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Alteration of Bending Properties of Wood Due to Ammonia Treatment and Additional Densification

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Abstract: This paper deals with comparative studies of bending behavior of untreated and modified European beech (*Fagus sylvatica* L.), European oak (*Quercus* spp.) and black locust (*Robinia pseudoacacia* L.). The modification of the woods included both ammonia treatment and ammonia treatment in combination with mechanical densification. For each ammonia treatment, pure gaseous ammonia was used. The investigations were conducted by means of three-point bending tests. The bulk density increases significantly due to ammonia treatment and, furthermore, due to additional mechanical densification. The modulus of rupture is not affected by ammonia treatment. Additional mechanical densification, however, leads to a strong increase in the strength and stiffness. The deflection behavior changes in such a way that the ammonia treatment leads to an increase in deflection, and the additional mechanical densification further reinforces this trend.

Keywords: gaseous ammonia treatment; beech wood; bending test; densification; mechanical properties; deflection

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1. Introduction

Improving the mechanical properties of indigenous wood species is essential to develop fields of application such as mechanical engineering. It is known that compression of the wood structure leads to a higher bulk density and thus higher rigidity and hardness [1]. In order to allow minor structural damage and low pressing forces, the wood is usually plasticized before densification. Wood as a viscoelastic material is conventionally plasticized by high moisture and/or heat [2]. However, if the wood is subjected to renewed climate stress, densified wood tends to spring back to its original shape, which is known as the set recovery. Therefore, fixation of the densified wood structure is absolutely necessary in a second step. This has already been successfully proven with the help of a subsequent thermal modification in the form-fixed state of the compacted wood [3].

An alternative method, which ensures both plasticization and fixation in one step, is ammonia treatment [4–7]. The ammonia penetrates deeper into the wood than water and also swells the crystalline areas of the cellulose. This notably plasticizes the wood, and a permanent displacement of molecules becomes possible as the cellulose changes its morphology because new bonds are formed [8]. Ammonia can be brought into contact with the wood by various methods. First of all, impregnation in liquid anhydrous ammonia is possible [9]. Ammonia must be cooled to −33 °C at normal pressure or kept in a pressure vessel to obtain a liquid state. Second, plasticizing with ammonia in a gaseous atmosphere is also possible [10]. The last plasticizing method is the impregnation with aqueous ammonia solution [11]. The method used in this study is the plasticization in gaseous atmosphere at almost saturated vapor pressure to prevent condensation effects. The important advantages of gaseous treatment are the ability to influence the intensity of the treatment by means of pressure and temperature. The system technology is limited to a temperature-controlled autoclave. During the treatment, there are no boiling phases, and the ammonia can be easily drained from the autoclave. It is also a relatively fast process, as the ammonia is gaseous, has very small molecules and saturates the wood sample very quickly.

The aim of this study was to investigate the bending behavior and selected property changes of ammonia-treated and densified wood in comparison to untreated and only ammonia-treated wood of three indigenous wood species.

2. Materials and Methods

Three different indigenous wood species have been modified using gaseous ammonia and a subsequent mechanical densification. The investigated wood species were European beech (*Fagus sylvatica* L.), European oak (*Quercus* spp.) and black locust (*Robinia pseudoacacia* L.). The specimens of one wood species were taken from the same defect-free plank of wood cut to the dimensions of $10 \times 33 \times 200$ mm^3 (R × T × L), dried at 103 °C and afterward conditioned at 65% relative humidity (RH) and 20 °C. The dimensions were chosen because further investigations were carried out on the samples (experimental modal analysis). The series of tests can be divided into untreated series, solely ammonia-treated (AT) series and ammonia-treated and subsequently densified (ATD) series. Each series included 7 specimens from each wood series.

The ammonia treatments were performed in a stainless steel autoclave, which was kept isothermal at 20 °C through active temperature control. Preliminary to ammonia treatment, the autoclave and the specimens positioned in it had been evacuated for 5 min to a pressure of 50 hPa. Gaseous ammonia treatment was conducted at a relative vapor pressure (total pressure to saturated vapor pressure ratio) of 0.9 at 20 °C for 6 h. Thus, the resulting pressure was 7710 hPa. Gaseous ammonia (99.98% purity) was taken from a pressurized gas bottle. The pressure was controlled by an electric valve actuation. When the treatment time was over, excess pressure was drained and specimens could be removed from the autoclave.

The test plan provided that one-third of the samples of each wood species was kept as a reference series without modification. Another one-third was only treated with gaseous ammonia (AT), and the last one-third of the samples was treated with gaseous ammonia and densified in radial direction by 20% of the swollen radial dimension (ATD). A universal test machine was used to ensure a constant compression speed of 1 mm/min (TIRAtest 28100 with 100 kN load sensor). Before densification, specimens were placed between aluminum plates that could be bolted together. The duration of the densification process was approximately 2 min and was performed at 65% RH and 20 °C. At the end of the densification, the aluminum plates were bolted together in order for the distance to remain constant, and the testing machine was opened again. The AT and ATD samples were stored under a fume hood for two weeks to allow the ammonia to evaporate. Afterward, all specimens were oven dried at 103° to remove ammonia completely followed by conditioning at 20 °C and 65% RH until constant mass was achieved. All specimens were formatted to the final dimensions of $6.5 \times 28 \times 190$ mm^3 (R × T × L). Deformations caused by the modification could thus be eliminated. The equilibrium moisture content (EMC) was calculated from the ratio of the difference between the dry and conditioned weight to the dry weight.

The investigations were conducted by means of three-point bending tests according to DIN EN 310 [12]. Deviating from the standard, the diameter of all rollers was set at 15 mm and the support spacing at 150 mm according to comparable studies by Krüger et al. [13]. A universal test machine was used (Hegewald & Peschke Inspekt 10 with 10 kN load sensor), and the test speed was determined to be 3 mm/min. The static modulus of elasticity (MOE) and the modulus of rupture (MOR) were evaluated with load in the radial direction. Furthermore, the change in strain behavior was investigated.

Statistical evaluation was conducted with the software IBM SPSS Statistics Version 25. ANOVA was used for the comparison of the different groups followed by Bonferroni post hoc test. The value for statistically significant differences was set at $p < 0.05$. Data are reported as means ± standard deviations.

3. Results

The EMC and change in mass are shown in Table 1. The density and results of mechanical testing are shown in Figure 1. After the ammonia treatment, it was observed that dark-colored condensate had collected at the bottom of the autoclave.

Table 1. Determined equilibrium moisture content (EMC) and change in mass.

Series		**EMC** [1]				**Change in Mass** [2]			
		(%)		***p*-Value**		**(%)**		***p*-Value**	
Beech	untreated	8.7	(±0.1)	ref		−0.20	(±0.06)	ref	
	AT	6.7	(±0.2)	$p < 0.001$	ref	−0.21	(±0.15)	n.s.	ref
	ATD	5.8	(±0.3)	$p < 0.001$	$p < 0.001$	0.17	(±0.15)	$p < 0.001$	$p < 0.001$
Oak	untreated	10.8	(±0.1)	ref		−0.10	(±0.31)	ref	
	AT	10.1	(±0.3)	$p < 0.001$	ref	−0.28	(±0.11)	n.s.	ref
	ATD	9.8	(±0.3)	$p < 0.001$	n.s.	−0.36	(±0.56)	n.s.	n.s.
Black locust	untreated	7.9	(±0.4)	ref		−0.21	(±0.06)	ref	
	AT	6.6	(±0.3)	$p < 0.001$	ref	0.88	(±0.13)	$p < 0.001$	ref
	ATD	5.8	(±0.2)	$p < 0.001$	$p < 0.001$	0.83	(±0.19)	$p < 0.001$	n.s.

[1] conditioning at 20 °C/65% relative humidity; [2] oven dry state before and after modification; ref: reference, AT: ammonia treated, ATD: ammonia treated and densified, n.s.: not significant.

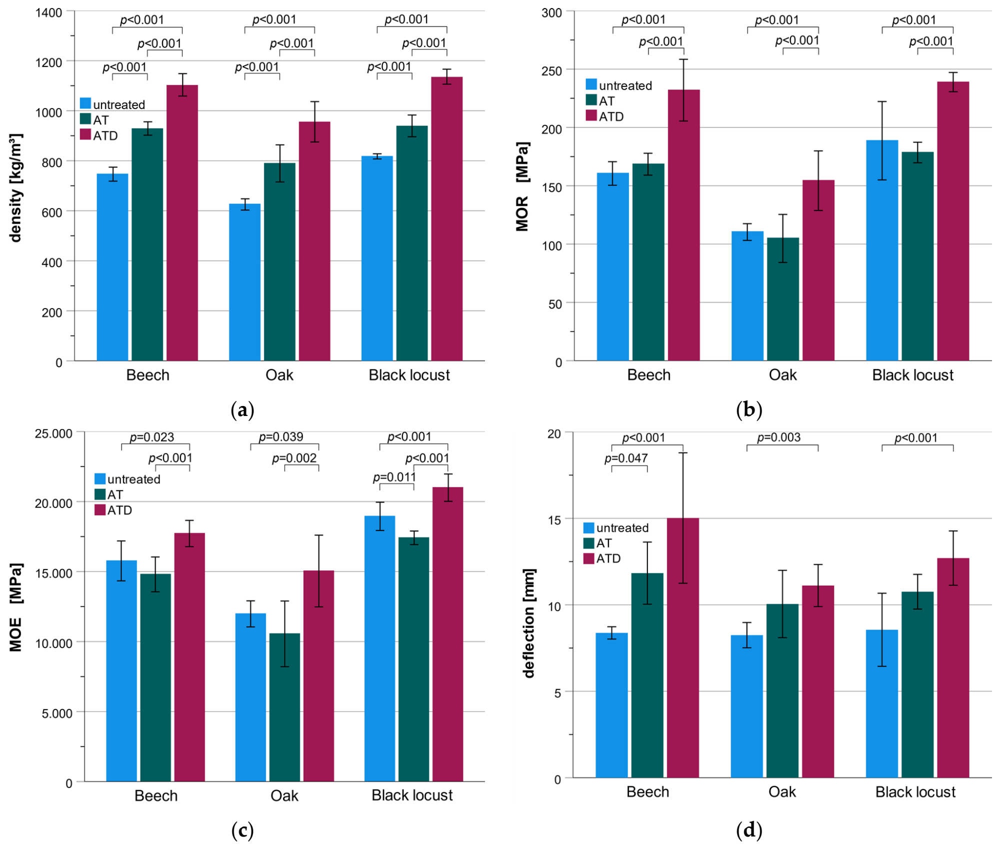

Figure 1. Three-point bending test [1] and density [1] of beech, oak and black locust depending on modification [2]: (**a**) density, (**b**) modulus of rupture, (**c**) modulus of elasticity and (**d**) maximum deflection during bending test. [1] conditioning at 20 °C/65% relative humidity. [2] untreated, AT (ammonia treated) and ATD (ammonia treated and densified).

4. Discussion

The EMC is lowered by the ammonia treatment (Table 1), and the mechanical densification leads to a further decline in the EMC. In the case of the AT series, a possible explanation for this behavior may be that the reduction in the highly hydrophilic acetyl groups causes a decline in the EMC [9]. Furthermore, the reduction in EMC due to gaseous ammonia treatment was also observed in birch wood samples [14]. The author assumed that hygroscopic components may have been removed from the samples due to a detected loss of mass. The additional change in EMC for the ATD series may be the result of a longer exposure time to the ammonia. Due to the storage between aluminum plates, the ammonia could not easily evaporate from the samples, and the reaction time of the chemical changes was prolonged.

The change in mass (Table 1) is not expressed by a clear trend, which is probably caused by a superposition of several influences. The untreated samples were dried twice according to the modified samples. A slight loss of mass was observed in all wood species. For oak, the mass changes of the AT and ATD series did not differ significantly from the untreated series. In the case of beech wood, only the ATD series differs from the others and, in contrast to the AT series, shows an increase in mass. Since both modified series were treated identically with ammonia and the standard deviations are high, the changes seem to lie within the range of measurement accuracy. The only clear changes are shown by black locust. Here, the AT and ATD series show an increase of almost 1%. Ammonia leads to the formation of amides, which is possibly followed by an increase in mass [8]. However, it is unclear why this cannot be observed in the other wood species. At this point, the formation of dark-colored condensate at the bottom of the autoclave must be mentioned. This observation confirms that components were extracted from the wood, but their quantity could not be determined due to the chosen experimental setup. Possibly, this leaching process and the increase in mass overlap. In combination with a small number of samples and since the findings are already in the range of measurement accuracy, a final clarification of the changes in mass is not possible. At this point, a further investigation with an adapted test setup is necessary.

A significant increase in bulk density (Figure 1a) can be observed for all process steps. Ammonia fumigation and subsequent degassing has already been frequently described [15–18]. The increase is attributed to a collapse of the cells. This causes the cell lumens to shrink and the bulk density to increase. The phenomenological description of the shrinkage process at the cellular level was first performed by Pollisco et al. [18], who divided the process into five stages. These five stages include the initial situation of the dry cell, the first ammonia adsorption and swelling into the lumen, the swelling of the entire wooden cell, the desorption and consolidation of the reduced dimensions beginning in the lumen and the completely shrunken dried cell. The density increases between 15% and 26%. The highest density increase can be observed in the wood with the lowest initial density (oak). The smallest increase is seen in the wood with the highest initial density (black locust). It is conceivable that in the case of high initial densities, the effect of self-compaction has a smaller effect on the wood, as the difference to the maximum possible density is smaller. As the increase in beech wood of 24% is similar to that of oak, there is no difference between diffuse porous and ring porous wood. The further increase in bulk density is caused by mechanical densification. The specimens do not spring back after being removed from the press plates. It is possible that new or altered cross-links will stabilize the previously plasticized wood structure. An indication of this may be the ammonia-induced conversion of cellulose I to cellulose III [19]. The good plasticization was also demonstrated by densification using a roller press [11,20]. In this case, there are no mechanisms to prevent springback, but extremely high bulk densities can still be achieved. Mechanical densification shows similar density changes for the woods: 19% for beech and 21% for oak and black locust.

Ammonia treatment has no significant effect on MOR. MOE is significantly lowered in the case of black locust, but the mean values of beech and oak are likewise diminished. Due to the similar behavior of all three wood species, the significance in black locust appears to be caused by sample selection and low sample numbers rather than structural or chemical differences between species. Important at this point is that the density increases sharply at the same time, and the specific values therefore decrease. Native wood generally shows an increase in strength properties with increasing density and decreasing EMC [21]. Ester bonds between hemicelluloses and lignin are easily separable in alkaline environments [22]. As a result, the wood loses its structural cohesion and is less able to absorb forces. A structural investigation is needed to determine the extent to which degree damage is caused by cell collapse.

The mechanical densification leads to a significant increase in MOE and MOR according to the strong increase in bulk density. This behavior corresponds to other plasticizing and compaction processes, e.g., high-pressure treatment [23]. Compared to the measured strength values, deflection behavior changes most in relation to the change in bulk density. A strong increase in the deflection can be observed on all wood types already at the AT series. Therefore, ammonia treatment as such must have an influence on the structural composition of the wood. At this point, self-compression plays an important role, as it creates a reserve of deformation. Zauer et al. [10] show that self-compression is accompanied by a collapse of the vessels and buckling of the cell walls. The buckling allows an increase in elongation during bending, as the buckling can first unfold and then the cells fail [24].

The schematic explanation of the processes that could lead to higher deflection is shown in Figure 2. In the upper part, it is shown that both the ammonia modification and the mechanical densification lead to a buckling of the cell walls. In terms of mechanical densification, cell wall buckling as a result of transversal densification is adequately described [25]. Moreover, with regard to ammonia treatment, it is known that cells buckle [10]. The lower part of the figure shows that buckling causes a strain reserve. This reserve is expressed by the fact that the cells must first unfold again before they fail. Since both modifications, the ammonia treatment and the mechanical densification, lead to a buckling of the cell walls, a higher deflection can be explained with both processes (AT and ATD).

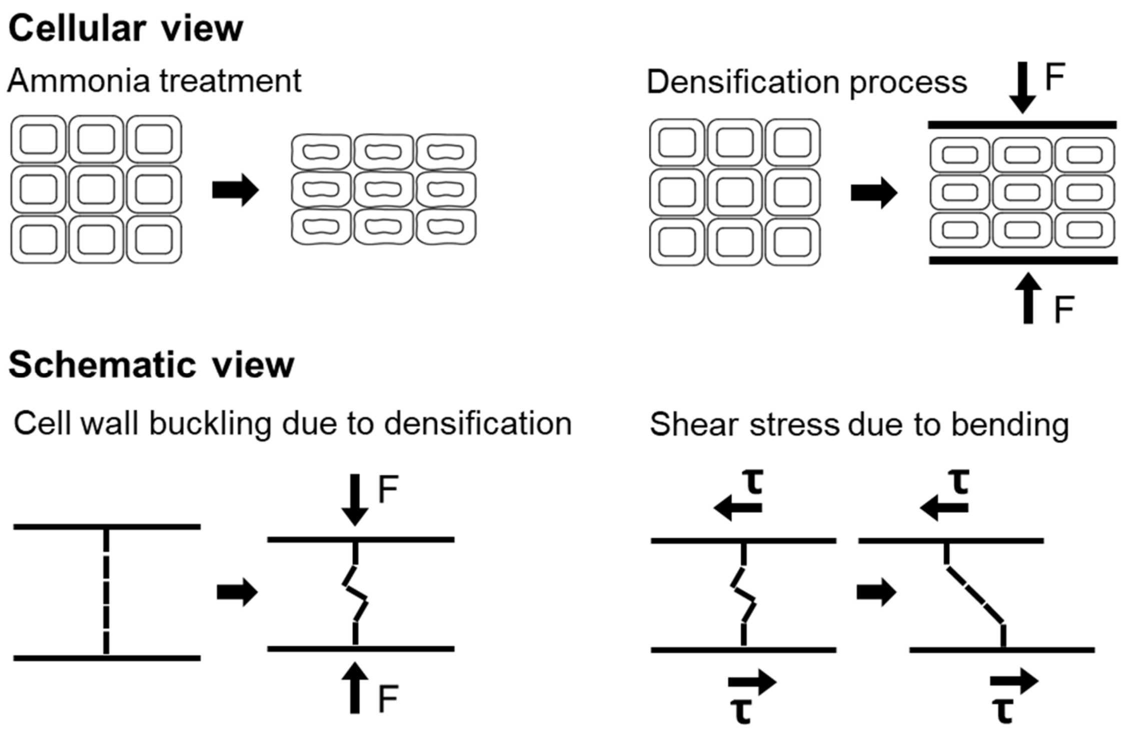

Figure 2. (**Top**): cellular view: both ammonia treatment and mechanical densification lead to cell wall buckling. (**Bottom**): schematic view: cell wall buckling leads to higher deflection during bending test.

All types of wood become much tougher but also more ductile as a result.

The limitations of our study are the following: 1. The number of samples was limited, but the experimental effort for a larger dataset is rather challenging and was not feasible within the scope of this study. 2. The background of the mass change could not be clearly identified, since a quantification of the leaching processes was not possible. A quantitative analysis of the leaching would imply a rather challenging experimental set-up with collection and measurement of the extract.

5. Conclusions

The alteration of bending properties of wood due to ammonia treatment and additional densification were investigated in the present work, and the following conclusions can be drawn:

1. Treatment with anhydrous gaseous ammonia lowers the equilibrium moisture content of beech, oak and black locust wood.
2. Bulk density is increased by both ammonia treatment and mechanical densification.
3. Ammonia treatment has a lowering effect on MOE. Additional mechanical densification raises MOE above reference level.
4. MOR is not significantly affected by ammonia treatment. Mechanical densification leads to a strong increase in MOR.
5. Deflection is increased by the ammonia treatment. The additional mechanical densification leads to a further increase in the deflection. The modified wood has a higher bending strength compared to the reference wood and shows a more ductile material behavior.

These material properties can be particularly interesting for applications where high ductility and strength are required. This is the case, for example, in mechanical engineering or even in safety-related components with special needs for ductility. The application to veneer materials could lead to further areas of interest, such as forming technology.

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