WOOD RESEARCH
61 (1): 2016
01-12

THE EFFECT OF COMBINED MELAMINE- RESIN-COLOURING-AGENT MODIFICATION ON WATER RELATED PROPERTIES OF BEECH WOOD

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(Received August 2015)

ABSTRACT

Beech wood (*Fagus sylvatica* L.) was modified with aqueous solutions of methylated N-methylol melamine (NMM) and a metal-complex dye and the water related properties were determined. Wood blocks, treated to the highest weight percent gain (WPG), attained approximately 5 % cell wall bulking and 30 % anti-swelling efficiency (ASE) after ten cycles of water saturation and drying. The metal-complex dye was stably fixed in the resin matrix and was hardly washed out. The equilibrium moisture content of the modified samples related to the dry mass of untreated beech wood (EMC_R) was not considerably reduced compared to the EMC of the control. The maximum swelling of the modified samples as a result of vapour sorption was only reduced above 65 % relative humidity compared to the control. Capillary water uptake of wood was significantly reduced by the resin modification. The results indicate the potential of the combined modification to improve the water related properties of wood.

KEYWORDS: Wood modification, melamine resin, colouring agent, dimensional stability, water uptake, moisture sorption.

INTRODUCTION

In the modern society, wood cannot only be appreciated for its functional properties but also for its aesthetic appearance, i.e. homogeneity, texture, figure and coloration (Janin et al. 2001). Various paints, varnishes and other coatings are available on the market to enhance or maintain the aesthetic appearance of wood surfaces, and contribute to better performance and prolong the service life of wood. Coating problems due to defects in varnish materials and their application, as well as failure of the wood substrate at the wood-coating interface (e.g through high moisture content, dimensional changes, photo-degradation, colonisation by staining fungi), however, bring about additional maintenance costs during service life (Miller and Boxall 1984).

Permanent staining of the wood products through combined impregnation modification of N-methylol melamine (NMM) resin and a metal-complex dye provides an alternative option to surface coating systems (Kielmann et al. 2014). The combined treatment is expected not only to improve the performance of wooden items exposed outdoors but also to increase the value of wood by enhancing its aesthetic quality (Kielmann et al. 2013a, b, 2014).

It is established that wood modification with NMM resin is able to influence water related properties (Pittman et al. 1994, Deka and Saikia 2000, Lukowsky 2002, Epmeier et al. 2004, 2007). It is an alternative to conventional preservation of wood and enhances the resistance to biological decay agents without using biocidal compounds. Treatment of wood with melamine-formaldehyde is classified as a passive (impregnation) modification, where the chemical is deposited in the cell wall without chemically reacting with the matrix polymers (Norimoto and Gril 1993). NMM resins are able to penetrate into various morphological regions of wood tissues and into the cell wall by diffusion (Gindl et al. 2002, 2003, Sint et al. 2013, Kielmann et al. 2013a). After curing, fixation of the resin is provided by the formation of a three-dimensional network. Dimensional stabilisation due to NMM modification is attributed to cell wall bulking. Bulking reduces the pore size in the cell wall matrix so that less space can be occupied by the water molecules. This results in reduced cell wall moisture content, limited access to the cell wall interior by decay agents (Lukowsky 2002), and, as a consequence, in high resistance to decay fungi (Lukowsky 2002, Gsöls et al. 2003, Kielmann et al. 2014).

Recent studies reported on the modification of three hardwood species with an aqueous NMM resin solution containing a metal complex dye (Kielmann et al. 2013a, b, 2014). The aim was not only to improve the performance of wood exposed outdoors, but also to enhance its aesthetic quality by a permanent staining of the whole wood substrate. It was shown that the combined resin modification and staining is possible and that NMM resin causes fixation of the water-soluble dye (Kielmann et al. 2013a). The modified wood performed better than untreated controls under weathering conditions according to the European standard EN 335 (2006) (Kielmann et al. 2012). With respect to changes in strength properties, the modified wood appeared suitable for most structural uses, but the problems associated with increased brittleness should be considered (Kielmann et al. 2013b). This study aims at investigating the effect of aqueous NMM solutions combined with a metal-complex dye to enhance the water related properties of modified beech wood.

MATERIAL AND METHODS

Wood and chemicals

Sapwood of air dried (12 % moisture content) European beech (*Fagus sylvatica* L.) logs of 100 year old trees from the forest of Göttingen (Germany) was cut into planks of approximately 60×300×3000 mm^3 (radial×tangential×longitudinal). The planks were cut to the specific specimen sizes described below. The specimens were oven-dried at 103 ± 2°C for 48 h and weighed in order to be able to determine the solution uptake and weight percent gain (WPG) after modification. Prior to treatment with N-methylol melamine (NMM), the dried wood specimens were conditioned at 20°C and 65 % relative humidity (RH) to a constant weight. The wood density amounted to approximately 680 $kg.m^{-3}$ and the average annual ring widths to 4-5 mm. The NMM resin Madurit MW840/75WA (Ineos Melamines GmbH, Frankfurt, Germany) was supplied as an aqueous stock formulation with a solid content of approx. 75 %, density of 1.245–1.260 $g.ml^{-1}$ at 23°C, dynamic viscosity of 430 mPa s, and pH value of 9.3 (all values at

25°C). The NMM resin is partly methylolated (with residual amino groups of the melamine) and partly methylated. The aqueous metal-complex dye Basantol Brown 269 liquid (BS) was provided by BASF SE (Ludwigshafen, Germany) with 30 % solid content, density of 1.12 $g.cm^{-3}$, pH 7. Triethanolamine was purchased from Th. Geyer GmbH & Co. KG (Hamburg, Germany).

NMM resin and NMM resin-dye treatment

Aqueous NMM formulations were prepared with 10, 20, and 30 % Madurit MW840/75WA (final concentration), triethanolamine (1 %) and tap water. For NMM-BS, a final concentration of 5 % (of stock solution) dye (BS) was established in the resin formulation. For all formulations, a pH of 10 was adjusted with sodium hydroxide. The conditioned wood specimens were impregnated at 23°C in a stainless steel vessel using a full cell process which included an initial vacuum phase of 5 kPa (1 h) and a pressure phase of 1200 kPa (2 h). After impregnation, the excess solution from the surface of the samples was removed with a paper towel and the samples were weighed. Then they were exposed to the following temperatures regime in a drying oven: 20, 40, 60, 80, 100°C (24 h each), 120°C (48 h), 103°C (24 h). Solution uptakes (SU) after treatment and the weight percent gain (WPG) after drying were related to the dry mass of the untreated beech wood.

Fixation of chemical

The fixation of the chemicals in beech wood was assessed after leaching of the specimens (25 × 25 × 10 mm, r × t × l) with water for 14 days according to EN 84 (1997). The specimens were subsequently dried at 103°C and weighed. Weight percent gain (WPG) and mass loss due to leaching were calculated as percentage of the dry weight of the specimens after the modification. Ten replicates were used per treatment and untreated specimens served as controls.

Bulking, anti-shrink efficiency, maximum swelling

The bulking was assessed as cross sectional area change (%) of specimens (25 × 25 × 10 mm, r × t × l) in the dry state before and after modification (Ohmae et al. 2002, Klüppel and Mai 2013). Anti-shrink efficiency (ASE) was determined after cyclic water soaking and drying (Xiao et al. 2010). Ten specimens per treatment and 10 untreated specimens were subjected to 10 cycles of water saturation (1 h with distilled water at 8 kPa, 24 h stored under water at atmospheric pressure) subsequently oven drying (40, 80, 103°C; 24 h each). After each cycle, the dimensions at oven dry state and water saturation were determined.

Maximum swelling was determined after water saturation and related to the cross sectional area of the dry specimens before modification. The maximum swelling (Sw_{max}) was calculated as follows:

$$Sw_{max} = \frac{A_{tw} - A_{ud}}{A_{ud}} \times 100 \qquad (\%) \qquad (1)$$

where: Sw_{max} - the maximum swelling,
A_{tw} the cross sectional area of the treated specimen in water saturated condition;
A_{ud} - the area of the untreated specimen in dry condition.

Equilibrium moisture content (EMC)

The specimens (25 x 25 x 10 mm, r x t x l) were conditioned to the equilibrium moisture content (EMC) for approximately 4 weeks in a climate chamber (CTS C+10/200, Clima Temperatur Systeme GmbH, Hechingen, Germany) at 20°C and at increasing RH (30, 50, 65, 80, 90 and 95 %), before decreasing to 30 % RH in the reverse. The moisture content was related to the mass of modified wood (EMC) and to the mass of the same specimen before modification (EMC_R), respectively (Hill 2006, Xiao et al. 2010, Himmel and Mai 2014). The EMC ratio was calculated by dividing the EMC_R of the modified specimens through the EMC of the control (Himmel and Mai 2014). Swelling (Sw) was determined based on the cross sectional area at each RH step. Ten replicates were used per treatment; untreated specimens served as controls.

Capillary water uptake

Capillary water uptake along three directions (radial, tangential and longitudinal) was tested according to DIN 52617 (1987) using cubic specimens (40 x 40 x 40 mm, r x t x l) to test radial and tangential uptake and rod-like samples (20 x 20 x 200 mm, r x t x l) for longitudinal uptake. Ten replicates were used per treatment; untreated samples served as a control. The surfaces of the specimens were sealed with the waterproof coating Pyrotect Schutzlack, 2K (Rütgers Organics GmbH, Mannheim, Germany) along four faces keeping only the cross sections, the radial or the tangential faces open. Prior to the test, all specimens were conditioned at 20°C and 65 % RH for two weeks. The wood samples were set on a sponge saturated with distilled water in a basin (20°C) so that the specimens took up liquid water only through the face in contact with the sponge. The contact surface of wood was ca. 2 mm under the water surface.

Water uptake was assessed after 1, 2, 3, 4, 5, 6, 8, 12, 24, 36, 48, 72 h; up to 600 h (25 days). The uptake coefficient was calculated as follows after 24 h:

$$W_t = \Delta W_t \times \Delta t^{-0.5} \qquad (\text{kg.m}^{-2}\ \text{h}^{-0.5}) \qquad (2)$$

where: W_t - the water uptake coefficient,
ΔW_t - the mass of water uptake per area;
t - the time (h) (Xiao et al. 2010).

Micro-computed tomography

Micro-computed tomography (µCT) acquisitions were conducted with the X-ray scanning tube nanotom® s (phoenix/x-ray) (GE Sensing & Inspection Technologies GmbH, Wunstorf, Germany). For the tomographic run, specimens were prepared by cutting a small wood section of approximately 1 x 1 x 10 mm^3 (radial x tangential x longitudinal) out of a larger block. Subsequently, specimens were vertically glued onto cylindrical glass rods (0.5 cm diameter) using hot wax. The final processing and reconstruction were performed by the software Avizo® 9 (FEI Visualization Sciences Group, Mérignac Cedex, France). To visualize both samples in a proper detail, small subvolumes of interest with a dimension of approximately 160 x 200 x 300 μm^3 were extracted of the µCT raw data volumes. Once extracted, these subvolumes were denoised and binarized before surface reconstruction.

RESULTS AND DISCUSSION

Weight percent gain and solution uptake

Solution uptake (SU), retention, and weight percent gain (WPG) demonstrated that *Fagus sylvatica* L. was easily treatable with the various NMM resin formulations (Tab. 1).

Tab. 1: Solution uptake, retention, WPG and mass loss after leaching of beech specimens treated with NMM resin and NMM-dye (BS) resin; mean value of 40 replicates ± standard deviation.

Treatment/	Solution uptake (%)	Retention (kg.m^{-3})	WPG (%)	EN 84 Mass loss (%)
Control	-	-	-	0.92±0.1
10% NMM	113.8±2.2	86.6±4.7	16.1±0.6	2.07±0.4
20% NMM	119.2±1.4	132.2±2.3	24.5±0.2	2.70±0.3
30% NMM	118.5±1.5	173.9±2.1	31.7±0.4	2.93±0.2
10% NMM-BS	120.3±2.0	69.8±1.5	14.5±0.3	2.88±0.1
20% NMM-BS	121.4±1.2	137.5±3.1	26.4±0.3	3.13±0.3
30% NMM-BS	126.0±1.4	189.3±2.5	35.3±0.3	3.22±0.3

Both parameters linearly increased with the solid content in the treating solution. As observed previously (Kielmann et al. 2013a), the weight-based solution uptake (SU) tended to slightly increase with the solid content as the density of the treating solution increases with the solid content. It is assumed, however, that the volumetric uptake and, thus, the penetration are not influenced by the solid content. A similar behaviour with respect to NMM treatment was recently observed for *Bombax* species (Sint et al. 2013). The modified specimens exhibited a somewhat higher mass loss as the controls after leaching with water (EN 84, 1997). This can be attributed to the removal of not covalently fixed NMM resin or dye as the mass of leachable chemicals slightly increased with the WPG. Also water-soluble wood extractives and wood degradation products might contribute to the mass loss during water leaching (Xie et al. 2007). Previous studies reveal better fixation of NMM in the temperature range of 120-140°C than in the range of 85-90°C (Devallencourt et al. 2000, Sint et al. 2013).

Bulking, anti-shrink efficiency, and maximum swelling (Sw_{max})

Cell wall bulking, ASE and Sw_{max} indicate dimensional stabilisation of modified beech wood. Depending on the treatment concentration, modification with NMM and NMM-dye induced moderate bulking in the range of 5-9 % prior to leaching (Fig. 1a, b). The low bulking values are attributed to the relatively great dimensions of the NMM molecules. In addition, drying prior to the modification might have reduced the nano-pore diameters of cell wall pores as compared to never dried wood (Hill and Papadopoulos 2001).

Sw_{max} of the beech controls amounted to approximately 24 %; this means that bulking makes up 21-38 % of Sw_{max}. During ten leaching cycles, bulking decreased to the range of 4-5 %. As a consequence of bulking, the modifications imparted moderate ASE and reduced Sw_{max}, which was continuously decreased by leaching. Bulking and ASE increased with increasing WPG. With respect to the high WPG attained at high treatment concentration, however, bulking and ASE were relatively low compared to active modifications such as acetylation. This indicates that major proportion of the NMM was not accommodated in the cell wall (Fig. 1c, d, e, f) and confirms the results of previous studies (Pittmann et al. 1994, Lukowsky 2002, Deka et al. 2007). It was additionally confirmed by 3-dimensional X-ray scanning imaging (nano-CT) of modified specimens, which shows that lumens are filled with NMM-resin (Fig. 6).

Sw_{max} of the controls decreased, while that of the modified specimens increased with the number of leaching cycles. The former is attributed to leaching of hydrophilic extractives and to hornification of the cell wall due to high temperature drying (Kato and Cameron 1999). The latter can be explained by bulking reduction due to leaching and rearrangement of the resins in the cell wall. The decreasing ASE with increasing number of leaching cycles is due to a combined

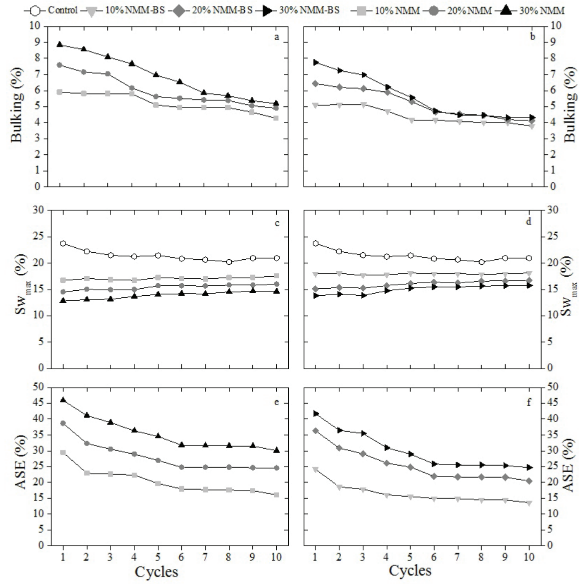

Fig. 1: Bulking (a, b), maximum swelling (b, c) and anti-swelling-efficiency [ASE] (e, f) of beech wood specimens treated to various WPGs with NMM resin (a, c, e) and NMM-dye resin (b, d, f) over 10 cycles of water saturation and oven drying; 10 replicates were used per treatment.

effect of a slightly increasing Sw_{max} of the resin-modified specimens and a lower Sw_{max} of the control. This steady minor loss in ASE indicates that the long-term dimensional stability of resin-treated beech wood must be called into questions.

Equilibrium moisture content

The moisture content was only assessed for NMM-dye modified samples, because the results principally did not deviate from those obtained with only resin-modified samples. The sorption isotherms show reduced EMC with increasing WPG of the samples (Fig. 2).

Generally, EMC decreases with increasing WPG, if the added chemical does not contribute to sorption because the amount of water adsorbed is related to a higher mass of the sorbent. By definition, EMC_R, which is related to the mass of the sample prior to modification, is not influenced by the weight of the added chemical (Himmel and Mai 2014). The EMC_R of the NMM-dye modified samples was not noteworthy reduced compared to the control, irrespective of the WPG attained. The sorption of NMM-dye-modified samples is obviously determined by two effects. On the one hand, cell wall bulking should reduce vapour sorption, because the chemical occupies cell wall nano-pores which cannot accommodate water molecules. On the other hand, cured melamine resin, which is located in the cell lumens, obviously adsorbs water vapour, in spite of its high water repellence (Pittmann et al. 1994). Even increasing EMC was reported after treatment with increasing concentrations of NMM formulations (Epmeier et al. 2004, 2007). This indicates that the effect of bulking can be offset by water vapour sorption of NMM resin in the cell lumens. Location of the resin is also shown by nano-CT (Fig. 6). In some cases, the EMC ratios for adsorption and desorption exceeded the value of 1 particularly at high WPG and low RH indicating that EMC_R was higher than the EMC of the controls.

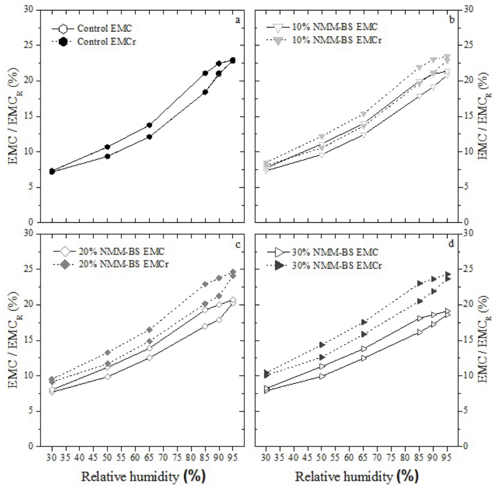

Fig. 2: Sorption isotherms of beech wood specimens; a): control, b): 10 % NMM-dye, c): 20 % NMM-dye, d): 30 % NMM-dye indicated as equilibrium moisture content (EMC) and reduced equilibrium moisture content (EMC_R); 10 replicates were used per treatment.

Generally, the EMC ratio at RH below 80 % was higher for samples with high WPG (Figs. 3 a-d). This indicates that the modification chemical in the cell lumens contributes to vapour sorption. The minor reduction in EMC_R observed in some cases is explained by the fact that sorption is reduced by the resin chemical in the cell wall. This reduced amount of water is greater than vapour adsorbed by the resin chemical in the cell lumens (Pittmann et al. 1994, Hosseinpourpia et al. 2015).

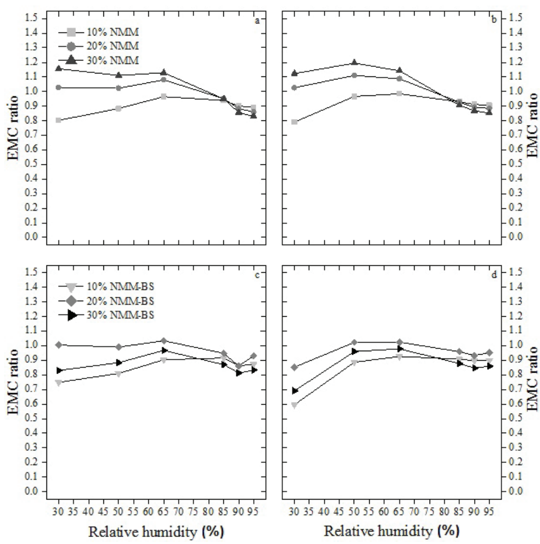

Fig. 3: EMC ratios of modified beech specimens (EMC_R) related to their untreated control at adsorption (a, c) and desorption (b, d); 10 replicates were used per treatment.

Swelling at various relative humidities (RH)

Up to approximately 65 % RH, the cross-sectional swelling (Sw) of untreated and treated wood increased linearly. Above 65 % RH, Sw decreased with increasing WPG of NMM resin and NMM-dye resin compared to the control. Below 65 % RH, the Sw hardly differed between the resin treated samples and the control (Fig. 4 a-d). The changed behaviour above 65 % RH is attributed to softening of amorphous polymers such as hemicelluloses (Vrentas and Vrentas 1991); at 20°C, softening of hemicelluloses occurs above 65 to 70 % RH. It decreases rigidity of the cell wall matrix and allows the accommodation of more water molecules in the cell wall (Olsson and Salmén 2004). NMM resin might interfere with the softening of hemicelluloses and reduce accommodation of water molecules in the gel-like structure of the cell wall. After 10 leaching cycles, the difference above 65 % RH between the control and the resin treated samples became minor (Figs. 4 b, d). This is attributable to leaching of modification chemical, which resulted in somewhat stronger Sw, and to a significant reduction in Sw of the control. The latter might be explained with stiffening ("hornification") of the cell wall matrix (Kato and Cameron 1999, Borrega and Kärenlampi 2010, Suchy et al. 2010) due to repeated swelling and drying.

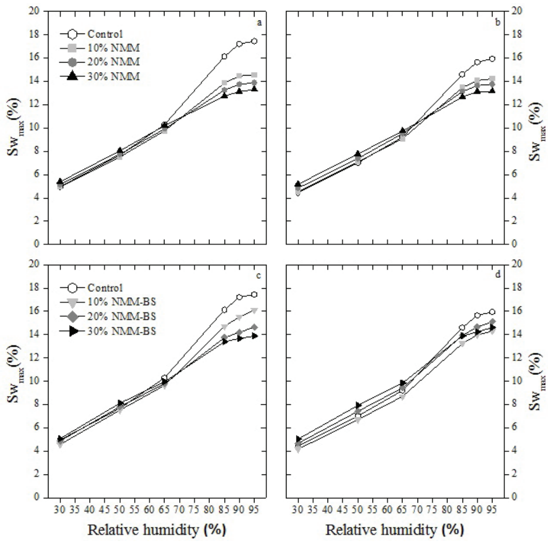

Fig. 4: Maximum swelling (Sw_{max}) of beech wood modified with NMM (a, b) and NMM-dye (c, d) during moisture adsorption; a, c specimens without leaching, b, d after 10 cycles of leaching (EN 84, 1997); 10 replicates were used per treatment.

Capillary water uptake

The liquid water uptake is only illustrated for NMM-dye modified specimens, because the results principally did not deviate from those obtained with only resin-modified samples. Water uptake of all treated and untreated wood specimens was fastest and highest in the longitudinal direction (Fig. 5c) followed by the radial (Fig. 5a) and tangential direction (Fig. 5b). After approx. 36 h, the water reached the surface of the unmodified specimens and of those treated with 10 % NMM-dye resin in the longitudinal direction. The radial water uptake proceeded faster than tangential uptake (Fig. 5 a, b), due to high permeability through ray cells (Banks 1970, Xiao et al. 2010). Treatment with NMM resin and NMM-dye resin clearly reduced water uptake of wood in each direction. Major differences in water uptake occurred between 10 % and higher treatment concentration, while the difference between 20 and 30 % were minor (Fig. 5 a-d). The water uptake coefficient after 24 h (ΔW_t) (Fig. 5 d) was reduced for the radial direction by approximately 18 at 30 % NMM-dye treatment; these values change considerable after 600 h to approx. 47 %. In contrast, 30 NMM-dye resin treatment reduced the tangential ΔW_t by approx. 21 and up to approx. 49 % for 600 h. These values were comparable to those of radial water uptake after the same exposure time (Fig. 5d).

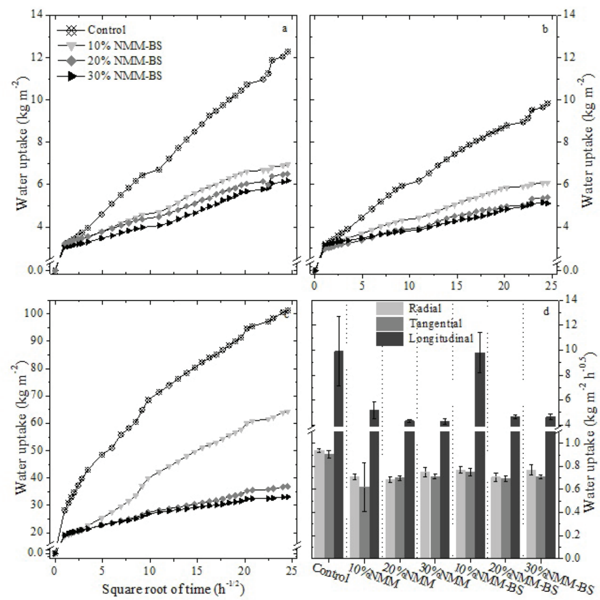

Fig. 5: Radial a), tangential b) and longitudinal c) water uptake (average of 20 samples) and the water uptake coefficient d) of untreated beech wood and wood treated with NMM resin respectively NMM-dye (BS) resin (10 %, 20 %, 30 %).

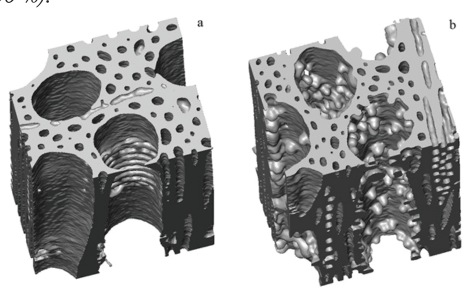

Fig. 6: Three-dimensional (3D) imaging of beech control a) size 0.929 µm and of NMM-dye resin treated beech wood b) size 1 µm.

For the longitudinal direction the ΔW_t was reduced by approx. 53 % after 24 h and for approx. up to 67 % after 600 h. The water uptake reduction may be attributed to a hydrophobation effect due to the non-polar nature of the three-dimensional resin network in the cell wall and the lumens. A considerable amount of resin in the lumens is shown by nano-CT (Fig. 6).

CONCLUSIONS

It can be concluded that the treatment of beech wood with a solution of low-molecular weight N-methylol melamine (NMM) combined with a metal-complex dye can improve water related properties, such as dimensional stability and water repellence. The relative low bulking and anti shrink efficiency (ASE) were increased with increased WPG. The modifications induce only minor reduction in moisture adsorption but major reductions in capillary water uptake. The metal-complex dye had no detrimental effect on the water related properties compared to sole treatment with NMM.

ACKNOWLEDGMENTS

The authors would like to thank the companies BASF SE and Ineos Melamines GmbH for their cooperation. The support from AIF through the ZIM cooperation program (KF 2454601GZ9) is also acknowledged. We would like to thank Tim Koddenberg for his assistance with the micro-computed tomography.

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