

**INFLUENCE OF BORON COMPOUNDS IN ADHESIVES
ON THE BONDING QUALITY AND FUNGICIDAL
PROPERTIES OF WOOD**

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ABSTRACT

Recent progress in bonding and wood preservation solves the problems with limited dimensions and insufficient durability of the wooden constructional material. The preservation of glued wood is elucidated in this paper. Through the addition of boric acid to adhesives, we tried to improve the fungicidal properties of glued wood. The results of mechanical testing (shear strength and delamination) showed that the addition of boric acid to glue did not have a negative impact on the performance of the glued wood. On the contrary, some properties were even improved. Unfortunately, the addition of boric acid to impregnated wood does not improve the resistance of the glued wood to brown rot fungi.

KEYWORDS: Adhesive, boric acid, delamination, diffusion, shear strength, wood.

INTRODUCTION

Despite the best efforts a protection of the wooden structural composites is a still open problem to improve the durability of these elements exposed to outdoor conditions.

There have been several attempts to improve the durability of glued wood. The easiest and the most frequently applied procedure is surface treatment, such as brushing or spraying the glued composites. The surface treatment of glued wood is not sufficient, since only the outside

layer of the wood is protected, and the major part of the wood remains untreated (Walker et al. 1993). Unfortunately, impregnation procedures are not feasible for glued wood, since glued woods are difficult to impregnate, and impregnation can also result in shrinking, swelling and unwanted cracking of the wood or adhesive bond lines. One of the most promising techniques for the treatment of glued wood, particularly glued laminated beams is supercritical impregnation (Morrell et al. 2005). Under supercritical conditions, substances can diffuse through solids like a gas, and dissolve materials like a liquid. Additionally, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties to be "tuned". Supercritical fluids are very suitable as a substitute for organic solvents. Of various chemicals, carbon dioxide is the most commonly used supercritical fluid for the impregnation of wood. Unfortunately, there is only one supercritical plant operating, since this process is currently fairly expensive compared to traditional treatments (Kjellow and Henriksen 2009).

There have also been parallel attempts to impregnate wood before bonding with adhesives (Janowiak et al. 1992). However, there is a technical problem, since most glued laminated wood production processes require the lamellas to be planed prior to bonding in order to achieve good contact between the lamellas in the process of bonding. Therefore it does not make sense to impregnate lamellas and then remove a significant portion of the protective layer with planning. Thus, in our research it was decided to include biocides in the adhesive and merge two phases: bonding and preservation. Boric acid was chosen as a model biocide, since it is one of the few remaining diffusible biocides since implementation of the Biocidal Products Directive (Köse et al. 2009). Boron compounds are prone to diffuse from places with a higher concentration to those with lower concentrations, if the moisture content of wood exceeds 22 % (Morell et al. 1992). Secondly, boric acid is a very effective fungicide and insecticide, even at relatively low concentrations. An important advantage of boric acid is its water solubility and general environmental sensitivity (Drysdale 1994, Baysal et al. 2006). However, some boron compounds have recently been classified as toxic for reproduction in Europe (Directive 2008/58/EC, 2008), which will presumably influence their use in wood preservation.

MATERIAL AND METHODS

Material

The experiments were performed on Norway spruce (*Picea abies* L. Karst.) wood of an average density of $450 \pm 100 \text{ kg}\cdot\text{m}^{-3}$. This material was chosen because Norway spruce is the most important wood for construction in our region. The dimensions of the lamellas were 105(t) \times 35(r) \times 900 mm(l). The lamellas were conditioned at a relative humidity (RH) of 65 % and a temperature (T) of 20°C for one month.

Two types of adhesives were used for bonding: melamine-urea formaldehyde (MUF) (Akzo Nobel) and polyurethane (PUR) (H.B. Fuller, ICEMA R 145/12). Boric acid (Merck) was added to the adhesive mixture to achieve two different final concentrations of boron: 0.5 % and 0.1 %.

Bonding of the wood

Prior to bonding two lamellas together, the surface layer of each lamella was removed by planning. The adhesive mixture was applied uniformly to the surface of one lamella using a roller at an application rate of $200 \pm 50 \text{ g}\cdot\text{m}^{-2}$. Pressing was carried out at room temperature ($20 \pm 2^\circ\text{C}$) for 2 hours at a specific pressure of about 0.5 MPa. After pressing, two layered samples were conditioned in a standard climate (RH = 65 %, T = 20°C) until testing.

Shear test of the bond line

The shear test of the bond line was performed according to the standard EN 392: 1995 on specimens with a nominal size of 40 (t) × 70 (r) × 40 mm (l), which were cut out of the bonded assemblies. Twenty-four specimens for each adhesive mixture were tested. The specimens were tested “dry” (conditioned in the standard climate). Shear strength (f_v) was determined from the equation:

$$f_v = k \frac{F_v}{A}$$

where: k is the modification factor ($k = 0,78 + 0,0044 t$), t is the specimen thickness (mm), F_v is the shear force applied (N), and A is the cross sectional area (mm^2).

The shear test was carried out with a ZWICK/Z100 universal testing machine.

Delamination of the bond line

The delamination test of the bond line was conducted according to the EN 391: 2001 on specimens with a nominal size of 80 (t) × 70 (r) × 75 mm (l). Four specimens for each adhesive mixture were tested. The delamination test cycle used method B, subsection 6.4.4 of the EN 391: 2001 standard.

Determination of diffusion

Two types of specimens were prepared from the bonded assemblies, 10 (t) × 70 (r) × 20 mm (l) (type A) and 3 (t) × 50 (r) × 25 mm (l) (type B), for the diffusion test. These specimens were conditioned in a chamber with RH = 100 % and T = 25°C, since preliminary experiments showed that the diffusion of boron is fairly slow with wood conditioned at a lower relative humidity. The boron diffusion was monitored occasionally over the course of a 14-week period. In order to visualize the boron in the wood, a color spot reagent was used. Comparison of two components: a saturated solution of salicylic acid in an ethanol (70 %) and HCl (30 %) mixture was performed. The second component was ethanol extract of curcuma (*Curcuma* sp.). In the presence of boron, the wood is colored red, while the untreated part remained yellow (Theden and Kottlors 1965).

In the second part, type B specimens were used. They were conditioned for 0, 7 and 14 days in a chamber with a relative humidity of 100 % and temperature of 25°C. The diffusion of the boron from the adhesive bond line was determined by means of laser ablation sampling (solid-state Nd: YAG laser, model UP 213 A/F, New Wave Research) in conjunction with inductively coupled plasma–mass spectrometric detection (octopole reaction system ICP–MS 7500 ce&cs, Agilent Technologies). Since wood is a fairly inhomogeneous material, it is difficult to prepare a calibration curve. The concentration of boron was therefore expressed in arbitrary units.

A 213 nm laser was operated at 20 Hz with a typical fluence of 2.5 J.cm⁻² and spot size of 100 μm. A scan speed of 500 μm.s⁻¹ was used. A 0.9 L.min⁻¹ flow of helium carrier gas was used to entrain sample aerosols from the ablation cell to the plasma torch. The optimal operation conditions for ICP–MS, determined by the NIST 612 glass standard, were a plasma gas flow rate of 13 L.min⁻¹, auxiliary gas flow rate of 0.85 L.min⁻¹ and RF power of 1500 W. Ion intensities of ¹¹B⁺ were acquired in the time resolved analysis (TRA) mode. An ablation line in the middle of the specimens was chosen. It started 2 mm below and stopped 25 mm above the adhesive bond line. Prior to ablation, the surface of the specimens was cleaned with pre-ablation.

Fungicidal properties

Fungicidal properties were determined according to a modified EN 113: 2002 procedure. Specimens of 10 (t) × 30 (r) × 40 mm (l) (the adhesive bond line was in the middle of the specimens 15 mm from the tangential plane) were exposed to three brown rot fungi: *Gloeophyllum trabeum* (ZIM L017), *Antrodia vaillantii* (ZIM L037) and *Serpula lacrymans* (ZIM L057). Brown rot fungi were chosen since they predominately degrade softwoods and glued wood in indoor applications. Steam sterilized specimens were placed in jars with overgrown nutrient medium above a plastic net for 16 weeks, according to the EN 113: 2002 protocol. After the period of exposure, the specimens were isolated and weight loss was determined gravimetrically.

RESULTS AND DISCUSSION

The shear strength, percentage of wood failure and delamination of the wood specimens bonded with the MUF and PUR adhesive mixtures are shown in Tab. 1. The shear strength was highest for pure MUF adhesive (8.65 N.mm⁻²) and dropped slightly in specimens that were bonded with MUF adhesives containing boron compounds, but this reduction was not significant. On the other hand, the percentage of wood failure increased from 83 % (MUF) to 95 % for both MUF adhesives containing boron. Delamination was 0 % for all MUF adhesive mixtures. It can be concluded that the inclusion of boric acid compounds in the MUF adhesive did not significantly affect the bonding quality. In terms of performance requirements for glued laminated timber (EN 386: 2001), all the specimens bonded with MUF adhesive mixtures fulfilled the requirements.

Tab. 1: Shear strength, amount of wood failure, and delamination of adhesive bond lines.

Adhesive mixture	Shear strength (N.mm ⁻²)	Wood failure (%)	Total delamination (%)	Maximum delamination (%)
MUF	8.65	83	0	0
MUF c _B = 0.5 %	8.07	95	0	0
MUF c _B = 0.1 %	7.71	95	0	0
PUR	7.37	74	9.8	13.1
PUR c _B = 0.5 %	7.54	80	2.4	4.8
PUR c _B = 0.1 %	7.93	75	1.2	2.4

Specimens bonded with PUR adhesive exhibited shear strength of 7.37 N.mm⁻² and 74 % of wood failure. The inclusion of boron in the PUR adhesive increased both the shear strength and the percentage of wood failure, but the difference was not significant. Total delamination was high for specimens bonded with pure PUR adhesive (9.8 %) but was significantly reduced for specimens bonded with PUR adhesive containing boron. The improvement of the bonding quality of PUR adhesives containing boron can be ascribed to crystal water in the boron acid, which promotes curing. It is known that PUR adhesives react with water molecules (particularly with OH groups) during the curing process (Marra 1992). In terms of performance requirements for glued laminated timber (EN 386: 2001), the specimens bonded with pure PUR adhesive did not fulfil the requirements, whereas both PUR adhesive mixtures containing boron were satisfactory.

The object of the second part of the research was to investigate whether boron remained in the adhesive bond line or whether it diffused from the adhesive bond line to the wood. In order to elucidate this issue, two sets of experiments were performed. In the first, the boron concentration was determined using a color spot reagent. This is a very sensitive and reliable technique (Grell et al. 1994). The results showed that there is virtually no boron diffusion with wood conditioned in a chamber with a relative humidity of 88 %. The moisture content of the wood was obviously too low. This is in line with statements in the literature, that boron diffusion starts when the wood moisture content exceeds 20 % (Morell et al. 1990). Considerably more prominent diffusion from the adhesive bond line was observed with specimens conditioned in a chamber with a relative humidity of 100 %. However, the concentration of boron in lamellas prepared with adhesives in which 0.1 % of boron added to the adhesive mixture, was too low to be monitored with color reagents (Fig. 1 A). On the other hand, the concentration of boron in wooden lamellas bonded with adhesives with the highest concentration of boron was sufficient to be monitored using color spot reagent. The first signs of diffusion were observed after the second day of observation. The boron had diffused approximately 1 mm from the adhesive bond line. The boron diffusion increases fairly fast during the process of conditioning. After 13 days of conditioning, the boron diffused approximately 4 mm from the adhesive bond line (Fig. 1 A). However, it must be taken into account that boron diffusion was monitored on the surface of the wooden specimens. The surface has higher moisture content in the process of conditioning than the inner part of the specimens, so it can be assumed that the moisture content in the center of the specimens was lower, and consequently the boron diffusion was also slower. Furthermore, visual observation showed that the pattern of boron diffusion was also influenced by other parameters, one of which is growth rings. Annual rings form a barrier that slows down boron diffusion in wood. Darker/denser late wood slows down boron diffusion more than lighter/light late wood.

In the second step, diffusion was additionally monitored with a more accurate technique. The surface layer was laser-ablated and analyzed with ICP-MS. From the results presented in Fig. 1 B, it is clearly evident that the boron concentration in the control wood was fairly low. The most interesting concentration gradient was observed in specimens that had not been conditioned in a chamber with high humidity. It is clear that the concentration of boron in the adhesive bond line or close to the adhesive bond line is considerably higher than in untreated specimens. Secondly, from the concentration gradient in the unconditioned specimens it can be seen that the boron diffuses from the adhesive bond line in the process of bonding. However, after 12 days of conditioning the specimens in a chamber with RH of 100 %, there was almost equal distribution of boron determined in the area 10 mm from the adhesive bond line. The boron concentration thereafter decreased and almost reached the background level 25 mm from the glue line. Comparable results were observed in spruce wood bonded with MUF and PUR based adhesives. This is clear evidence of increased boron diffusion with high moisture contents. It can be concluded that none of the adhesives used immobilized the boron in the adhesive bond line. The boron remained mobile and began diffusing from the adhesive bond line during the process of bonding, but boron diffusion became particularly notable in a moist environment.

The last question related to the addition of boron to the adhesives was how the addition of boron influences wood decay fungi. Mass losses of the control specimens, bonded with adhesives without biocides, varied between 25 % (*A. vaillantii*, PUR) and 54 % (*S. lacrymans*, MUF). This clearly showed that the fungal strains were vital and that the used wood was susceptible to fungal decay. The adhesive itself has an insignificant influence on decay fungi.

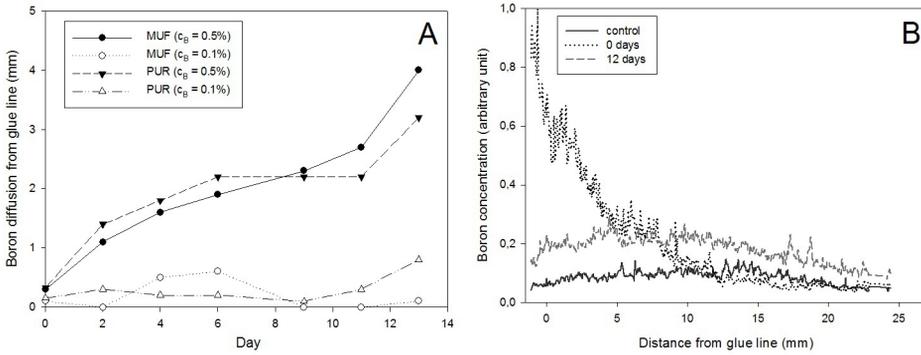


Fig. 1: Influence of time on boron diffusion from glue line to wooden lamellas (A), concentration gradient of boron in wooden lamellas at the beginning and after 12 days of conditioning in a humid environment (B).

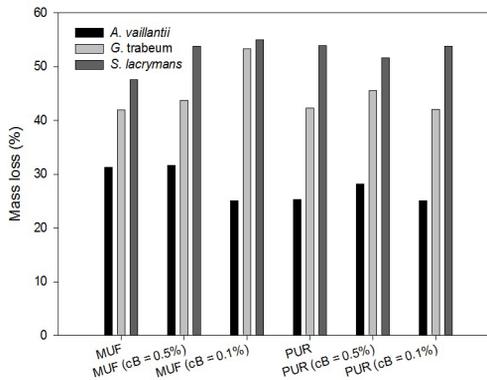


Fig. 2: Mass loss of glued wooden specimens after 16 weeks of exposure to wood decay fungi in terms of type of glue used.

However, as can be seen from Fig. 2, the concentration of boron added to the adhesive was not sufficient to protect the wood against fungal decay. Mass losses of the wooden lamellas bonded with adhesive enriched with boron were comparable to the control ones. It seems that the wood volume to adhesive bond line ratio was too high to achieve sufficient protection against fungal decay. It is therefore believed that the proposed technique is not suitable for protection of glued laminated beams but for the production of plywood or OSB, for example. This issue needs to be addressed in future studies.

CONCLUSIONS

The inclusion of boron compounds in the MUF adhesive did not significantly affect the bonding quality. In terms of performance requirements for glued laminated timber, all the specimens bonded with MUF adhesive mixtures fulfilled the standard requirements. The

inclusion of boron in PUR adhesive increased both the shear strength and the percentage of wood failure but the difference was not significant. The total delamination was high for specimens bonded with pure PUR adhesive but was significantly reduced for specimens bonded with PUR adhesive containing boron. The specimens bonded with pure PUR adhesive did not fulfil the standard requirements, whereas both PUR adhesive mixtures containing boron were satisfactory. The concentration of boron in the adhesive bond line was not sufficient to protect spruce wood against wood decay fungi. The mass loss of specimens made of bonded wood in which the adhesive was supplemented with boron was comparable to the mass loss of the control specimens. It is assumed that a considerably better effect would be achieved with thinner lamellas or veneers.

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