WOOD RESEARCH
58 (3): 2013
343-350

STRENGTH CHANGES IN ASH, BEECH AND MAPLE WOOD MODIFIED WITH A N-METHYLOL MELAMINE COMPOUND AND A METAL-COMPLEX DYE

Bodo Caspar Kielmann, Holger Militz, Carsten Mai*
Georg-August-University Göttingen, Burckhardt Institute
Wood Biology and Wood Products
Göttingen, Germany

Stergios Adamopoulos
Technological Educational Institute of Thessaly
Department of Wood & Furniture Design and Technology
Karditsa, Greece

ABSTRACT

Ash, beech and maple wood was modified with aqueous solutions of methylated N-methylol melamine (NMM) and a metal-complex dye (BS) consisting of 10, 20, and 30 % NMM and 5 % BS. Static bending strength and stiffness, impact bending strength and hardness were examined to evaluate the suitability of modified wood for structural uses. The combined NMM-BS modification resulted in significant higher dynamic (MOE_{dyn}) and static (MOE) moduli of elasticity for all species. Beech and maple exhibited enhanced static bending strength (MOR), while that of ash was unchanged. The higher stiffness and strength of NMM-BS modified wood is attributed to its higher wood density and lower EMC and to the stiff character of NMM resin incorporated in the wood matrix.

Impact bending strength decreased substantially after modification as a result of reduced pliability of treated wood. Brinell hardness significantly increased with the weight percent gain (WPG) due to modification, and, unlike the other properties, it was positively correlated with the WPG.

KEYWORDS: N-methylol melamine, colouring agent, static bending, dynamic modulus of elasticity, impact bending strength, hardness.

INTRODUCTION

Wood modification with condensation resins has been reported to influence water related properties and mechanical properties. While the moduli of rupture (MOR) and elasticity (MOE) are mostly unchanged, work to maximum load in bending and impact bending strength are clearly reduced. Hardness in contrast significantly increases after modification with condensation resins (Stamm 1964, Lutomski and Lawniczak 1977, Meyer 1981).

The effect on the properties and the magnitude of changes depend on the type of modification (chemical, impregnation, thermal) and wood species. Impregnation modification of wood with melamine resins has shown its potential to provide various physical improvements and decay resistance (Rapp and Peek 1999, Krause et al. 2004, Hansmann et al. 2006). Modification with melamine leads to increased hardness, MOE and MOR (Miroy et al. 1995, Deka and Saikia 2000, Gindl et al. 2004), but also to reduced impact bending strength, i.e. embrittlement which has been attributed to the incorporation of cured resin inside the wood matrix (Pittman et al. 1994, Epmeier et al. 2004). Melamine resins penetrate the cell wall and cause bulking by diffusion and form a three-dimensional network within the cell wall rather than covalent chemical bonds to the cell wall polymers (Lukowsky 1999).

A treatment with a low molecular weight melamine formaldehyde resin (N-methylol melamine, NMM) and a metal-complex dye was proposed recently (Kielmann et al. 2013). Three hardwood species (ash, beach, maple) were treated with the aim to improve the performance of wood exposed outdoors but also to enhance its aesthetically pleasant characters. The suitability of wood modified with combined NMM and metal-complex dye as a structural material should be established on the basis of its strength properties. The studied properties were chosen with respect to their importance for structural purposes, such as strength and stiffness, impact bending strength and hardness.

MATERIAL AND METHODS

Wood and chemicals

The wood material used in this study was ash (*Fraxinus excelsior* L.), beech (*Fagus sylvatica* L.), and maple (*Acer platanoides* L.) originating from air-dried boards. The methylated N-methylol melamine (NMM) resin Madurit MW840/75WA was supplied by Ineos Melamines GmbH (Frankfurt, Germany) with a solid content of approx. 75 % and a specific gravity of 1.245-1.260 g. ml^{-1} at 23°C. The metal-complex dye (BS) Basantol® Brown 269 was supplied by BASF SE (Ludwigshafen, Germany) with 30 % solid content, density of 1.14 $g.cm^{-3}$, pH 6.5 and fastness 6-7. Ethanolamine was purchased from Th. Geyer GmbH & Co. KG (Hamburg, Germany).

Wood treatment

Aqueous NMM-dye solutions were prepared consisting of 10, 20, and 30 % NMM (final solid content) and 5 % BS (of stock solution) by diluting with tap water. Ethanolamine (1 %) was added and the pH of the final solution was adjusted to 10 by adding sodium hydroxide.

The specimens were impregnated in a full cell process with an initial vacuum phase of 50 mbar (1 h) and a pressure phase of 12 bar (72 h). In a drying oven the impregnated specimens were exposed to the following temperature cycle: 20, 40, 60, 80, 100°C (24 h each), 120°C (8 h), 103°C (24 h). The weight percent gain (WPG) was calculated by relating the increase in mass after drying and resin curing to the dry mass prior to the treatment.

Mechanical properties

After the treatment, all the specimens were conditioned at 20°C and 65 % RH for 4 weeks. The density under standard conditions was determined by dividing the weight to volume calculated from the three dimensions of orthogonal wood specimens. The equilibrium moisture content (EMC) was based on the weight under standard conditions and the dry weight of specimens. On average, a set of 40 specimens were used for each species, modification level and test.

The dynamic MOE (MOE_{dyn}) was determined on specimens with dimensions 20 × 20 × 360 mm^3 by using a GrindoSonic MK 4-1 device (J.W. Lemmens N.V., Leuven, Belgium). The MOE_{dyn} calculation was based on the formula (Hearmon 1966):

$$MOE_{dyn} = \frac{4 \times \pi^2 \times l^4 \times f^2 \times \rho \times A}{m_l^4 \times I} \times \left(l + \frac{I}{l^2 \times A}\right) \times K_l$$

where: MOE_{dyn} - dynamic modulus of elasticity ($N.mm^{-2}$),
I - moment of inertia (mm^4) ,
A - area of the cross section (mm^2),
f - frequency (kHz),
ρ - density ($g.mm^{-3}$),
l - length (mm),
K_l - 49.48,
m_l - 4.72.

Moduli of rupture (MOR) and elasticity (MOE) in static bending were determined with specimens of the same dimensions (20 × 20 × 360 mm^3) according to the German standard DIN 52186 (1978) using a universal testing machine equipped with a 10 kN load head and the software testXpert II (Zwick GmbH & Co. KG, Ulm, Germany).

Impact bending strength was assessed following DIN 52189-1 (1981) with modified specimen's dimensions of 10 × 10 × 180 mm^3. The testing machine was a CEAST Resil Impactor (Instron, Norwood MA, USA) equipped with a 25 J hammer and an integrated force-measuring device. The bearing width was 120 mm.

Brinell hardness was determined perpendicular to the grain according to the European standard EN 1534 (2000). Four measurements were performed on each specimen, two on the tangential and two on the radial surface by using a steel ball of 10 mm and a load of 1000 N.

RESULTS AND DISCUSSION

The combined NMM-BS modification resulted in a statistically significant increase in dynamic and static moduli of elasticity (Tab. 1). The increase was higher in the case of ash, 12-23 % for MOE and 16-27 % for MOE_{dyn}, while a similar increase of 6-19 % for MOE and 7-19 % for MOE_{dyn} was observed for beech and maple. Although the values of treated specimens were higher than those of the controls, it seemed that the WPG did not reveal a significant effect from a statistical point of view. Static bending strength (MOR) was found to increase significantly in beech and maple (8-15 %), while no change was observed for ash. Again, the solid content of NMM in the modification solution, i.e. the WPG, played a minor role. The increase in stiffness and strength of NMM-BS modified wood could be attributed to the significant increase of wood density by 4-23 % and the incorporation of a stiff thermosetting polymer in the wood matrix. Increased stiffness might also be attributed to the significant reduction of EMC by 4-32 % (Tab. 1). The lower weight percent gain (WPG) of ash might be responsible for the deviations observed in stiffness and strength for this species as compared to beech and maple. According to Epmeier et al. (2004), modification with methylated melamine formaldehyde resin led to a slight increase in bending strength. On the other hand, increased MOR and MOE were obtained after treatment with melamine formaldehyde at 33-35 % WPG possibly due to the fact that the volumes of the treated samples remained unchanged as compared to the controls (Deka and Saikia 2000).

Tab. 1: Static bending strength (MOR), and static (MOE) and dynamic (MOE_{dyn}*) modulus of elasticity of NMM-BS modified ash, beech and maple wood (mean values ± standard deviations)[1].*

Species / Treatment	WPG (%)	Density ($kg.m^{-3}$)	EMC (%)	MOR ($N.mm^{-2}$)	MOE	MOE_{dyn}
Ash						
Control	-	645±57.6 ^{a}	10.7±0.2^{a}	100±13.1^{a}	9.734±1.305^{a}	10.923±1.575^{a}
10% NMM-BS	7.0±1.2	755±34.5^{b}	10.3±0.2^{ab}	110±16.3^{b}	11.320±1.347^{bc}	13.164±1.774^{bc}
20% NMM-BS	15.6±3.3	810±25.9^{c}	9.8±0.2^{b}	100±12.4^{a}	10.926±1.030^{b}	12.647±1.375^{b}
30% NMM-BS	16.6±4.5	823±25.6^{c}	8.9±0.5^{c}	109±11.6^{ab}	11.975±1.056^{c}	13.904±1.285^{c}
F-value		138.6*	30.7*	5.0*	18.5*	22.7*
Beech						
Control	-	697±15.9 ^{a}	10.4±1.3^{a}	118±8.6^{a}	12.509±987^{a}	14.610±1.119 ^{a}
10% NMM-BS	8.5±0.6	749±23.1^{b}	9.8±0.2^{ab}	128±12.3^{b}	13.465±1.032^{b}	15.809±1.143^{b}
20% NMM-BS	17.9±1.0	823±33.7^{c}	9.3±0.3^{ab}	131±16.6^{b}	14.276±757^{c}	16.394±1.575^{bc}
30% NMM-BS	28.6±2.1	899±17.7^{d}	8.6±0.3^{b}	130±16.3^{b}	14.522±864^{c}	17.209±1.223^{c}
F-value		435.2*	5.3*	5.9*	28.9*	23.4*
Maple						
Control	-	670±11.4 ^{a}	12.4±0.3 ^{a}	119±9.3 ^{a}	11.670±878^{a}	13368±1.003^{a}
10% NMM-BS	8.9±0.9	697±14.8^{b}	9.5±0.2^{b}	129±8.9^{bc}	12.400±845^{b}	14303±1.101^{b}
20% NMM-BS	19.6±1.6	758±14.1^{c}	8.9±0.2^{c}	129±12.5^{b}	12.603±854^{b}	14800±1.319^{bc}
30% NMM-BS	27.9±1.8	826±15.8^{d}	8.4±0.2^{d}	137±14.6^{c}	13.871±1.148^{c}	15926±1.503^{c}
F-value		432.2*	254.1*	12.4*	27.7*	21.1*

1 values followed by a different letter within a column are statistically different according to ANOVA and Tukey HSD test

* differences statistically significant at P = 5 %

Impact bending strength of melamine-treated wood has been reported to considerably decrease apparently because the cured resins formed inside the wood are rigid and brittle (Pittman et al. 1994, Epmeier et al. 2004). In this study, substantial reductions (>35 %) in impact bending strength were induced by NMM-BS modification, but the values did not significantly change with the WPG. The loss in impact bending strength was approximately the same in ash and beech and ranged between 35 to 48 %, while it was highest in maple (55-67 %). This result might be attributed to the higher WPG achieved in maple. On the other hand, the significant changes in density and EMC due to modification were similar in all three species (Tab. 2).

Treatment with NMM-BS did not significantly change the maximum force at the specimen's break (Fig. 1). This indicates that the treatment does not cause strength losses due to cell wall degradation. Although the treatment solution was alkaline, it did not attack cell wall polymers which contribute to impact bending strength. The major reason for the decreased impact bending strength was a reduction in the degree of deformation at break due to NMM-BS treatment; this reduction slightly increased with increasing WPG. Reduction in impact bending strength is, thus, almost exclusively attributable to a reduction in pliability due to a rigid, tree-dimensional corset of melamine resin in the wood structure.

Tab. 2: Impact bending strength of NMM-BS modified ash, beech and maple wood (mean values ± standard deviations)[1].

Species / Treatment	WPG	Density	EMC	Impact bending strength
	(%)	(kg.m^{-3})	(%)	(KJ.m^{-2})
Ash				
Control	-	571±19.0^{a}	8.9±0.2^{a}	26.4±4.1^{a}
10% NMM-BS	13.2±1.4	634±19.2^{b}	8.4±0.1^{b}	17.2±4.2^{b}
20% NMM-BS	21.0±3.3	672±18.3^{c}	8.2±0.1^{bc}	16.3±3.6^{b}
30% NMM-BS	30.0±5.8	707±33.3^{d}	8.1±0.1^{c}	15.3±4.5^{b}
F-value		188.2*	24.8*	46.1*
Beech				
Control	-	707±13.3a	9.8±0.2a	34.1±6.6a
10% NMM-BS	12.9±0.7	788±16.8^{b}	8.8±0.1^{b}	21.2±5.5^{b}
20% NMM-BS	22.2±0.8	846±18.6^{c}	8.7±0.1^{b}	17.9±4.7^{b}
30% NMM-BS	31.7±1.2	908±15.1^{d}	8.1±0.1^{c}	17.8±4.4^{b}
F-value		852.7*	89.7*	59.0*
Maple				
Control	-	626±13.2^{a}	10.0±0.1^{a}	36.2±7.2^{a}
10% NMM-BS	14.6±0.7	689±14.9^{b}	9.0±0.1^{b}	16.3±3.1^{b}
20% NMM-BS	24.9±1.0	757±12.9^{c}	8.5±0.1^{c}	13.4±2.4^{bc}
30% NMM-BS	37.4±1.5	806±11.2^{d}	7.9±0.1^{d}	11.8±2.2^{c}
F-value		1,078.8*	414.9*	206.6*

1 values followed by a different letter within a column are statistically different according to ANOVA and Tukey HSD test

* differences statistically significant at P = 5 %

The high loss in impact bending strength of treated maple (see above) is due to the greatest reduction in deformation at break as compared to the controls (Fig. 1).

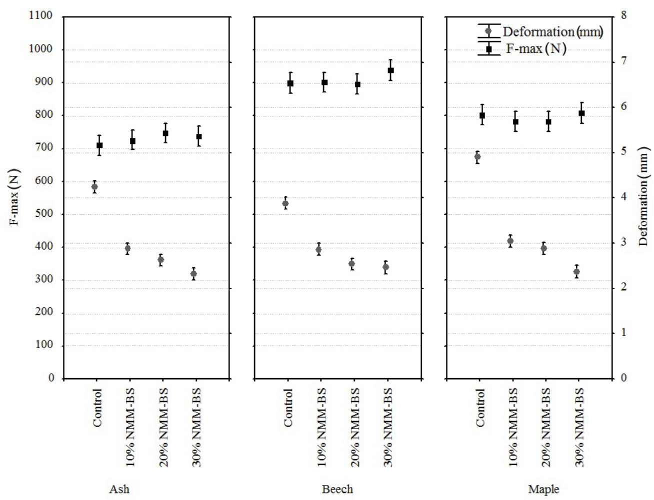

Fig. 1: Maximum load (F-max) and deformation corresponding to maximum load in impact bending of NMM-BS modified ash, beech and maple wood.

Tab. 3: Brinell hardness of NMM-BS modified ash, beech and maple wood (mean values ± standard deviations)[1].

Species / Treatment	WPG (%)	Density ($kg.m^{-3}$)	EMC (%)	Brinell hardness ($N.mm^{-2}$) Radial	Tangential	Axial
Ash						
Control	-	739±2.7^a	10.8±0.1^a	53±14.1^a	50±5.0^a	75±5.7^a
10% NMM-BS	8.0±0.8	774±23.3^b	10.2±0.5^b	55±12.0^a	51±10.7^a	85±10.7^a
20% NMM-BS	15.8±4.2	805±18.5^c	9.9±0.2^b	73±14.2^b	62±9.5^b	106±12.0^b
30% NMM-BS	22.1±1.9	846±10.1^d	9.5±0.2^c	85±16.7^c	69±9.7^b	115±15.3^b
F-value		81.5*	35.9*	22.3*	15.3*	40.3*
Beech						
Control	-	689±4.5^a	10.6±0.1^a	43±5.8^a	35±2.2^a	74±4.9^a
10% NMM-BS	12.6±1.1	736±16.1^b	10.0±0.1^b	51±7.2^a	47±4.2^b	98±7.6^b
20% NMM-BS	24.7±1.5	803±23.7^c	9.6±0.1^c	79±16.6^b	68±8.5^c	121±18.6^c
30% NMM-BS	33.5±1.4	860±26.8^d	8.6±0.1^d	105±25.2^c	100±18.6^d	137±18.6^d
F-value		142.7*	635.6*	65.2*	146.7*	80.5*
Maple						
Control	-	592±41.9^a	11.1±0.1^a	42±3.6^a	31±2.4^a	73±6.3^a
10% NMM-BS	9.8±1.1	663±25.3^b	9.0±0.4^b	65±3.8^b	41±2.9^b	104±6.5^b
20% NMM-BS	20.5±1.2	722±27.4^c	8.3±0.3^c	75±8.3^c	56±4.9^c	108±6.9^b
30% NMM-BS	30.0±1.0	761±36.1^c	8.1±0.1^c	87±4.7^d	76±4.0^d	129±6.9^c
F-value		48.4*	289.9*	245.7*	566.2*	243.1*

1 values followed by a different letter within a column are statistically different according to ANOVA and Tukey HSD test

* differences statistically significant at P = 5%

Brinell hardness clearly increased with increasing WPG, especially in beech and maple which showed a higher WPG than ash (Tab. 3). The increase of transverse hardness was up to 186 % for beech and up to 145 % for maple, while smaller changes up to 77-85 % were found axially for these species. It was previously shown that only transverse mechanical properties were significantly affected by melamine modification (Gindl et al. 2002). For ash, the respective increase in hardness perpendicular and parallel to the grain ranged between 2-60 % and 13-53 %. The findings were in agreement with previous results on wood hardening due to treatment with melamine resins (Miroy et al. 1995, Deka and Saikia 2000, Gindl et al. 2004).

CONCLUSIONS

The strength changes of ash, beech and maple wood after the combined NMM-BS modification can be summarised as follows:

- Bending and dynamic properties (MOR, MOE, MOE_{dyn}) increased significantly, with the exception of MOR in ash. This was a result of several properties, specifically the increased density of the modified wood, the incorporation of the stiff polymer in the wood matrix, and the reduction of EMC. WPG had no major effect.
- Impact bending strength was substantially reduced (especially in maple) apparently because NMM treatment reduced pliability of the wood. This is proved by the fact that the modified specimens maintained a maximum load in impact bending equal to the untreated wood, while deformation corresponding to maximum load was significantly reduced.

- Brinell hardness considerably increased, especially in beech and maple, and was very dependent to the resin load in the modification solution.

On the basis of strength changes, NMM-BS treated wood of ash, beech and maple appears suitable for most structural uses. However, the severe reduction in impact strength could limit the use of modified wood in applications where high impact strength is required.

ACKNOWLEDGMENT

The authors would like to thank the companies BASF SE, Fehrensen GmbH, and Ineos Melamines GmbH for their cooperation. The support from AIF through the ZIM cooperation program (KF 2454601GZ9) is also acknowledged.

REFERENCES

1. Deka, M., Saikia, C.N., 2000: Chemical modification of wood with thermosetting resin: Effect on dimensional stability and strength property. Bioresource Technology 73(2): 179-181.
2. Epmeier, H., Westin, M., Rapp, A., 2004: Differently modified wood: Comparison of some selected properties. Scandinavian Journal of Forest Research 19(5): 31-37.
3. EN 1534, 2000: Wood and parquet flooring-determination of resistance to indentation (Brinell)-test method.
4. DIN 52186, 1978: Prüfung von Holz; Biegeversuch.
5. DIN 52189-1, 1981: Prüfung von Holz; Schlagbiegeversuch Teil 1: Bestimmung der Bruchschlagarbeit.
6. Gindl, W., Zargar-Yaghubi, F., Hansmann, C., Gupta, H.S., Wimmer, R., 2002: Improving the mechanical properties of wood by impregnation with a water soluble melamine-formaldehyde resin. In: Proceedings 6th Pacific Rim Bio-Based Composites Symposium, Oregon State University, Corvallis, USA. Pp 509-513.
7. Gindl, W., Hansmann, C., Gierlinger, N., Schwanninger, M., Hinterstoisser, B., Jeronimidis, G., 2004: Using a water-soluble melamine-formaldehyde resin to improve the hardness of Norway spruce wood. Journal of Applied Polymer Science 93(4): 1900-1907.
8. Hansmann, C., Deka, M., Wimmer, R., Gindl, W., 2006: Artificial weathering of wood surfaces modified by melamine formaldehyde resins. Holz als Roh- und Werkstoff 64(3): 198-203.
9. Hearmon, R.F.S. 1966: Vibration testing of wood. Forest Products Journal 16(8): 29-39.
10. Kielmann, B.C., Militz, H., Adamopoulos, S., 2013: Combined n-methylol melamine-colouring agent modification of hardwoods to improve their performance under use class 3 situations. In: Proceedings of the Sixth European Conference on Wood Modification 2012, Ljubljana, Slovenia. Pp 437-446.
11. Krause, A., Hof, C., Militz, H., 2004: Novel wood modification processes for windows and cladding products. In: Proceedings 35th Annual Meeting on the International Research Group on Wood Preservation, IRG/WP 04-40285, Ljubljana, Slovenia.
12. Lukowsky, D., 1999: Holzschutz mit Melaminharzen. PhD thesis, University of Hamburg.
13. Lutomski, K., Lawniczak, M., 1977: Polymerholz und seine Widerstandsfähigkeit gegen biotische Einflüsse. Holz als Roh- und Werkstoff 35(2): 63-65.

14. Meyer, J.A., 1981: Wood polymer materials: State of the art. Wood Science 14(2): 49-54.
15. Miroy, F., Eymard, P., Pizzi, A., 1995: Wood hardening by methoxymethyl melamine. Holz als Roh- und Werkstoff 53(4): 276.
16. Pittman, C.U., Kim, M.G., Nicholas, D.D., Wang, L., Kabir, F.R.A., Schultz, T.P., Ingram, L.L., 1994: Wood enhancement treatments. I. Impregnation of southern yellow pine with melamine formaldehyde and melamine-ammeline-formaldehyde resins. Journal of Wood Chemistry and Technology 14(4): 577-603.
17. Rapp, A.O., Peek, R.D., 1999: Melaminharzimprägniertes so wie mit Wetterschutzlasur oberflächenbehandeltes und unbehandeltes Vollholz während zweijähriger Freilandbewitterung. Holz als Roh- und Werkstoff 57(5): 331-339.
18. Stamm, A.J., 1964: Wood and cellulose science. Ronald Press Company, New York, 549 pp.

Bodo Caspar Kielmann, Holger Militz, Carsten Mai*
Georg-August-University Göttingen
Burckhardt Institute
Wood Biology and Wood Products
Büsgenweg 4
37077 Göttingen
Germany
Phone: +49-(0)551-393558
Corresponding author: cmai@gwdg.de

Stergios Adamopoulos
Technological Educational Institute of Thessaly
Department of Wood & Furniture Design and Technology
43100 Karditsa
Greece