

Original Article

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Wood-water interactions of thermally modified, acetylated and melamine formaldehyde resin impregnated beech wood

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Abstract: The wood-water interactions of modified beech wood (*Fagus sylvatica* L.) were studied. Specimens were thermally modified at 180 (TM₁), 200 (TM₂) and 220 °C (TM₃), acetylated (Acet), and melamine formaldehyde (MF) resin (Mel) modified. Afterwards, the water vapour characteristics, i.e. water vapour sorption isotherms, equilibrium moisture content (EMC), dimensional stability of specimens conditioned at 30, 65 and 90% RH and liquid water characteristics, i.e. water absorption, maximum moisture content (MC), leachability and swelling kinetics, were determined and the results compared with reference (Ref) specimens. From the results, it is evident that the scale of wood-water interactions was highly dependent on the thermal modification temperature and type of chemical modification. The water vapour isotherms of thermally modified wood decreased, whereas more severe treatment exhibited more distinct reduction. The EMC values of the Mel and TM₁ specimens decreased only at high RH, whereas the most significant decrease, within the whole range of observation, was found in the Acet group. The maximum MC reduction was achieved by acetylation. As a consequence of swelling reduction, dimensional stability expressed as anti-swelling efficiency (ASE) was considerably improved. A relatively high initial linear-phase swelling rate was found

for the Ref specimens, whereas modified wood exhibited comparatively slow and gradual swelling.

Keywords: acetylation; dimensional stability; melamine formaldehyde (MF) resin; sorption isotherm; thermal modification; wood modification.

1 Introduction

Wood is an important natural and renewable resource, which has many technical advantages, such as its mechanical strength and stiffness in relation to its weight, processing energy and aesthetic properties. However, despite these unquestionably positive benefits, wood exhibits some disadvantageous properties, such as dimensional instability and susceptibility to fungal decay, which are both strongly influenced by the absorption and desorption of water from and to the surroundings. Water absorption generally results in a decrease in strength and leads to dimensional changes until the wood reaches the fibre saturation point (FSP). These dimensional changes caused by moisture content (MC) variations lead to internal stresses, checks and other undesirable defects. Therefore, the dimensional instability of wood affects its functionality and the aesthetics of wood products during their service life. Modifying wood reduces these natural disadvantages considerably, enhancing its properties during its service life. According to Sandberg et al. (2017), there are four main types of treatment: (1) thermo-hydro (TM) and thermo-hydro-mechanical (THM); (2) chemical; (3) those based on biological processes and (4) physical treatments using electromagnetic irradiation or plasma. In the present research, the first two types of treatment will be studied and discussed, i.e. thermal modification and two chemical treatments: acetylation using acetic anhydride and modification using melamine formaldehyde (MF) resin.

Thermally modified timber is usually produced at a temperature between 160 and 240 °C, which results in

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thermal degradation of the cell-wall components associated with chemical and structural changes (Boonstra and Tjeerdsma 2006; Fengel and Wegener 1989). There are various types of thermal modification, depending on the applied temperature, time of treatment, treatment atmosphere (inert gas, air, vacuum), closed or open systems, wood species (important difference between softwoods and hardwoods) and wet and dry systems (Hill et al. 2021). The presence of water vapour or water in the thermal modification process significantly affects the heat transfer and the chemical reactions taking place in the wood. Thermal modification results in mass loss (M_L) which is related to the time and temperature of treatment, the wood species – with hardwoods exhibiting greater mass loss than softwoods under the same conditions (Čermák et al. 2021) – and employed conditions. Thermal degradation starts by deacetylation, and the release of acetic acid acts as a depolymerisation catalyst, which further increases polysaccharide decomposition (Esteves and Pereira 2009). At the same time, hemicelluloses, which are considered the most thermally labile of the wood cell-wall polymers, undergo dehydration reactions associated with a decrease of hydroxyl (OH-) groups (Weiland and Guyonnet 2003). In addition, cellulose crystallinity proportionally increases due to the degradation of the amorphous part of cellulose (Boonstra and Tjeerdsma 2006). Furthermore, new extractive compounds emerge from wood as a by-product of degradation (Hakkou et al. 2005) and cross-linking occurs in lignin, depending on the amount of water present during the process (Altgen et al. 2016; Tjeerdsma and Militz 2005). As a result of these chemical changes, the concentration and accessibility of hydroxyl (OH-) groups are reduced, leading to less wood-water interactions (Rautkari and Hill 2014). Although thermal modification of wood results in a reduction of equilibrium moisture content (EMC), the effect may be partially reversible depending on the conditions as mentioned by Hill et al. (2021), Endo et al. (2016) and Čermák et al. (2015). When water enters the cell walls of wood, they swell, which is macroscopically reflected in a dimensional change in the transverse directions of the wood. The dimensional stability of thermally modified wood is typically improved by (1) thermally degraded compounds remaining in the cell wall, where they have a bulking property, and this filled space is not available to water molecules; (2) removal of OH- groups after thermal degradation of the cell wall, which reduces the hygroscopicity and surface wetting and (3) increased crosslinking within the cell-wall polymers, which restricts the ability of the cell-wall matrix to swell and accommodate sorbed water molecules (Hill et al. 2021).

The acetylation of wood using acetic anhydride – $(\text{CH}_3\text{CO})_2\text{O}$ – is one of the chemical modifications most studied and most commonly used commercially. The

reaction of acetic anhydride with wood polymers results in the esterification of accessible hydroxyl groups in the cell wall and the formation of a by-product, acetic acid, which is mostly removed from the modified wood at the end of the process. Acetylation leads to an increase in the weight of the wood due to the addition of non-polar acetyl groups. Acetylated wood EMC reduction is attributed to the presence of covalently bonded acetyl groups in the nanopores in the cell-wall matrix, which is consequently not available for sorbed water molecules (Hill 2006; Papadopoulos and Hill 2003; Popescu et al. 2014). The dimensional stability of wood improves with increasing weight percentage gain (WPG), due to this chemical reaction. However, other studies favour different mechanisms, reporting that dimensional stability is closely related to WPG or the bulking effect of the cell wall and that the extent of OH-substitution is irrelevant (Jones and Hill 2007; Papadopoulos 2010).

The swelling and water uptake of wood can be reduced by impregnation with thermosetting resins, forming a wood-resin composite; research into wood modification with MF resins has increased recently (Altgen et al. 2020a,b; Behr et al. 2018; Kielmann et al. 2014; Merline et al. 2012; Sandberg et al. 2017; Sint et al. 2013). MF resins are formed by the reaction of the primary amino groups of melamine with formaldehyde to form methylol melamines (Pizzi 2003). Methylation of the methylol melamine with methanol improves its miscibility with water, limits self-condensation during storage and allows the use of aqueous solutions of low molecular weight for polymerisation inside the wood. The molecules are small enough to enter not only the wood lumens but also the nanopores in the water-swollen cell wall (Gindl et al. 2003; Rapp et al. 2005). Heat curing at elevated temperatures removes the water and induces self-condensation of the MF resin via methylene bridges or ether bonds (Pizzi 2003). This forms highly cross-linked MF resin macromolecules that are no longer water-soluble and are irreversibly fixated in the hierarchical structure of the wood (Rapp et al. 2005). When the resin polymerises within the wood cell wall, it fills the free space between the cell-wall matrix polymers to keep the cell wall in a permanently swollen state, i.e. cell-wall bulking (CWB). Therefore, water uptake into the cell wall is reduced, which limits the dimensional changes of wood and enhances its decay resistance. According to Altgen et al. (2020b), the applied conditions (dry or wet) during heat-curing had a significant effect on the moisture uptake of MF resin modified wood. Dry curing resulted in more CWB and, therefore, in less moisture uptake than in wood treated under wet curing conditions. This consequently reduced the water-accessible cell-wall pore volume in dry cured wood and counterbalanced the moisture uptake by the resin itself.

European beech (*Fagus sylvatica* L.) is one of the most widespread and important tree species in Europe. Its proportion is currently increasing in Central Europe, particularly where coniferous plantations are being converted into mixed forests (Brunetti et al. 2020). Beech wood is preferred due to its material properties, especially because it is easily workable and impregnable. However, it suffers from low resistance to fungi and insects, and dimensional instability when the wood's MC changes below the FSP (e.g. by weathering), so a means of modifying its properties would be of great value. It is well known that the chemical and thermal modifications discussed above improve the water-related characteristics of wood. Although the effect of these modifications has already been evidenced (Hill et al. 2021; Sandberg et al. 2017), comprehensive and comparable experimental data for beech wood modified by various treatments are not available. Therefore, this study aims to analyse (a) the water vapour and (b) the liquid water related characteristics of modified beech wood. The work described in this paper will be followed by mechanical tests of modified wood under various moisture conditions to produce comprehensive performance data.

2 Materials and methods

European beech (*F. sylvatica* L., dry density 727 kg/m³) wood harvested from the Training Forest Enterprise, Masaryk Forest Křtiny of Mendel University in Brno, Czech Republic, was studied. Logs harvested from 17 different trees were sawn using a plain-sawn cutting pattern to achieve central planks with quarter-sawn grain (symmetrical around the pith), with a thickness of 65 mm and length of 3000 mm. Planks were kiln-dried to 12% of MC before further processing. Each plank was cut into six beams (60 × 110 × 650 mm; $R \times T \times L$) representing the modification groups, i.e. untreated reference (Ref), MF resin modified (Mel), thermal modified at 180 (TM₁), 200 (TM₂) and 220 °C (TM₃) and acetylated (Acet). Each beam was further cut to make the samples (60 × 25 × 650 mm; $R \times T \times L$) used for modification processes.

2.1 Wood modification

2.1.1 Melamine formaldehyde resin modification: The samples were vacuum-impregnated at 10 kPa (absolute pressure) for 1 h with an aqueous solution of low molecular weight melamine resin (Madurit MW 840/75WA; Prefere Melamines GmbH, DE) using a laboratory vacuum pressure impregnation plant (J. Hradecký spol. s r.o., CZ, vessel volume 50 l). The MF resin was supplied as an aqueous stock solution with a pH of 9.7 (50% non-ionic water at 20 °C). Solutions with solid contents of 25% (dilution with deionised water) were selected for testing based on preliminary test studies. After vacuum impregnation, the samples were kept in the solution at ambient pressure for 1 h. They were then removed from the aqueous solution and carefully dried to prevent cracking. After two weeks at laboratory conditions (20 ± 1 °C), the samples were placed in the oven and exposed to the following

temperature sequence: 30, 60 and 103 °C for 48 h each. WPG (%), R (kg/m³) and CWB (%) values were used as indicators of impregnation quality and calculated according to Equations (1)–(3).

$$\text{WPG (\%)} = (\text{dry mass}_{\text{[modified]}} - \text{dry mass}_{\text{[unmodified]}}) / \text{dry mass}_{\text{[unmodified]}} \quad (1)$$

$$R \text{ (kg/m}^3\text{)} = (\text{dry mass}_{\text{[modified]}} - \text{dry mass}_{\text{[unmodified]}}) / \text{dry volume}_{\text{[unmodified]}} \quad (2)$$

$$\text{CWB (\%)} = (\text{dry volume}_{\text{[modified]}} - \text{dry volume}_{\text{[unmodified]}}) / \text{dry volume}_{\text{[unmodified]}} \quad (3)$$

2.1.2 Thermal modification: Thermal modification at 180 (TM₁), 200 (TM₂) and 220 °C (TM₃) was carried out in a laboratory chamber (Katres spol. s r.o., CZ, volume 0.7 m³) in a superheated steam environment at atmospheric pressure. The treatment was performed in five stages: an initial heating rise at 10 °C/h to drying temperature (103 °C); 70 h at this temperature; a second rise at 4 °C/h to reach 130 °C; a third rise at 30 °C/h until the maximum temperatures (180, 200 and 220 °C) were reached; maintained at maximum temperature for 3 h; and natural cooling. The process intensity and degree of thermal modification was determined by mass loss (M_L ; %), based on oven-dry (103 ± 2 °C) mass before and after the thermal modification process. The M_L was calculated according to Equation (4).

$$M_L \text{ (\%)} = (\text{dry mass}_{\text{[unmodified]}} - \text{dry mass}_{\text{[modified]}}) / \text{dry mass}_{\text{[unmodified]}} \quad (4)$$

2.1.3 Acetic anhydride modification – acetylation: The oven-dried samples were vacuum-impregnated at 10 kPa (absolute pressure) for 0.5 h with acetic anhydride (Acet) using a laboratory vacuum-pressure impregnation plant (J. Hradecký spol. s r.o., CZ, vessel volume 50 l). After vacuum impregnation, the samples were kept in the chemical at ambient pressure for 0.5 h, then placed in stainless-steel containers and sealed during the acetylation. The acetylation reaction took place at 120 °C in a hot-air oven (Sanyo MOV-212P) for 24 h. On completion, the samples were dried to 0% MC (12 h at 30 °C, 12 h at 60 °C and 48 h at 120 ± 2 °C). The WPG, R and CWB values were calculated according to Equations (1)–(3).

2.2 Chemical analysis

The reference, MF resin modified, thermally modified and acetylated specimens were disintegrated into sawdust (fraction size 0.5–1.0 mm) and extracted in a Soxhlet apparatus with a mixture of ethanol and toluene according to ASTM D 1107-96 (2013). The lignin content was determined according to ASTM D 1106-96 (2013), the holocellulose content according to the method reported by Wise et al. (1946) and the cellulose content according to the method by Seifert (1956). The hemicellulose content was calculated as the difference between the holocellulose and cellulose contents. The result was taken as the mean percentage of three oven-dry wood repetitions.

2.3 Wood-water interaction measurements

2.3.1 Dynamic water vapour sorption: The sorption behaviour of the modified beech wood was analysed with dynamic vapour sorption (DVS) equipment (DVS Resolution, Surface Measurement Systems Ltd., UK) using liquid deionised water. The device consists of a microbalance in a cabinet with controlled temperature and RH. The latter was achieved by mixing dry and saturated carrier gas (N₂) using a digital mass flow controller. Prior to the sorption measurements, 30 mg samples of wood were cut from each specimen group with a

razor blade in a sledge microtome (WSL, Switzerland) and placed on the sample holder in the DVS microbalance. Sorption isotherm analysis was carried out for three repetitions for each group. The sorption isotherms were determined in the following sequence: 0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 85, 90 and 95% RH, which was followed by the same sequence in reverse order to 0% RH. The sorption measurements were run at a constant temperature of 25 ± 0.1 °C and a nitrogen flow of 200 sccm. The first step of 0% RH was combined with preheating (103 °C, 240 min) to reach the dry mass of the sample. Based on pre-test results, the optimal time for reaching the equilibrium state at individual steps of the TM_3 samples was determined. These step time intervals were further applied to other tested samples and ranged from 240 min (low RH) to 3020 min (95% RH). Data from the microbalance were acquired every 10 s. The MC was determined based on the sample mass at the end of each RH step using the oven-dry method according to EN 13183-1 (2002). The results were taken as the mean of three repetitions.

2.3.2 Equilibrium moisture content: The oven-dried specimens of dimensions $20 \times 20 \times 20$ mm ($R \times T \times L$) were measured (accuracy of 0.01 mm), weighed (accuracy of 0.001 g) and conditioned at various relative humidities (RHs), i.e. 30, 65 and 95% RH at 20 ± 1 °C until the specimens reached EMC, i.e. when less than 0.5% weight difference between measurements (five days) was found. The EMC data were further recalculated to reduced equilibrium moisture content (EMC_R) according to Equation (5), which is the mass ratio of moisture to dry wood substance, i.e. where the mass of the modification agent is deducted from the dry mass. The radial, tangential and volumetric swelling (S) was calculated at each RH level according to Equation (6). The anti-swelling efficiency (ASE) and moisture exclusion efficiency (MEE) were calculated according to Equations (7) and (8).

$$EMC_R (\%) = EMC(1 + WPG)/100 \quad (5)$$

$$S_{R,T,V} (\%) = (\text{dimension}_{[at EMC]} - \text{dimensions}_{[oven-dry]}) / \text{dimension}_{[oven-dry]} \quad (6)$$

$$ASE (\%) = (\text{swelling}_{[unmodified]} - \text{swelling}_{[modified]}) / \text{welling}_{[unmodified]} \quad (7)$$

$$MEE (\%) = (EMC_{[unmodified]} - EMC_{[modified]}) / EMC_{[unmodified]} \quad (8)$$

$$WRE (\%) = (MC_{[unmodified]} - MC_{[modified]}) / MC_{[unmodified]} \quad (9)$$

2.3.3 Water soaking and leachability: The oven-dried specimens of dimensions $20 \times 20 \times 20$ mm ($R \times T \times L$) were measured (to an accuracy of 0.01 mm), weighed (to an accuracy of 0.001 g) and immersed in deionised water (20 °C) in laboratory glass beakers; the wood-to-water ratio was approx. 1/5. The specimens' mass was measured after 2, 4, 6, 10, 24, 48, 72, 144, 168, 192, 384 and 720 h and expressed as a function of water uptake (MC) over time. After each measurement the deionised water was renewed. The specimens were left soaking in the water to reach maximum MC. Maximum swelling, ASE and WRE were calculated according to Equations (6), (7) and (9). The leachability of the analysed specimens was determined on oven-dried mass before and after water soaking (approx. three months).

2.3.4 Swelling kinetics: The oven-dried specimens of dimensions $20 \times 20 \times 20$ mm ($R \times T \times L$) were measured (accuracy of 0.01 mm), weighed (accuracy of 0.001 g) and immersed in deionised water for 48 h at 20 °C. The radial and tangential dimensions of the specimens were continuously measured by displacement transducers (WA/20 mm, HBM, Inc., USA, accuracy of 0.02 mm) and data were transmitted by an acquisition system (QuantumX, MX440A, HBM, Inc.,

USA) and software (catman Easy, HBM, Inc., USA) to the computer every 5 s. Afterwards, the radial and tangential swelling were calculated. The radial and tangential swelling kinetics of all groups were compared using the relative slopes of the linear part of the swelling curves calculated as a function of a tangent as follows: $\Delta y/\Delta x$. The beginning and end of the linear phase of the plots were determined at intervals of 10% and 50% of the maximum swelling after 48 h of immersion. The swelling kinetics are presented as relative swelling rate per time unit. Results were taken as the mean of five repetitions.

2.4 Data processing and statistical analysis

The data were processed, evaluated using one-factor analysis of variance (ANOVA), completed with Tukey's honest significance test (HSD) and graphed by OriginPro (version 9.0). Statistically significant differences were considered at $p \leq 0.05$.

3 Results and discussion

3.1 Wood modification efficiency indication

The values of WPG, R and CWB of MF resin modified and acetylated specimens, and the mass loss (M_L) of thermally modified specimens are listed in Table 1. These values are generally considered the first indicators of the degree of modification achieved (Esteves and Pereira 2009; Hill 2006; Sandberg et al. 2017).

As expected, higher M_L values were achieved as more severe thermal treatments were applied. These results are in agreement with previous findings reported by Čermák et al. (2021), Ferrari et al. (2013) and Esteves and Pereira (2009). According to Ferrari et al. (2013), the mass loss of spruce, beech and oak wood thermally modified at 220 °C for 3 h was 5.7%, 9.4% and 13.0%, respectively. The influence of treatment temperature on M_L is generally more pronounced than the influence of the treatment time. According to previous studies, it is evident that the thermal degradation reaction kinetics are strongly influenced by the wood species and their respective chemical compositions

Table 1: Average densities, mass loss, weight percentage gain (WPG), retention (R) and cell-wall bulking (CWB) effect for modified groups.

	ρ_0 (kg/m ³)	M_L (%)	WPG (%)	R (kg/m ³)	CWB (%)
Ref	727 (44)	–	–	–	–
Mel	841 (35)	–	19.4 (1.9)	696 (36)	2.9 (1.3)
TM_1	715 (36)	1.4 (0.1)	–	–	–
TM_2	708 (27)	2.7 (0.2)	–	–	–
TM_3	694 (51)	8.6 (0.6)	–	–	–
Acet	746 (26)	–	24.9 (1.2)	463 (30)	18.4 (1.7)

Numbers in parentheses represent standard deviation.

which undergo thermal decomposition; hardwoods have been shown to be more sensitive to thermal degradation than softwoods (Chaouch et al. 2013). These differences may be explained by the different types of hemicellulose or the higher lignin content of softwoods compared to hardwoods (Fengel and Wegener 1989), the greater amount of acetic acid released from hardwood hemicelluloses (Candelier et al. 2011; Prins et al. 2006) or the heat transfer phase defined by the thermal properties of wood (Chaouch et al. 2010).

The extent of the reactions of acetic anhydride and MF resin with wood are invariably reported as WPG and CWB, indicating the mass and volume change after curing. Behr et al. (2018a) reported a WPG of 15.4% for beech wood modified by MF resin (19% solid content), which is in agreement with the present study. Similar results were published by Behr et al. (2018b) and Altgen et al. (2020b), who reported WPG of 13.7% and 11.9 (10% solid content) and 26.1% (25% solid content) for beech and pine wood, respectively. CWB was reported to be 2.8–3.6%, depending on the solid content and curing conditions. According to Altgen et al. (2020b) and Biziks et al. (2019), the CWB is dependent on the molecular size and concentration of treatment solution and used curing conditions.

As reported earlier by Minato et al. (2003), Obataya and Minato (2009) and Popescu et al. (2014), WPG results are influenced by wood species, the reaction temperature and time and the type of catalyst, if any, used during acetylation. For instance, Beckers and Militz (1994) reported that a WPG of 10% was already sufficient to reduce EMC and protect acetylated beech wood against soft-rot attack, while a WPG of more than 20% was required to prevent acetylated pine from being degraded by brown rot fungus. Bollmus et al. (2015) reported WPGs of 20.7, 23.4, 19.3 and 20.0% for beech, alder, lime and maple wood, respectively. However, only maple and alder wood specimens provided high quality after acetylation, while further adapted process parameters or a limitation in board width are suggested for the acetylation of a highly unstable wood species like beech. Dong et al. (2016) reported CWBs of 11.8 and 6.8% for acetylated pine and poplar wood (4 h reaction time) with WPGs of 23.0 and 18.7%, respectively. In the present study the WPG and CWB were higher, most probably due to the different wood species and time of the acetylation reaction.

3.2 Analysis of chemical changes

Thermal modification and acetylation led to significant changes in chemical composition, whereas MF resin

modification shows only minor chemical composition changes (Table 2). The thermal modification of wood resulted in a decrease in the amount of polysaccharide, and the decrease was more noticeable at higher temperatures. The content of holocellulose in TM₃ was approximately 81% of its content in the reference group. This is caused by the degradation of hemicelluloses which are the most thermally labile of the cell-wall polymers. The degradation of wood starts with the deacetylation of hemicelluloses, followed by the release of acetic acid, which catalyses the depolymerisation reactions of polysaccharides, first degrading hemicelluloses and the amorphous regions of the cellulose macromolecule. The crystalline regions of cellulose are more thermally stable due to their organised structure. Therefore, the cellulose content relatively increased with increased modification temperature. A lignin content of 20.5% was determined in the reference specimens. Under the influence of heat and also acetic acid released by the degradation of hemicelluloses, the cleavage of aryl-ether linkages may occur. Consequently, more reactive and unstable free radicals are formed, leading to condensation reactions of lignin with hemicellulose cleavage products or to lignin macromolecule cross-linking (Da Silva et al. 2013; Nuopponen et al. 2004; Tumen et al. 2010; Wikberg and Maunu 2004). The emerging products have greater stability. This may be a reason for the increase in lignin content in the thermally modified groups. Thermal modification also resulted in a significant increase in extractive content. This can be explained by the release of the degradation products of lignin and saccharides into the extraction mixture, or by their condensation reactions with the extractives originally present in beech wood. A similar trend was obtained also in other studies (Severo et al. 2016; Wang et al. 2015).

Cellulose, which makes up more than 38% of the wood structure, is less reactive with acetic anhydride and more thermally stable than hemicelluloses. According to Zhao et al. (1987), cellulose reacts during wood acetylation only above 20% WPG and the degree of crystallinity changes above 25% WPG. Sun et al. (2019) found that the degree of acetylation of larch and pine wood cell-wall polymers increased with increasing WPG until all the main components of wood (cellulose, hemicelluloses and lignin) were acetylated. However, during the acetylation process, acetic acid was formed and the degradation of lignin and the acid hydrolysis of carbohydrates occurred simultaneously. Hemicelluloses have shorter polymer chains, are not crystalline and are composed of both hexose and pentose sugars. Hemicelluloses are very reactive and proportionally contain the most hydroxyl groups (Sadeghifar et al. 2014; Winandy and Rowell 1984). When hydroxyl groups

Table 2: Results of chemical analysis of reference and modified groups expressed in relative %.

	Holocellulose (%)	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Extractives (%)
Ref	76.9 (0.1)	38.4 (0.3)	38.5 (0.3)	20.5 (0.1)	2.6 (0.1)
Mel	76.7 (0.2)	35.5 (0.1)	41.2 (0.3)	22.3 (0.2)	1.0 (0.1)
TM ₁	75.9 (0.5)	41.9 (0.1)	34.0 (0.6)	21.4 (0.1)	2.6 (0.1)
TM ₂	71.8 (0.1)	46.1 (0.6)	25.7 (0.6)	24.2 (0.2)	3.9 (0.1)
TM ₃	62.4 (0.1)	52.2 (0.3)	10.2 (0.3)	30.6 (0.1)	7.0 (0.1)
Acet	81.4 (0.2)	31.1 (0.1)	50.3 (0.2)	15.9 (0.2)	2.7 (0.1)

Numbers in parentheses represent standard deviation.

are substituted by acetyl groups, hemicelluloses are mostly acetylated and increase the weight of the polymer. This is reflected by the increase from 38.5% to 50.3%. Lignin also reacts with acetic anhydride (Hill 2006; Sadeghifar et al. 2014), but it has fewer -OH groups available for acetylation than hemicelluloses. The proportion of lignin was reduced from 20.5% to 15.9%.

The chemical changes in the main wood components caused by MF resin modification were minor compared to other treatments. While the cellulose content decreased by almost 3%, in contrast, the hemicellulose content increased by approximately the same proportion. Bollmus et al. (2020) also mentioned the possible effect of formaldehyde, which can react with cellulose and cause its hydrolysis. The lignin and extractives content were affected slightly by the MF resin modification.

3.3 Dynamic water vapour sorption

The sorption isotherms shown in Figure 1 provide important information on changes in the adsorption and desorption process due to the experimental modifications. It is evident from the plots that the scale of the EMC decrease is dependent on the TM temperature and type of chemical modification. A more distinct reduction in the EMC was observed as more severe thermal treatments were applied. The EMC (at 95% RH) decreased from 22.3% to 20.3, 18.1 and 11.5% for TM₁, TM₂ and TM₃, respectively, which represents 8.9, 18.8 and 48.3% reduction. The reduction in EMC is commonly explained by a decrease in hydroxyl groups, mainly in the least thermally stable hemicelluloses, having active sorption sites available within the wood cell walls (Table 2). It was also reported

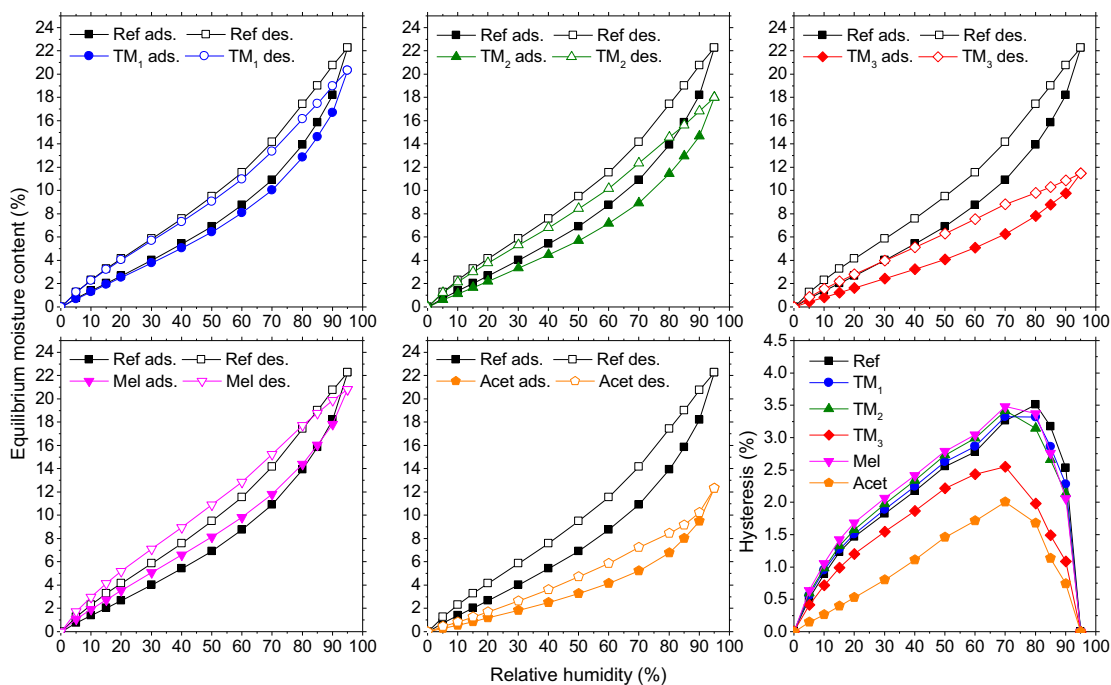


Figure 1: Sorption isotherms (adsorption and desorption) and hysteresis plotted as a function of relative humidity (RH) for reference and modified wood specimens measured by dynamic vapour sorption (DVS) (Ref – untreated beech, TM₁ – thermally modified at 180 °C, TM₂ – thermally modified at 200 °C, TM₃ – thermally modified at 220 °C, Mel – melamine resin modified, Acet – acetylated).

that the TM may cause additional ultrastructural reorganisation of cellulose from the less ordered amorphous state to the crystalline one, which further effects a reduction in the available sorption sites (Hill et al. 2013; Olek et al. 2013). Below ca. 60% RH, TM₁ showed almost identical EMC to the reference specimens. This can be assigned to the insufficient M_L at 180 °C (1.4%). MF resin modified specimens exhibits even higher EMC over whole range of RH, which can be assigned to additional water adsorption by MF resin itself as reported by Altgen et al. (2020b).

After conditioning at 95% RH, the EMC of MF resin-modified specimens decreased to 20.8%, which represents a 6.7% reduction. Altgen et al. (2020b) studied the effect of curing conditions on the sorption behaviour of MF resin modified Scots pine (*Pinus sylvestris* L.) sapwood. EMC reductions of 10 and 15% were reported only above ca. 80% RH for dry-cured samples with 10 and 25% solid content of MF resin, respectively. The opposite effect was reported for wet-cured samples within the whole range of RH as well as for dry-cured samples at RH below ca. 80%, which was further discussed by Altgen et al. (2020b). The same results were reported by Hosseinpourpia et al. (2016), who measured only a slight reduction of the EMC in the high RH (above 70–80%) range of adsorption and desorption isotherms of MF resin modified wood (WPG 18%). Bollmus et al. (2020) reported lower EMCs for methyl-etherified MF resin treated Scots pine at all concentrations tested. However, the reduced EMC, which was on the basis of dry weight before modification and which eliminated the additional weight of the modification agent in wood, showed any no significant decrease in EMC. Evidence for covalent bonding between MF resins and both the lignin and cellulose components of wood have been reported (Troughton 1969). The MF resin occupied space within the cell wall that would otherwise be used by water molecules, which led to a reduction in the hygroscopic properties of the wood (Qin et al. 2019). The EMC values of acetylated specimens in the adsorption and desorption isotherms significantly decreased and the slope (EMC/RH) of the isotherm was significantly reduced compared to the reference (Figure 1), similarly to TM₃. The EMC of acetylated wood, measured at 95% RH, decreased to 12.3%, which represents a 44.7% reduction. Himmel and Mai (2015) reported a reduction of 45% for acetylated Scots pine wood with a WPG of 20.4%. Similar results were reported by Popescu et al. (2014), who reported 11.6, 18.9, 32.3 and 46.5% reductions for acetylated birch wood at WPGs of 3, 7, 10 and 16%, respectively. The EMC reduction of the acetylated wood was reported to be because the bonded reagent bulks the cell wall or because hygroscopic OH- groups are blocked (Hill 2006).

According to the results shown in Figure 1, it is evident that the reference and all modified groups exhibit the

hysteresis phenomenon common in wood (Hill et al. 2009; Skaar 1988; Walker 2006). However, with the same exposure history, modification reduced hysteresis, although the TM₁, TM₂ and MEL specimens showed no significant difference from the reference. The hysteresis effect has been explained in the literature, and various explanations have been proposed from chemical and physical viewpoints, such as different concentrations of the hydroxyl groups taking part in adsorption and desorption (Urquhart 1959), the formation of metastable states of adsorbate in fixed pores (Neimark et al. 2000; Sander et al. 2005) and relaxation of swelling stress due to matrix stiffness of glassy solids below the glass transition temperature, which leads to different physical states during adsorption and desorption (Hill et al. 2010; Lu and Pignatello 2002). The most significant difference between the sorption and desorption process was found for the TM₃ and Acet specimens, especially at a RH range of ca. 60–80%. This is consistent with previous observations that the effects of wood modification mainly occur at the high end of the RH range, as reported by Popescu et al. (2014), Hill et al. (2013) and Xie et al. (2011a,b). However, it is important to note that recent studies have shown that there is a significant difference between the determination of sorption hysteresis by scanning and desorption isotherms (Fredriksson and Thybring 2018) and therefore it may be difficult to interpret these results; further detailed study is needed.

3.4 Equilibrium moisture content

The EMC values measured on the microtome slice (30 mg) by means of the DVS apparatus were further verified by solid wood specimens conditioned at 30, 65 and 90% RH; the results are expressed as MEE (Figure 2A). When results were compared with those of sorption isotherms, only minor differences, within the range of 0.1–1.7%, were found. The maximum values of MEE, measured at 90% RH, were achieved for thermally modified (TM₃) and acetylated wood, i.e. $\pm 56.5\%$. Even though the slightly different EMC reduction was measured by means of DVS at 95% RH, when EMC values were compared at 90% RH, both analyses showed almost the same value (less than 1% of MEE).

3.5 Maximum moisture content and leachability

The maximum MC and leachability of wood specimens after water soaking are shown in Figure 2B. The reference beech wood reached maximum MC (with standard deviation) of 101% (9%), which significantly decreased for all

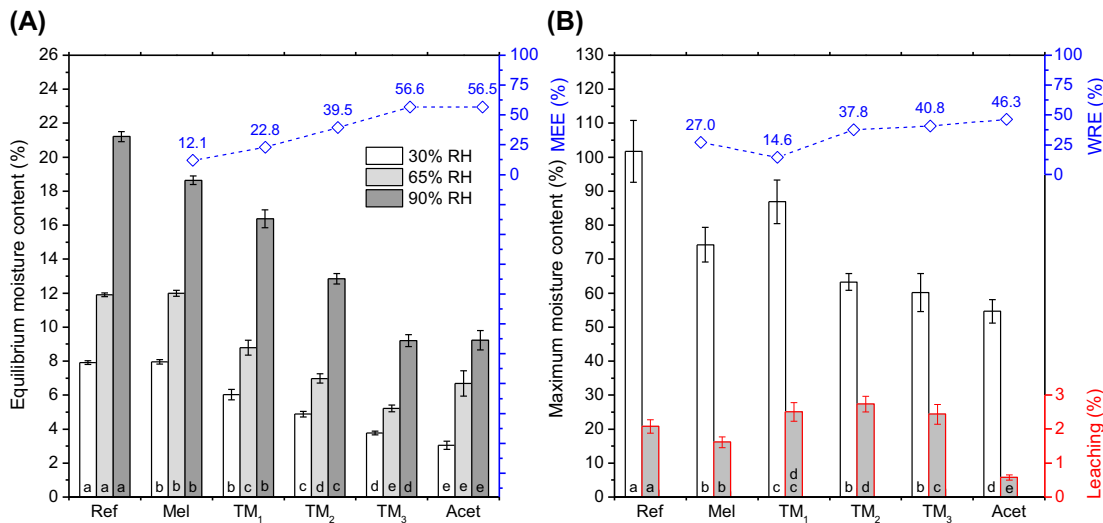


Figure 2: Equilibrium moisture content (EMC_R) of solid specimens measured at 30, 65 and 90% RH, together with moisture exclusion efficiency (MEE) (A), and maximum moisture content (MC) after water soaking together with water repellence efficiency (WRE) and specimen leaching (B). The same letters between the modified groups indicates that the difference of the means is not significant at the 0.05 level (Ref – untreated beech, TM₁ – thermally modified at 180 °C, TM₂ – thermally modified at 200 °C, TM₃ – thermally modified at 220 °C, Mel – melamine resin modified, Acet – acetylated).

modified groups. The Mel, TM₂ and TM₃ exhibit almost identical values with no statistical differences between groups. The maximum water repellence efficiency (WRE) was achieved by acetylation (46.3%). In all treatments, the WRE must be at least partly attributed to a reduction of bonded water in the cell wall. However, the significant decrease of maximum MC is in contrast to increased pore size and the total porosity of thermally treated wood (Jang and Kang 2019), which should allow more liquid water to be absorbed. Moghaddam et al. (2016) showed almost unchanged porosity in Southern yellow pine after acetylation, whereas acetylation strongly decreased swelling but the effect on capillary uptake was minor. On the other hand, a significant water uptake decrease after acetylation was shown by Adebawo et al. (2016) for obeche wood (WRE 20–60%). In general, water uptake of wood can be reduced through (a) altering the surface properties of the wood in a way that hinders water uptake and (b) blocking penetration pathways for capillary water uptake (Pries et al. 2013). It is believed that alteration of the cell-wall surface by increasing its hydrophobicity – i.e. contact angle – leads to decreased water uptake of acetylated and thermally modified wood (Adebawo et al. 2016; Esteves and Pereira 2009). Decreased porosity caused by cell-wall swelling into the lumina and occluding some of them in the latewood of beech after acetylation (WPG around 20%), which was observed by Sander et al. (2003), can also lead to lower water uptake. When wood is impregnated with thermo-setting resin, it partly diffuses into the cell wall and partly fills the cell-wall voids and cell lumina after curing

(Altgen et al. 2020a; Qin et al. 2019), thereby blocking the space for free water and preventing water penetration into the cell wall.

The leaching of tested specimens did not exceed 3%, while the highest values were found in thermally modified specimens (2.5%) and the lowest in acetylated (0.6%). According to the chemical analysis, the number of extractives within thermally modified wood was increased significantly (Table 2) and therefore these newly formed extractives can leach out. This has previously been reported by Biziks et al. (2015); Čermák et al. (2015), who noted the deterioration of water-related properties after several soaking cycles. It is believed that the majority of the newly formed extractives could be leached out, which would hinder the penetration of water molecules into the cell wall (Biziks et al. 2015). It was found that the mass losses of PF, MF and UF treated softwood samples were less than those of the untreated samples, indicating that resins were retained by wood components (Deka and Saikia 2000). Similar results are presented by Behr (2019), when leaching of cured MF impregnated beech wood led to slightly less mass loss than reference beech (0.8 and 1.3%, respectively).

3.6 Wood swelling

The effects of the experimental modifications on the dimensional stability of wood at various RH levels and after water soaking were compared to untreated specimens as a

reference and expressed as radial, tangential and volumetric swelling (Figure 3). The swelling of untreated wood is known to be highest in the tangential direction, and even if previous studies have reported a reduction in anisotropic behaviour due to wood modification (Esteves et al. 2008; Sailer et al. 2000), it was only partly confirmed in the present study. The radial and tangential swelling ratio of reference specimens measured at 90% RH was approximately 0.53 (0.07) and changed for the TM₃, Mel and Acet groups, i.e. 0.59 (0.09), 0.60 (0.06) and 0.64 (0.07), respectively. A statistically significant difference was proved only for the Acet group at the 0.05 level. Even though the differences between the radial and tangential swelling still remains, the experimental modification partly contributed to the decrease of wood anisotropy. Volumetric swelling (with standard deviation), measured at 90% RH, decreased from the original 15.0 (0.7) to 11.0% (0.7%) for mild thermal modification (TM₁) and to 8.5% (0.4%) and 5.8% (0.4%) for severe treatments (TM₂, TM₃), respectively. MF resin specimens exhibited almost identical results to TM₁, which was already observed from the EMC results.

A large swelling reduction was achieved by wood acetylation, where radial, tangential and volumetric swelling was 1.2 (0.2), 1.9 (0.3) and 3.1% (0.4%). As a consequence of swelling reduction, the dimensional stability expressed as ASE was considerably improved. The dimensional stability improvement was more significantly pronounced at higher RH levels. A similar trend in the swelling behaviour of modified wood was found after exposure to liquid water (Figure 3B). However, the radial, tangential and volumetric swelling depended on the water phase used in the test – water vapour (RH 90%) or liquid water (RH 100%). These conditions create different equilibrium moisture levels in the wood and therefore different swelling values. According to Engelund and Fredriksson (2021), cell-wall water absorption is significantly more pronounced at higher RH (above 90% RH), which causes more swelling.

Water absorption of modified beech wood specimens measured as a function of immersion time was significantly lower than for the corresponding reference specimens (Figure 4). These results are in line with reported increases of dimensional stability, reduced hygroscopicity and water

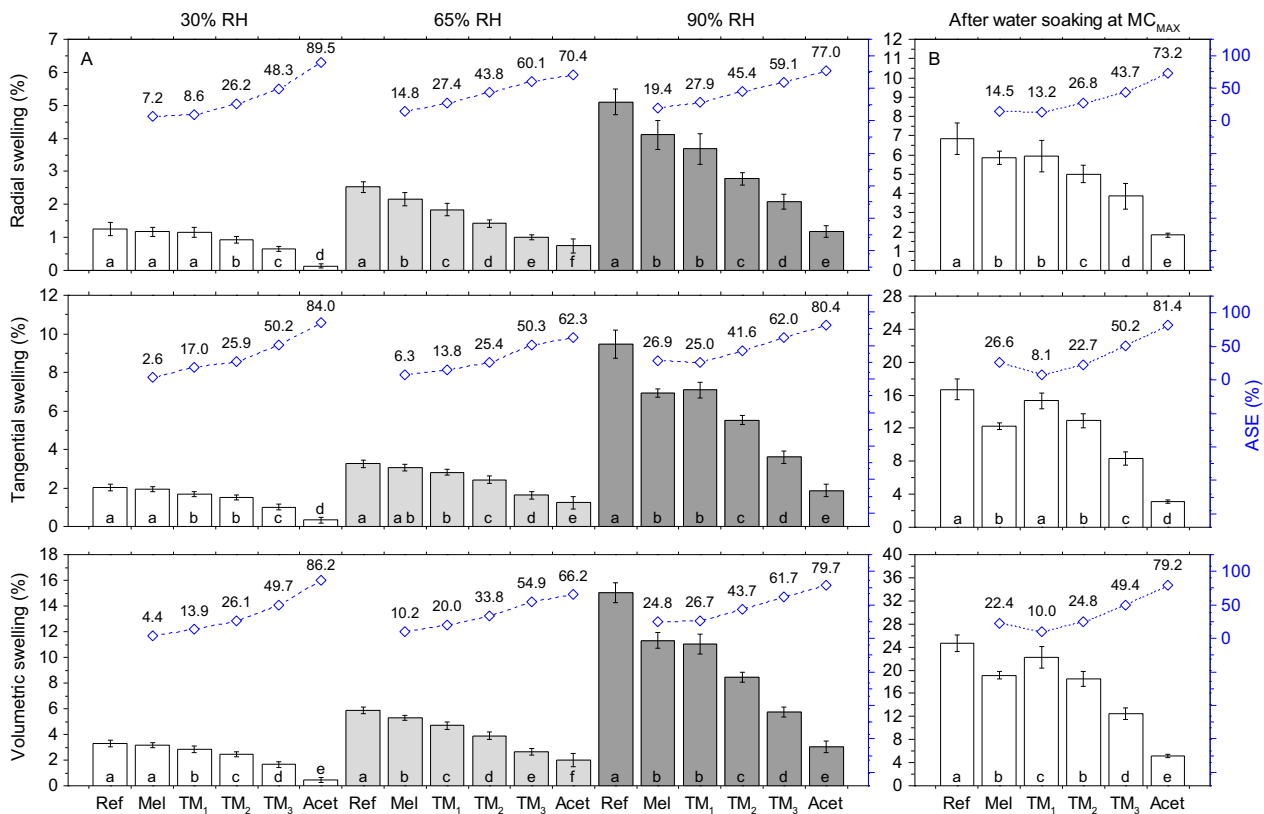


Figure 3: The radial, tangential and volumetric swelling of reference and modified specimens conditioned at 30, 65 and 90% RH (A), and after water soaking (B), both expressed as an ASE. The same letters between the testing groups indicates that the difference of the means is not significant at the 0.05 level (Ref – untreated beech, TM₁ – thermally modified at 180 °C, TM₂ – thermally modified at 200 °C, TM₃ – thermally modified at 220 °C, Mel – melamine resin modified, Acet – acetylated).

adsorption by the cell wall after thermal modification, acetylation and MF resin modification. For all tested groups, the wood specimens exhibited an initially high rate of water uptake followed by a relaxation phase in which water uptake was very slow (Kumar and Flynn 2006). It is evident that, during the first phase of water soaking, reference and thermally modified specimens quickly (2–6 h) reached a moisture level in excess of the original FSP ($\pm 25\%$), whereas MC of acetylated and MF resin impregnated specimens increased more gradually, as can be seen in the magnified area in Figure 4. At the beginning of the water immersion, capillaries and cavities near the surface are filled up with water very fast. Hence, it can be assumed that the water concentration on the surface is raised to saturation almost immediately. However, the water moves freely in large cavities, but in small ones the presence of trapped air bubbles influences the water movement inside the material. The surface hydrophobicity increases as a result of wood modification and therefore the water absorption decreases and water molecules cannot penetrate into previously available pores. At the same time, the diffusion of water from capillaries into the cell wall is ongoing phenomenon (Engelund et al. 2013; Noorolahi et al. 2008).

During the diffusion process, a difference in concentration between the various cellular layers is established. Water migrates from the more concentrated medium towards the less concentrated one. The rate of water absorption depends on the difference between the saturation water content and water content at a given time, which is called the driving force. In other words, moisture diffusion into the wood takes place because of the moisture gradient

between the surface and the centre of the wood specimens. As water absorption proceeds, the MC increases, decreasing the driving force and consequently the absorption rate. The process ceases when the wood attains the FSP. In general, the force which retains the interstitial water molecules is weaker than that exerted on the bound water molecules (Fotsing and Tchagang 2005; Skaar 1954; Stamm 1959). The most significant water uptake reduction was recorded for acetylated specimens, i.e. 70% MC was measured for reference and 44% for acetylated. However, after 720 h of water soaking, the TM_2 , TM_3 , Acet and Mel groups exhibited only a minor MC increase ($\pm 1\text{--}5\%$), whereas the MC of Ref and TM_1 gradually increased and reached maximum after prolonged water soaking as shown in Figure 2B.

3.7 Swelling kinetics

The radial and tangential swelling kinetics of the reference and modified specimens during 48 h of water immersion are shown in Figure 5. A relatively high initial linear-phase swelling rate (LS_r) was found for the reference specimens, while modified specimens exhibited comparatively slow and gradual swelling.

Even though MF resin modified specimens exhibited similar linear phase swelling as the reference during the first few hours, it slowed down gradually afterwards. The linear-phase swelling rate provides interesting information about how the native and modified wood behaved in the initial swelling period of wood-water interaction. However, Čermák et al. (2021) and Nopens et al. (2019) reported that

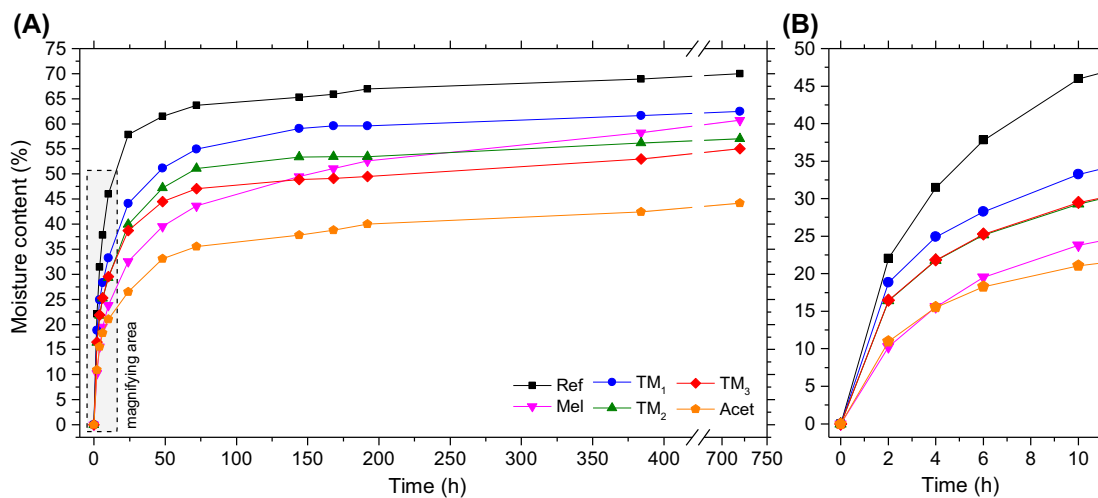


Figure 4: Water uptake of reference and modified specimens during 720 h of water soaking (A), and magnified area of 0–10 h (B) (Ref – untreated beech, TM_1 – thermally modified at 180 °C, TM_2 – thermally modified at 200 °C, TM_3 – thermally modified at 220 °C, Mel – melamine impregnated, Acet – acetylated).

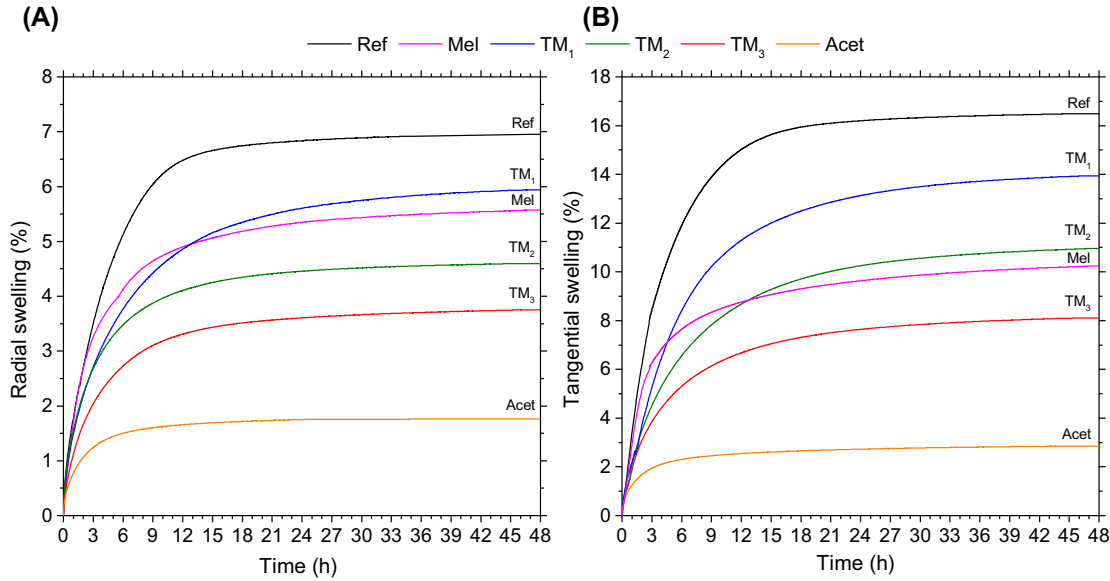


Figure 5: The radial (A) and tangential (B) swelling kinetics of reference and modified beech specimens (Ref – untreated beech, TM_1 – thermally modified at 180 °C, TM_2 – thermally modified at 200 °C, TM_3 – thermally modified at 220 °C, Mel – melamine impregnated, Acet – acetylated).

the linear-phase swelling rate depended on the size of the specimen and therefore it is suggested to relate the observed swelling kinetics of modified wood to that of the reference to produce a linear-phase swelling ratio.

The linear-phase swelling rates and ratios are presented in Table 3. These results may be used to predict the swelling of modified specimens based on the knowledge of swelling kinetics of native beech wood. The decrease in swelling kinetics reflects the reduced ability of modified wood to absorb water molecules (liquid water and water vapour) after acetylation, thermal modification and MF resin impregnation as a result of bulking of the cell wall by bounded acetyl, OH- group blocking and the thermal degradation of the cell wall (Altgen et al. 2020a,b; Čermák et al. 2021; Popescu et al. 2014).

From the linear-phase swelling ratios it can be concluded that wood modification was more significantly pronounced at tangential swelling, which is partly confirmed by Figure 3B, especially for the TM_3 and Acet groups. The maximum radial and tangential swelling

results observed during dynamic swelling analysis are in agreement with previous findings shown in Figure 3B, even though data variability has to be taken into account due to the shorter time of water immersion (48 h) when compared to the water soaking test (over 30 days).

4 Conclusions

The water vapour and liquid water related characteristics of beech wood treated by thermal modification, acetylation and MF resin impregnation were significantly improved. As a result of a significant decrease in the amount of polysaccharide, mainly caused by the degradation of hemicelluloses which are the most thermally labile components of wood, the EMC of thermally modified wood decreased and radial, tangential and volumetric swelling was reduced. The swelling kinetics of thermally modified wood reflect the reduced ability of specimens to absorb water molecules; and the decrease was more noticeable at higher temperatures.

Table 3: The linear-phase swelling rate (LS_i) and ratio for reference and modified wood.

	Linear-phase swelling rate (%/min)						Linear-phase swelling ratio
	Ref	Mel	TM_1	TM_2	TM_3	Acet	
<i>R</i>	0.034	0.032	0.026	0.025	0.018	0.015	10:9.7:7.7:7.4:5.3:4.4
<i>T</i>	0.077	0.070	0.039	0.032	0.030	0.024	10:9.1:5.1:4.2:3.9:3.1

MF resin impregnated specimens exhibited comparable behaviour to those thermally modified at lower temperatures; however, significant changes were found at the higher end of the RH range and after liquid water exposure. Even though MF resin modified specimens exhibited a similar linear phase to the reference during initial swelling, this slowed gradually afterwards. The most significantly pronounced improvement in the water-related properties was found for acetylated wood, where improvement of 50% or more was achieved for all studied wood-water related characteristics. Reported wood modifications also partly contributed to the reduction of the hysteresis effect between adsorption and desorption curves and a decrease of beech wood anisotropy. All studied wood modifications provided a high efficiency against interactions between wood and water, whereas more detailed analysis of MF resin modified wood needs more attention, as heat-curing conditions may have a significant effect on the water-related properties, as reported recently in the scientific literature.

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