Cent. Eur. For. J. 69 (2023) 120–125 sciendo DOI: 10.2478/forj-2023-0009
CENTRAL EUROPEAN Forestry Journal

ORIGINAL PAPER

The effect of chemical modification of the surface of the glued surface on the strength of the structural joint of oak wood

Lukáš Sahula, Přemysl Šedivka*, Tadeáš Zachara, Vlastimil Borůvka

Czech University of Life Sciences Prague, Faculty of Forestry and Wood Sciences, Kamýcká 129, CZ-16500 Praha 6 – Suchdol, Czech Republic

Abstract
As a result of climate change, the species structure of forest stands is gradually changing when the growing share of core species of deciduous trees at the expense of conifers places demands on its future efficient processing into final products. This study evaluates the influence of the surface modification of the heartwood of oak (*Quercus robur*) with five selected chemical modifiers on the strength of the glued joint with the used one-component PUR adhesive for interior and exterior structural applications. Samples of test bodies produced according to the standards were exposed to the given environment and subsequently subjected to a test using the method of determining the longitudinal shear strength under tensile stress. By applying a chemical modification to the surface layers of the glued surfaces of oak wood, the tannins in the surface layers were neutralized, increasing the adhesion of the glued surface. The resulting values of the strength of the glued joints with the applied chemical modification of the heartwood surface also confirmed this.

Key words: adhesive; oak; chemical modification; glued joint; strength

Editor: Tomáš Gergeľ

1. Introduction

Due to the increase in average temperatures and the uneven distribution of annual rainfall averages, spruce forest stands are dying in Central Europe due to bark beetle infestation (Yadav & Kumar 2021; Nardi et al. 2022). The absence of spruce wood on the market for processing into final products due to the bark beetle calamity and the gradual change in the species structure of forest stands more resistant to climate changes in the future. Selected species of deciduous trees can potentially replace it. Hardwood is already commonly used in a range of final products (Krackler et al. 2011). Oak wood is attractive as a structural application for the exterior due to the advantageous ratio of mechanical properties for structural timber and natural resistance when exposed to the cover. Thanks to its high density and cell structure, it has beneficial strength properties. Thanks to the high content of tannins in the oak wood core, it is highly resistant to degradation by biotic and abiotic factors. However, the disadvantage is the low pH, from 6.3 to 7.0, of tannins and other extractive substances in the core (Terrasse et al. 2021), which eliminates the strength of the glued joint or completely prevents the hardening of the glued joint when applied in the glued laminated timber program.

There are many types of wood surface modification before gluing. The effect of the mechanical unevenness of the surface of plywood panels before gluing on the strength of the glued joint was discussed by Aydin (2004), and the study shows that the smaller the surface roughness after the sanding process before gluing, the higher the strength of the glued joint. Bongers et al. (2016) focused on gluing wood for non-structural applications with a chemically modified wood surface by acetylation. During delamination tests, the increased strength of the glued joint was proven for acetylated wood. The study by Klébert et al. (2022) mentions the possibility of increasing the adhesion of the wood surface by plasma modification, while the effectiveness of this type of surface modification depends on the type of gas used and the plasma system while treating the surface with plasma can increase its adhesion. Still, this procedure is technologically and cost-intensive compared to chemical modification. In a study by Tymyk et al. (2013), the positive

*Corresponding author. Přemysl Šedivka, e-mail: sedivka@fld.czu.cz, phone: +420 2 24 38 37 79
© 2023 Authors. This is an open access article under the CC BY 4.0 license.

effect of chemical change of the surface of veneers with the chemical modification agent hydrogen peroxide on the increase of surface adhesion was demonstrated.

The study focuses on the influence of chemical modification of the oak heartwood surface before gluing to increase adhesion and the strength of the glued joint to produce the supporting lamella program for the interior and exterior. The high tannin content eliminates the degradation of core wood (fungi, mushrooms, decaying wood insects) and abiotic factors (UV radiation, frost, rain, dust particles), so this wood is suitable for exterior exposure (Zahri et al. 2007; Sivrikaya et al. 2009; Oberhofner et al. 2019).

2. Material and methods

2.1. Types of modification and adhesive

They have tested a total of five types of chemical modifications, three principles based, and two esters, which are primarily developed for other applications or are basic chemicals. The parameters of the changes tested are listed in Table 1. The adhesive used for testing is one-component polyurethane adhesive (PUR), developed for gluing the load-bearing structural wood, specified in Table 2.

Table 1. Tested chemical modifiers.

Sign.	Type of chemical modifier	Formula	Concentration [%]	CAS registration number
1.	Aqueous solution of hydrogen peroxide	H_2O_2	3.0	7722-84-1
2.	Aqueous solution of potassium hydroxide	$KOH \cdot H_2O$	2.0	1310-58-3
3.	Aqueous solution of ammonium hydroxide	$NH_3 \cdot H_2O$	5.0	1336-21-6
4.	Tetrachlorethylene	C_2Cl_4	100	127-18-4
5.	Hydrochloric acid	HCl	2.5	7647-01-0
6.	Reference without modifier	—	0.0	—

Table 2. Type of adhesive.

Adhesive parameters	Type of PUR adhesive
Adhesive resistance class	D3
Chemical composition	Polyol (1,500–2,000 g/mol) (432.0 g) + catalyst (1.4 g) + polyisocyanate (566.6 g)
Application quantity [g m^2] (glue applied to both adherends)	120 – 200
Viscosity by +20 °C [mPas]	7,900 ±1,000**
Minimum process temperature [°C]	+ 6
Open time [min]	10 – 15
Application wood moisture [%]	10 – 12
Pressing pressure [N mm^2]	min. 0.5
Density [g cm^3]	1.04
Pressing time at 20 °C of the glued joint [min]	minimum 60*

* The pressing time of the tested samples was 6 h;
** The Brookfield method was used to determine the viscosity.

Wood samples

Test bodies for implementing experiments were made of oak wood according to the procedure defined by ČSN EN 302-1 (2013). Twelve test specimens were produced for each measured group so that a minimum of 10 valid measurements were always achieved. So a total of 144 test bodies were to complete 120 valuable measures. Testing boards were made of strong, unread, conditioned prying plates, first dried naturally and then dried artificially of oak wood (*Quercus robur*) with straight fibres with a nominal density of 680 ±50 g and humidity 12 ±1% (Fig. 1). The angle between the annual rings and the surface of the slat was between 30° and 90°. The slats were conditioned for seven days under standard conditions, i.e. in our case, at a temperature of 20 ±2 °C and a relative air humidity of 65 ±5% so that the wood moisture was maintained at 12 ±1%. On the surfaces intended for gluing, the given modifier was applied with a deposit of 110 ±10 g m^2 using a brush so that the modifier penetrated at least to a depth of 1.0 mm from the top surface of the wood lamella. After that, the slats were again conditioned for seven days under standard conditions at a temperature of 20 ±2 °C and relative humidity of 65 ±5% so that after the application of the modifying agent, the moisture content of the wood was equalized again to a value of 12 ±1%.

In order to achieve the ideal roughness of flatness and roughness, the surfaces intended for adhesive application were subsequently sanded with sandpaper in order to eliminate protruding wood fibres, which occurred due to an increase in the moisture of the fibres on the surface after the application of the given modifier. This re-sanding has always been practised a maximum of 30 minutes before the gluing process in order to eliminate the re-emergence of wood fibres in the surface layers due to surface exposure to the environment, due to which the volume of wood fibres could change again due to the surrounding higher air humidity.

In the next phase, an adhesive with a coating of 200 ±10 g m^2 was applied to both glued surfaces with a brush. For seven days until the adhesive has completely cured and the glued joints are glued. Subsequently, the glued slats were formatted to the final dimension of the test bodies (Fig. 2). As part of the tests to determine the longitudinal shear strength under tensile stress, two exposures and conditioning of test specimens were chosen, namely exposure type A1 and A5 (ČSN EN 302-1) (Table 3).

Table 3. Exposure time and type of environment for testing test specimens.

Designation	Exposure type and type of environment
A1	Air-condition the glued wood samples for 7 days at 20 ± 2 °C and 65 ±5%. Then testing of the samples in a dry state.
A5	Boil in water for 6 hours. For 2 hours in water of 20 ±5 °C. Air-condition the glued wood samples for 7 days at 20 ±2 °C and 65 ±5%. Then testing of the samples in a dry state.

Source: ČSN EN 302-1.



Fig. 1. Oak wood lamellas for the production of test specimens.

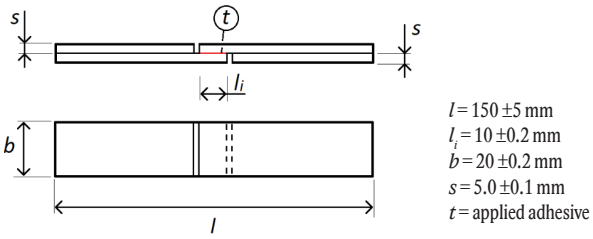


Fig. 2. Test specimens made of oak wood.

For the test to determine the longitudinal shear strength under tensile stress, the test device of the universal test tearing machine type TIRA test 2850 (manufactured by TIRA GmbH, Germany) with feed was used (Fig. 3). The test samples were fastened at both ends to the jaws of the universal tear-off machine of 45 ±5 mm. Finally, they were burdened with tensile strength until its violation, and the highest developed F_{max} force in Newton (N) was recorded. The feed rate of the tensile testing machine was offered at 5 mm min.

Wood pH estimation

To determine the pH values of the heartwood and sapwood surface of oak with and without chemical surface modifiers, a direct contact method was chosen using the combined pH electrode for surface measurement SenTix Sur (WTW Wissenschaftlich GmbH, Germany). The measurement procedure is determined according to the standard STN 50 0374. The testing is based on the measurement of pH values on the surface of a wood sample moistened with one drop of water or the modified surface of an oak wood sample with a given chemical modifier moistened with one drop of the given chemical modifier when applying a planar combined electrode. For each sample, the pH was measured with a ten-fold repetition.

3. Results

3.1. Values of pH

The pH values in the surface layers of chemically modified surfaces before gluing oak wood were determined using the direct contact method (Fig. 4), while the positive effect of the modification was demonstrated when applying Aqueous solution of hydrogen peroxide (H_2O_2) with a concentration of 3.0%, Aqueous solution of potassium hydroxide ($KOH \cdot H_2O$) with a concentration of 2.0% and Aqueous solution of ammonium hydroxide ($NH_3 \cdot H_2O$) with a concentration of 5.0%, when the pH was increased above 7.0 and thus the tannins in the surface layers were neutralized.

On the contrary, the modifiers Tetrachlorethylene (C_2Cl_4) with a concentration of 100% and Hydrochloric acid (HCl) with a concentration of 2.5% compared to the reference sample with an unmodified surface of the glued surfaces of oak wood show either slight or no neutralization, respectively the pH of the surface is still below 7.0 in the acidic environment. If the PUR adhesive has a pH above 7.0, strong covalent bonds will not form between the wood surface and the adhesive. The results of measured pH values in the surface layers of oak wood were processed and evaluated by the statistical method of one-way analysis of variance (ANOVA) of Statistica 12 software (StatSoft Inc., USA).

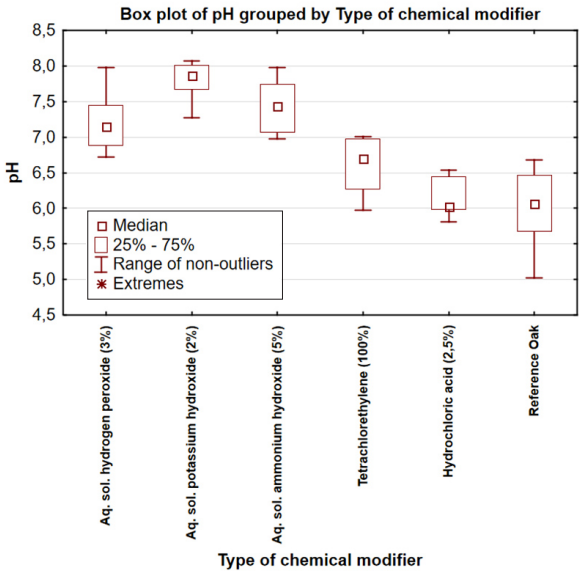


Fig. 3. Determined values of chemically modified oak wood surface before gluing.

3.2. Expression of strength results according to ČSN EN 302-1

The measurement determined the ultimate longitudinal shear strength under tensile stress of the glued joint when the test specimens were exposed to environments of type A1 and A5 (ČSN EN 302-1). The strength of the glued joint (τ) is expressed in MPa and calculated according to Eq. 1:

$$\tau = \frac{F_{max}}{l_2 \cdot b} \quad [1]$$

where F_{max} is the ultimate force in Newtons (N), l_2 is the length of the bonded test surface in millimetres (mm), and b is the width of the related test surface in millimetres (mm).



Fig. 4. Test to determine the longitudinal shear strength under tensile stress.

In the case of air-conditioning of glued joint samples in environment A1, the highest shear strength under tensile stress was achieved when the surface was treated with an aqueous solution of potassium hydroxide ($KOH \cdot H_2O$) with a concentration of 2.0% and an aqueous solution of ammonium hydroxide ($NH_3 \cdot H_2O$) with a concentration of 5.0%, i.e. 10.3–10.5 MPa (Fig. 5). These basic modifiers neutralized the pH of tannins in the surface layers of heartwood above pH 7.0, and thus a large number of covalent bonds were formed during the interaction of the surface area of the oak heartwood with the applied polyurethane adhesive, which has a pH above 7.0, i.e. it is basic. This resulted in an increase in the adhesion of the oak wood surface and spatial cross-linking of the glue with the glued oak wood surface. A less strong bond is shown by the connection where the surface of the oak wood was modified with Aqueous solution of hydrogen peroxide with a concentration of 3.0%. On the contrary, the lowest strength values are shown by the glued joint, in which tetrachorethylene (C_2Cl_4) with a concentration of 100% and hydrochloric acid (HCl) with a concentration of 2.5% were used as modifiers, which modified the pH of the oak heartwood surface below 7.0. In the case of application of tetrachorethylene (C_2Cl_4), only partial neutralization of the modifications occurs, in the case of application of hydrochloric acid (HCl), neutralization of the surface did not occur at all (Fig. 4). This eliminated the formation of chemical bonds and the quality of the crosslinking of the PUR adhesive and the surface of the heartwood of the oak, therefore the strength of the glued joint is lower.

In the case of exposure of samples of glued joints before the test to determine the ultimate longitudinal shear strength under tensile stress to the A5 environment, the highest strength was achieved when the surface was treated with Aqueous solution of ammonium hydroxide ($NH_3 \cdot H_2O$) with a concentration of 5.0%, while the surface modified showed lower strength Aqueous solution of potassium hydroxide ($KOH \cdot H_2O$) with a concentration of 2.0%.

The results of the measured values of the ultimate longitudinal shear strength under tensile stress of the glued joint of oak wood were processed and evaluated by the statistical method of one-way analysis of variance (ANOVA) of the Statistica 12 software (StatSoft Inc., USA).

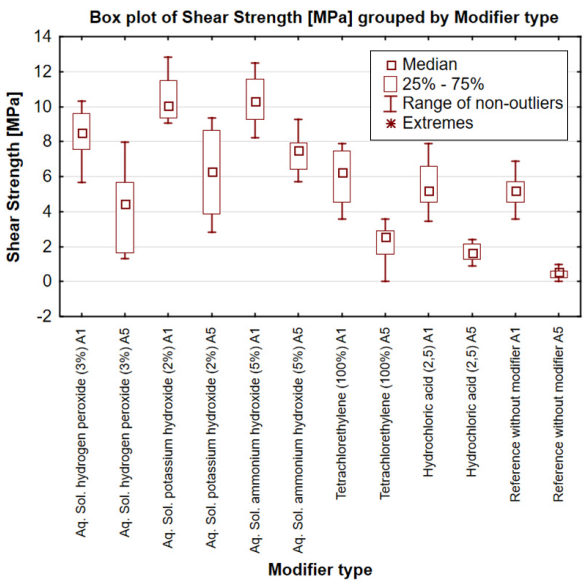


Fig. 5. Shear strength under tensile stress.

4. Discussion

Demands for the future increase in the volume of felling of deciduous wood species for structural applications due to global climate change impose requirements on the development of effective gluing systems to achieve glued joints with load-bearing capacity according to valid standards while requiring technological, economic and environmental sustainability. The solution of surface chemical modification can be an effective solution for achieving the required strength parameters of structural glued joints of deciduous wood species.

In the case of use aqueous solution of potassium hydroxide ($KOH \cdot H_2O$) with a concentration of 2.0% and an aqueous solution of ammonium hydroxide ($NH_3 \cdot H_2O$) with a concentration of 5.0% as surface modifiers was achieved the highest shear strength under tensile stress. According to the study by Blasi et al. 2009, potassium hydroxide ($KOH \cdot H_2O$) even at low concentrations of 0.2–0.6% dissolves part of furfuryl alcohol, some saccharides (3-ethyl-2-hydroxy-2-cyclopentenone, 3-methyl-2-cyclopentenone, 1-hydroxy-2-butanone) and phenols (phenol, cresols, hydroquinone, guaiacol, isoeugenol-trans, isoeugenol-cis, 4-acetoneguaiacol, 4-ethylguaiacol). At the same time, the binding of hydrogen bridges in the surface layers of the wood to the adhesive increases. According to the study by Stanciu et al. (2020) is Ammonium hydroxide (NH_3) causes a hydrolytic reaction, during which not only the neutralization and partial leaching of tannins from the surface layers of the core part of the core wood species occurs, according to a study by Albano et al. (2022) also the partial hydrolysis of hemicellulose chains and a slight decrease in the crystallinity of cellulose in the surface layers with the formation of a larger number of free hydrogen bridges of cellulose, which are binding for the applied adhesive.

The chemical modification of the surface of the wood Aqueous solution of hydrogen peroxide ($KOH \cdot H_2O$) with a concentration of 3.0% showed an unexpectedly lower strength of the glued joint, which may be caused by the partial oxidation of hydrogen peroxide in the surface layers of the heartwood, while the fiber structure is disturbed and thus to reduce the compact flatness of the wood surface and thereby reduce adhesion (Xie et al. 2010). Tetrachlorethylene (C_2Cl_4) with a concentration of 100% and Hydrochloric acid (HCl) with a concentration of 2.5% are acidic and lead to esterification of the surface layers, when the surface of the wood is constantly acidic below pH 7.0, i.e. the surface layers of the core will not be neutralized wood and the PUR-based adhesive repels the surface of the wood (Rowell 2021).

5. Conclusions

Research has shown an increase in the strength of the glued joint when the surface of the glued surfaces of oak wood is modified with an aqueous solution of potassium hydroxide ($KOH \cdot H_2O$) with a concentration of 2.0% and ammonium hydroxide ($NH_3 \cdot H_2O$) with a concentration of 5.0%, namely 10.3–10.5 MPa (Fig. 4) compared to the surface without chemical modification. The reason was an icrease of the pH on the surface of the glued surfaces of the oak heartwood above the value of 7.0, which resulted in the neutralization of the tannins contained in the surface layer of the wood and better interaction with the polyurethane adhesive used.

Acknowledgements

The research was carried out as part of the project entitled "Optimization of wood core surface adhesion to increase the strength of the glued joint", no. A_04_22 of the program of the Internal Grant Agency of the Faculty of Forestry and Wood, Czech University of Life Sciences in Prague.

References

Albano, M., Comelli, D., Fiocco, G., Mattonai, M., Lucejko, J. J., Zoia, L. et al., 2022: Chemical modification of wood induced by the traditional making procedures of bowed string musical instruments: the effect of alkaline treatments. Heritage Science, 10:1–12.

Aydin, I., 2004: Activation of wood surfaces for glue bonds by mechanical pre-treatment and its effects on some properties of veneer surfaces and plywood panels. Applied Surface Science, 233:268–274.

Blasi, C. D., Galgano, A., Branca, C., 2009: Effects of potassium hydroxide impregnation on wood pyrolysis. Energy Fuels, 23:1045–1054.

Bongers, F., Meijerink, T., Lütkemeier, B., Lankveld, C., Alexander, J., Militz, H. et al., 2016: Bonding of acetylated wood. International Wood Product Journal, 2016:102–106.

Klébert, S., Mohai, M., Csiszár, E., 2022: Can plasma surface treatment replace traditional wood modification methods? Coatings, 12:1–20.

Krackler, V., Keunecke, D., Niemz, P., Hurst, A., 2011: Possible fields of hardwood application. Wood Research, 56:125–136.

Nardi, D., Jactel, H., Pagot, E., Samalens, J. Ch., Marini, L., 2022: Drought and stand susceptibility to attacks by the European spruce bark beetle: A remote sensing approach. Agricultural Forest Entomology, 2022:1–11.

Oberhofnerová, E., Šimůnková, K., Dvořák, O., Štěrbová, I., Hiziroglu, S., Šedivka, P. et al., 2019: Comparison of exterior coating applied to oak wood as a function of natural and artificial weathering exposure. Coatings, 9:1–15.

Rowell, R. M., 2021: Chemical modification. In: Handbook of wood chemistry and wood composites. Boca Raton: CRC Press LLC, p. 35–74.

Sivrikaya, H., Hafizoglu, H., Yasav, A., Aydemir, D., 2009: Natural weathering of oak (*Quercus petrae*) and Chestnut (*Castanea sativa*) coated with various finishes. Color Research and Application, 36:72–78.

Stanciu, M. D., Sova, D., Savin, A., Ilias, N., Gorbacheva, G. A., 2020: Physical and mechanical properties of ammonia-treated black locust wood. Polymers, 12:1–17.

Terrasse, F., Brancheriau, L., Marchal, R., Boutahar, N., Lotte, S., Guibal, D. et al., 2021: Density, extractives and decay resistance variabilities within branch wood from four agroforestry hardwood species. Biogeosciences and Forestry, 14:212–220.

Tymyk, D., Bekhta, P., Sedliačik, J., 2013: The effect of chemical modification of wood veneer surfaces on their bondability. Forestry and Wood Technology, 81:269–273.

Xie, Y., Xiao, Z., Goodell, B., Jellison, J., Militz, H., Mai, C., 2010: Degradation of wood veneers by Fenton's reagents: Effects of wood constituents and low molecular weight phenolic compounds on hydrogen peroxide decomposition and wood tensile strength loss. Holzforschung, 64:375–383.

Yadav, R., Kumar, J., 2021: Engineered wood products as a sustainable construction material: A review. Engineered Wood Products for Construction, p. 1–112.

Zahri, S., Belloncle, C., Charrier, F., Pardon, P., Quideau, S., Charrier, B., 2007: UV light impact on ellagitannins and wood surface color of European oak (*Quercus petraea* and *Quercus robur*). Applied Surface Science, 253:4985–4989.

Other sources

ČSN EN 302-1 Lepidla pro nosné dřevěné konstrukce. Zkušební metody. Část 1: Stanovení podélné smykové pevnosti lepeného spoje. 2013 Úřad pro technickou normalizaci. (In Czech).

STN 50 0374 Testing of pulp and paper. Surface pH measurement of paper and pulp. 1996 Úrad pre normalizáciu, metrológiu a skúšobníctvo SR.