J Wood Sci (2017) 63:338–349
DOI 10.1007/s10086-017-1632-5

ORIGINAL ARTICLE

Plywood made from plasma-treated veneers: melamine uptake, dimensional stability, and mechanical properties

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Received: 20 January 2017 / Accepted: 14 April 2017 / Published online: 29 May 2017

Abstract This study investigates the dimensional stability and mechanical properties of plywood boards made of thermally modified and unmodified beech veneers that have undergone plasma pre-treatment before melamine resin impregnation. The water and melamine resin uptake and resulting weight percent gain of the veneers were investigated, whereby the air plasma pre-treated veneers showed improved liquid uptake. Five-layer plywood boards were then manufactured and tested for their dimensional stability, compressive strength, bending strength, and tensile strength. Plywood boards made of thermally modified and plasma pre-treated veneers showed a significantly improved dimensional stability, along with small influences on their mechanical properties.

Keywords Dimensional stability · Mechanical properties · Plasma treatment · Thermally modified wood veneer · Plywood

Introduction

In the last decades chemical modification of wood has attracted increasing interest in scientific terms as well as from an economic point of view [1]. Chemical wood modification processes, e.g., acetylation, furfurylation, or the treatment with 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU), are characterized by modification agents penetrating the wood structure and the reaction of these chemicals with functional groups (e.g., hydroxyl groups) of the lignocellulosic material of the cell wall polymers [2–5]. These modification processes are aimed at improving wood properties such as its resistance against biological decay by fungi, insects or marine organisms, its dimensional stability, or the reduction of its interaction with water in general.

Moreover, the impregnation of wood with melamine resin has proven to be an effective method of wood modification, leading to increased water repellence efficiency (WRE), decreased swelling [6], and delayed discoloration after natural and artificial weathering [7]. Besides the aforementioned wet chemical processes, thermal modification techniques have been developed to improve the dimensional stability and durability of wood [1, 8]. However, the heat treatment of wood results in the adverse side effect that the surface becomes more hydrophobic due to losses of oxygen functionalities during the process [9], which can negatively affect the adhesion or penetration of coatings and modification agents [10, 11]. Furthermore, a reduction of the mechanical strength behavior of thermally modified wood has been reported in the literature [12].

Recent research has also showed that wood surfaces can be altered by exposure to gas discharges (also known as plasma). Plasma-based modification of wood surface using air as the process gas is known to improve wetting characteristics [13–15], which enhances the adhesion of

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coatings and adhesives [16–19]. Additionally, the uptake characteristics of wooden materials for water and water-based modification agents are positively affected by plasma modification [20–23] as well as the penetration depth of adhesives applied to pre-treated wood surfaces [24]. Chen et al. reported an increase in the adhesive strength of plywood made of plasma-treated poplar veneers [25].

In this study, the water uptake and the melamine resin uptake of thermally modified and unmodified beech veneers (*Fagus sylvatica*) in untreated and plasma-pretreated state were determined. Furthermore, the dimensional stability of plywood boards made of these veneers was investigated. As part of this work, tensile strength, compressive strength, and bending strength were tested.

Experimental

Materials

Thermally modified and not-modified rotary cut beech (*Fagus sylvatica*) veneers (thickness 1.2 mm) were purchased from OWI GmbH, Germany. Thermally modified veneers were produced from veneers with a residual moisture of 12% at a treatment temperature of approximately 200 °C and exposure duration of 20 min [26]. The veneers were used for the immersion tests and for the manufacture of five-layer plywood boards. Samples were stored at standard condition (20 °C and 65% RH) for 24 h, resulting in an equilibrium moisture content (EMC) of approximately 10% for unmodified beech and 7.7% for thermally modified beech. Melamine resin (Madurit MW 840, solid content 75%) was purchased from INEOS Group AG.

Plasma setup

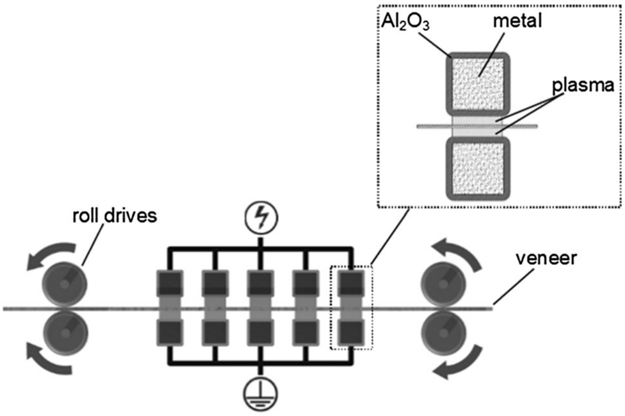

Fig. 1 Plasma setup

Figure 1 depicts the dielectric barrier discharge (DBD) setup used for the pre-treatment of the veneers. The veneer sheets were transported centrally by a roll-conveyer through the gap (5 mm) between two electrode arrays. Each electrode array consisted of 5 single electrodes of rectangular Al_2O_3 tubes ($15 \times 15 \times 400$ mm^3, $t = 2.5$ mm) filled with bronze powder with a distance of 5 mm between the single electrodes [27], similar to the setup used in [21]. Two radial fans above and below the electrode arrays generated an ambient air stream towards the electrode arrays (cooling and discharge homogenization). The upper electrode array was connected to a power supply generating a pulsed (2 µs) voltage of ≈16–21 kV (peak) with alternating polarity, and a pulse repetition frequency of 15 kHz; the lower array was grounded. During plasma treatment, a total power in the range of 380–860 W was injected into the discharge system. During the plasma treatment gas temperatures were measured using a fibreoptic thermometer (FTI-10, FISO Technologies) and did not exceed 60 °C.

Liquid uptake and weight percentage gain (WPG)

The liquid uptake (water and melamine solution) of the samples was measured using an immersion test at atmospheric pressure and at a liquid temperature of 20 °C directly after plasma treatment. In order to determine the water (deionized) uptake, circular samples (diameter 60 mm) were punched out from the veneer. The water uptake measurements were made using the test setup described in Wascher et al. [27], which allows automated measurements with high reproducibility. To determine the melamine resin uptake, veneers with the dimensions of $300 \times 300 \times 1.2$ mm^3 were completely immersed in an impregnating bath. The residual liquid was removed from the veneer surface with a scraping device. All samples were weighed before plasma treatment (digital scale SSH93, SCALTEC Instruments GmbH, Germany). After immersion and removal of residuals from the surface, the samples were weighed and the percentage of increase in mass was calculated according to Eq. (1) [1, 28]:

$$\text{Solution uptake } (\%) = ((m_2 - m_1)/m_1) \times 100, \quad (1)$$

where m_1 is the mass before immersion (at corresponding EMC) and m_2 is the mass after immersion.

In order to determine the solid content of melamine in wood after impregnation with melamine solution, the WPG was calculated by Eq. (2):

$$\text{WPG } (\%) = ((m_m - m_u)/m_u) \times 100, \quad (2)$$

where m_{m} is the weight of the oven-dried immersed samples and m_{u} is the weight of the oven-dried untreated samples [1].

Plywood

For the production of plywood, veneer sheets ($300 \times 300 \times 1.2\ \mathrm{mm}^3$) were first impregnated ("reference" and "plasma" samples) in a melamine solution (melamine + deionized water) with a solid content of 25 or 50% (immersion duration 1 s). The impregnated veneers were dried for 24 h and subsequently manufactured into cross-wise assembled five-layer plywood by hot pressing (press power 250 N/cm^2, pressing time 3 min/mm, temperature 130–140 °C) using a LAP 40 hot press (Gottfried Joos Maschinenfabrik GmbH & Co. KG). No additional adhesive between the single veneer sheets was applied—in accordance with the standard production process of plywood made of thermally modified beech veneers at the OWI GmbH (Germany), which saves one process step in this way. The glue line generated by the melamine resin present within the impregnated veneers creates the bond between the single veneers.

In addition, non-impregnated veneers ("reference^0") were glued using melamine formaldehyde [45% MF-resin (Madurit MW 840, 75% solids), 15% hardener (Prefere 26F782; 3–5% ammonium chloride), 40% water] applied between single veneer sheets under the same pressing conditions as the impregnated samples ("reference", "plasma").

Dimensional stability

Changes in the external dimensions of a wood sample provide information on its dimensional stability under stress during a swelling–drying process. Quantitatively, an increase or decrease in the dimensional stability of the sample is represented by the values of the swelling test.

$$S\,(\%) = ((V_{\mathrm{WS}} - V_{\mathrm{OD}})/V_{\mathrm{OD}}) \times 100, \qquad (3)$$

where V_{WS} is the water-swollen volume of the sample and V_{OD} is the oven-dried volume of the sample [1]. In calculating the swelling coefficients in the plywood, only the radial direction (thickness) was used, since tangential and longitudinal direction cannot be measured separately due to the typical 90° arrangement of the veneer layers of plywood [29]. Therefore, Eq. (3) was accordingly adapted to

$$S^{*}(\%) = ((l_{\mathrm{WS}} - l_{\mathrm{OD}})/l_{\mathrm{OD}}) \times 100, \qquad (4)$$

where l_{WS} is the water-swollen thickness of the sample and l_{OD} is the oven-dried thickness of the sample. To measure the thickness (sample dimension $25 \times 25\ \mathrm{mm}^2$), a dial indicator was used.

Tensile strength, bending strength and compression strength

Tensile strength and the corresponding modulus of elasticity (MOE) were determined according to DIN 52 377 [30] ($n = 10$). However, the lateral dimensions of the tensile bars were reduced by a factor of 2.3 (overall length according to DIN 52 377 [30]: 400 mm) due to the maximum treatment width (300 mm) of the plasma system that was used. Bending tests in accordance with DIN EN 310 [31] were executed ($n = 10$) to determine bending strength or modulus of rupture (MOR) and its related MOE. The compression strength was determined according to DIN 52 376 [32] ($n = 20$).

For each test parameter two types of plywood panels were tested: samples manufactured with the grain of the outer layers parallel to the direction of force, and samples with the grain of the outer layers perpendicular to the force direction. The tests according to DIN 52 377 [30], DIN EN 310 [31], and DIN 52 376 [32] were carried out on a 100-kN universal testing machine (Zwick GmbH & Co. KG, Germany) and evaluated by the corresponding software TEST EXPERT II (Zwick GmbH & Co. KG, Germany).

Results

Injected power and exposure time

Experiments were performed to ascertain process parameters showing the highest efficiency in terms of injected electrical power (dependent on the applied voltage) and treatment duration. The efficiency of treatment was evaluated by the water uptake capabilities of the veneers in untreated and plasma-treated state. Figure 2 (left) displays the water uptake vs. injected power of untreated or thermally modified beech veneers. Plasma treatment duration was set at 2 s and the immersion time was set at 1 s. Unmodified veneers show highest improvement in water uptake of approximately 50% at a power density of 3.5 W/cm^2 ($U \approx 18$ kV), whereas the uptake of thermally modified veneers was increased by fivefold (3.7 W/cm^2, $U \approx 18$ kV). Only marginal differences in means of water uptake can be observed between the chosen power densi-

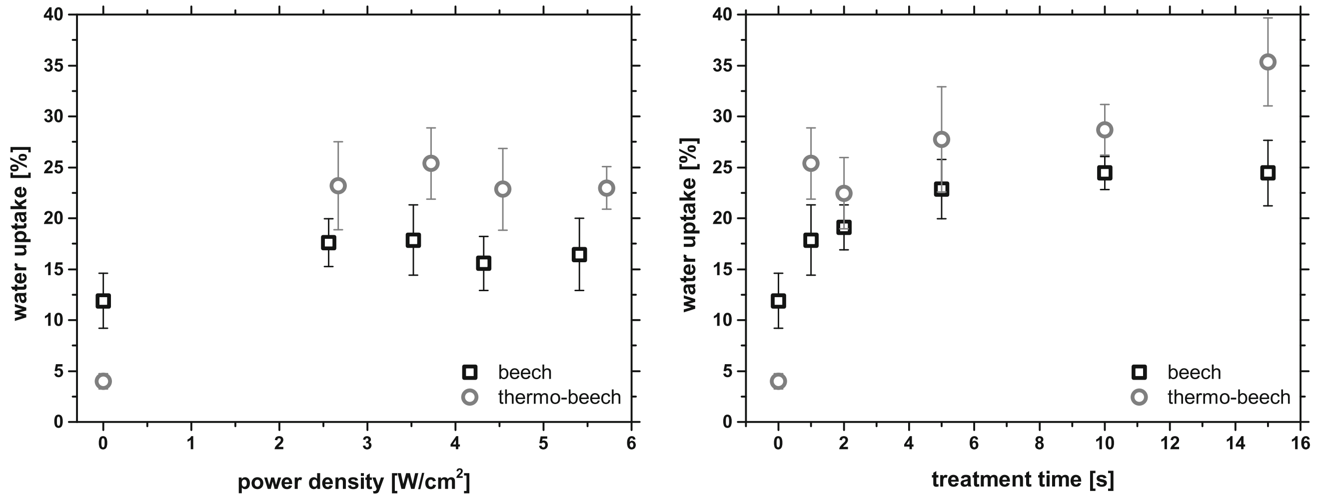

Fig. 2 Water uptake of modified and thermally modified beech veneers in relation to power density (*left*) and treatment time (*right*). *Error bars* display the standard deviation

ties. Differences in injected power at the same applied voltage were attributed to the differences in the EMC of unmodified and thermally modified beech [33]. Therefore, for all subsequent experiments the power density was set to the aforementioned values.

At the selected injected power, the plasma treatment time was varied within a range of 0–15 s (immersion duration 1 s). Unmodified beech veneers attain a water uptake of approximately 20% after plasma treatment duration of 5 s and show only marginal alterations with increasing treatment duration. Whereas thermally treated veneers reach a water uptake of approximately 25% after 1 s which remains stable up to 10 s, at a plasma exposure time of 15 s a distinct increase can be observed. The reasons for this behavior are hypothetical and cannot be discussed in the frame of this study. For all following experiments, the treatment duration was set to 5 s.

Generally, thermally modified beech veneers are more affected by plasma in terms of water uptake than are unmodified beech veneers.

Melamine uptake

In order to evaluate the uptake of modification agents and the resulting WPG according to Eqs. (1) and (2), respectively, untreated and plasma-treated (5 s) unmodified and thermally modified beech veneers were immersed in melamine solution for 1 s using melamine concentrations of 25 and 50% (Fig. 3).

Generally, the plasma-treated samples show enhanced uptake of melamine resin (Fig. 3, left) and increased WPG (Fig. 3, right) compared to the references. It is obvious that the effect is more pronounced for higher concentrations of melamine resin and thermally modified beech samples, respectively. Whereas the 25% solution results in an uptake-improvement of 24%, the 50% solution shows an improvement of 65% for unmodified beech. The increase in uptake of the thermally modified samples was 39% for the 25% solution, whereas the uptake of the 50% solution was doubled. The WPG follows the trend, but the differences are less pronounced for the unmodified beech veneers.

Dimensional stability and mechanical properties

Thermally modified, 25% melamine concentration

The results of the plywood panels made of thermally modified beech veneers impregnated with 25% melamine resin solution (Fig. 4) will first be discussed. Considering the thickness swelling and the thickness change in wet and dry conditions of the "reference^0" (not impregnated, melamine resin only as glue between single layers), the slopes of the corresponding curves (Fig. 4a, c, d, dark grey line, square data points) show a large discrepancy between the initial and final values, indicating a strong permanent swelling of "reference^0" in the dry state. The differences in these values amount to an increase of about 13% (reference^0), 8.8% (reference), and 3.9% (plasma) in the thickness in dry state ("thickness$_{dry}$"; Fig. 4c), and an increase of 4.4% (reference^0), 2% (reference), and 1.1% (plasma) in the thickness in the wet state ("thickness$_{wet}$"; Fig. 4d). This means that the thickness$_{dry}$ of the "reference^0" grows faster than the thickness$_{wet}$ with progressing cycle number. Therefore in the following, thickness swelling S^* and the absolute thickness of the samples in the dry and wet states were presented as criteria for dimensional stability.

The changes to the weight in the dry state provide information on the possible leaching of the modifying agent from the bulk material. The plasma-treated samples

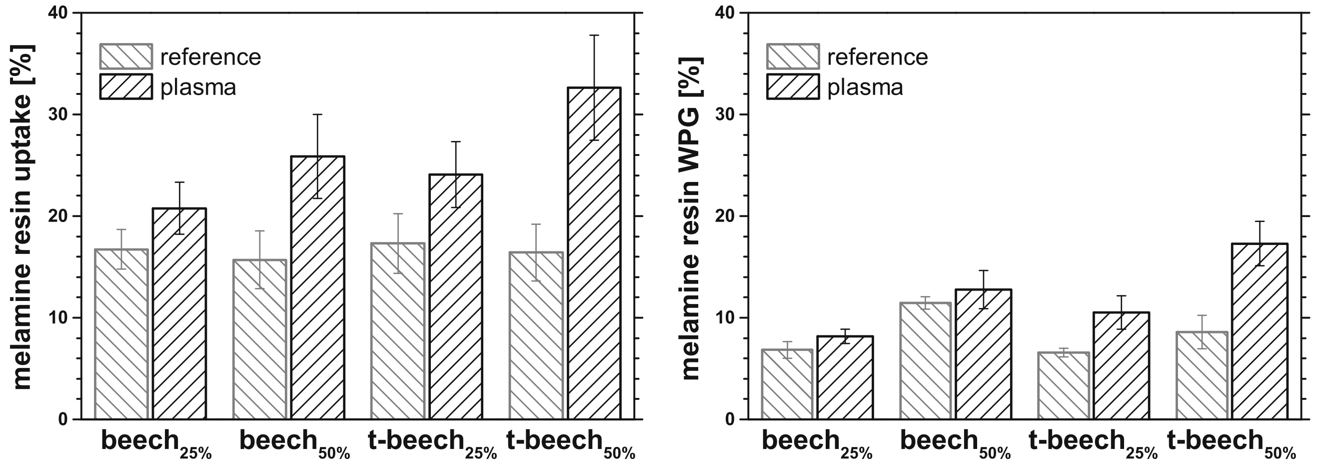

Fig. 3 Melamine uptake (*left*) and corresponding WPG in relation to veneer types and melamine concentration (*beech* unmodified, *t-beech* thermally modified, *subscript percentage value* refers to concentration of melamine solution). *Error bars* display the standard deviation

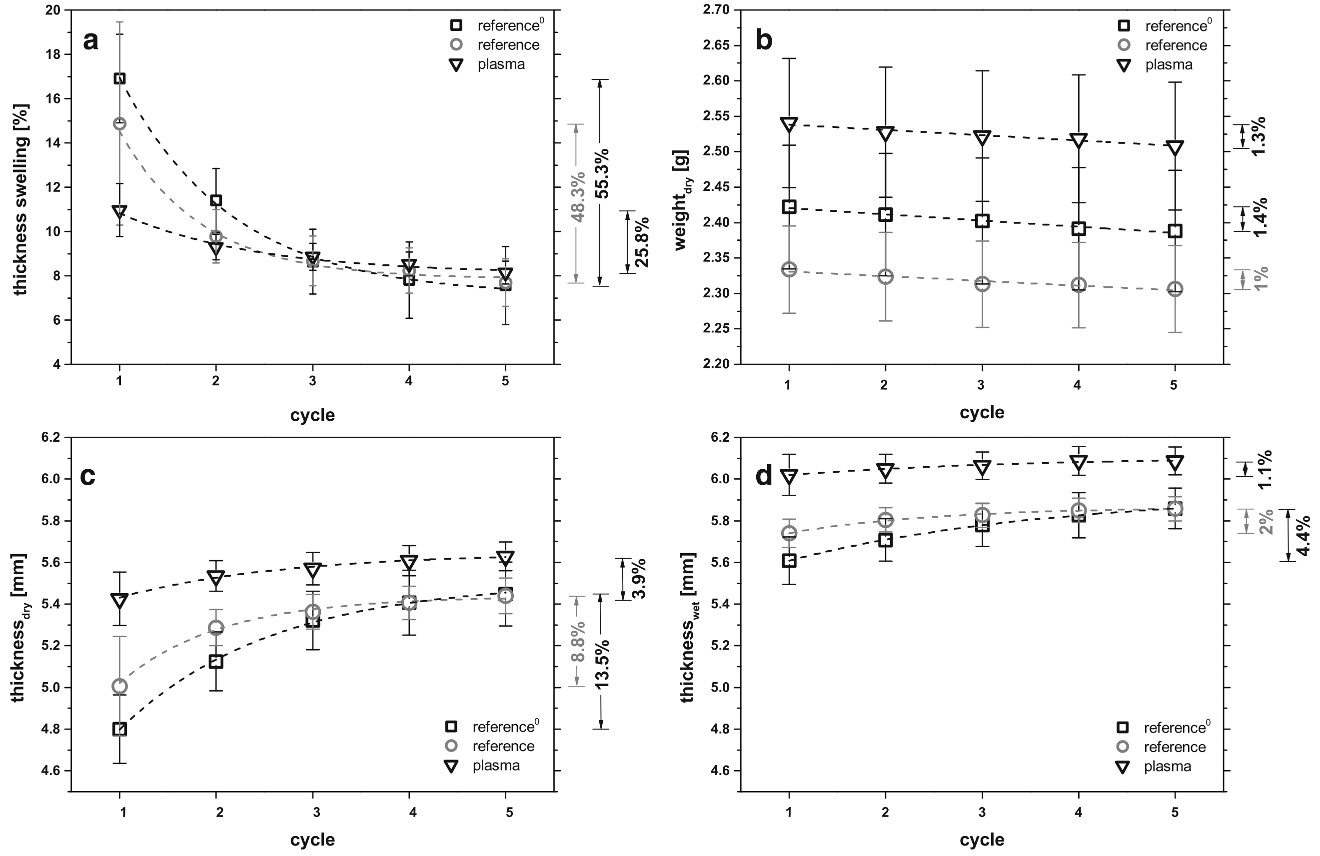

Fig. 4 Thickness swelling (**a**), thickness in dry state (**c**), thickness in wet state (**d**), and weight in dry state (**b**) of plywood made of thermally modified beech veneers impregnated with 25% melamine solution in relation to series of cycles for determining dimensional stability. *Error bars* display the standard deviation

for both melamine concentrations have a higher weight in the dry state, than do the "reference^0" and reference, which is in accordance with the WPG (Fig. 3, right). In this study, no leaching of melamine could be detected in any of the samples (Figs. 4b, 5b, 6b, 7b), since all variants show equal weight loss, attributed to accessory material of wood.

Table 1 displays the values of the collected data corresponding to DIN 52 377 [30], DIN EN 310 [31], and DIN 52 376 [32]. As expected, all variants show significant

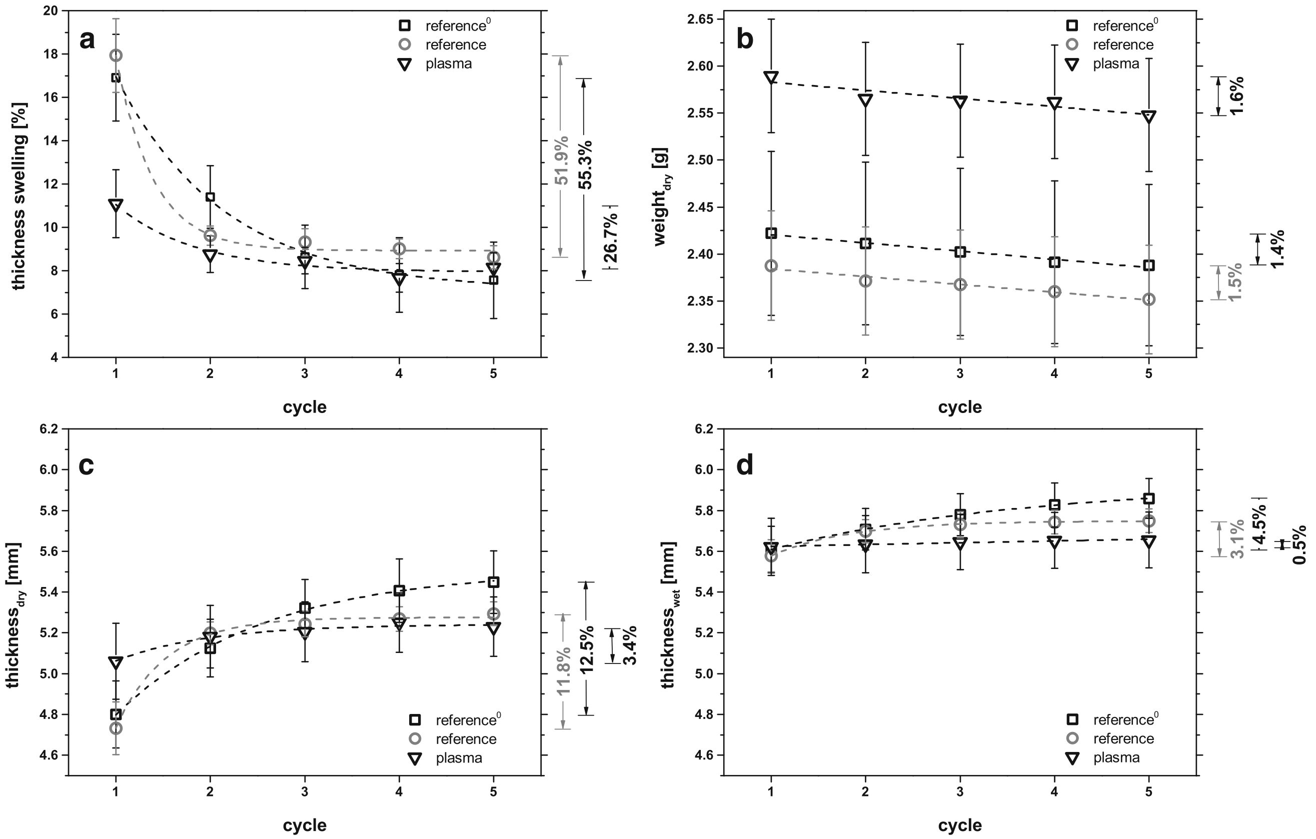

Fig. 5 Thickness swelling (**a**), thickness in dry state (**c**), thickness in wet state (**d**), and weight in dry state (**b**) of plywood made of thermally modified beech veneers impregnated with 50% melamine solution in relation to series of cycles for determining dimensional stability. *Error bars* display the standard deviation

differences between parallel and perpendicular test direction, an observation that has already been reported in several studies [29, 34]. For compressive strength, only marginal differences could be observed between reference^0, reference and plasma samples independent of grain direction of the outer layers (whereas “reference^0” shows the highest value in perpendicular direction and “plasma” in parallel direction, respectively). This applies also for tensile strength in perpendicular direction, whereas in parallel direction distinct differences occur (“reference^0” shows approximately 30% higher σM than “plasma”). MOE shows a similar behavior for parallel direction, although the differences were less distinct. In perpendicular direction, MOE behaves similar to σM; however, the value of “reference^0” is 20% above the values of “reference” and “plasma”. The bending strength, also known as MOR, shows similar values for all variants in perpendicular direction; in parallel direction the plasma value is 10% lower compared to “reference^0”. In both test directions, the corresponding MOE for reference and plasma shows generally higher values than the “reference^0”.

Thermally modified, 50% melamine concentration

Plywood samples made of thermally modified beech veneers impregnated with a 50% melamine resin solution (Fig. 5) show similar results as the thermally modified veneers impregnated with 25% melamine solution for the swelling, whereby the differences between the plasma samples and reference or reference^0, respectively, are more significant. A comparison of the plasma samples impregnated with the 25% solution and the 50% solution reveals a slight improvement for the latter ones, which is due to the higher WPG. The plasma samples show no significant changes in thickness in dry and wet state and remain almost dimensionally stable.

For this specimen set, the plasma samples exhibit distinctly higher compressive strength in both test directions than the reference samples. Compared to the reference^0 samples, they display a similar compressive strength in perpendicular direction and a 15% increase in parallel direction (Table 2). The tensile strength and the corresponding MOE of the plasma and reference samples (in

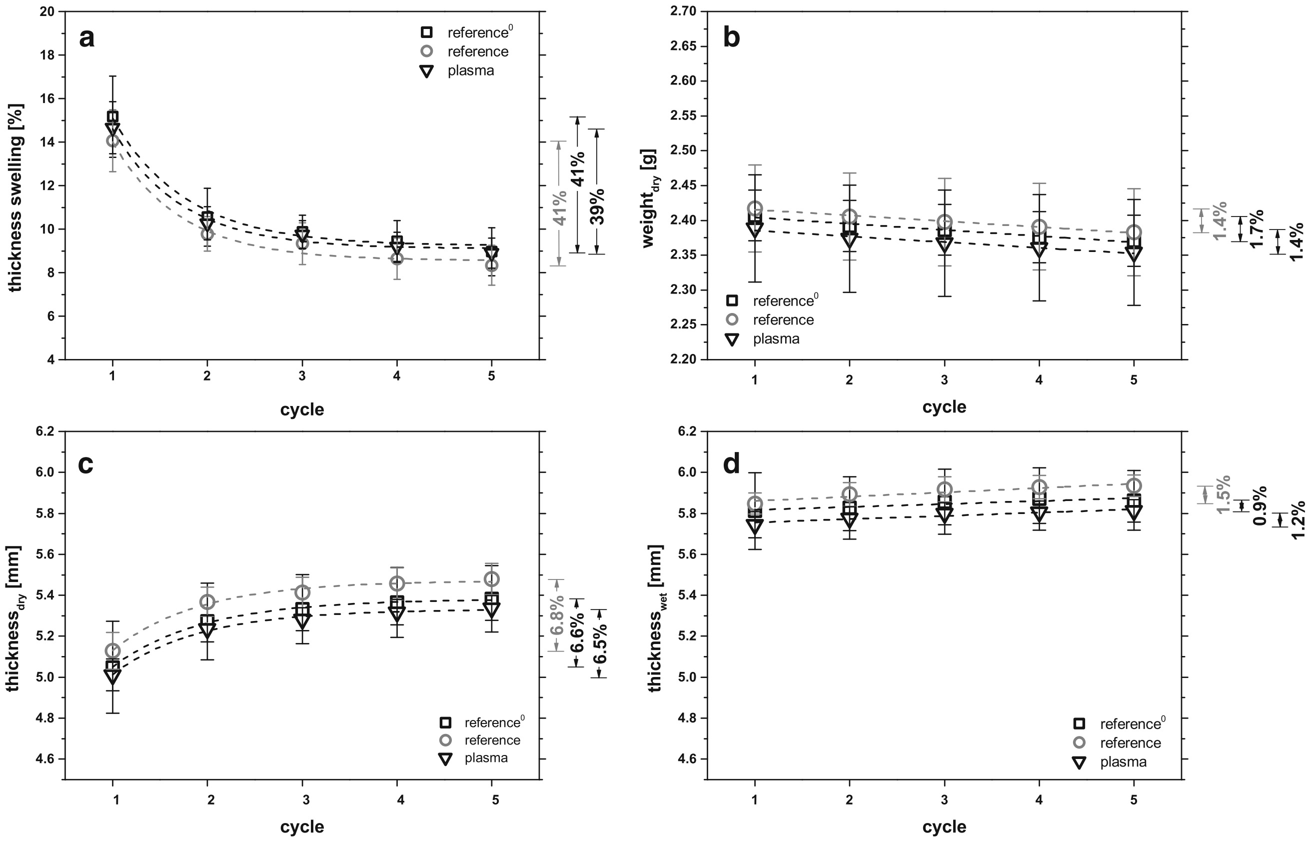

Fig. 6 Thickness swelling (**a**), thickness in dry state (**c**), thickness in wet state (**d**), and weight in dry state (**b**) of plywood made of unmodified beech veneers impregnated with 25% melamine solution in relation to series of cycles for determining dimensional stability. *Error bars* display the standard deviation

both grain orientations) are significantly lower than the values of the "reference^0". The MOR-values of "reference^0" and "plasma" are 20 and 15% higher, respectively, than the values of the reference in perpendicular test direction; in the parallel test direction, "reference^0" also shows a higher MOR than the reference and plasma samples but the differences are less pronounced. All three variants present approximately equal MOE in parallel direction: in the perpendicular direction, "plasma" samples show approximately 1 kN/mm^2 higher MOE than "reference^0" and "reference".

Not modified, 25% melamine concentration

Plywood samples made of unmodified beech veneer show noticeable differences in contrast to plywood made of thermally modified veneers for both melamine resin concentrations. Figure 6 depicts the results of plywood samples made of unmodified beech veneers impregnated with a 25% melamine resin solution. In dry state, the thickness follows a distinctly asymptotic slope even for the samples made of plasma-pretreated veneers, whereas for the thickness in the wet state all variants follow a linear slope. For both concentrations in all three variants, the thickness swelling amounts approximately 40%, so no significant improvement in dimensional stability is observable for the plasma samples.

Table 3 depicts similar values for the compressive strength for both test directions of reference^0 and plasma, whereas the reference values exhibit a significant drop in perpendicular direction. Only slight differences could be observed for all variants with regard to tensile strength and related MOE in perpendicular test direction; in parallel direction, the values of reference and plasma samples are lowered by 10 and 25%, respectively, regarding σM, and 25 and 15%, respectively, regarding MOE. Considering the modulus of rupture as well as the MOE, the values are comparable for all variants in perpendicular grain orientation. In parallel direction, however, reference samples show a 15% drop in MOR (compared to "plasma" and "reference^0"), whereas for the MOE the "reference^0" shows a significantly lower value than the plasma samples (approximately 25%).

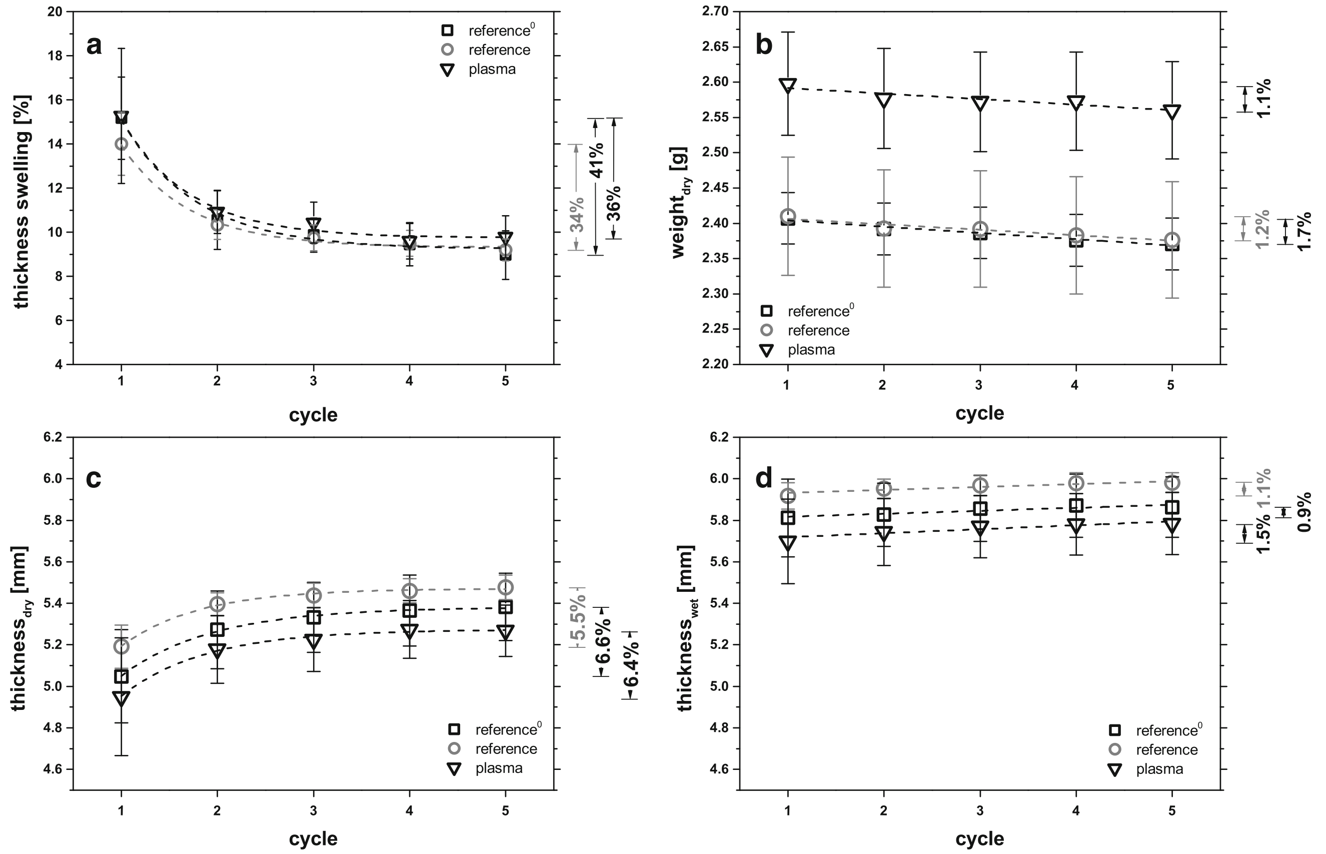

Fig. 7 Thickness swelling (**a**), thickness in dry state (**c**), thickness in wet state (**d**), and weight in dry state (**b**) of plywood made of unmodified beech veneers impregnated with 50% melamine solution in relation to series of cycles for determining dimensional stability. *Error bars* display the standard deviation

Table 1 Mechanical properties of plywood made of thermally modified beech veneers impregnated with 25% melamine solution (± = standard deviation)

Sample	Direction	Compressive strength (N mm^{-2})	Tensile strength		Bending strength	
			σM[a] (N mm^{-2})	MOE (kN mm^{-2})	MOR (N mm^{-2})	MOE (kN mm^{-2})
Reference^0	Parallel	38 ± 2	69 ± 9	8.8 ± 0.9	126 ± 10	12.9 ± 1.1
	Perpendicular	55 ± 2	88 ± 11	13.2 ± 1.3	54 ± 4	3.8 ± 0.2
Reference	Parallel	36 ± 2	60 ± 6	7.7 ± 0.7	124 ± 11	14.7 ± 1.5
	Perpendicular	52 ± 5	83 ± 8	11 ± 1	60 ± 3	4.5 ± 0.2
Plasma	Parallel	40 ± 3	52 ± 5	6.9 ± 0.5	116 ± 5	13.4 ± 0.7
	Perpendicular	52 ± 3	82 ± 8	11 ± 0.9	57 ± 3	4.4 ± 0.2

MOE modulus of elasticity, *MOR* modulus of rupture

[a] Tensile strength

Not modified, 50% melamine concentration

In the case of 50% concentration of melamine resin (Fig. 7), the percentage thickness swelling of the reference (34%) and plasma samples (36%) shows slightly lower values than the variants impregnated with 25% solution (41 and 39%, respectively).

For this parameter set the plasma samples show higher values in compressive strength as reference or reference^0 in both directions. However, for tensile strength and related MOE the plasma samples show a distinct decline of up to 40% compared to “reference^0”, independent of the test direction. For modulus of rupture, the reference samples show a slight increase in perpendicular direction but a distinct decrease in parallel direction compared to the reference^0 and plasma samples. In contrast, the MOE of the plasma samples is up to 20% higher than the reference and reference^0 samples in both directions (Table 4).

Table 2 Mechanical properties of plywood made of thermally modified beech veneers impregnated with 50% melamine solution (±standard deviation)

Sample	Direction	Compressive strength (N mm^{-2})	Tensile strength		Bending strength	
			σM[a] (N mm^{-2})	MOE (kN mm^{-2})	MOR (N mm^{-2})	MOE (kN mm^{-2})
Reference[0]	Parallel	38 ± 2	69 ± 9	8.8 ± 0.9	126 ± 10	12.9 ± 1.1
	Perpendicular	55 ± 2	88 ± 11	13.2 ± 1.3	54 ± 4	3.8 ± 0.2
Reference	Parallel	37 ± 3	49 ± 3	6.8 ± 0.6	93 ± 7	11.6 ± 0.6
	Perpendicular	47 ± 4	66 ± 8	8.8 ± 0.9	45 ± 3	3.6 ± 0.2
Plasma	Parallel	44 ± 1	52 ± 7	7.5 ± 0.7	107 ± 8	12 ± 1.1
	Perpendicular	56 ± 4	68 ± 10	9.9 ± 1.1	52 ± 4	4.9 ± 0.4

MOE modulus of elasticity, *MOR* modulus of rupture

[a] Tensile strength

Table 3 Mechanical properties of plywood made of unmodified beech veneers impregnated with 25% melamine solution (± = standard deviation)

Sample	Direction	Compressive strength (N mm^{-2})	Tensile strength		Bending strength	
			σM[a] (N mm^{-2})	MOE (kN mm^{-2})	MOR (N mm^{-2})	MOE (kN mm^{-2})
Reference[0]	Parallel	38 ± 2	82 ± 7	9.3 ± 1.1	136 ± 12	12.1 ± 1.2
	Perpendicular	51 ± 2	94 ± 9	11.3 ± 1.6	60 ± 3	4 ± 0.4
Reference	Parallel	40 ± 3	74 ± 5	7.4 ± 0.5	120 ± 13	13.8 ± 1.1
	Perpendicular	47 ± 3	93 ± 7	11.1 ± 0.6	59 ± 5	4.3 ± 0.2
Plasma	Parallel	40 ± 2	65 ± 10	8 ± 1.1	137 ± 12	15.1 ± 0.9
	Perpendicular	51 ± 3	90 ± 9	10.8 ± 0.9	61 ± 4	4.4 ± 0.3

MOE modulus of elasticity, *MOR* modulus of rupture

[a] Tensile strength

Table 4 Mechanical properties of plywood made of unmodified beech veneers impregnated with 50% melamine solution (± = standard deviation)

Sample	Direction	Compressive strength (N mm^{-2})	Tensile strength		Bending strength	
			σM[a] (N mm^{-2})	MOE (kN mm^{-2})	MOR (N mm^{-2})	MOE (kN mm^{-2})
Reference[0]	Parallel	38 ± 2	82 ± 7	9.3 ± 1.1	136 ± 12	12.1 ± 1.2
	Perpendicular	51 ± 2	94 ± 9	11.3 ± 1.6	60 ± 3	4 ± 0.4
Reference	Parallel	36 ± 2	59 ± 7	6.9 ± 0.5	114 ± 15	12.5 ± 0.2
	Perpendicular	46 ± 3	80 ± 9	9.1 ± 0.4	64 ± 3	4.5 ± 0.2
Plasma	Parallel	41 ± 2	51 ± 8	6.2 ± 0.6	128 ± 8	14.6 ± 0.9
	Perpendicular	53 ± 5	71 ± 12	9.7 ± 1	61 ± 4	4.8 ± 0.3

MOE modulus of elasticity, *MOR* modulus of rupture

[a] Tensile strength

Discussion

Water uptake and melamine resin uptake

In general, atmospheric pressure air–plasma pre-treatment of beech veneers leads to enhanced water uptake and melamine uptake (and as a consequence, increased WPG).

These observations are attributed to an accelerated inflow of solution into the wood capillaries due to the improved wetting and opening of the capillaries as a result of the plasma-induced generation of functional groups [35] and the degradation of the pit membrane [36], respectively. Wascher et al. [37] demonstrated plasma-induced effects within the bulk of beech veneers and ascribed these effects to the occurrence of discharges within the wood capillaries leading to enhanced capillary penetration.

However, thermally modified beech veneers show a more pronounced effect in terms of water uptake, melamine uptake, and the corresponding WPG when plasma-treated as unmodified beech veneers, which is reflected in the dimensional stability of plywood. This behavior is attributed to the hydrophobic character of thermally modified wood products [9], which hampers the uptake of water and water-based modification agents into the bulk along with an over-proportional plasma effect in comparison to unmodified beech, as has already been reported for thermally modified wood specimens in comparison to unmodified ones [38].

Dimensional stability

The differences in thickness swelling of "reference^0" in dry and wet state, with progressing cycle number are attributed to a more distinct spring-back effect (expansion of the densified wood structure due to the pressing process) compared to the samples made of impregnated and plasma-treated veneers. This also has consequences for the percentage thickness swelling S^* (see Eq. 4), as can be seen in Fig. 4a, where the initial value for "reference^0" amounts to 17% and ends at 7.5% below the final value of the plasma samples (8%, starting value 11%). Considering the equation frequently used in the wood science literature for the anti-swelling efficiency (ASE), characterizing dimensional stability,

$$\mathrm{ASE}\ (\%) = ((S_\mathrm{u} - S_\mathrm{m})/S_\mathrm{u}) \times 100, \tag{5}$$

where S_u is the swelling coefficient of unmodified samples and S_m is the swelling coefficient of modified samples [1], the observed behavior would lead to a negative ASE for the plasma samples, despite the fact that the plasma samples show only small alterations in the thickness during the cycle runs. This means that when the benchmark S_u for the ASE calculation (in our case, thickness of "reference^0") is derived from a sample which shows permanent swelling in dry state, the use of the ASE is not reasonable. Although the use of ASE would be appropriate in the case of plywood made of unmodified beech veneers—since it does not show distinct permanent swelling in dry state—it has been omitted for the sake of consistency.

All three plywood variants made of unmodified beech veneers showed comparable dimensional stability, irrespective of plasma pre-treatment, production process, and melamine resin concentration. The authors attribute this behavior on the one hand to the generally low WPG-value of the unmodified beech veneers after the chosen immersion duration (plasma/reference). On the other hand, it might also be explained by a possible penetration of the melamine resin from the glue line (despite the presence of additives) during the pressing process of "reference^0", leading to a certain impregnation effect of these samples, which in consequence diminishes the differences between "reference^0" and "plasma". In contrast, the samples made of thermally modified beech veneers showed distinctly improved dimensional stability when veneers are plasma pre-treated, compared to reference^0 and reference samples (for both concentrations). This can be explained by the fact that the hydrophobic properties of thermally modified veneers impede the penetration of melamine resin into the bulk (applies to the reference and reference^0 samples). The improved dimensional stability of plasma-treated samples made from thermally modified veneers results in a significantly higher melamine uptake (see Fig. 3)—due to the over-proportional plasma effect displayed by the thermally modified beech veneers in comparison to unmodified beech.

Mechanical properties

Similar to the discussion of dimensional stability, a direct comparison of the results with other scientific studies is difficult, because no values were found in the literature either for the impregnation of beech veneers with melamine resin after a plasma treatment in particular (along with the production of plywood without an additional adhesive layer between the single veneers) or for plywood production from thermally modified beech veneers generally. Trinh et al. tested the bending strength of five-layer plywood samples made from vacuum-impregnated beech veneers with melamine resin (solution solid content 5–10%) and bonded with phenol formaldehyde (PF) resin [34]. Dieste et al. presented similar results of plywood samples made from DMDHEU vacuum-impregnated beech veneers [39]. In both studies, the reported MOR of the references is 85–100 N/mm^2 in parallel direction and 45–55 N/mm^2 in perpendicular direction, and the corresponding MOE is 10–12.5 and 3–4 kN/mm^2, respectively. The obtained values of MOR and MOE (for plywood made from unmodified beech veneers) in the present study are largely in accordance with these values in the literature. As here, the MOR and MOE values in the cited works vary at a similar level, depending on treatment options. This means no adverse side effects in bending strength and the corresponding MOE due to the veneer modification in general and plasma treatment in particular could be observed.

With regard to tensile strength, the force required to fracture and the related MOE are lower for samples made of impregnated veneers than the corresponding values of conventionally produced plywood. Xie et al. [40] ascribed the reduction of the tensile strength of Scots pine wood (*Pinus sylvestris* L.) impregnated with dimethylol dihydroxyethylene urea (DMDHEU) to the fact that the natural elasticity of the wood fibers is restricted by a deposition of the modification agent in the cell wall and the frictional resistance between the fibers are increased as a result of cross-linking. Since a partial penetration into the cell wall occurs during the impregnation with melamine resin [41, 42], this explanation might also apply to the fracture behavior of plywood made of melamine-impregnated veneers.

With regard to compressive strength, the results indicate only a marginal influence of plasma pre-treatment. Nevertheless, thermally modified samples as well as unmodified specimens show a slight increase in compressive strength in parallel direction (exception: unmodified beech, 25% melamine concentration) compared to "reference" and "reference^0". Gindl et al. reported increased compressive strength of melamine resin-impregnated spruce wood [43]. The strength increase for samples made of plasma pre-treated veneers can therefore be attributed to the higher loading with melamine resin (see Fig. 3).

Conclusion

Generally, it can be stated that with regard to the mechanical properties of the plywood, no distinct differences could be measured among all tested variants, with the exception of tensile strength for plywood made from thermally modified veneers.

The obtained data clearly show that:

- Plasma pre-treatment reverses the undesirable hydrophobic effects of thermal modification of wood.
- Plywood made of thermally modified and impregnated veneers achieves a significant improvement in dimensional stability after undergoing air plasma pre-treatment.
- Plasma pre-treatment of the veneers has no influence on compressive strength and bending strength of the manufactured plywood; however, a slight decrease in tensile strength was observed.

This means that two factors compromising the use of thermally modified wood products in the building sector—the loss in strength properties and the hydrophobic character—can be successfully remedied through plywood that has undergone hydrophilization by plasma pre-treatment of the veneers.

The application of plasma technology in plywood production shows particularly beneficial effects with regard to outdoor contexts where thermally modified wood is used, for example in decking or facade elements. For application as structural timber in construction, however, the decrease in tensile strength has to be taken into account.

Acknowledgements This work was funded by the German Federal Ministry of Education and Research (BMBF), under the supervision of Dr.-Ing. Karen Otten, in Jülich, Germany, and the joint research project "PlaNaWood 2" (Grant No. 03XP0015B). The authors would like to thank Roger Skarsten from the HAWK.

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