

BEECH WOOD MODIFICATION WITH AMMONIA GAS – IMPROVED PROPERTIES

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Abstract

*European beech wood (*Fagus sylvatica*) is common hardwood in the Czech Republic and an important material in industry. However, the demand for this renewable material is not sufficient. In order to improve its utilization as a high value material, wood properties can be modified and new material can be developed. This paper is focussing on ammonia modification, which has been known for decades mainly for the plasticization effect, but commonly used only for wood darkening. The first part of this paper presents selected properties of ammonified and densified beech wood, called lignamon (mechanical properties, swelling and durability). The second part compares the plasticization effect of ammonia gas with the common method using hot saturated steam. The last part shows the influence of ammonia gas treatment on glued joint strength.*

Very good properties of lignamon were proved. It is a strong material with permanent compression even after 2 cycles of swelling in water and subsequent drying. Durability is significantly improved. Ammonia plasticization effect at 0.2MPa alone is low compared to hot steam. The best results were achieved by the methods combined. It was found that ammonia treatment can improve strength of glued joint in the case of beech veneers.

Key words: wood modification; densification; ammonia gas; durability; bonding strength.

INTRODUCTION

European beech (*Fagus sylvatica*) is the most common broadleaved species in the Czech Republic. Its annual harvest is almost one million cubic meters of wood, which is more than 45% of all hardwoods (Czech Statistical Office 2015) and it is expected to increase in future. This wood is suitable mainly for furniture and indoor applications. Demand of this wood in industry is still lower than supply and this high quality wood is often used as fuel wood. A possible way to increase the utilization of this renewable material is wood modification.

Beech wood can be modified with ammonia, which seems to be a promising method. It was investigated by many authors in the 1960s and the 1970s. Nowadays, only few scientists publish on this field of research (Rosca *et al.* 2002, Weigl *et al.* 2012). The main focus was on wood plasticization

by liquid anhydrous ammonia, which is very efficient and rapid (Schuerch 1963). Also ammonia gas plasticization works well and is much easier to carry out (Davidson and Baumgardt 1970). During this process wood becomes darker (Miklečić *et al.* 2012). Material based on ammonia gas modification called lignamon was developed by Stojcev (1979). This dark brown material was industrially produced mainly from European beech. The process consists of vacuum-pressure impregnation with ammonia gas, transversal compression at an increased temperature and a phase of drying and thermal stabilization (180°C). The whole process was carried out in a closed vessel equipped with a hydraulic press. Lignamon was presented as material with considerably improved properties (Stojcev 1979, Pařil *et al.* 2014). Despite this, the factory was closed and lignamon is not produced any more.

Wood plasticized by gaseous ammonia can be bent in sharper curve without damage than after traditional plasticization with hot saturated steam (Pandey *et al.* 1991). After evaporation of ammonia, wood becomes rigid again without a negative influence on mechanical properties (Weigl *et al.* 2012). Moisture in wood can improve the plasticization effect of ammonia gas and reduce wood stiffness (Davidson and Baumgardt 1970) but the optimal moisture content for this method is not clearly defined. The values can vary from 10% to 20% according to several authors (Davidson and Baumgardt 1970, Sharma *et al.* 1988, Pandey *et al.* 1991). The common steam plasticization works the best at 100°C and moisture content at the fibre saturation point. The influence of moisture content and temperature on compression strength of beech wood in the transversal direction was well described by Kúdela (1996). Conditions during lignamon process indicate that higher temperature and higher saturation due to gas pressure could result in better plasticity of wood. To understand the process better a comparison of these two methods is needed.

Not only solid wood modification can improve beech utilization, but also new or improved composites. This requires bonding of modified wood with adhesives. It is known that ammonia can penetrate cell wall more than moisture (Davidson and Baumgardt 1970), which results in a permanent change of its properties (Bariska 1975). This modification can influence glue adhesion and bonding strength of glued solid wood (Minelga *et al.* 2013). Special laminated products, for example chairs, are made of veneers. If the plasticization effect of ammonia is employed due to complicated shape, the influence on glue adhesion and bonding strength is needed.

OBJECTIVE

The main objective of the present research was to evaluate beech wood modification with ammonia gas and to find advantages and reasons for using this chemical for new material development. Firstly, selected properties of ammonia plasticized and compressed beech wood called lignamon were evaluated. Then the plasticization effect of ammonia gas on beech wood was investigated and compared with the traditional method using hot saturated steam. Also the influence of this modification on glued joint strength was measured.

MATERIAL, METHOD, EQUIPMENT

Lignamon material (15 prisms with dimensions of 740×80×35mm³) came from old Czech industrial production. It was made from beech sideboards, so that the direction of compression was not purely tangential or radial. One board of native European beech (*Fagus sylvatica*) was used for reference specimens and also for the preparation of compressed beech. Twelve prisms of beech wood with dimensions 350×50×50mm³ were plasticized in hot saturated steam and consequently compressed in hydraulic press. The temperature of pressing plates was 90°C and conditioning proceeded for 10 days. The resulting compression ratio was about 45%.

Mechanical properties of lignamon

Specimens for bending strength test with dimensions of 14×14×210mm³ were made from all three materials described above - lignamon (147 specimens), compressed beech (30 specimens), native beech (30 specimens). The ratio of these dimensions followed the British Standard BS 373-1957. The static bending test was carried out with universal testing device Zwick Z050 in compliance with this standard. Modulus of rupture (MOR) and modulus of elasticity (MOE) were determined during the static bending test by the central loading method (three-point bend). The span of supports was 196 mm. Specimens were conditioned before measurement at 20 ± 3°C and a relative humidity of 65 ± 2%. They were divided in two groups. 50% of them were loaded parallel to the direction of compression. The other 50% were loaded perpendicular to the direction of compression. Density was measured after conditioning.

Swelling of lignamon

Swelling was measured using the same material as mechanical properties (lignamon, compressed beech and native beech), but specimen dimensions were $14 \times 14 \times 42 \text{ mm}^3$. This investigation consisted of two cycles of swelling and drying. First, specimens were dried in order to measure dimensions at 0% moisture content. After 2 days of conditioning, the specimens were immersed in distilled water for 5 weeks. Then, they were slowly dried to 0% moisture content. This procedure was repeated in the second cycle. Swelling was evaluated in the direction of compression and compared with swelling of native beech in the tangential direction.

Durability of lignamon

Specimens were prepared from 15 prisms of lignamon. Two specimens with dimensions $15 \times 25 \times 50 \text{ mm}^3$ were cut from each prism. One specimen from each couple was subjected to the leaching procedure for 14 days in compliance with EN 84. The third set of reference specimens was prepared from native beech wood. Durability test was carried out according to standards EN 350-1 and EN 113. Mass loss due to fungus *Trametes versicolor* was evaluated after 16 weeks of the test.

Plasticizing wood with ammonia gas – a comparison of methods

One board of European beech wood (*Fagus sylvatica*) was used to produce anatomically perfectly oriented specimens with dimensions $20 \times 20 \times 30 \text{ mm}^3$. They were divided into four groups based on the planned treatment. Reference specimens with moisture content 12% were directly loaded in the tangential direction with testing device Zwick Z050. The speed of compression was set to $8 \text{ mm} \cdot \text{min}^{-1}$ for all measurements. The second group with the same moisture content was plasticized with ammonia gas in a small autoclave. The vessel with specimens was evacuated first and then filled with gaseous ammonia. Gas pressure of 0.2 MPa was maintained for 3 hours. Plasticized specimens were sealed in a small plastic bag and consequently loaded on the testing device. The specimens from the third group, which had been moistened to 25% in humid air, were plasticized in hot saturated steam with temperature of 100°C for 10 minutes. To prevent cooling during measurement, the specimens were compressed between small heated plates. The plasticization process of the last group combined both of the described methods. First, ammonia gas was applied and consequently, steam plasticization was carried out.

Improvement of glue adhesion by ammonia gas modification

Specimens for this research were made of peeled beech veneer 2.5mm thick. Ammonia treatment was carried out in a sealed plastic bag. First, vacuum was applied and then veneers were treated in gaseous ammonia at normal pressure for 3 hours.

One group of veneers was used as reference without ammonia modification. The other group was glued just after ammonia treatment (fresh). Veneers of the third group were conditioned one week until free ammonia disappeared and then glued together. Three types of adhesives were applied - polyvinyl acetate (PVAc), polyurethane (PUR) and urea formaldehyde (UF with ammonium chloride as a hardener). Pairs of veneers with adhesive were pressed at temperature of 80°C and pressure of 1 MPa for 12 minutes. Specimens were prepared in compliance with standard ČSN EN 205 and dimensions of glued area were $20 \times 10 \text{ mm}^2$. All 12 groups of specimens were conditioned for 7 days at a temperature of 23°C and relative humidity of 60%

Shear strength testing was performed by universal testing machine Zwick Z050. Shear strength of bonded joint was calculated by equation (1)

$$T = \frac{F_{\max}}{b \cdot L} \quad [\text{MPa}] \quad (1)$$

F_{\max} is the maximum force, b is the width of tested bonded surface, L is the length of the tested bonded surface.

RESULTS AND DISCUSSION

Mechanical properties of lignamon

Fig. 1 shows an improvement of MOR and MOE in both cases of plasticization. In the case of lignamon, the MOR and MOE increased by about 78 and 86%, respectively, compared to native beech. The MOR and MOE of steam-densified (compressed) beech increased by about 69% and 51%, respectively, compared to native beech, which is in agreement with observations by other authors (Blomberg *et al.* 2005, Kamke 2006).

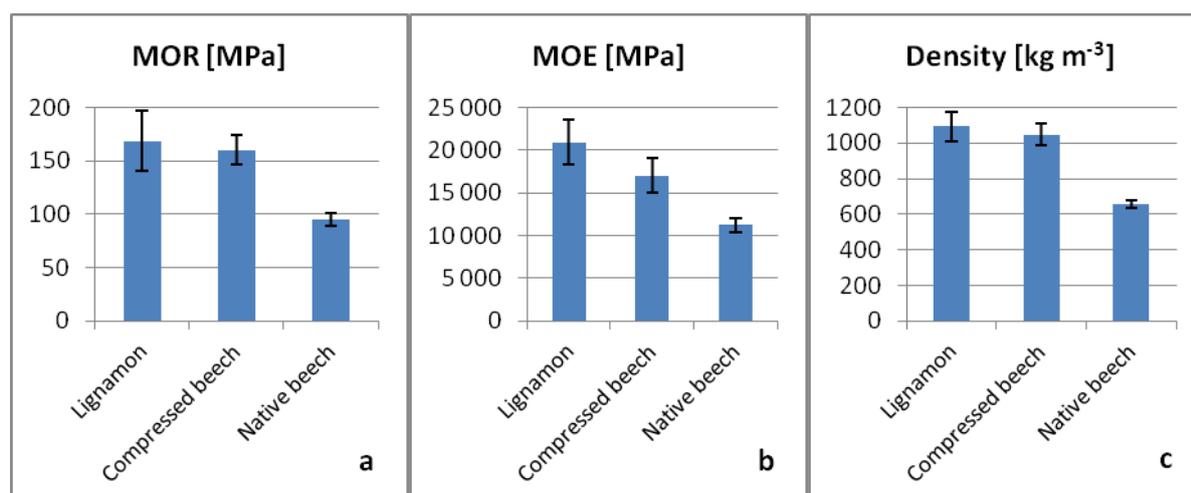


Fig. 1.

**Selected properties of lignamon, compressed beech and native beech obtained from bending strength test
Strength MOR (a), modulus of elasticity MOE (b) and density (c)**

Although lignamon and compressed beech are insignificantly different in the density, lignamon shows higher values of MOE by about 23% compared to compressed beech, meanwhile the results of the MOR are almost similar (Table 1). Bach and Hastrup (1973) also observed that compressed wood plasticized by ammonia exhibits higher mechanical properties compared to compressed wood plasticized by steam or native wood with similar density. They suggested that it is attributable to a mechanism involving no-fracture buckling of the cell walls and forming of the new secondary bonds. This assumption was confirmed by Bariska (1975). The increase in MOR due to ammonia treatment of wood was also found by Mahdalk *et al.* (1971).

Table 1

Selected properties of lignamon, compressed beech and native beech obtained from bending strength test (Coefficient of variation in parenthesis)

	Strength MOR [MPa]	Modulus of elasticity MOE [MPa]	Density [kg m ⁻³]
Lignamon	168.7 (16.6)	20 894 (12.7)	1092 (7.5)
Compressed beech	160.3 (8.4)	17 002 (11.7)	1048 (6.1)
Native beech	94.6 (6.4)	11 266 (7.3)	657 (3.1)]

Swelling of lignamon

Results show significant improvement in swelling of lignamon compared to compressed beech (Fig. 2). Although swelling of lignamon in the direction of compression (23.7%) was almost double compared to native beech (13% in the tangential direction), this modified material shrank back to its initial dimensions after drying. Lignamon reached almost the same value of swelling in both cycles (increased by 0.3%). In the case of compressed beech, swelling increased much more (from 62.5% to 70.1%). Compressed beech (CB) showed significant recovery of its structure that reached 35.4% (Fig.3). Both lignamon (L) and native beech (NB) shrank even slightly under their initial dimensions. It may be caused by leaching. Mass loss due to leaching was 1.08% for compressed beech, 2.27% for lignamon and 1.57% for native beech. Reduced swelling of lignamon may be influenced by forming of new secondary bonds (Bach and Hastrup 1973) and by heat treatment (Inoue *et al.* 1993).

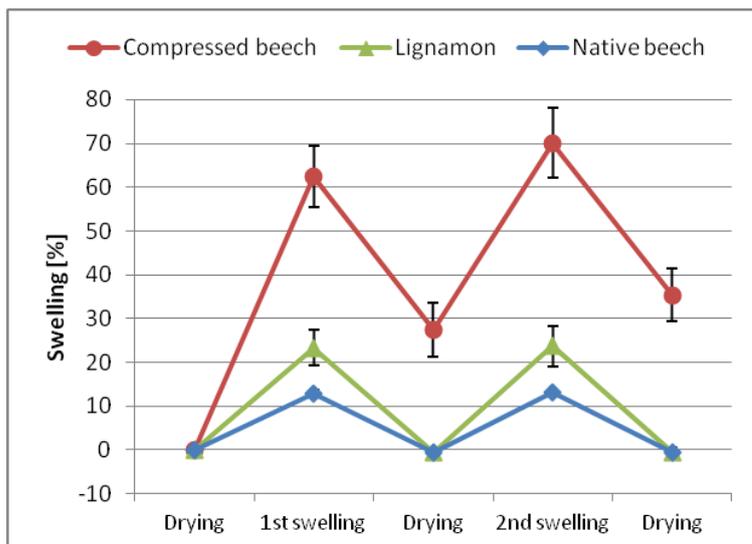


Fig. 2.
Two cycles of swelling in water and drying.
Error bars show standard deviation

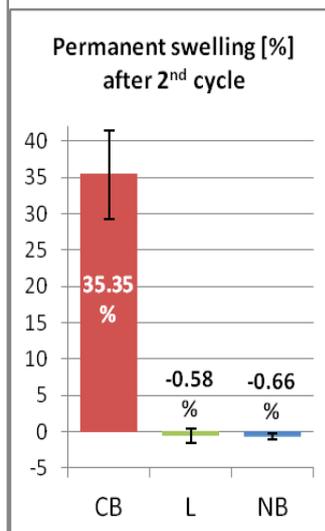


Fig. 3.
Results of permanent swelling after last drying

Durability of lignamon

The degradation activity of white-rot fungus *Trametes versicolor* led to a considerably lower average mass loss of lignamon (3.96%) in comparison with reference untreated beech wood (35.5%) (see Fig. 4). The mass loss high variability (ranges between 1.1 to 13.3%) is probably caused by the nonobservance of technological process parameters which could influence final chemical changes in wood and its consequent decay resistance. The leaching of lignamon samples usually resulted in slightly higher mass loss (6.37%), but differences are not significant. During the production process different treatments are involved and have changed wood chemical and morphological structure. The higher density of densified material can positively influence decay resistance due to restricted space for fungi hyphae spreading (Skyba *et al.* 2009). Hemicelluloses, amorphous cellulose, and lignin are subject to degradation or modification during the heating stabilization phase with higher temperatures (180°C). The ammonification increases the amount of nitrogen in wood (Rosca *et al.* 2002), an important source for fungi synthesis of proteins or chitin, but ammonia supplement may affect media pH and therefore fungi growth responses (Zabel and Morrell 1992).

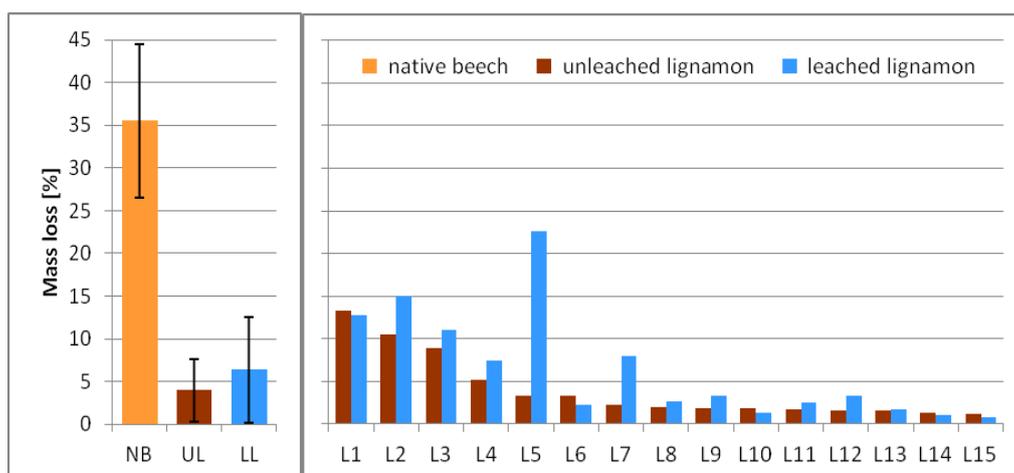


Fig. 4.
Lignamon decay test with *Trametes versicolor*, 16 weeks.

Left – mass loss mean values of native beech (NB), unleached lignamon (UL) and leached lignamon (LL). Error bars show standard deviation. Right – mass loss of single lignamon specimens (L1 – L15)

Plasticizing wood with ammonia gas – a comparison of methods

Stress-strain diagrams (Fig. 5) demonstrate big differences between plasticization methods. Ammonia gas treatment at pressure of 0.2MPa reduced compression stress significantly. Compared to hot saturated steam, it was less efficient. Weight percent gain (WPG) of ammonia reached average value of 9.1%. The best plasticization effect was achieved by combining of these two methods – first ammonia treatment and then steaming.

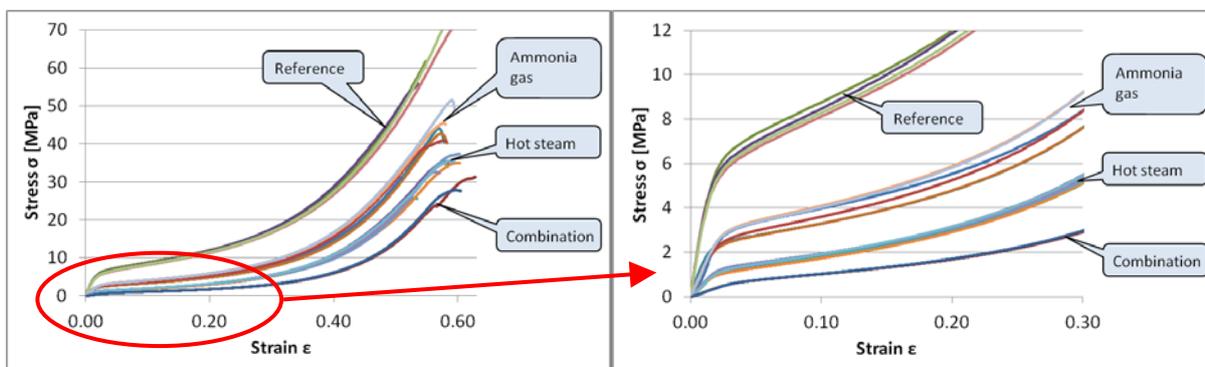


Fig. 5.

Compression strength test of European beech wood (*Fagus sylvatica*) in the tangential direction – the whole diagram (left) and detail (right). Specimens were plasticized by ammonia gas, hot steam, combination of these methods or remained untreated as reference

The plasticization methods were compared at three deformation levels (Table 2). Stress at these levels was also expressed as percentage of the reference values (Fig. 6). The highest plasticization effect was observed at the beginning of the compression. Ammonia treatment decreased pressure to 44.5% of the reference values. Hot saturated steam and the combined method reached 20.5% and 10.5% of the reference values respectively.

Table 2

Plasticization effect of three different methods at three deformation levels. Stress is expressed in MPa and also as percentage of reference values

Treatment	Stress [MPa] at deformation of:			Stress [%] at deformation of:		
	5%	20%	45%	5%	20%	45%
Reference	6.94	11.65	36.07	100	100	100
Ammonia gas	3.09	5.33	21.44	44.46	45.74	59.43
Hot steam	1.42	3.05	14.92	20.49	26.18	41.35
Combined method	0.73	1.69	9.09	10.53	14.48	25.21

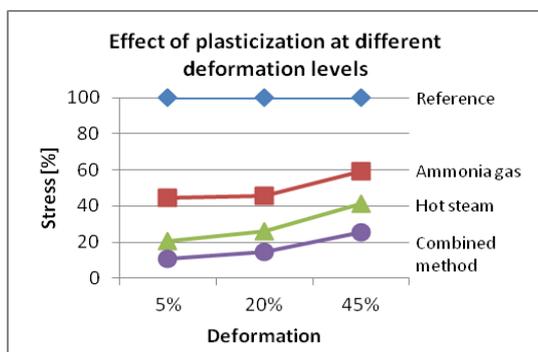


Fig. 6.
Influence of plasticization methods on stress values (in %)

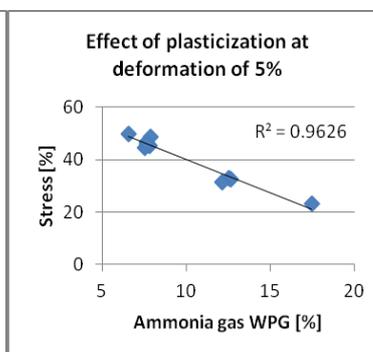


Fig. 7.
Dependency of stress on ammonia weight percent gain (WPG). Stress is expressed as percentage of reference values

Plasticization effect of ammonia gas significantly depends on WPG (Fig. 7). It seems to be linear in this short range, but the influence of WPG probably decreases at higher values. Beech wood can reach WPG of ammonia gas around 30% if the maximal gas pressure is applied (Bariska 1971). Stress during compression could be reduced significantly under 20% of reference values.

The combined method resulted in 28.6% of total content of ammonia and moisture. This method was the most efficient because moisture in wood can improve the plasticization effect of ammonia gas (Davidson and Baumgardt 1970). Also ammonia treatment can increase accessibility of polar groups in cell walls for water molecules (Bariska 1975) which results in better plasticization.

Improvement of glue adhesion by ammonia gas modification

Glued joint of ammonia modified and native beech wood can have different mechanical properties (Fig. 8). Results show significant improvement in case of polyvinyl acetate adhesive (PVAc) and polyurethane adhesive (PUR). Strength of joint with urea formaldehyde adhesive (UF) decreased. Ammonia modified and conditioned specimens showed slightly better results compared to fully saturated ones.

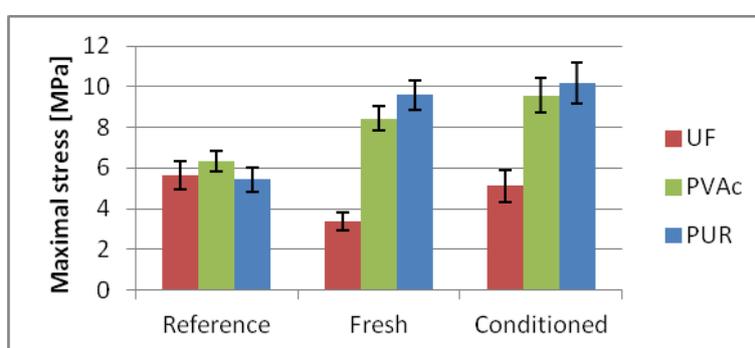


Fig. 8.

Influence of ammonia treatment on strength of glued veneer-joints with three types of adhesives. Error bars show standard deviation

Reference specimens were expected to reach values around 11 MPa, which is typical for solid beech wood and PVAc or PUR adhesive (Král *et al.* 2015). Lower values around 6 MPa (Table 3) can be caused by lower mechanical properties of peeled veneers compared to solid wood. Results of other wood species can also differ. Minelga *et al.* (2013) found that ammonia modification of oak decreased strength of joints glued with PVAc adhesive. Ammonia reacts especially with extractives of wood (Miklečić *et al.* 2012). Different chemical composition of extractives in oak and beech can explain different behaviour of glued joint. To confirm these assumptions, further research with solid beech wood will be carried out.

Table 3

Influence of ammonia treatment on strength of glued joint with three types of adhesives

Adhesive	Condition	Maximal stress [MPa]	Failure of samples	Decrease/increase in strength
UF	Reference	5.63	wood	0%
	Fresh	3.39	bond line	-39.8%
	Conditioned	5.12	wood	-9.1%
PVAc	Reference	6.35	wood	0%
	Fresh	8.44	wood	+32.8%
	Conditioned	9.58	bond line	+50.2%
PUR	Reference	5.43	wood	0%
	Fresh	9.59	wood	+76.6%
	Conditioned	10.19	wood	+87.8%

CONCLUSIONS

The results obtained within the present research demonstrated that the properties of European beech wood (*Fagus sylvatica*) can be successfully improved by ammonia gas modification. Ammonia plasticized and heat treated beech wood called lignamon showed significantly improved mechanical properties. The increased MOR and MOE allow the utilization of modified wood in applications where natural wood would fail. Durability is increased and swelling is reduced. Lignamon shrinks to its initial dimensions after a cycle of swelling and consequent drying.

Ammonia plasticization effect at 0.2MPa gas pressure reduces the compression force significantly and it is sufficient for successful densification. Compared to hot steam, it was less efficient. It could be increased by applying higher gas pressure. The best plasticizing effect was reached by combining these two methods.

It was found that ammonia gas can also improve strength of glued joint in case of peeled veneers from European beech. Results show that ammonia plasticized veneers can be used for laminated veneer products.

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