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# Caractéristiques chimiques et anatomiques de la ligne de soudure du bois

Maria Inès Placencia Pena

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# Caractéristiques chimiques et anatomiques de la ligne de soudure du bois

## THÈSE

Présentée et soutenue publiquement le 15 décembre 2014

pour l'obtention du titre de

**DOCTEUR DE L'UNIVERSITÉ DE LORRAINE, NANCY**

**Specialité : Sciences du Bois et des Fibres**

Par

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## Résumé

Ce travail présente une série d'études concernant différents aspects de la technologie de soudage du bois. Les objectifs de la thèse sont les suivants. Déterminer la composition chimique et le comportement du matériau soudé par rapport à l'eau. Déterminer des relations possibles entre la composition chimique de la matière soudée et les propriétés mécaniques. Etudier des méthodes capables d'améliorer la performance mécanique et la résistance à l'eau du joint soudé. Déterminer l'influence des paramètres de soudage dans l'anatomie, la composition chimique et les propriétés mécaniques du joint soudé.

Le premier chapitre présente une introduction. Le deuxième présente l'état de l'art dans le domaine du bois et du soudage par friction. Le troisième chapitre décrit des résultats. Ce chapitre est composé de deux parties, une première concernant la compréhension des aspects chimiques, anatomiques et son lien avec les propriétés mécaniques du bois soudé et une deuxième partie concernant les améliorations de la résistance mécanique et de la résistance à l'eau du bois soudé.

Dedans le premier groupe de résultats trois études sont présentées. Une première étude comprendre la composition chimique et la solubilité dans l'eau de la matière soudée pour le hêtre et l'épicéa, ceci pour des temps de soudage progressifs. Dans cette étude les composants du matériau soudé ainsi que les composants de dégradation solubles dans l'eau sont identifiés et quantifiés. Une deuxième étude montre les caractéristiques topo-chimiques des sections transversales du bois soudé. Ici, la modification de la lignine dans la zone soudée et dans les fibres environnantes est établie. La troisième étude établit des corrélations obtenues entre la composition chimique du bois soudé et les propriétés mécaniques.

Dans le deuxième groupe de résultats trois études sont exposées. Une première montre le changement de la résistance au cisaillement du joint soudé par la densification du bois avant le soudage. Les deuxième et troisième études comprennent l'utilisation d'additifs pour l'amélioration de la résistance à l'eau des joints soudés. Le deuxième concerne le soudage linéaire et le troisième le soudage rotatif par tourillons. Pour finir, les conclusions et perspectives sont présentées dans le chapitre quatre de ce travail.

## **Abstract**

This work presents a series of studies on various aspects of the welding technology of wood. The objectives of this thesis are as follows. To determine the chemical composition and the behavior of the welded joint into water. To determine possible relationships between the chemical composition and mechanical properties of the welded material. To study methods capable of improving the mechanical strength and the water resistance of the welded joints. To determine the influence of welding parameters in the anatomy, chemical composition and mechanical properties of the welded joints.

The first chapter presents an introduction. The second chapter shows the state of the art in the field of wood and friction welding. The third chapter describes the results and is divided in two parts. The first one is related to the comprehension of the chemical and anatomical aspects and its relation with the mechanical properties of the welded joint and the second part covers the improvements in the mechanical resistance and in the water resistance of the welded joints.

In the first group of results three studies are included; the first one presents the chemical composition and solubility in water of the welded beech and spruce material at progressive welding time. In this study the components of the welded material and the degradation products of welded wood soluble in water are determined and quantified. The second work shows a topo-chemical study of cross sections of welded wood. Here, the modification of the lignin in the welding zone and the surrounding fibers is established. The third study establishes correlations between the chemical composition and mechanical properties of the welded joint.

The second part of the results includes three studies; the first one describes the changes in the shear strength of the welded wood joints by wood densification before welding. In the second and third studies the use of additives in order to improve the water resistance of the welded joints is described. The second study deals with linear friction welding and the third one with rotational wood dowel friction welding. Finally, conclusions and perspectives are presented in the fourth chapter.

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# 1. Introduction

## 1.1 Contexte et défis

La technologie du soudage du bois par friction est une alternative aux procédés traditionnels d'assemblage du bois tels que le collage ou l'utilisation de connecteurs. Cette technologie a comme avantage la très courte durée du procédé, de l'ordre de quelques secondes, pour obtenir un joint soudé. Aussi, le soudage du bois ne requiert pas d'adhésifs ni une préparation de surface spéciale autre que le rabotage (soudage linéaire) pour garantir un bon contact entre les surfaces. Il est actuellement indispensable de trouver des alternatives aux adhésifs qui proviennent principalement des matières fossiles non renouvelables. En plus, puisque le bois a des propriétés mécaniques spécifiques très performantes, il est l'un des matériaux le plus utilisé pour la construction et l'ameublement. L'utilisation du bois comme matière première renouvelable et l'élimination des adhésifs dans l'assemblage du bois font du soudage une technologie très intéressante et prometteuse.

Les premières recherches sur la technologie du soudage du bois par friction ont commencé vers les années 2000. Plusieurs institutions, telles que la Haute école spécialisée bernoise, BFH-AHB, à Bienne; l'Institut de recherche sur le bois, IBOIS, de l'EPFL à Lausanne et le Laboratoire d'études et recherche sur le matériau bois, LERMAB de l'Université de Lorraine à Epinal ont été pionnières dans ce domaine. Afin de bien comprendre les phénomènes du soudage et pousser la technologie vers des applications industrielles, un projet synergique entre les institutions mentionnées ci-dessus en plus du laboratoire d'études de bois de l'EMPA à Zurich a été mis en place. Cette thèse fait partie de ce projet et traite les caractéristiques chimiques et anatomiques des joints soudés en bois, leurs caractéristiques par rapport aux propriétés mécaniques et des possibilités d'amélioration des performances mécaniques et de résistance à l'eau. Les autres sujets du projet ont été la modélisation du procédé de soudage, la modélisation de la mécanique de la fracture des joints soudés et l'adaptation des joints soudés pour des applications à grande échelle.

L'un des défis de la technologie de soudage du bois est la faible résistance à l'eau des joints soudés, qu'elle soit en état liquide ou vapeur (Gfeller et al. 2003, Mansouri et al. 2009, Vaziri et al. 2010, Mansouri et al. 2011, Vaziri et al. 2011, Pizzi et al. 2011, Rhême et al. 2013a, Rhême et al. 2013b). Aussi, la variabilité des propriétés mécaniques des joints soudés a été mise en évidence (Gineste et al. 2012, Rhême et al. 2013a, Rhême et al. 2013b, Ganne-

Chédeville 2008a). Puisque le bois en soi est un matériau sensible à l'eau et que ses propriétés mécaniques varient conformément à l'orientation des fibres, la variabilité des propriétés mécaniques du bois soudé restent jusqu'à un certain point inhérente. Par contre les paramètres de soudage sont maîtrisables. Ceux-ci ont été étudiés avec une approche statistique (Vaziri et al. 2011, Vaziri et al. 2010), comme fonction des résistances mécaniques maximales et de résistance à l'eau liquide (Mansouri et al. 2009, Mansouri et al. 2011, Omrani et al. 2009a), jusqu'à en déterminer des combinaisons de paramètres spécifiques optimales. Néanmoins, en raison de la grande variabilité des résistances maximales du bois soudé et du fait que les paramètres de soudage sont restreints ou dépendent de la technologie utilisé i.e., la fréquence de soudage ne peut pas être changée dans tous les types de machines de soudage, il serait préférable d'établir des fenêtres de paramètres dans lesquelles les propriétés du bois soudé peuvent être considérées stables.

Des améliorations de la résistance à l'eau du bois soudé ont été obtenues par la diminution du temps de soudage (Omrani et al. 2009a) et par l'utilisation d'additifs tels que la colophane (Mansouri et al. 2011). Le temps d'immersion à l'eau des joints soudés sans endommagement a été allongé, nonobstant, le problème de la solubilité dans l'eau de la matière soudée n'a pas été traité auparavant. L'étude des composants dissous dans l'eau permet de mieux comprendre les phénomènes de dégradations dues au soudage.

Dans la perspective que la technologie du bois soudé reste un système d'assemblage robuste qui permette d'utiliser différentes essences de bois avec des propriétés mécaniques performantes, une partie de ce travail a été dédié à étudier les modifications possibles du bois pour obtenir des améliorations de la résistance mécanique. Le procédé de densification du bois préalablement au soudage a été notamment utilisé.

Il est bien connu dans tous les domaines d'étude des matériaux que les propriétés mécaniques sont liées à la composition chimique et à la conformation physique (anatomie) des composants. La matière soudée se forme en très petites quantités à l'interface de deux planches en bois massif. C'est donc un défi de trouver des méthodes permettant de caractériser la composition chimique et les propriétés mécaniques afin de trouver des corrélations entre elles. Ceci a été un des plus grands challenges dans ce travail.

### ***Objectifs***

Toutes les problématiques mentionnées ci-dessus ont mené aux objectifs suivants, qui ont été abordés tout au long de ce travail de thèse:

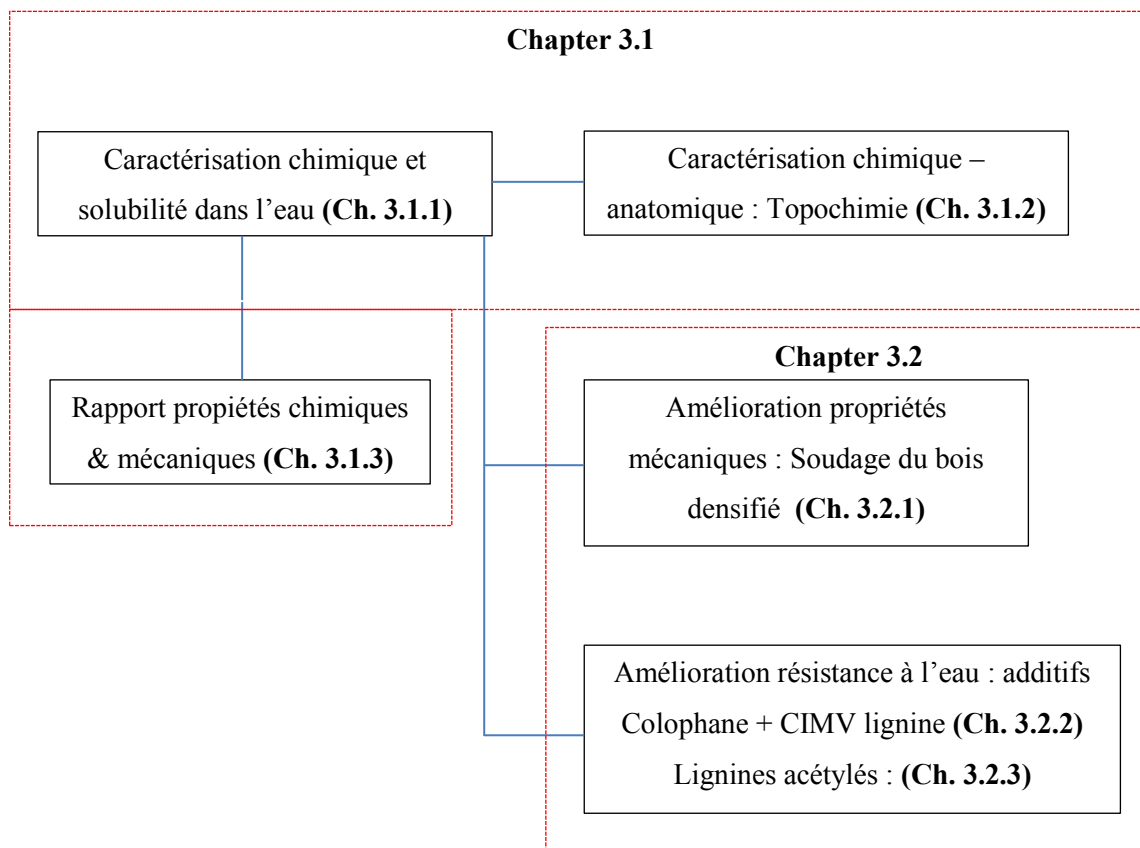
- Déterminer la composition chimique et le comportement du matériau soudé par rapport à l'eau.
- Déterminer des rapports possibles entre la composition chimique de la matière soudée et les propriétés mécaniques.
- Etudier des méthodes capables d'améliorer la performance mécanique et la résistance à l'eau du joint soudé.
- Déterminer l'influence des paramètres de soudage dans l'anatomie, la composition chimique et les propriétés mécaniques du bois soudé.

## **1.2 Approche**

Le premier chapitre présente une introduction. Le deuxième chapitre inclut un état de l'art dans le domaine du bois et du soudage. Dans le chapitre trois les résultats obtenus dans cette thèse sont présentés. Ce chapitre est divisé en deux parties, la première regroupe des études liées à la compréhension des aspects chimiques et anatomiques du bois soudé et son rapport avec des propriétés mécaniques. La deuxième partie présente des études concernant l'amélioration des propriétés mécaniques et de résistance à l'eau des joints du bois soudé. Chaque étude est présentée sous forme de papier pour publication. Chaque papier contient alors les parties de matériels, des méthodes, des résultats et discussion et de conclusions. Un diagramme des résultats est dessiné dans la figure 1.

Dans le chapitre 3.1, le premier papier présente une étude de la composition chimique et la solubilité dans l'eau de la matière soudée du hêtre et d'épicéa à temps progressifs de soudage. Le deuxième papier montre une étude topo-chimique des sections transversales de bois soudé. Le troisième papier montre des corrélations obtenues entre la composition chimique du bois soudé et des propriétés mécaniques.

Dans le chapitre 3.2, la première étude expose les améliorations dans les performances mécaniques, obtenues par la densification du bois avant le soudage. Les deuxième et troisième études portent sur l'utilisation des additives pour l'amélioration de la résistance à l'eau des joints soudés. La deuxième concerne le soudage linéaire et la troisième le soudage rotatif par tourillons. Finalement, les conclusions et perspectives sont présentées dans le chapitre quatre.

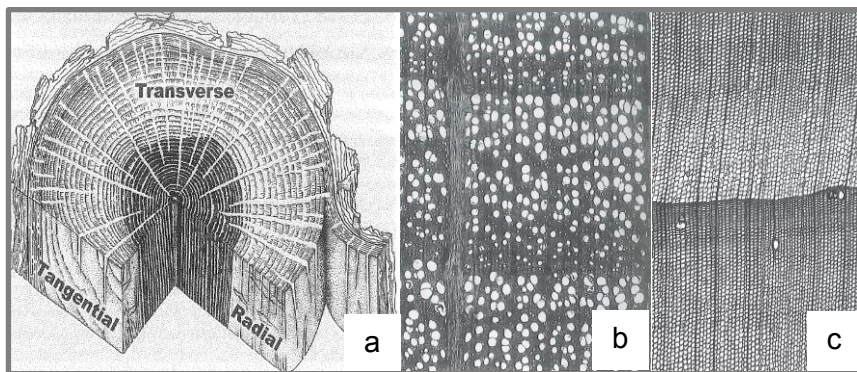


**Figure 1.1.** Diagramme des résultats présentés dans le chapitre 3.

## 2. Etat de l'art

### 2.1 Matériau bois

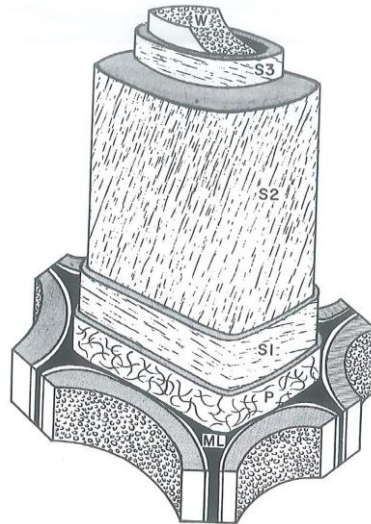
Le bois est un matériau organique composé par des cellules allongées, la plupart orienté dans la direction longitudinale du tronc. Elles sont connectées par des punctuations et leur forme varie en dépendant de leurs fonctions. Elles sont chargées du support de l'arbre, de la conduction de l'eau et des nutriments, et accomplissent les fonctions de stockage des substances nécessaires pour la croissance de l'arbre. Le bois est un matériau anisotropique, ses propriétés varient selon la direction considérée: longitudinale, radial et tangential.



**Figure 2.1.** Illustrations des sections du bois. a: Trois directions anatomiques (De : Biology of Plants 4 ed., Peter H. Raven et al. 1999 © 1971, 1976, 1986 Worth Publishers), b : section transversale du hêtre, c : section transversale d'épicéa. (b et c : Wagenführ, R. 2000).

#### 2.1.1. Structure anatomique

Les cellules de bois sont formées de cellulose, de hémicellulose et de lignine. La cellulose forme un squelette qui est entouré des autres composants, qui fonctionnent comme matrice. La ultrastructure des cellules de bois est conformé par la paroi primaire (P), paroi secondaire (S) qui est divisé en trois couches (S1, S2, S3), et les verrues. Entre les cellules adjacentes se trouve la couche intercellulaire. Le terme *lamelle moyenne composée* est utilisé pour faire référence à la zone composée par la couche intercellulaire et la paroi primaire. Cette dernière est caractérisée par une composition très élevée en lignine. Néanmoins, la paroi secondaire, que constitue la partie la plus volumineuse et que possède en majorité de la cellulose, contient une quantité de lignine plus grande que la lamelle moyenne composée. La représentation d'une cellule de bois avec les différentes couches est illustrée dans la figure 2.2.

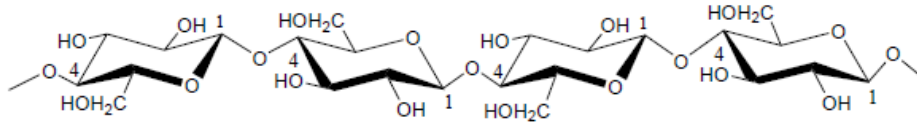


**Figure 2.2.** Représentation d'une cellule de bois avec les couches composant la paroi cellulaire (P), paroi secondaire (S) qui est divisé en trois couches (S1, S2, S3), et verrues (W) (Côté, 1967)

### 2.1.2. Composition chimiques du bois

#### *Cellulose*

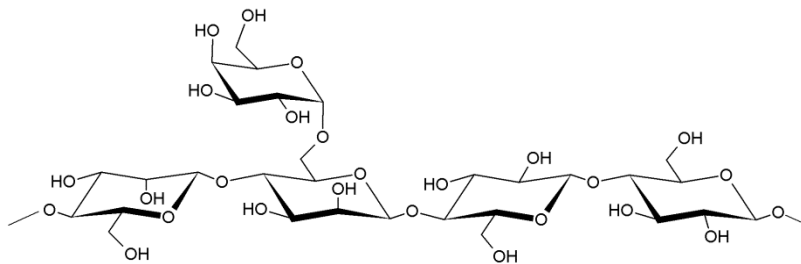
La cellulose est le composant du bois qui se trouve en quantité plus élevée et contribue à environ 40-45% au poids sec du bois (Sjöstrom, E. 1993). Elle est localisée principalement dans la paroi secondaire des cellules du bois. La cellulose est un homopolysaccharide composée des unités de  $\beta$ -D-glucopyranose liés par des liaisons glycosidiques  $\beta$ -1 $\rightarrow$ 4. Les chaînes de cellulose ont une conformation linéaire et ont tendance à former des liaisons hydrogène intra et intermoléculaire. Des faisceaux des chaînes de cellulose sont rassemblés et forment donc des microfibrilles. Ces microfibrilles ont des régions ordonnées cristallines et moins ordonnées amorphes. Les microfibrilles forment les fibrilles et celles-ci forment les fibres de cellulose. Dû à cette structure fibreuse et à des liaisons hydrogène fortes, la cellulose confère au bois une forte résistance à la tension dans la direction longitudinale du bois. Aussi, son structure moléculaire confère à la cellulose ses propriétés d'hydrophilicité, chiralité et dégradabilité. Bien que les mesures du poids moléculaire de la cellulose native soient influencées par la méthode utilisée, des valeurs d'environ 10 000 unités de glucose ont été rapportés pour le bois (Sjöstrom, E. 1993).



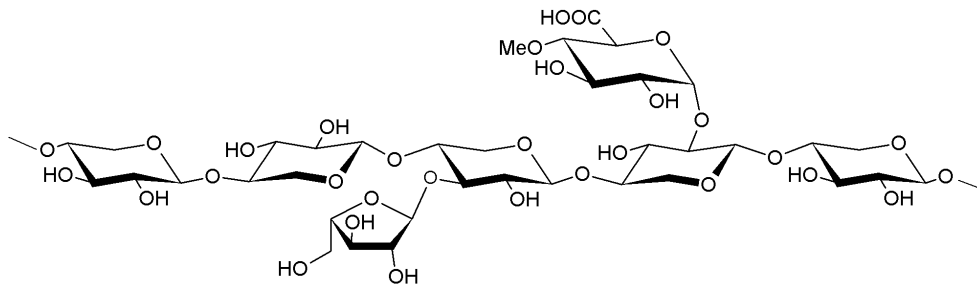
**Figure 2.3.** Structure partielle de la cellulose

### *Hémicelluloses*

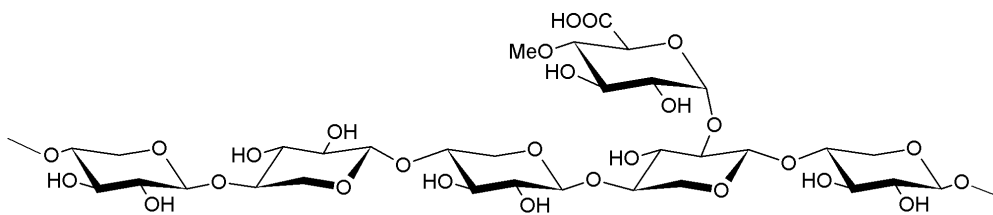
Différentement à la cellulose, les hémicelluloses sont des polysaccharides hétérogènes formés par des unités monomériques de pentoses, hexoses, des acides hexuriques et des deoxyhexoses (Fengel, D. & Wegener, G. 2003). Elles comprennent du 20 à 30% du poids sec du bois et ont un degré de polymérisation de 50 à 300. Les hémicelluloses des feuillus sont principalement formées de glucuronoxylans (15-30%) et de glucomannane (2-5%). Les glucuronoxylans sont composées d'unités  $\beta$ -D-xylopyranose avec des groupes O-acétyles (7 groupes acétyles par unité de xylose) et un résidu d'acide glucuronique O-méthyle pour dix unités de xylose (Sjöström, E. 1993). Les hémicelluloses des résineux sont principalement composées de galactoglucomannans (environ 20%) et d'arabinoglucuronoxylan (5-10%). La base des galactoglucomannans est composée de  $\beta$ -D-glucopyranose et d'unités de  $\beta$ -D-mannopyranose; deux types sont décrits dépendant du rapport de contenu galactose:glucose:mannose, qui peut être de 0.1:1:4 ou de 1:1:3. Additionnement, les groupes O-acétyle sont présents avec une moyenne de 1 pour 3-4 unités (Sjöström, E. 1993). Les figures 2.4 au 2.6 montrent les principales structures des hémicelluloses.



**Figure 2.4.** Structure principale des résineux : galactoglucomannane (15-20%) (hexosane)



**Figure 2.5.** Structure partielle des résineux : Ara-4-O-MeGluA-Xylan (8-12%) (pentosane)

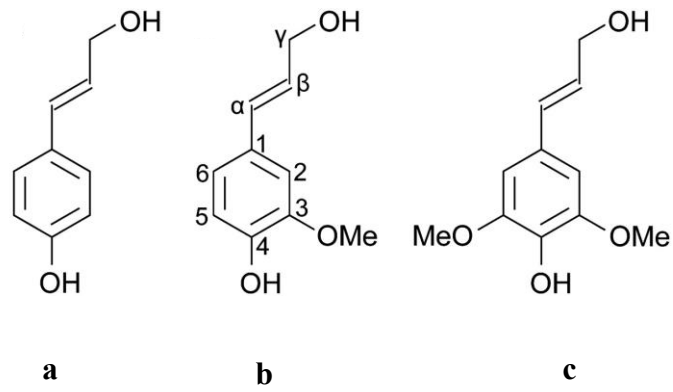


**Figure 2.6.** Structure principale des feuillus : Acetyl-4-O-MeGluA-Xylan (20-30%) (pentosane)

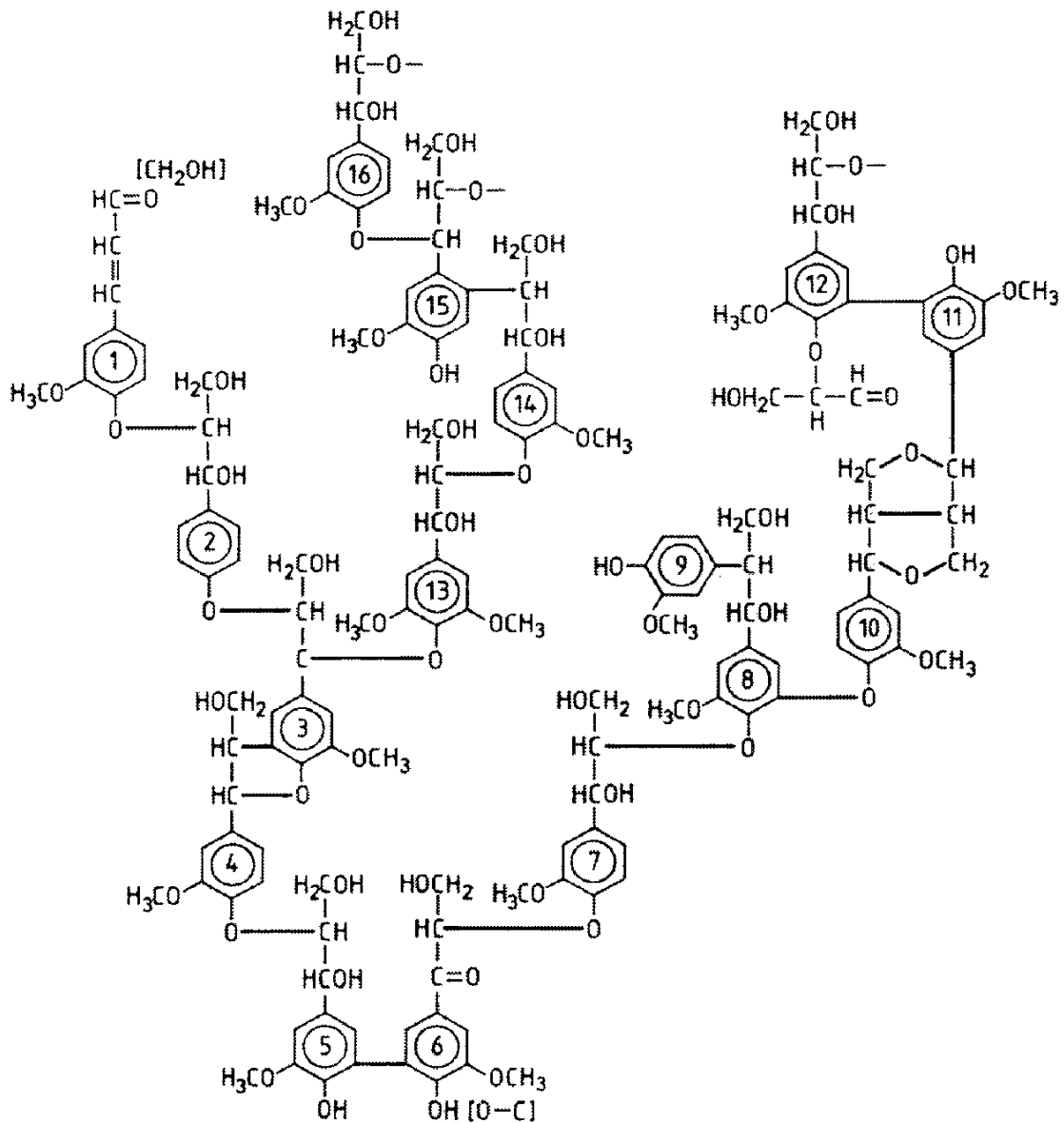
### ***Lignine***

La lignine est un polymère hétérogène amorphe dérivé des monomères de phénylpropane. Les précurseurs de la lignine sont l'alcool p-coumarylique, l'alcool coniferylque et l'alcool sinapylique (figure 2.7). Ces précurseurs donnent lieu aux macromolécules de lignine à travers des synthèses biochimiques. La contribution de chaque précurseur varie en dépendant de la source de lignine. La lignine des gymnospermes (résineux) est basée seulement sur l'alcool coniferylque, tandis que la lignine des angiospermes (feuillus) est basée principalement sur les deux l'alcool coniferylque et l'alcool sinapylique. Les polymères résultants sont la lignine p-hydroxyphényle, guaiacyle, et syringyle. Les résineux contiennent de 25 à 35%, tandis que les feuillus en contiennent de 18 à 35%. Des représentations de l'structure de la lignine de l'épicéa et du hêtre sont présentés dans les figures 2.8 et 2.9. Les liaisons entre les monomères de phénylpropane sont du type C-O-C (ether) et C-C. Les plus fréquentes sont les C-O-C (approximativement deux tiers par rapport à un tiers des liaisons C-C). Dans la figure 2.10 les liaisons typiques dans la lignine sont représentés.

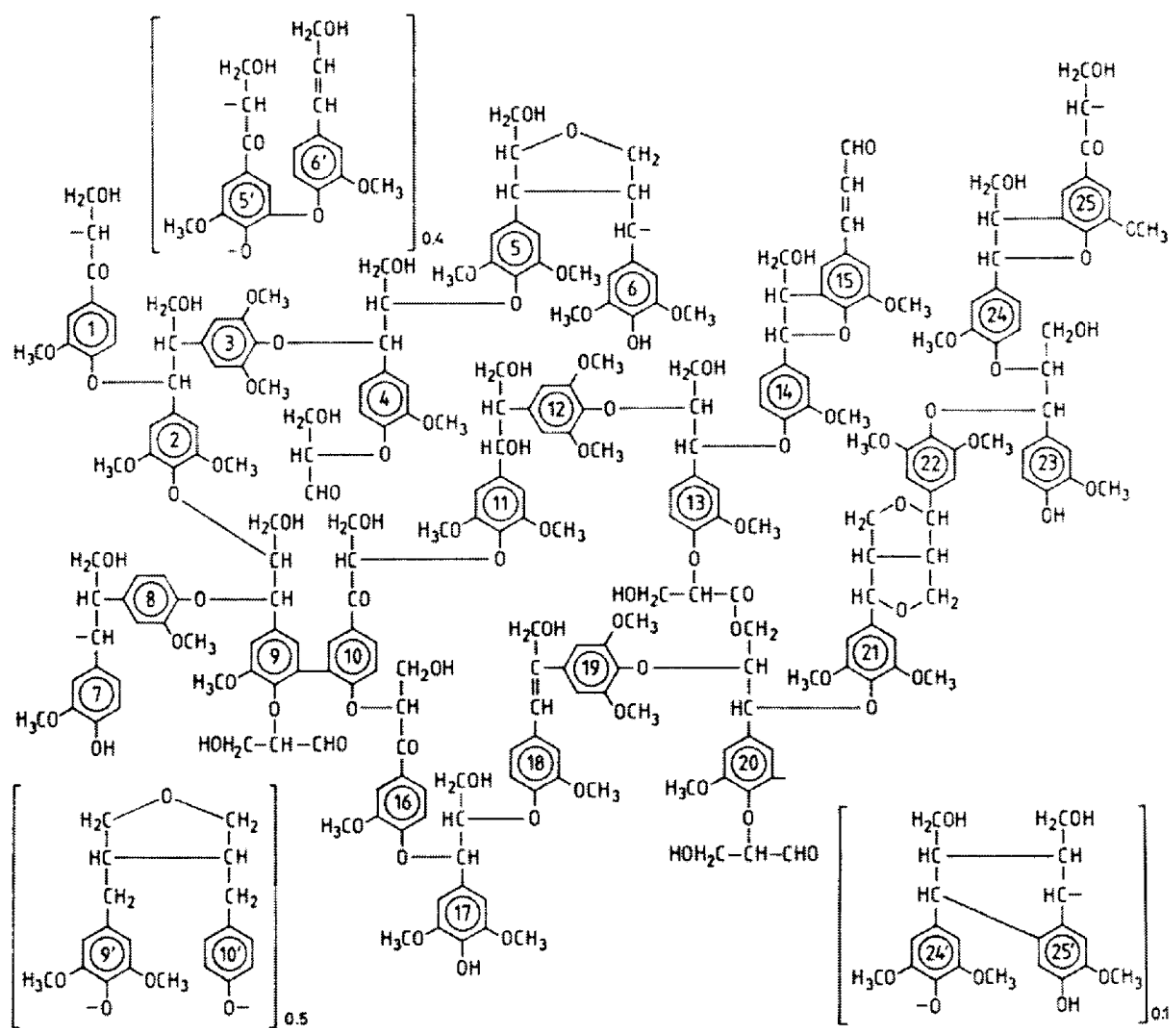




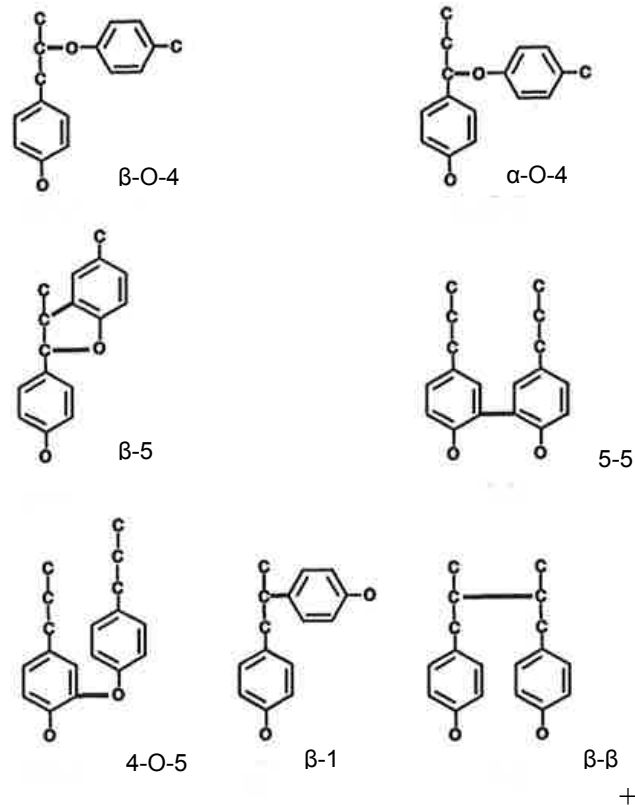
**Figure 2.7.** Précurseurs de la lignine. a : alcool p-coumarylique, b : alcool conifèrylique et c : alcool sinapylique



**Figure 2.8.** Structure de la lignine de l'épicéa (d'après Fengel et Wegener 2003)



**Figure 2.9.** Structure de la lignine du hêtre (d'après Fengel et Wegener 2003)

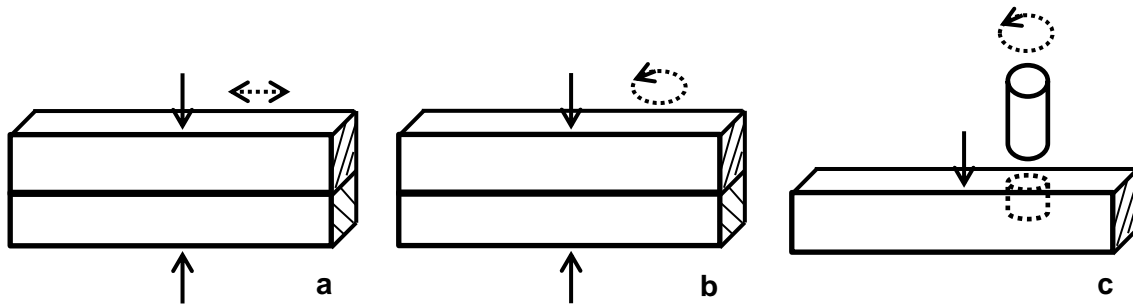


**Figure 2.10.** Liaisons typiques entre les monomères phénylpropane dans la structure de la lignine (d'après Sjöström 1993)

## 2.2 Soudage du bois par friction

### 2.2.1 Généralités

Le soudage par friction est une technologie largement employée pour les métaux et les plastiques. Les domaines d'application sont principalement dans l'industrie automobile, aéronautique et dans la fabrication de pièces en général. Il est bien connu que l'effet de la friction, apart l'usure est la génération de chaleur, principe qui est optimisé dans les machines d'assemblage par friction. La première machine à souder des tuyaux a été patentée par Bevington (1981); et les premières pièces soudées en plastique ont été fabriqués par Henning (1942). Le premier indice de l'utilisation du soudage par friction pour le bois est une patente allemande (Suthoff et al. 1996). Les différentes technologies de soudage par friction peuvent être classifiés d'accord à la direction du mouvement de friction appliqué. Le mouvement peut être dans la direction linéaire, circulaire ou rotative. Une vue d'ensemble de ces techniques du soudage appliqués au bois est présenté ci-dessous (figure 2.11):



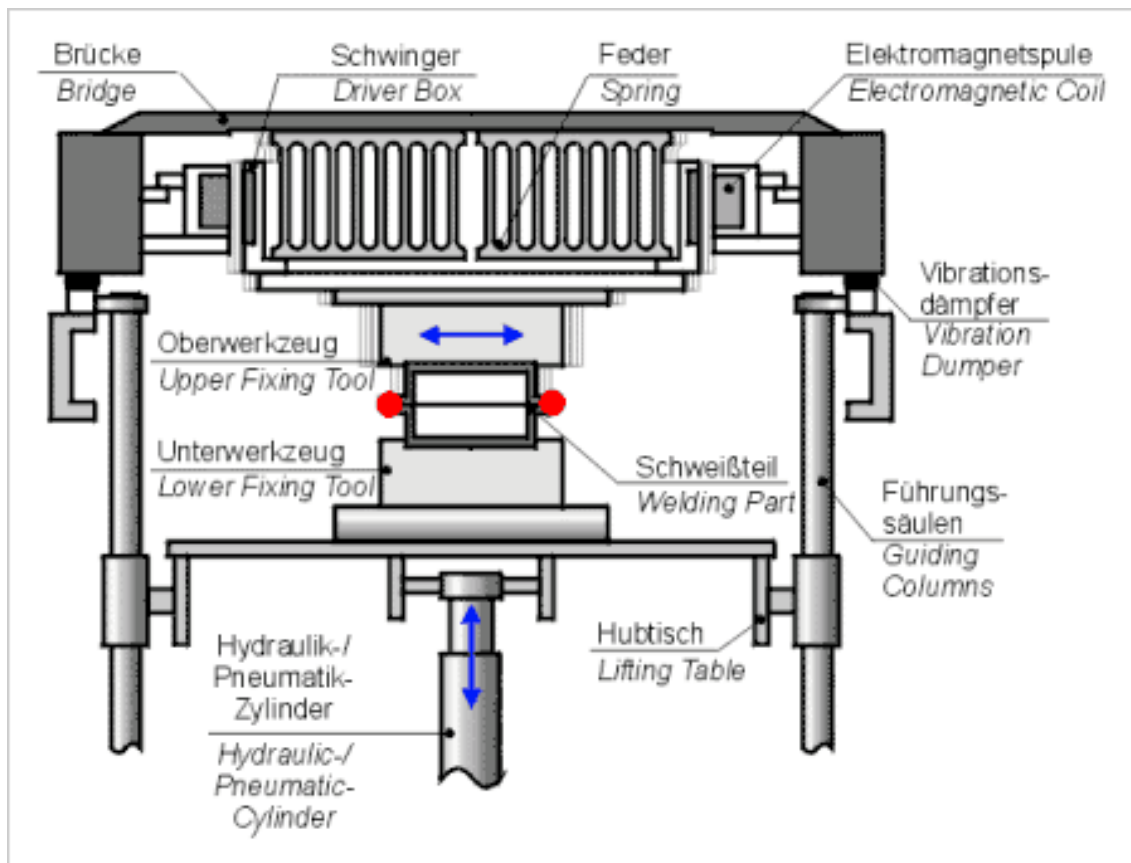
**Figure 2.11.** Représentation schématique des types de soudage, a: linéaire, b: circulaire, c: rotatif. Les flèches avec lignes à tiret uni indiquent la direction de la pression, les flèches en pointillé indiquent la direction du mouvement.

### 2.2.2 Soudage par friction linéaire

#### *Principe de fonctionnement et procédé*

Une machine de soudage linéaire typique est pourvue d'une table inférieure mobile dans l'axe verticale à travers d'un vérin hydraulique/pneumatique. Cette table dispose d'un outil de fixation où les pièces à souder sont placées. La table inférieure est soulevée jusqu'à ce que la latte en bois en dessus soit en contact avec la fixation de l'outil supérieur. La table inférieure reste fixe dans cette position lors du mouvement de friction de l'outil supérieur. Ce mouvement (friction linéaire) est généré grâce à un dispositif électromagnétique aimanté capable d'entraîner des oscillations à une fréquence et amplitude données. L'esquisse d'une machine de soudage linéaire est présentée dans la figure 2.12. Dans d'autres types de machines de soudage linéaire les systèmes d'entraînement de l'oscillation sont de type mécanique ou hydraulique. Pour que la friction à l'interface ait lieu, une pression dans le sens perpendiculaire aux pièces à souder est fournie. De même, une pression de maintien est appliquée pour assurer la cohésion des pièces soudées lorsque le mouvement de friction est arrêté.

Les paramètres à définir/contrôler dans le soudage linéaire du bois sont donc la fréquence et l'amplitude de vibration, le temps de soudage, la pression de soudage, le temps de maintien et la pression de maintien.



**Figure 2.12.** Esquisse de fonctionnement d'une machine de soudage par friction linéaire à entraînement électromagnétique (Branson Ultraschall, Dietzenbach-Allemagne)

### Caractérisations chimiques du bois soudé

Des études qui caractérisent le matériau soudé ont été réalisées avec différentes techniques, qui sont nommés ci-dessous:

### **Résonance magnétique nucléaire du solide**

Au début des recherches sur le bois soudé, des études ont été menés en utilisant la résonance magnétique nucléaire en état solide (CP-MAS  $^{13}\text{C}$ -NMR). Ces études ont montré la déméthoxylation de la lignine, une faible augmentation des hydrates de carbone amorphes, l'auto-condensation de la lignine, la déacétylation des hémicelluloses, des réactions de condensation de la lignine avec du furfural dérivé d'hydrates de carbone ou l'auto-polymérisation du furfural pendant le soudage (Gfeller et al. 2003, Pizzi et al. 2006, Ganne Chédeville 2008a).

## **Spectroscopie infrarouge à Transformée de Fourier**

En combinaison avec des études par CP-MAS  $^{13}\text{C}$ -NMR, des études avec l'spectroscopie infrarouge à Transformée de Fourier (FTIR) ont démontré la formation de quinones par oxydation de phénols, et le mécanisme de condensation des lignines avec des liaisons aryle-aryle et aryle- $\text{CH}_2$ -aryle (Delmotte et al. 2008).

## **Hydrolyse acid avec de l'acide trifluoroacétique**

Stamm et al. (2005b; 2006b) ont effectué des extractions du matériau soudé d'épicéa (friction circulaire) suivi par une hydrolyse. L'extraction a été effectuée avec de l'acétone et l'hydrolyse avec de l'acide trifluoroacétique (TFA). Dans le matériau soudé la quantité des hémicelluloses décroît, la lignine augmente, la cellulose augmente et aproximativement 15% du matériau est extrait en acétone.

L'hydrolyse du bois par TFA a besoin des conditions strictes de manière à atteindre une hydrolyse complète de la cellulose. Lorsque ces conditions sont respectées les xylandes se décomposent non seulement en monomères mais donnent aussi lieu à une perte de valeur de leur contenu original (Fengel and Wegener 1979). Inversement, appliquant des conditions plus souples, une hydrolyse incomplète des hexoses se produit. Conformément à Puls (1993), une hydrolyse analytique est toujours un compromis entre une hydrolyse incomplète et une destruction des sucres. L'usage du TFA est le bon choix lorsque les polysaccharides solubles ont besoin d'être hydrolysés ; cependant son usage fait encourir le risque d'une hydrolyse incomplète lorsque les matériaux lignifiés dégènèrent en sucres monomériques, ce qui implique de plus grandes productions de teneur en lignines et de productions comparablement basses de sucres.

## **Thioacidolyse-chromatographie en phase gazeuse – spectrometrie de masse**

Stamm et al. (2006b) ont analysé les fragments de lignines du matériau soudé d'épicéa par thioacidolyse-GC/MS; cette méthode permet déterminer la structure chimique des portions des lignines ayant un poids moléculaire bas. Les composés dérivés de la lignine hautement condensées ne sont malheureusement pas possibles d'être analysés par cette méthode. Ces derniers composés sont communément admis d'apparaître lors du processus de soudage.

## **Aminolyse**

Stamm et al. (2005b, 2006b) ont utilisé l'aminolyse pour montrer l'augmentation des groupes phénoliques OH dans le matériau soudé d'épicéa, ce que indique le clivage des macromolécules de lignine. D'un autre côté la diminution des groupes aliphatiques OH dans le matériau soudé d'épicéa a été aussi déterminé, ceci montre la dégradation des polysaccharides (Stamm 2006a).

## **Autres méthodes**

Sun et al. (2010) ont étudiés du bois soudé par tourillons (rotatif) avec haute vitesse par pyrolyse-GC-MS, DSC et XPS. Les pourcentages des lignines guaiacycle et syringyle et de produits reliés aux hydrates de carbone issus de la pyrolyse GC-MS sont présentés; cependant ces pourcentage sont basés sur des produits identifiés et diffèrent des références de la composition typique du bois (Wagenführ 2000; Fengel and Wegener 2003). Aussi, Belleville et al. (2013) ont étudié du bois soudé par tourillons (rotatif) par pyrolyse-GC-MS, XPS et ATR-FTIR. Les résultats du XPS montrent une augmentation du rapport O/C dans l'érable soudé; augmentation qui est attribuée à une formation de substances contenant une fonctionnalité oxygénée.

## **Caractérisations microscopiques du bois soudé**

La structure du matériel soudé de bois a été observée dans des images acquises au microscope électronique à balayage (SEM). Celle-ci a été décrite comme un enchevêtrement des fibres partiellement détruites avec du matériau amorphe (Gfeller et al. 2003, Properzi et al. 2005, Mansouri et al. 2009). Des études du matériel soudé d'épicéa ont été réalisées à l'aide de la microscopie optique par Stamm (2006b), et de l'érable soudé par Ganne-Chédeville et al. (2006). Aussi, la microscopie confocal laser a été utilisé par Stamm (2006) pour analyser des joints soudés d'épicéa.

## **Caractérisations mécaniques du bois soudé**

Des essais de cisaillement des joints soudés du hêtre et d'épicéa par soudage par friction linéaire ont été rapportés par Gfeller et al. (2003). Aussi, Ganne-Chédeville et al. (2008a) présentent les valeurs de résistance au cisaillement des joints du hêtre soudé (friction linéaire)

dans un éventail de temps de soudage de 0 à 11 s. Stamm et al. (2005a, 2005b) présentent des valeurs de résistance au cisaillement pour des joints soudés du hêtre et d'épicéa par soudage par friction circulaire.

Des mesures de taux de restitution d'énergie dans des éprouvettes du type double-levier (DCB) du hêtre soudé sont présentées par Ganne-Chédeville et al. (2008d). Les études sur la mécanique de rupture ont été également effectuées par Omrani et al. (2009b), et des recherches sur l'influence de la direction du grain dans les joints soudés ont été exécutées par Properzi et al. (2005), Omrani et al. (2009b), Omrani et al. (2010). Aussi, Gineste et al. (2012) ont effectué des tests de cisaillement sur des éprouvettes soudées de hêtre. Selon Omrani et al. (2009a), l'amélioration des performances mécaniques sur des joints fabriqués par soudure linéaire seraient obtenues par le raccourcissement du temps de soudage (1.5 s), amplitude décroissante (2 mm) et l'augmentation de fréquence (150 Hz). L'amélioration est attribuée à un endommagement réduit des composants du bois dans l'interface de soudure.

Essais de résistance au cisaillement ont été réalisés en pin sylvestre par Vaziri et al. (2012), et Mansouri et al. (2011). Aussi, tomographie à rayons X a été utilisé pour étudier le développement de fissures dans les joints soudés du pin sylvestre (Vaziri et al. 2010, 2011). Il a été montré dans Brunner et al. (2010a, 2010b) et de la Vallée et al. (2011) que la capacité de charge des joints soudés d'épicéa augmente avec la longueur de chevauchement. Cependant, cette augmentation est limitée à des longueurs de chevauchement plus élevés avec une valeur critique d'environ 300 mm, au-delà aucune augmentation n'est atteinte. Enfin, le comportement des joints soudés du hêtre dans des différents modes de rupture et d'environnements de conditions d'humidité a été étudié par Rhême et al. (2013a, 2013b) et Rhême (2014). Il a été constaté que la résistance des joints soudés en hêtre diminue au-delà de 16% EMC (contenu d'humidité à l'équilibre). En outre, il a été déterminé que la traction et la résistance au cisaillement ne dépendent pas de l'orientation des fibres.



### **3. Résultats**

Les résultats de ce travail sont présentés sous forme de publications. Une première partie regroupe des études liées à la compréhension des aspects chimiques et anatomiques du bois soudé et son rapport avec des propriétés mécaniques (3.1), et la deuxième partie présente des études concernant l'amélioration des propriétés mécaniques et de résistance à l'eau des joints du bois soudé (3.2), ceux-ci ont été réalisés par moyen de la prédensification du bois et l'utilisation des additives avant le soudage. Ci-dessous la description des titres des publications:

#### ***3.1 : Compréhension des aspects chimiques et anatomiques et rapport avec les propriétés mécaniques***

3.1.1 : Etude de la solubilité et composition chimique du bois soudé

3.1.2 : Caractérisation topo-chimique de la lignine sur la zone soudé du bois

3.1.3 : Corrélation entre les propriétés mécaniques et chimiques du bois soudé à différents temps de soudage

#### ***3.2 : Amélioration des propriétés mécaniques et de résistance à l'eau***

3.2.1 : Soudage du bois densifié : propriétés physiques, anatomiques, chimiques et mécaniques

3.2.2 : Révision des acquis dans le domaine de soudage linéaire par friction

3.2.3 : Amélioration de la résistance à l'eau des joints de bois soudé par tourillons par la lignine acétylée



### **3.1 Compréhension des aspects chimiques et anatomiques et rapport avec les propriétés mécaniques**

#### **3.1.1 Etude de la solubilité et composition chimique du bois soudé**

Publication soumise au journal “European Journal of Wood and Wood Products”

#### **Résumé**

La solubilité dans l'eau et la composition en hydrates de carbone/lignine après hydrolyse du matériau soudé de bois par friction linéaire ont été étudiées. Du hêtre (WB : “welded beech”) et de l'épicéa soudés (WS : “welded spruce”) ont été analysés pour des temps de soudage de 1, 1.5, 2, 2.5, 3 s, et 2, 4, 6, 8, 10, 12 s respectivement. Le matériau soudé isolé a été d'abord extrait dans l'eau, séché, cryo-broyé puis hydrolysé avec de l'acide sulfurique. Les pourcentages maximaux des solides dissouts dans l'eau ont été de 17.7 pour le WB, de 10 pour le WS, de 2.2 pour le hêtre non soudé et de 1.4 pour l'épicéa non soudé. De la lignine, des mono-oligosaccharides, de l'acide acétique, de la vanilline, du furfural, de l'hydroxyméthylfurfural 5 (5HMF) et du syringaldéhyde ont été quantifiés dans les extraits d'eau. Les pourcentages de lignine soluble dans l'eau dans le WB et le WS furent de 5 et 3,6 respectivement; le poids moléculaire et la polydispersité ont également été déterminés. Concernant les hydrates de carbone dans les extraits d'eau, un maximum de 1.4% d'oligosaccharides dans le WB et de 1% de monosaccharides dans le WS ont été détectés. Après l'hydrolyse une quantité plus élevée de lignine Klason et une diminution progressive de certains sucres ont lieu à des temps de soudage consécutives pour le WB et le WS. Ce travail permet d'expliquer dans une large mesure le comportement des joints soudés placés dans l'eau. De plus, la dégradation de certains composants du bois est clairement présentée.



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

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Pizzi <sup>(2)</sup> • Frédéric Pichelin <sup>(1,\*)</sup>**

## **Abstract**

The solubility in water and carbohydrates/lignin composition after hydrolysis of welded wood by linear friction welding was studied. Welded beech (WB) and welded spruce (WS) were analyzed at welding times 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 correspondingly. Among water extracts, lignin, mono-oligosaccharides, acetic acid, vanillin, furfural, 5 hydroxymethylfurfural (5HMF), syringaldehyde and levoglucosan 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 maximal of 1.4 oligosaccharides in WB and 1% monosaccharides in WS were detected. After hydrolysis, an increasing amount of Klason lignin and a progressive diminution of some sugars take place at consecutive welding times of WB and WS. This study allows explaining in a good extent the behavior of welded joints face to liquid water. Moreover, degradation of certain wood components is clearly presented.

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## Introduction

Linear friction welding for wood is an assembly technology that requires short process time, no glue nor special preparation of surface. Owing to its mechanical resistance welded wood can be used for internal applications (Gfeller et al. 2003; Stamm 2006a; Ganne-Chédeville 2008c; Omrani 2009b) with caution on high relative humidity environments (Rhême et al. 2013a; Rhême et al. 2013b). Outdoor applications are not possible due to the lack of resistance of welded wood to water. Some improvements in the water resistance have been reported by using rosin or shortening welding time (Wt) (Mansouri et al. 2009; Omrani et al. 2009a; Mansouri et al. 2011; Pizzi et al. 2011; Vaziri et al. 2011). However, the problem of the partial dissolution of welded material into water has not been tackled before. This is studied in the present work.

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 2006a; Ganne-Chédeville 2008c; Omrani 2009b). Fibers get detached, partially “ground” and welded material is formed. When friction is stopped pressure is still applied until solidification-compaction of the joint. Densification of the welded material and nearby zones goes together with chemical and anatomical changes.

Chemical modifications produced in the welded material have been studied with several methods. Solid state CP-MAS  $^{13}\text{C}$ -NMR was used to show lignin demethoxylation, apparent 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). Also, the formation of quinones by oxidation of phenols, dehydration, and mechanism of condensation of lignins by aryl-aryl and aryl- $\text{CH}_2$ -aryl links have been reported by Delmotte et al. (2008) in coupled studies with FTIR. Delmotte et al. (2009) argues 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 in welding times from 0 to 11s. Pizzi et al. (2006) mentioned that is not possible to draw conclusions about the relative proportions of lignin and carbohydrates from CP-MAS  $^{13}\text{C}$ -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). Also, 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. (2006b) analyzed lignin fragments of WS by thioacidolysis-GC/MS; this method is limited to determine the chemical structure of low molecular weight portions of lignin but not the higher condensate/cross-linked lignin derived compounds, which are most likely considered to occur. In the same study, aminolysis was used to show the increase of phenolic OH and decrease of aliphatic OH groups in WS. 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.

Stamm et al. (2005b; 2006b) performed extraction and hydrolysis of spruce welded by circular friction welding. Extraction was carried out with acetone and hydrolysis with trifluoroacetic acid (TFA). Even if circular and linear welding differ in the friction direction implying distinct conditions at the interface, i.e. temperature, welding pressure and times, the mechanisms are similar. In welded material the amount of hemicelluloses decrease, lignin increases, cellulose in this case increases and an important quantity of material is extracted in acetone. Hydrolysis of wood with TFA needs severe conditions to achieve complete hydrolysis of cellulose. When these conditions are used, xylans decompose not only in monomers but further giving place to a loss in their original content value (Fengel and Wegener 1979). Conversely, when mild conditions are applied, incomplete hydrolysis of hexoses occurs. According to Puls (1993), analytical hydrolysis is always a compromise between incomplete hydrolysis and sugar destruction. The use of TFA is a right choice when soluble polysaccharides need to be hydrolyzed; however, its use carries the risk of incomplete hydrolysis when lignified materials are degraded to monomeric sugars, which implies higher yields in lignin content and comparatively low sugar yields.

For lignocellulosic materials the hydrolysis in two steps with sulfuric acid is highly recommended over other methods as hydrolysis with TFA, methanolysis or enzymatic hydrolysis. This method has been carefully developed for beech and spruce to keep optimal sugar survival (Puls 1993). In the present work, where different welding times for beech and spruce have been 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.

## **Materials and methods**

### **Raw materials**

Beech (*Fagus sylvatica*) and Spruce (*Picea abies*) were assembled by linear friction welding during 1, 1.5, 2, 2.5, 3 s, and 2, 4, 6, 8, 10, 12 s respectively. 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 correspondingly. The process was carried out in a Branson M-DT24L linear welding machine. Size of welded specimens was 500x80x24 mm<sup>3</sup> for beech and 500x50x24 mm<sup>3</sup> for spruce. Thinner sections of spruce specimens were selected since larger sections without defects, i.e. knots, were not available. The welding surface was 500x80 and 500x50 mm<sup>2</sup> 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° respect to the welding interface. Wood was acclimatized at 23°C and 50% RH before welding. Testing material was obtained by scratching with a razor blade the surface of opened welded pieces. Care was taken to remove just welded material (dark/brown colored) and avoid wood fibers.

### **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 in holes of 0.5 mm diameter, from the back of the wood specimens.



### **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 distilled water. 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.

### **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.

### **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<sub>2</sub>SO<sub>4</sub> at 72% w/w is added to 100 mg of sample. The mixture is kept during 1 h in a thermal bath at 30°C. The reaction is stopped by diluting the solution with ionized H<sub>2</sub>O until a concentration of 4% of H<sub>2</sub>SO<sub>4</sub>. In the second step, dilute solutions are placed in an autoclave at 120°C and 1.2 Bar, during 40 min for WS and 30 min for WB. Time is optimized for maximal recovery of monomeric sugars (Puls 1993). Then, solutions are cooled down and filtered in a G4 sintered glass crucible. Klason lignin is the solid residue and liquid solution contains the hydrolyzed sugars.

### **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 bichinchonate 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).

### **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, and 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 300x7.5 mm columns plus guard column 50x7.5 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 kit, Megazyme, Ireland) and UV spectroscopy with the detection at a wavelength of 205 nm.

## **Results and discussion**

### **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. Welding material is expelled out 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 so 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 as well found by Stamm (2005a), where thermocouples placed directly in the welding interface were also used. Other authors (Delmotte et al. 2008; Ganne-Chédeville et al. 2008a; Ganne-Chédeville et al. 2008b), 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 later cases was performed by infrared thermography on the edge of the welding line.

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

<b>Beech</b>				
Wt (s)	1	2	3	-
T (°C)	203	291	380	-
<b>Spruce</b>				
Wt (s)	1	2	6	12
T (°C)	107	182	368	400

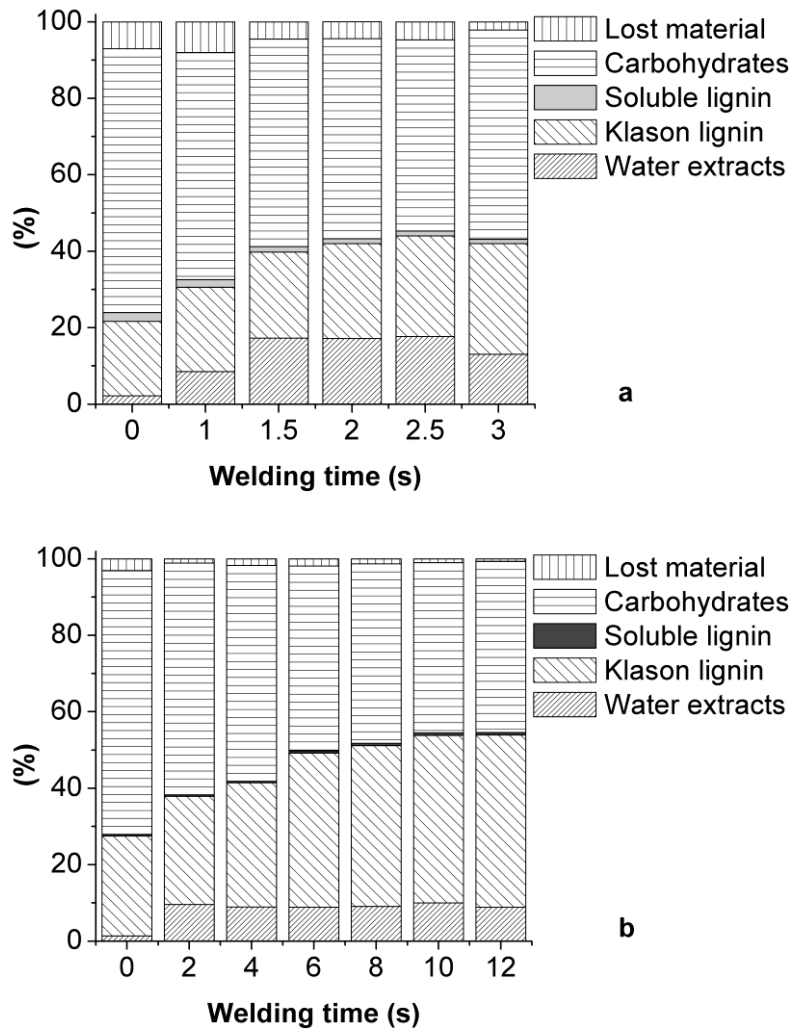
### **Composition of pre-extracted welded material after hydrolysis**

In figures 1 to 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 (figure 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 into 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 into water.

Klason lignin shows a clear ascent for longer welding times for both species. It increases to 28.9% after 3 s 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 e.g. condensation with furans (Gfeller et al. 2003, Stamm 2006a, Delmotte et al. 2008) and other carbohydrate degradation products can

be conceived. In welded wood, Klason lignin represents the lignin that has been thermal- 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 2003). Even if the rise of temperature in the welding interface of spruce is slower than in beech, due to the longer required welding times higher temperatures are reached in welded spruce. Therefore, hemicelluloses in WS are affected in a greater extent than in WB, leading to a higher increase of lignin content. Further, guaiacyl (G) units in spruce lignin are more susceptible for 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.

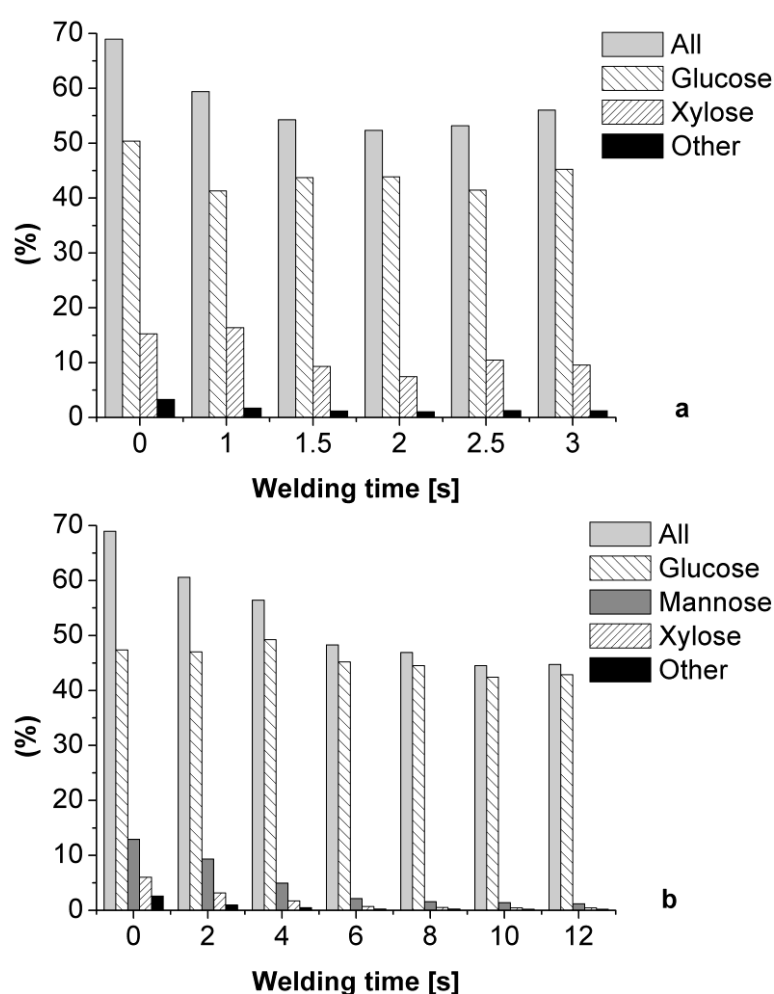
It is well known that lignin and cellulose (crystalline) are the most thermally resistant components in wood, and hemicelluloses the more sensitive (Fengel and Wegener 2003; Garrote et al. 1999). In general, the total carbohydrate percentage decreases with Wt (figure 1). It diminishes from 69% in un-welded 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; 2006a; 2006b), around 45%, at welding times 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).



**Fig. 1** Effect of welding time on the composition of welded material as determined after water-extraction and hydrolysis. a beech, b spruce

The differentiation of monosaccharides coming from hemicellulose and cellulose is depicted in figure 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 steply. 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 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 entails 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).



**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

## **Water extracted components in welded material**

### **General description**

Degraded materials generated in the welding interface can either form condensed products, remain as single substances, be liberated as volatile products or be expelled as “ground black fibers” through the edges of the welding interface, when Wt is prolonged. In figure 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. More components could be dissolved if other solvents would be used. Windeisen and Wegener (2008) found a lignan (syringaresinol) from thermal treated beech extracted with acetone/cyclohexane. Stamm et al. (2005b) found 15.8% of acetone extractives in WS from circular welding. As it can be seen, 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 is 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 get brown. At 8-10 s the welded line is formed and it is almost completely dark. At 12 s it is black.

### **Carbohydrates degradation products**

Under acidic conditions and high temperature furans are formed as carbohydrate degradation products. 5HMF is a decomposition product from hexoses, either derived from glucomannan (Janzon et al. 2013), the main hemicellulose of softwoods in general; 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 (Figure 3). Therefore it is most likely that they have been lost as volatiles or that they have further reacted with themselves or with lignin to form condensed products. Acetic acid is a typical degradation product of thermal treated wood (Tjeerdsma et al. 1998; Sivonen et al. 2002; Windeisen et al. 2007) and it is generated by the de-acetylation of hemicelluloses. Hence, it is logical to find it

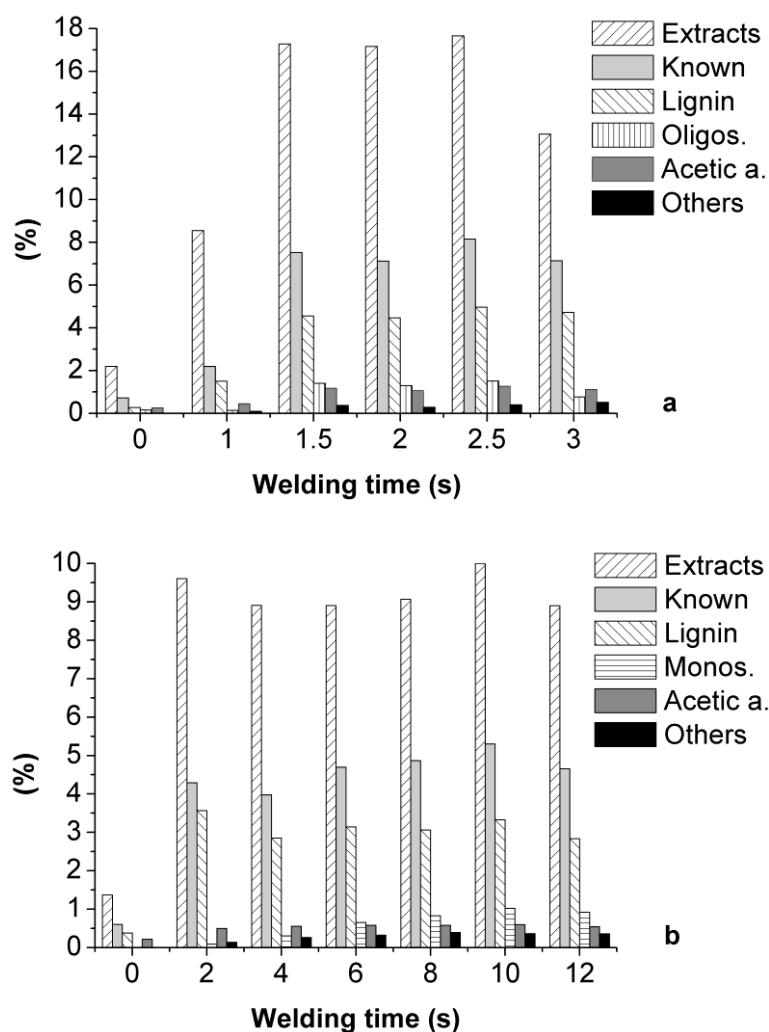
in higher amounts in WB than in WS, due to the higher content of acetyl groups in hardwoods than in softwoods. However, as for other degradation products of welded material, part of organic acids escapes with the volatiles (Omrani et al. 2009c; Ganne-Chédeville 2008c). The presence of acetic acid together 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.

### **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 (figure 1).

Milled wood lignins are reported to have a weight average molar mass ( $M_w$ ) of 20 000 g mol<sup>-1</sup> in softwood and a lower  $M_w$  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 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 in a higher extent than glucomannan-linked lignin (in spruce); this last one undergoes a partial condensation to form more high molecular mass material. It would go along with the higher percentages of klason lignin in WS vs WB (figure 1). The higher sensitivity of hardwood Syringyl-moieties is also noticed in a study of welded wood (Sun et al. 2010).





**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

### Molecular weight and polydispersity of water dissolved lignins

The Mw and PD 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 masses of  $7900 \text{ g mol}^{-1}$  for beech and  $4100 \text{ g mol}^{-1}$  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 PD. As depolymerization and repolymerization 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 repolymerization 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 extend. High molar masses are achieved especially at low reaction times.

**Table 2.** Molecular weight and polidispersity of water soluble lignin

Sample	Wt (s)	Mw (g mol <sup>-1</sup> )	PD (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

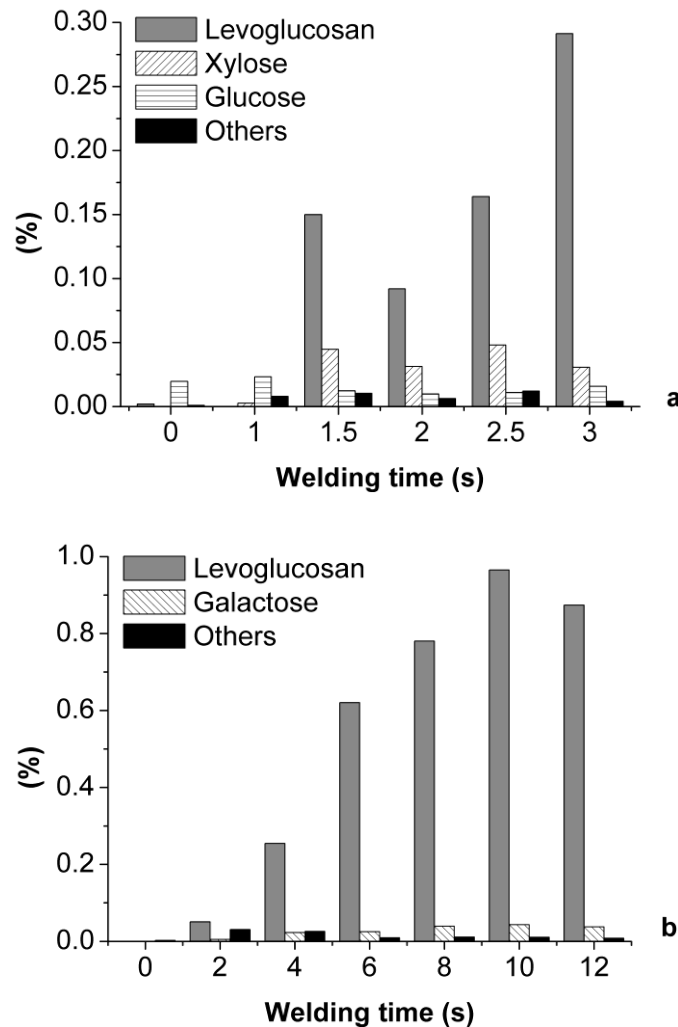
### **Monosaccharides, anhydrosugars and oligosaccharides in water extracts**

In figures 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 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<sup>-1</sup> (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<sup>-1</sup> (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<sup>-1</sup> (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 (figure 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 0.04% in water extracts of WS, and it is almost not present in hydrolyzed sugars (figure 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 near to up 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). Also, 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). At such short welding times it is presumable that levoglucosan comes from glucose from galactoglucomannan rather than cellulose, which corresponds with 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°C vs. 200-400°C, and

oligosaccharides that are found in the welding interphase are not necessary present in pyrolysis products. Moreover, the mixing effect of the frictional movement does not occur in pyrolysis.

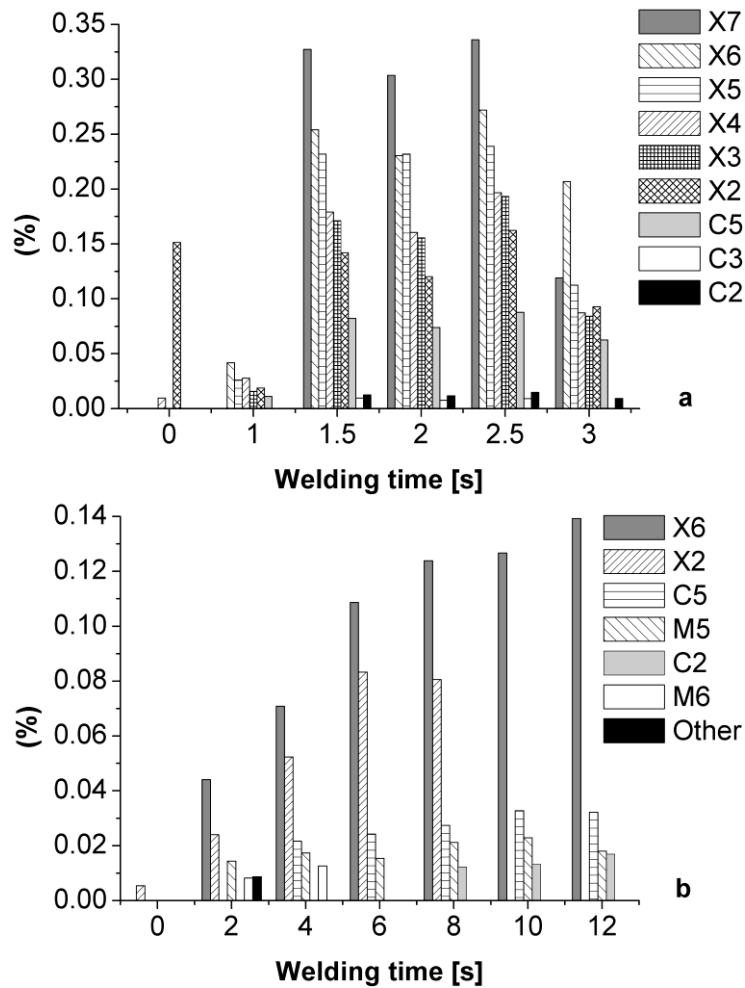


**Fig. 4** Monosaccharides and anhydrosugars in water extracts of welded material. a beech, b spruce. Others beech: arabinose, galactose, mannose. Others spruce: arabinose, glucose, xylose, mannose

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 et al. (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. 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 (Lepänen et al. 2011). Additionally, solubility of cleaved oligosaccharides during welding could be affected by their deacetylation (see free acetic acid in figure 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; Song et al. 2011; Grénman et al. 2011).

Regarding figure 5a, a well-defined distribution of xylooligomers is delineated. Between welding times 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 (kason lignin) of xylooligomers at higher temperature and longer Wt. According to Bobleter (1994), cellulose-derived oligosaccharides are soluble in water up 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 process. In flow through extraction of spruce in water, apparently part of cellulose is removed at 240°C (Leppänen et al. 2011). Cellooligomers 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 figure 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 mannoooligomers 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 attacked would be the amorphous part. It is worthy 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.



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

## Conclusions

In the field of linear friction welding for wood this work presents for first time a study of 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 even not completely formed. Similarly, water extracts in WS get over 9% at just 2 s of Wt. Since at least welding times of 2 s for WB or 8s for WS are needed to get a homogeneous joint, the degradation due to the process is not avoidable. Longer welding times

in both cases imply further degradation of the welded material and new input wood material entering the welding interface.

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 1.5s of Wt for WB and 2s for WS. The series of xylooligomers of 7 to 2 units and celooligomers from 5 to 2 units in water extracts from WB and corresponding oligosaccharides from WS clearly illustrate it. Levoglucosan, that appears significantly in the water extracts of WB at 1.5 s and at 4 s in WS most likely demonstrate the degradation of glucose coming from glucomannans. Acetic acid that catalyzes the depolymerization of hemicelluloses, the condensation reactions of lignin, the dehydration of certain sugars and decreases the solubility of oligosaccharides in water, also appears from the early stages of the welding process.

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 will be of great benefit in the understanding of mechanical properties of the welded joints. The selected analytical protocols will be useful tools to further understand and characterize the phenomena taking place in the welding process of wood.

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### 3.1.2 Caractérisation topo-chimique de la lignine sur la zone soudée du bois

#### Résumé

Les sections transversales du hêtre soudé (*Fagus sylvatica*) et de l'épicéa soudé (*Picea abies*) à des temps de soudage successifs ont été caractérisées avec un microspectrophotomètre UV. La zone soudée du hêtre et de l'épicéa est identifiée comme une surface discontinue avec une absorption UV irrégulière qui augmente pour des temps de soudage consécutifs. L'absorption plus grande est liée aux modifications chimiques dans la structure de la lignine par l'effet de la température et de la friction. La modification des cellules dans les couches plus profondes à la zone soudée est détectée comme une augmentation dans l'absorption dans la paroi secondaire et la lamelle moyenne. Cette modification diminue graduellement depuis la zone soudée. De plus fortes modifications sont mises en évidence dans l'épicéa soudé que dans le hêtre soudé. Ceci s'explique par une plus grande propension de la lignine guaiacyle à former des produits condensés et par des conditions plus sévères de température et de temps de soudage pour l'épicéa soudé.





# Topochemical characterization of welded wood at different welding times

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## Abstract

The transversal sections of welded beech (*Fagus sylvatica*) and spruce (*Picea abies*) at successive welding times were characterized topochemically by means of cellular UV microspectrophotometry. The welded zone in beech and spruce is recognized as a discontinuous area with uneven UV absorbance of the individual cell wall layers that increases at consecutive welding times. The increased UV absorbance is related to the chemical modifications in the lignin structure by the effect of temperature and friction. The chemical modification of the cells in the deeper layers to the welded zone is noticed as a distinct increase in the UV absorbance in the secondary wall and middle lamella. The absorbance intensity decreases gradually, at longer distances from the welded zone. Stronger modifications are evidenced in welded spruce than in welded beech. It is explained by the higher propensity of guaiacyl lignin to form condensed products and the more severe temperature and welding time conditions undergone by welded spruce.

**Keywords:** linear friction welding, beech, spruce, lignin, topochemical characterization, thermal degradation.

## Introduction

The technology of linear friction welding for wood has been studied since the earlier 2000s. The BFH-AHB in Bienne (Gfeller et al. 2003) and the institute IBOIS in Lausanne (Stamm et al. 2005a) published the first scientific studies in this field. Welded wood is an alternative to conventionally glued wood and can be used for indoor applications (Rhême et al 2013a and 2013b, Stamm 2006a, Ganne-Chédeville 2008a; Omrani 2009). The advantages of this technology are the very short time of processing, the dispensable use of adhesives and the possibility to weld any kind of wood.

In linear friction welding, pressure and continuous frictional movement between two wood surfaces is supplied (Gfeller et al. 2003, Stamm et al. 2006a, Ganne-Chédeville 2008a, Delmotte et al. 2008). Fibers in the welding interface get detached, partially “milled” and mixed by the frictional movement and generated heat. When the “welded material” in the interface is formed, friction stops and the wood specimens are held together under compression so the welded material solidifies.

Temperature is maximal in the welding interface and it gradually decreases in the deeper zones (Stamm 2006a, Omrani et al. 2009a). Temperature increase in the welding interface depends on the wood species, i.e. temperature rises faster in welded beech than in spruce (Stamm et al. 2005a). Welding parameters as frequency, amplitude, and welding time also affect this temperature; i.e. higher temperatures are reached at longer welding times (Stamm 2005a, Stamm 2006a, Ganne-Chédeville et al. 2008b, Omrani et al. 2009a).

Temperature and frictional movement cause chemical modifications of carbohydrates and lignin in the welding interface and neighbor zones of the wood tissue. Autocondensation of lignin, lignin demethoxylation, deacetylation of hemicelluloses, crosslinking reactions of lignin with carbohydrate-derived furfural or self-polymerization of furfural in the welded material have been already analyzed by Solid State CP-MAS <sup>13</sup>C-NMR, and FTIR (Gfeller et al. 2003, Pizzi et al. 2006, Delmotte et al. 2008, Ganne-Chédeville et al. 2008b). The increase in phenolic OH groups in welded material as determined by aminolysis reveals the splitting of lignin macromolecules due to temperature, as demonstrated by Stamm et al. (2005b). On the other hand, the decrease of aliphatic OH groups shows the degradation of polysaccharides and aliphatic side chains by dehydration (Stamm 2006a). In welded beech and spruce, the

percentage of modified lignin in the interfacial welded material increases at consecutive welding times (Placencia Peña et al. 201x).

The heat affected zone of welded spruce and maple tissue is microscopically analyzed (and described) by Stamm (2006b) and Ganne-Chédeville et al. (2006). Also, the entanglement of partially destroyed fibers with amorphous material is observed in SEM images of welded wood (Gfeller et al. 2003, Properzi et al. 2005, Mansouri et al. 2009). However, a quantification of the chemical changes, especially the modification of lignin in combination with the anatomical features of welded wood has not been performed so far. In the present study, the local distribution and thermal modification of lignin in the welded zone and neighbor regions are topochemically analyzed by cellular UV microspectrophotometry (UMSP). This improved analytical technique has been successfully used to characterize, e.g., the topochemical distribution of lignin and/or phenolic extractives in kiln-dried beechwood and American black cherry (Koch et al. 2003, Mayer et al. 2006), the heat affected zone during laser material processing of wood and wood composites (Barcikowski et al. 2006) or the topochemistry of heat-treated and N-methylol melamine modified wood of Koto and Limba (Mahnert et al. 2013). The UMSP is used for the first time to characterize welded beech and spruce tissue at progressive welding times. This characterization provides a better understanding of the chemical changes produced in welded wood and neighbor zones.

## **Materials and methods**

### **Welded specimens preparation**

Beech (*Fagus sylvatica*) and spruce (*Picea abies*) samples were assembled by linear friction welding during 1, 1.5, 2, 2.5, 3 s, and 2, 4, 6, 8, 10, 12 s, respectively. The process was carried out in a Branson M-DT24L linear welding machine. The welding parameters were frequency 100 Hz and welding pressure 1.5 MPa for both species; amplitude 2.8 and 3.0mm, holding time 5 and 40s, holding pressure 2.0 and 1.5 MPa for beech and spruce, respectively. Wood was acclimatized at 23°C and 50% RH before welding. Sizes of welded specimens were 500x80x24 mm<sup>3</sup> (LxRxT) for beech and 500x50x24 mm<sup>3</sup> (LxRxT) for spruce. The thinner sections of spruce specimens were selected since larger sections without defects, i.e. knots and resin canals, were not available. In both cases, welding is performed in the LR plane.

## **Temperature in the welding interface**

Temperature measurements in the welding interface during the LFW process were performed to control and record the process temperature. 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 per welded specimen were used. They were positioned in the center and at approximately 6 cm from the edges, in the middle part through the length direction. The thermocouples were inserted in holes of 0.5 mm diameter, from the back of the wood specimens, as described by Placencia Peña et al. (201x).

## **UV microspectrophotometry (UMSP)**

The topochemical characterization of the distribution and the thermal modification of lignin in welded wood were performed by cellular UV microspectrophotometry. Small wood blocks of approximately 2x1x5 mm<sup>3</sup> of transversal section of welded beech and spruce at successive welding times were dehydrated in a graded series of acetone and embedded with Spurr's epoxy resin (Spurr 1969). Ultrathin sections of 1 µm thickness were cut with a diamond knife, transferred to quartz microscope slides and immersed in glycerine. For additional light microscopic analyses, ultrathin sections were prepared from the same embedded blocks and stained with a toluidine-blue solution.

The topochemical analyses were performed with a Zeiss UMSP 80 microspectrophotometer equipped with a scanning stage thus the determination of image profiles at constant wavelengths with the scan programme APAMOS® (Zeiss) was possible. For the detection of lignin in untreated and welded spruce a wavelength of 280nm (absorbance maximum of softwood lignin) was selected. For untreated and welded beech the wavelength was 278nm (Koch and Kleist 2001, Koch and Grünwald 2004). The scan program digitizes rectangular fields of the sections with a local geometrical resolution of 0.25µm x 0.25µm and yields a photometrical resolution of 4096 grey scale levels, which are converted into 14 basic colors to visualize the absorbance intensities (Koch and Grünwald 2004). The scans can be depicted as two- or three-dimensional image profiles including a statistical evaluation (as histogram) of the UV absorbances.

Photometric point by point measurements were also performed with a spot size of  $1 \mu\text{m}^2$  between 250nm and 500nm wavelength. The programme LAMWIN<sup>®</sup> (Zeiss) was used which records the spectra of the lignified and thermally modified cell walls and tissues. For quantitative studies, 10 spectra were taken from each individual cell wall layer and cell type, respectively.

## **Results and discussion**

### **Temperature**

Temperatures in the welding interface of beech and spruce tissues are reported in Table 1. The welding interface in beech reaches temperatures up to 380 °C in 3 s of welding. In spruce, the welding interface reaches near 390°C at about 8 s and gets 400°C at 12 s. The faster increase in temperature in the interface of welded beech than in welded spruce are attributed to the different surface properties between both wood species (Stamm et al. 2005a). Also, the different wood densities may also influence the temperature profiles. According to Stamm (2006a) in spruce welded by circular welding, temperature at 2.1 mm distance from the welding interface is lower than 50°C, while interfacial temperature is over 400°C at 12 to 14 s of welding. At 20 s, during the cooling step, temperature at 2.1 mm from the welding interface is 78°C while the interfacial temperature is still 231°C. Omrani et al. (2009a) found that in linear friction welding of beech at 150 Hz, temperature at 1 mm distance from the welding interface was 100°C, while temperature in the welding interface was about 160°C, at 1.5 s of welding.

According to Niemz et al. (2010) thermal conductivity is higher in beech tissue than in spruce in all anatomical directions. Thermal conductivity is higher in longitudinal than in radial and tangential directions, respectively. Moreover, moisture content increases the thermal conductivity. As these properties were measured at maximum temperature of 40°C, these trends in thermal conductivity are at least referential since temperatures during welding are much higher. Additionally, phenomena as densification in the welding interface and deeper layers, and the released moisture during welding facilitate the heat transfer from the welded zone to the deeper layers. In the present study heat is transferred perpendicular to the grain, in the tangential direction. It is important to consider that even if the thermal conductivity in

beech would be higher than in spruce at such temperatures, interfacial temperatures reached in welded spruce are higher and welding time is longer in welded spruce than in welded beech. According to the temperature measurements of the deeper zones from the welded line (Stamm 2006a, Omrani et al. 2009a), the heat affected zones in welded beech and spruce are in the range of microns.

**Table 1.** Temperature measurements in the welding interface of beech and spruce tissue by linear friction welding (Placencia Peña et al. 201x)

<b>Beech</b>				
Wt (s)	1	2	3	-
T (°C)	203	291	380	-
<b>Spruce</b>				
Wt (s)	1	2	6	12
T (°C)	107	182	368	400

### Cellular UV microspectrophotometry

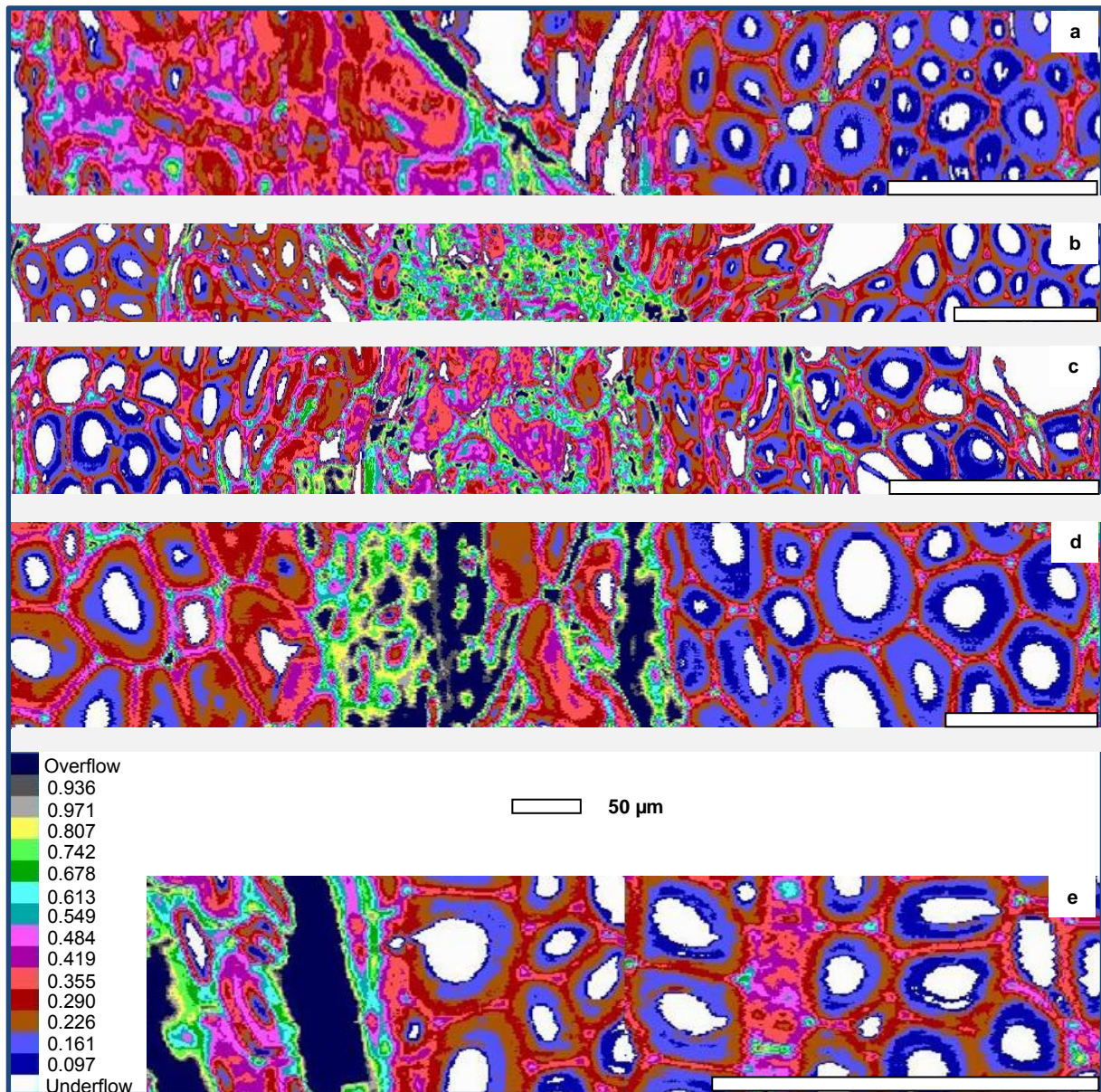
In figures 1 and 2, typical two dimensional UV microscopic scanning profiles for transversal sections of welded beech and spruce tissues are given. Each image is obtained by the gathering of two to six single scans of each transversal section including more than 20,000 individual measuring points. The color pixels show distinct intensities of UV absorbance within the different cell wall layers and welded zones. The typical absorbance values for untreated beech vary in the secondary wall (Abs<sub>278 nm</sub> 0.1 to 0.29), compound middle lamella (Abs<sub>278 nm</sub> 0.29 to 0.41), and cell corners (Abs<sub>278 nm</sub> 0.48 to 0.74) (Koch et al. 2003). In comparison to beech, untreated tracheids of spruce present higher absorbance values in the secondary wall (Abs<sub>280 nm</sub> 0.35 to 0.54), in the cell corners and compound middle lamella (Abs<sub>280 nm</sub> 0.61 to 0.87) (Koch and Kleist 2001). The higher UV absorbance of the S<sub>2</sub> layer of spruce tracheids compared to beech is related to the presence of the strongly absorbing guaiacyl-lignin (e.g., Fergus and Goring 1970b, Koch and Kleist 2001). Beech secondary wall is composed by syringyl-guaiacyl lignin characterized by a higher symmetry of the phenyl propane units with absorbance values decreasing with an increase in the OCH<sub>3</sub>/C<sub>9</sub> ratio (Musha and Goring 1975). The welded zones of beech and spruce in figures 1 and 2 are distinguished as a discontinuous area with destructed cellular tissue characterized by distinctively increased absorbance values (Placencia et al. 2012).

In figure 1, the scans of the transversal sections of beech tissue welded at 1, 1.5, 2, 2.5 and 3 s are shown. At welding time 1 s (203°C, figure 1a) most of the welded material presents absorbance values in the range of  $Abs_{278\text{ nm}}$  0.23 to 0.42, as depicted by the brown-red and violet color pixels. At welding times 1.5 and 2 s (250 to 291°C, figures 1b and 1c), some parts of the welded zone show increased absorbance values in the range of  $Abs_{278\text{ nm}}$  0.42 to 0.74 visualized by the violet and green color pixels. At welding times 2.5 and 3 s (340 to 380°C, figures 1d and 1e) local regions with strongly varying absorbance values between ( $Abs_{278\text{ nm}}$  0.22 to 0.48), ( $Abs_{278\text{ nm}}$  0.48 to 0.8) and ( $Abs_{278\text{ nm}} > 0.94$ ) are distinguished. These results demonstrate the uneven and wide distribution of modified UV absorbing components through the welded zone.

In figure 1, beech fibers in the deeper layers to the welded zone also show a detectable increased UV absorbance. A larger portion of brown-red pixel colors showing higher absorbance in the secondary wall ( $Abs_{278\text{ nm}}$  0.22 to 0.48) and pink-violet pixels showing higher absorbance in the middle lamella ( $Abs_{278\text{ nm}}$  0.42 to 0.74) are clearly depicted. In general, the cells closest to the welded zone present the strongest modification. It would suggest that the changes in the UV absorbance are initiated from the welded zone, where the temperature generated by the friction is maximal, towards the coldest deeper layers. While at welding time 1 s, the chemical modification appears in the first to second fiber rows (< 50  $\mu\text{m}$  from the welding line), at 2.5 to 3 s, the UV absorbance modification is still observed at 50 to 100  $\mu\text{m}$  from the welding zone.

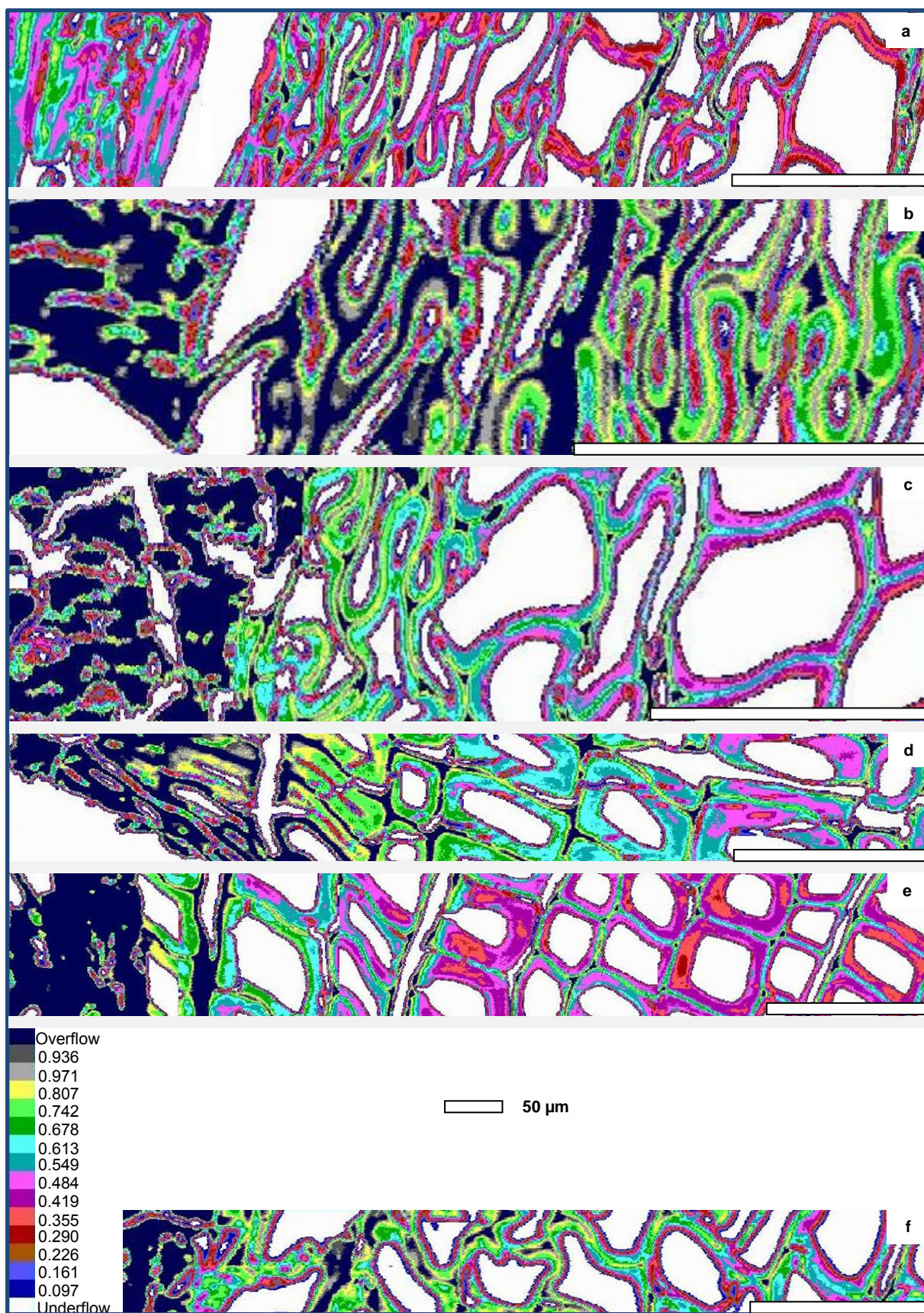
In figure 2, representative scans of the transversal sections of spruce tissue welded at 2, 4, 6, 8, 10 and 12 s are depicted. UV absorbance in the welded zone changes from ( $Abs_{280\text{ nm}}$  0.35 to 0.74) at welding time 2 s (182°C, figure 2a) to ( $Abs_{280\text{ nm}} > 0.94$ ) from 4 to 12 s of welding time (300 to 400°C, figures 2b to 2f). Defects, e.g., blow holes are more often found than in welded tissue of spruce as compared to the welded beech. They frequently arise from the detachment of tracheids or fibers from the massive wood, from spaces produced by the smoke generated in the welded zone, and spaces between the uneven fibers detachment in the early-late wood transition. A densification of the thin-walled early wood in preference to thick-walled late wood tracheids close to the welded zone is also clearly shown (Leban et al. 2004, Stamm 2006a, Ganne-Chédeville 2008a).

In figure 2, tracheids in the deeper layers to the welded zone show strongly increased absorbance in the S<sub>2</sub> (Abs<sub>280 nm</sub> up to 0.81) and middle lamella (Abs<sub>280 nm</sub> 0.94 or more). These chemical modifications are clearly noticed in transversal sections from 4 to 12 s of welding time. As compared to welded beech, the strongest modification is observed in the cells directly linked to the welded zone. The modification is observed in thin and thick cells even at approximately 200 μm from the welded zone (figure 2e and 2f).



**Figure 1.** UV microscopic scanning transversal sections of welded beech at successive welding times a: 1 s, b: 1.5 s, c: 2 s, d: 2.5 s, e: 3 s. The colour pixels represent different UV absorbance values measured at  $\lambda_{278\text{nm}}$  with a geometrical resolution of  $0.25 \mu\text{m} \times 0.25 \mu\text{m}$





**Figure 2.** UV microscopic scanning transversal sections of welded spruce at successive

welding times, a: 2 s, b: 4 s, c: 6 s, d: 8 s, e: 10 s, f: 12 s. The colour pixels represent different UV absorbance values measured at  $\lambda_{280\text{nm}}$  with a geometrical resolution of  $0.25\ \mu\text{m} \times 0.25\ \mu\text{m}$

Scans performed by UMSP-technique allow making semi-quantitative evaluation of the lignin distribution and concentration in the wood cells (Koch and Grünwald 2004). Lignin absorbance at defined wavelengths of 278nm and 280nm, respectively, is estimated according to Lambert-Beer's law (Scott et al. 1969); however it does not allow the chemical identification of the pure UV absorbing components. In a previous study (Placencia Peña et al. 201x), the chemical composition of welded beech and spruce material after water extraction was determined by a two-step hydrolysis with sulfuric acid. The used welding time and other welding parameters were the same as for the present study (2, 4, 6, 8, 10, 12 s for welded spruce and 1, 1.5, 2, 2.5, 3 s for welded beech, see paragraph "Welded specimens preparation"). The results of this chemical analyses showed that Klason lignin percentages increase at longer welding times in both welded beech and spruce. In welded wood tissue, Klason lignin represents a water insoluble complex mixture of modified native lignin due to condensation reactions, either with lignin itself or furan like components (Gfeller et al. 2003, Stamm 2006a, Delmotte et al. 2008, Placencia Peña et al. 201x). The increase of Klason lignin percentage in the composition of the welded material is in accordance with the topochemically detected increase of UV absorbance at progressive welding times observed by UMSP. In addition to the determined Klason lignin, cleaved lignin components and other UV absorbing degradation components dissolved in water contribute to the increased UV absorbance in the welded zone of beech and spruce (Placencia Peña et al. 201x).

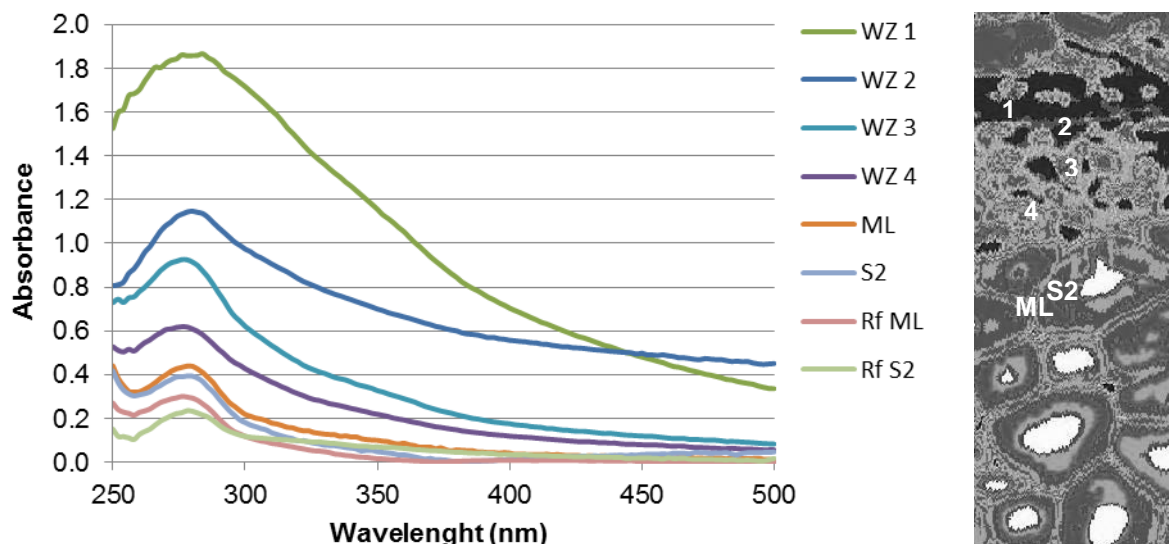
### **Thermal modification of lignin**

Thermal modification of lignin in welded beech and spruce tissue was additionally studied by evaluating the UV-absorbance spectra in the selected wavelength range from 250 to 500nm.

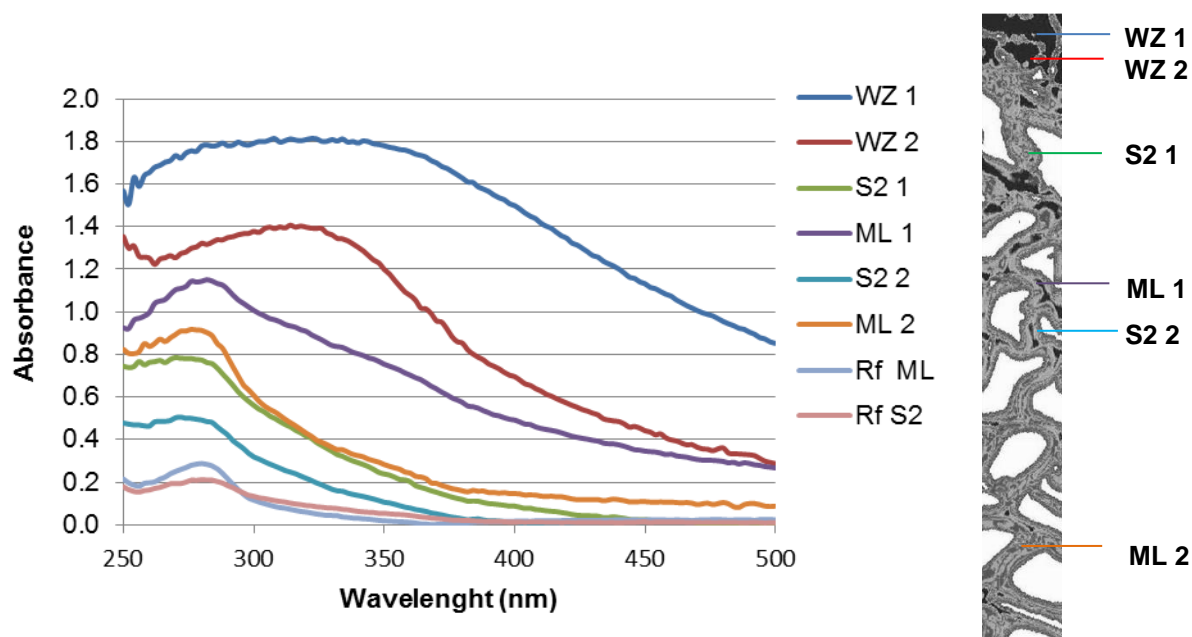
In figure 3 characteristic spectra of individual cell wall layers of beech fibres in the welded zone and adjacent fibers welded at 2.5 s are depicted. The reference spectra (Rf S2 and Rf ML) show the typical spectral behavior of hardwood lignin with a distinct maximum at 278 nm and a local minimum at about 250 nm (Fergus and Goring 1970a, 1970b, Takabe et al.

1992, Koch and Grünwald 2004). The maximum absorbance in the reference secondary wall and reference middle lamella is ( $Abs_{278\text{ nm Rf S2}} 0.24$ ) ( $Abs_{278\text{ nm Rf ML}} 0.30$ ), while in the fiber tissue adjacent to the welded zone a continuous increase of the UV absorbance ( $Abs_{278\text{ nm S2}} 0.39$ ) ( $Abs_{278\text{ nm ML}} 0.44$ ) is observed. The spectra of the four selected measured points in the welded zone show the highest UV absorbance values ( $Abs_{278\text{ nm}} 0.6$  to  $1.9$ ) respect to the reference secondary wall and middle lamella, and a broadening shape of the bands with increased absorbance towards the higher wavelengths.

In figure 4, representative UV absorbance spectra of S2 and ML of spruce tracheids in the welded zone, bordering tissue welded at 12 s and references of the untreated cells are shown. The spectra of the untreated cell walls (Rf S2 and Rf ML) reveal the typical UV-absorbance of a softwood lignin, with a maximum at 280nm indicating the presence of strongly absorbing guaiacyl-lignin (Fergus and Goring 1970b) and a local minimum at about 250nm. The maximum absorbance value in the reference middle lamella ( $Abs_{280\text{ nm Ref ML}} 0.28$ ) is higher than in the reference secondary wall ( $Abs_{280\text{ nm Rf S2}} 0.21$ ) which is in accordance with the values reported in Koch and Kleist (2001). In contrast, the maximum absorbance in the secondary wall of tracheids directly connected to the welded zone (S2 1) is significantly higher and amounts to a value of  $Abs_{280\text{ nm S2 1}} 0.78$ . Also, the maximum absorbance in the middle lamella of a tracheid in the second layer from the welded zone (ML 1) is distinctively higher ( $Abs_{280\text{ nm ML 1}} 1.14$ ), and the maximum absorbance in the middle lamella of a tracheid in the sixth layer from the welded zone (ML 2) is still on a very high level ( $Abs_{280\text{ nm ML 2}} 0.91$ ). The spectra 1 and 2 of the thermally merged cell wall material in the welded zone show the highest increase in UV-absorbance up to ( $Abs_{280\text{ nm}} 1.6 - 1.8$ ) and also a distinct shift in the maximal absorbance from 280 to about 340nm (widening of the UV band). The wider bands and shifts can be explained as follows.



**Figure 3.** Representative UV absorbance spectra of a transversal section of welded beech at 2.5 s (WZ stands for welded zone, ML middle lamella, S2 secondary wall, Rf ML reference middle lamella, Rf S2 reference secondary wall). Rf ML and Rf S2 are measured in a separated tissue of un-treated beech.



**Figure 4.** Representative UV absorbance spectra of a transversal section of welded spruce at 12 s. (WZ stands for welded zone, ML middle lamella, S2 secondary wall, Rf ML reference middle lamella, Rf S2 reference secondary wall). Rf ML and Rf S2 are measured in a separated tissue of un-treated spruce.

In thermo-treated wood, the increase in the UV absorbance values is attributed to the condensation of lignin due to temperature (Fengel and Wegener 1989, Funoaka et al. 1991, Jamalirad et al. 2012,). According to Barcikowski et al. (2006), the typical wavelength shift (shoulder) at about 340 nm is based on modifications of the chemical constitution of lignin molecules, i.e. chromophoric and optically more active groups due to the formation of conjugated double bonds (Koch et al 2003). The higher degree of conjugation stabilizes  $\pi$ - $\pi^*$  transitions resulting in absorbance bands shifted to the higher wavelength (Goldschmid 1971). In welded wood material, not only high temperatures but also the mixing effect of the frictional movement contributes to the chemical modifications of lignin. In fact, friction is a key factor in the modification of lignin. In a separated experiment where massive beech was treated with temperatures of 350 and 400°C by direct contact and pressure with a heated plate during periods of up to 15 s, any lignin modification was observed in the tissue of semi-thin sectionings analyzed by UMSP. In addition, the modification is not just restricted to water-insoluble condensation products of lignin (Klason lignin) but also to depolymerized residues, and degradation products absorbing in the UV range as shown in (Placencia Peña et al. 201x). Depolymerization and repolymerization of lignin occur simultaneously (Li et al. 2007). The main referred depolymerization mechanism in lignin is the cleavage of  $\beta$ -O-4 linkages (Stamm 2006a, Belleville et al. 2013). Also, some lignin re-polymerization routes are depicted in Li et al. (2007), and furfural – lignin and similar reactions are described in Stamm (2006a). As observed from figures 3 and 4, lignin modifications are expected to be stronger in the welded zone of spruce than in welded beech (broader absorbance bands in the welded zone), which is plausible since a higher amount of guaiacyl lignin is present in spruce tissue (G:S:H = 94:1:5; H = p-hydroxyphenylpropane) in comparison to beech (G:S:H = 56:40:4) (Fengel and Wegener 2003). Guaiacyl lignin is well known to be more affine than S-lignin to form condensation products (Saka and Goring 1985). Modifications (higher UV absorbance) observed in the secondary wall and middle lamella in the deeper fibers and tracheids to the welded zone are also expected due to the chemical changes i.e. lignin condensation/depolymerization occurring from the more thermally/frictionally affected welded zone to the cooler deeper layers. In addition to temperature, the furfural-like degradation components from hemicelluloses diffused in the smokes from the welded interface can facilitate the condensation reactions with ML or S2 lignin in the adjacent zones.

## Conclusions

The UV absorbance of the welded zones of beech and spruce tissue gradually increase with welding time, and therefore with temperature. A wider range of UV absorbance from ( $Abs_{278\text{ nm}} 0.22$  to  $> 0.94$ ) in different regions of the welded zone of beech is observed from welding time 2.5 to 3 s (340 to 380°C). In welded spruce, even if the welded zone begins to appear at 2 s of welding time, the strongest changes in the UV absorbance ( $Abs_{280\text{ nm}} > 0.94$ ) occur from 4 to 12 s (300 to 400°C). The progressive increase in UV absorbance in the welded zones is in good agreement with the ascent of Klason lignin percentage in the welded material, for both welded beech and spruce (Placencia Peña et al. 201x). However, not only Klason lignin but also water soluble lignin and other degradation products account for the increased UV absorbance.

Defects in the welded material are observed more intensely in welded spruce than in welded beech. Also, highly densified fibers, especially compressed early wood spruce tracheids connected to the welded zone are clearly distinguished. The thermal modification in the deeper layers to the welded zone is also evidenced as high absorbance values in the secondary wall and middle lamella, with a gradient decreasing affectation from the welded zone. More pronounced modifications are found in the deeper layers of welded spruce, where increased absorbance values are observed even at distances up to 200  $\mu\text{m}$  from the welded line. In the deeper layers of welded beech, modified cells are still observed up to 100  $\mu\text{m}$ . The higher affectation of spruce cells is related to the presence of guaiacyl lignin, which is more affine to condensation reactions than syringyl moieties.

Changes in the chemical structure of lignin, i.e. the presence of chromophoric and optically more active groups due to the formation of conjugated double bonds are possible in both welded beech and welded spruce; however, they are definitively more explicit in the welded zone of spruce, where a broader UV absorbance spectrum and shift to a higher wavelength is observed. It could be explained by the more reactive nature of guaiacyl lignin and the higher temperatures and longer welding times occurring in welded spruce. However, not only high temperatures but also friction is a key factor for the modification of lignin in the welding interface. Without friction the formation of the welded joint would not be possible.

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### **3.1.3 Corrélation entre les propriétés mécaniques et chimiques du bois soudé à différents temps de soudage**

#### **Résumé**

Les propriétés de cisaillement des joints soudés du hêtre et de l'épicéa à des temps de soudage progressifs sont mesurées et contrastées avec le pourcentage de lignine klason dans le matériau soudé. Les résultats montrent que pour des temps de soudage plus longs le module de cisaillement croît lorsque le pourcentage de lignine klason augmente. Néanmoins, la déformation maximale au cisaillement diminue à des pourcentages plus hauts de lignine klason (temps de soudage plus longs). D'un autre côté les valeurs de résistance au cisaillement sont relativement constantes dans un éventail sélectionné de temps de soudage et elles sont plus basses pour des temps de soudage très courts lorsque le joint n'a pas encore développé sa résistance maximale.



# Correlation between the mechanical and chemical properties of welded wood at different welding times

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## Abstract

The shear properties of welded joints of beech and spruce at progressive welding times are measured and contrasted with the percentage of Klason lignin in the welded joint material. Results illustrate that at longer welding time the shear modulus shows an ascent as the percentage of Klason lignin increases. In contrast, maximal shear strain decreases. It results in a diminution of the work to failure at higher percentages of Klason lignin (longer welding time). On the other hand, tensile shear strength values are relatively constant in a selected range of welding time and they are lower at very short welding times when the welded material has not yet developed its maximal strength.

**Keywords:** shear modulus, maximum shear strain, shear toughness, Klason lignin, welded material, beech, spruce.

## Introduction

The contribution of the single components of wood fibers to the mechanical and physical properties of wood has been widely studied (Keckles et al. 2003, Navi and Heger 2005, Burget et al. 2005a, Burget et al. 2005b, Eder et al. 2008, Salmén and Burget 2009). Besides their individual properties, the polymers interactions govern the properties of the cell wall assembly (Salmén and Burget 2009). Cellulose microfibrils are the strengthening part which is embedded in a less resistant hemicellulose-lignin matrix (Spatz et al. 1999, Keckles et al. 2003). Secondary wall is regarded as the main part of the cell regarding the mechanical performance (Booker 1996, Bergander and Salmén 2002, Burget et al. 2005). The angle of the semicrystalline cellulose microfibrils is considered to be the decisive parameter on the wood stiffness (Keckles et al 2003), as well as the density of the tissues (Salmén and Burget 2009). Not only microfibrils angle but its local variation, i.e. around the pits, and natural defects in the fibers need to be considered in the mechanical properties of fibers (Navi and Heger 2005). As in other composite materials, the stresses need to be transferred through the matrix to the fibers; hemicelluloses are apparently charged of this transmission of stress (Carpita and Gibaut 1993, Cosgrove 2001, Salmén and Burget 2009). Lignin is considered to contribute to the compressive strength of the cell wall (Wardrop 1971). On the other hand, in peeling tests performed in isolated fibers of spruce, delamination occurred mainly in the secondary cell wall and compound middle lamella, this last one being a lignin rich region (Burget et al. 2005). In coupled loading-dynamical FTIR tests, it has been demonstrated that when a load is charged on cellulosic material, the cellulose stretching vibration including the C-O-C bridge at  $1165\text{ cm}^{-1}$  wave number is the most dominant structure taking the load during deformation (Salmén 2005).

In studies performed by Windeisen et al. (2008) on thermally treated beech, an increase of the modulus of elasticity (MOE) up to  $200^{\circ}\text{C}$  and a decrease of modulus of rupture (MOR) are observed. The increase in MOE is explained by the formation of new chemical bonds with a higher binding energy than the cleaved hydrogen bonds, by the settlement of the cellulose chains until a certain level and by the decrease of equilibrium moisture content (EMC) that implies a decrease in free accessible hydroxyl groups. The loss of MOR goes along with a decrease in xylan and other polysaccharides. In thermo-treated wood (Tjeerdsma et al. 1998) the improved hydrophobicity and dimensional stability are explained by the inelastic network



surrounding cellulose microfibrils, which is formed by the increased crosslinking within the lignin complex. Either in untreated single fibers or in thermo-treated wood, hints are available on the relations between chemical and mechanical properties. However, absolute correlations are difficult to set due to the complexity of the interactions of the chemical components and of the wood ultrastructure.

In welding of wood, the first shear tests performed in welded beech and spruce joints by linear friction welding were reported in Gfeller et al. (2003). Stamm et al. (2005a, 2005b) present shear strength values for welded beech and spruce joints welded by circular friction welding. Chemical composition analyses of welded material have been also performed (Stamm 2006a, Stamm et al. 2005c, 2006b) however no trial to correlate the mechanical and chemical properties of welded wood has been stated. The shear strength values of beech joined by linear friction welding from 0 to 11 s and the possible chemical changes in this range of welding time have been described in Ganne-Chédeville et al. (2008a). The mode I energy release rate measurements with double cantilever beams of welded beech were presented in Ganne-Chédeville et al. (2008b). Studies on fracture mechanics have been also carried out by Omrani et al. (2009a), and researches on the influence of grain direction in welded joints have been performed in Properzi et al. (2005), Omrani et al. (2009b), Omrani et al. (2010). Also, Gineste et al. (2012) performed tension-shear tests on welded specimens of beech. According to Omrani et al. (2009c), improved mechanical performances in linear welding would be obtained by shortening welding time (1.5 s), decreasing amplitude (2 mm) and increasing frequency (150 Hz). It is attributed to a reduced damage in the welded interface.

Tensile shear strength tests have been carried out in Scots pine in Vaziri et al. (2012), in *Pinus sylvestris* in Mansouri et al. (2011). Also, X-ray Computed Tomography has been used to study cracks development in welded joints of Scots pine (Vaziri et al. 2010, 2011). It has been shown in Brunner et al. (2010a, 2010b) and Vallée et al. (2011) that the capacity of the welded spruce joints increases with overlap length. However, this increase is limited towards higher overlap lengths with a critical value of approximately 300 mm, beyond this no further increase is expected. Finally, the behavior of welded beech joints in different fracture modes and moisture condition environments has been studied by Rhême et al. (2013a, 2013b) and Rhême (2014). It was found that the strength of the welded beech joints decreases beyond

16% EMC. Also, it was determined that the tensile and shear strength do not depend on the fibers orientation (parallel, cross grain or in-plane loading direction).

The studies above give rich information on the tensile and shear strength, fracture and dependence of these properties on moisture content and welding parameters, or overlap length of the joint. However, no correlation between the mechanical properties and the quantified chemical composition of the welded material (dark thermal/frictionally modified material formed in the welding interface) has been presented so far. Furthermore, no measurement on the displacement of the welded material during tensile shear tests has been yet performed. This study presents shear properties of welded beech and spruce material (shear modulus, maximum shear strain and work to failure) in relation with Klason lignin percentage and welding time.

## **Materials and methods**

### **Welded specimens**

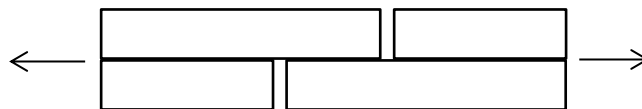
Beech (*Fagus sylvatica*) and Spruce (*Picea abies*) were assembled by linear friction welding with friction time of 1.5, 2, 2.5, 3, 3.5 s, and 4, 6, 8, 10, 12 s respectively. Frequency was 100 Hz and welding pressure 1.5 MPa for both species. Amplitude was 2.8 and 3 mm, holding time 5 and 40 s, holding pressure 2 and 1.5 MPa for beech and spruce correspondingly. The process was carried out with a Branson M-DT24L linear welding machine. Wood was acclimatized at 23°C and 50 %RH at least 20 days before and after welding. The angle of the year-rings with respect to the welding line was ranging from 60 – 90° for welded beech and 80 – 90° for welded spruce. The size of the specimens varied: 326x37x11 mm<sup>3</sup> (for welded beech and welded spruce, mechanical and chemical tests), 500x80x24 mm<sup>3</sup> (welded beech, chemical tests) and 500x50x24 mm<sup>3</sup> (welded spruce, chemical tests). Since the amount of welded material in the opened surfaces after shear tests is not enough for the chemical tests, additional material not just from the shear tested samples, but also from the same welded specimen and specimens welded with the same welding parameters are used.

### **Chemical analysis**

The analysis was performed in the welded material of beech welded at 1.5, 2, 2.5 and 3 s; and in spruce welded at 4, 6, 8, 10 and 12 s. After the welding, some specimens were intentionally delaminated, and the welded material was collected by scratching the welded interface with a razor blade. About 600 mg of each type of welded material were subjected to water extraction, cryo-milling and two steps acid hydrolysis, as reported in Placencia Peña et al. (201x). The percentage of Klason lignin in welded material was determined gravimetrically, as the solid residue after the two stage acid hydrolysis.

### Shear properties

Shear properties were measured in specimens of welded beech joined at 1.5, 2, 2.5, 3, 3.5 s, and welded spruce at 4, 6, 8, 10, 12 s. The specimens had a single lap joint shape (figure 1) with a total size of 50 x 8 x 11 mm<sup>3</sup> and testing surface: 10 x 8 mm<sup>2</sup>. Ten samples per each welding time condition were measured. The tests were carried out on a universal Zwick machine with a cell force of 2.5 kN operated with the TestExpert I software. The displacement speed was 4 mm•min<sup>-1</sup> for all specimens. Simultaneously, an external Zwick video-extensometer provided with the videoXtens software was installed and used to record the displacement of the welded zone in the direction of the traction. The files of force and displacement were matched with the help of a Matlab routine. Computation of the shear modulus, maximum shear strain, work to failure and shear strength were performed. The shear modulus is calculated as the slope of the line stress vs. strain in a range from 10 to 40 % of the failure stress. The work to failure is calculated as the area under the stress vs. strain curve at failure.

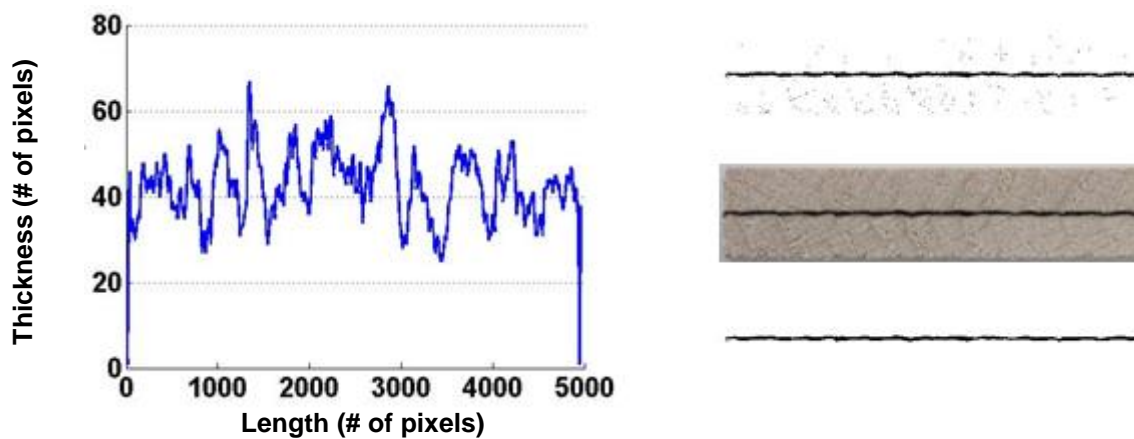


**Figure 1.** Sketch of a single lap welded joint for tensile shear test

### Thickness of the welded line

The thickness of the welded line was measured to enable calculating the shear modulus and maximum shear strain. Optical photographs of both transversal sides of rectangular pieces of

50x37x11 mm<sup>3</sup> were made. Two or three shear specimens were cut from each rectangular piece. The contrast between the black welded line and the “white” massive wood was analyzed by means of an image analysis program set in Matlab. The thickness of the welded line is defined in terms of number of pixels. The conversion of pixels to metric units is obtained by a reference picture of a gauge of known dimensions. All photos (transversal sections and references) are taken at the same position, distance from the camera and light conditions. A contrast image of the welded line is generated by the Matlab program. An example is presented in figure 2.



**Figure 2.** Thickness of the welded line. Left: representation of the welded line as function of the number of pixels. Right: contrast images of a welded line, up: binary image, middle: optical image, down: refined welded line.

## Results and discussion

### Chemical analysis background

The composition of the welded material of beech and spruce at progressive welded times was described in a previous study (Placencia Peña et al. 201x). It was shown that at longer welding time the percentage of Klason lignin rises. The increase was from 19.5% of a starting reference beech (not welded) to 28.9% for welded beech 3 s; and from 26.1% for reference spruce to 45% for welded spruce 12 s. This ascent is explained as a reduction in the carbohydrate proportion in the welded material, and as an increase due to condensation

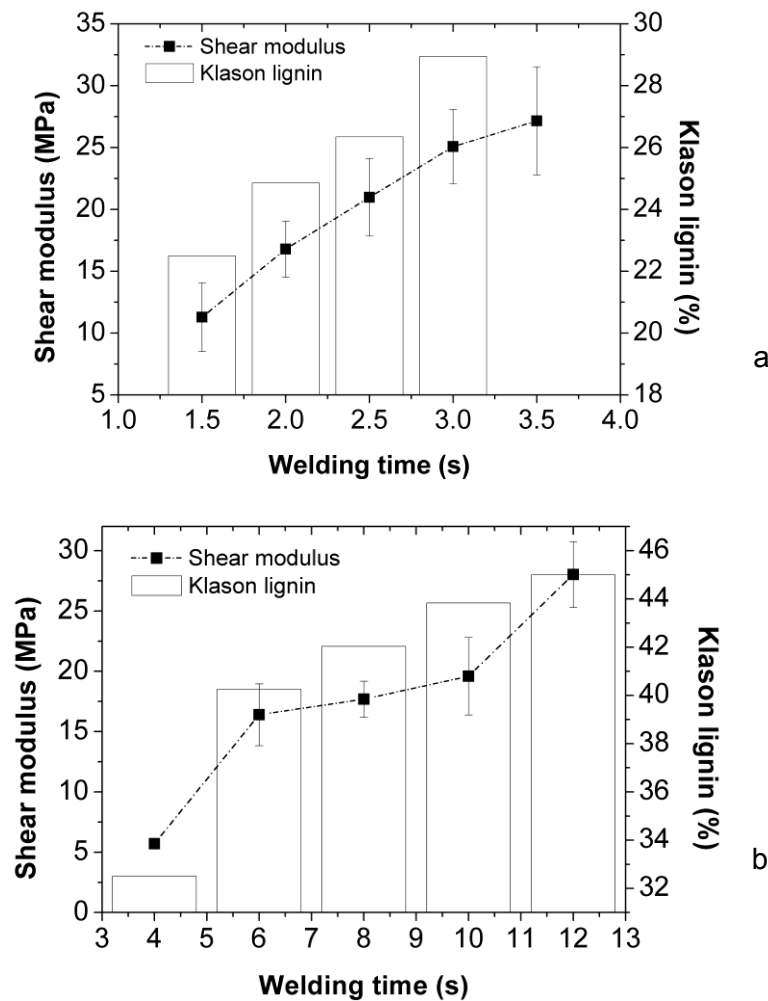
reactions of lignin with furans and other degradation products (Gfeller et al. 2003, Stamm 2006a, Delmotte et al. 2008).

### **Shear properties**

The welded material is surrounded by massive wood and the compaction produced by densification makes it harshly isolable. Moreover, it is not possible to obtain a welded block wide enough for testing (Ganne-Chédeville et al. 2008b). The welded material presents an amorphous structure formed by a melted-modified matrix, partially detached fibres and thermally/mechanically (by friction) decomposed wood cells (Gfeller et al. 2004, Stamm 2005a), distinct to the massive wood. Even though its complex structure, as a product of a mixture in a called “molten state”, welded material could be considered as an isotropic material. Latest results in the mechanical properties of the welded joints (Rhême 2014) show that the grain direction during welding has not a strong influence in the strength properties of welded beech. Among the components of the welded material, lignin is the only one that shows an increasing trend of proportion with welding time. Glucose, at least the semicristalline or crystalline portion of undestroyed fibers/microfibrils slightly decreases (Placencia Peña et al. 201x). Moreover, even if fibres/microfibrils potentially reinforce the welded material, its size and shape are random and change locally. Hemicelluloses are strongly degraded. Lignin percentage in the mixture should therefore play an important role in the mechanical properties of the welded joint.

All the tested specimens present a linear load displacement behavior with a brittle failure. This type of failure has been already observed for welded joints in Vallée et al. (2011). As observed in figure 3, for both welded beech and welded spruce material, the shear modulus shows an increasing trend with welding time. It indicates that the welded material becomes stiffer as longer welded times are used. In principle, lignin itself has a rigid nature, as it is characteristic for aromatic polymeric structures. Therefore, an increased amount of lignin in any mixture/copolymer would already imply an increase in the rigidity of a material. However, not only the aromatic structure but also the crosslinking effect of condensed lignin, which is also expected to increase at longer welding times, contributes to the augmentation in the shear modulus of the welded material. The shear modulus values of welded beech and spruce material are in the range of 5 to 27 MPa. Shear modulus values of wood are in the range of GPa, i.e. the shear modulus of beech in the LT direction is 1.05 GPa and in the LR

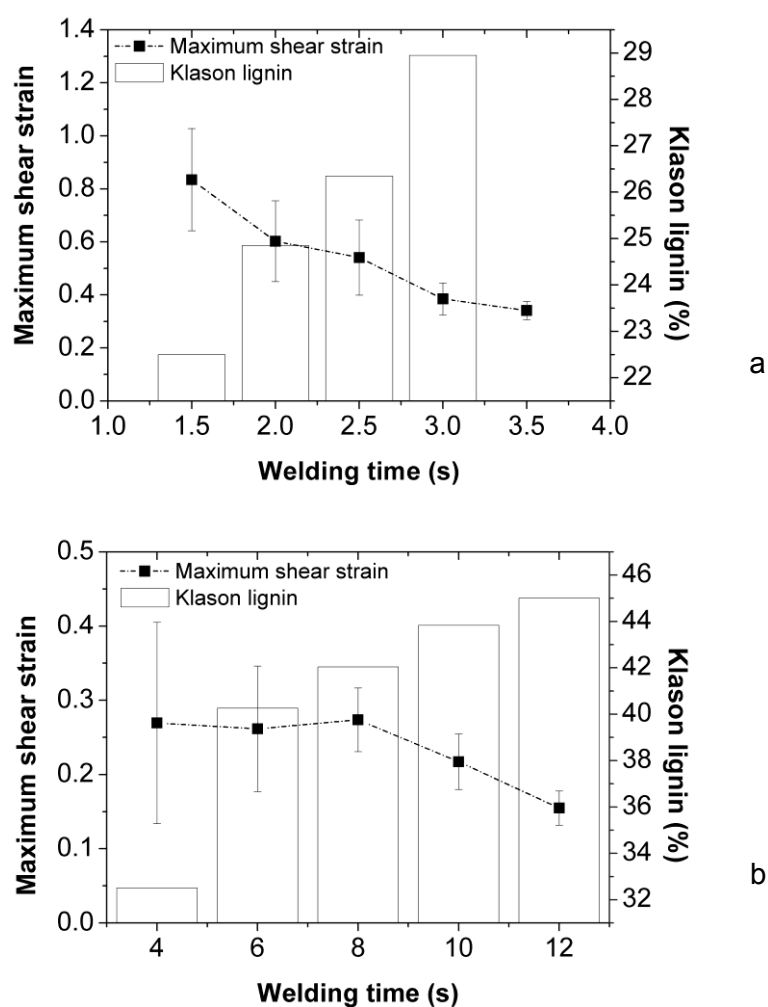
direction 1.61 GPa (Kollmann, 1982). This difference in order of magnitude clearly shows the completely new structure formed in the welded interface.



**Figure 3.** Shear modulus and Klason lignin percentage of welded material at progressive welding times. a: beech, b: spruce.

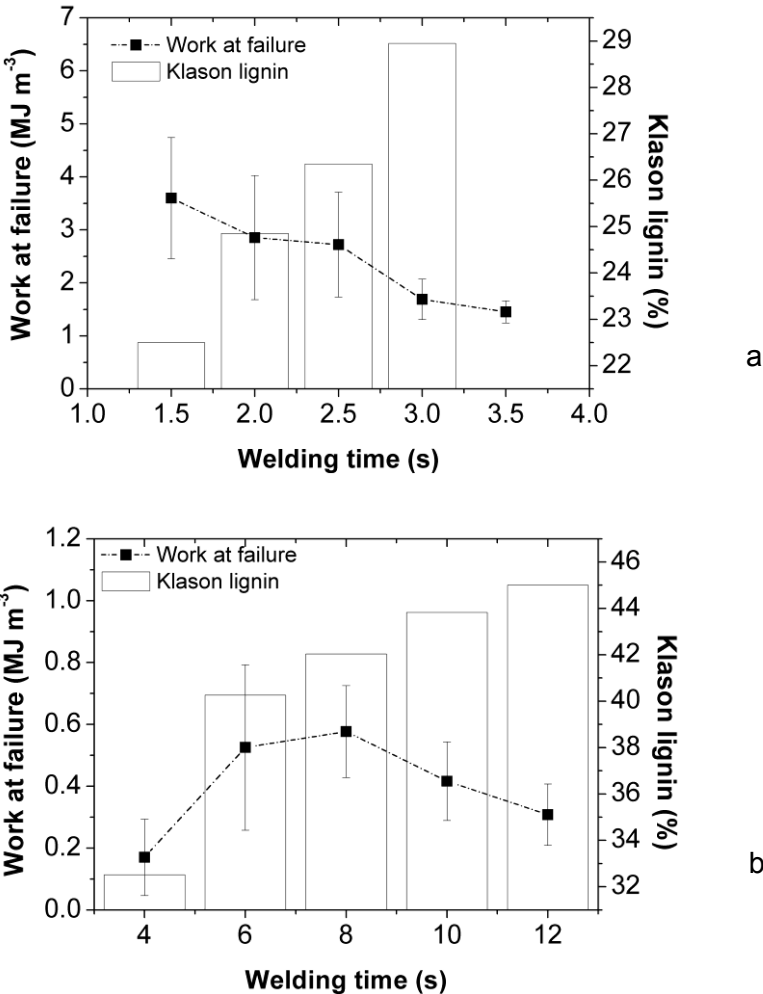
On the other side, the cross linking effect goes together with an intra and intermolecular reduction of movement and therefore a loss of elasticity. In addition, the lessening of some hemicelluloses, (Stamm et al. 2005c, 2006b, Placencia Peña et al. 201x) decreases as well the elastic properties of the welded material rendering it more brittle. According to Sivonene et al. (2002) depolymerization of hemicelluloses could have an effect of reduction of toughness of heat treated wood. This effect is observed in figure 4, where maximum shear strain clearly decreases at longer welding times and increasing amounts of Klason lignin.

It is interesting to notice that the maximum shear strain range in welded spruce is from 0.28 to 0.15, while for welded beech this range is from 0.83 to 0.34. It gives hints on the more rigid nature of welded spruce. This behavior, besides the fact that higher amounts of lignin are found in welded spruce, is also related to the presence of guaiacyl lignin in spruce. Guaiacyl, in preference to syringyl lignin is well known to produce condensed reactions (Saka and Goring 1985). This is due to the availability of the C5 position of guaiacyl lignin to form potential bonds of the C-C ( $\beta$ -5 and 5-5), and 4-O-5 type (Sun et al. 2010). Thus, a higher extent in the crosslink could be also at the bases of the lesser maximum shear strain of welded spruce material.



**Figure 4.** Maximum shear strain and Klason lignin percentage of welded material at progressive welding times. a: beech, b: spruce

Finally, the combination of increasing shear modulus and decreasing maximum shear strain result in a lessening of the work to failure at increasing welding times (figure 5). This trend is clearly developed in welded beech. In welded spruce, a slight maximum of the work to failure is depicted at 8 s. As maximum shear strain values from 4 to 8 s are close but standard deviations values are noticeable smaller towards 8 s, the maximum value of work to failure at 8 s could be related to an optimum in the lignin condensation reactions in which the strengthened lignin is more evenly distributed through the whole welding interface.



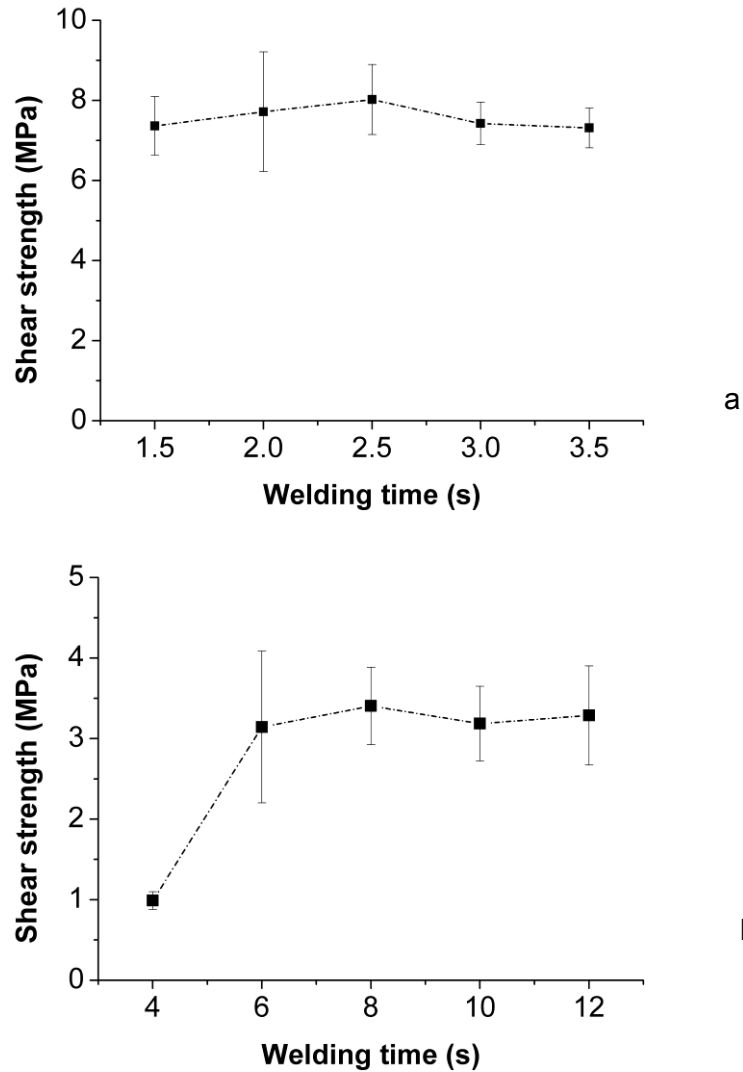
**Figure 5.** Work to failure, i.e. area under stress strain curve at failure, and Klason lignin percentage of welded material at progressive welding times. a: beech, b: spruce



As depicted in figure 6, the shear strength values of welded beech joints from 1.5 to 3.5 s and welded spruce joints from 6 to 12 s are quite constant in the mentioned ranges. Shear modulus and maximal shear strain are intrinsic properties of the welded material, whereas shear strength can be considered as a property of the joint that depends on the local features of the tested area. Thus, homogeneities as porous, locally more degraded material, or lower molecular weight components could produce a decrease in the maximum shear strength.

The shear strength values of welded beech are in good agreement with those found by Ganne-Chédeville et al. (2008a), where an average of 7 MPa was determined for welded beech in a range of 2 to 6.5 s, even if a slight difference in the welded pressure and amplitude were used in this study (1.3 instead of 1.5 MPa, and 3 instead of 2.8 mm respectively). The lower shear strength value of welded spruce at a welding time 4 s can be explained as a too early state of the lignin condensation reactions where the maximal strength is not yet completely developed. It is also macroscopically evidenced in opened joints by a slight brown color of the welded material, much lighter than the dark brown observed beyond 6 s of welding time. In addition, it is also corroborated with observations made by UMSP (Placencia Peña et al. 20xx), where the main increases in UV absorbance in the transversal sections of welded spruce were observed from 4 s. Therefore, it would indicate that lignin modification related to strength development begins at 4 s.

Differences in the chemical composition of the welded material influence its shear properties. On the other side, wood anatomy plays also an important role. Porosity in the welded material is not avoidable even at high welding and holding pressure. The difference between early and late wood produce an irregular shape with areas of different local densification (Leban et al. 2004, Stamm 2006a, Properzi et al. 2005, Ganne-Chédeville 2008c). These phenomena affect both welded beech and welded spruce, but probably welded spruce in a greater extent due to the lower average density and marked difference between early and late wood. Voids were more often found in welded spruce than in welded beech (Placencia Peña et al. 20xx). In addition to the chemical composition local defects as voids could be also at the origin for the lower shear strength of welded spruce in comparison to welded beech.



**Figure 6.** Shear strength of welded material at progressive welding times. a: beech, b: spruce

## Conclusions

Chemical composition of the welded material influences its intrinsic shear properties. A clear increase of shear modulus and decrease of maximum shear strain is observed with a growing percentage of Klason lignin. It demonstrates that at longer welding times and therefore ascent percentages of lignin, the welded material becomes more rigid and brittle. The range of maximum shear strain observed in the welded material of spruce is below the corresponding range for beech. It is most probably related to the higher amounts of lignin observed in welded spruce and to the more condensable nature of guaiacyl lignin present in spruce. Apart from the chemical composition, welded line defects, i.e. porosity has an important role in the

shear properties of welded wood. Even if porosity in the welded line has not been measured its contribution to the shear strength could be of great interest. Welded spruce is probably more intensely affected by the lower average and different early/late wood density that could lead to a more irregular (with defects) welded interface. Shear strength of welded beech and spruce remain constant in the range from 1.5 to 3.5 s and from 6 to 12 s respectively. It could be said that when the welded material is “completely” formed, tensile shear strength better reflects the local features of the welded zone than chemical composition itself.

### **Acknowledgements**

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## **3.2 Amélioration des propriétés mécaniques et de résistance à l'eau**

### **3.2.1 Soudage du bois densifié: propriétés physiques, anatomiques, chimiques et mécaniques**

#### **Résumé**

La densification plus un traitement thermique avant le processus de soudage par friction linéaire ont été étudiés comme une alternative pour améliorer les propriétés mécaniques des joints soudés d'épicéa. Les résultats montrent que la résistance au cisaillement de l'épicéa soudé augmente jusqu'à 2.4 fois sa valeur en comparaison avec les joints soudés non densifiés correspondants. Cette amélioration s'explique par la plus haute compactation de la matière soudée d'épicéa et par la compression locale plus régulière entre les zones du bois de printemps-printemps et printemps-été accomplies avec les échantillons pré-densifiés/post-densifiés. Cette amélioration est aussi liée à la densité plus haute de bois massif et au profil de densité plus homogène entre la ligne soudée et l'épicéa massif densifié. La ligne de soudure de l'épicéa densifié/post-traité montre une forme droite comparée à la ligne de soudure de l'épicéa non densifié qui ressemble à une onde. La dégradation de certains hydrates de carbon après la densification et le post-traitement thermique n'interfère pas avec la formation de la matière soudée.



# **Welding of densified spruce: anatomical, chemical, physical, and mechanical properties**

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## **Abstract**

The densification and a thermal post/treatment previous to the linear friction welding process has been studied as an alternative to improve the mechanical properties of welded joints of spruce. Results show that effectively the tensile shear strength of welded spruce increases up to 2.4 times its value compared with the corresponding un-densified welded joints. This improvement is explained by the higher compaction of the welded spruce material and the more even local compression between the early-early and early-late wood zones achieved with the pre-densified/post-treated specimens. The improvement is also related to the higher density of the massive wood and the more homogeneous density profile between welded line and massive densified spruce. The welded line of welded densified/post-treated spruce shows a straight shape compared with the wave-like welded line of un-densified spruce. The degradation of some carbohydrates after the densification and thermal post-treatment do not interfere with the formation of the welded material.

**Keywords:** welded spruce, densification, thermal post-treatment, carbohydrates degradation, tensile shear strength, welded line, density profile

## **Introduction**

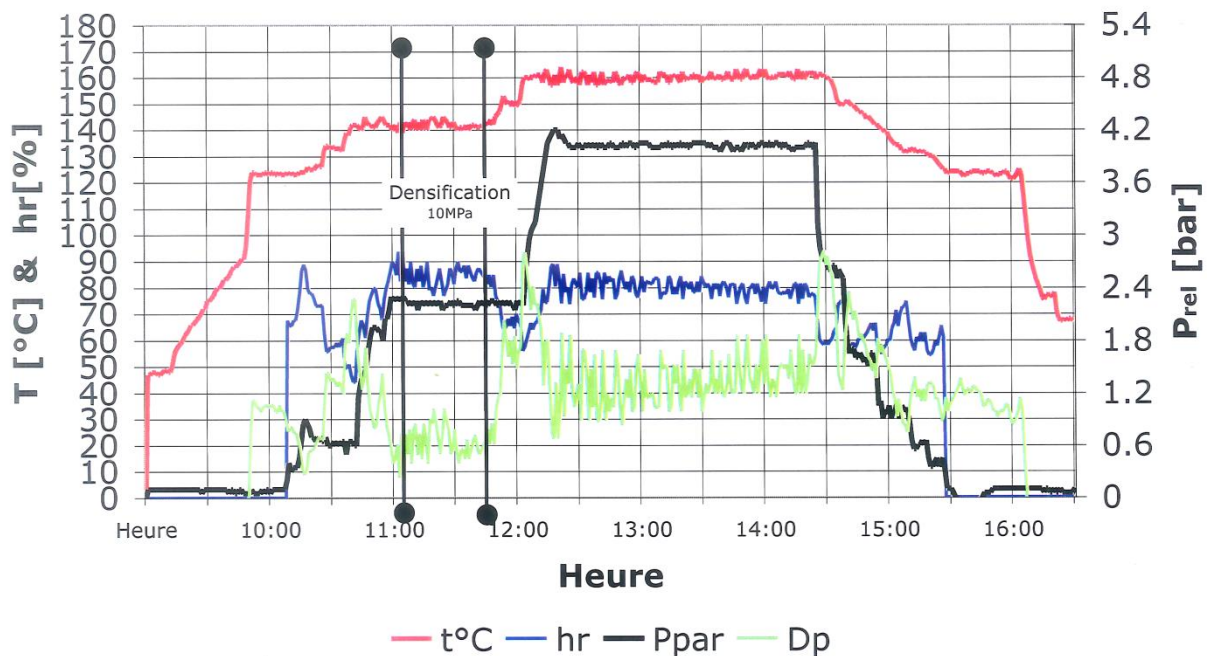
The improvement of the mechanical performance of welded joints of wood has been investigated by several authors. An increase of 50% in the shear strength of welded joints of spruce (circular welding) was obtained by the pre-treatment of the wood specimens with mannose (Stamm 2006). The pre-treatment with xylan and xylose lead to an increase of shear strength of 5 and 9% respectively. These pretreatments improved the performance of welded spruce but the same effect was not achieved for welded beech. Thermal treated wood (beech, birch and poplar) by the industrial Plato process previous to the welding process showed lower mechanical performances than the corresponding untreated wood (Boonstra et al. 2006). The mechanical properties certainly change with the welding parameters (Gfeller et al. 2003, Ganne-Chédeville et al. 2006, Ganne-Chédeville et al. 2008a, Omrani et al. 2009, Vaziri et al 2012), however, their improvement by varying the welding parameters is limited due to the degradation of wood components intrinsic of the welding process (Stamm 2006, Placencia Peña et al. 201x). It is well known that during the linear friction welding process, certain densification occurs in the welding interface (Gfeller et al. 2003, Leban et al. 2004, Stamm 2006, Ganne-Chédeville 2008b). In fact, this process has been used to increase the surface hardness of single wood specimens (Pizzi et al. 2005, Rautkari et al. 2009). However, densification generated during welding of wood is not homogeneous for wood species with a marked difference between early and late wood as spruce (Leban et al. 2004). It would be one of the factors leading to poor mechanical properties. In the present study, the potential improvement of the tensile shear strength of welded spruce by a previous densification is investigated. The welding of densified spruce is for the first time presented.

## **Materials and Methods**

### **Wood densification**

The densification of spruce was carried out in a closed THM (Thermo-Hydro-Mechanic) reactor conceived in the EPFL (École Polytechnique Fédérale de Lausanne). This reactor is able to produce densified wood specimens of defined shapes. Laths of spruce of 240x80x10 mm<sup>3</sup> (LxRxT) were densified up to 240x80x4 mm<sup>3</sup> (densification factor of 2.5, in the tangential direction). The selected laths were free of defects (knots or resin canals). The

process is carried out in four steps. In the first step temperature increases up to 140°C and pressure continuously ascents up to 10 MPa. In the second step both temperature and pressure are hold (140°C, 10 MPa) during about 45 min. Temperature is set through a controlled saturation steam pressure. The hot steam facilitates the “plastification” of the wood and the densification is achieved. The next step is the so called “post-treatment”, which is necessary to conserve the densified form and avoid the shape recovery. In this step (third), temperature is set at 160°C and maintained during approximately 2.5 h under 10 MPa. A fourth cooling step follows. Densified samples are finally dried. A diagram of the densification and post-treatment process is presented in figure 1. In the rest of the text “densified spruce” refers to “densified/post-treated” spruce.



**Figure 1.** Parameters diagram during the densification process. T [°C] measured in the mold; (hr) stands for relative humidity, (Ppar) partial vapor pressure, (Dp) difference of pressure (between partial vapor pressure and pressure in the chamber, an indicative to avoid excessive drops in pressure that could damage the wood structure)

### Welding process

Spruce and densified spruce were welded in a Branson M-DT24L linear friction welding machine. The parameters during welding were frequency 100 Hz, amplitude 3 mm, welding time 8 s. Welding pressure was 1.5 and 1.4 MPa, holding pressure 1.5 MPa and 2 MPa and

holding time 40 and 60 s for spruce and densified spruce respectively. The size of the welded specimens was 326x37x11 mm<sup>3</sup> and 240x80x8 mm<sup>3</sup> for reference spruce and densified spruce accordingly. Reference spruce and densified spruce were welded in the RL plane (rings at 90° respect to the welded line). Additional spruce specimens with rings at approximately (30 - 60°) respect to the welded line were also welded. Since the surfaces of densified spruce were completely smooth after the densification, the sides to be welded were previously sanded. Wood was acclimatized at 23°C and 50 %RH at least 20 days before and after welding.

## **Chemical analysis**

### **Raw materials**

Small cubes of reference spruce and densified spruce of cross section of about 4 x 4 mm<sup>2</sup> were cut in thin layers of about 20 µm thickness with a microtome. Also, the “black” (welded) material from the opened welded spruce joints was scratched with a razor blade and collected. The three types of samples (spruce, densified spruce and welded spruce material) were subjected to water extraction followed by cryo-milling and two-step acid hydrolysis.

### **Extraction of soluble components**

About 600 mg of each sample were extracted in distilled water in an ASE accelerated solvent extractor (ASE 200, Fa. Dionex). 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, as in Placencia Peña et al. (201x).

### **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 materials was placed into liquid nitrogen. 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 as in Placencia Peña et al. (201x).

### **Acidic hydrolysis of welded-extracted material**

Carbohydrates and lignin content were analyzed in triplicate on acclimatized extracted-dried-milled material (reference spruce, densified spruce and welded material) by two-stage acid hydrolysis (Placencia Peña et al. 201x). In the first step, 1 ml of H<sub>2</sub>SO<sub>4</sub> at 72% w/w is added to 100 mg of sample. The mixture is kept during 1 h in a thermal bath at 30°C. The reaction is stopped by diluting the solution with ionized H<sub>2</sub>O until a concentration of 4% of H<sub>2</sub>SO<sub>4</sub>. In the second step, dilute solutions are placed in an autoclave at 120°C and 1.2 Bar, during 40 min. Time is optimized for maximal recovery of monomeric sugars (Puls 1993). Then, solutions are cooled down and filtered in a G4 sintered glass crucible. Klason lignin is the solid residue and liquid solution contains the hydrolyzed sugars.

### **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 bicinchonate 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).

### **Shear strength**

The tensile shear strength of welded spruce and welded densified spruce joints was measured in a universal Zwick machine provided with a charge cell of 2.5 kN. The speed was set at 4 mm min<sup>-1</sup>. The specimens had a single lap joint shape with a total size of 50 x 8 x 8 mm<sup>3</sup> and a test surface of 10x8 mm<sup>2</sup>. A total of 25 samples of welded-densified spruce, 10 of reference welded spruce (rings at 90° from the welded line, the same rings orientation as used for densified spruce), and 10 samples with rings at (30-60°) from the welded were tested.

### **X-ray densitometry**

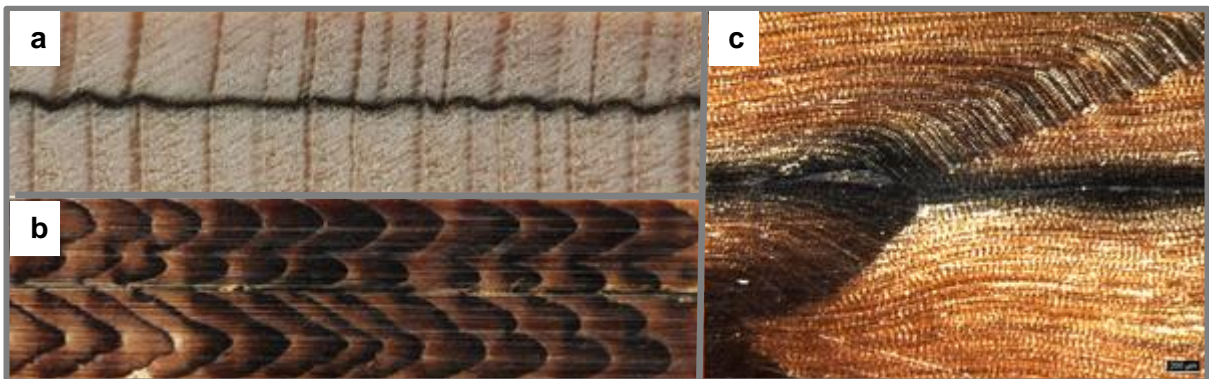
The density profiles of the transversal sections of welded spruce (reference and densified) were performed in an X-ray densitometer GreCon DAX 5000. The X-ray densitometer works with a X-ray source of 33000 V, 432 μA and an internal temperature of 45°C. The measurements are performed with increments of 20 μm. Sections of 50 x 50 x 8 mm<sup>3</sup> (LxRxT) of welded spruce (reference and densified) were measured.

## Results and Discussion

### Color and anatomical features

The densification/post-treatment induces important color changes in spruce. The darkening of the whole structure is macroscopically noticeable. Late wood zones are more pronouncedly dark. Changes in color in thermal treatments are related to the hydrolysis of hemicelluloses (Koch et al. 2003). Also, color changes can be caused by the reactions of sugars (mono, oligo or polysaccharides) with amino-acids that result in Amadori-Maillard-type reactions (Kollmann et al. 1951). Other causes as the condensation and oxidation of phenolic compounds are also possible (Frey-Wyssling and Bosshard 1959, Mayer et al. 2006). Although the dark color in the densified spruce, the welded line is clearly differentiated.

As depicted in figure 2, the welded line formed between the two densified specimens has a noticeable more “straight” shape in contrast to the “wavy” welded line formed between the no densified spruce laths. The densified structure of spruce allows for a more homogeneous joint where the zones of different compression between early and late wood almost completely disappear (figure 2 c). The local inhomogeneity between early and late wood in the welded line of spruce has been earlier reported by Leban et al. (2004) and Stamm (2006).



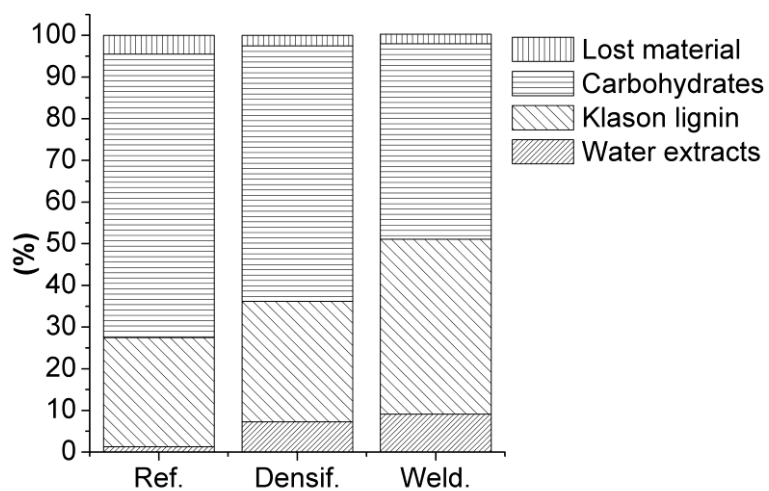
**Figure 2.** Transversal sections of welded reference spruce (a) and welded densified spruce (b and c)



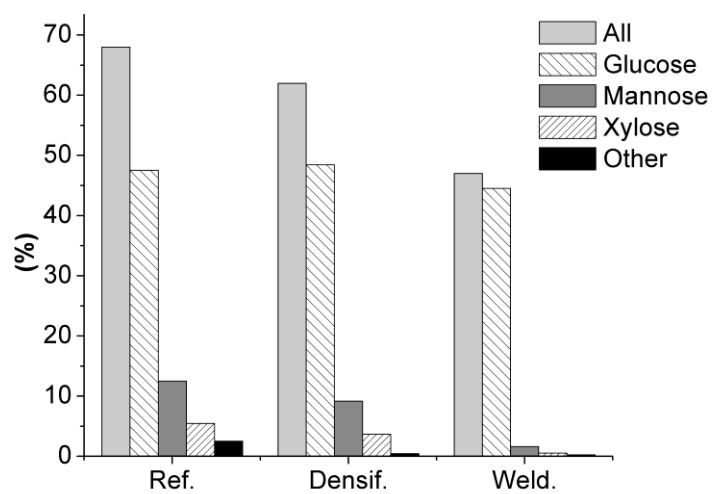
## Chemical composition

In figures 3 and 4, weight percentages based on dry wood (or welded wood) are presented. In figure 3, the composition of spruce, densified spruce and welded spruce was determined after water extraction by acid hydrolysis. The percentage of carbohydrates in spruce after the densification process shows a descent from 68 to 61.3 %. The percentage of klason lignin slightly increases from 26.2 to 28.9 %, and the percentage of water extracts increases from 1.3 to 7.3 %. Sugars as arabinose, rhamnose and galactose almost completely disappear from the hydrolyzed sugars after densification (figure 4: “Others” from 2.5 to 0.4%). Mannose and xylose decrease from 12.1 to 9.2 and from 4.9 to 3.7% respectively, and glucose remains practically constant near 48%. These results are in good agreement with the work of Heger (2004), where decreases in mannose (from 13.6 to 9.7 %), xylose (from 5.6 to 4.7), galactose (from 2.8 to 1.2), and arabinose (from 1.2 to 0.7) identified and measured by gas chromatography (analyses made at CERMAV, CNRS, Grenoble) are reported. Even though, the water extracts of densified spruce have not been identified and analyzed, it is more likely that the depolymerized sugars during the densification-post treatment process are at least partially dissolved. Probably not only depolymerized sugars but also acetic acid, and other degradation products could be present in water extracts. However, the solubility in water of galactoglucomannan oligosaccharides is affected if the deacetylation happens in important extent (Willför et al. 2003, Song et al. 2008, Song et al. 2011, Grénman et al. 2011).

The main changes between reference spruce and densified spruce occur therefore in carbohydrates, and more particularly in hemicelluloses. The slight lignin increase could be more likely due to the relative decrease in the amount of carbohydrates and in a minimum extent to possible condensation reactions of lignin. In welded spruce material about 9% is extracted in water, 42% is klason lignin and 46.9% carbohydrates (Placencia Peña et al. 201x). Even though the composition of the welded densified spruce was not determined due to the much reduced amount of material available, a further decrease in carbohydrates (i.e. mannose and xylose) and increase in the amount of klason lignin would be expected.



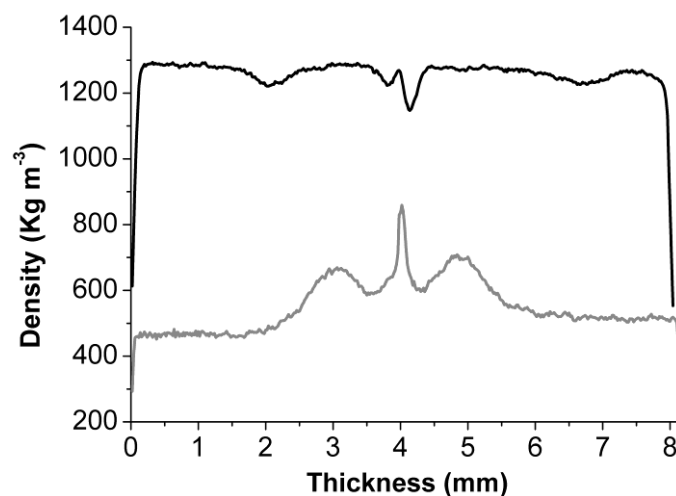
**Figure 3.** Composition of spruce, densified spruce and welded spruce material after water-extraction and hydrolysis



**Figure 4.** Carbohydrate composition of spruce, densified spruce and welded spruce material as determined after water-extraction and hydrolysis. Other: cellobiose, rhamnose, arabinose, galactose

## Density profiles

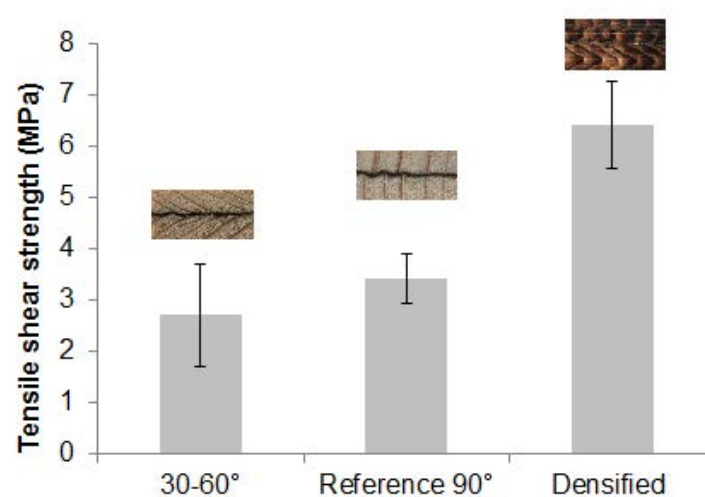
Representative density profiles of two sections of a welded reference spruce (rings 90°) and a welded densified spruce are depicted in figure 5. The profiles show average values of density of blocks of 50 x 50 mm<sup>2</sup> (LxR) in a width of 8 mm (T). The X-rays go through the R direction, parallel to the welded line plane. Therefore, due to the “wave” shape of the welded line, a direct measurement of the thickness of the welded line or densified zones would not be precise. However, the different features of each welded section are clearly defined. The density profile of the welded reference spruce shows a maximum in the welded line of 860 kg m<sup>-3</sup>. The bulkiness at both sides of the welded line reflects the densification of the massive wood and presents maximums between 660 and 690 kg m<sup>-3</sup>, while the average density of the massive wood is 460 and 520 kg m<sup>-3</sup> at both sides of the bulkiness. The density profile of the welded densified spruce shows a slight minimum of 1150 kg m<sup>-3</sup> in the welded line, which is still higher than the maximum of welded reference spruce. The density of massive densified spruce is between 1270 – 1280 kg m<sup>-3</sup>.



**Figure 5.** Density profiles of welded reference spruce (black) and welded densified spruce (grey)

## Tensile shear strength

In figure 6, the tensile shear strength of the different welded spruce specimens is presented. The tensile shear strength value of densified welded spruce is  $6.4 \pm 0.86$  MPa, while for welded spruce (30-60°) it is  $2.7 \pm 1.01$  MPa and for welded spruce (90°) it is  $3.4 \text{ MPa} \pm 0.48$  MPa. In contrast to beech, in which the slight difference between early and late wood density allow the formation of a moderately straight welded line, whether the rings direction are at 90° or 30-60° respect to the welding plane, in spruce, samples welded with rings direction 30-60° give lower tensile shear strength than the 90° configuration. Since tensile shear strength depends on the local features of the joint, apparently more zones of lower compression (between two early wood sections) would be formed with the 30-60° configuration. Also, with the 30-60° configuration, a less stable joint would be formed, since the potential hygro-expansion of massive wood linked to the welded line would be higher than with the 90° configuration (i.e. higher deformation of the fibers due to moisture in the tangential is higher than in the radial direction). Leban et al. (2004) attribute the poor bonding of welded spruce to the intra-ring wood heterogeneity, considered as the limiting factor for reaching high local compression rates during the welding process. The higher tensile shear strength of welded densified spruce can be explained by the following reasons.



**Figure 6.** Tensile shear strength of welded spruce with rings direction (30-60° respect to the welded line), welded reference spruce with rings direction (90° respect to the welded line) and welded densified spruce joints (densification in the T direction: rings direction 90° respect to the welded line).

Welded densified spruce has a more compact welded line, whose density is higher than a conventional welded line with un-densified spruce. Also, the density profile of the welded densified spruce shows a more homogeneous density distribution between massive wood and welded line, in contrast to the density profile of un-densified spruce that depicts big gaps of density between the peak (welded line) and neighbor zones. The higher density and homogeneous density profile between massive wood and joint material is well known to positively affect the mechanical performance of the joint. Moreover, in welded densified spruce, the welded line presents a more homogeneous straight shape with noticeable reduced zones of uneven compression between early wood – late wood, and early wood – early wood. Additionally, due to the post-treatment, densified/post-treated spruce is expected to have a low shape memory (higher dimensional stability), and also less water adsorption at the equilibrium conditions than un-densified spruce. Therefore, it would be expected that densified/post-treated spruce would better stand the stresses entailed by the welding process than un-densified spruce, which would lead to a more stable joint. Considering the lowest shear strength value (2.7 MPa), the tensile shear strength of welded spruce can increase up to 2.4 times if wood is predensified. The improvement of the tensile shear strength of welded densified spruce goes together with the improvement of other mechanical properties in densified wood. Brinell hardness, shear strength in the LT plane, elastic modulus and tensile strength in the L direction have been reported to increase due to densification by Navi and Girardet (2000), Heger (2004), Navi and Heger (2005). The improvements are always limited by the temperature of the densification and post-treatment. The post-treatments with temperatures higher than 160°C induce important degradation and therefore loss of properties respect to the densified wood.

## **Conclusions**

The waved shape of the welded line of un-densified spruce is noticeably straightened when densified spruce is welded. It goes together with a high compaction of the welded material and a diminution or even disappearance of uneven local compression zones between early-early or early-late wood, frequently found in welded un-densified spruce. Also, the density

profile of the welded densified spruce shows a more homogeneous and closer density between the welded line and neighbor zones of densified spruce than in conventional welded spruce. Moreover, the welded densified joints would be expected to be more stable regarding residual stress generated in the massive wood during and interface during the welding process, due to the higher dimensional stability achieved by the post-treatment after densification. These anatomical and physical modifications are the basis for the improvement of tensile shear strength of welded densified spruce. Thus, the densification of spruce previous to the linear friction welding process is probed as an effective method to increase the tensile shear strength of welded spruce.

The decrease in the amount of carbohydrates in spruce after densification does not affect the formation of the welded line. An increase in Klason lignin and decrease in carbohydrates percentage respect to densified spruce are expected in the welded densified spruce material composition. Besides the chemical changes necessary for the formation of the welded line, the anatomical features of wood have been proved to be of great importance on the mechanical performance of the welded joint.

### **Acknowledgements**

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### **3.2.2 Influence des additifs dans la solubilité, la composition et la résistance au cisaillement du hêtre soudé**

#### **Résumé**

Les joints du bois soudé sont connus par sa faible résistance à l'humidité et à l'eau liquide. Afin d'améliorer cette résistance, l'influence d'additifs naturels tels que la colophane et la lignine sur l'interface du bois avant le soudage a été étudié. La composition chimique et la solubilité dans l'eau du matériau soudé avec des additifs ont été déterminées. En outre, la résistance au cisaillement des joints après trempage à l'eau et acclimatation a été évaluée. En comparaison avec les joints soudés sans additifs, ceux soudés avec des additifs résistent plus longtemps sous l'eau liquide. La solubilité dans l'eau du matériau soudé est plus faible lorsque les additifs sont utilisés. À température ambiante, la résistance au cisaillement en traction des joints soudés avec des additifs est plus petite que dans les joints soudés sans additifs. Néanmoins, les joints soudés avec des additifs montrent une plus grande résistance au cisaillement en traction après trempage et ré-acclimatation. Les additifs naturels à l'interface du bois avant le soudage ont un effet positif sur la résistance à l'eau des joints; cependant, le matériau soudé est encore partiellement soluble dans l'eau.



# **The influence of additives on the solubility, composition and shear strength of welded beech**

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## **Abstract**

Welded joints of wood are well known to have a poor resistance to moisture and liquid water. In order to improve this resistance the influence of natural additives (rosin and lignin) in the interface previous to welding is studied. The chemical composition and the water solubility of the welded material with additives were determined. Also, the shear strength of the joints after water soaking and acclimatization was evaluated. In comparison to welded joints without additives, those welded with additives resist longer time under liquid water. The water solubility of the welded material is lower when additives are used. At room conditions, tensile shear strength of welded joints with additives is lesser than in welded joints without additives. Nevertheless, joints welded with additives show higher tensile shear strength after soaking and re-acclimatization. Natural additives in the interface previous to welding have a positive effect regarding the water resistance of the joints to water; however, the welded material is still partially water soluble.

**Keywords:** rosin, lignin, carbohydrates, linear friction welding, water extracts, thermal degradation, tensile shear strength.

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## **Introduction**

The use of wood joints assembled by linear friction welding is restricted to internal applications (Gfeller et al. 2003, Stamm 2005a, Ganne-Chédeville 2008, Omrani 2009), since the welded joints have poor resistance to liquid water and the mechanical properties deteriorate in humid environments (Rhême et al. 2013a, Rhême et al. 2013b). According to Placencia Peña et al. (201x), about 18% of welded beech and 10% of welded spruce material can be dissolved in water, in contrast to 2.2% and 1.4% for reference wood respectively. This largely explains the poor resistance of welded joints to water. Improvements in the water resistance of welded joints have been reported by Mansouri et al. (2009), Omrani et al. (2009a), and Vaziri et al. (2011) by reducing the welding time and by tuning the frequency and welding pressure. Additionally, substances as rosin (Mansouri et al. 2011) and lignin acetate (Pizzi et al. 2012) have been reported to improve the water resistance of welded joints. The feasibility of using two additives: rosin and lignin as agents to improve the water resistance of welded beech in water was evaluated in the work reported herein. The solubility of the welded material in water provides useful information on its water resistance.

## **Materials and Methods**

### **Raw materials**

Rosin was provided by Kemtan AG, Switzerland. It is a yellow vitreous natural resin that principally contains abietic, levopimaric, neoabietic, and palustric acids. The rosin was dissolved in ethylic alcohol 94% (v/v) at 50% (w/w). Beech (*Fagus Sylvatica*) laths with a surface of  $500 \times 80 \text{ mm}^2$  (for the L and R directions, respectively) were immersed in the rosin solution for approximately 15 min, after which they were dried at 23 °C and 60% RH for around 48 h. The amount of solution retained by each lath after impregnation varied from 15 to 50 g. Both surfaces of the lath to be welded were impregnated. Lignin, provided by the “Compagnie Industrielle de la Matière Végétale” (CIMV), Neuilly sur Seine, France, was obtained from wheat straw by a procedure carried out at atmospheric pressure using a catalyst solvent system of formic and acetic acid (Banoub and Delmas 2003). Before welding, 1 g of the CIMV lignin powder was distributed over a surface area of  $500 \times 20 \text{ mm}^2$  of one of the two beech laths.

## **Welding process**

Welding was performed on a Branson M DT24L welding machine that operates at a fixed frequency of 100 Hz. The parameters for beech impregnated with rosin were: amplitude 2.8 mm, welding pressure 1.8 MPa, welding time 10 s, holding pressure 2 MPa and holding time 60 s. For beech with CIMV lignin, the parameters were: amplitude 2.8 mm, welding pressure 1.8 MPa, welding time 7 s, holding pressure 2.2 MPa and holding time 60 s.

## **Water solubility and chemical composition of welded wood**

The welded material was collected by scratching with a razor blade the opened welded surfaces. The solubility of the welded material was determined after extraction of the scratched welded material in water. After extraction, the residue was subjected to cryo-milling and two stage acid hydrolysis. The hydrolysis residue, representing the Klason lignin, was determined gravimetrically. Carbohydrates were hydrolysed and determined by borate-anion-exchange-chromatography (Placencia Peña et al. 201x). Mono-, oligosaccharides and anhydrosugars in water extracts were analysed by anion exchange chromatography; soluble lignin was analysed by size exclusion chromatography; furfural and 5-hydroxy methyl furfural (5HMF) were determined by reversed-phase high performance liquid chromatography (Placencia Peña et al. 201x).

## **Tensile shear strength**

The tensile shear strength of the welded beech with rosin, lignin and without additives was measured according to EN 205:2003. The displacement speed employed was 2 mm min<sup>-1</sup>. The specimens welded with rosin and lignin were evaluated after soaking in water at ambient temperature for 30 min. Specimens welded with lignin were also tested after 12 h water soaking. All specimens whether they had been water soaked or not, were conditioned for at least 7 days at 23°C and 65% RH before testing. A minimum of 10 specimens per treatment were evaluated.

## **Results and discussion**

### **Composition of welded material after extraction and hydrolysis**

In figures 1 and 2, the values shown are the weight percentages based on dry welded material. As depicted in figure 1, water extracts from welded beech with rosin and CIMV lignin amount to about 11%, which clearly represents a lower level of solubility compared to welded beech without additives (17.7%), but which is still higher than the reference beech (2.2%). Rosin is a hydrophobic resin; it reduces the sensitivity to water absorption and thereby the solubility of the welded material. In figure 1, water extracts, carbohydrates and Klason lignin of the samples are also shown. In sample WB-R-10s, welded beech with rosin for 10 s, the Klason lignin determination is falsified by the rosin which is included in the hydrolysis residue. However, the rosin was not extracted prior to the water extraction and acid hydrolysis in order to have the same comparative analytical protocol used in welded beech without additives. The Klason lignin in welded beech with rosin was 37.4%, whilst in welded beech it was 26.3 and 19.5% in the beech reference. The presence of CIMV lignin as part of the welding material most likely contributes to the formation of un-hydrolysable condensate products of lignin which is reflected in the higher amount of Klason lignin (43.7%).

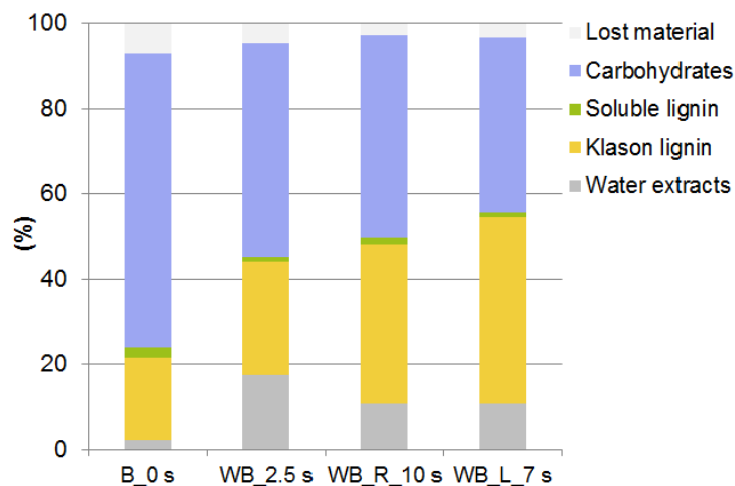


Figure 1. Effect of rosin and CIMV lignin in the composition of the welded material as determined after water extraction and hydrolysis. Legend, “B” stands for beech reference not welded, “WB” for welded beech, “L” for CIMV lignin, “R” for rosin, the time at the right side indicates the welding time

In welded material, either with or without additives, the increase in Klason lignin over that of the beech reference is also explained by the simultaneous decrease (degradation) of carbohydrates and its capability to form condensation products with lignin, e.g. condensation with furans and other carbohydrate degradation products (Placencia Peña et al. 201x). The



percentage of carbohydrates decreased from 69% in un-welded beech to 50, 47.7 and 41.3% for beech welded without additives, and beech welded with rosin and CIMV lignin respectively. In figure 2a, the differentiation of hydrolysed monosaccharides from carbohydrates is shown. Glucose represents cellulose and part of glucomannan (Sjöström 1993). It clearly diminishes in all welded material. Also, the amount of xylose is reduced, especially in welded beech with additives, where longer welding times were used. Mannose, arabinose, galactose and rhamnose, which total 3.3% in untreated beech, were reduced by up to between 0.6 and 0.7% in welded beech with additives.

The composition of water extracts from welded beech with rosin, CIMV lignin, welded beech and reference beech is shown in figure 2b. Water extracts contain lignin, acetic acid, oligosaccharides, monosaccharides, anhydrosugars, 5HMF and furfural. The slightly lower amount of lignin observed in extracts from welded beech with additives (4%) than in welded beech (5%) might be due to a higher tendency for lignin to form condensation products at longer welding times. Highly condensed lignin may be less affected by the extraction, thereby increasing the percentage of Klason lignin in the solid extraction residue (Placencia Peña et al. 201x).

In general as the percentage of dissolved lignin or, more accurately, the UV absorbing components, in the beech reference is much lower (0.27%) than in the welded beech with or without additives, the presence of soluble lignin clearly demonstrates the cleavage of native lignin (or the corresponding CIMV lignin) during the welding process. The molecular weight (Mw) and polydispersity (PD) of water extracted lignin is shown in table 1. The values of Mw and PD were lower in welded beech with additives than in beech welded for 2.5 s. The decreased Mw and PD of welded beech with additives most probably indicates a further cleavage of lignin in the welded material due to the longer welding times applied, i.e. Mw = 3100 g mol<sup>-1</sup> and PD = 3 at welding time 10 s for welded beech with rosin (table 1) and Mw = 7900 g mol<sup>-1</sup> and PD = 6.6 at welding time 1 s for welded beech without additives (Placencia Peña et al. 201x).

Table 1. Molecular weight and polydispersity of water soluble lignin

Sample	Wt (s)	Mw (g mol <sup>-1</sup> )	PD (au)
Beech	0	1500	1.7
Beech	2.5	4700	3.9
Beech rosin	10	3100	3.0
Beech lignin	7	3000	3.0

5-hydroxy methyl furfural is a decomposition product from hexoses, most likely from glucose coming from the amorphous part of cellulose and mannose from glucomannan (Fengel and Wegener 2003). Furfural appears from the decomposition of pentoses, mainly xyloses in beech (Sjöström 1993). 5HMF and furfural were present in very small amounts in the water extracts of welded beech with and without additives due to their high volatility and tendency to form condensed products with themselves and with lignin (Placencia Peña et al. 201x). Acetic acid is generated by the de-acetylation of hemicelluloses and it classically appears in the thermal treatment of wood (Tjeerdsma et al. 1998, Sivonen et al. 2002, Windeisen et al. 2007, Placencia Peña et al. 201x). The amounts determined in welded beech with rosin and CIMV lignin were close to the amount in welded beech. Part of the acetic acid generated evaporates within the volatiles produced during welding (Omrani et al. 2009b and Ganne-Chédeville 2008, Placencia Peña, et al. 201x). The acidic environment generated at the welding interface by acetic acid favours the condensation reactions of lignin and the depolymerization of hemicellulose.

The oligosaccharides, monosaccharides and anhydrosugars found in the water extracts are shown in figures 2c and 2d. They almost all appear exclusively in welded beech with or without additives and not in the reference beech. Therefore they can be attributed to the cleavage of hemicelluloses during welding. Their amount in the water extracts is not very high, but they are evidence of the cleavage and degradation of carbohydrates. Further, the solubility of cleaved oligosaccharides is, in general, affected by their degree of acetylation, i.e. acetic acid in water extracts reflects the deacetylation of hemicelluloses during welding. Galactoglucomannan oligosaccharides from spruce require a high degree of acetylation to be

dissolved in water (Willför et al. 2003; Song et al. 2008; Song et al. 2011; Grénman et al. 2011, Placencia Peña et al. 201x). Xylooligomers of up to 7 units were present in the water extracts from welded beech. In welded beech with rosin and CIMV lignin, xylooligomers of mainly 2 units were detected. At longer welding times (welding with rosin and CIMV lignin) bigger molecules are cleaved and the formation of smaller molecules is favoured (Placencia Peña et al. 201x). Cellooligomers of up to 5 units were found specifically in welded beech and in welded beech with CIMV lignin. They did not appear in welded beech with rosin probably due to the prolonged welding time (10 s). Cellooligomers show the degradation of cellulose, certainly the amorphous part.

The levels of glucose, xylose and levoglucosan found are depicted in figure 2d. In general, monosaccharides have a poor dissolution in water. They begin to dissolve in significant amounts at about 160 – 240°C (55 mg g<sup>-1</sup> of spruce monosaccharides are hydrolysed and extracted in water) (Leppänen et al. 2011). Xylose and glucose were present in relatively small amounts in the water extracts from all welded material. Xylose reflects the depolymerization of xylans, the main hemicellulose of beech wood. It is important to notice that small quantities of arabinose and galactose were only dissolved in beech welded for 2.5 s. In welded beech with additives, these two sugars are no longer dissolved, most likely because they have been degraded due to the longer welding times. Levoglucosan is an anhydrosugar formed through the dehydration of glucose. It is a degradation product from cellulose (Fengel and Wegener 2003), as well as from glucose from galactoglucomannans from spruce (Xu et al. 2009). Since very short welding times were used and the amounts are relatively small, it is logical to ascribe it to the dehydration of glucose from galactoglucomannan that is present in small amounts in beech (Placencia Peña et al. 201x). Greater amounts of levoglucosan were present in the water extracts of welded beech with additives since longer welding times were used. The dissolution in water of a certain amount of wood degradation components is not completely avoidable. Degradation of wood occurs as part of the welding process either with or without additives (Placencia Peña et al. 201x).

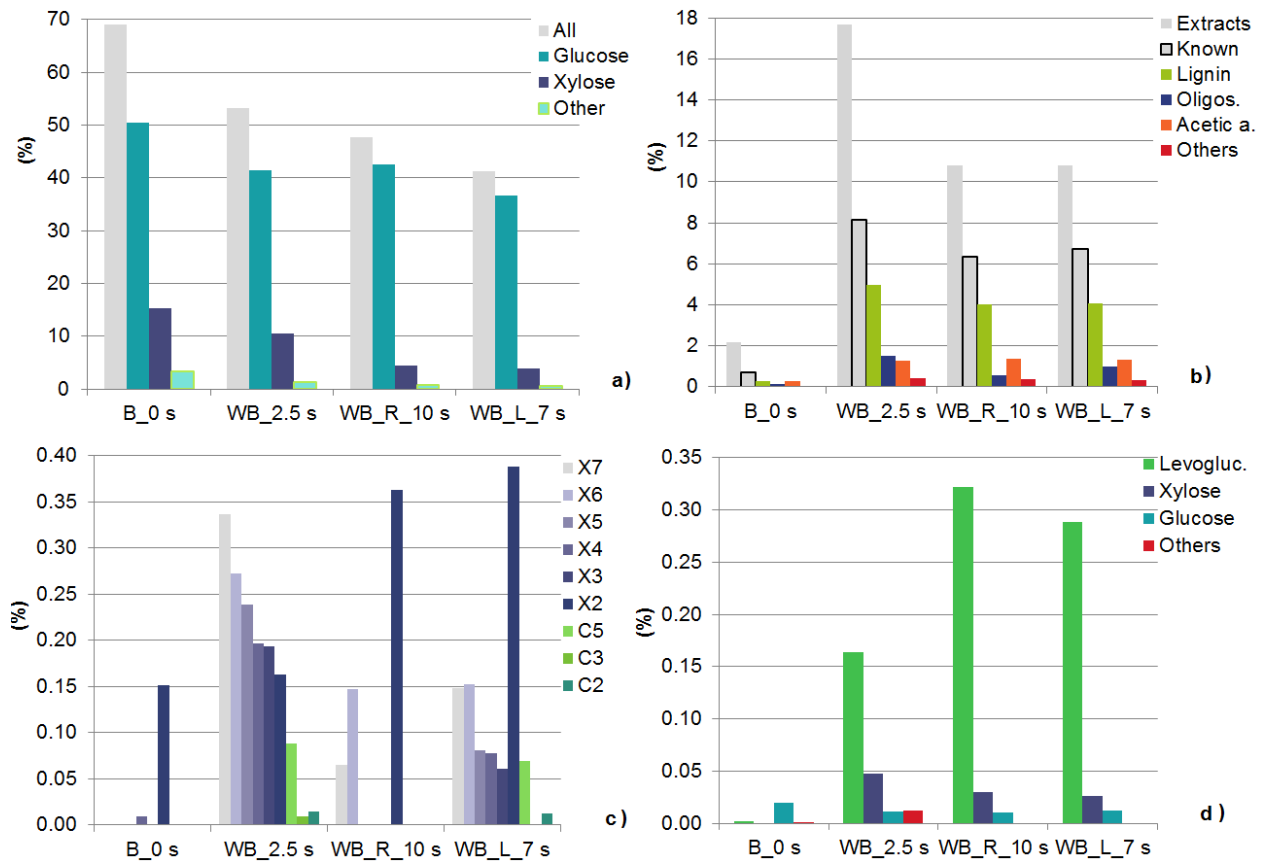


Figure 2. a) Carbohydrate composition of welded material after water extraction. Other sugars: mannose, arabinose, galactose, rhamnose. b) Water extracts components from welded material. Others: monosaccharides, levoglucosan, 5HMF, furfural. c) Oligosaccharides in water extracts solution of welded material. “X” stands for xylooligomers, “C” celooligomers. The number at the right side means the degree of polymerization. d) Monosaccharides and anhydrosugars in water extracts of welded material. Others: arabinose, galactose. Legends, “B” stands for beech reference not welded, “WB” for welded beech, “L” for CIMV lignin, “R” for rosin, the time at the right side indicates the welding time

### Tensile shear strength

In figure 3, the decrease in the tensile shear strength of welded wood with rosin and CIMV lignin after water soaking is shown. It is important to mention that beech welded without additives breaks apart after 0.5 – 3 h of soaking in water, therefore the tensile shear strength cannot be measured. Welded beech with rosin and CIMV lignin show lower tensile shear strength than welded beech. Rosin, apart from giving the welded interface and the adjacent

massive beech substrate, hydrophobic characteristics, also acts as a kind of insulation medium between the two wood surfaces. That is why longer welding times are needed to achieve a minimum interface strength. On the other hand, since rosin is a mixture of relatively low molecular weight components and their participation in the welded wood material is mainly physical and not in the formation of the chemical bonds present in the welded material, rosin tends to decrease the strength of the welded joint. Similarly, the utilization of a layer of powder CIMV lignin at the welding interface also produces a sort of isolation between the welding interfaces; consequently, longer welding times are needed. However, unlike rosin, CIMV lignin most likely participates in the formation of the condensation products of lignin. The effect of welding with these two additives extends the time that the welded joint can withstand water without breaking; however it does not avoid a decrease in the tensile shear strength after soaking. The diminution in mechanical properties is probably related to the continuous dissolution of the degraded material into the water. Failure is therefore induced by the combined action of the moisture on the joining material and of the stresses induced by hygro-expansion of the wood. Hence, in order to improve the water resistance of linearly welded, large dimension pieces further, more investigation is needed.

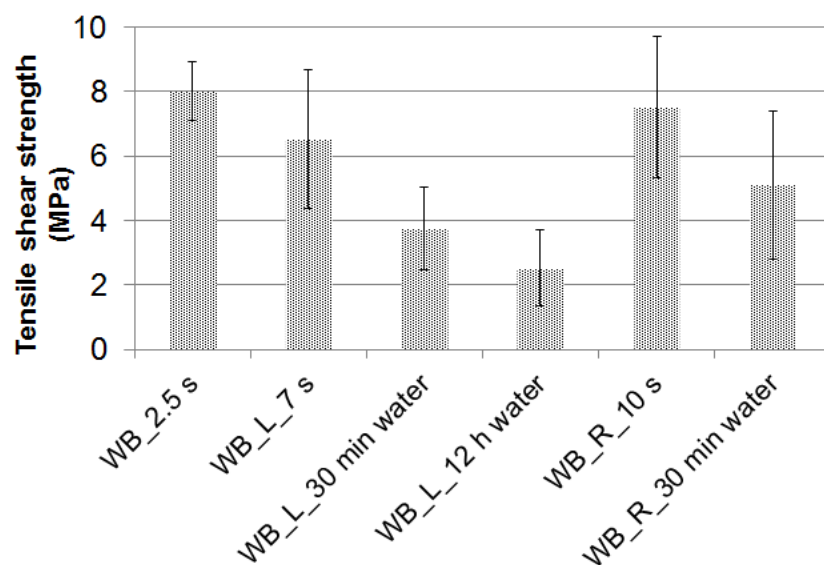


Figure 3. Effect of water soaking in the tensile shear strength of welded beech with additives. Legend, WB stands for “welded beech”, “L” for CIMV lignin, “R” for rosin; the time at the right side stands for welding time or the time of “water soaking”.

## **Conclusions**

It has been shown that the use of rosin reduces the sensitivity to water absorption and thereby the solubility of the welded material. On the hand, CIMV lignin most likely contributes to the formation of un-hydrolysable condensate products of lignin, decreasing the solubility of the welded material in water. In both cases, the solubility decrease is unfortunately not great enough to allow good water resistance of the joint for long water exposure times. The main causes of failure can be attributed to the combined actions of degraded material dissolution and stresses induced by hygro-expansion of the wood.

## **Acknowledgements**

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### **3.2.3 Amélioration de la résistance à l'eau des joints de bois soudé par tourillons par la lignine acétylée**

#### **Résumé**

La lignine organosolv acétylée de bas poids moléculaire provenant de la paille de blé et la lignine organosolv de bas teneur en soufre provenant du bois ont sensiblement amélioré la résistance à l'eau et amélioré les performances mécaniques des joints soudés par tourillons. La distribution des oligomères acétylés des deux types de lignines a été déterminée par MALDI-TOF-spectrométrie de masse. Une vaste acétylation a été confirmée par CP-MAS <sup>13</sup>C NMR spectrométrie. Les courbes force-déplacement des joints testés qui ont été additivés avec la lignine acétylée provenant du bois ont montré un comportement ductile. Ceci est expliqué par l'interpénétration de la lignine acétylée élastique et le plus rigide réseau composite de l'interphase de soudure.



# Enhancing water resistance of welded dowel wood joints by acetylated lignin

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## ABSTRACT

Low molecular mass acetylated organosolv lignin from wheat straw and from depolymerized low sulfur organosolv wood lignin have been shown to markedly improve both the water resistance and the mechanical performance of welded dowel wood joints. The acetylated oligomers distribution and extent of acetylation of the two lignins was determined by Matrix Assisted Laser Ionization Desorption-Time Of Flight (MALDI-TOF) mass spectrometry. Extensive acetylation was confirmed by CP-MAS <sup>13</sup>C NMR spectrometry. Force-displacement measurements on welded dowel joints to which acetylated wood lignins were added showed a ductile behavior. This is due to the interpenetration of the elastic acetylated lignin network and of the more rigid composite network of the welded interphase.

**Keywords:** Wood welding, welded dowels, water resistance, waterproofing additives, lignin, acetylated lignin, ductile behavior, interpenetrating network, environment friendly, biosourced additives

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## 1. Introduction

Mechanically induced friction welding techniques have recently been employed to join wood, without the use of any adhesives [1-3]. While rotational wood dowel welding [4-6] yields joints that possess a certain degree of long-term resistance to water due to the geometry of the joint [7-9]; this is not the case for linear vibration welding of a flat wood surface to another flat wood surface [1]. Thus, linear vibration-welded wood joints are rather sensitive to water attack, thus the joints being suitable exclusively for interior grade applications such as furniture, in spite of their dry strength being at the structural level. There has been interest in overcoming this limitation without the use of synthetic waterproofing chemicals, which would spoil the totally environment-friendly characteristics of such welded joints.

Recently, however, exceptional water resistance, well in excess of 400 days immersion in water, was obtained by adding small amounts of rosin [10] to the weldline. Rosin consists of a mix of a number of sesquiterpenoid acids derived from wood itself [11]. The enhancement in the water resistance of the weldline was obtained both for linear friction welding as well as for dowel rotational welding [12,13]. Rosin is inexpensive and easily commercially available from the pulp and paper industry, melts at about 80°C, is natural and non-toxic hence maintaining environment-friendly characteristics of the joint. Most importantly, it is water repellent, hence it protects the weldline. This development opened the door to the utilisation of wood welded joints for exterior applications [12].

Once a natural oligomer capable of waterproofing the welded interphase had been found the search was on to find possible alternative compounds capable of yielding the same or at least a similar effect. Not many compounds that are naturally-derived, non toxic and that can melt and solidify similarly to rosin exist. However, a compound that showed promise was acetylated lignin. Acetylated lignin is known for quite some time, and so is the method of its preparation [14]. It has the characteristic to be easily prepared and that it melts, although the melting temperature range depends on the type of lignin used and its level of acetylation.

This paper thus deals with (i) the acetylation of either a naturally low molecular mass lignin, namely an organosolv lignin [11] from wheat straw [15], or a kraft wood lignin obtained from the pulp and paper industry and subsequently depolymerized [16,17], and (ii) the use of these two lignins as a waterproofing additive in wood dowel welding.

## **2. Experimental**

The lignins used for acetylation were a wheat straw organosolv lignin of low molecular mass supplied by the Compagnie Industrielle de la Matière Végétale (CIMV), Levallois-Perret, France, a grass organosolv lignin supplied by Granite (Switzerland) and a depolymerized desulfurized organosolv wood lignin supplied by Inventia, Stockholm, Sweden.

### **2.1. Lignin acetylation**

Lignin 100 g were placed in a 50:50 mixture by weight of pyridine and acetic anhydride [14]. The mixture was refluxed at 60-65°C for 8 h and then cooled. The acetylated lignin was then precipitated with ice water, the mix was centrifuged and the acetylated lignin solid was separated from the supernatant residual solution. The acetylated lignin was then washed with cold water five times and separated by centrifugation at every wash. The acetylated lignin was then allowed to air dry at ambient temperature.

### **2.2. MALDI-TOF Sample Preparation**

The lignin samples were dissolved in acetone (4 mg/ml). The sample solutions were mixed with an acetone solution (10 mg/ml in acetone) of the matrix. As the matrix, 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation NaCl was added to the matrix (10mg/ml in water). The solutions of the sample and the matrix were mixed in the proportions three parts by mass matrix solution + three parts polymer solution + one part NaCl solution and 0.5 to 1  $\mu\text{L}$  of the resulting solution mix were placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer. To each peak value in the resulting positive mode spectrum the 23 Da of the  $\text{Na}^+$  of the matrix must be subtracted to obtain the molecular mass of the chemical species.

### **2.3. MALDI-TOF Mass Spectrometry**

The spectra were recorded on a KRATOS Kompact MALDI AXIMA TOF 2 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. Each laser pulse was 3 ns. The measurements were carried out using the following conditions: positive polarity, linear flight path, and high mass (20 kV acceleration voltage), and 100-150 pulses per spectrum. The delayed extraction technique was used by applying delay times of 200-800 ns.

### **2.4. CP-MAS $^{13}\text{C}$ NMR**

The acetylated organosolv lignin was dried before being ground finely for NMR analysis. The hardened lignins were analysed by solid state CP MAS  $^{13}\text{C}$  NMR. Spectra were obtained on a Bruker AVANCE II 400 MHz spectrometer at a frequency of 100.6 MHz and at sample spin of 12 kHz, using a recycling delay of 1s, and contact time of 1 ms. Number of transients was about 15000, and the decoupling field was 78 kHz. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control. The spectra were accurate to 1 ppm. The spectra were run with suppression of spinning side bands so that each peak observed corresponded to a chemical group and no reflected multiple peaks corresponded to any one single group. Only the spectra of the unreacted lignin and of the lignin dried directly at 103°C for 2 hours are reported, as the spectrum of the latter was the same as that of the glyoxalated lignin precipitated by any other method.

### **2.5. Welding**

Rotational dowel welding was done using beech (*Fagus sylvatica*) dowels of 10 mm diameter inserted in pre-drilled holes of 8 mm diameter, with a rotation speed of 1600 rpm as optimised in previous work [4-6]: (a) in the radial direction of single pieces of beech (*Fagus sylvatica*) wood of dimensions 50x50x38 mm<sup>3</sup> and 12% equilibrium moisture content (e.m.c.) up to a depth of 20 mm, and (b) through two pieces of beech wood as defined in previous work [4,5]. The acetylated lignin was dissolved in ethanol and applied on the surface of the dowels by immersing them in the alcoholic 25% solids content solution for a few minutes and then allowed to dry for a few minutes until the layer of deposited lignin was dried. Non-acetylated lignin was used as control but as it was not soluble in an ethanol solution it was added to the joint by wetting the dowel and powdering the surface of the wetted dowel with fine, non-acetylated lignin powder. When the welding was achieved the rotation of the dowel was stopped and the pressure on it was briefly maintained. Welding time was 1.5-2 seconds and holding time after rotation was stopped was 5 s. The dowel and substrate moisture contents were 12%. The substrate was also a block of beech wood. The samples were tested in tension (by pulling the dowel out of the substrate where it had been welded) with an Instron universal testing machine at a displacement rate of 2 mm/s. The samples were tested dry, after 24 hours cold water immersion and after air redrying after the specimens were taken out of the water. Each test value reported was the average of 10 test specimens.

Joints in which the dowel insertion was only of 20 mm were tested because if the dowel is inserted deeper it breaks. In such cases, only the material strength of the dowel was being tested and not the strength of the welded interphase.

## **3. Results and Discussion**



Three different organosolv lignins of low molecular mass were acetylated according to the procedure outlined in the Experimental part. Two of these were straw lignins (one wheat straw lignin) which are naturally of low molecular weight and one a desulfurized depolymerized wood lignin. The two straw lignins gave equal results due to their similarity and thus only the results of one of them are reported. To determine what was obtained by acetylation, the acetylated lignins were analyzed by MALDI-TOF mass spectrometry. The results obtained for two of the lignins so tested are reported in Tables 1 and 2, and Figures 1 and 2. From the values in Figs 1 and 2 of the experimental peaks 23 Da due to the Na<sup>+</sup> residual of the matrix must be subtracted to obtain the molecular mass of the oligomer observed. Thus, the MW of the various fragments involved can be interpreted as follows [11]:

**-COCH<sub>3</sub> = 43 Da**

**C<sub>10</sub>O<sub>2</sub>H<sub>10</sub> = 162 non-acetylated lignin guayacyl unit**

**C<sub>12</sub>O<sub>3</sub>H<sub>13</sub> = 205 acetylated lignin guayacyl unit**

**C<sub>11</sub>O<sub>2</sub>H<sub>11</sub> = 175 acetylated lignin hydroxyphenyl unit (thus minus one -OCH<sub>3</sub> group from the preceding one)**

Table 1. Oligomers distribution of acetylated wheat straw organosolv lignin obtained by MALDI-TOF

Experimental (Da)	Calculated (Da)	Distribution (%)	Oligomer type
318	318	16	175+(94+30)Fragment+23
333.7	335	10	175+1x(94+43)Fragment+23
346.0	347	60	2x162 + 23
355.9	352	43	1x205 + 1x (94+30) Fragment +23
372.1	373	15	2x175 + 23
377.9	373	59	2x175 + 23
403.2	403	15	1x175+1x205+23
408.0	408	100	1x162 + 1x205 (- 1x OH) +23
430.2	433	37	2x205 +23
510.6	509	23	3x162 + 23
608	608	22	1x175 + 2x205 + 23
639.2	638	36	3x205 + 23
810-813	813	13	1x175 + 3x205 + 23
848.1	845	20	4x205 + 23
1056.5	1049	10	5x205 + 23

Table 2. Oligomers distribution of acetylated depolymerized organosolv wood lignin obtained by MALDI-TOF

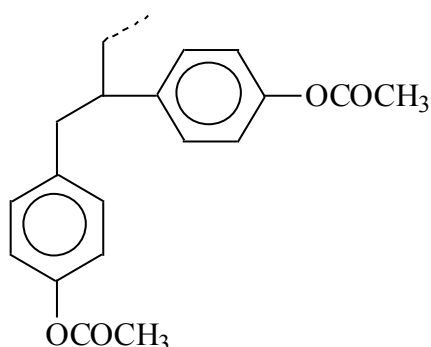
Experimental (Da)	Calculated (Da)	Distribution (%)	Oligomer type
333.5	335	100	175+1x(94+43)Fragment+23
346.0	347	22	2x162 + 23
355.6	352	100	1x205 + 1x (94+30) Fragment +23
377.9	373	76	2x175 + 23
469.6	471	42	2x175 + 1x(94) + 23
671.4	674	42	1x205 + 2x175 + 1x (94) + 23 or 3x205 (+1xCH <sub>2</sub> OH terminal) +23
889.8	891	40	2x205 + 2x175 + 1x (94-CH <sub>3</sub> ) + 23 or 4x205 + (1x -COCH <sub>3</sub> more) + 23
1098.2		5	3x205 + 2x175 + 1x (94-CH <sub>3</sub> ) + 23 or 5x205 + (1x -COCH <sub>3</sub> more) + 23

**94 Da = lignin hydroxyphenyl unit fragment**

**94+30 Da = lignin guayacyl fragment (94+ -OCH<sub>3</sub>) linked on the C $\beta$  of another lignin unit [11]**

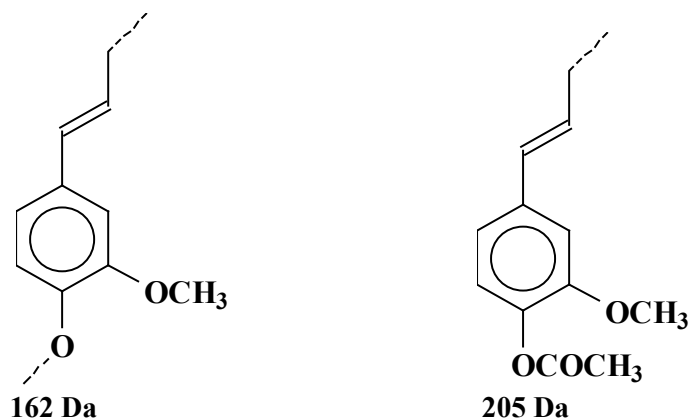
**94+43 Da= acetylated lignin phenyl unit fragment (94+-COCH<sub>3</sub>) on the C $\beta$  of another lignin unit [11]**

The main difference between the results in Figures 1 and 2 and Tables 1 and 2, is that the low molecular weight oligomers of the depolymerized wood (kraft) lignins are more acetylated (333.5, 355.6 and 377.9 Da) than for the wheat straw lignin (highest peak at 408 Da). The two lignins appear to have low molecular masses, with the depolymerized wood lignin having perhaps a slightly lower molecular mass but showing more fragments presumably derived from the depolymerization process it has undergone. The two lignins are very similar. Thus, for example, for both lignins from Tables 1 and 2, the common oligomer at 333.7 Da (calculated 335 Da) has the structure although with different peak intensities and different oligomer relative abundance.

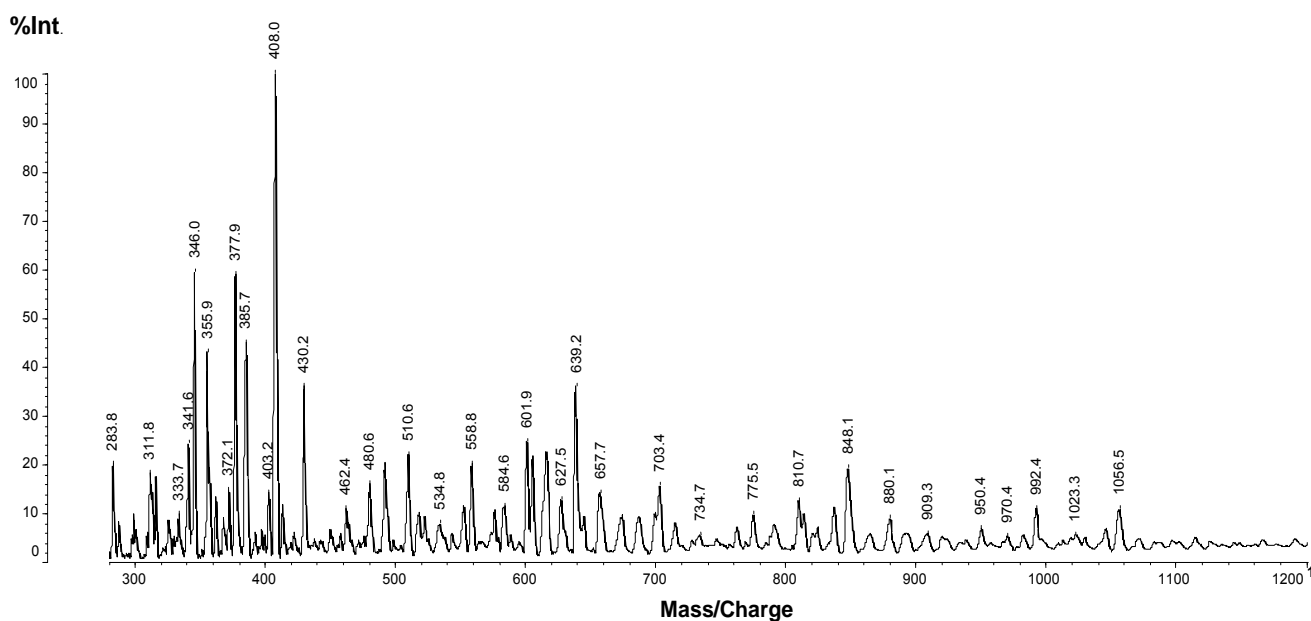


$$312 \text{ Da} + 23 \text{ Da (Na}^+) = 335 \text{ Da}$$

The structures belonging, respectively, to non-acetylated and acetylated lignin units and fragments can be represented as:

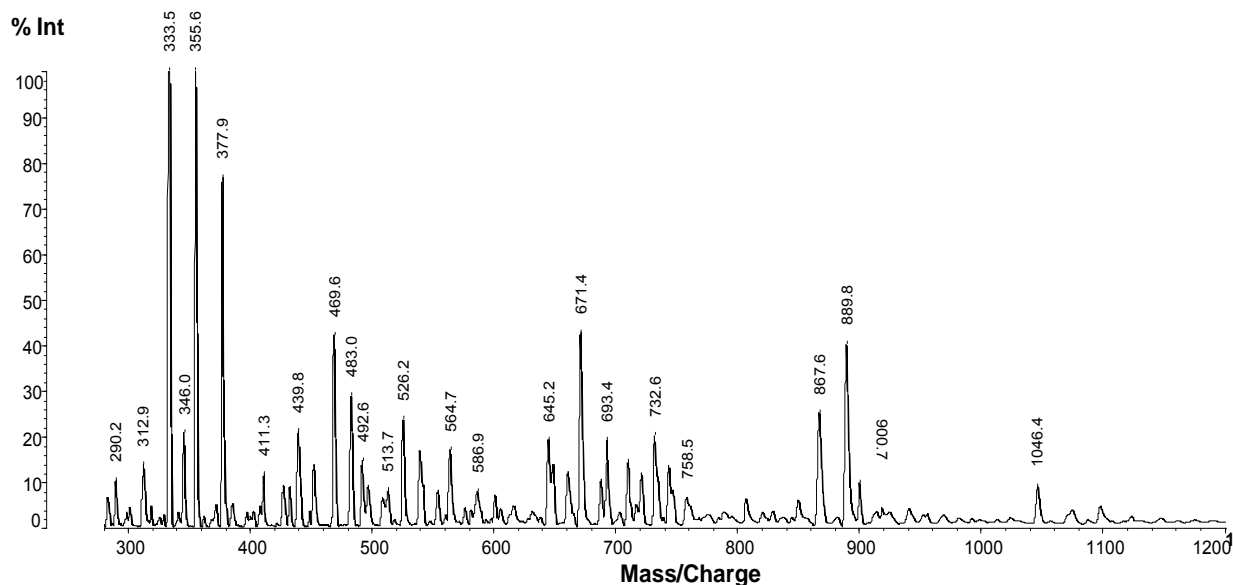


In very pure depolymerized non-sulfur acetylated organosolv wood lignin, there is a series of peaks each separated by 202-210 Da. This indicates clearly the presence of acetylated guayacyl unit in the system. Thus the peak at 889.8 Da is composed of  $4 \times 205$  Da + (plus  $1 \times -\text{COCH}_3$  group more) + 23 Da ( $\text{Na}^+$ ), thus a fully acetylated lignin tetramer [11]. The peak at 671.4 Da is composed of  $3 \times 205$  Da



(+ $1 \times \text{CH}_2\text{OH}$  terminal) + 23 Da ( $\text{Na}^+$ ), hence is a trimer. The peak at 469.6 Da is composed of  $2 \times 75$  Da + ( $1 \times 94$  Da nonacetylated) fragment + 23 Da ( $\text{Na}^+$ ).

**Fig. 1.** MALDI-TOF mass spectrum of acetylated organosolv wheat straw lignin

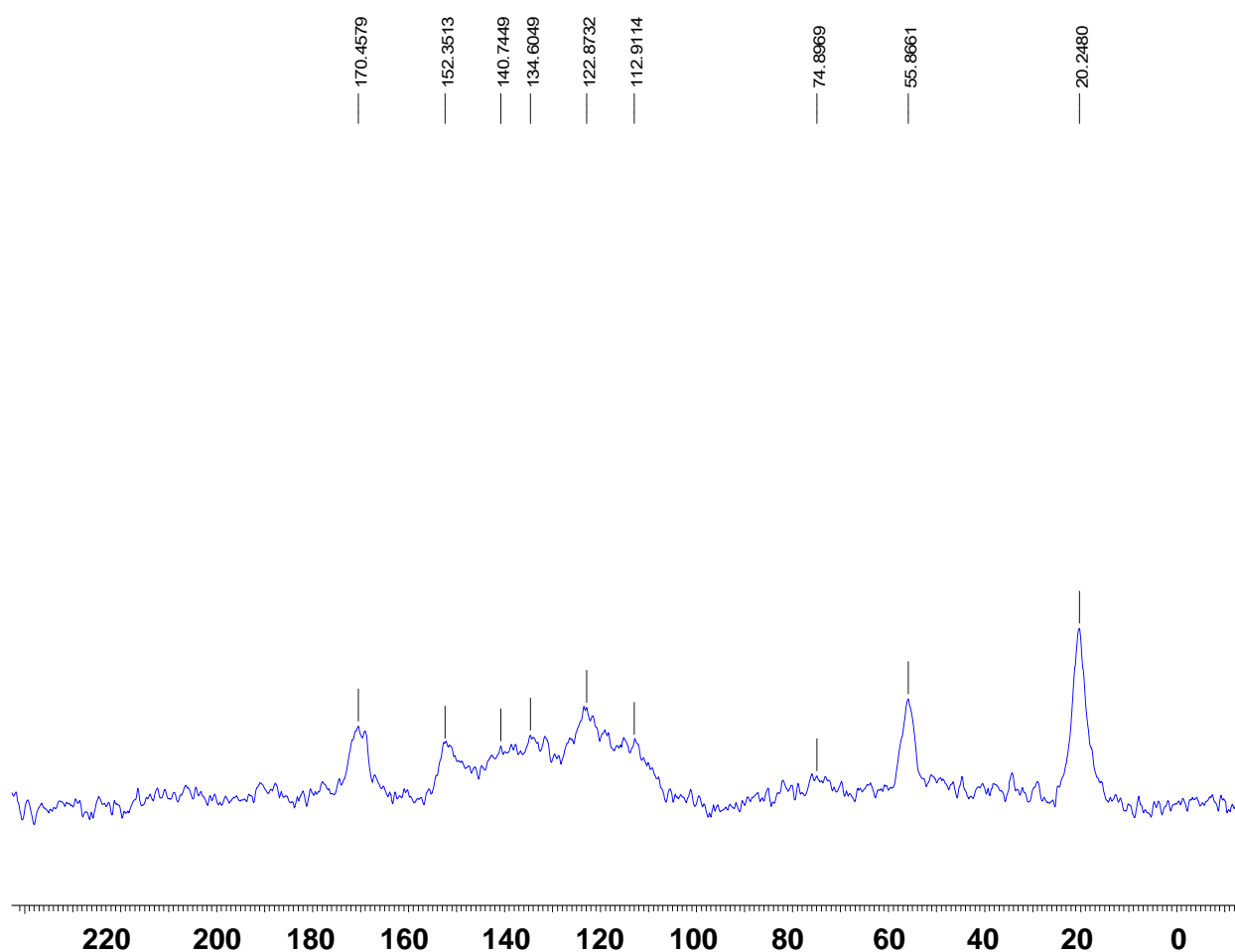


**Fig. 2.** MALDI-TOF mass spectrum of acetylated organosolv wood lignin

The indications are that the depolymerized wood lignins are depolymerized zero-sulphur content organosolv wood lignins while the straw lignins are organosolv wheat straw lignins naturally of low molecular weight. Thus, in Tables 1 and 2 wherever a 94 +43 Da fragment is indicated the oligomer such a fragment belongs is an acetylated oligomer. This is the case for the oligomers at 333, and 355 Da. Equally acetylated are the oligomers where the 175 Da fragment (acetylated lignin hydroxyphenyl unit) appears, hence the peaks at 377, 402-403, and 608 Da. All the oligomers containing the 205 Da group are also acetylated. Thus the acetylated oligomers are in majority in the reaction mix obtained (Tables 1 and 2), and multiacetylated oligomers such as the 639 and 848 Da ones also occur in noticeable quantities (Tables 1 and 2; Figures 1 and 2).

The  $^{13}\text{C}$  NMR spectrum of acetylated wheat straw lignin confirms that extensive acetylation has occurred. Thus the peaks at, respectively, 170 and 20 ppm in Figure 3 indicate the CO of the  $-\text{COCH}_3$  of the phenolic oxygen of the lignin aromatic ring and the  $-\text{CH}_3$  of the acetyl group of acetylated lignin [18]. Proper acetylation is also evident from the 148 ppm and 152 ppm bands, the first representing the aromatic carbon of unsubstituted phenolic groups  $(\text{Ar})\text{C}-\text{OH}$ , and the second the same carbon once the phenolic hydroxygroup has been acetylated, i.e.  $(\text{Ar})\text{C}-\text{OCOCH}_3$  [18]. The prominent 123 ppm band and characteristic of a  $(\text{Aromatic})\text{C}-\text{C}(\text{Aliphatic})$  bond indicates that some substitution on the free sites of the aromatic nuclei of lignin has occurred [18-23]. This coupled with the fairly low intensity of the 112 ppm band indicates that substitution at position 5 of the aromatic nuclei of lignin has occurred

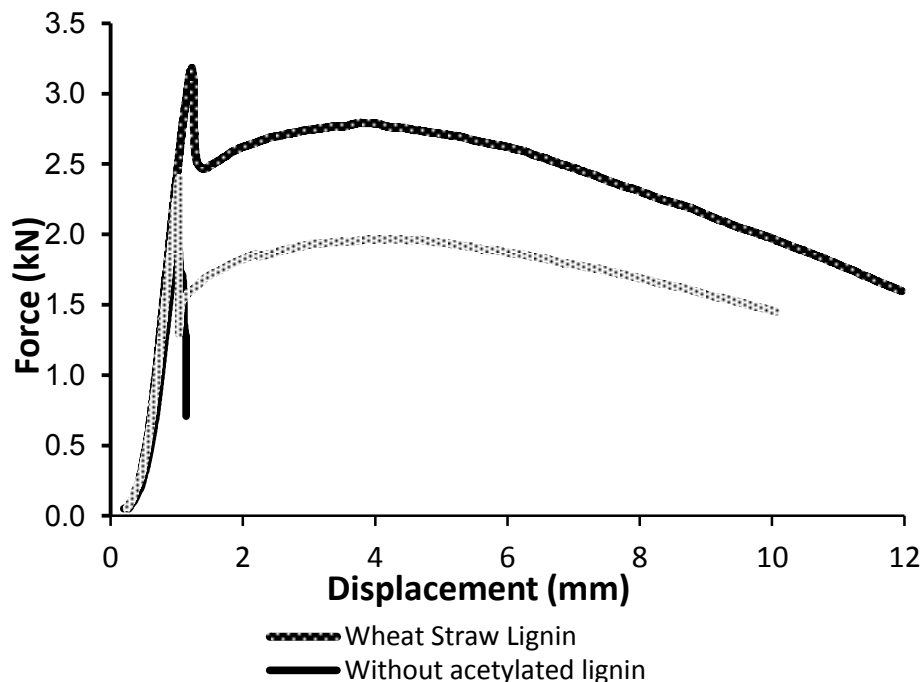
[18]. The relative intensities of these two bands indicate an initial substitution of an acyl group on the aromatic ring of lignin as already reported in other investigations [18-23]. Some low level of substitution on the aromatic ring of lignin can be deduced by the small 138 ppm band indicative of a different type of (Ar)C-C(-O-) grouping than that represented by the 134 ppm band of unaltered lignin [18]. The bands at 74 ppm and 55 ppm are characteristic of the  $-\text{CH}_2\text{OH}$  and methoxy ( $-\text{OCH}_3$ ) groups of all lignins.



**Figure 3.** CP-MAS  $^{13}\text{C}$  NMR spectrum of acetylated organosolv wheat straw lignin

Of interest are the graphs of the force applied as a function of the displacement during testing to welded joints with and without acetylated lignin. In Figure 4 the graphs indicate that for the same force applied to a joint with acetylated lignin yields a much greater displacement than for joints for which acetylated lignin has not been used. Thus, in Figure 4, while for the joint welded with no acetylated lignin a clear breaking force is observed for the two samples with acetylated lignin; the maximum force is a limit at which flowing of the samples subsequently starts. Thus, the former describes a rigid behaviour of the joint while the latter describe a clear ductile behaviour of the welded

joint. Thus, the welded joint without acetylated lignin breaks at 1.8 kN and 1.1 mm displacement, while the joint with acetylated lignin for an applied force of 1.8 kN presents still a displacement of 10 mm for the joint with both acetylated lignins. More interesting is that while the welded joint without acetylated lignin breaks at 1.1 mm displacement, the joints with acetylated lignin show considerable plasticity, deforming more and more as the force continues to be applied (Figure 4) and this without breaking, although at this elongation the joint has lost its functionality. This indicates a plastic joint and a clear ductile behaviour of the weldline contrasting with the rigid weldline behaviour of the joint without lignin. Equally, the maximum resistance of the joints to which acetylated lignin has been added is markedly higher at 2400 and 3200 N in the rigid behaviour part the joint test curves in Figure 4, and of 2500 to 2800 N in the ductile parts of the curve (Figure 4) than for joints where acetylated lignin has not been added at 1800 N (Figure 4). One can only speculate about this behaviour of welded joints with acetylated lignin. Acetylated lignin being thermoplastic creates a mass of entangled but non-cross-linked chains that is intermeshed with the two wood surfaces in the welded interphase. The interphase thus at first has a rigid response to the force applied as can be seen from the sharp peak at the beginning of the graphs in Figure 6, followed by the difference in behaviour that follows. Thus, after the sharp peak the plastic network of the acetylated lignin intermeshed with the welded interphase takes over causing the force vs displacement curve which follows (Figure 4). This behaviour is the same as observed for synthetic thermoplastic wood binder.



**Fig. 4.** Tensile force applied as a function of displacement of welded dowel joints with and without addition of acetylated lignin. Note the break at low displacement of the welded joint without acetylated lignin (rigid behaviour) and the ductile behaviour of the joints welded with the acetylated lignins

In Table 3 are reported the variation of the tensile force (see Experimental for method) applied to welded dowel joints with and without addition of acetylated lignin. In the case of a dowel just welded in a single substrate piece (Figure 5) the results with and without lignin are comparable, with perhaps the joint with acetylated wood lignin appearing to be weaker. This is not the case as the dowel itself breaks. Thus, the force reported in this case has no relation to the weld strength: the only conclusion possible in this case is that the welding is always stronger than the dowel itself. The situation is different for both the force applied to a dry joint of two pieces of wood held together by a welded dowel (Figure 6) and for a dowel welded to a single piece of wood after the joint has undergone water impregnation followed by air drying. For the variation of the force applied to a dry two-piece joint the results indicate that acetylated lignin contributes to the resistance of the joint. Thus acetylated lignin reinforces the weldline (Table 3). From Table 3 the application of non-acetylated lignin results in the same behaviour of welded joints without any lignin, thus application of lignin alone appears to contribute but little to the strength of the joint. This can be attributed to two reasons: (i) lignin alone is not soluble in the alcohol solution as acetylated lignin and thus must be added in powder form with lower effectiveness of application, and (ii) the melting and flowing point of non-acetylated lignin is much higher than that of acetylated lignin, limiting the flow of the material at the temperatures reached. The difference between joints welded with either no lignin or with non-acetylated lignin and joints welded with acetylated lignins is significant. The difference between the joints with the two acetylated lignins is also significant: acetylated wheat straw lignin appears to give better joints than acetylated depolymerized wood lignin. This could correlate with the different distribution in molecular masses observed by MALDI-TOF in Tables 1 and 2 and Figures 1 and 2. Thus, from Figures 1 and 2 it is apparent that the acetylated depolymerized wood lignin has a higher relative proportion of higher molecular mass oligomers. This difference, although small, may influence the temperature of melting and thus the extent of flowing of the acetylated lignin during welding, a relatively higher proportion of higher average molecular mass oligomers will then increase the melting/flowing temperature with relatively lower strength results of the joint. The curves in Figure 6 confirm the results in Table 3, namely that the interphase is held together not only by welding but by a thermoplastic elastic material. This gives to the interphase considerable elongation without breaking of the joint, thus a ductile behaviour. In Table 3 are shown the results of a joint formed by a dowel welded to a single piece of wood after the joint has undergone water impregnation followed by air drying with and without acetylated lignin. The joint without lignin presents a certain residual strength as found and explained in a previous article [7]. The presence of both acetylated organosolv lignins markedly improves the water protection of the joint, especially the wheat straw organosolv lignin, although this improvement does not appear to be as marked as materials previously tested for the same purpose, such as rosin

[10,12,13]. The advantage of acetylated lignin over native lignin of the same molecular mass is likely to be due to their very different melting and flowing temperatures.

Table 3. Tensile strength results of welded dowel joints with and without addition of acetylated lignin.

Joint type	without any lignin (kN)	with non-acetylated wheat lignin (kN)	with wheat straw acetylated lignin (kN)	with depolymerized acetylated wood lignin (kN)
Assembly of two pieces of wood, held by a welded dowel, weld depth = 50 mm	1.97	2.00	2.85	2.74
Dowel welded in a single piece of wood, weld depth = 24 mm	3.98	3.12	3.87	2.99
Dowel welded in a single piece of wood, weld depth = 24 mm after 24 h cold water soaking+ +72 hours air drying	1.84	1.87	2.43	2.22

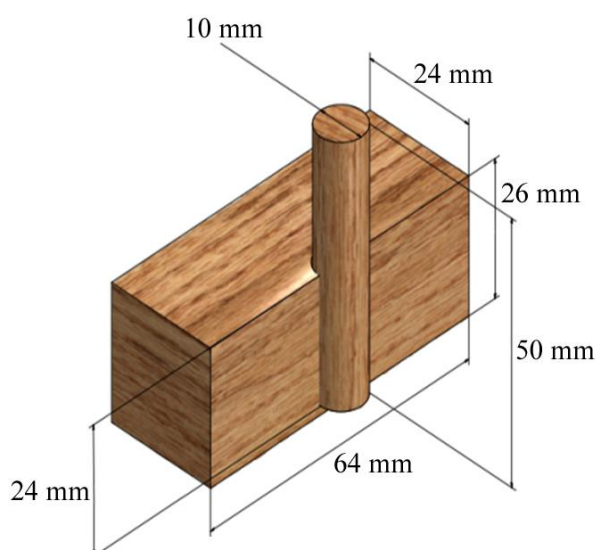
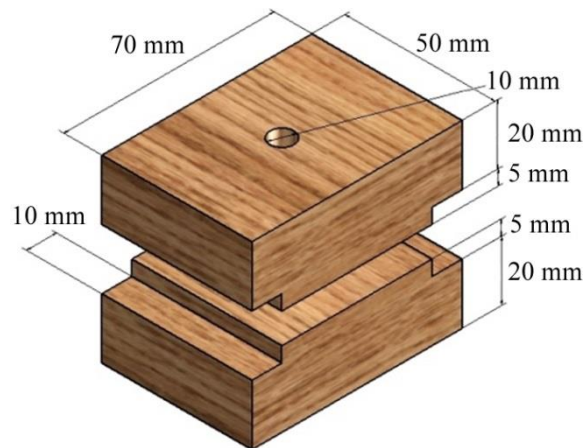


Fig. 5. Design of a joint of a dowel welded to a single piece of wood





**Fig. 6.** Design of a joint of two pieces of wood held together by a welded dowel

#### 4. Conclusion

Low molecular weight acetylated organosolv lignins from wheat straw and from degradation of organosolv wood lignin have been shown to markedly improve both the water resistance and the mechanical performance of welded dowels wood joints. The water resistance obtained for the joints is not as good as obtained previously by rosin addition. The use of a biosourced material such as lignin is environment-friendly but after its acetylation is, however, somewhat less acceptable than the addition of a totally natural material such as rosin. The joints present a ductile behaviour that is absent in the relatively rigid dowel-welded joints both with rosin added or without any additives. Such ductile behaviour appears to be due to an acetylated lignin network interpenetrating the welded interphase. Such a behaviour, less acceptable for exterior structural joints, is nonetheless of interest in other applications, or when a certain extent of plasticity is needed in water-resistant weldlines.

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## 4. Conclusions et perspectives

### *Composition chimique*

La composition chimique du matériau soudé du hêtre et de l'épicéa a été déterminée après une extraction à l'eau par hydrolyse acide. Ceci pour un éventail de temps de soudage adéquat pour les deux espèces, de 1 à 3 s pour du hêtre et de 2 à 12 s pour l'épicéa. Le bilan de masse des composants a montré une tendance à l'augmentation du pourcentage de lignine Klason et à la diminution du pourcentage des hydrates de carbone lorsque le temps de soudage est plus long, ceci pour les deux essences. Une quantité non négligeable du matériau soudé était soluble dans l'eau (jusqu'à 17.7% pour le hêtre soudé et jusqu'à 10% pour l'épicéa soudé), ce qui explique en bonne partie la faible résistance à l'eau des joints soudés. Parmi les extraits à l'eau, de la lignine, de l'acide acétique des mono et oligosaccharides, du lévoglucosane, de la vanilline, du syringaldéhyde, du furfural et du 5-hydroxyméthylfurfural ont été identifiés et quantifiés. Les quantités légèrement supérieures de lignine soluble dans les extraits à l'eau du matériau soudé du hêtre mettent en évidence le caractère plus labile de la lignine syringyle comparés à la lignine guaiacyle pour la dégradation.

La diminution du poids moléculaire de la lignine soluble à l'eau pour des temps de soudage allant en augmentant montre la dépolymérisation de la lignine due au processus de soudage. La dégradation de la lignine est aussi mise en évidence par la présence de vanilline et de syringaldéhyde dans les extraits à l'eau. Cependant non seulement la dépolymérisation mais aussi des réactions de re-polymérisation peuvent probablement simultanément se produire. Des réactions de condensation lignine-lignine ou lignine avec des produits de dégradation des hémicelluloses, i.e. furfural, sont aussi plausibles. Ces réactions expliquent l'accumulation ou la tendance à l'augmentation de la lignine Klason dans le matériau soudé. La dégradation des hémicelluloses est mise en évidence par la présence d'acide acétique, de mono et oligosaccharides, de furfural, de 5-hydroxyméthylfurfural et de lévoglucosane dans les extraits à l'eau.

### *Analyse topochimique du bois soudé*

L'augmentation de l'absorbance UV observé dans la zone soudée du hêtre et d'épicéa à une longueur d'onde de 278 et 280 nm respectivement obtenues par l'analyse UMSP est liée aux

modifications chimiques dans la structure de la lignine par l'effet de la température et de la friction. Le pourcentage en augmentation de la lignine Klason dans la matière soudée pour des temps de soudage plus longs est en accord avec cette augmentation de l'absorbance UV. La plus grande tendance de la lignine guaiacyle à entamer des réactions de condensation est aussi mise en évidence par les hautes valeurs d'absorbance, les larges bandes d'absorption et le décalage vers des longueurs d'onde plus grandes observés dans les spectres UV de la matière soudée de l'épicéa.

La modification graduelle de la lignine à partir de la zone soudée vers les zones plus profondes est aussi observée dans les sections transversales analysées par UMSP et dans les spectres de la paroi secondaire et de la lamelle moyenne des cellules adjacentes à la zone soudée. La modification de la lignine (i.e. une plus haute absorbance UV en comparaison aux valeurs de référence) est exclusivement observée lorsque l'effet combiné de la friction et de la température sont appliquées; si une surface en bois est soumise par conduction sous pression à des températures dans le même éventail que celle du soudage durant une période d'au plus 15 s, aucune modification à la surface n'est observée. Ceci démontre l'importance de la friction et non seulement de la température dans la modification de la lignine et la formation du matériau soudé; et donc cela différencie le processus de soudage de tout autre processus thermique dans lequel seule la température est appliquée (par exemple la pyrolyse). En plus de la modification de la lignine, la densification des cellules plus profondes adjacentes à la zone soudée et la présence de pores dans le matériau soudé sont clairement représentées dans les sections transversales, notamment de l'épicéa soudé analysé par UMSP.

### ***Rapport entre propriétés chimiques et mécaniques***

La composition du matériau soudé influence fortement ses propriétés mécaniques. Des quantités augmentées de lignine Klason (pour des temps de soudage plus longs) impliquent un module de cisaillement plus haut mais aussi des déformations maximales plus basses. C'est-à-dire que le matériau soudé devient plus rigide mais aussi fragile. Cela indique que même si le développement du renforcement du matériau soudé par les réactions de condensation de la lignine pouvait encore continuer à des temps de soudage plus grands, le processus serait limité par la perte d'élasticité générée par la dégradation des composants du bois. L'éventail plus petit de la déformation maximal au cisaillement de l'épicéa soudé comparé à l'éventail correspondant du hêtre soudé est probablement lié à la lignine guaiacyle dans l'épicéa et à sa

plus grande habilité à se réticuler et à former des produits de condensation en comparaison avec la lignine syringyle-guaiacyle présente dans le hêtre. Bien que le temps de soudage devrait être limité au minimum nécessaire pour former un matériau soudé renforcé et éviter une dégradation excessive, il y a une certaine flexibilité pour le choix du temps de soudage puisque la résistance maximale au cisaillement par traction reste pratiquement constante dans un éventail donné de temps de soudage. En contraste avec le module de cisaillement et de la déformation maximale au cisaillement qui sont des propriétés intrinsèques au matériau soudé, la résistance maximale au cisaillement reflète mieux les propriétés locales du joint. En plus de la composition chimique du bois soudé, des défauts locaux (porosité) ont aussi une influence sur les propriétés mécaniques, des analyses dans cette direction seraient donc un bon complément dans la compréhension des propriétés mécaniques.

### ***Soudage du bois densifié***

La résistance au cisaillement de l'épicéa soudé a été améliorée avec succès en utilisant une densification/post-traitement avant le processus de soudage. Le procédé de densification, comme l'indique son nom, permet d'avoir un matériel bois de densité plus élevée que le bois non densifié du départ. La densification est complétée avec un post-traitement en ayant comme finalité la diminution de la mémoire de forme du bois densifié. La résistance au cisaillement du joint d'épicéa densifié/post-traité soudé est 2.4 fois supérieure par rapport à un joint soudé d'épicéa non densifié. Cette amélioration est liée au compactage plus élevé de la ligne de soudure et aux zones de compression locale plus homogènes entre les bois de printemps-printemps et printemps-été dans l'épicéa densifié/post-traité soudé. Aussi, la densité plus haute et le profil de densité plus homogène entre la ligne de soudure et l'épicéa massif densifié sont la raison de cette amélioration. De plus on s'attendrait à une plus grande stabilité des joints soudés de l'épicéa densifié/post-traité en raison de la plus grande stabilité dimensionnelle de l'épicéa massif densifié après post-traitement, par exemple, l'hygro-expansion de l'épicéa massif proche de la ligne de soudure serait attendue à être moindre dans le bois soudé densifié/post-traité par rapport au bois pas densifié mais principalement pas post-traité. La dépolymérisation partielle des hémicelluloses due à la densification/post-traitement n'affecte pas la formation de la ligne de soudure de l'épicéa soudé. En plus des réactions chimiques de repolymérisation i.e. lignine-lignine ou condensation de lignine avec des composants de dégradation des hémicelluloses, essentielles pour la formation de la ligne

de soudure, les propriétés physiques et anatomiques du bois affectent profondément les propriétés mécaniques du joint soudé.

### ***Paramètres de soudage***

D'entre tous les paramètres de soudage, le temps de soudage (temps d'application de la friction) est l'un des plus importants par rapport aux propriétés mécaniques. Par rapport aux aspects pratiques de la technologie de soudage linéaire, tant pour du hêtre que pour l'épicéa il est convenable de parler de fenêtres de paramètres où les résistances maximales (au cisaillement dans ce cas) sont stables. Pour du hêtre ce range correspond à un range de temps de soudage de 2 à 3 s et pour l'épicéa de 8 à 12 s. Des temps de soudage plus courts peuvent impliquer des zones pas totalement soudés, et des temps plus longs peuvent impliquer une dégradation excessive. Ceci, en considérant une pression de soudage de 1.3 - 1.5 MPa, une amplitude de 2.8 - 3 mm, une fréquence de 100 Hz, une pression de maintien de 2 MPa (hêtre) et de 1.5 MPa (épicéa), et un temps de maintien de 5 s (hêtre) et de 40 s (épicéa).

### ***Soudage avec des additives***

L'utilisation de colophane et de lignine CIMV comme additifs avant le processus de soudage linéaire améliore partiellement la résistance à l'eau des joints soudés de hêtre. L'amélioration par l'utilisation de la colophane est expliquée par la faible sensibilité à l'eau et donc par la faible solubilité dans l'eau du matériau soudé. La lignine CIMV est supposée contribuer aux réactions de condensation de la lignine native à l'interface de soudage, améliorant de ce fait l'effet de résistance à l'eau. La résistance à l'eau du joint soudé peut certainement être améliorée et sa solubilité dans l'eau diminuée, cependant éviter les tensions induites par l'hygro-expansion du bois massif est encore un défi. L'hygro-expansion fait référence aux variations dimensionnelles du bois massif dues à l'absorption d'humidité. Dû à la structure et la composition distinctes entre le bois massif et le matériau soudé, une différente absorption d'humidité est plausible, entraînant ainsi des variations dimensionnelles différentes et donc de fortes contraintes mécaniques. Ceci pourrait causer la propagation des défauts dans la ligne de soudure et sa fragilisation. Le faible poids moléculaire des lignines acétylés organosolv de l'épi de blé et de la dégradation des lignines de bois organosolv est connu pour améliorer la résistance à l'eau et les performances mécaniques des joints soudés par tourillon.

## *Perspectives*

Dans l'étude sur la composition chimique du soudage du bois, un grand pourcentage de la matière dissolue à l'eau a été identifié et quantifié, cependant il reste encore de la place pour analyser des extraits à l'eau inconnus, par exemple des sucres anhydres comme le cellobiosane ou d'autres composants comme l'acide formique. Aussi, il serait très intéressant de continuer la recherche concernant la structure chimique des lignines dans les extraits à l'eau. Des études dans l'NMR à l'état liquide pourraient être faites dans ce but. Ceci pourrait donner des informations clés sur les réactions de la lignine durant le soudage. De plus, des études par UMSP du matériau soudé déjà extrait à l'eau pourraient éclaircir la nature des composants du matériau soudé absorbant fortement les UV.

La présence de défauts (porosité) dans la ligne de soudure a été observée par microphotospectroscopie UV et par d'autres méthodes microscopiques, cependant des études plus approfondies seraient nécessaires pour caractériser systématiquement la porosité dans la ligne de soudure en fonction des paramètres de soudage. Sans doute, des méthodes de préparation des échantillons en évitant la formation des fentes est encore un défi. Une méthode prometteuse semble être la microscopie confocale par auto-fluorescence (Rhême 2014); cette méthode donne un très bon contraste entre les fibres détachées, la matrice modifiée et les trous. La caractérisation des défauts (porosité) dans la ligne de soudure permettrait de mieux expliquer les mécanismes de propagation de la fracture et aussi les mécanismes liés à la diffusion d'eau et à la solubilité dans l'eau liquide des joints soudés.

Il serait très intéressant de mener de plus amples recherches sur le soudage de matériau densifié/post-traité pour d'éventuelles futures applications, puisque la combinaison de ces deux technologies pourrait donner des solutions concernant l'homogénéité du bois massif avec des propriétés mécaniques performantes.

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