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Change of chemical composition and FTIR spectra of Turkey oak and Pannonia poplar wood after acetylation

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ABSTRACT

In this research, acetylation was applied under industrial conditions to improve the properties of Turkey oak and Pannonia poplar wood. Both species are potential "climate winners" in Hungary, yet they are currently underused due their low durability and poor dimensional stability. Acetylation modification process may be a suitable method to improve their properties. In order to verify the effectiveness of the process, comparative chemical analyses (cellulose, hemicelluloses, lignin, extractives, and ash, buffering capacity and pH) of the untreated and acetylated heartwood and sapwood was carried out for both species for the first time. Diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy was also used to support the evaluation of the chemical analyses. The Weight Percent Gain was 11.54% for poplar and 0.94% for Turkey oak, indicating poor treatment efficiency for the latter. The cellulose, hemicellulose and lignin content changed significantly in poplar, having the highest change (+81%) by acetylating the hemicelluloses. Only the alpha-cellulose content decreased significantly in Turkey oak, presumably due to the degradation of the non-crystalline part of cellulose. Acetylation may improve the resistance of Pannonia poplar against moisture, weather, decay and wood-boring insects, but the process parameters need to be optimized in order to prevent degradation and discoloration in poplar. Turkey oak was found to be less suitable for acetylation due to its low permeability and tendency to crack.

INTRODUCTION

A significant part of Hungary's wood production is made up of Pannonia poplar (*Populus* × *euramericana* cv. Pannónia) (1,306,000 m^3) and Turkey oak (*Quercus cerris* L.) (801,000 m^3) (HCSO 2021). However, due to their unfavorable properties (e.g. low natural durability, poor dimensional stability) they are mainly used as firewood and in the wood-based panel production and packaging industry. One possible way of improving wood quality is the application of modification methods, which have proven their efficiency and potential in the last decades (Mai and Militz 2023).

Poplar species, specifically Pannonia poplar, are hard to dry and modify because the freshly-cut heartwood (ripewood) has higher moisture content than its sapwood. Also, more tyloses and extractive substances form in older trees which enable false heartwood formation and discoloration, which impairs their quality and value (Komán 2012). Because of this phenomenon, hybrid poplar species such as Pannonia poplar are mainly felled at about 15 years, especially those that are intended for veneer production. Usually its sapwood, heartwood and juvenile wood are hard to differentiate, especially after drying (Németh et al. 2013). In Pannonia poplar, the borderline of sapwood and heartwood is faintly visible (Horváth and Schantl 2017). The difference between the physical properties of sapwood and heartwood is not significant (Molnár et al. 2002). There is no visible distinction between earlywood and latewood within the annual rings. The annual ring width varies between 2-30 mm (Molnár and Bariska 2002). Pannonia poplar has higher density than most poplar species (> 401 kg/m^3), which makes it suitable for structural applications and the furniture industry (Mirzaei et al. 2017).

The color of Pannonia poplar was successfully modified to a darker tone by steaming (Banadics and Tolvaj 2019; Banadics et al. 2022), thermal modification (Molnár et al. 2006) and heat-treatment in different oils (Bak and Németh 2012; Bak et al. 2012). Heat treating it at 180°C and 200°C improved its durability, dimensional stability, and compression strength (Molnár et al. 2006; Horváth 2008).

Similar results were found for oil-heat-treated Pannonia poplar (Bak and Németh 2012; Bak et al. 2012). On the other hand, its color was not stable against weathering (Bak et al. 2012). Promising results were found with the thermo-mechanical densification of Pannonia poplar with increased mechanical properties (Ábrahám et al. 2010).
There are several publications regarding the chemical modification and impregnation modification of poplar species – these processes could be applied to Pannonia hybrid as well, in order to improve its physical and mechanical properties, and to modify its color.
Turkey oak logs grown in optimal sites can have a diameter of 30 – 50 cm and length of 12 – 15 m, usually smaller than sessile or pedunculate oak species. This is due to their short lifespan: they are attacked by diseases and grow slowly after an age of 60 – 80 years. They are usually harvested at this age. If they grow in closed stands, they usually develop straight, cylindrical trunks, which is more favorable for industry. They have wide, light-grey sapwood and dark, reddish-brownish heartwood, often having a false heart. The wood is prone to have frost ribs or cracks, ring shakes, crooks or springs, tapered trunk, warping, splitting, and knots. Due to its inhomogeneous annual ring structure and density, its high shrinkage anisotropy, the stress results in ring shakes and cracks; their wood is less suitable for sawlog production (Molnár and Bariska 2002). Its usage is also hindered by having low durability against fungi species and wood-boring insects (Bajraktari et al. 2018). Due to its disadvantages and high calorific value (11,592 MJ/m^3 for air-dry wood), it is mainly used as firewood. Turkey oak has somewhat higher density than that of other oaks (720-810 kg/m^3) so it can be used for similar purposes, except for the production of barrels and outdoor, durable wood products. Its low extractive content, and low amount of polyphenols are connected to its low durability (Lavisci et al. 1991; Molnár and Bariska 2002; Bajraktari et al. 2018).
The modification of Turkey oak was less studied in scientific literature. Hydrothermal (steaming) and thermal treatments have been carried out with promising results, like reduced equilibrium moisture content, anti-swelling efficiency and homogenized color (Tolvaj and Molnár 2006; Todaro et al. 2013, 2018; Cetera et al. 2016, 2019). Steaming enables the homogenization and darkening of wood color, but compared to thermal modification it is less suitable for durability enhancement. There was no report found on the acetylation of Turkey oak. If high dimensional stability and durability are achieved, it could be used for glulam production (Uzelac Glavinić et al. 2023). The gluing difficulties of Turkey oak are the same as of other oaks: too high variation in density and permeability between earlywood and latewood, which hinders an adequate adhesive bond (Lavisci et al. 1991). Chemical surface modification could enable better interaction between the surface of oakwood and polyurethane (PUR) adhesives (Sahula et al. 2023).
In the present work the acetylation modification of Pannonia poplar and Turkey oak has been carried out for the first time using a semi-industrial process by investigating both sapwood and heartwood. The main chemical constituents (cellulose, hemicelluloses, and lignin) as well as extractive content, ash content, buffering capacity and pH were measured and compared in untreated and acetylated wood. Diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy supported the evaluation of the chemical analysis. The results contribute to the understanding of the chemical changes taking place during the acetylation of Pannonia poplar and Turkey oak and provide data for the elaboration of techniques for the acetylation and better utilization of these currently underused wood species.

MATERIALS AND METHODS

Wood material

One Pannonia poplar log was obtained from Újrónafő 11/G and one from Győr 540/B (Hungary), with breast height diameter of 21.3 cm and 39.5 cm, from 22 and 24 year-old trees, respectively. The logs were about 150 cm long. The density of the sapwood was 444 and 427 kg/m^3 for the poplar from Győr and Újrónafő, respectively (Horváth and Csiha 2022). The heartwood density was 470 and 413 kg/m^3 for the poplar from Győr and Újrónafő, respectively.
One Turkey oak log was from the mountains of Sopron forestry (Hungary), with breast height diameter of 30 cm and length of about 150 cm.

Acetylation

The logs were sawn into 30 and 50 cm thick boards. There were 10 pcs of thinner and 4 pcs of thicker Pannonia poplar boards, and 7 pcs of thinner and 6 pcs of thicker Turkey oak boards. Half of them were acetylated at Accsys Technologies (Arnhem, the Netherlands) under semi-industrial conditions (Girotra 2013). The process was carried out with batches of Radiata pine with corresponding thickness and process parameters. The WPG was determined at Accsys Technologies, where it was calculated by dividing the density change after acetylation by the initial oven-dry density of the boards.

Preparation of particles for chemical analysis

Samples (about 100-200 g) were ground in a hammer mill and sieved. The 0.2-0.63 mm sieve fraction was taken for chemical analyses. All measurements were run in triplicates and the results were given based on dry wood mass. The particles were stored at 20°C 65% relative humidity until reaching constant mass.

Measurement of wood polymers, total extractive and ash content

For determining the holocellulose content, 2.5 g of wood particles were transferred into an Erlenmeyer flask. Subsequently, 80 mL of hot distilled water, 0.5 mL of acetic acid (96%), and 1 g of sodium chlorite were added. The mixture was heated in a water bath at 70 °C for 1 h. After each succeeding hour, portions of 0.5 mL acetic acid and 1 g sodium chlorite were added by shaking. This process was repeated 7 times. After six cycles, the samples were left in the water bath overnight. At the end of 24 h of reaction, samples were cooled and filtered on a G2 glass funnel filter and the holocellulose was washed with 10 mL acetone and water until the yellow color was removed (Rowell 2012). The prepared holocellulose was dried at 105 °C and then weighed.

Then the alpha-cellulose content was determined by transferring the previously prepared holocellulose into a 250-mL glass beaker, and adding 10 mL of 17.5% NaOH solution. At 5-min intervals, portions of 5 mL NaOH solution were added until the holocellulose was fully covered with solution. The reaction time was 1 h. The α-cellulose was filtered on a G2 porosity glass funnel filter and washed with 5% NaOH, acetic acid, and water. This washing cycle was repeated twice. The prepared α-cellulose was dried at 105 °C and then weighed (Rowell 2012). Similar methods were used in recent articles (Ghavidel et al. 2020b, a; Amato et al. 2021).

The hemicellulose content was calculated by the subtraction of the alpha-cellulose content from the holocellulose content.

The acid-insoluble lignin content was determined using Klason's method (TAPPI standard T 222).

Two solvent-systems were used to assess its extractive content: cyclohexane:ethanol 50:50 (v/v) and methanol:water 50:50 (v/v). 0.4 g sample was mixed with 40 ml solvent in a 100 ml glass beaker. The beaker was covered with aluminium foil to avoid evaporation. Samples were placed in an ultrasonic bath (Elma Transsonic T570, Elma Schmidbauer GmbH, Singen, Germany) and extracted for 60 min. Extract solutions were filtered through filter paper and 10 ml of the clean solutions were evaporated to dryness at room temperature; then the remaining solids were weighed. Results for the total extractive content are given as the sum of the values obtained by the two solvent systems.

Determination of pH and buffering capacity

In order to measure the pH and buffering capacity, extraction was carried out as follows: 2.5 g of wood was extracted with 50 ml water for 24 h in a closed beaker. The solutions were filtered and the particles were washed with water into a conical flask to a final volume of 100 ml.

The pH of the remaining part of the aqueous extract solution was determined by a Hanna HI 2550 pH meter, which corresponded to the pH of the wood. The buffering capacity of the solution was measured by titration using 0.02 M NaOH to pH=7.00.

Equillibrium moisture content

An Ohaus MB 23 moisture analyzer (Ohaus Corporation, Parsippany, Unites States) was used to determine the equilibrium moisture content of the samples.

FTIR analysis

The tangential surface was analyzed and samples of 5 mm thickness × 10 mm width × 30 mm length (t × w × l) were used for diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy with a JASCO FT/IR-6300 spectrophotometer and Spectra Manager program. First, the background spectrum was obtained against an aluminum plate in order to see the contribution of the instrument and environment to the spectrum.

These effects were removed from the samples' spectrum by making a ratio of the sample single beam spectrum to the background spectrum. Secondly, the spectrometer did 50 scans of each sample. There were 8 untreated and 48 acetylated Pannonia poplar samples, and 10 untreated and 44 acetylated Turkey oak samples. After measurement, the spectra were smoothed with 15 points convolution. A two-point base line correction was made by setting the lowest point between 3800 cm^{-1} and 1900 cm^{-1} to a zero absorbance. The intensity of the infrared peaks was converted to Kubelka-Munk (K-M) units for quantitative analysis. The chemical changes in wood were evaluated observing the difference of the spectra of untreated samples subtracted from the spectra of acetylated samples. Here, the absorption increase was represented by positive band while an absorption decrease was represented by a negative band. The band assignments were made using the difference of the two spectra.

Statistical analysis

All wet-chemical analyses have been conducted in duplicates. Statistical analysis was performed using the Dell Statistica software (version 13, Dell Inc., Round Rock, TX, USA). Factorial analyses of variances (ANOVA) combined with the Tukey's HSD test and Levene's test for homogeneity of variances were conducted, and the differences were considered significant at $p < 0.05$.

RESULTS AND DISCUSSION

Although the sapwood of Pannonia poplar seemed to be successfully acetylated, degradation and discoloration was visible in the sapwood-heartwood transition zone. The density of Pannonia poplar increased from 453 to 486 kg/m^3 (Újrónafő), and from 476 to 489 kg/m^3 (Győr). The (indicative) WPG was 11.72 % and 11.36 % for poplar from Újrónafő and Győr, respectively.

After acetylation, the quality of Turkey oak wood was impaired by a significant amount of cracks. The density of Turkey oak decreased from 796 to 757 kg/m^3. The (indicative) WPG was low, only 0.94 %.

Table 1 and Table 2 lists the chemical composition, pH and buffering capacity of Pannonia poplar and Turkey oak, respectively. Table 3 lists the most important wavenumbers for both species after acetylation which are assigned in their difference spectra in Figure 1. The band numbers are referred in brackets in the text. Structural changes in the wood were evaluated according to these results and compared to the relevant literature.

The moisture content of Pannonia poplar and Turkey oak decreased significantly by 20-58 % due to the incorporation of acetyl groups in their cell walls. Positive and negative peaks were observed between 3200-3600cm^{-1} (1) on the spectra of both species, which are the signs of OH group rearrangement in the wood structure. Their lower moisture content indicates that the wood of Pannonia poplar and Turkey oak absorbs less moisture after acetylation, and thus the material swells less in humid or wet conditions, and its dimensional stability is higher when exposed to changing climatic conditions. The degraded part of acetylated poplar had a little higher moisture content than its sapwood and heartwood, which may indicate lower acetyl content. Acetylation reduced the moisture content of Turkey oak less than Pannonia poplar, probably due to its lower permeability and higher density. The difference between the moisture content of sapwood and heartwood evened after acetylation.

The holocellulose content is made up of the cellulose and hemicellulose content of the wood material. In Pannonia poplar, the hemicellulose content increased significantly after acetylation from 33.52 % to 60.68 % for sapwood, and from 33.81 to 58.08 % for heartwood. For Turkey oak, where the hemicellulose content increased from 29.66 % to 44.95 % for sapwood, and from 31.73 % to 38.85 % for heartwood. The increase was higher in sapwood than heartwood, for both wood species.

During acetylation, some of the hydroxyl groups are substituted by acetyl groups, which increase the weight of the polymer. As the hemicellulose fraction has proportionally the most hydroxyl groups, its weight increased after acetylation. Higher absorption of carbonyl groups in xylan (2), symmetric C-H deformation in hemicelluloses (3), and absorption of C-O stretching in xylan (4) confirm this finding on the differential spectrum. The increment at these wavenumbers after acetylation was found by other

researchers as well (Stefke et al. 2008), e.g. for spruce (Schwanninger et al. 2011), for Scots pine and beech (Mohebby 2008), and for European hornbeam (Fodor et al. 2018; Bari et al. 2019).

Table 1: Chemical composition, pH and buffering capacity of untreated and acetylated Pannonia poplar, showing results for sapwood (S), heartwood (H) and degraded part separately. Average values are presented with standard deviation in brackets. Different superscript letters in a row denote significant difference at p<0.05 level

Chemical composition	Untreated		Acetylated		Difference (pp)		Percent change (%)		Acetylated
	S	H	S	H	S	H	S	H	Degraded
Moisture content [%]	5.9	5.9	2.5	2.5	- 3.40	- 3.40	- 58	- 58	2.8
Holocellulose content [%]	77.59^{a} (2.65)	78.47^{a} (0.34)	91.55^{b} (1.03)	90.26^{b} (4.26)	+ 13.96	+ 11.79	+ 18	+ 15	84.36^{ab} (2.60)
Hemicellulose content [%]	33.52^{a} (3.64)	33.81^{a} (1.45)	60.68^{b} (0.19)	58.08^{b} (0.59)	+ 27.16	+ 24.27	+ 81	+ 72	54.44^{b} (2.99)
Alpha-Cellulose content [%]	44.07^{bc} (0.98)	44.66^{c} (1.11)	30.87^{a} (0.84)	32.19^{ab} (3.67)	- 13.20	- 12.47	- 30	- 28	29.92^{a} (5.59)
Klason lignin content [%]	17.10^{b} (0.43)	19.11^{b} (1.95)	6.47^{a} (0.47)	8.14^{a} (1.98)	- 10.63	- 10.97	- 62	- 57	7.17^{a} (0.23)
Extractive content [%]	4.41^{c} (0.03)	3.38^{b} (0.14)	2.72^{a} (0.15)	2.41^{a} (0.01)	- 1.69	- 0.97	- 38	- 29	3.79^{b} (0.13)
Ash content [%]	0.90^{b} (0.06)	1.11^{b} (0.10)	0.22^{a} (0.08)	0.88^{b} (0.19)	- 0.68	- 0.23	- 75	- 20	0.83^{b} (0.03)
pH	5.79^{a} (0.01)	6.59^{b} (0.12)	5.35^{a} (0.21)	6.52^{b} (0.10)	-	-	-	-	5.70^{a} (0.07)
Buffering capacity [mg/g]	0.36^{b} (0.03)	0.11^{a} (0.03)	0.35^{b} (0.08)	0.13^{a} (0.05)	- 0.01	+ 0.02	- 3	+ 18	0.56^{c} (0.00)

Table 2: Chemical composition, pH and buffering capacity of untreated and acetylated Turkey oak, showing results for sapwood (S) and heartwood (H) separately. Average values are presented with standard deviation in brackets. Different superscript letters in a row denote significant difference at p<0.05 level

Chemical composition	Untreated		Acetylated		Difference (pp)		Percent change (%)	
	S	H	S	H	S	H	S	H
Moisture content (%)	5.4	4.1	3.3	3.3	- 2.10	- 0.80	- 39	- 20
Holocellulose content (%)	77.87^{a} (0.08)	75.96^{a} (1.91)	79.27^{a} (2.77)	76.26^{a} (5.23)	+ 1.40	+ 0.30	+ 2	+ 0
Hemicellulose content (%)	29.66^{a} (0.95)	31.73^{a} (4.65)	44.95^{a} (0.29)	38.85^{a} (7.51)	+ 15.29	+ 7.12	+ 52	+ 22
Alpha-Cellulose content (%)	48.21^{c} (0.87)	44.23^{bc} (2.74)	34.32^{a} (2.47)	37.41^{ab} (2.28)	- 13.89	- 6.82	- 29	- 15
Klason lignin content (%)	16.27^{a} (0.23)	16.20^{a} (1.60)	13.25^{a} (1.07)	17.27^{a} (2.16)	- 3.02	+ 1.07	- 19	+ 7
Extractive content (%)	4.89^{a} (0.09)	5.09^{a} (0.11)	4.70^{a} (0.23)	5.64^{b} (0.04)	- 0.19	+ 0.55	- 4	+ 11
Ash content (%)	1.13^{a} (0.22)	1.16^{a} (0.27)	0.60^{a} (0.10)	0.61^{a} (0.08)	- 0.53	- 0.55	- 47	- 47
pH	5.58^{a} (0.04)	5.39^{a} (0.04)	5.86^{a} (0.47)	5.13^{a} (0.24)	-	-	-	-
Buffering capacity (mg/g)	0.45^{b} (0.01)	0.48^{b} (0.00)	0.27^{a} (0.04)	1.02^{c} (0.03)	- 0.18	+ 0.54	- 40	+ 113

In the transition zone of acetylated Pannonia poplar, the hemicellulose content was only 54.44 %, lower than that of sapwood and heartwood. This may indicate a lower rate of acetylation and WPG. On the other hand, there was no remarkable difference between the FTIR spectrum of acetylated Pannonia poplar sapwood, heartwood or the degraded part.

In a study where *Populus ussuriensis* was acetylated under laboratory conditions at 100 °C, 120 °C and 140 °C, a WPG of 12.6 %, 19.7 % and 21.3 % were achieved, respectively (Chai et al. 2016). According to their report, the intensities at peaks 1740, 1370, and 1230 cm^{-1} increased with increasing WPG, which correspond to our results.

Table 3: Wavenumber characterization (Mohebby 2008; Tolvaj 2013) of the infrared spectra of untreated and acetylated Pannonia poplar and Turkey oak. (Band number): numbers assigned to the bands in Figure 1

Band number	Wavenumber (cm^{-1}) Pannonia poplar	Wavenumber (cm^{-1}) Turkey oak	Functional group	Assignment
1	3534 3351 3201	3567 3348 3135	OH stretching (bonded)	
2	1761	1765	C=O (carbonyl) stretching in unconjugated acetyl groups	Xylan (hemicellulose)
3	1378	1382	Symmetric C-H deformation in CH3	Cellulose and hemicelluloses
4	1260	1267	Syringyl ring and C-O stretching in the ester bond	Lignin and xylan (hemicellulose)
5	1174	1177	Asymmetric C-O-C stretching	Cellulose and hemicelluloses

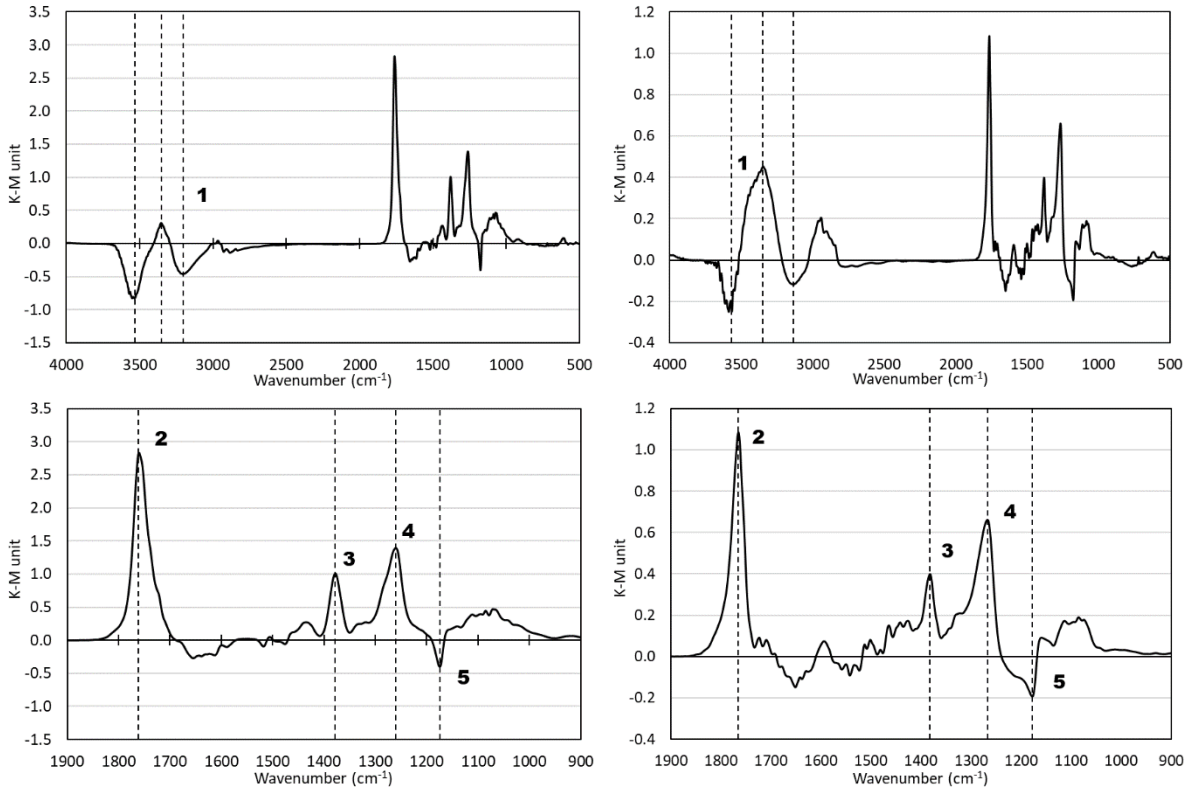

Figure 1: FTIR difference spectrum of Pannonia poplar sapwood (left) and Turkey oak sapwood (right). The spectra above are shown between wavenumbers 4000 – 500 cm^{-1}, and the fingerprint regions are highlighted from it in the bottom between wavenumbers 1900 – 900 cm^{-1}. The differential spectrum was calculated by subtracting the spectrum of untreated wood from that of acetylated wood. Description and assignments of band numbers are listed in Table 3

The alpha-cellulose content of both wood species decreased significantly by 15-30 % after acetylation. There was a negative peak of C-O-C stretching in cellulose (5) on the FTIR differential spectra. As the cellulose, hemicellulose and lignin fractions were not analyzed separately by FTIR, only assumptions can be drawn. The increase of hemicellulose content and the reduction of cellulose content can be explained by the difference in reactivity. Acetylation mainly affects the hemicelluloses and lignin as they are more reactive than cellulose (Ohkoshi and Kato 1997; Cetin and Ozmen 2011; Schwanninger et al. 2011). This leads to their increased share in chemical composition. As only the cellulose changed significantly in Turkey oak, here the amorph parts of the cellulose chains were degraded in the acidic medium, reducing its crystallinity. Fodor and colleagues examined acetylated hornbeam, and reported

no remarkable elevation of the soluble carbohydrate content or the levunilic acid concentration, which are the main breakdown products of cellulose (Fodor et al. 2018). Comparing the results of these species, Pannonia poplar had higher WPG then Turkey oak, which corresponds to the higher increment of hemicellulose content. On the other hand, the reduction of cellulose content was comparable, leading to the assumption that cellulose did degrade during acetylation.

The lignin content of Pannonia poplar decreased significantly by more than half after acetylation, while the lignin of Turkey oak changed at a lower rate. The initial values were not remarkably different between its sapwood and heartwood, similar to literature (Todaro et al. 2013). The higher the rate of acetylation is, the more lignin is degraded or dissolved in the acidic medium (Rowell 2012). Here, Klason (acid-insoluble) lignin content decreases by acetylation because some parts of lignin (e.g. ester bonds) hydrolyze during reaction with acetic anhydride and dissolve (Ying et al. 2022). In a study on acetylated hornbeam, only internal structural changes took place in the lignin matrix without any significant change in the lignin content (Fodor et al. 2018). The color darkening was also attributed to the change in lignin and extractive content.

The extractive content was exceptionally higher for sapwood than heartwood in Pannonia poplar, and decreased after acetylation. As the tested material was felled after its "optimal" age (after 15 years), it also had higher extractive content than the corresponding literature data. After acetylation, the difference between the extractive content of sapwood and heartwood is less remarkable. It can be hypothesized that there is no actual difference between the extractive content in sapwood and in heartwood, as Pannonia poplar has no colored heartwood which would indicate that. The sapwood contains more sugars and starch, which may explain its higher water-soluble extractive content. Related scientific articles report an average extractive content of poplar species below 3 % (Osman et al. 2013; Szadkowska et al. 2021).

Turkey oak has low extractive content corresponding to its low durability. Compared to pedunculate oak, it has similar content of proanthocyanidins (condensed tannin). However, it cannot accumulate ellagitannins as much as pedunculate oak which reduces its biological resistance (Lavisci et al. 1991). In general, heartwood has higher durability due to its higher extractive content, which was true in the case of Turkey oak. Similar results were found for Turkey oak (Todaro et al. 2013). The extractive content did not change remarkably after acetylation, indicating low rate of acetylation.

It is known that the anatomy and components of sapwood and heartwood are the same, except for extractives (Rowell 2012). These impregnate the individual cells after they die to form heartwood. The heartwood of Pannonia poplar and Turkey oak can develop tyloses which inhibit the rate of acetylation. The ash content seemingly decreased for both wood species, but it was probably not affected by acetylation.

As the acetylation process takes place in an acidic medium, and acetic acid forms as a byproduct, the acetylated material becomes more acidic, having a lower pH and a higher buffering capacity (Bongers et al. 2016). In Pannonia poplar and the heartwood of Turkey oak, the pH decreased accordingly. The buffering capacity results did not show a clear trend or a great difference. The compatibility of the wood material with adhesives and coatings is influenced by its pH and the buffering capacity, and thus it is an important factor of the finished product. If it is too acidic, base needs to be added for better bonding strength or coating stability. Turkey oak fundamentally has problems with bonding and surface finishing (stains) (Lavisci et al. 1991).

Based on the work of Beckers et al., the degree of acetylation or HPLC acetyl content can be determined approximately by correlating the peak of 1740 to 1510 cm^{-1} (Beckers et al. 2003). Here, the HPLC acetyl content is only an indicated value. It was determined 24% or more for acetylated Pannonia poplar, and 15% and 8% for acetylated Turkey oak sapwood and heartwood, respectively. The values for Pannonia poplar and Turkey oak were read from the correlation diagram for acetylated poplar and beech, respectively. The results are higher than the WPG calculated from weight, which was also shown in the acetylated hornbeam (Fodor et al. 2018).

As diverse as they are, wood species react to the same acetylation process diversely and show different properties, which have been studied well in literature (Sandberg et al. 2021).

The degraded part of Pannonia poplar was found on the borderline of sapwood and heartwood, in the transition zone. This part may have been a wet pocket in the original material. The initially higher moisture content in these parts can account for their lower acetyl content. Poplars are well-known for having wet pockets, water pockets or wetwood which complicate the drying process and cause the

formation of wood defects like warping, splitting, checks and collapses (Boever et al. 2011). These are associated with a bacterial infection of the living tree, where the moisture content grows as the bacteria grows while a bacterial slime prevents the moisture from leaving the wetwood zone thus it will have an exceedingly (at least +5 %) higher moisture content compared to the rest of the wood (Ward and Pong 1980).
Turkey oak was not successfully acetylated under industrial conditions, which was confirmed by its low WPG and slight changes in its chemical properties and FTIR differential spectrum.

CONCLUSIONS

In this research, semi-industrial acetylation was carried out on Pannonia poplar and Turkey oak. These wood species are less utilized and have not been subjected to acetylation before. The moisture content of both Pannonia poplar and Turkey oak decreased significantly by 20-58 % after acetylation. The ratio of alpha-cellulose decreased significantly by 15-30 % for both wood species. A higher hemicellulose content was experienced after acetylation for both wood species, by 22-81%. The increase was higher in sapwood than in heartwood, in Pannonia poplar than in Turkey oak. The lignin content decreased for both wood species, indicating that a part of the lignin degraded or dissolved in the acidic medium during acetylation. The extractive and ash content was not affected by acetylation for neither tested wood species. The wood material became more acidic as the pH decreased after acetylation. After acetylation, the changes were less significant in the degraded part than in the rest of Pannonia poplar, which indicates a lower WPG, lower acetyl content. Sapwood is more suitable for acetylation than heartwood, having a higher WPG. Based on these results, acetylation may improve the resistance of Pannonia poplar against moisture, weather, decay and wood-boring insects, but the process parameters need to be optimized in order to exclude the probability of degradation in poplar. Turkey oak was found to be less suitable for acetylation due to its low permeability and tendency to form cracks.

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