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Comparative adhesion analysis at glue joints in European beech and Norway spruce wood by means of nanoindentation

Samuel Ammann [a,*], Michael Obersriebnig [b], Johannes Konnerth [b], Wolfgang Gindl-Altmutter [b], Peter Niemz [a]

[a] Institute for Building Materials, Department of Civil, Environmental and Geomatic Engineering, ETH Zurich, Zurich, Switzerland
[b] Institute of Wood Technology and Renewable Resources, Department of Material Sciences and Process Engineering, University of Natural Resources and Life Sciences, Vienna, Austria

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ABSTRACT

To gain a better insight into the delamination behaviour of glue joints in hardwood, the adhesion at the cell wall level was investigated. By the use of nanoindentation techniques, the adhesion, hardness and Young's modulus of adhesively bonded European beech wood (*Fagus silvatica* L.) was analysed. To highlight differences between soft- and hardwood adherends, Norway spruce wood (*Picea abies* KARST.) was also investigated. One-component polyurethane (PUR) and phenol resorcinol formaldehyde resin (PRF) were used for bonding. Untreated and aged samples (artificially and naturally weathered) were analysed and compared to silylated samples as reference, assuming the silylation reduces the adhesion to a minimum. From the gathered results it can be concluded that artificial ageing has the same effect as natural weathering on, both, adhesion and the properties of the single components of a bond. In beech wood, weathering increases the adhesion of PUR significantly. For PUR in spruce wood, the adhesion is not affected by any treatment. Tensile shear tests signified a reduced adhesion in all silylated samples. Additionally, the stiffness and hardness of both adhesives were found to be reduced by approximately 10%. As a consequence, the applied silylation is not considered as adequate treatment for reference samples.

1. Introduction

Reinforcing softwood timber constructions locally with hardwood components, or hardwood constructions generally, can improve the competitiveness of timber designs compared to those made of steel or concrete. To safely estimate the durability of such structures it is essential to understand possible failure mechanisms. In hardwood elements, the critical zones normally are the glue joints. Delamination is a potential consequence if the glue joints are not designed properly.

In Europe the standard delamination test for glued-laminated timber is specified in DIN EN 391 [1]. Basically, short glulam elements are soaked in water under alternating vacuum and high pressure and then dried afterwards in a warm and dry air current. This procedure was developed for softwood and has proven its validity. Hardwood elements however barely pass this test because of their high modulus of elasticity (MOE, E) combined with high shrinkage and swelling coefficients [2]. Moreover, adhesive systems are generally designed for use with softwoods and thus might not be suitable for the demands of hardwoods. The vessel network in beech wood for example may lead to starved glue joints, if adhesives are not properly adapted to hardwood applications [3].

In general, standards have to be feasible and cannot claim to be realistic or scientific. Hence the testing method DIN EN 391 [1] is not suitable for hardwood elements, whether they are manufactured properly or not. Firstly the mechanisms of the wood adhesive system have to be investigated based on their basic behaviour in order to later be able to assess the durability of adhesively bonded hardwood elements. Nanoindentation (NI) is a technique that allows investigating one fundamental mechanism of adhesive bonding: the adhesion at the interface of the wood cell wall and the adhesive at the micron scale level [4].

2. Materials and methods

2.1. Sample preparation

Before sample preparation the wood was stored at standard atmospheric conditions (20 °C and 65% relative humidity) until

* Correspondence to: Institute for Building Materials, Department of Civil, Environmental and Geomatic Engineering, ETH Zurich, HIF E 27, Schafmattstrasse 6, 8093 Zürich, Switzerland. Tel.: +41 44 6337156.
E-mail address: ammanns@ethz.ch (S. Ammann).

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equilibrium moisture content was reached. After each procedure step, the samples were again stored at standard atmosphere.

To emphasise differences between adhesively bonded hard- and softwood, one prominent species of each was analysed. Adhesive bonds were manufactured according to the requirements indicated in DIN EN 302-1 [5] for lap-joint specimens. Therefore, boards of European beech (*Fagus silvatica* L., density: 635 kg/m^3 at standard atmospheric conditions) and Norway spruce (*Picea abies* KARST., density: 435 kg/m^3 at standard atmospheric conditions) wood were planed with sharp blades to a thickness of 5 mm. For all boards, the annual ring angle was between 60° and 90°. Adhesives were applied directly after planing and processed according to the manufacturers′ guidelines. The adhesives used were one-component polyurethane (1C PUR) and phenol resorcinol formaldehyde (PRF) resin. The 1C PUR (HB S 309) was provided by Purbond AG, Sempach-Station, Switzerland. The applied PRF (Aerodux 185, hardener 180) was provided by Dynea AS, Lillestrøm, Norway.

Samples of approximately 2 mm × 2 mm × 2 mm containing the glue line were cut out of the bonded boards. After embedding the samples in epoxy under vacuum, they were attached to the NI sample holders and the surface was prepared with a Leica ultramicrotome using a histo diamond knife. Details regarding the specimen preparation procedure can be found in Konnerth et al. [6]. The cutting direction was perpendicular to the wood fibres, parallel to the glue joint.

2.2. Artificial and natural weathering

Samples were available from PUR bonded beech boards that were directly exposed to the weather for a period of 45 months (February 2009 to November 2012). These boards were prepared as described in Section 2.1. The weathering took place on a flat roof in Zurich, Switzerland. To avoid standing water on the wood, the samples were inclined by 45°, facing south.

For quick ageing simulations, the procedures from DIN EN 302-1 [5] Table 1 can also be applied. Kläusler et al. [7,8] found a significant increase in tensile strength of flawless 1C PUR films after A5 treatment according to DIN EN 302-1 [5]. For PUR glue joints in beech wood they found that the shear strength after A5 treatment is at the same level as the untreated reference (A1). For this reason, A5 treated samples were also investigated here to compare the artificial with the natural weathering and highlight possible differences and changes in the mechanical behaviour of 1C PUR.

2.3. Silylation

By the silylation of wood, the hydroxyl groups react with silanes [25], resulting in an increased hydrophobicity of the wood surface. Half of the boards were silylated after planing to reduce wettability with water and, consequently, also with adhesives of polar character. Such samples were intended to serve as references for the zero adhesion (see Section 2.4). Based on results from Obersriebnig et al. [9], the silylation was adapted from Mohammed-Ziegler et al. [10]. For the silylation treatment, samples were kept first in a 1 vol% n-hexane solution of Trichloro(octadecyl)silane (CAS no. 112-04-9) under continuous stirring for 1 h, rinsed afterwards with pure n-hexane and then air-dried. This procedure was repeated with a 1 vol% n-hexane solution of chlorotrimethylsilane (CAS no. 75-77-4). After these silylation steps the sample preparation continued as described in Section 2.1.

Table 1
Tensile shear strengths of the glue joints with corresponding confidence intervals and wood failure percentages.

	τ_u [MPa]	Wood failure [%]	n [–]
Spruce	10.98 ± 1.40	100	15
Spruce silylated	5.01 ± 1.26	0	5
Beech	12.80 ± 1.30	≥ 90	8
Beech silylated	1.02 ± 0.93	0	5

2.4. Testing methodology

The NI experiments were conducted according to the procedure proposed by Obersriebnig et al. [4] and performed on the Hysitron TI 900 Triboindenter. A force controlled function was used for the material characterisation with a single loading increment (400 μN) and unloading after a holding time of 5 s. Four indents (uniformly distributed around the lumen, see Fig. 1) were performed per analysed wood cell wall to avoid artefacts due to varying angles between the microfibrils and the indenter tip, as observed by Konnerth et al. [11]. Hardness (H) and MOE of the wood cell wall and adhesive were measured with a Berkovich-type tip with a total opening angle of 142.3°. The experimental data was evaluated according to Oliver and Pharr [12]

$$E = \frac{S}{2}\left(\frac{\pi}{A}\right)^{1/2}$$

$$H = \frac{F_{max}}{A}$$

wherein S is the unloading stiffness, A is the contact area of the indentation tip and F_{max} indicates the maximum force.

The adhesion between adhesive and wood cell wall was investigated by directly placing the indentation spots at the interface. The interface at the third layer of the secondary cell wall was investigated, either directly at the glue joint or inside adhesive filled lumen (see Fig. 2). A cone shaped diamond tip with an opening angle of 60° and a tip radius of approximately 10 nm was used in combination with a four-step displacement controlled load function (see Fig. 3). This load function was found to work best for this type of experimental setup by Obersriebnig et al. [4] and was thus adapted. The total indentation work W_I, i.e. integrating force over displacement, at the interface was taken as a measure for the adhesion. Silylated samples served as references, assuming the silylation reduces the adhesion to a minimum (see Section 2.3) [9]. The difference between regular and silylated samples should therefore indicate the energy needed to overcome the adhesion force (see Fig. 5 for example). The validity of the assumption can be assessed on the macroscopic scale with ordinary tensile shear tests according to DIN EN 302-1 [5]. A significant reduction in shear strength together with a significant

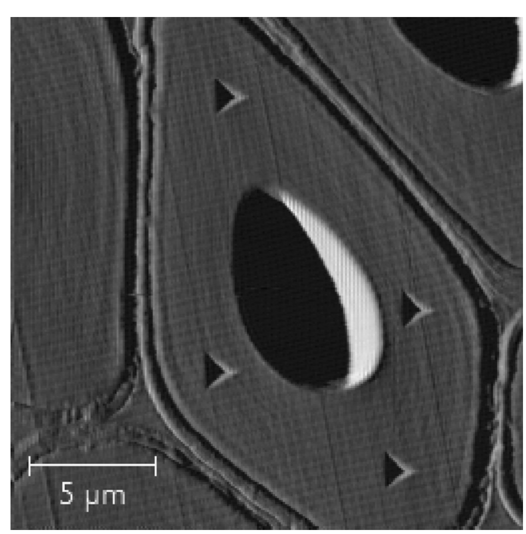

Fig. 1. Indentation spots in the wood cell wall (beech).