Wood Technology/Products

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Chemical changes in thermally modified, acetylated and melamine formaldehyde resin impregnated beech wood

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Abstract: Wood modification (by thermal or chemical treatment) helps to improve the dimensional stability of wood and enhance its resistance to biological agents. Beech wood is non-durable and exposure in exterior settings dramatically shortens its service life. To determine the full potential of beech wood for advanced applications, a better understanding of the chemical changes induced by modification is needed. Two chemical treatments (acetylation and melamine formaldehyde resin impregnation) and three thermal treatments (heating to 180, 200 and 220 °C) were performed on beech wood. The modification effect was examined based on (i) molecular changes in functional groups by Fourier-transform infrared spectroscopy (ATR-FTIR); (ii) extractive content; and (iii) pH changes. Moreover, the explanation of these changes was supported by the FTIR-analysis of isolated main wood components (cellulose, holocellulose and lignin) from the modified wood. The high temperatures applied to samples during thermal modification promoted the deacetylation and degradation of hemicelluloses. Hemicelluloses were targeted also by acetic anhydride and melamine resin, the bonding of which was confirmed by FTIR analysis. The formation of fewer methylene bridges affected the properties of the melamine network. This observation suggests the need to determine optimal curing conditions in future research, to reduce melamine-wood hydrophilicity.

Keywords: acetylation; Fourier-transform infrared spectroscopy (FTIR); hydrophilic extractives; melamine formaldehyde (MF) resin; thermal modification; wood chemistry

1 Introduction

Wood is a lignocellulosic complex whose three main biopolymer components are located in the cell walls: cellulose, hemicelluloses and lignin. The cellulose molecules form long unbranched chains called microfibrils, which are embedded in a matrix composed of short branched chains of hemicelluloses and of amorphous phenolic lignin (Fengel and Wegener 1989). Hemicellulose molecules contain many accessible hydroxyl groups, making them interact easily with sorbed water (Hill 2006). The hygroscopic character of hemicelluloses and, in part, of non-crystalline cellulose, means that the physical and mechanical properties of wood are strongly affected by the moisture content of wood (Engelund et al. 2013; Skaar 1988).

Wood may be modified with the aim of decreasing its hygroscopicity, while improving its dimensional stability (Čermák et al. 2022) and biological durability (López-Gómez et al. 2022; Rowell 2005; Sandberg et al. 2017). A common chemical method, acetylation uses acetic anhydride to esterify accessible hydroxyl groups in the cell wall with the release of acetic acid (Rowell 2005). This reaction causes significant changes in wood at the molecular level which are visible by infrared spectroscopy (Fodor and Hofmann 2024; Gaitán-Alvarez et al. 2020; Mohebby 2008) and also Raman spectroscopy (Digaitis et al. 2021; Ponzecchi et al. 2022). Alternatively, attempts to induce chemical changes are made using

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melamine resins (Altgen et al. 2020a,b; Behr et al. 2018; Gindl et al. 2003; Sultan et al. 2024). Melamine formaldehyde resins (MF) are synthesised by the condensation reaction of melamine molecules with formaldehyde in water (Pizzi 2003). Vacuum-pressure impregnation allows the MF solution to enter the lumens of the wood matrix. A subsequent diffusion phase allows the impregnation solution and the included monomers to enter the cell wall cavities (Gindl et al. 2003; Rapp et al. 1999). The reaction, when carried out at elevated temperature, produces hydrophobic intermediates, the molecular size of which is increased through the presence of methylene and ether bridges (Pizzi 2003), forming irreversible fixation points with the wood structure (Rapp et al. 1999).

During thermal modification, wood is exposed to a temperature higher than 160 °C in an oxygen-depleted environment, such as superheated steam, nitrogen, vacuum or oil (Sandberg et al. 2017). Under these conditions, the chemical structure of the wood changes, making it darker (Bekhta and Niemz 2003; Hill et al. 2021). At temperatures above 100 °C carbohydrates and lignin start to degrade (White and Dietenberger 2001), while water evaporates. During treatment at the highest temperatures, typically in the range 160–240 °C, several reactions can be observed, for example: (i) the generation of degradation products (acetic acid, methanol, formic acid, furfurals, aldehydes and lignin breakdown products); (ii) the hydrolysis of the amorphous polysaccharide content; (iii) an increase in the relative crystalline polysaccharide content; (iv) the loss of acetyl content; (v) an increase in the relative proportion of lignin; and (vi) the loss of methoxy groups (Hill et al. 2021). Demethoxylation and the other cleavage reactions mentioned lead to cross-linking and improvements in the dimensional stability of wood (Tjeerdsma et al. 1998). The effects of thermal modification have been investigated in various softwood and hardwood species on both a laboratory scale and an industrial scale for a few decades (Esteves and Pereira 2009; Hill et al. 2021; Militz and Altgen 2014). The initial cell wall moisture content and thermal treatment by dry or saturated steam affects the kinetics of the degradation profiles of wood components (Hill et al. 2021; Marcon et al. 2021). These authors have noted a lack of available research on combinations of wood species, applied thermal treatment and resulting observations on chemical changes.

The lack of available data comparing different modification methods applied to the same wood species will become more critical with changing climate conditions as species traditionally used in Central Europe (e.g., spruce) will need to be replaced by those that are currently less used or those that become more available (e.g., beech wood). The potential of beech wood for exterior use can only be properly assessed following a comprehensive analysis of its properties based on several aspects. The study by Čermák et al. (2022) examined one such aspect – the behaviour of modified beech exposed to water or a humid environment. The present study aimed to research a second aspect – to locate and explain the changes observed at the molecular level, using the same beech wood batch as in the 2022 study by Čermák et al. Fourier-transform infrared spectroscopy (FTIR) was used to track the impact of the modification of beech wood and of its main biopolymers (cellulose, holocellulose and lignin). The hypothesis was that an explanation of the chemical changes in functional groups when wood is modified could help us understand the changes in physical, mechanical and biological properties.

2 Materials and methods

European beech (*Fagus sylvatica* L.) specimens were taken from 17 trees (average dry density 727 kg/m^3) from the Training Forest Enterprise of Mendel University in Brno (Křtiny, Czech Republic). One group without any treatment served as a reference (Ref), two groups were allocated to chemical modification (acetylation and melamine formaldehyde resin impregnation), and three groups to thermal treatment at three temperatures. The level of wood modification was expressed in terms of weight-percentage gain (WPG) or mass loss (ML).

2.1 Wood modification

2.1.1 Acetylation (Acet)

The acetylation of beech wood specimens was performed using acetic anhydride (Penta Chemicals, Czech Republic) in a vacuum (absolute pressure 10 kPa). The reaction then proceeded at atmospheric pressure at 120 °C, reaching a WPG of 24.9 ± 1.2 % (Čermák et al. 2022).

2.1.2 Melamine formaldehyde resin impregnation (Mel)

Melamine formaldehyde resin (Madurit MW840/75WA) was supplied as an aqueous solution of modified MF resin with 75 wt% of solid content by Prefere Melamines GmbH (Germany) with a pH of 9.7 (measured at 20 °C in 50 % de-ionised water). The beech wood specimens were impregnated with diluted MF resin solution containing 25 % of solids and further processed as reported by Čermák et al. (2022). The WPG reached 19.4 ± 1.9 %.

2.1.3 Thermal modification (TM1, TM2, TM3)

Thermal modification was carried out at three temperatures: 180 °C (TM1), 200 °C (TM2) and 220 °C (TM3) in a superheated steam environment, keeping the specimens at maximum temperature for 3 h. The mass loss was 1.4 ± 0.1, 2.7 ± 0.2 and 8.6 ± 0.6 % for TM1, TM2 and TM3, respectively (Čermák et al. 2022).

2.2 Chemical analysis

2.2.1 ATR-FTIR spectroscopy of modified wood and isolated main wood components

The changes in functional groups of reference and modified wood specimens as well as the isolated main wood components were analysed by means of ATR-FTIR spectroscopy. The specimens were milled (fractions 0.5–1.0 mm) and holocellulose, Seifert's cellulose and lignin were isolated by extraction according to ASTM D 1107-96 (2013) and ASTM D 1106-96 (2013). The hemicellulosic content was calculated by subtracting the dry weight of cellulose from that of holocellulose (Čermák et al. 2022). The measurements were carried out using a Nicolet iS10 FTIR spectrometer equipped with Smart iTR attenuated total reflectance (ATR) (a sampling accessory with a diamond crystal – Thermo Fisher Scientific, Madison WI, USA). The resolution was set at 4 cm^{-1}, 32 scans were recorded for each analysis and the wavenumber range was from 4000 to 650 cm^{-1}. Four analyses were performed on each specimen. The spectra were further evaluated using OMNIC 8.0 software (Thermo Fisher Scientific, Madison WI, USA).

2.2.2 Preparing samples for pH determination

Eight specimens from each group were cut into small pieces using a rasp and those pieces were then powderised with a mixer mill (Retsch MM 400, Germany) at an oscillation frequency of 30 Hz for 150 s. Three grams (with an accuracy of 0.0001 g) of ground specimen were mixed with 30 mL of demineralised water in a beaker. The mixture was shaken on an orbital shaker (Miulab, China) at 130 RPM for 30 min at room temperature (25 ± 2 °C). The pH of the mixture was measured on a calibrated pH meter (XS Instruments, Italy) using a CHS FermPro pH sensor (Chromservis, Czech Republic) with 0.01 accuracy.

2.2.3 Extractive content

Two grams (with an accuracy of 0.0001 g) of powdered, ground specimen were put into a stainless steel extraction cell and topped up to 90 % volume with an inert material. Eight specimens from each tested group were processed with an automated solvent extractor Dionex ASE 350 (Thermo Fisher Scientific, USA) under the following extraction conditions (Table 1) using methanol of HPLC grade (Mikrochem, Slovak Republic) diluted with demineralised water.

At the end of the extracting program the extract volume was topped up to the final volume of 25 mL with the same solvent. The extracts obtained from automated extraction were quantitatively transferred to dry, weighed glass beakers. Each glass reservoir was flushed with a few millilitres of pure methanol to avoid leaving any extractives behind. The beakers were left at room temperature (25 ± 2 °C) for a few days to let the solvent evaporate. Afterwards, the beakers with extractives were fully dried at 103 ± 2 °C, cooled in a desiccator and re-weighted. The final extractive content was calculated from the weight gain of the beakers after solvent evaporation and expressed in mg/g based on the starting wood powder weight used for ASE.

3 Results and discussion

3.1 Chemical changes detected by FTIR

3.1.1 Acetylation

FTIR spectra of acetylated specimens (Figure 1) highlighted the following changes: (i) a decrease in intensity of absorption bands at 3348 cm^{-1} (OH stretching) and (ii) a parallel increase in intensity of absorption bands at 1739 cm^{-1} (C=O stretching in esters), 1369 cm^{-1} (CH in-plane bending in carbohydrates) and 1221 cm^{-1} (C–O stretching in xylan). A

Table 1: Conditions for the automated solvent extraction (ASE) of modified wood.

Extraction cell volume	Solvent	Extraction cycles	Static time	Extraction temperature	Flush volume	Purging with nitrogen
10 mL	50 % (v/v) methanol	2	5 min	50 °C	50 % of the cell volume	90 s

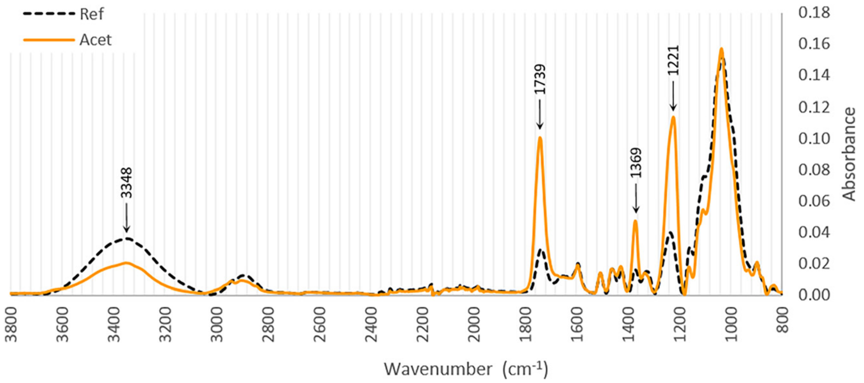

Figure 1: ATR-FTIR spectra of reference (Ref – black dashed line) and acetylated wood specimens (Acet – orange line).

similar response was observed in acetylated tropical hardwood species by Gaitán-Alvarez et al. (2020) who used the last three bands mentioned as an indicator of the degree of acetylation.

Wood acetylation is based on an esterification reaction in which hydroxyl groups in the wood components are replaced by acetyl groups (Rowell et al. 1994). Changes induced by the acetylation process are detectable also in the spectra of isolated main wood components: holocellulose, cellulose and lignin (Supplementary material, Figures S1–S3). In the spectrum of holocellulose, the intensity of the absorption band at 3348 cm^{-1} significantly decreased, while the intensity of absorption bands at 1739, 1369 and 1221 cm^{-1} simultaneously increased (Figure S1). A similar decrease at 3338 cm^{-1} and an increase at 1729 cm^{-1}, as in the case of holocelullose, can be seen in the spectrum of isolated cellulose (Figure S2) as well as in the spectrum of lignin (Figure S3; broader peak tip at around 3423 cm^{-1} and a slight position shift to 1719 cm^{-1} when comparing it with the spectra of cellulose Figure S2). The absorbance differences between the main wood components (compare Figures S1, S2 and S3) show that the components most esterified with acetic anhydride were hemicelluloses. This statement confirms the quantification of isolated main wood components made with the same beech wood batch by Čermák et al. (2022). They found larger amounts of hemicelluloses in acetylated specimens (50.3 relative % vs. 38.5 rel.% for Ref), while the lignin (15.9 rel.% vs. 20.5 rel.% for Ref) and cellulose content was smaller than in reference specimens (31.1 rel.% vs. 38.4 rel.% for Ref). Since the relative percentage was calculated from oven-dried weight, the increase in hemicellulose content must be derived from the substitution of hydroxyl groups in hemicellulosic side chains by acetyl groups. It is important to mention that an acetyl group has 2.5× the molecular weight of a hydroxyl group.

To quantify newly formed acetylated functional groups in wood and isolated components in the frame of FTIR, the intensities (H) of two relevant bands were compared to each other (Table 2). The substitution of hydroxyl groups by acetyl groups was followed by a decrease in the number of –OH groups and a corresponding increase in the number of C=O groups; this is expressed as a decrease of their intensity ratios after acetylation.

A 6.8× decrease was caused by the acetylation reaction in the spectra of wood and a 5.7× decrease in holocellulose, while in isolated cellulose and lignin the changes were smaller and quite similar to each other (2.9× and 2.2×, respectively). It should be noted that the absorption band at

Table 2: Absorption changes of main relevant bands (hydroxyl and carbonyl groups) induced by acetylation.

Type	–OH group Wavenumber (cm^{-1})	C=O group Wavenumber (cm^{-1})	$H_{(-OH)}/H_{(C=O)}$	Absorption change (–OH) after acetylation
Ref-wood	3348	1736	1.30	6.8× decrease
Acet-wood	3349	1739	0.19	
Ref-holocellulose	3340	1732	1.32	5.7× decrease
Acet-holocellulose	3348	1739	0.23	
Ref-cellulose	3336	1725	11.11	2.9× decrease
Acet-cellulose	3338	1729	3.89	
Ref-lignin	3423	1718	2.71	2.2× decrease
Acet-lignin	3423	1719	1.21	

1725 cm^{-1} in the FTIR spectrum of cellulose isolated from reference specimens has a minimum height; according to Kubovský et al. (2020) it is associated with the hemicellulose complex. Rowell et al. (1994) investigated the reactivity of isolated wood polymers with acetic anhydride. Industrial kraft-lignin was shown to be the most reactive, with hemicelluloses second, while cellulose did not react at all (within the 4 h reaction time). The tendency changed slightly after 1 h when the acetyl content in hemicelulloses overtook that in lignin (i.e., hemicelulloses gained up to 30 % of acetyl content). Whole pine wood produced a similar trend to isolated lignin, with a maximum of 18 % acetyl content after 4 h. The authors explain the slower rate in the case of whole wood by the diffusion (rate) problem of getting the chemical into the cell. Since lignin creates lignin-carbohydrate complexes (Rowell et al. 2012), there is less opportunity to react directly with acetic anhydride due to steric hindrance. Acetylated lignin can also lose acetyl groups in the process of isolation from modified wood samples. For these reasons absorbance change after acetylation was not very significant in lignin in the present study. However, due to thermal effects during the acetylation process, the exposure of wood to a higher temperature for some time cannot be excluded. Apart from the substitution mentioned, other reactions by increased treatment temperature could also have contributed to absorption changes of selected bands to an unknown extent.

3.1.2 Melamine resin impregnation

In the fingerprint region of the spectra of wood specimens impregnated with melamine formaldehyde resin, absorption changes at the following wavenumbers were observed: 1736, 1558, 1462, 1335, 1232, 1030 and 811 cm^{-1} (Figure 2). Three of these are characteristic absorption regions of the melamine molecule: (1) in the region between 1650 and 1500 cm^{-1}; (2) at 1462; and (3) at 811 cm^{-1} (Huang et al. 2021; Seidl et al. 2021; Wang et al. 2012). These bands belong to a triazine, which is composed of three nitrogen atoms and three carbon atoms in a six-membered ring. The band at 1558 cm^{-1} corresponds to the stretching vibration of C=N bonds in the triazine ring (Merline et al. 2013; Seidl et al. 2021).

The spectra of MF modified wood (Figure 2) and holocellulose (Figure S4) confirmed a decrease in the absorption bands of C=O groups at 1736 and 1232 cm^{-1}. This decrease points to the extinction of C=O and C–O bonds in hemicelluloses. Because no significant changes in cellulosic (Figure S5) or lignin spectra (Figure S6) were observed, it can be concluded that the melamine molecule might be attracted by hemicelluloses. This assertion is confirmed by comparative spectra, where the line of MF-modified wood closely matches that of isolated holocellulose (Figure 3; blue and brown lines). Hemicellulosic macromolecules are characterised by shorter branched chains and a less ordered structure than cellulosic macromolecules, which creates more favourable spatial conditions for melamine to enter and bond.

The curing parameters of melamine resin play an important role in its final properties and distribution at the cellular level. Altgen et al. (2020a,b) reported different MF resin depositions in the wood cell lumen when applied using dry and wet curing (resulting in resin film and resin droplets, respectively) without exceeding a temperature of 103 °C. The effect of curing temperature, duration and relative humidity on the final degree of conversion of the MF resin was examined by Behr et al. (2018) by means of differential scanning calorimetry (DSC). Better fixation of the resin was achieved at 105 °C and higher relative humidity; however, the optimal temperature for complete resin curing based on DSC was reported as above 110 °C in their study. The highest curing temperature in the present study was 103 °C. Depending on the temperature applied, a flexible network with mainly ether bridges but less cross-linking (more free methylol functional groups) (Weiss et al. 2020) could have been formed. Increased absorption at about 1355 cm^{-1} is a

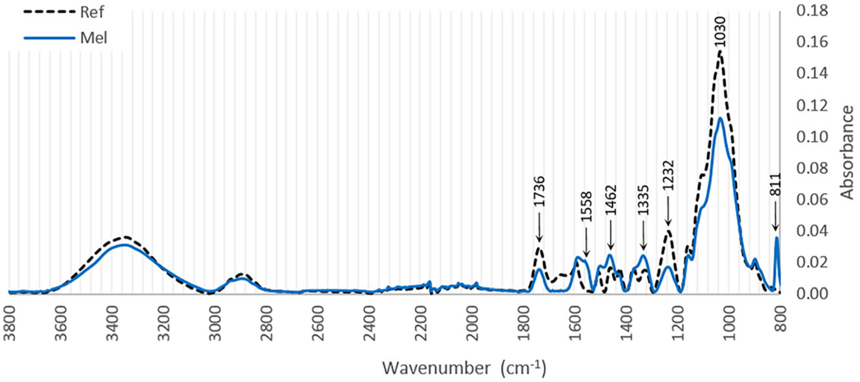

Figure 2: ATR-FTIR spectra of reference (Ref – black dashed line) and melamine formaldehyde resin modified wood specimens (Mel – blue line).

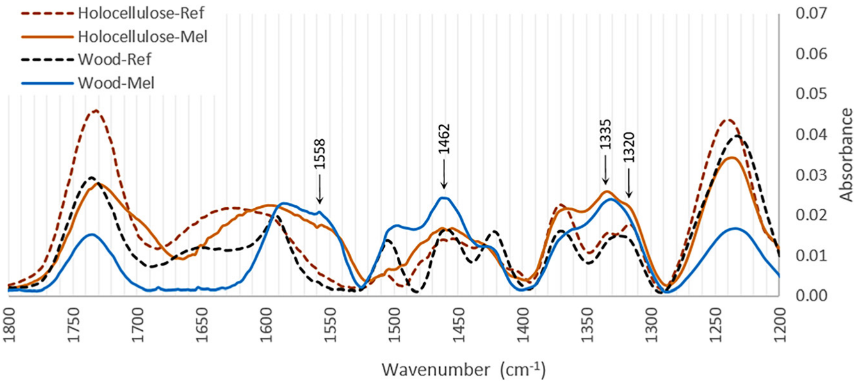

Figure 3: Comparison ATR-FTIR spectra (region 1800–1200 cm^{-1}) of holocellulose isolated from specimens modified with melamine resin (brown line) and holocellulose from reference wood specimens (brown dashed line); melamine resin modified wood (blue line) and reference wood spectra (black dashed line).

sign of the presence of more methylol moieties, which are formed at lower curing temperatures, while their conversion to methylene ether or methylene bridges would be seen as a shift to around 1320 cm^{-1} (Weiss et al. 2019). This shift is visible only slightly in the holocellulosic spectrum (Figure 3, see arrows). Weiss et al. (2020) investigated the main melamine resin spectral components *in situ* during curing: methylol-rich, ether-rich and methylene-rich "network components", whose amounts vary in the curing process. Based on their investigation, the temperature range applied in this study favoured the formation of ether bridges over methylene bridges.

The type and quantity of linkages created during curing significantly affect the hydrolytical stability of the resin (Weiss et al. 2021). At lower temperatures (below 120 °C) MF resin shows less conversion and lower resistance to acidic hydrolysis (i.e., a higher level of free formaldehyde content) (Weiss et al. 2021). This is in accordance with the observation of Čermák et al. (2022), using the same beech wood batch as was used in the present study, who detected a slightly decreased level of cellulose being possibly hydrolysed by formaldehyde present in MF modified beech.

3.1.3 Thermal modification

Figure 4 shows the FTIR spectra of reference and thermally modified wood specimens. During thermal treatment several processes take place in wood simultaneously with different effects on the intensity of the absorption band between 1780 and 1670 cm^{-1} (Kačík et al. 2006; Windeisen et al. 2009). While an increase in its intensity can be caused by the opening of the glucopyranose ring, by the formation of new carbonyl and carboxyl groups or by the cleavage of β-alkyl-aryl ether bonds in lignin, conversely, a decrease in its intensity may be linked either to (a) lignin condensation reactions; (b) the deacetylation of hemicelluloses; or (c) the decomposition of compounds containing C=O bonds (e.g., aldehydes, carboxylic acids and their esters). In order to evaluate which of these processes dominates and which of the main wood components are responsible for this change of that absorption band, FTIR analysis of isolated main wood components was also carried out.

In the FTIR spectra of wood mainly at a temperature of 220 °C (TM3) a decrease in the intensity of absorption bands at 1736 and 1233 cm^{-1} was observed. The first of these is attributed to C=O carbonyl groups and the second is assigned to C–O or O=C–O groups of acetylated xylan and uronic acids (Bhagia et al. 2022; Windeisen et al. 2007). The intensities of both peaks also markedly decreased in holocellulose thermally modified at 200 and 220 °C (TM2 and TM3) (Figure 5, whole spectrum Figure S7). In contrast, in the case of cellulose the intensity at 1725 cm^{-1} reached a maximum when treatment was at 220 °C (Figure 6, whole spectrum Figure S8). This may be the result of oxidation reactions induced by heat treatment. However, in the spectrum of cellulose, the intensity of the absorption band of C=O is much lower than in the spectrum of holocellulose. Based on the above, it can be concluded that a drop in the intensity of bands attributed to C=O in holocellulose is caused by the deacetylation and degradation of hemicelluloses. The process begins with the partial degradation of long hemicellulose chains into shorter ones and then follows with their decomposition through monosaccharides to volatile products (Hill 2006).

With increasing modification temperature, the intensity of the absorption band of carbonyl groups at 1718 cm^{-1} in lignin increases, while the peak maximum moves to lower wavenumbers (1702 cm^{-1} at 220 °C) (Figure S9). The formation of new C=O functional groups and the cleavage of β-alkyl-aryl ether bonds in lignin can be explained in this way, as suggested in the case of similar thermal treatment of oak wood by Kubovský et al. (2020). Additionally, intensity at 1216 cm^{-1} goes along with temperature that might mean generation of new C–O or C=O bonds via oxidation reactions, which naturally take part in thermally modified wood.

From a comparison of changes in the spectra of wood, holocellulose, cellulose and lignin (Figure 4 and Figures S7–S9),

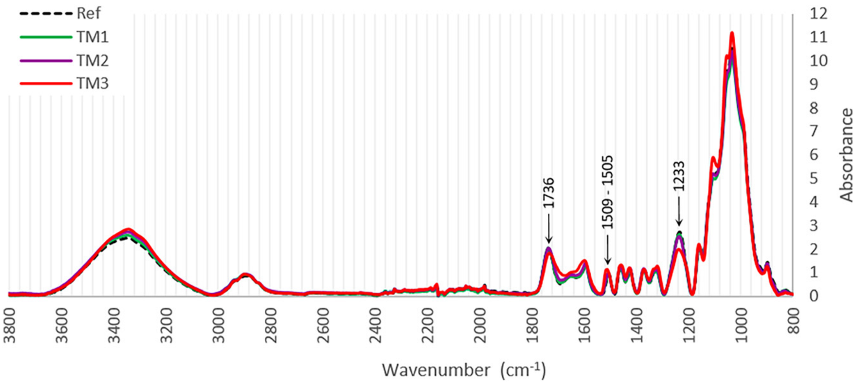

Figure 4: ATR-FTIR spectra of reference (Ref – black dashed line) and thermally modified wood specimens at 180 °C (TM1 – green line), 200 °C (TM2 – violet line) and 220 °C (TM3 – red line); all spectra normalised at 1370 cm^{-1}.

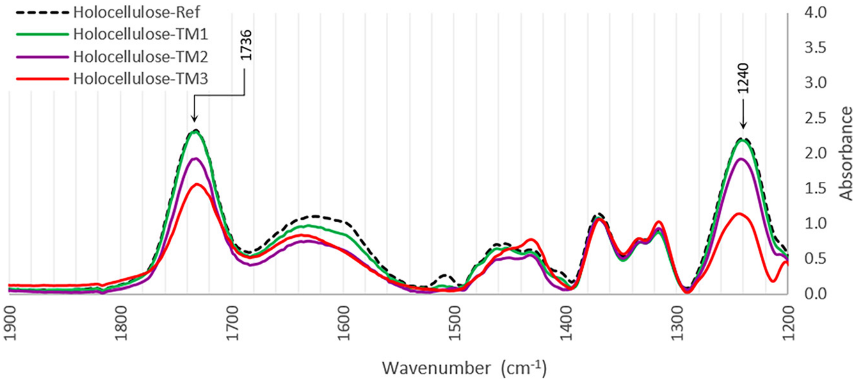

Figure 5: Comparison of ATR-FTIR spectra (region 1900–1200 cm^{-1}) of holocellulose isolated from reference (Ref – black dashed line) and thermally modified wood specimens at 180 °C (TM1 – green line), 200 °C (TM2 – violet line) and 220 °C (TM3 – red line); all spectra normalised at 1370 cm^{-1}.

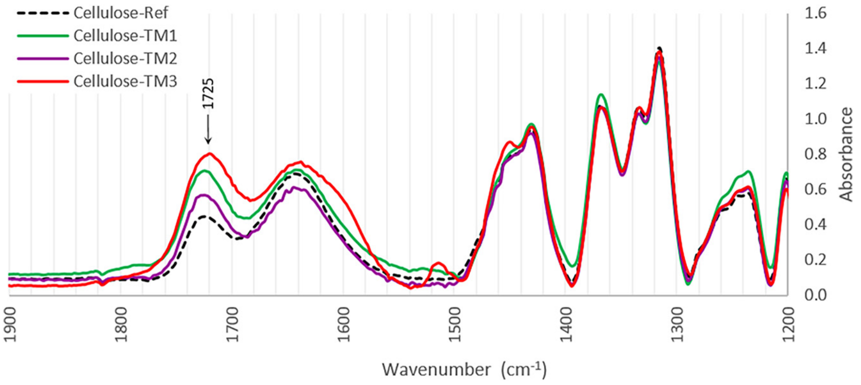

Figure 6: Comparison of ATR-FTIR spectra (region 1900–1200 cm^{-1}) of cellulose isolated from reference (Ref – black dashed line) and thermally modified wood specimens at 180 °C (TM1 – green line), 200 °C (TM2 – violet line) and 220 °C (TM3 – red line); all spectra normalised at 1370 cm^{-1}.

it can be concluded that the biggest impact on intensity at 1736 cm^{-1} is made by the deacetylation and degradation of hemicelluloses (Figure 5 and Figure S7). This peak can be assigned to xylan (Wang et al. 2022). It should be emphasised that heat caused changes in the intensity of the absorption band of carbonyl or carboxyl groups according to the treatment conditions as well as depending on the wood species (Geffert et al. 2019b, 2020; Özgenç et al. 2017). Similar decreasing intensity with increasing treatment temperature in holocellulosic spectra was also observed by Tjeerdsma and Militz (2005) in beech and pine wood.

Further changes in the FTIR spectra of reference and thermally modified wood specimens can also be observed (Figure 4). In the reference wood the characteristic peak for aromatic rings in the lignin macromolecule at 1505 cm^{-1} was observed. The maximum of this peak shifts with increased treatment temperature to a higher wavenumber of 1509 cm^{-1}. In spectra of lignin (Figure S9) this shift is noticeable from 1500 to 1509 cm^{-1}. According to Faix (1991), the shifting of peak maximum to the higher wavenumber can be due to a decrease in the methoxyl groups in the lignin macromolecule or to a loss of syringyl units. Because the syringyl monomers are less condensed by C–C bonds than guaiacyl monomers, they are more liable to be released by thermal degradation (Faix et al. 1990).

3.2 Extractive content and pH

Wood extractives are a mixture of chemical compounds with diverse functional groups and structures, so wood modification affects their structure differently. The appearance of wood extractives in FTIR spectra often overlaps with the vibration responses of the main wood components. Additionally, their significantly lower content in wood than of the main components (i.e., cellulose, hemicelluloses and lignin) makes their traceability more difficult. Therefore changes in extractive content and the pH effects of modification were tracked (Figure 7).

Reference beech contained 2.05 % (with standard deviation of 0.22 %) of hydrophilic extractives. Using the same solvent (50 % methanol) other studies have reported similar values in the sapwood (2.41 %) and mature wood (2.19 %) of the same wood species (Sablík et al. 2016; Výbohová and Oberle 2023). Beech wood is known for its low extractives content of only 3–5% (Wagenführ 1996). Based on the study by Vek et al. (2015) on methanolic extractives of beech wood, the hydrophilic spectrum includes mono- and oligosaccharides, sugar acids, sugar alcohols, carboxylic acids, simple phenols and flavonoids. Wood extractives belong to the most temperature-sensitive wood constituents due to their low boiling point (Jones and Sandberg 2020). Therefore, the largest polar extractive content was achieved after thermal modification at 220 °C (TM3) with 4.26 (0.57) %, followed by 200 °C (TM2) with 3.93 (0.41) % and 180 °C (TM1) with 2.97 (0.19) %. Some wood extractives naturally present are degraded at higher temperatures, whereas new ones are simultaneously formed from degrading wood polymers (Kačík et al. 2022). While the concentration of some extractives decreases with increasing temperature from 170 to 200 °C (robinetinidin, dihydrorobinetin, phenol), other extractives increase (furfural, robinetin, syringic acid, xyloses) (Sablík et al. 2018). Although phenolic compounds mentioned in the last literature source were detected in black locust heartwood, the extraction solvent was the same and temperature range very similar to the present study.

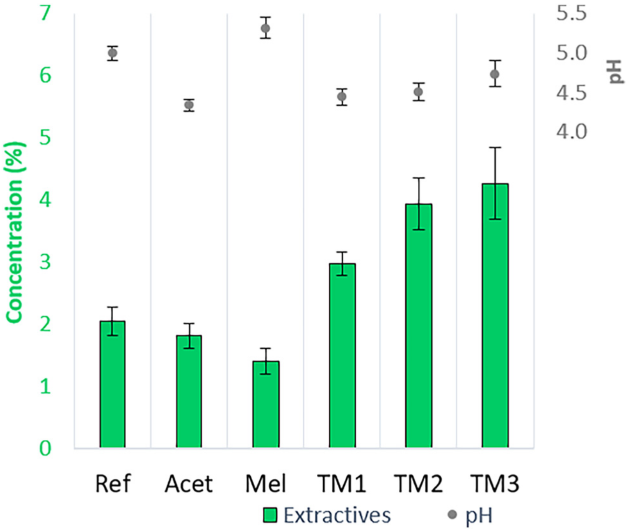

Figure 7: pH (grey) and extractive content (green, %) present in water-methanolic extract from Ref – reference beech wood and modified wood: Acet – acetylated wood; Mel – wood impregnated with melamine resin; TM1 – wood thermally modified at 180 °C; TM2 – wood thermally modified at 200 °C; TM3 – wood thermally modified at 220 °C; error bars represent standard deviation.

A slightly lowered extractive content was observed in the cases of acetylated (1.82 ± 0.20 %) and melaminated (1.41 ± 0.21 %) specimens. There are two possible reasons for this observation: (1) hydrophilic extractives are leached out during the modification process (specimens were soaked during those two modifications); (2) (the remaining) extractives are modified; thus, as hydrophobic compounds, they cannot be extracted and work as a blockade (Moghaddam et al. 2016) against solvent molecules entering.

Chemical modification altered the pH of beech wood slightly (Figure 7, grey). The reference wood had a pH of 4.99 (standard deviation, SD: 0.09), acetylation decreased the value to 4.34 (SD: 0.07). The pH plays a role in reactivity and might induce the hydrolysis of wooden polymers (Fengel and Wegener 1989). Therefore, the elimination of splitting acetic acid being formed during the acetylation process is desired. A similar pH reduction resulting from the residual acid after wood acetylation was found by Fodor et al. (2018). In the case of Mel wood the alkaline environment increased the pH to 5.32 (SD: 0.13).

Thermal modification slightly decreased the pH in the following order: TM3 > TM2 > TM1 (i.e., 4.74 > 4.51 > 4.45). An increase in the pH of heat treated beech wood has been observed by other researchers (Gérardin et al. 2007; Hofmann et al. 2013). Heating wood releases organic acids, such as acetic acid, formed mainly from thermally labile acetyl groups in hemicelluloses (Hill 2006). The elimination of present volatile acids could explain the positive correlation between the pH of the TM series and increasing temperature. The concentration of acetic acid released from modified wood has been investigated in several studies (Fodor et al. 2018; Hill et al. 2021; Hofmann et al. 2013; Sundqvist et al. 2006; Xu et al. 2019). However, the pH of heat-treated wood varies with temperature-duration settings as well as with wood species, why the tendency might be the opposite (Jirouš-Rajković and Miklečić 2019).

The measurement procedure also affects the final pH, which can be measured directly from sawdust or indirectly by cold or hot water extraction (Geffert et al. 2019a). Direct sawdust measurement of pH in maple and beech has shown a greater decrease in value after 12 h of thermal treatment (from 5.1 to 3.4 for beech and from 5.0 to 3.3 for maple, respectively) (Dzurenda and Dudiak 2021; Dzurenda et al. 2020), even at lower treatment temperatures than those used in the present study. Since pH is dependent on the concentration, the values for cold water wood extracts in this case must have been affected by dilution. This resulted in relatively smaller variation between the modification groups as compared with direct sawdust measurement.

4 Conclusions

This study presents chemical changes in beech wood induced by three different modification methods. While two of these use added chemicals (acetic anhydride and melamine-formaldehyde resin), the third uses heat to change the properties of beech wood. The ATR-FTIR technique allows modified wood to be analysed without difficult sample preparations. However, the complexity of the wood composition leads to overlaps of the absorption bands in the spectra and to issues with identifying the type and extent of the modifying effects on the individual components. That is why ATR-FTIR analysis was applied to the isolated wood components (i.e., holocellulose, cellulose and lignin) from modified wood. Their spectra confirmed the main changes and explained the location of the interactions happening within the beech wood.

The main observations can be listed: (1) hemicelluloses were targeted by the substitution of OH-groups with C=O groups during acetylation to the greatest extent; (2) the curing temperature of MF resin favoured the formation of ether bridges over methylene bridges; (3) the partial degradation of hemicelluloses, oxidation reactions and a loss of methoxyl groups in lignin were observed following thermal treatment; the effect was greater with increasing treatment temperature; (4) pH was slightly affected by all modifications; and (5) hydrophilic wood extractive content was decreased by chemical modification (leaching and changed chemistry by treatment) and increased by thermal modification due to thermal degradation.

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