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ATR-FTIR SPECTROSCOPIC ANALYSIS OF THERMALLY MODIFIED WOOD DEGRADED BY ROT FUNGI

The resistance of thermally modified oriental spruce, Scots pine, and oriental beech wood samples against fungi is investigated under different temperatures. Thermally modified wood samples are subjected to brown-rot fungi or white-rot fungi. In the control samples, 32-43% of the total mass losses are caused by fungal degradation, but only 0.47-0.78% was caused by the thermally modified wood samples. The changes in the wood cell walls main components, in the wood samples were analysed via attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The thermally modified and the control wood samples' spectra after the decay test exhibit different intensities. Thermal modification increases wood's resistance against decay by removing hemicellulose polymers from the wood cell wall. The resistance against the decay of thermally modified wood is quite high due to the loss of hemicellulose polymers in the wood cell wall. The thermally modified wood structure was also investigated via scanning electron microscopy (SEM) after decay testing. SEM images clearly elucidate that fungal degradation was not effective on the thermally modified wood samples. Conclusively, our study reveals that thermal modification improves some wood's resistance in Turkey against fungal activity.

Keywords: ATR-FTIR spectroscopy; decay test; thermal modification; SEM; wood durability

Introduction

Thermal modification (TM) is a useful technique for protecting wood from fungal decay by changing its chemical composition [Akgül et al. 2007]. According to Windeisen et al. [2007], the modification of the chemical structure of lignin, cellulose, and hemicellulose blocks reabsorbing of water molecules, which tend to attach themselves between as well as within the wood cell wall

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polymers [Boonstra et al. 2006a; 2006b; Boonstra et al. 2007]. The changes in the relative amounts of crystalline and amorphous cellulose due to thermal modification also improves the wood's dimensional stability, thereby reducing wood shrinkage and swelling [Brito et al. 2008; Calonega et al. 2010]. Consequently, by increasing its dimensional stability and decreasing its hygroscopicity, TM increases the wood's biological resistance against fungi [Daniel 2003; Kačiková et al. 2013]. Furthermore, the alteration of the wood substrate's chemical structure through TM changes hinders several processes involved in fungal decay and the enzymatic systems' supporting metabolism [Boonstra and Tjeedsma 2006]. The physical and chemical degradation of wood exposed to decay is altered according to the type of fungus. Brown rot is mainly caused by basidiomycete fungus, which is a prominent degrader of wood cell wall components [Durmaz et al. 2016]. White rot is caused by the decay of lignin and structural carbohydrates at a similar rate in the wood structure, resulting in cell wall degradation [Pandey and Pitman 2004; Hakkou et al. 2006].

TM increases wood durability against rot fungi. Several studies reported improvements to wood's resistance to fungal decay by changing its chemical structure through TM [Gündüz et al. 2008; Irbe et al. 2011]. In particular, the lignin content was reported to increase due to thermal modification, but the reduction of the holocellulose content is caused by dehydration reactions, which depend on the decrease of the carbon content or of the O/C ratio [Kotilainen et al. 2000; Kamdem et al. 2002; Kačiková et al. 2013].

Bazyar [2012] found that the oil TM process increases decay resistance by improving the physical properties of wood such as its equilibrium moisture content and volumetric shrinkage. Some research demonstrated that due to thermal modification, hydroxyl groups diminished and were replaced with hydrophobic acetyl groups resulting in cross-linking along fibres [Korkut et al. 2008a; 2008b; Kačiková et al. 2013].

Several studies investigated thermally modified wood using SEM microscopy. TM caused small cracks between tracheids in some softwood and hardwood species, but the margo fibrils appeared undamaged. The ray parenchyma pit membranes, bordered pits, and large window pit membranes were not damaged in thermally modified wood [Boonstra et al. 2006a; 2006b].

The objective of the present research is to investigate the effect of TM on the fungal resistance of different wood species of Turkey. For this purpose, oriental spruce, oriental beech, and Scots pine samples were selected and TM using the ThermoWood® process. Sapwood was used in this study due to its low resistance against fungal resistance in comparison to heartwood. Changes in the chemical structure of the wood were examined with attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The effect of fungal degradation was monitored via scanning electron microscopy (SEM). The results could provide primary information to the industry and academic environment

with regards to the chemical behaviour and decay resistance of Turkey's wood species, which are enhanced using the ThermoWood process.

Materials and methods

Preparation of wood samples

As raw materials, oriental beech (*Fagus orientalis* L.), oriental spruce (*Picea orientalis* L.), and Scots pine (*Pinus sylvestris* L.) wood samples were acquired from the Black Sea Region in Turkey. Defect-free samples with dimensions of 300 mm (length) × 70 mm (wide) × 20 mm (thick) from sapwood of these three species were placed in a climate room at 20°C and 65% relative humidity (RH) until their moisture content reached approximately 12%. A LOYKA NSP-100 MC meter (AKYOL Company, Istanbul, Turkey) was used to determine the moisture content of the three wood species.

Thermal modification (TM) process

TM was then applied to four samples from each species in an oven. The temperature was controlled with ±1°C sensitivity, at two different temperatures (oriental beech at 190°C for 90 min; oriental spruce and Scots pine at 212°C for 90 min) under a steam atmosphere (ThermoWood process) in an industrial plant, in Novawood, Gerede, Turkey.

Decay test

The thermally modified wood samples were cut into pieces with dimensions of 0.5 × 1.0 × 2.5 cm (tangential × radial × longitudinal) for decay testing. Straight--grained, defect-free sapwood samples were then placed in an oven at 103°C to determine the oven-dry weight before the decay test. Then, the samples were conditioned at 20°C and 65% RH until they reached a constant weight (about two weeks). Subsequently, all wood samples were sterilized in an autoclave at 120°C for 30 min. The prepared wood samples were exposed to white-rot fungi (*Trametes versicolor* (L.) Lloyd (Mad-697)) for beech and brown-rot fungi (*Coniophera puteana* (L.) (Schumach.) P. Karst. (Mad-515)) for spruce and Scots pine for 90 days, according to EN 113 standards. After the decay test, the oven-dried weights of the decayed samples were determined, and the mass loss of the samples was calculated by dry weight before and after the decay test.

Fungi were grown on a 4.8% malt extract agar medium. The media were steam-sterilized at 120°C for 20 min before being poured into petri dishes. After inoculation, the petri dishes were held at 23 ±2°C and 65 ±5% RH so that the fungi could spread over the entire surface of the petri dishes. After the specimens were steam-sterilized under the same conditions, the fungal test was initiated.

ATR-FTIR spectroscopic measurements

The ATR-FTIR spectra were recorded using a Thermo Nicolet iS50 FTIR (Thermo Fisher Scientific Co., Waltham, MA, USA) spectrometer equipped with a single bounce diamond crystal and a deuterated triglycine sulphate detector. The FTIR spectra of all wood samples were determined in the range of 4000--400 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum was collected after 32 scans in the absorbance mode. The ATR-FTIR spectra of wood samples were analysed using the OMNICTM software (Thermo Electron Corporation, Madison, WI, USA). The peak heights, constructed by connecting the lowest data points on either side of the peak, were measured from the baseline. The intensities of the lignin-associated band were rationed against the carbohydrate band in unmodified and thermally modified samples for the decay test [Pandey and Nagvani 2007].

Scanning electron microscopy (SEM)

For SEM (Zeiss Evo LS10, Germany), test and control samples were oven-dried and coated with gold under vacuum to increase conductivity (Emitech SC7620, France). The microscope was operated at 5 kV. The thermally modified and unmodified wood structures and the degradation caused by fungi were observed.

Results and discussion

Mass loss data

Thermal modification (TM) is an important modification method that causes both physical and chemical changes. Mass loss occurs due to the TM, which results in a decrease of the mechanical properties of the wood [Korkut et al. 2008a; 2008b]. Additionally, a part of the hemicellulose is also soluble under high temperatures [Nuopponen et al. 2003; Esteves et al. 2013]. The deacetylation of hemicelluloses triggers acetic acid formation, which catalyses depolymerization reactions and results in wood mass loss [Windeisen et al. 2007; Esteves et al. 2013]. Table 1 displays the wood mass-loss percentage following the TM process.

Table 1. The mass loss of the thermal modified wood samples

Mass loss of thermal modified wood (%)	
Oriental beech	Scots pine
14.3 ±1.1	17.3 ±0.8

The mean mass-loss percentages for unmodified and thermally modified wood samples exposed to *C. putuena*, for pine and spruce wood samples, and

T. versicolor, for beech wood samples, are given in table 2. After the decay test, the measured wood mass losses in unmodified samples are around 32-42%, confirming the virulence of fungi under the test conditions [Eriksson et al. 2012]. The mean mass losses for unmodified pine and spruce by *C. putuena* are 32.16% and 42.23%, respectively. They are 0.78% and 0.53% for thermally modified pine and spruce wood samples, respectively, after fungal exposure. Meanwhile, the mean mass losses in unmodified and thermally modified beech decayed by *T. versicolor* are 32.32% and 0.47%, respectively.

Brown and white decay fungi are important fungus species that damage the wood significantly [Daniel 2003; Ek et al. 2009]. The chemical changes as a result of the TM prevent the fungus from destroying the wood. High temperature causes the degradation of a significant portion of the hemicellulose and amorphous cellulose [Nuopponen et al. 2005; Kocaefe et al. 2008; Awoyemi and Jones 2011; Esteves et al. 2013]. As a result, a decrease in the free hydroxyl groups occurs, which affects the wood wetting phenomenon [Esteves et al. 2013; Özgenç et al. 2017]. Therefore, it can be stated that the TM modifies the main components of the wood cell wall (cellulose, hemicellulose, and lignin) and improves the resistance of wood against fungal decay [Boonstra and Tjeedsma 2006; Lekounougou et al. 2009]. The results of this study show the protective effect of TM of Turkey's wood species against fungal decay.

ATR-FTIR spectroscopic studies

The chemical composition of the wood cell wall has also been examined through ATR-FTIR spectroscopy due to the easy sample preparation, requiring a small sample size and rapid analysis [Ferraz et al. 2000; Pandey and Nagvani 2007; Özgenç et al. 2017]. In this study, FTIR data was obtained to characterize the FTIR bands belonging to thermally modified and unmodified wood samples. The ATR-FTIR spectra of decayed unmodified and thermally modified beech, pine, and spruce wood showed differences in the characteristic bands of the wood cell wall components (figs. 1-3). The IR spectra of wood species include a strong hydrogen-bonded (OH) stretching absorption and a prominent C-H stretching vibration between 4000-400 cm^{-1} [Kotilainen et al. 2000]. Therefore, there are many well-defined peaks in the fingerprint region of 1800-800 cm^{-1}. The assigned peaks in this region are: 1730-1731 cm^{-1} for unconjugated C=O in xylans (hemicellulose) [Kotilainen et al. 2000; Nuopponen 2005; Kocaefe et al. 2008]; 1593, 1598, and 1595 cm^{-1} for conjugated C-O stretching [Naumann et al. 2005; Rowell 2012; Durmaz et al. 2016]; 1506-1509 cm^{-1} for aromatic skeletal in lignin [Nuopponen et al. 2003; 2005; Mohareb et al. 2012]; 1451--1456 cm^{-1} and 1422-1424 cm^{-1} for C-H deformation in lignin and carbohydrates [Kihara et al. 2002; Ishimaru et al. 2007; Mohareb et al. 2012]; 1368-1372 cm^{-1} C-H deformation in cellulose and hemicellulose [Nuopponen 2005 ; Kocaefe et al. 2008]; 1316-1326 cm^{-1} for C-H vibration in cellulose and

C1-O vibration in syringyl derivatives [Kocaefe et al. 2008]; 1265 cm^{-1} for guiacyl ring breathing, C-O stretch in lignin, and C-O linkage in guiacyl aromatic methoxyl groups [Kotilainen et al. 2000]; 1234 cm^{-1} for syringyl ring and C-O stretch in lignin and xylan [Kotilainen et al. 2000]; 1156, 1155, and 1155 cm^{-1} for C-O-C vibration in cellulose and hemicellulose [Nuopponen et al. 2003; 2005]; 1050-1051 cm^{-1} for C-O stretch in cellulose and hemicellulose [Hakkou et al. 2006]; 895-897 cm^{-1} for C1-H group vibration in cellulose and hemicellulose [Nuopponen et al. 2003; 2005; Hakkou et al. 2006]. The average mass losses and intensity ratios of the lignin-associated band with the carbohydrate band in unmodified and thermally modified samples for the decay test are shown in table 2.

ATR-FTIR spectroscopic analysis of beech wood

The ATR-FTIR spectra of undecayed and decayed beech samples that were exposed to decay by *T. versicolor* for 90 days are shown in figure 1. The difference between the intensities of the spectra is remarkable. White-rot fungi primarily decay lignin [Mohebby 2005], but also polysaccharide in the wood cell wall. In fact, in unmodified beech (fig. 1), the intensity reduction of the carbohydrate bands at 1731, 1372, 1156, and 897 cm^{-1} after exposure to white-

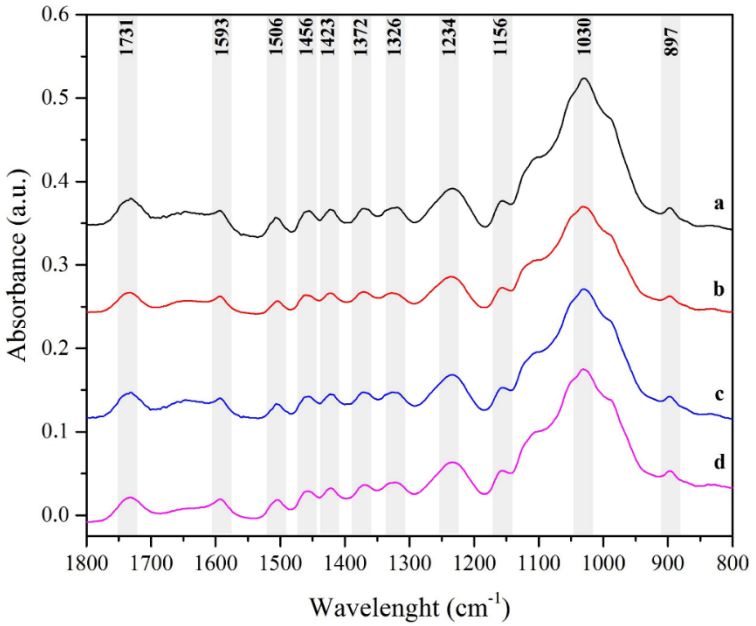

Fig. 1. ATR-FTIR spectra of thermal modified and unmodified beech samples after the decay test. (a): unmodified beech, (b): unmodified beech exposed to *T. versicolor*, (c): thermal modified beech, and (d): thermal modified beech exposed to *T. versicolor*

Table 2. Average mass losses and ratios of the intensity of the lignin-associated band with the carbohydrate band in thermal modified and unmodified samples for the decay test

Wood species	Decayed or undecayed		Fungus	Average mass loss (%)	Relative intensities of aromatic skelatel vibration (I_a)[b] against typical bands for carbohydrates			
					I_a/I_{1731}	I_a/I_{1372}	I_a/I_{1156}	I_a/I_{897}
Beech	Decayed	Untreated	*T. versicolor*	32.32 ±9.3	0.55 (0.022)	1.12 (0.011)	0.89 (0.014)	1.39 (0.009)
		Treated	*T. versicolor*	0.47 ±0.08	0.80 (0.020)	1.6 (0.010)	1.27 (0.012)	2.13 (0.007)
	Undecayed	Untreated	–	–	0.76 (0.026)	1.48 (0.013)	1.27 (0.015)	1.89 (0.010)
		Treated	–	–	0.60 (0.023)	1.22 (0.012)	1.09 (0.013)	1.53 (0.009)
					I_a/I_{1731}	I_a/I_{1368}	I_a/I_{1155}	I_a/I_{897}
Pine	Decayed	Untreated	*C. puteana*	32.16 ±8.9	6.20 (0.008)	5.23 (0.010)	3.46 (0.014)	9.28 (0.005)
		Treated	*C. puteana*	0.78 ±0.1	3.34 (0.010)	3.06 (0.010)	1.74 (0.018)	4.90 (0.006)
	Undecayed	Untreated	–	–	1.27 (0.017)	1.54 (0.014)	0.97 (0.023)	2.24 (0.010)
		Treated	–	–	2.18 (0.011)	2.21 (0.011)	1.31 (0.018)	3.58 (0.006)
					I_a/I_{1730}	I_a/I_{1368}	I_a/I_{1155}	I_a/I_{895}
Spruce	Decayed	Untreated	*C. puteana*	42.23 ±11.2	8.96 (0.006)	7.48 (0.007)	9.16 (0.006)	17.65 (0.003)
		Treated	*C. puteana*	0.53 ±0.09	2.17 (0.009)	2.75 (0.007)	1.55 (0.013)	3.91 (0.005)
	Undecayed	Untreated	–	–	2.21 (0.013)	2.02 (0.015)	1.47 (0.020)	2.95 (0.010)
		Treated	–	–	1.20 (0.013)	1.47 (0.011)	0.88 (0.017)	2.13 (0.007)

[a]Quantities given in the parentheses correspond to values calculated from the band area measurements. The values above the parentheses are ratios based on peak heights. Beech 1506 cm^{-1}; Pine 1509 cm^{-1}; Spruce 1508 cm^{-1}.

-rot fungi is greater than that of thermally modified beech wood. TM also reduces the intensities of the carbohydrate peaks. The variation between the intensities of unmodified and thermally modified beech wood peaks after decay testing indicates that thermally modified wood shows increased resistance to *T. versicolor.*

Furthermore, the average relative intensities of the lignin peak at 1506 cm^{-1} (for beech) against the carbohydrate peaks at 1731, 1372, 1156, and 897 cm^{-1} are calculated using the peak height ratios to clarify the changes in the wood cell walls main component, which are summarized in table 2 [Pandey and Pitman 2003]. It is determined that the values of I1506 /I1731, I1506 / I1372, I1506 /I1156 and I1506 /I897 for unmodified beech wood are higher than those for thermally modified beech wood.. This is because the decrease in the absorption band at 1506 cm^{-1} is mainly due to the condensation reactions and splitting of the aliphatic side chains in the lignin in thermally modified beech wood. The decrease in the absorption band at 1731 cm^{-1} leads to a decrease in the amount of absorbed water in cellulose [Kotilainen et al. 2000; Kocaefe et al. 2008]. The TM chemically modifies the main components of wood; thus, these modifications alter or block the decay mechanism in this study. The white rot species *T. versicolor* is unable to attack beech wood treated at 190°C, indicating that the chemical modification of the wood's main components increases its resistance.

ATR-FTIR spectroscopic analysis of Scots pine wood

Figure 2 shows the ATR-FTIR spectra of the Scots pine samples decayed by *C. putuena* and those of the undecayed samples. The relative intensities of the bands belonging to various wood cell wall components are summarized in table 2, where the differences are striking. *C. putuena*, as a brown-rot fungus, has the characteristic capacity to depolymerize and extinguish cellulose and hemicellulose in the wood cell wall [Moore and Owen 2001; Mohebby 2005; Mburu et al. 2007]. It can also modify the lignin in the wood cell wall [Moore and Owen 2001]. As seen in figure 2, TM decreases the intensity of hemicellulose and cellulose (1731 and 897 cm^{-1}), whereas there is no significant difference in the intensity of the lignin peaks (1509, 1598, 1265, and 1155 cm^{-1}). However, TM also triggers condensation reactions and splitting of the aliphatic side chains in the lignin, which changes the intensity of the lignin peaks [Korkut et al. 2008a; Nuopponen et al. 2013].

The height ratios of the lignin and carbohydrate peaks (I1506 /I1731, I1506 / I1372, I1506 /I1156, I1506 /I897) are also estimated, in order to evaluate the effect of TM. It is found that TM degrades the hemicellulose in the wood cell wall and results in condensation reactions, which affect the intensity of the lignin peaks. The carbohydrate bands in thermally modified wood degrade only a little. Conversely, the control samples show significant degradation. In the thermally modified wood, after the decay test, the intensities of the absorption bands at 1598, 1509, 1451, 1424, 1265, and 1026 cm^{-1} are considerably higher, and the well-resolved lignin bands at 1222 and 1104cm^{-1} increase. The relative lignin content in the wood cell wall increases due to carbohydrate degradation,

affecting the intensity of the lignin bands [Chaouch et al. 2010; Fackler et al. 2010].

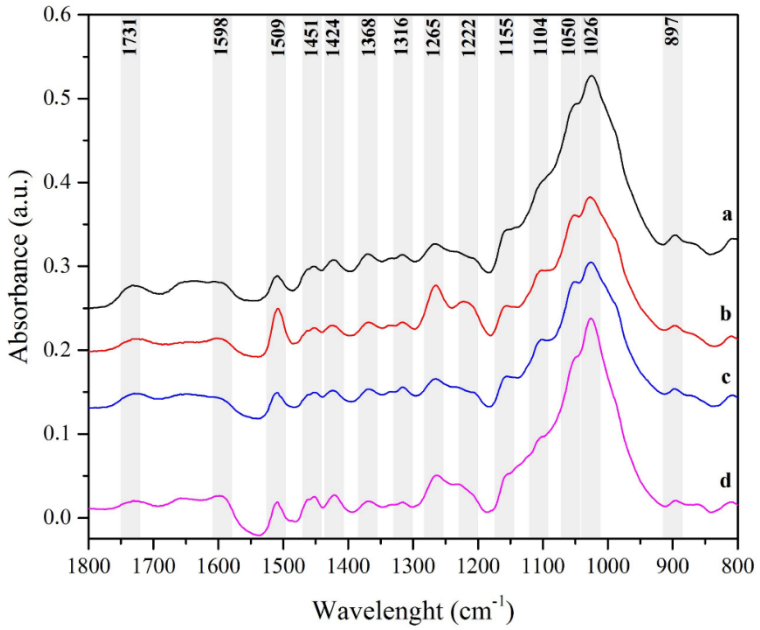

Fig. 2. ATR-FTIR spectra thermal modified and unmodified pine samples after the decay test. (a): unmodified pine, (b): unmodified pine exposed to *C. puteana*, (c): thermal modified pine, and (d): thermal modified pine exposed to *C. puteana*

ATR-FTIR spectroscopic analysis of spruce wood

Figure 3 shows the ATR-FTIR spectra of spruce samples undecayed and decayed by *C. putuena* for 90 days. The reduction in the intensity of the lignin bands at 1508 and 1265 cm^{-1} and of xylan bands at 1730 cm^{-1} for unmodified spruce is more significant than that of thermally modified spruce samples. Hemicellulose is soluble due to the TM [Chaouch et al. 2010]. Organic acid (acetic acid, formic acid) formation degrades the hemicellulose and the cellulose structure during the TM process [Kocaefe et al. 2008; Özgenç et al. 2017]. The condensation reaction and the degradation of the aliphatic side chain in the lignin structure causes a reduction in the intensity of the lignin bands. Additionally, the lignin in the decayed wood is chemically altered by the brown-rot fungus [Kotilainen et al. 2000].

The height ratios of the lignin and the carbohydrate peaks (I1508 /I1730, I1508 / I1368, I1508 /I1155, I1508 /I895) are also calculated to determine the effect of high temperature on the wood structure. The obtained results show that the reduction in the ratio of thermally modified spruce is not significant after the

decay process, whereas there is a striking change in the ratio of unmodified spruce wood samples after the decay test.

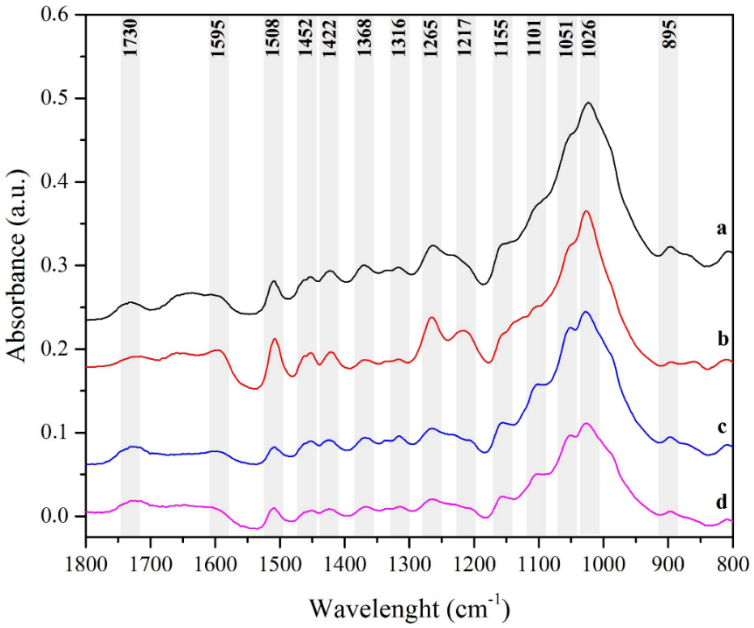

Fig. 3. ATR-FTIR spectra of thermal modified and unmodified spruce samples after the decay test. (a): unmodified spruce, (b): unmodified spruce exposed to *C. puteana*, (c): unmodified spruce, and (d): unmodified spruce exposed to *C. puteana*

The mass losses and the ATR-FTIR spectral results indicate that TM improves the resistance of wood against white-rot (*T. versicolor*) and brown-rot fungi (*C. putuena*). The molecular formation responsible for the improvement of rot resistance in thermal modification wood was previously reported by several researchers [Pandey and Pitman 2003; Ek et al. 2009; Chaouch et al. 2010; Mohareb et al. 2012]. During the TM process, some molecules such as furfural, hydroxylmethyl furfural, acids, methanol, and other condensation products can disappear [Zheng et al. 2012]. In addition, carbohydrates may be modified, and/or toxic compounds may be formed [Lekounougou et al. 2009]. Therefore, the fungal enzymatic system does not recognize the substratum after the TM and cannot degrade the wood cell wall components [Boonstra and Tjeedsma 2006]. Another major requirement for fungal growth in wood is the presence of free water on the surfaces of the cell luminas [Durmaz et al. 2016; Özgenç et al. 2017]. However, the peaks at the 1506-1509 cm^{-1} band in figures 1-3 demonstrate the breaking of the aliphatic side chains in lignin and the formation of new cross-linking. New cross-linking in lignin decreases the hygroscopicity of wood [Gündüz et al. 2008].

SEM Images

After TM, the fungal resistance of the different wood species was determined. Spruce and pine wood samples were exposed to *C. puteana*, whereas beech wood samples were exposed to *T. versicolor*. The SEM images of the thermally modified wood samples exposed to fungi appear in figure 4.

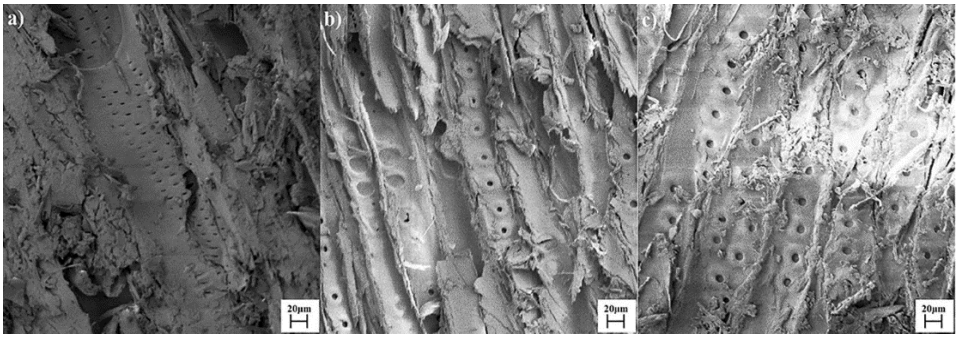

Fig. 4. SEM images of thermal modified wood samples after the decay test: a) beech wood, b) spruce wood, and c) pine wood

In previous studies, the changes in the anatomical structure of the wood by TM were investigated by SEM analysis [Boonstra et al. 2006a; 2006b; Li et al. 2011]. The sapwoods of Scots pine after TM reveal some damage to parenchyma cells in the rays and epithelial cells; whereas the radial cracks in spruce sapwood occur mainly in impermeable wood, as indicated by SEM analysis [Boonstra et al. 2006a; 2006b]. Besides, the collapse of the vessels and some deformation of the libriform fibres have been observed through SEM analysis in thermally modified beech wood [Boonstra et al. 2006a; Popescu et al. 2010].

The SEM images are interpreted through comparison with the normal wood structure, which is known from previous studies. Indeed, the wood structure is well preserved, and fungal degradation is inhibited after TM. After the decay test, the wood samples tend to be fibrous because of the extensive degradation [Pandey and Pitman 2003; 2004].

As shown in figure 4, fungal hyphae are located in the wood tracheid and vessels. Fungal hyphae secrete enzymes and/or low molecular agents at the contact with the tertiary wall, effect a degradation of the wood samples [Moore and Owen 2001; Li et al. 2011]. They bear pit membranes and spread over the other wood cell lumens. In fact, the pit membranes and the cell wall structure are preserved from the decay process because of the TM, which improves the wood's properties.

Conclusions

Thermal modification (TM) is one of the most preferred methods for improving wood properties. This study investigated the influence of TM on the fungal resistance of different wood species. SEM images clearly indicated how the TM inhibited fungal activity. The cell wall structure changed through TM, hindering the spread of fungal hyphae over the wood structure. Nondegraded pit structure showed the effectiveness of TM against fungal activity. ATR-FTIR spectroscopy was also used to compare relatively qualitative and quantitative changes in the lignin and carbohydrate components between unmodified and thermally modified wood decayed by *T. versicolor* and *C. putuena*. Improvement of decay resistance is associated with the modification during the TM process. High temperature leads to the modification of lignin and decomposition of a large portion of the hemicellulose in the wood cell wall in the thermally modified beech, Scots pine, and spruce wood samples. ATR-FTIR spectra results exhibited that there were significant differences between decayed and undecayed thermal modified wood samples after the decay test. This study clearly reveals that modification at high temperature definitely improves wood resistance, which provides more benefits in its service. FTIR spectra could be used for explaining the chemical changes in the wood structure and thus for evaluating wood for its service life span in future studies. Main conclusions, concise summary of research results.

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