Assessment of Thermo-treated Bonded Wood Performance: Comparisons among Norway Spruce, Common Ash, and Turkey Oak

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Polyvinyl acetate (PVA) exhibits fine adhesion qualities when bonded to wood. However, when using thermo-treated wood, a number of different unstudied factors (such as the water stress condition) influence the wood bonding effectiveness. The main goal of this study was to evaluate how different treatments affect the shear bonding strength for three cases of thermo-vacuum treated woods. Wood from both Norway spruce (*Picea abies* Karst.) and common ash (*Fraxinus excelsior* L.) was thermo-treated at 190 °C for two hours under vacuum conditions (250 mbar). Turkey oak (*Quercus cerris* L.) logs were separately steamed at 110 °C for 24 h, then thermo-vacuum treated at 160 °C for three hours. The bonding shear strength between the PVA adhesive and treated wood was evaluated using water stress condition. The results were compared with the adhesive bond line properties of the untreated wood. The shear strength and wettability of the produced material were measured. Tests for the shear resistance, performed in accordance with the standard DIN EN 204, revealed dissimilar behavior as well as the influence of treatment schedules for the different wood species. Consequently, the tests performed allowed a detailed characterization of the effect of the thermo-vacuum process on the bonding quality of three common woods in different water stress conditions.

Keywords: Wettability; DIN EN 204; Shear strength; Thermo-vacuum

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INTRODUCTION

Thermo-treated wood is a new generation of wood material. It is well known that by using heat and steam, without the addition of any chemical additives, it is possible to improve the properties of the material, resulting in a new and environmentally friendly material. The cumulative results of the different studies indicate modifications in the dimensional stability, surface hardness, durability, and mechanical properties (Korkut and Hiziroglu 2009). Esteves and Pereira conducted research on the advantages and drawbacks of using different thermal methods on wood materials (2009). The modification of wood via induced heat can affect several characteristics, such as the resistance and bonding performance of wood (Mirzaei *et al.* 2012).

Adhesives are commonplace in the wood industry, as more than 70% of wood products utilize some form of an adhesive (Zhao *et al.* 2011). Additionally, hydro-thermal treated wood needs to be glued for certain applications. The DIN EN 204 standard classifies thermoplastic resin based wood adhesives that will be used for non-structural applications into durability classes. The classes range from D1 to D4 based on the dry and wet strengths of the bond-lines measured under specified conditions after various conditioning treatments. The adhesives described in this standard are suitable for the bonding of furniture and interior structures, paneling, doors, windows, and stairs that are made of wood or derived timber products.

Polyvinyl acetate (PVA) is widely used in wood processing because of its low cost and effective polymerization under normal pressure. Even though it is difficult to make generalizations regarding the properties of polyvinyl acetate, for Jaffe *et al.* (1990) the balance of strength and flexibility makes it an ideal adhesive for wood materials in many different conditions. However, certain problems, such as the adhesive's propensity to sharply decrease the bond strength under hot and humid conditions, limit its application (Zhao *et al.* 2011). Currently, no conclusive results have been obtained regarding the performance of thermo-treated wood after external adhesive application (Hill 2007). On testing thermo-treated glulam specimens bonded using PVAc adhesive, Bengtsson *et al*. (2003) highlighted extremely poor performance, with a large number of glulam beams failing in the delamination test.

Norway spruce and common ash woods are commonly used for building and indoor applications. The two species were selected based on their commercial interest in the European market, as modified solid wood products with improved performances. The last of the three species, Turkey oak, is a poorly investigated material (Todaro *et al*. 2012). It is widely distributed in Southeastern Europe; however, its relatively poor dimensional stability, elevated internal tensions, and a low durability tend to detract from its use. In addition, gluing issues (Lavisci *et al.* 1991), stain, and a typically unattractive color surface (Tolvaj and Molnár 2006), essentially limits the use of Turkey oak to firewood. Some recent investigations on the thermal treatment of Turkey oak under a vacuum demonstrated the influence of a pre-steaming treatment on the final quality of the thermo-treated Turkey oak boards (Ferrari *et al.* 2013a).

The aim of this research is to study the influence of thermal-vacuum treatment on the moisture content (MC), pH, wettability, and shear strength, for both the wood and bond-lines of three wood species: Norway spruce (*Picea abies* Karst.), common ash (*Fraxinus excelsior* L.), and Turkey oak (*Quercus cerris* L.).

For this study, the null hypothesis stated that there would be differences between the shear strength of treated and untreated wood, for each of the three species. It was also hypothesized that the exposition of wood samples to the water stress condition (DIN EN 204) would induce a strong decrease in the shear strength along the bonded line for a given species.

EXPERIMENTAL

Wood Material

Six sawn boards (32 mm × 150 mm × 1000 mm, having initial moisture content around 20%) of ash and spruce were randomly disposed in a stack, and they were treated together. Meanwhile, turkey oak boards were 40 mm × 150 mm × 1000 mm.

In order to minimize the wood variability, all of the wood properties were measured and compared by matched samples cut from the same board 2 m long, which was initially sawn into two parts, *i.e.* a treated and untreated control piece. Three boards for each treatment and for each wood species were sampled from different parts of the stack for the characterization tests.

Drying and Thermo Vacuum Processes

The thermo-vacuum plant used for the test, as described by Ferrari *et al.* (2013b), was a semi-industrial prototype with an internal diameter of 1.7 m, modified to perform thermo-vacuum treatments at high temperature (up to 250 °C). During the wood's exposure to the vacuum, the heat from the hot walls was conventionally transferred to wood by means of a high efficiency fan (diameter 500 mm) with external motors as well as a mechanical vacuum-proof and temperature-resistant transmission. The fan speed was proportional to the internal air pressure, ranging from 635 rpm at atmospheric pressure, to a maximum speed of 1930 rpm at a vacuum pressure of 250 mbar. A water ring type pump, equipped with a heat exchanger, provided the vacuum. An oil-air heat exchanger unit assisted during the cooling procedure. The temperatures of the oil, air, and wood core were measured by means of thermocouples.

The thermo-vacuum treatments of spruce and ash woods were applied to boards after they were dried to a moisture content (MC) of 0%. The drying process was carried out at low temperatures, and the vacuum conditions were created in the same cylinder where the thermo-vacuum treatment later took place. Each thermo-vacuum treatment consisted of a heating phase that started at 100 °C and maximized at the air temperature set value (190 °C); a thermal treatment phase at a constant air temperature (190 °C) and a defined duration (2 hours); and a three hour cooling phase that decreased the wood's temperature to 100 °C. A heating rate of 12°C/hour was selected for control of the air temperature setting.

In the case of Turkey oak, the logs were initially steamed at 110 °C for 24 h, and then cut into 32-mm-thick boards. The steamed boards were then subjected to drying and thermal modification under low-pressure conditions (250 mbar) in a thermo-vacuum cylinder. Finally, the wood was dried until its MC was 0%, and then the dried wood was thermally treated at 160 °C for 3 h.

Bonding

Three boards, one for each glued specimen, were assembled in accordance with the standard DIN 68602/EN 204, and to the specifications of the adhesive manufacturer (Table 1). The sample sets were planed to a thickness of 20 mm, then bonded together (three layers) into small samples, as shown in Fig. 1. Polyvinyl acetate (PVA), mixed with the additive hexamethylene diisocyanate, was used as an adhesive. Some of the advantages of the adhesive are its good adhesion to different surfaces, its high molecular weight at low viscosity, and its relatively low cost.

The adhesive was applied at the rate of 180 g/m^2 on a double bonding surface of boards. The glues were spread uniformly on the board samples surface by a machine, with plates at 60 °C. Then samples were exposed to pressure of 50 bar for 20 min, at 20 °C. The samples were tested after being subjected to 8 weeks of conditioning at 20 ± 2 °C and 65 ± 3% relative humidity. After conditioning, the specimens from the glued boards were cut as reported in Fig. 1.

A total of 540 samples was used, (2 treatments for each wood species, 3 sequences (Seq.), and 30 replications). In addition, another 180 samples, equally divided among species and treatments, were used to measure the non- bonded wood specimens' strength.

Table 1. Adhesive Specification and Conditioning Sequence, According to DIN EN 204

Adhesive	Density (23 °C) (g/cm^3) (ISO8962)	Viscosity mPa s (ISO2555)	Rupture load (kg/ cm^2) (DIN68602/EN204)	pH
Polyvinyl acetate + Hexamethylene diisocyanate	1	9000-15000 + 3000	1100	2.8-3.6
Conditioning			Kind and duration	
Seq. 1 (D4-1)			7 days in standard atmosphere	
Seq. 3 (D4-4)			7 days in standard atmosphere and 4 days in cold water (20 °C)	
Seq. 5 (D4-5)			7 days in stand atm., 6 h in hot water (60 °C), 2 h in cold water (20 °C)	

Experimental Tests

The moisture content (MC) of each specimen was determined using the gravimetric method.

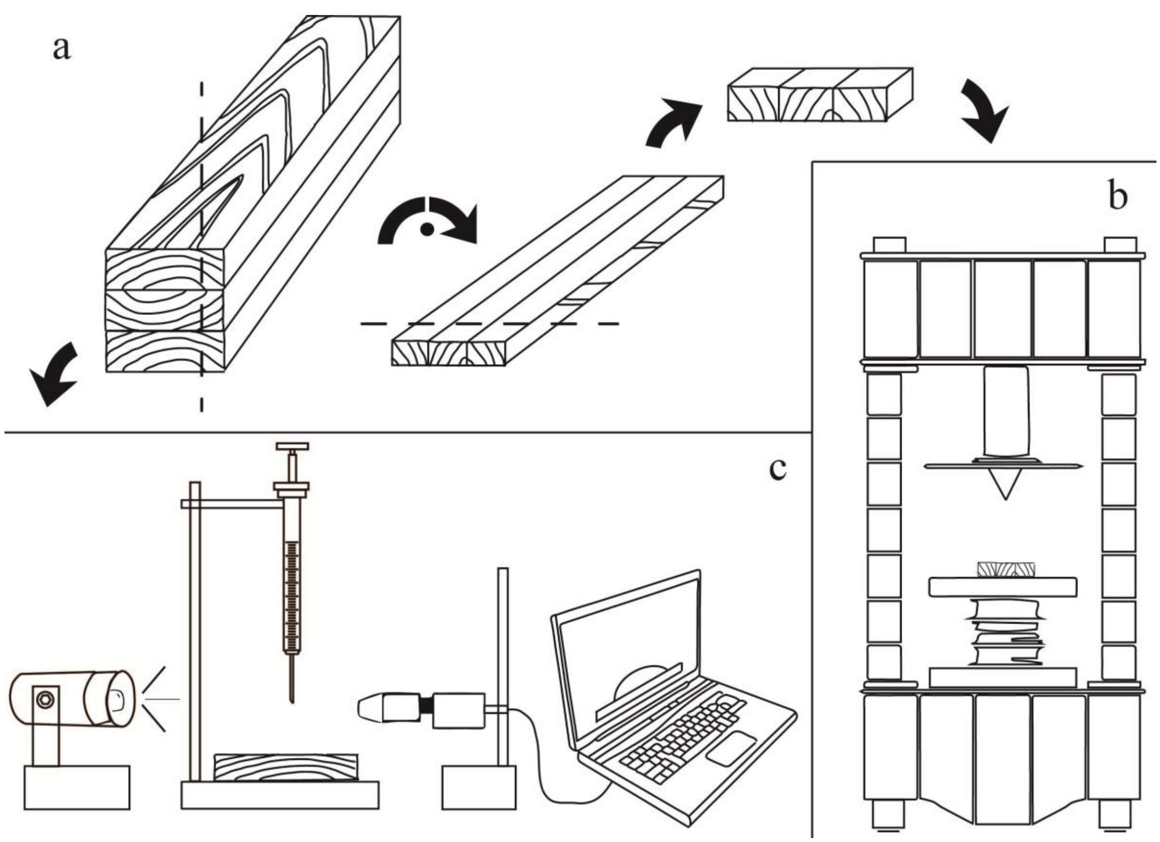

Fig. 1. Schematic illustration of the experimental set-up for (a) the wood material, (b) mechanical tests, and (c) contact angle measurements

The surface wettability of the three treated and untreated boards was evaluated using contact angle measurements in parallel experiments, in accordance with Sernek's method (2002). A total of 420 contact angle measurements, 70 for each treatment, were obtained. The determination of the pH levels for the wood samples was performed in accordance with Shitole's finding (2005).

The bond strength was tested by means of a test machine Galdabini (SUN/10-P/S), as shown in Fig. 1. The test machine's tensile test utilized a feed rate of 10 mm/min. The shear strength, T (Nmm^{-2}), in both bonded and non-bonded wood, was calculated according to Eq. 1:

$$T = F_{max} / A \quad (1)$$

where F_{max} is the maximum force (N), and A (mm^2) is the area of the tested bonded surface. Loading was applied until adhesive or cohesive breakage of the sample occurred.
Analysis of the statistical variance (ANOVA), performed with SPSS v.21 software (IBM Corp.), was applied to test the difference in variance between treated and untreated samples for each species. For the variance, a 5% difference ($p < 0.05$) was considered to be statistically significant.

RESULTS AND DISCUSSION

The results of the non-bonded wood shear strength tests (Table 2) highlighted a significant decrease in strength for the treated spruce and oak. However, the highest reduction in the shear strength for Turkey oak (-32.3%) could be related to the previous steaming treatment, according to Todaro *et al.* (2012). On the contrary, ash wood did not exhibit a significant difference between the treated and untreated wood. Considering that spruce and ash were subjected to the same treatment, the results for the shear strength tests suggested a greater effect of thermo-vacuum treatment on softwoods compared to hardwoods, as reported by Green *et al.* (1999). This correlation can be attributed to the strong relation between the heat treatment and the polymeric structural wood constituents such as cellulose, hemicelluloses and lignin. Indeed, as extensively reported by Boonstra *et al.* (2007), the degradation of hemicelluloses has been proposed as the major factor for the loss of shear strength.

Table 2. MC, pH, and Shear Strength (± SD) of Non-Bonded Wood Specimens

	Treatments	MC *(%)*	pH	Strength (N/mm^2)	*sign*	D *(%)*
Spruce	Ctrl	11.7	5.10	14.6±1.2	***	
	Treated	9.7	4.64	12.6±2.3		-13.7
Ash	Ctrl	11.1	5.14	22.1±3.8	*ns*	
	Treated	8.0	4.94	21.0±3.3		-1.8
Oak	Ctrl	10.9	4.90	29.7±3.6	***	
	Treated	8.9	4.78	20.1±2.5		-32.3

(*) indicates significant differences between treatments at $p<0.05$. Letter D means decreasing compared to untreated (Ctrl).

As expected, the results for the shear strength of bonded wood for Sequence 1 (Fig. 2) confirmed the statistical difference observed for non-bonded wood, as shown in Table

2. The results showcased spruce and oak's suitability (both the treated and untreated woods) for indoor application, following the standard D4-1 class (EN 204).

After soaking the wood in the cold water for 4 days (Seq. 3), the bonding strength of modified spruce, ash, and oak wood decreased in comparison to unmodified wood, by 16.3%, 10.7%, and 7.9%, respectively.

This phenomenon may result in a weak bond-line resistance for the PVA adhesive, especially if the specimens were submerged numerous times in cold water (Seq. 3). The results in Fig. 2 showed that when wood is kept in water, a strong reduction of shear strength occurs, which was particularly evident for ash and Turkey oak. Although it is well known that heat treatments reduce the rate of water absorption (Esteves and Pereira 2009), it was found that an extreme immersion in the water led to a significant change in the wood's mechanical properties, resulting in a decrease in the stiffness of the wood. Indeed, when dry timber has its water content increased to the levels found in green timber, the cell walls fill with water. This causes dimensional changes in the wood due to the expansion of the cell walls. The expansion had repercussions on the bonding line performance.

The values for Sequence 5 were similar to those of Sequence 3, even if the untreated and treated Turkey oak wood didn't reach the threshold value to be considered in the D4-4/D4-5 class (DIN EN 204). However, the effect of the treatment on the shear strength was not statistically significant for all species in Sequence 5, as shown in Fig. 2.

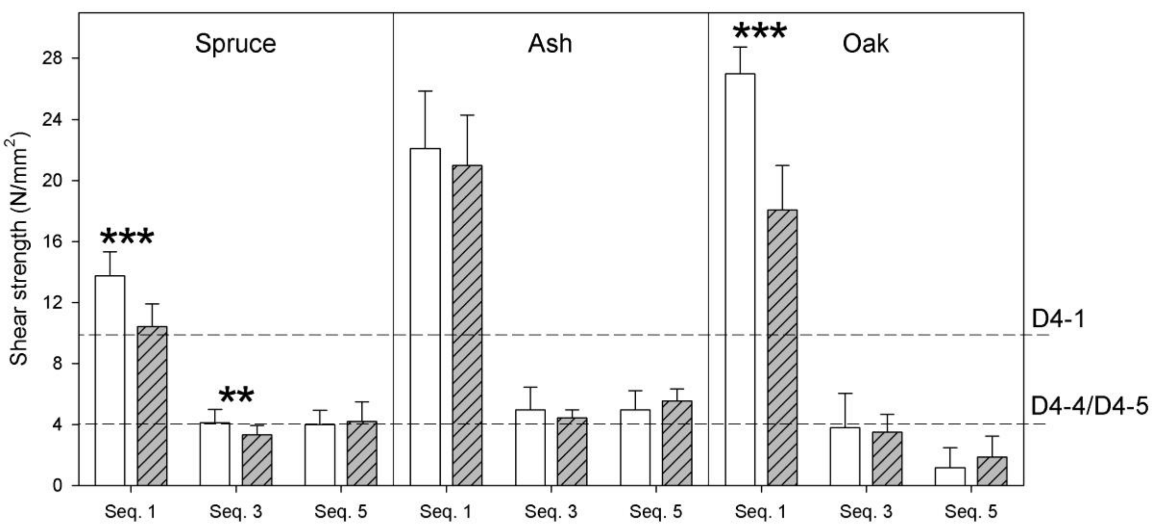

Fig. 2. Shear strength (+SD) of the bonded wood specimens. White and gray bars represent the untreated and treated wood, respectively. The stars indicate significant differences between the treatments (*** p<0.001, ** p<0.01). The horizontal reference lines are the durability threshold class (EN 204).

To quantify an adequate bonding performance, several characteristics should be considered, including the wettability, which is an indicator of the quality of the adhesion. Wettability is directly related to the contact angle; as the smaller the contact angle, the better the wettability.

The wood is expected to become more hydrophobic as the heat-treatment temperature increases. The wood's increases in hydrophobicity can also be attributed to the chemical changes taking place within the material. Accordingly, the contact angle for all wood species was found to increase significantly after treatment (Fig. 3), as evidenced by the claims of other researchers (*e.g.*, Kocaefe *et al*. 2008; Aleš *et al*. 2013). Moreover, Fig. 3 highlights a large difference in the pattern of the contact angles between treated and untreated ash wood. As suggested by Hakkou *et al.* (2005), the high change in the wettability for ash wood might be due to the modification of the conformational arrangement in wood biopolymers, which results from residual water or the plasticization of lignin. In addition, the improvement in the hydrophobic character of the wood is mainly by hemicelluloses degradation, in which there is reduction in the hydroxyls groups that connect to the water. However, it should be noted that despite a clear difference in the wettability between treated and untreated ash, there was no difference in the bond shear strength.

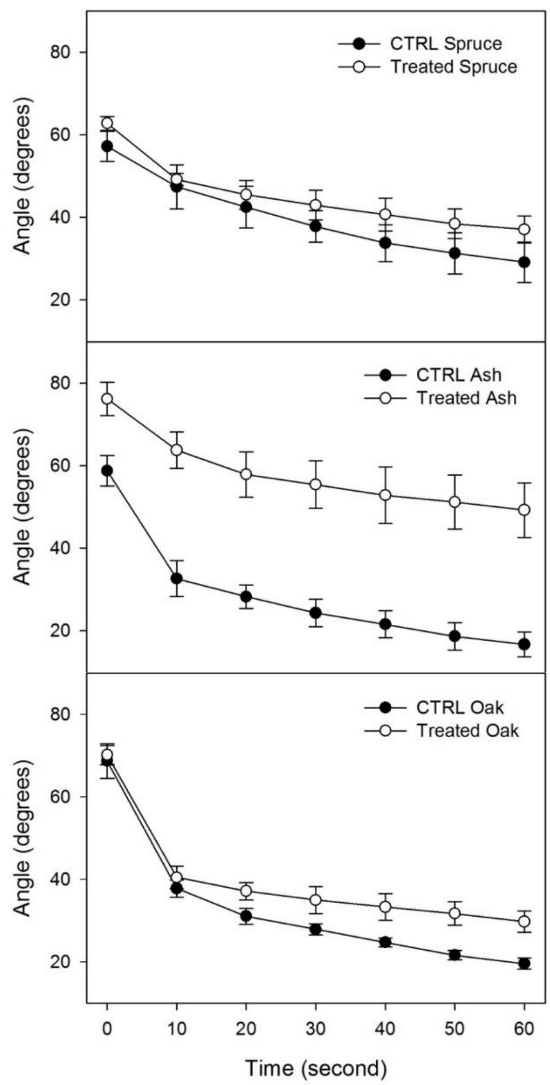

Fig. 3. The effect of thermo treatment on contact angle *vs.* time

However, according to Marra (1992), wettability is not the only factor responsible for the formation of an adhesive bond. Other factors, such as flow, transfer, penetration, and solidification should be taken into account. In addition, the ability of the adhesive to cure properly on a substrate depends highly on the surface properties (Blomquist *et al.*

1981), as the rate of cross-linking for most thermosetting adhesives is pH-dependent. The results in Table 1 are consistent with other studies that highlight a reduction of the pH level in wood after the thermo-treatment.

It can be hypothesized that the change in pH may be one of the factors in determining the net effect on the shear strength of the bonded wood. This is because the efficiency of the adhesive properties in a PVA (hexamethylene diisocyanate) system depends on the formation of polyurethanes between the alcoholic groups of wood and the reagents.

It is well known that thermal treatment induces an oxidation process on the surface of the wood (Todaro *et al.* 2013). The effect of this oxidation process is the reduction of free hydroxyl groups, coupled with a subsequent reduction of the efficiency of both the adhesion and wettability. Further demonstration of this point is provided in the works of Lavisci *et al.* (1991), who found that, for Turkey oak, the surface inactivation is affected by the alteration in the pH levels of the wood.

CONCLUSIONS

In this research, the bonding shear strength and wettability for different wood species were investigated. The following conclusions can be drawn from this study:

1. The null hypothesis that the shear strength was different between treated and untreated wood was partially rejected. In fact, a significant difference was observed for spruce and oak, while it was negligible in case of ash.
2. After water soaking, the untreated and treated Turkey oak wood didn't reach the threshold value to be considered in the D4-4/D4-5 class (DIN EN 204). Therefore, the PVA adhesive performed poorly for the Turkey oak wood, highlighting the need for other specific adhesives.
3. It was also hypothesized that sample exposure to the water stress condition could cause a strong reduction of the shear strength. This hypothesis was confirmed, with the most obvious reduction occurring from sequence 1 to the sequences 3 and 5 for ash and oak, in comparison to spruce.

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