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ORIGINAL RESEARCH

The effect of ageing on bonding performance of plasma treated beech wood with urea-formaldehyde adhesive

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Abstract In the process of wood bonding, the usage of aged and inactivated wooden elements can cause a reduction in mechanical properties of products containing wood-adhesive joints. Treating wood with an atmospheric air plasma represents a sophisticated technique for surface activation. With this regard, to enhance the bondability of normal beech wood (*Fagus sylvatica* L.) with urea-formaldehyde (UF) adhesive, a dielectric barrier discharge plasma in floating electrode configuration was implemented. In this study, fresh and aged wood specimen both, untreated and plasma treated, were investigated. X-ray photoelectron spectroscopy revealed promotion of carbon-rich species with ageing, but generation of a new functional oxygen-containing functional groups after plasma treatment. Microscopic observations with scanning electron microscope showed no obvious changes in the wood structure after plasma treatment. Surface oxidation consequently improved the wettability of the wood surface with water and UF adhesive. However, this enhanced wettability slightly diminished over time. As shown with dynamic mechanical analysis, the rheological properties of the UF adhesive in wood-adhesive joints were not affected by aging nor by plasma treatment. The positive influence of plasma treatment and negative impact of substrate ageing to the shear strengths of wood lap-joints were determined using an automated bonding evaluation system. Similarly, the negative effect of wood ageing and the positive effect of plasma pre-treatment were reflected in the bending strengths of the produced laminated veneer lumbers. Results showed that plasma treatment of beech wood improves the bonding performance of both fresh and aged wood.

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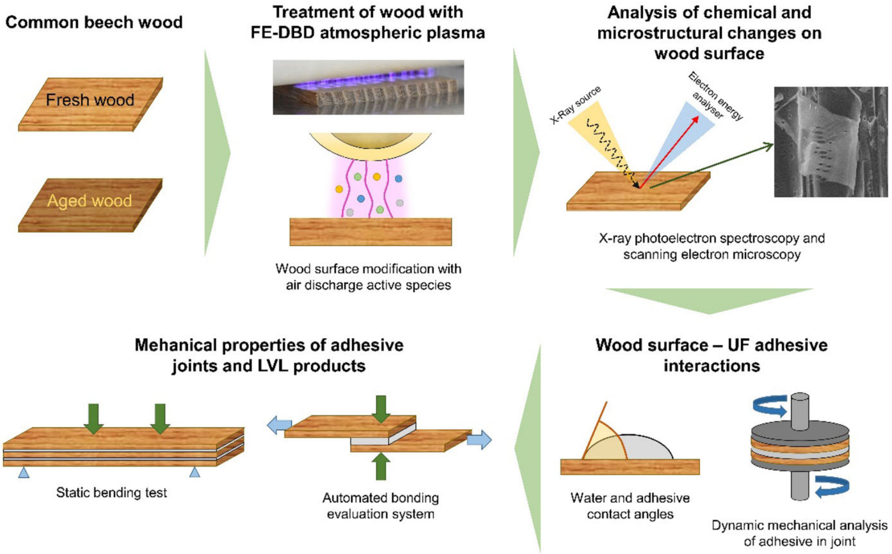
Graphic abstract



Keywords Ageing · Bonding · Wood · Plasma · Surface · Urea-formaldehyde adhesive

Introduction

The performance of a bond between wood and adhesive depends on various properties of the wooden substrate and the adhesive used, as well as on the bonding process. In wood bonding process the selection of adhesive for a specific purpose of use, and a proper selection and preparation of wooden material present a critical step. Urea-formaldehyde (UF) adhesives are the most prominent waterborne thermosetting amino resins in the wood products industry (Conner 1996).

Immediately after mechanical preparation, the wood surfaces are exposed to atmospheric influences, including oxidation, temperature, humidity, light irradiation, airborne contaminants and by that become inactivated (Nussbaum 1999; Aydin 2004a, b). Wood ageing is related also to surface inactivation caused by the migration of extractives from the bulk to the surface and changes in the chemistry (Bryne and Wålinder 2010). Surface inactivation is attributed by a poor wettability. Such reduced ability of wood to interact with various liquid adhesives negatively affects the establishment of a good wood-adhesive bond (Šernek et al. 2004). Therefore, when bonding wood, the time between mechanical preparation of wood material and bonding process must be as short as possible, preferably within 2–3 days (Nussbaum 1996). Besides improving the adhesion strength of wood joints, the modern mantra in wood bonding processes is to use environmentally benign processes (Pizzi and Mittal 2010).

One of the possible surface treatment techniques of wood is the treatment using plasmas (Jamali and Evans 2020). Plasma treatment (PT) of different types of materials, including wood, is a well reported environmentally friendly surface treatment technique for promotion of adhesion of coatings or adhesives to the substrates (Mittal and Pizzi 1999; Vander Wielen et al. 2006). The use of different kinds of atmospheric air pressure plasma systems (Förster et al. 2005; Baltazar-Y-Jeminez and Bismarck 2007) allows selective modification of the topmost layers without affection the bulk material (Jordá-Vilaplana et al. 2015; Kulyk et al. 2020). Non-thermal dielectric barrier discharge (DBD) plasma holds the advantages of high degree of technological maturity, low energy consumption, uniform and stable discharge features, and uniform plasma spatial distribution (Profili et al.

2017; Guo et al. 2020). Enhanced adhesion between wood and adhesive, gained by pre-treatment of wooden constituents (particles, chips or veneers) with air electrical discharge, reflects in generation and promotion of active functional groups on the surface (Avramidis et al. 2009), improved surface wettability with waterborne adhesives (Altgen et al. 2015) and finally enhanced mechanical and physical properties of wood-based products (Rao et al. 2018; He et al. 2019; Kettner et al. 2020). For instance, alteration of the surface chemical properties and etching of the wood surface with atmospheric DBD PT significantly improves the interfacial adhesion between adhesive and wood, thus enhancing the mechanical properties of plywood (Cao et al. 2020) or particleboards (Altgen et al. 2015, 2016). Furthermore, PT of wood has the ability to enhance or re-activate the wettability of both, fresh and aged (i.e. inactivated) wood surfaces (Aydin and Demirkir 2010). However, the effect of PT on wood is not permanent (Altgen et al. 2020).

During the curing of the adhesive in the bondline of the wood-adhesive joint, chemical and physical aspects are important due to the possible effect of the wood surface that is being bonded (Winter 2001; Ugovšek and Sernek 2013; Ormondroyd 2015). The conditions in the hot press (including temperature, pressure and time) and the curing of the adhesive during wood bonding can be simulated with dynamic mechanical analysis (DMA) (Núñez-Regueira et al. 2005). DMA enables monitoring and evaluation of various rheological parameters of the adhesive, placed between two wooden plates (Lodeiro and Mulligan 2005).

The mechanical properties of established wood-adhesive joints can be evaluated by different test methods (Šernek et al. 2004). The automated bonding evaluation system (ABES) (Humphrey 1993) technique allows to simulate the mechanical bond strength development of wood-adhesive joints, at adjustable pressing conditions, including pressure, temperature, time and substrate type (Ferra et al. 2011; Costa et al. 2014). Up to now, Yamamoto and co-authors (2017) were the only one reporting on bond performance between wood treated with plasma discharge (more precisely corona discharge) and phenol-formaldehyde resin, evaluated by ABES.

Indeed, the performance of wood-adhesive joints reflect in the mechanical properties of wood products including bonded elements. One example of a load-bearing engineered wood product material is laminated veneer lumber (LVL). LVL is produced from layered, parallel configured veneers, primarily obtained from both hardwood (e.g. European beech) (Knorz and Van de Kuilen 2012; Saražin et al 2017) or softwood species (Volsky et al. 1994; Hunger et al. 2016). Layered wooden elements can have equal or different thicknesses (Youngquist et al. 1984; De Melo et al. 2014) and can be obtained from the same or different type of wood (Burdurlu et al. 2007). Compared to solid wood, LVL exhibits higher strength and stiffness properties (Fonselius 1997; Pot et al. 2015). This makes LVL mainly useable for load carrying timber structural purposes, but also in furniture industry (Gaaf and Gašparik 2015). In LVL, wooden layered veneers are bonded together with structural adhesives (phenol–formaldehyde or UF) (Dunky 1998; Dill-Langer and Aicher 2014), which mass share in LVL product can reach up to 20% (Daoui et al. 2011).

The objective of this research was to examine the effects of wood ageing and treatment with floating electrode DBD plasma on the bonding performances of common beech with UF adhesive. The experimental part of the study was based on the hypothesis that treatment with a novel kind of DBD plasma is a suitable technique for wood surface reactivation. Further on, the properties of such reactivated wood surface could influence on the interactions with adhesive as well as on the formation process of adhesive bond. The pre-treatment of wood with plasma could possibly influence the mechanical properties of wood-adhesive bonds. In this study, the wood was exposed to ageing in dry and dark indoor conditions for 21 days. Chemical changes caused by ageing of wood and PT of wood were determined with X-ray photoelectron spectroscopy. To examine the influence of PT on surface morphology, surfaces of untreated (UT) and plasma treated (PTd) samples were analyzed with a scanning electron microscope. Wettability changes of samples were assessed by measuring the contact angles of water and adhesive at different time intervals of storing. To evaluate the possible influence of the wooden substrate properties (ageing and PT) on the curing of the UF adhesive, the DMA of adhesive joints were performed. The shear strength development of wood-adhesive joints, including either fresh or aged UT or PTd beech veneers, was determined with ABES. Finally, the influence of ageing and PT on mechanical properties of loading engineered wood products was evaluated with bending strength test of produced LVLs.

Materials and methods

Materials

Common beech (*Fagus sylvatica* L.) wood with a moisture content of 11.8% and nominal density of 715 kg m^{-3} (both determined gravimetrically) was used.

Specimens with dimensions depending on the particular part of the study, were sawn out of straight grain industrial scale planks. All the studies reported in this paper were performed on surfaces with radial orientation of wood grain. After mechanical preparation, the samples were stored in a climate chamber at a temperature of 20 °C and relative humidity (RH) of 65% for at least 7 days before usage.

Commercial urea-formaldehyde (UF) adhesive W-Leim Plus 3000 was obtained in the form of powder from Dynea AS (Lillestrøm, Norway). The adhesive mixture was prepared by mixing UF adhesive and deionized water in two different ratios for different parts of the experiment.

Plasma treatment of wood

Treatment with plasma was performed with a newly developed device generating a non-thermal plasma discharge in air at atmospheric pressure (Fig. 1). The device was constructed and manufactured at University of Ljubljana, Biotechnical faculty. The details of the setup are described in previous publications (Žigon et al. 2019, 2020a). The DBD plasma device operates with configuration of a floating electrode (FE-DBD), where the treated wood sample represents an opposite active electrode at a floating potential with required electric capacity for charge storage. Alternating high voltage (frequency 5 kHz, 15 kV peak voltage) is supplied by high voltage power supply into two parallel insulated brass electrodes. In the present study the distance between the insulated electrodes was 5 mm, whereas the gap between the dielectrics and the surface of the beech wood workpiece was 1 mm. PT of individual workpiece was performed at a moving rate of 2 mm s^{-1} at a room temperature of 20 °C and RH of 50%.

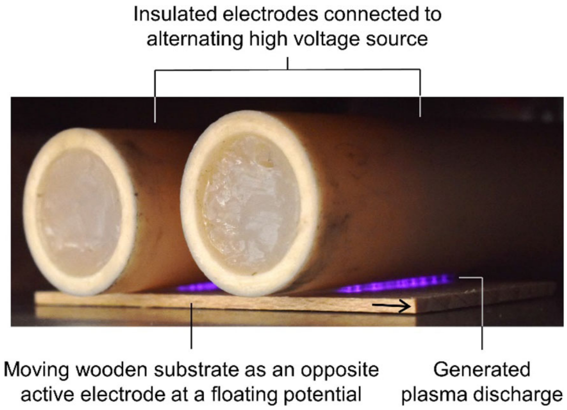


Fig. 1 The FE-DBD plasma reactor in operation during treatment of a beech wood substrate. The photo was taken with a Nikon D5600 photo camera (f/14, 0.5 s, ISO 1600)

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was employed to identify changes in the surface chemical composition of beech wood induced by the PT, and to detect chemical species on fresh wood surfaces and wood surfaces aged for 21 days in a dark ambient atmosphere (20 °C, 30%) (Sinn et al. 2001; Gindl et al. 2004). XPS analyses were performed on 3–4 beech wood samples (1 analyzing spot per sample) from each series of approximately (5 × 2 × 2) mm^3 in size, using a TFA-XPS spectrometer (Physical Electronics, Inc. Chanhassen, Minnesota, USA). For fitting C 1 s high-resolution spectra the XPS analysis was additionally performed on clean ash-free 100% cellulosic filter paper (Macherey-Nagel MN 640 d), acting as an in-situ reference (Johansson et al. 2012, 2020). The spectra were acquired at a base pressure of 10^{-9} hPa using a focused monochromatic Al Kα source (photon energy 1486.68 eV, power 200 W), from an area of 400 μm in diameter. Excited photoelectrons were emitted at 45° to the samples' surface normal. Typical information depths of the XPS method are in the range of 3–5 nm. Data elaboration, including spectral calibration, processing, fitting routines, and atomic concentration calculations, was done using the XPS database and the Multipak v.8.1 software. Surface concentration of C and O was calculated with relative sensitivity factor 0.296 for C 1 s and 0.711 for O 1 s. The measured photoelectron spectra were decomposed using a Gaussian–Lorentzian sum curve with about 95% contribution of Gauss curve. High-energy C 1 s spectra were decomposed into four subcomponents (Chen and Tanaka 1998) at the following bonding energies: C_1 (at 284.6 eV, representing C–C and C–H groups), C_2 (at 286.3 eV, representing C–O and C–O–C groups), C_3 (at 287.5 eV, representing C=O and O–C–O groups) and C_4 (at 288.9 eV, representing O–C=O and C(=O)OH groups).

Microscopic analysis

Microscopic structure of UT and PTd beech wood was analyzed with scanning electron microscope (SEM) FEI Quanta 250 (FEI, Hillsboro, OR, USA). Samples of dimensions (5 × 5 × 2) mm^3 were sprayed with a gold conductive layer. The analysis of the samples' surfaces were performed in a high vacuum of $1.06e^{-4}$ Pa, the electron source voltage was 10.0 kV, and the spot size was 3.0 nm. The images were captured by the time of the beam transition through the sample of 45 μs.

Determination of wood wettability

The surface wetting properties of UT and PTd wood with water and UF adhesive were estimated on the basis of contact angle (CA) measurements of liquids droplets. The adhesive mixture was prepared by mixing UF adhesive and deionized water in ratio 1:0.85 (wt). Fifteen 5 μL-droplets of each liquid were applied on 3 (60 mm × 30 mm) samples from UT series and PTd series with optical goniometer Theta (Biolin Scientific Oy, Espoo, Finland). The corresponding goniometer software was used to record the motion of the droplet, and to measure the CA between the substrates surface and tangent fitting to shape of droplet, following the Young–Laplace analysis (Adam 1957). In order to detect the effect of wood ageing on surface wettability, additional sets of samples were left in a dark ambient atmosphere (20 °C, 30%) for 5 h, 24 h, 48 h, 168 h, 336 h and 504 h (21 days) after mechanical preparation (UT samples) or mechanical preparation and treatment with plasma (PTd samples), respectively. After each ageing period the contact angles (CAs) of UF adhesive and deionized water were determined as described.

Dynamic mechanical analysis of adhesive joints

Rheological tests of the UF adhesive mixtures (UF:deionized water ratio 1:0.85 [wt]) were utilized in order to evaluate the influence of the wooden substrate properties on the curing of the UF adhesive. Here, a stress control rheometer instrument ARES G2 (TA Instruments, New Castle, DE, USA) was used. Two 0.9 mm thick beech wood plates, with diameter of 25 mm, were glued on aluminum disks with polyurethane adhesive (Mitopur E45, Mitol d.o.o., Sežana, Slovenia). The aluminum disks with glued wooden plates were conditioned in a climate chamber (20 °C, 65%) for 7 days and mounted in the jaws of the rheometer. UF adhesive was applied ([2 ± 0.001] g) with a spatula on one UT or PTd wooden plate and a bondline with a gap of 0.5 mm was created. The rheological oscillation tests were performed at a frequency of 10 rad s^{-1}, at a strain of 1.0%, and at a heating rate of 10 °C min^{-1} within a temperature range from 25 to 130 °C. The rheological tests were performed also by using wooden plates aged for 21 days in a dark room at temperature of 20 °C and RH of 30%, following the same described procedure.

Information about the adhesive curing are gained in terms of the storage modulus (G') and the loss modulus (G'') or complex viscosity (η^*). G' is a measure of the deformation elastic energy stored in the sample during the shear process, whereas G' is a measure of the deformation viscous energy used in the sample during the shear process and afterwards lost to the sample (Mezger 2002). The loss tangent (tanδ) is the ratio between G'' and G', and it can be used to define the gel point (at tanδ = 1). Another criterion is that gelation and vitrification occur when the curve of G' starts to increase towards the infinity (Winter 1987; Núñez-Regueira et al. 2005) or when the tangent line to the curve of G' crossovers a value close to 0.1 MPa and a baseline of $G' = 0$ (Laza et al. 1998). Complex viscosity η^*, as the vectorial sum of the elastic and loss component of the dynamic viscosity, expresses the general resistance of the material to flow as a function of the stress rate (Garnier et al. 2002), and can be also used for interpretation of the hardening behavior of the adhesive. With elevated temperature the viscosity of UF adhesive starts to increase near the gel point (Malkin and Kulichikhin 1991).

Adhesive bond shear strength development

ABES (Adhesive Evaluation Systems, Corvallis, Oregon, USA) was used to evaluate the adhesive bond strength development. Cut beech veneer strips with dimensions (117 × 20 × 0.9) mm^3 were conditioned at a temperature of 23 °C and RH of 65%. Here, the veneers reached the MC of 10.2%. The UF adhesive mixture (UF:deionized water ratio 1:0.85 [wt]) was applied manually with a spatula on overlapping area of (20 × 5) mm^2 of one UT or PTd veneer strip. The spread rate of the adhesive ([250 ± 10] g m^{-2}) was controlled in a precision balance. Adherent pairs of strips (either both UT or both PTd) were mounted in the system and pressed together at 1.2 N mm^{-2} for a certain time (10–120 s, with steps of 10 s). The press temperature was 100 °C. After the elapsed pressing time followed the 5 s of cooling. The bond strength was determined in shear mode at loading rate of 1 kN s^{-1} with computer-controlled and pneumatically driven system. Five measurements at each pressing time were performed. The tests were performed also by using veneers aged for 21 days, following the same described procedure.

The data of shear strength obtained by ABES was fitted to a three-parameter logistic model, using IBM SPSS Statistic software (IBM, Armonk, NY, U.S.A.). This model describes the shear strength as a function of a press time (Seber and Wild 1989; Jost and Sernek 2009):

$$\tau(t) = \frac{\beta}{1 + exp^{(-\kappa\cdot(t-\gamma))}}, \tag{1}$$

where τ [MPa] is the shear strength, t [s] is the press time, β [MPa] determines the upper asymptote of shear strength, γ [s] is the time when maximum growth occurs, and κ is the slope of the curve at the point of the maximum growth rate. The maximum growth rate w_m was calculated as (Eq. 2).

$$w_m = \beta \cdot \frac{\kappa}{4} \tag{2}$$

LVL manufacturing and determination of bending strength

Beech wood lamellas of dimensions (210 × 45 × 1.5) mm^3 (L × R × T) were prepared from raw material conditioned at temperature 20 °C and RH of 65%. Each LVL sample consisted of 3 lamellae, either PTd or not. PT was performed immediately after mechanical preparation of lamellae. On the outer lamellae, only the surface facing the bondline was treated with plasma, whereas the middle lamellae were treated with plasma on both sides. UF adhesive mixture was applied on a single surface of each bonding layer by spraying ([120 ± 2] g m^{-2}). Due to the application technique used, the adhesive mixture contained higher amount of water (UF:deionized water ratio 1:1.16 [wt]) than in the other experiments. The glued lamellae were assembled one on the top of the other and pressed together in a hot press under a pressure of 0.5 N mm^{-2} for 4 min at temperature of 100 °C. For each type of LVL (UT and PTd) 20 samples were prepared. Control solid beech wood samples and manufactured 5.5 mm-thick three-ply LVL samples (Fig. 2) were cut to final dimensions ([200 × 20] mm^2, L × R) and kept in an acclimatization chamber (20 °C, 65%) for 7 days before the start of bending test. The LVL samples were prepared also by using lamellae aged for 21 days, following the same described procedure.

Bending strength and the static modulus of elasticity (MoE) of the manufactured LVL products (EN 14374 2004) were determined according to standard EN 408 (2010) with 4-point bending using a Zwick/Roell Z005 testing machine (Zwick GmbH & Co. KG, Ulm, Germany). Individual specimens were placed on two round (10 mm in diameter) metal supports, with the distance between them set to 110 mm. The loading force was applied perpendicular to the sample surface via two round (10 mm in diameter) metal loading pads which were 40 mm apart. The loading rate was set to 10 mm min^{-1} by which the breakage occurred in less than 60 s after the start of the measurement. The MoE [N mm^{-2}] was determined from the slope of the stress–strain curve in the range between 10 and 40% of maximum force, and calculated as follows (Eq. 3):

$$MoE = \frac{3\cdot a\cdot l^2 - 4\cdot a^3}{2\cdot b\cdot h^3\left(2\cdot\frac{w_2-w_1}{F_2-F_1} - \frac{6\cdot a}{5\cdot G\cdot b\cdot h}\right)} \tag{3}$$

where F_2–F_1 [N] is applied force on the regression line with a correlation coefficient, w_2–w_1 [mm] is the deformation in the range between F_2 and F_1, l [110 mm] is a span in bending, a [35 mm] is the distance between individual loading pad and individual support, b [mm] and h [mm] present width or height of the sample cross-section, whereas G is the shear modulus [N mm^{-2}, infinite because unknown].

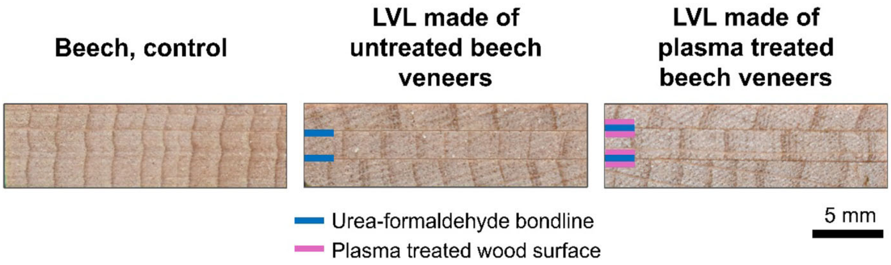


Fig. 2 Cross-section composition of different samples, used for the determination of bending strength

Results and discussion

XPS spectra

The XPS analysis has revealed change in surface chemistry of beech wood, both after ageing and after PT. The results are presented in Fig. 3 as XPS carbon C 1s spectra decomposed into C_1, C_2, C_3 and C_4 components showing different types of bonds of carbon atoms. XPS results are also presented in Table 1 as surface chemical composition in relative concentration of C_1–C_4 components in C 1s spectra. The predominant acquired chemical elements were carbon (C 1 s at 285.2 eV) and oxygen (O 1s at 532.9 eV). The differences between chemical composition of UT aged and PTd aged wood were detected in all four subcomponents of C 1s spectra, despite 21 days passed between the sample preparation and XPS study. On a long term, the ageing of wood causes the decomposition of cellulose and hemicelluloses (Kačík et al. 2014). High intensities of C_1 and C_2 peaks on aged UT samples are related with presence of some carbon-rich species (maybe of the non-cellulose origin) on the surface (Flynn et al. 2013). With the time of exposure of wood to atmospheric air, non-polar extractives molecules migrate from bulk towards the surface due to thermodynamic conditions (Gindl et al. 2004; Šernek et al. 2004; Fardim et al. 2005). In the detected XPS spectra this was expressed in larger share of C 1s spectra and smaller share of O 1s spectra on aged wood. In addition, the air pollutants deposit on the surface during ageing, consequently together with the migrated non-polar extractives making wood surface less acceptable to water (Bryne and Wålinder 2010; Bryne et al. 2010). Samples exposed to plasma discharge and aged for 21 days exhibited higher presence of oxygen containing chemical groups in comparison to aged UT samples (increase of C_3 by 136% and C_4 by 129%). The chemical effects of the plasma species caused various changes over the surface composition and generated new functional oxygen-containing functional groups, like C–O, C=O, O–C–O and O–C=O (Karahan and Özdoğan 2008; Klarhöfer et al. 2010). DBD plasma used in this work mainly consist of active species originating from nitrogen and oxygen present in the atmospheric air (Žigon et al. 2020a). Surface oxidation is caused due to strong oxidizing effect of atomic oxygen (Belgacem et al. 1995; Cao et al. 2020). The contribution of PT to surface oxidation remained still after the time of ageing (Kolářová et al. 2013). In aged PTd samples, inorganic particles (Ca and K) were detected in amount of about 1%, originating either from the wood bulk during the treatment of wood surface with plasma (Yang et al. 2004; Vesel et al. 2007; Inari et al. 2011) or from some artifacts present in the laboratory air (Bryne et al. 2010).

The C 1s spectra of fresh UT wood samples, mechanically prepared just before the XPS study, was very similar to spectra of PT aged samples. However, the smaller C_1 (by − 16%) component indicate that fresh UT sample contained more oxygen-containing groups on surface. The treatment of fresh wood surfaces with plasma additionally promoted the C_4 component (by 33%), but decreased the C_1 (by − 4%) and C_3 (by − 26%) components. This is signalizing additional enrichment of freshly prepared wood surface mainly with O–C=O functional group. Inorganic elements (Ca and K) were detected in quantities of about 1% on fresh PTd samples, again confirming the generation of these elements or their migration from the wood bulk after treatment of wood with plasma (Deslandes et al. 1998; Avramidis et al. 2012).

The corresponding O 1s spectral region at 532.9 eV are identified as –OH and –O– chemical

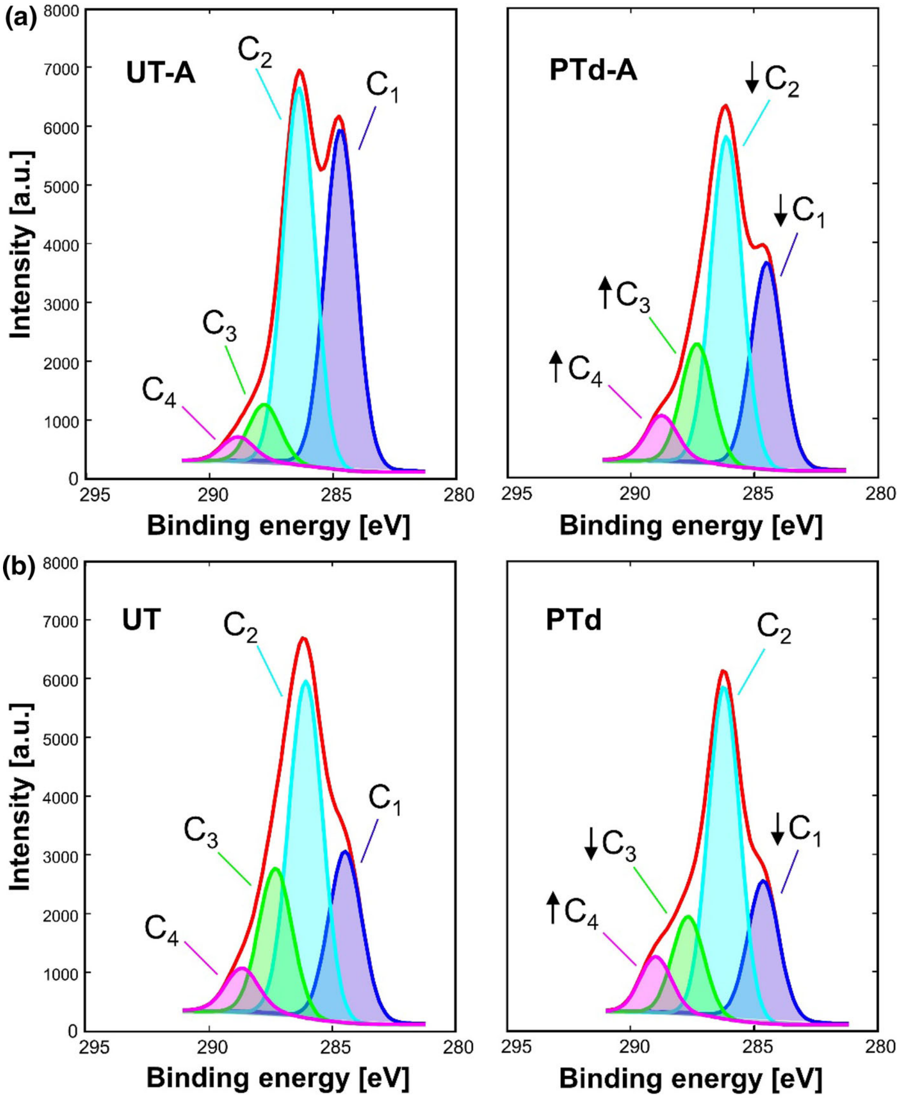


Fig. 3 Representative XPS high-energy resolution C 1 s spectra, decomposed into components C_1–C_4: aged (**a**) and fresh (**b**) untreated (UT) and plasma treated (PTd) beech wood

Table 1 Chemical composition (in at%), O/C atomic ratios and relative concentrations of C_1–C_4 components in C 1s spectra obtained by XPS method

Sample type	O 1s	C 1s	C 1s % area				O/C
			C_1	C_2	C_3	C_4	
Cellulose	40.5 (0.9)	59.5 (0.9)	12.1	66.7	19.2	2.0	0.68 (0.02)
UT-A	28.8 (1.1)	71.2 (1.1)	43.3	46.7	7.1	3.0	0.41 (0.02)
PTd-A	34.0 (1.0)	66.0 (1.0)	29.8	46.6	16.7	6.9	0.52 (0.02)
UT	34.3 (0.3)	65.7 (0.3)	25.0	47.8	20.6	6.6	0.52 (0.01)
PTd	39.6 (0.8)	60.4 (0.8)	23.9	52.1	15.3	8.7	0.65 (0.02)

*Standard deviation is shown in the brackets

groups (Flynn et al. 2013). The O 1s spectra and their summarized data are presented in the supplemental materials (Žigon et al. 2020b). The O 1s spectra between fresh, aged and PTd wood samples differed in their atomic concentrations. A good indicator of the surface oxidation are the mean values of oxygen-to-carbon atomic (O/C) ratio (Uehara and Sakata 1990). Higher O/C ratio increases polar part of surface free energy which contributes to enhanced wettability of wood surface with polar liquids (Talviste et al. 2020) like water and UF adhesive. The lowest O/C ratio was found on aged UT samples (0.41). An air PT of the wood surface results in an increase of the O/C ratio (to 0.52) (Tóth et al. 2007; Král et al. 2015) due to surface oxidation and surface cleaning with removal of pollutant volatile organic compounds or dust from the wood surface (Fras et al. 2005; Avramidis et al. 2012). In general, lower O/C ratio on aged wood surfaces is an indicator of the presence of more hydrophobic material after ageing on the outermost surface (around 10 nm in depth) (Bryne et al. 2010; Calienno et al. 2014). The fresh wood samples exhibited O/C ratio comparable to aged PTd samples (0.52). Treatment of fresh wood surface with plasma additionally promoted the O/C ratio (to 0.65) and it was found as the most comparable to those found on pure reference cellulose (0.68).

Microstructure of wood

Treatment of beech wood with FE-DBD plasma discharge caused no distinct morphological changes in the wood structure. As seen in the Fig. 4, the wood microstructure elements like scalariform vessel perforations, vessel pits and bordered pits remained intact after PT. No erosion or etching of the wood cell wall was detected. Similar findings about no influence of treatment with DBD plasma on wood microstructure were reported by Altgen and co-authors (2020). However, different findings with presence of wood etching were reported from other authors, for instance when performing the treatment by lower pressures (Jamali and Evans 2011; Chen et al. 2017) or other process gasses (Yuan et al. 2004; Demirkir et al. 2014). The presence of surface etching seems to arise also with the prolonged time of PT (Jamali and Evans 2020).

Wettability of wood with water and UF adhesive

The presence of the effect induced by PT and its stability over a duration of ageing was assessed from CA measurements. The detected initial (2 s after contact with the surface) CAs of water (W-) and UF adhesive are shown in Fig. 5. The fresh wood surfaces are more easily wetted by water then the aged surfaces, as consistently was found in the literature (Gindl et al. 2004). PT improved the spreading and absorption of water and UF adhesive on the wood surface. CA values of both liquids showed that the effect of PT enhancing wood wettability was not permanent and diminished over time, as already reported in previous studies (Yamamoto et al. 2017; Altgen et al. 2020). Despite the reduction in the effect of PT, the treated wood surfaces were notably more active through 21 days after the preparation than the UT surfaces.

The differences in water CAs on UT and PTd surfaces were noticeable from the beginning of ageing (0 h, W-UT 45.7°, W-PTd 17.9°) and remained large until the end of ageing period (504 h, W-UT 83.7°, W-PTd 43.3°). On the other hand, the differences in UF adhesive CAs (UF-) on UT and PTd surfaces were smaller, but still noteworthy: At the beginning of ageing UF-UT samples exhibited CAs of 63.5° and UF-PTd 52.6°, and after 504 h of ageing UF-UT 70.1° and UF-PTd 65.6°. On the basis of these results we can conclude that pre-treatment of wood with plasma enhanced the wetting of the wood surface, which is typically accompanied by enhanced penetration of water into the bulk and thus a reduction of water in the UF adhesive (Altgen et al. 2016).

The increase in CAs of liquids is in line with the results of XPS study regarding the influence of ageing on wood surface chemical composition. Increased presence of oxygen-containing groups on the wood surface after PT contributed to better compatibility of the wood specimen with waterborne UF adhesive (Marvel et al. 1946; Altgen et al. 2020), the fluidity of which is largely dependent on the flow properties imparted by the water component (Sernek et al. 1999).

Rheological response of UF adhesive

Since the curing and hardening of UF adhesive is dependent on water evaporation and absorption into the substrate, it was hypothesized that the increased hydrophilicity of PTd wood has an effect on the curing of UF adhesive. The effect of the wood substrates' pre-treatment with plasma, and the effect of time after the pre-treatment on the curing of UF adhesive were evaluated by a rheological study. Curves in the Fig. 6 provide curing profiles of the joints between UF

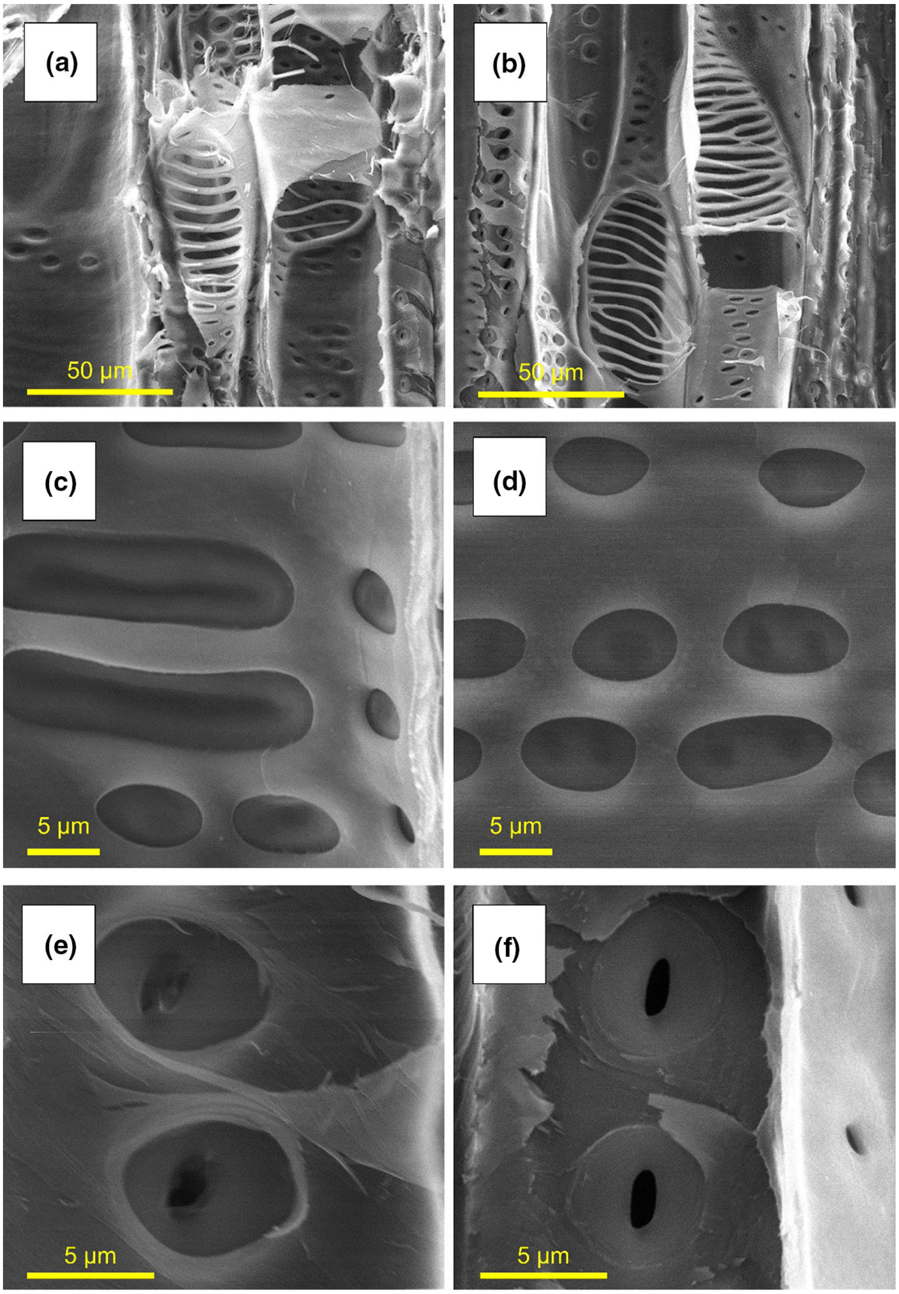


Fig. 4 Images of untreated (UT) and plasma treated (PTd) radial sections of beech wood obtained with SEM: **a** Scalariform vessel perforations in UT wood, **b** scalariform vessel perforations in PTd wood, **c** vessel pits in UT wood, **d** vessel pits in PTd wood, **e** bordered pits in UT wood, and **f** bordered pits in PTd wood

adhesive and beech wood (UT and PTd for both, fresh and aged) by means of adhesive rheological response to an oscillating load generated by the instrument.

The rheological responses of UF adhesive (including increase of G', G'' and η^*) are related to the evaporation of water from adhesive, the penetration of adhesive into the substrate, and hardening of the adhesive in the joint (Ugovšek and Sernek 2013). In case of fresh UT and fresh PTd wood the adhesive started to become more viscous in the temperature

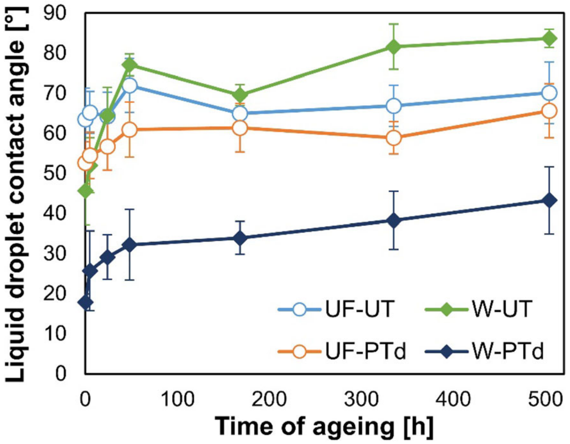


Fig. 5 Changes in water (W-) and UF adhesive (UF-) CAs on untreated (UT) and plasma treated (PTd) beech wood samples, in the period of 504 h of ageing

range between 90 and 100 °C. This temperature range is the range of UF adhesive gelation and bond formation, which, again, did not differ between the measurements on UT and PTd wood substrates. Despite enhanced wetting and typically a reduced surface moisture content, it does not seem to be a faster drying or curing on the PTd specimen and even contrary to possible expectations, the viscosity reaches higher levels for the UT than for the corresponding PTd samples. However, the actual gel point of the UF adhesive is rather hard to determine. From 110 to 115 °C the slope of the G' curve reached the maximum, signalizing that UF adhesive was finally cross-linked and hardened. Regarding gelation temperature, the rheological response of UF adhesive, including aged UT and PTd beech wood substrates, did not differ from fresh wood. The only difference in the curves of G', G'' and η^* was detected at the end of the measurements, where the curves of these three parameters ended at higher values for fresh wood substrates than for aged wood substrates. However, higher final values of G', G'' and η^* did not influence the entire gelation and curing process of the UF adhesive. Therefore, it can be concluded that neither PT nor aging of the wooden substrates influenced the rheological properties of the UF adhesive. Despite enhanced wettability of PTd wood with water and UF adhesive, including more effective spreading of UF adhesive (Altgen et al. 2016), the PT of wood does not influence (e.g. accelerates) the curing of adhesive in the adhesive joint.

Shear strength of adhesive bonds

The bonding quality of joints is dependent on UF resin curing characteristics and applied pressing parameters (pressure, time and temperature) (Martins et al. 2013). The actual shear strength developments of the created adhesive joints are presented in left Fig. 7. When using fresh beech wood veneers, the minimum press time for detection of minimum strength was 20 s. With longer press time the shear strength was increasing. Pre-treatment of the substrate with plasma contributed to higher shear strengths, which became evident at press time of 50 s and longer. At the longest press time (120 s) the joints shear strength including PTd veneers was 10.4% higher than those with UT veneers (9.9 MPa compared with 8.8 MPa). Shear strengths of joints created with veneers aged for 21 days were evidently lower, regardless whether they were treated with plasma or not before the start of ageing. Here, the joints exhibited some strength after minimum 30 s of pressing. The following measurements with longer press times did not show differences between aged (-A) UT and aged (-A) PTd samples. At press time of 120 s the UT-A and PTd-A joints had the same shear strengths (6.3 MPa). This is 29% lower than for fresh UT samples or 37% lower than for fresh PTd samples, respectively. The predicted values of the shear strength, calculated according to equation (Eq. 1) of the model, are presented in the right Fig. 7. The model predicted that longer press times would no longer contribute to rise in joints shear strengths, but the differences between the joint series would remain. The other calculated parameters of the logistic model are presented in Table 2. All model predictions had quite good corresponding with the measured data (all R^2 higher than 0.9). Both series of fresh samples had better fit with the model (R^2 equal or higher than 0.98), however aged samples had little bit lower correspondences (R^2 0.938 and 0.956). The biggest difference between model predictions and measured values was for aged samples above 100 s of press time, where model underestimated the actual shear strength values.

Bending strength

The nominal densities of the samples used for determination of bending strength were as follows: Control beech wood (712.5 ± 38.6) kg m^{-3}, UT LVL (750.3 ± 20.1) kg m^{-3} and PTd LVL

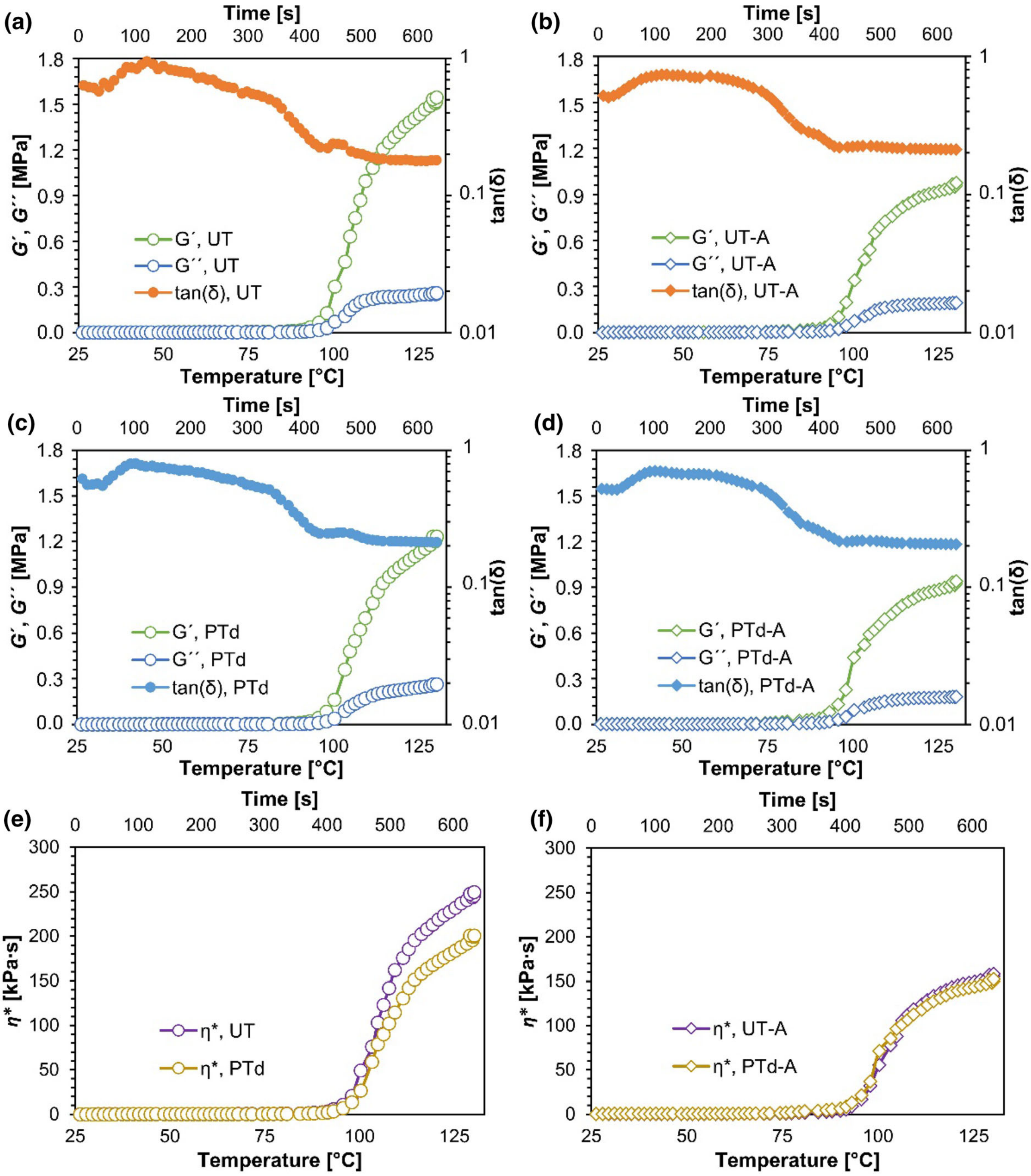


Fig. 6 Rheological response (including storage modulus G', loss modulus G'', loss tangent tanδ) of UF adhesive during its curing and bonding of beech wood: **a** fresh untreated (UT) wood, **b** aged (-A) UT wood, **c** fresh plasma treated (PTd) wood, **d** aged (-A) PTd wood. The curves of UF adhesive complex viscosity η^* in the adhesive joint are presented separately: **e** fresh wood and **f** aged (-A) wood

(749.2 ± 27.9) kg m^{-3}. As reported by Aydin et al. (2004a, b) the higher density of LVL is the consequence of UF adhesive presence in the product and the pressure applied during manufacturing. The bending strengths curves of the individual tested products, with respect to test time or samples deflection, are presented in Fig. 8. As it can be seen, the slope of the bending strength of solid beech wood is lower than of any kind of LVL samples.

Considering other characteristics of static bending test performed stated in Table 3, the best bending performances were found by LVL samples made of fresh veneers (particularly made of fresh PTd veneers). When comparing the performance of LVL-PTd and LVL-UT, the reason for higher strength of LVL-PTd may lay in the improved mechanical properties (i.e. adhesion, shear strength and cleavage strength) of the joint between PTd veneers and UF adhesive (Aydin et al. 2004a, b). However, the differences in MoE between LVL-UT and LVL-PTd are too negligible to make a general conclusion about the contribution of PT to enhanced bending strength of LVL.

On the other hand, LVL products made of veneers aged for 21 days after processing exhibited lower bending strengths and lower values of MoE. Reduced bending strength properties of LVL made of aged veneers are attributed to decreased bonding strength because of inactivated wood surfaces (Aydin and Demirkir 2010). LVL made of UT-A veneers showed higher strength values than LVL made of PTd-A veneers. But the differences in MoE values between LVL-UT-A and LVL-PTd-A are again too negligible to state a possible effect of PT of veneer, subsequently exposed to ageing. As already shown by the results gained in the study using ABES, however, the ageing of veneers seem to have here similar negative effect on bonding and consequently to worst properties of LVL produced.

Conclusions

In the process of wood bonding, the chemical composition influencing the ability of the wood surfaces to interact with applied liquid adhesive is an important

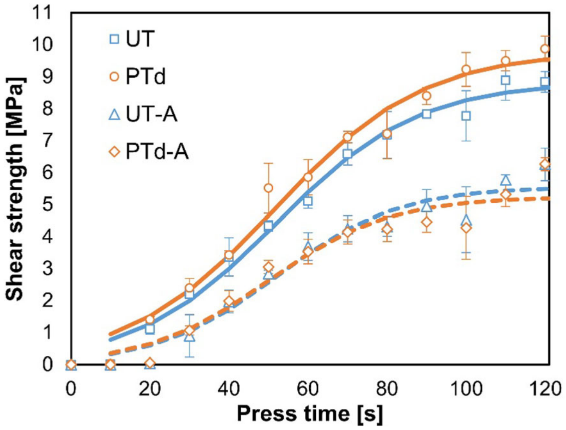


Fig. 7 Actual (markings) and modeled (lines) shear strength evolution with press time of fresh and aged (-A) untreated (UT) and plasma treated (PTd) beech wood veneers, bonded with UF adhesive

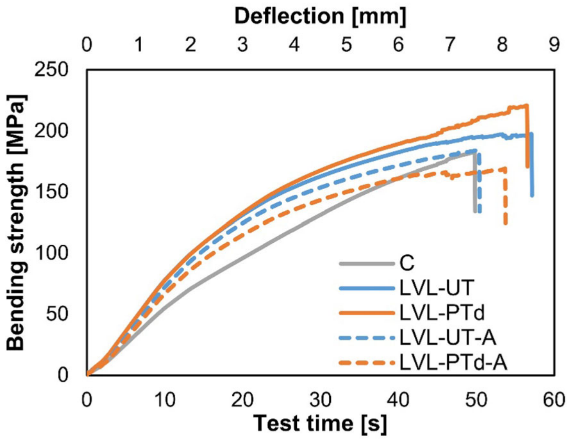


Fig. 8 Bending strength-deformation curves of control solid beech wood (C) and LVL products, composed of fresh and aged (-A) untreated (UT) and plasma treated (PTd) beech wood veneers

Table 2 Parameters for the modelling of the shear strength development of fresh and aged (-A) UT and PTd beech wood veneers, bonded with UF adhesive

Parameter	Sample series			
	UT	PTd	UT-A	PTd-A
β [MPa]	8.838 (0.317)	9.780 (0.447)	5.558 (0.345)	5.243 (0.372)
κ	0.056 (0.006)	0.053 (0.007)	0.066 (0.014)	0.066 (0.017)
γ [s]	51.989 (2.330)	51.786 (3.010)	52.302 (3.855)	49.979 (4.504)
w_m	0.124	0.131	0.091	0.086
R^2	0.987	0.980	0.956	0.938

*Standard deviation is shown in the brackets

Table 3 Results of the static bending performances on control solid beech wood samples, LVL products made of fresh UT and PTd beech wood veneers and LVL products made of aged (-A) UT and PTd beech wood veneers. Values in the brackets are standard deviations

Sample series	$F_{\max}$ [N]	Deflection [mm]	σ [MPa]	MoE [MPa]
Beech, control	875.5 (106.0)	7.5 (1.3)	183.9 (27.9)	14.742 (1.998)
LVL-UT	954.8 (36.0)	8.6 (1.6)	197.5 (10.7)	18.083 (1.424)
LVL-PTd	1081.8 (56.8)	8.5 (1.2)	224.3 (16.1)	18.090 (1.394)
LVL-UT-A	884.3 (42.3)	7.6 (0.9)	184.1 (42.3)	17.024 (1.402)
LVL-PTd-A	798.8 (192.1)	8.0 (2.8)	168.8 (20.3)	16.217 (2.238)

prerequisite for establishment of a good wood-adhesive joint. The surface of wood is in proper conditions for good bonding immediately after mechanical preparation (i.e. cutting or sanding). With the time after preparation, the wood surface is losing its ability to properly bond with polymer adhesives.

As shown in XPS, the chemical composition of the wood surface changes with ageing time. A migration of carbon-rich species of the non-cellulose origin and the presence of air pollutants on the surface make it more hydrophobic, which was evident in measurements of water and UF adhesive CAs. PT of beech wood with floating electrode DBD plasma changed the wood surfaces' characteristics and positively influenced the bonding performance of fresh wood and wood aged for 21 days. The plasma generated additional oxygen-containing functional groups (C–O, C=O, O–C–O and O–C=O) on the surface. As shown with XPS, the oxidation effect of wood originating from PT remained present even after 21 days of ageing.

Microscopic studies revealed that the treatment of wood with plasma discharge did not cause any detectable morphological or structural changes on the wood surface. With this regard, the process of wood treatment with atmospheric FE-DBD plasma can be denoted as more "soft" in comparison to other "harsher" plasma discharges generated at low pressures, causing etching or ablation of wood structure.

Pre-treatment of wood with plasma enhanced the wood wettability with water and UF adhesive. The effect was visible throughout the whole ageing period. The differences between UT wood and PTd wood were more pronounced in wettability of water. Lower CAs of UF adhesive on PTd wood surfaces were related to the improved reduction of water in the adhesive, as a consequence of an enhanced hydrophilicity of the treated substrates.

Dynamic mechanical analysis with determination of rheological properties of UF adhesive showed no influence of the wood substrates on adhesive curing and hardening. The formation process of wood-adhesive joints, including fresh and aged, UT and PTd, were not affected by the properties of the substrates, despite the differences in their chemical compositions and wetting abilities. However, the influences of the substrate properties were shown in shear strengths of wood lap-joints in dependence of press time, determined with ABES. In comparison to fresh UT veneers, pre-treatment of fresh wood veneers with plasma contributed to 10.4% higher shear strengths at the longest press times (120 s, at press temperature of 100 °C). Shear strengths of joints created with aged veneers, both UT-A and PTd-A, were evidently lower (29% or 37% after 120 s of pressing, respectively). In addition, the joints with aged veneer required longer minimum press times (30 s) than joints including fresh veneers (20 s) to exhibit minimum shear strength. The measured values of shear strengths of all types of the bonded samples were in good correlation with a three-parameter logistic model predicting the evolution of shear strengths in dependence of press time.

It was hypothesized in earlier studies (Daoui et al. 2011; Rescalvo et al. 2020) that the obtained differences in bonding abilities and performances among different types of wood substrates can be reflected also in the bending properties of the produced LVL, as an example load-bearing engineered wood product. However, this did not hold true in the current study, as the highest modulus of elasticities were determined in LVL made from fresh PTd (18,090 MPa) and fresh

UT veneers (18,083 MPa). Aged veneers were found to have a negative influence on the bending strength of LVL (UT-A 17,024 MPa, PTd-A 16,217 MPa). The reason for this lies in lower ability of aged wood to establish bonds with UF adhesive with sufficient bonding properties, as showed in previous experiments.

In conclusion, we can confirm our hypothesis that PT of beech wood with a recently developed floating electrode DBD plasma is a promising technique, which reactivates and improves the surface characteristic and bonding performance of both fresh and aged wood. Although the pre-treatment of wood with plasma did not influence the process of adhesive bond formation, it improved the shear strength of bonded samples. Potentially, this type of pre-treatment technique could be implemented in production LVL beams. The pre-treatment of wooden elements (veneers or lamellae) with plasma would reduce the amount of waste material, in the manner of rising the susceptibility of deactivated or aged wooden elements to bonding. In addition, the pre-treatment of wooden elements with plasma would positively reflect in enhanced mechanical properties of adhesive joints between individual wooden elements and at the end in the enhanced mechanical properties of the entire LVL products.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest, and the manuscript is approved by all authors. We confirm that neither the manuscript nor any parts of its content are currently under consideration or published in another journal.

Human and animal rights his article does not contain any studies with human participants or animals performed by any of the authors.

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