L linear welding machine. The size of the welded specimens was $500 \times 80 \times 24$ mm^3 for beech and $500 \times 50 \times 24$ mm^3 for spruce. Thinner sections of spruce specimens were selected since larger sections without defects, i.e. knots, were not available. The welding surface was 500×80 and 500×50 mm^2 for beech and spruce, respectively. The linear friction is performed parallel to the fibers length direction (500 mm). Annual rings have an inclination of 60–90° with respect to the welding interface. Wood was acclimatized at 23 °C and 50 % RH prior to welding. Testing material was obtained by scratching the surface of opened welded pieces with a razor blade. Care was taken to remove just welded material (dark/brown colored) and avoid wood fibers.

2.2 Temperature in the welding interface

Temperature measurements in the welding interface during the linear friction welding process were performed. The measurement system was made up of a thermo-element: thermocouples type K (Din EN 60584-2, alloy Ni–Cr, measurement range from −180 to 1300 °C), an amplifier HBM Spider 8 SR30, and the software HBM Catman professional. Three thermocouples were placed, one in the middle and two at approximately 6 cm from the edges in the length direction of the welded specimen. They were introduced into holes of 0.5 mm diameter, from the back of the wood specimens.

2.3 Extraction of soluble components of welded wood

Extraction of welded material was performed in an accelerated solvent extractor (ASE 200, Fa. Dionex). The

material was acclimatized and the moisture content was previously determined by gravimetry, drying three small fractions of each sample at 100 °C. About 600 mg of welded material at each condition were extracted in distillated water. The conditions were 100 °C, 100 bar, preheating 5 min, heating 5 min and static period 10 min. The extracted liquid was gauged to 25 ml. In order to determine the solids content, 10 ml of each extracted solution were placed in an aluminum pan and dried under vacuum. Weight was controlled and measured until it was constant. The remaining solution was frozen for further tests. Three extractions were performed per condition. Average % values are reported. A maximal error margin of ($\pm$12.7 %) of the absolute reported values was calculated for water extracts, for a confidence interval of 95 %.

2.4 Cryo-milling

Cryo-milling was performed in a vibration mill consisting of a polycarbonate flask with a metallic hammer cylinder inside, which is actuated by a magnetic field. The flask containing the dried-extracted welded material was placed into liquid nitrogen to cool down the system. The process consisted of a first cooling period of 15 min followed by 3 milling periods of 2 min each with intermediate cooling steps of 2 min. Milling allows having powder accessible enough for acid hydrolysis.

2.5 Acidic hydrolysis of welded-extracted material

Carbohydrates and lignin content was analyzed in triplicate on acclimatized extracted-dried-milled welded material by two-stage acid hydrolysis. In the first step, 1 ml of H_2SO_4 at 72 % w/w was added to 100 mg of sample. The mixture was kept in a thermal bath at 30 °C for 1 h. The reaction was stopped by diluting the solution with ionized H_2O until a concentration of 4 % of H_2SO_4. In the second step, diluted solutions were placed in an autoclave at 120 °C and 1.2 bar, during 40 min for WS and 30 min for WB. Time was optimized for maximal recovery of monomeric sugars (Puls 1993). Then, solutions were cooled down and filtered in a G4 sintered glass crucible. Klason lignin is the solid residue and liquid solution contains the hydrolyzed sugars.

2.6 Carbohydrates in hydrolyzed welded wood

In hydrolyzed samples, carbohydrates content was determined by borate-anion-exchange-chromatography. Detection was performed after post-column derivatization with cuprum bicinchoninate at 560 nm, as described by Sinner et al. (1975) and Sinner and Puls (1978). Soluble lignin was determined by UV spectroscopy at a wavelength of 205 nm, as described by Puls (1993).

2.7 Water extractives of welded wood

In water extracts, monosaccharides, anhydrosugars and oligosaccharides were determined by high performance anion exchange chromatography coupled with pulsed amperometric detection and a mass spectrometer (HPAEC-PAD/MS). Monosaccharides and anhydrosugars were analyzed on a CarboPac PA20 column and oligosaccharides on a CarboPac PA200 column. NaOH, Na-acetate/NaOH and water were used as eluents. Vanillin, furfural, 5HMF and syringaldehyde were determined by reversed-phase high performance liquid chromatography (RP-HPLC) on a C18 column (Aquasil, Thermo Scientific, Waltham, MA, USA) with UV detection at 210 nm as in Janzon et al. (2013). Soluble lignin in water extracts was determined by size exclusion chromatography (SEC) using PolarGel-M linear columns (2 300 × 7.5 mm columns plus guard column 50 × 7.5 mm; Agilent Technologies, Santa Clara, CA, USA). Dimethyl sulfoxide (DMSO) with addition of 0.1 % LiBr was applied as eluent and calibration was performed with polyethylene glycol standards. Detection was performed by refractive index (RI) and ultra violet (UV, 280 nm) detection as in Schütt et al. (2011). Acetic acid was quantified with an enzymatic assay (Acetic acid assay kid, Megazyme, Irland) and UV spectroscopy with the detection at a wavelength of 205 nm.

3 Results

3.1 Welding process

Welding process has a distinctive dynamic for beech and spruce due to factors as density, anatomy, surface and chemical composition. Beech requires shorter welding times than spruce. Welded material is expelled from the welding interface when excessive welding times are applied. It implies that "new" wood material is being frictioned and the process is somehow "repeated". In WB, no expelled material is observed until approximately 2 s, while in spruce it corresponds to around 8 to 10 s. However in spruce a further blackening—"hardening" of the same welded material also occurs. Analyzed ranges for both species include short welding times where no complete welded line is formed and welding times long enough that expelled welded material is observed.

Welding time defines the temperature and the duration of the mixing effect due to the linear friction. The rise of temperature in the welding interface is faster in beech than in spruce (see Table 1). The faster increase of temperature in the welding interface of beech than in spruce was also found by Stamm et al. (2005a), where thermocouples placed directly in the welding interface were also used.

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Table 1 Temperature measurements in the welding interface of beech and spruce

Beech				
Wt (s)	1	2	3	–
T (°C)	203	291	380	–
Spruce				
Wt (s)	1	2	6	12
T (°C)	107	182	368	400

Other authors (Delmotte et al. 2008; Ganne-Chédeville et al. 2008a, b) report lower maximal temperatures for welded beech: 250 °C for welding times 6–11 s. These differences probably arise from the measuring method which in the latter cases was performed by infrared thermography on the edge of the welding line.

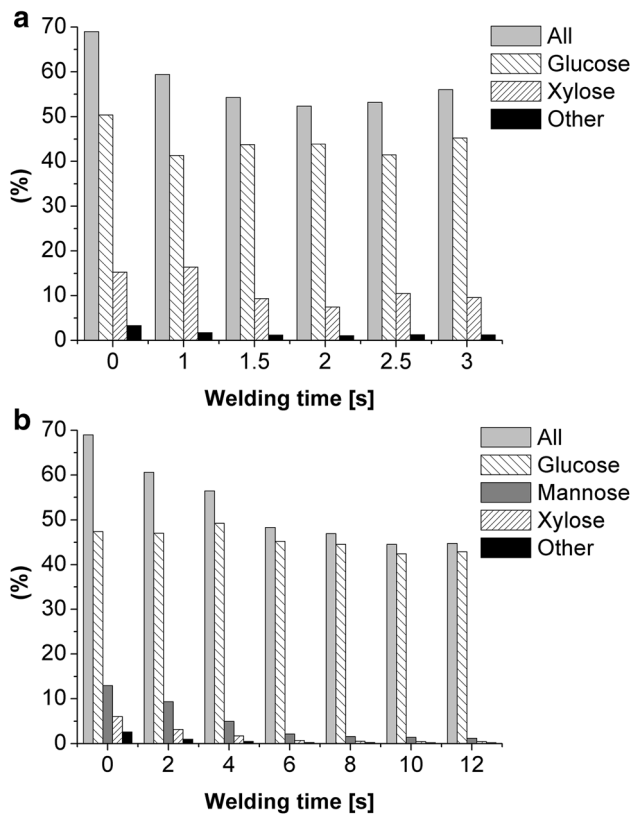### 3.2 Composition of pre-extracted welded material after hydrolysis

In Figs. 1, 2, 3, 4, 5, weight percentages based on dry welded wood are presented. The composition of welded wood after water extraction was determined by acid hydrolysis for beech and spruce at progressive welding times (Fig. 1). An important percentage of welded material of both species is dissolved in water. It reaches 17.7 and 10 % in welded beech and spruce in contrast to 2.2 and 1.4 % in un-welded wood, respectively. Evidently, dissolved material represents low molecular weight components which hardly contribute to the strength of the welded joint in liquid water. However, causes related to the stresses formed through the sudden increase–decrease of temperature in the welding interface (Rhême 2014) could also account for the low resistance of welded wood in liquid water.

Klason lignin shows a clear ascent for longer welding times for both species. It increases to 28.9 % after 3 s of welding for beech compared to 19.5 % on the starting sample. A gain from 26.1 to 45 % can be observed after welding of spruce for 12 s correspondingly. The increase of Klason lignins is partly due to the reduction of the carbohydrate proportion in welded wood. Further on an increase due to other reactions, for example condensation with furans (Gfeller et al. 2003, Stamm 2006, Delmotte et al. 2008) and other carbohydrate degradation products can be conceived. In welded wood, Klason lignin represents the lignin that has been thermally and chemically modified. This material together with carbohydrates is meant to bear the welded joint. Klason lignin contents are higher in welded spruce compared with welded beech. In general, spruce wood possesses a higher proportion of lignin than beech wood which is already apparent in the starting material (Wagenführ 2000; Fengel and Wegener
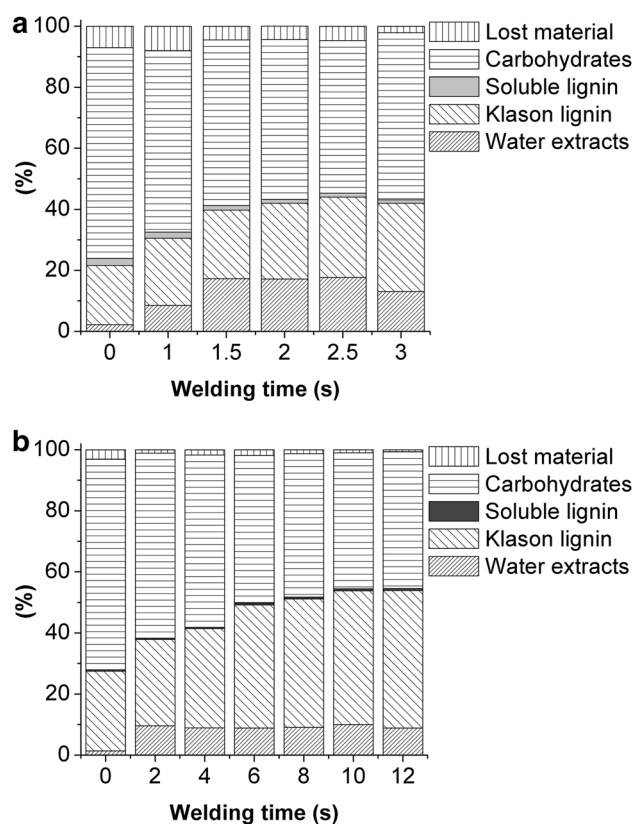
Fig. 1 Effect of welding time on the composition of welded material as determined after water-extraction and hydrolysis. **a** beech, **b** spruce

2003). Even if the rise of temperature in the welding interface of spruce is slower than in beech, due to the longer welding times required, higher temperatures are reached in welded spruce. Therefore, hemicelluloses in WS are affected to a greater extent than in WB, leading to a higher increase of lignin content. Further, guaiacyl (G) units in spruce lignin are more susceptible to condensation reactions during the welding which might as well favor increased proportions of lignin after welding. Maximal percentage of soluble lignin is 2.3 in WB and 0.7 in WS. According to Puls (1993) the amounts of acid soluble lignin in hydrolysates of hardwoods and softwoods are in the range of 2–3 and 0.4–0.9 %, respectively, which is in good accord with experimental data.
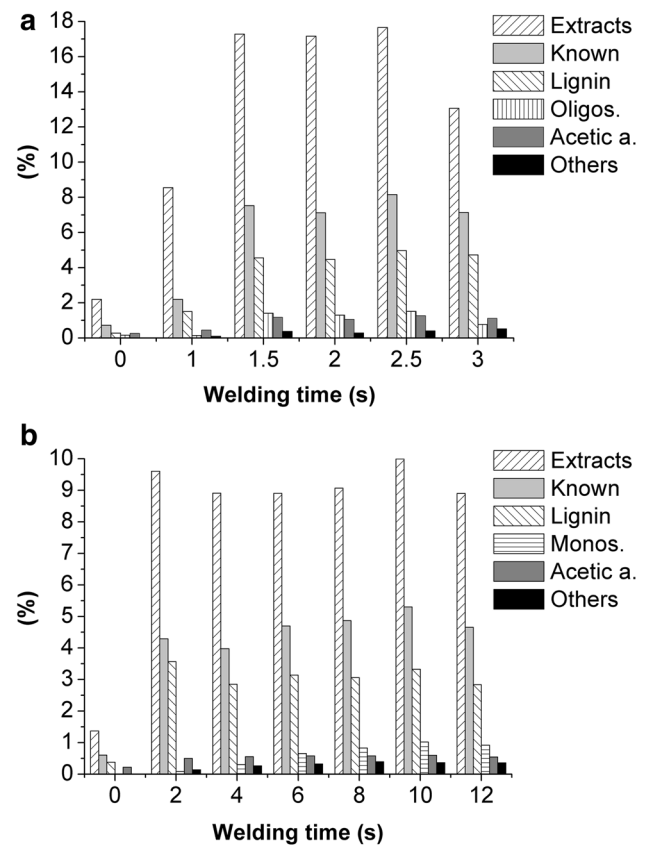
It is well known that lignin and cellulose (crystalline) are the most thermally resistant components in wood, and hemicelluloses the more sensitive ones (Fengel and Wegener 2003; Garrote et al. 1999). In general, the total carbohydrate percentage decreases with Wt (Fig. 1). It diminishes from 69 % in un-welded beech to 50–54.7 % in WB welded for 2.5–3 s. In spruce it decreases from 69 % in un-welded spruce to 44.5–44.8 % in spruce welded 10–12 s. The minimal amount of carbohydrates found in WS is similar to that found by Stamm et al. (2005b, 2006)

Fig. 2 Carbohydrate composition of welded material after water extraction. **a** beech, **b** spruce. Other beech: rhamnose, mannose, arabinose, galactose. Other spruce: rhamnose, arabinose, galactose

Fig. 3 Water extracted components from welded material. **a** beech, **b** spruce. Others beech: monosaccharides/anhydrosugars, syringaldehyde, vanillin, furfural, 5HMF. Others spruce: oligosaccharides, 5HMF, vanillin, furfural

(Stamm 2006), around 45 %, at welding times of 10–20 s, 420–440 °C, in WS by circular welding using acid hydrolysis with TFA. Small percentages of lost material in both welded species are observed. It is due to the decarboxylation of uronic acid and destruction of neutral sugars (Puls 1993).

The differentiation of monosaccharides coming from hemicelluloses and cellulose is depicted in Fig. 2. Xylose content in WB decreases approximately by half until Wt 2 s. For higher Wt some deviation is apparent regarding the xylose content. Other sugars which are present only in small amounts drop gradually. In WS, mannose, the main hemicellulose constituent, is constantly reduced. After 8 s the amount is very small and remains practically constant for further prolongation of welding time. Xylose and other minor sugar fractions in WS disappear completely after Wt 4–6 s. Despite the fact that beech xylans are rather labile compared to spruce glucomannans, further degradation is observed for the latter. This can be rationalized by the harsher thermal treatment consequence of the prolonged welding times in WS. In both welded species, glucose represents cellulose and also part of the glucomannan. Glucose content diminishes in respect to untreated wood for both species, but in a lesser relative proportion than

other sugars. As for beech xyloses, small relative increases in glucose content might be related to the new input material in the welding zone. The lower stability of hemicelluloses in respect to cellulose is well known and related to the difference in structure. The linearity of the cellulose chains and its intensive hydrogen bonding system entail its crystalline structure and therefore its higher thermal resistance. The ramified chains of hemicelluloses form an amorphous structure that together with the amorphous part of cellulose are more prone to thermal and hydrolytic attack (Sjöström 1993; Fengel and Wegener 2003).
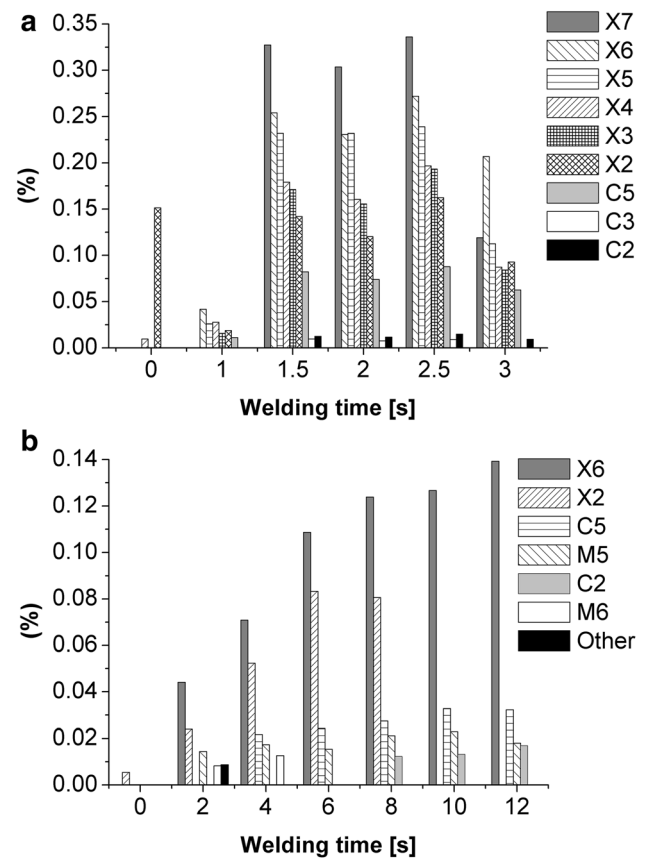
3.3 Water extracted components in welded material

3.3.1 General description

In the welded interface, degraded components are generated. These components can either form condensed products, remain as single substances, be liberated as volatile products or be expelled as "ground black fibers". These last ones are ruled out through the edges of the

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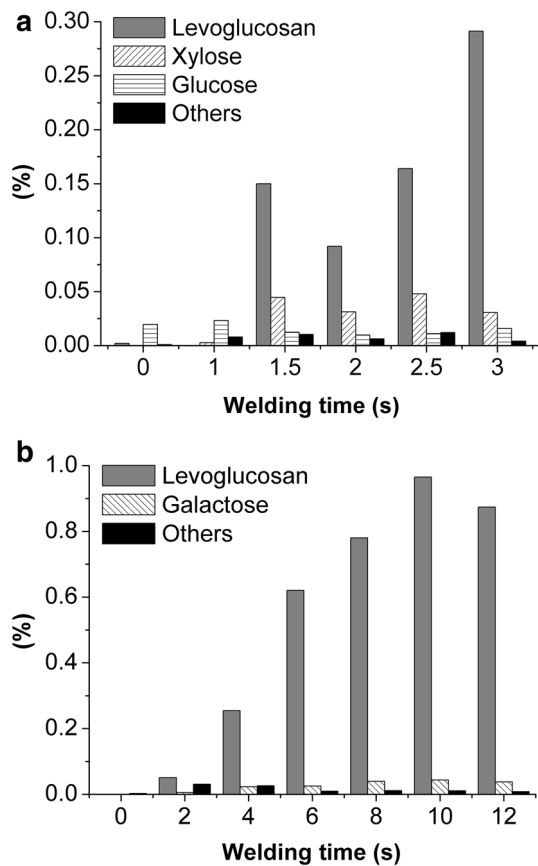
Fig. 4 Monosaccharides and anhydrosugars in water extracts of welded material. **a** beech, **b** spruce. Others beech: arabinose, galactose, mannose. Others spruce: arabinose, glucose, xylose, mannose

Fig. 5 Oligosaccharides in water extracts of welded material. **a** beech, **b** spruce. "X" stands for xylooligomers, "C" cellooligomers, "M" mannooligomers. The number at the right side means the degree of polymerization. Other spruce: M2, 3, 4

welding interface when the welding time is prolonged (i.e. Wt longer than 2 s for WB and 8 s for WS, see Sect. 3.1). In Fig. 3, the degradation products of the welded material that are soluble in water are shown. Among the identified ones there are lignin, oligo- and monosaccharides, acetic acid, and small fractions of anhydrosugars, syringaldehyde, vanillin, furfural and 5HMF. The depolymerization of lignin and carbohydrates occurs during welding. Simultaneously, further degradation of the depolymerized components also happens. At Wt 1 s for WB and 2 s for WS, already 8.5 and 9.6 % of welded material are extracted in water. At Wt 1 s (203 °C), the welded line of beech is not yet completely formed and its color is still pale. At 1.5 s it becomes brown and at 2–2.5 s it is darker and completely formed. At 3 s it is completely black. In WS, at 2 s (182 °C) just small pale agglomerations are formed. At 4–6 s, the welded line is almost completely formed and it begins to become brown. At 8–10 s the welded line is formed and it is almost completely dark. At 12 s it is black.

3.3.2 Carbohydrates degradation products

Under acidic conditions and high temperature furans are formed as carbohydrate degradation products. 5HMF is a decomposition product from hexoses. They are either derived from glucomannan (Janzon et al. 2013), the main hemicellulose of softwoods, or from glucose most likely originating from amorphous cellulose (Fengel and Wegener 2003). Furfural is generated from pentoses: xyloses (hardwood and softwood) or arabinose (softwoods) (Sjöström 1993). 5HMF and furfural are volatile and reactive. Further on they are easily dissolved in water. Surprisingly they are found only in very small amounts in the water extracts, although their percentage increases with welding time (Fig. 3). Therefore, it is most likely that they have been lost as volatiles or they have further reacted with themselves or with lignin to form condensed products. Acetic acid is a typical degradation product of thermally treated wood (Tjeerdsma et al. 1998; Sivonen et al. 2002; Windeisen et al. 2007) and it is generated by the deacetylation of hemicelluloses. Hence, it is logical to find it

in higher amounts in WB than in WS, due to the higher content of acetyl groups in hardwoods than in softwoods. However, as for other degradation products of welded material, part of organic acids escapes with the volatiles (Omrani et al. 2009b; Ganne-Chédeville 2008). The presence of acetic acid together with temperature and pressure in the welding interface favors the de-polymerization of carbohydrates, further degradation of sugars and condensation reactions of lignin. Dissolved anhydrosugars, mono and oligosaccharides will be discussed later.

3.3.3 Lignin degradation products

Vanillin and syringaldehyde are degradation products from guaiacyl (G) and syringyl (S) lignins, respectively. G-units, are the main lignin component in spruce wood (G:S:H = 94:1:5; H = p-hydroxyphenylpropane) while both, G- and S-units are characteristic for beech lignin (G:S:H = 56:40:4) (Fengel and Wegener 2003). Vanillin and syringaldehyde are present only in very small quantities in water extracts of all welded materials. However, they give evidence of some degradation and structural changes induced in lignin. The fact that only small amounts of lignin are solubilized matches the large content of acid soluble and insoluble lignins detected in all types of welded materials (Fig. 1).

Milled wood lignins are reported to have a weight average molar mass (Mw) of 20,000 g mol^{-1} in softwood and a lower Mw in hardwoods (Sjöström 1993). Splitting of lignin at elevated temperatures occurs via radical degradation reactions (Fengel and Wegener 2003). The slightly higher amount of soluble lignin in WB water extractives in respect to the corresponding ones in WS could be related to the higher thermal sensitivity of hardwood lignin compared to softwood lignins. According to Lawoko et al. (2005), in LCC (lignin carbohydrate complexes), the xylan-linked lignin (more likely in beech) is delignified to a higher extent than glucomannan-linked lignin (in spruce). This last one undergoes a partial condensation to form higher molecular mass material. It would go along with the higher percentages of Klason lignin in WS vs WB (Fig. 1). The higher sensitivity of hardwood Syringyl-moities is also noticed in a study on welded wood by Sun et al. (2010).

3.3.4 Molecular weight and polydispersity of water dissolved lignins

The Mw and D of water soluble lignins from WB and WS are listed in Table 2. For both starting materials the Mw of extracted lignin or more carefully phrased UV active components is very small. However, after short welding times the extracted materials have much higher molar

Table 2 Molecular weight and polydispersity of water soluble lignin

Sample	Wt (s)	Mw (g mol^{-1})	D (au)
Beech	0	1500	1.7
	1	7900	6.6
	1.5	5600	4.5
	2	5600	4.6
	2.5	4700	3.9
	3	3600	3.2
Spruce	0	1800	2.3
	2	4100	5.3
	4	3600	3.7
	6	2900	3.1
	8	2800	2.9
	10	2700	2.8
	12	2700	2.8

masses of 7900 g mol^{-1} for beech and 4100 g mol^{-1} for spruce. In both cases an increase of the polydispersity is observed. Considering the simultaneous increase of the extraction yield it can be concluded that the Mw increase is due to the fragmentation of lignin during the welding process. A further increase of Wt is reflected in a decrease of the Mw and D. As depolymerization and re-polymerization reactions of lignin happen simultaneously, it is possible that part of the cleaved molecules react to form higher molecular weight/condensed structures (Klason lignin) that render lignin insoluble in water. However the creation of free phenolic hydroxyl groups as a result of ether bond cleavage also increases the hydrophilicity of lignin, rendering it more soluble (Sjöström 1993). In any case, it is evident that at least the dissolved fraction in water has a certain hydrophilic character. The competition between depolymerization and re-polymerization reactions of lignins is evidenced by Li et al. (2007). Higher polydispersities (broad molecular weight distribution) accompanied by higher molecular weights might be associated with re-condensation reactions of lignins (Schütt et al. 2011). However, the data supports that some lignin degradation occurs to a significant extent. High molar masses are achieved especially at low reaction times.

3.3.5 Monosaccharides, anhydrosugars and oligosaccharides in water extracts

In Figs. 4 and 5, levoglucosan, mono and oligosaccharides from the water extracts of welded material are depicted. In general, all these components represent a small part of the welded material; nevertheless their identification and quantification require an intense effort and greatly contribute to the understanding of the welding process. According to Willför and Holmbom (2004) and Leppänen

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et al. (2011), most of the water soluble carbohydrates in spruce are oligo and polysaccharides. The amount of monosaccharides of spruce wood chips in water at 100 °C after 100 min was 3 mg g^{-1} (Song et al. 2008). Likewise, monomers of spruce galactoglucomannan released during hydrolysis at pH 1, 90 °C, after 10 min were 6.3 mg g^{-1} (Xu et al. 2009). Moreover, the amounts of dissolved monosaccharides from spruce in water increase with temperature in an extraction range from 160 to 240 °C, up to about 55 mg g^{-1} (Leppänen et al. 2011). Arabinose and galactose followed by xylose, mannose and glucose are the first water dissolved monosaccharides (Leppänen et al. 2011; Willför and Holmbom 2004; Song et al. 2011). In the current study, almost any monosaccharide is found in water extracts of spruce reference (Wt 0 s), and just a small quantity of glucose is present in beech reference. Therefore, monosaccharides found in water extracts can be ascribed to the depolymerization of oligosaccharides during the welding process. As the amounts of arabinose monomer in water extracts and in the hydrolyzed sugars of WS are extremely low (Fig. 2), one can say that arabinose is almost completely degraded during the welding process. In the arabinoglucuronoxylan framework of spruce, arabinose units are side chains that can be easily hydrolyzed under acid conditions (Sjöström 1993) and temperature. Galactose, the side chain in the galactoglucomannan framework (Sjöström 1993) amounts to up to 0.04 % in water extracts of WS, and it is almost not present in hydrolyzed sugars (Fig. 2). Therefore, it is clearly shown that galactose units are also degraded in the linear friction welding process. Xylose monomers in water extracts of WB are also present in amounts close to 0.05 %, showing that also monomers from the main chain of glucuronoxylans are detached during welding.

Levoglucosan (1.6-anhydro-β-D-glucopyranose) is an anhydrosugar formed from the dehydration of glucose. Acids and temperature catalyze its formation (Sjöström 1993). Levoglucosan has been ascribed to the decomposition of cellulose (Fengel and Wegener 2003). In addition, traces of levoglucosan come from glucose after hydrolysis of galactoglucomannan from spruce for 1 h at 90 °C and pH 1 (Xu et al. 2009). As in hydro-thermal treatments, traces of levoglucosan also appear during welding. At such short welding times it is presumable that levoglucosan comes from glucose from galactoglucomannan rather than cellulose. It corresponds to the higher levoglucosan amounts present in WS than in WB, explained by a higher amount of galactoglucomannan in spruce than in beech (Sjöström 1993). Other anhydrosugars, as cellobiosan are most likely present. A further analysis of the chromatograms would ascertain its detection and quantification. The oxygen-less conditions in the welding interface could be considered similar to those in pyrolysis, i.e. traces of

levoglucosan are found. However, temperatures in pyrolysis are higher than in welding interface, i.e. 500–600 vs. 200–400 °C, and oligosaccharides that are found in the welding interphase are not necessarily present in pyrolysis products. Moreover, the mixing effect of the frictional movement does not occur in pyrolysis.

Only small quantities of hemicelluloses from native hardwood can be extracted by water. Further on, arabinogalactans, which are found only in small quantities in most softwood species (Sjöström 1993) are first solubilized (Willför and Holmbom 2004). According to Bobleter (1994), temperatures of dissolution of hemicelluloses in hydrothermal processes begin at 180–230 °C. For spruce wood, the fraction of solubilized galactoglucomannan in water increases steadily from 160 to 200 °C (Song et al. 2008). At 220 °C all hemicelluloses from spruce wood can be removed, and at 240 °C apparently part of cellulose is also extracted (Leppänen et al. 2011). In the present tests, an insignificant amount of oligosaccharides are dissolved for beech and spruce reference (Wt 0 s). In contrast, from Wt 1.5 s for beech and Wt 2 s for spruce, oligosaccharides are clearly present in water extracts. Therefore, oligosaccharides found in water extracts can be ascribed to the depolymerization of hemicelluloses during the welding process. Temperatures reached at these welding times (see Table 1) correspond to literature temperatures mentioned above for dissolved carbohydrates in water. Amounts of dissolved oligosaccharides from welded wood are smaller probably due to the very short times of welding: maximum 3 s for WB and 12 s for WS, compared to batch: 5 min to 100 min (Song et al. 2008), or flow through extraction times: 1 to 30 min recollection (Leppänen et al. 2011). Additionally, solubility of cleaved oligosaccharides during welding could be affected by their deacetylation (see free acetic acid in Fig. 3). A high degree of acetylation of galactoglucomannan oligosaccharides from spruce is required for their higher dissolution in water (Willför et al. 2003; Song et al. 2008, 2011; Grénman et al. 2011).

Regarding Fig. 5a, a well-defined distribution of xylooligomers is delineated. Between welding times of 2.5 and 3 s, a general decrease in the amount of xylooligomers is observed. It could be explained as a further cleavage, degradation and volatilization or formation of condensation products (Klason lignin) of xylooligomers at higher temperature and longer Wt. According to Bobleter (1994), cellulose-derived oligosaccharides are soluble in water up to a degree of polymerization (DP) of around 8 glucose units. Köll et al. (1990) found that thermal degradation of cellulose gave water soluble oligomers at 250 °C and 4 h of processing. In flow through extraction of spruce in water, apparently part of cellulose is removed at 240 °C (Leppänen et al. 2011). Celloligomers in beech appear notably at Wt 1.5 s. Corresponding temperatures at Wt 1

and 2 s are 203 and 291 °C (see Table 1). In Fig. 5b, dissolved oligosaccharides of WS appear in smaller percentages than in WB. In WS, xylooligomers which are known to be more labile for degradation than mannooligomers have comparatively higher concentrations. In addition, 5-cellooligomers begin to appear just at Wt 4 s where T is certainly higher than 250 °C. Cellooligomers show some degradation of cellulose, probably the first to be attacked would be the amorphous part. It is worth noting that in general, the lesser amount of hemicellulose degradation products in the water extractives is related to their capability to form condensation reactions with lignin.

4 Conclusion

In the field of linear friction welding for wood this work presents for the first time a study on the water soluble components and a complete mass balance of the constituents of WB and WS at consecutive welding severities. It clearly appears that the linear friction welding process entails a progressive degradation of the welding material, which is evidenced by the water soluble components. Water extracts of WB reach over 17 % at already 1.5 s of Wt, when the welding interface is not even completely formed. Similarly, water extracts in WS get over 9 % at just 2 s of Wt.

Lignin is the identified component present in highest proportion in the water extracts of both WB and WS. Slightly higher amounts of lignin are found in water extracts from WB, probably due to the reduced recondensation of syringyl lignin. It is plausible that depolymerization and re-polymerization reactions of lignin occur during welding. The formed fractions with presumably stronger bonds and/or higher molecular weight belong to the Klason lignin and the rest (lower molecular weight/condensed lignin, vanillin, 5-HMF) would be part of the water extracts.

Degradation of polysaccharides is evidenced at already 1.5 s of Wt for WB and 2 s for WS. This is clearly illustrated by the series of xylooligomers of 7 to 2 units and cellooligomers from 5 to 2 units in water extracts from WB and corresponding oligosaccharides from WS. Levoglucosan, which appears significantly in the water extracts of WB at 1.5 and at 4 s in WS, most likely demonstrates the degradation of glucose coming from glucomannans. Acetic acid also appears from the early stages of the welding process. It catalyzes the depolymerization of hemicelluloses, the condensation reactions of lignin and the dehydration of certain sugars. In addition it decreases the solubility of oligosaccharides in water.

In general, the relatively small amounts of carbohydrates degradation products in water extracts are probably due to their aptitude to react forming condensate products

with lignin and to evaporate. The "accumulation" of lignin/condensate lignin in the welded material is noticed as Klason lignin increases with longer welding times while carbohydrates diminish. Even if welded material is a mixture of many components, hydrolyzed carbohydrates and Klason lignin are key components of the welded material, and their quantification is of great benefit in the understanding of mechanical properties of the welded joints. In fact, a positive correlation between the percentage of Klason lignin and the shear modulus of the welded material at consecutive welding times is established. However, a decrease in the maximal shear strain with increasing Klason lignin also occurs. The increase in Klason lignin indicates a higher proportion of condensed lignin products. This increased lignin proportion not only renders the welded joint material more rigid but also brittle. In a practical approach, a too long welding time (i.e. longer than 2.5 s for welded beech and 8 s for welded spruce) would not imply an improvement in the mechanical properties but a further degradation of the wood components. The determination of the chemical composition of the welded material at consecutive welding time is an important step towards a correlation with the mechanical properties of the welded joint. These correlations will be presented in a further work. The selected analytical protocols are of great benefit to further understand and characterize the phenomena taking place in the welding process of wood.

The dissolution in water of degradation components of the welded material is not avoidable in the windows of parameters studied (i.e. welding times). However the quantification of the water soluble material is an important step towards an optimization of the process. Future work needs to focus on possible additives in the welded interface that could improve the crosslinking reactions of the welded material. It could decrease the amount of welded material dissolved in water.

References

Belleville B, Stevanovic T, Cloutier A, Pizzi A, Prado M, Erakovic S, Diouf PN, Royer M (2013) An investigation of thermochemical changes in Canadian hardwood species during wood welding. Eur J Wood Prod 71:245–257

Bobleter O (1994) Hydrothermal degradation of polymers derived from plant. Prog Polym Sci 19:797–841

Delmotte L, Ganne-Chédeville C, Leban JM, Pizzi A, Pichelin F (2008) CP-MAS 13C NMR and FTIR investigation of the degradation reactions of polymer constituents in wood welding. Poly Deg Stab 93:406–412

Delmotte L, Mansouri HR, Omrani P, Pizzi A (2009) Influence of wood welding frequency on wood constituents chemical modifications. J Adhesion Sci Technol 23:1271–1279

Fengel D, Wegener G (2003) Wood-chemistry, ultrastructure, reactions. De Gruyter, Berlin

Ganne-Chédeville C (2008) Soudage linéaire du bois: étude et compréhension des modifications physico-chimiques et développement d'une technologie d'assemblage innovante (Wood welding by linear friction: investigations and understanding of the physical and chemical modifications and development of an innovative technology) (In French) Dissertation, University Henri Poincaré, Nancy

Ganne-Chédeville C, Properzi M, Leban JM, Pizzi A, Pichelin F (2008a) Wood welding: chemical and physical changes according to the welding time. J Adhesion Sci Technol 22:761–773

Ganne-Chédeville C, Duchanois G, Pizzi A, Leban JM, Pichelin F (2008b) Predicting the thermal behavior of wood during linear welding using the finite element method. J. Adhesion Sci. Technol. 22:1209–1221

Garrote G, Domínguez H, Parajó JC (1999) Hydrothermal processing of lignocellulosic materials. Holz Roh Werkst 57:191–202

Gfeller B, Zanetti M, Properzi M, Pizzi A, Pichelin F, Lehmann M, Delmotte L (2003) Wood bonding by vibrational welding. J Adhesion Sci Technol 17:1573–1589

Grénman H, Eränen K, Krogell J, Willför S, Salmi T, Murzin DY (2011) Kinetics of aqueous extraction of hemicelluloses from spruce in an intensified reactor system. Ind Eng Chem Res 50:3818–3828

Janzon R, Schütt F, Oldenburg S, Fischer E, Körner I, Saake B (2013) Steam pretreatment of spruce forest residues: optimal conditions for biogas production and enzymatic hydrolysis. Carbohydr Polym 100:202–210

Köll P, Borchers G, Metzger JO (1990) Preparative isolation of oligomers with a terminal anhydrosugar unit by thermal degradation of chitin and cellulose. J Anal Appl Pyrol 17:319–327

Lawoko M, Henriksson G, Gellerstedt G (2005) Structural differences between the lignin-carbohydrate complexes present in wood and in chemical pulps. Biomacromolecules 6:3467–3473

Leppänen K, Spetz P, Pranovich A, Hartonen K, Kitunen V, Ilvesniemi H (2011) Pressurized hot water extraction of Norway spruce hemicelluloses using a flow-through system. Wood Sci Technol 45:223–236

Li J, Henriksson G, Gellerstedt G (2007) Lignin depolymerization/ repolymerization and its critical role for delignification of aspen wood by steam explosion. Bioresour Technol. 98:3061–3068

Mansouri HR, Omrani P, Pizzi A (2009) Improving the water resistance of linear vibration welded wood joints. J Adhesion Sci Technol 23:63–70

Mansouri HR, Pizzi A, Leban JM, Delmotte L, Lindgren O, Vaziri M (2011) Causes for the improved water resistance in pine wood linear welded joints. J Adhesion Sci Technol 25:1987–1995

Omrani P (2009) Amélioration et nouvelle technologie de soudage linéaire et rotative du bois (Improvement and new linear and rotary welding technology of wood) (In French) Dissertation. University Henri Poincaré, Nancy

Omrani P, Pizzi A, Mansouri HR, Leban JM, Delmotte L (2009a) Physico-chemical causes of the extent of water resistance of linearly welded wood joints. J Adhesion Sci Technol 23:827–837

Omrani P, Masson E, Pizzi A, Mansouri HR (2009b) Emission gases in linear vibration welding of wood. J Adhesion Sci Technol 23:85–94

Pizzi A, Despres A, Mansouri HR, Leban JM, Rigolet S (2006) Wood joints by through-dowel rotation welding: microstructure, 13C-NMR and water resistance. J Adhesion Sci Technol 20:427–436

Pizzi A, Mansouri HR, Leban JM, Delmotte L, Pichelin F (2011) Enhancing the exterior performance of wood joined by linear and rotational welding. J Adhesion Sci Technol 25:2717–2730

Puls J (1993) Substrate Analysis of Forest and Agricultural Wastes. In: Saddler JN (ed) Biotechnology in agriculture; bioconversion of forest and agricultural plant residues. CAB Int 13–32

Rhême M (2014) Strength and fracture characterization of welded wood joints: effects of moisture and mixed mode loadings. Dissertation, Ecole polytechnique fédérale de Lausanne

Rhême M, Botsis J, Cugnoni J, Navi P (2013a) Influence of the moisture content on the fracture characteristics of welded wood joint. Part 1: Mode I fracture. Holzforschung 67:747–754

Rhême M, Botsis J, Cugnoni J, Navi P (2013b) Influence of the moisture content on the fracture characteristics of welded wood joint. Part 2: Mode II fracture. Holzforschung 67:755–761

Schütt F, Puls J, Saake B (2011) Optimization of steam pretreatment conditions for enzymatic hydrolysis of poplar wood. Holzforschung 65:453–459

Sinner M, Puls J (1978) Non-corrosive dye reagent for detection of reducing sugars in borate complex ion-exchange chromatography. J Chrom 156:197–204

Sinner M, Simatupang MH, Dietrichs HH (1975) Automated quantitative-analysis of wood carbohydrates by borate complex ion-exchange chromatography. Wood Sci Technol 9:307–322

Sivonen H, Maunu S, Sundholm F, Jämsä S, Viitaniemi P (2002) Magnetic resonance studies of thermally modified wood. Holzforschung 56:648–654

Sjöström E (1993) Wood chemistry: fundamentals and application. Academic Press Inc., San Diego

Song T, Pranovich A, Sumerskiy I, Holmbom B (2008) Extraction of galactoglucomannan from spruce wood with pressurized hot water. Holzforschung 62:659–666

Song T, Pranovich A, Holmbom B (2011) Effects of pH control with phthalate buffers on hot-water extraction of hemicelluloses from spruce wood. Bioresour Technol 102:10518–10523

Stamm B (2006) Development of friction welding of wood—physical, mechanical and chemical studies. Dissertation, École polytechnique fédérale de Lausanne

Stamm B, Naterrer J, Navi P (2005a) Joining wood by friction welding. Holz Roh Werkst 63:313–320

Stamm B, Windeisen E, Naterrer J, Wegener G (2005b) Thermal behavior of polysaccharides in wood during friction welding. Holz Roh Werkst 63:388–389

Stamm B, Windeisen E, Naterrer J, Wegener G (2006) Chemical investigations on the thermal behavior of wood during friction welding. Wood Sci Technol 40:615–627

Sun Y, Royer M, Diouf PN, Stevanovic T (2010) Chemical changes induced by high-speed rotation welding of wood—application to two canadian hardwood species. J Adhesion Sci Technol 24:1383–1400

Tjeerdsma BF, Boonstra M, Pizzi A, Tekely P, Militz H (1998) Characterisation of thermally modified wood: molecular reasons for wood performance improvement. Holz Roh Werkst 56:149–153

Vaziri M, Lindgren O, Pizzi A (2011) Influence of welding parameters and wood properties on the water absorption in scots pine joints induced by linear welding. J Adhesion Sci Technol 25:1839–1847

Wagenführ R (2000) Holzatlas (Wood atlas) (In German), 5th edn. Fachbuchverlag Leipzig im Carl Hanser Verlag, Leipzig

Willför S, Holmbom B (2004) Isolation and characterisation of water soluble polysaccharides from Norway spruce and Scots pine. Wood Sci Technol 38:173–179

Willför S, Sjöholm R, Laine C, Roslund M, Hemming J, Holmbom B (2003) Characterisation of water-soluble galactoglucomannans from Norway spruce wood and thermomechanical pulp. Carbohyd Polym 52:175–187

Windeisen E, Strobel C, Wegener W (2007) Chemical changes during the production of thermo-treated beech wood. Wood Sci Technol 41:523–536

Xu C, Provanovich A, Hemming J, Holmbom B, Albrecht S, Schols HA, Willför S (2009) Hydrolytic stability of water-soluble spruce O-acetyl galactoglucomannans. Holzforschung 63:61–68