Thermo-Vacuum Modification of Poplar Veneers and its Quality Control

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Poplar wood is commonly used for many purposes due to its easy machinability, low density, uniform light colour, and relatively low cost. Here, vacuum thermal treatment is proposed for upgrading veneers in the manufacturing of plywood panels with resulting reduced hygroscopicity, improved durability, and dimensional stability. Thirty-eight batch processes with different treatment conditions (temperature ranging from 150 to 240 °C, time from 0.5 to 22.5 h and pressure from 100 to 1000 mbar) were performed to characterize the influence of process parameters on the product properties. Samples were characterized considering their appearance (colour) and their physical (mass loss and equilibrium moisture content), mechanical (bending strength), and chemical (investigated with near infrared spectroscopy (NIR)) properties. The darkening of poplar veneers and the reduction of mechanical strength were observed with increased treatment time and intensity. Mass loss closely correlated with colour change, resulting from chemical changes in wood components. Principal component analysis (PCA) and partial least squares (PLS) were used for evaluation of near infrared spectral data. Both were correlated with several technical properties, and thus NIR allowed the simultaneous prediction of several of these properties. Both colour change and NIR could be used to optimize the thermal treatment of poplar veneers at the industrial scale and for real-time statistical process control.

Keywords: Plywood; Thermal treatment; Process control; Colour; Near infrared spectroscopy

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INTRODUCTION

Poplar is a rapid growing species that is economically important for several industrial and ecological purposes. It is widespread in plantations with a rotation period from five to twenty years. In Europe poplar plantations cover approximately 940,000 ha, and around 90% of their production is used for the manufacturing of plywood, sawn timber, pulpwood, packaging, and biomass for energy (Nervo *et al*. 2011). Recently, approximately 7,000 ha of short rotation coppices, mainly with selected clones, were cultivated in Italy, almost 80% of which are in the northern part (Bergante *et al*. 2014). Regular poplar plantations (estimated at 60,000 ha) cover only 0.5% of national forest areas, though they annually supply almost 50% of hardwood for industrial purposes (Castro and Zanuttini 2008).

Plywood is a wood-based panel composed of layers of veneer placed crosswise and bound with adhesives. This cross-bonded construction improves the dimensional stability and minimizes the movement of the panel due to swelling and shrinkage. The trend of replacing traditional materials with new ones that have improved characteristics has recently accelerated. Limited but growing amounts of modified wood-based products are currently appearing on the market. Their total production in Europe was estimated at 300,000 to 400,000 m^3 in 2015 (Militz).

Thermally modified wood (TMW) is an example that follows this trend. According to UNI CEN/TS 15679 (2008), TMW is defined as timber in which the chemical composition of constitutive woody polymers and the wood physical properties are modified by exposure to temperatures higher than 160 °C in conditions of reduced oxygen availability. Thermally modified wood shows better durability against decay, enhanced dimensional stability, reduced thermal conductivity, and lower equilibrium moisture content, but also, as a drawback, reduced mechanical performances.

Several researchers reported the advantages of the thermal modification (TM) of veneers used for the improvement of dimensional stability, the decrease of hygroscopicity, and the change in colour (Bak and Németh 2012; Goli *et al*. 2014; Lovrić *et al*. 2014). Many attempts to integrate TM technology with panel production can be found in the literature. Thermal treatment was first applied directly after the manufacturing of oriented strand boards (OSB) (Del Menezzi *et al*. 2009), and Zdravković *et al*. (2013) and Fioravanti *et al*. (2013) proposed the TM of veneers before plywood production. Ruponen *et al*. (2014) presented research regarding the auto-adhesion of veneers in plywood by using heat, moisture, and mechanical compression. All approaches presented had advantages and drawbacks. In general, the mechanical performance and bonding quality of treated plywood diminished after TM; the wooden surfaces exposed to high temperature might be subjected to surface inactivation with possible adhesion problems during its manufacturing (Ayrilmis and Winandy 2009). While the production of heat-treated poplar plywood is feasible, it needs important improvements to avoid reductions in mechanical properties (Goli *et al*. 2014).

The thermo-vacuum process is an alternative technology for the TM of wood where the reduction of oxygen content inside the reactor is obtained by applying a vacuum, while volatiles and water vapour are continuously removed using a vacuum pump. This process exhibits high energy efficiency, lower rate of wood mass loss (ML), and less corrosion compared with alternative treatment technologies (Allegretti *et al*. 2012). Moreover, the thermo-vacuum system does not cause a considerable reduction of the mechanical properties of wood (Candelier *et al*. 2014). Castro *et al*. (2016) confirmed that there are no statistically significant decreases in the bending strength of veneers treated with the thermo-vacuum process at temperatures below 190 °C.

Fourier transform near infrared spectroscopy (FT-NIR) is a technique capable of the fast and non-destructive measurement of organic materials. Quality assessment of thermally treated wood by means of NIR was previously investigated by several researchers (Schwanninger *et al*. 2004; Esteves and Pereira 2008; Bächle *et al*. 2012; Sandak *et al*. 2012, 2016). FT-NIR was also successfully used for characterizing defects in composite structures including detecting superficial resin pockets (Elhajjar *et al*. 2016), monitoring polymer matrix composites (Johnson *et al*. 2000), controlling the resin content (Jiang and Huang 2008), or discriminating panels with various urea formaldehyde contents (Sandak *et al*. 2015b).

FT-NIR is a useful tool in developing chemometric models to predict thermal modification advancement indicators, especially mass loss and equilibrium moisture content. Promising results previously obtained by Esteves and Pereira (2008) and Sandak *et al*. (2015a) suggested the implementation of FT-NIR for the quality control of thermally treated wood.

The thermo-vacuum modification system was tested within the framework of the ThermoPoplarPly project (Castro *et al.* 2016) on both veneers and plywood samples. The objective was to find an alternative use for low density European species such as poplar by developing a new family of products that could replace, in humid and/or exterior environments, the plywood made of tropical woods characterized by higher durability.

The study presents a comprehensive characterization of the properties of poplar veneers modified in thermo-vacuum conditions, considered here as a veneer upgrading process. The overall goal was to evaluate the influence of temperature, time, and pressure on the key indicators of the thermal modification process that included colour, mass loss, and equilibrium moisture content. A future goal is to develop reliable methodology that might be used for the quality control of treated veneers directly during the industrial production.

EXPERIMENTAL

Materials

Experimental samples used for vacuum thermal treatment were rotary-cut veneers of poplar clone 'I-214' (*Populus x canadensis* Moench) obtained from a 9-year-old monoclonal plantation established in the experimental farm managed by the CREA-PLF, in Casale Monferrato, Piedmont, Italy. The sample size was 360 mm × 150 mm × 2.5 mm (length × width × thickness, respectively).

Table 1. Process Parameters of Performed Tests and Measured *ML* and *EMC*

batch n°	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13
***t* (h)**	1.0	1.1	1.5	1.5	6.1	12.0	6.4	22.2	23.0	22.2	22.0	1.1	1.5
***T* (°C)**	240	240	240	240	195	150	175	195	175	212	240	250	240
***p* (mbar)**	1000	250	100	1000	1000	250	1000	250	250	250	250	250	1000
***ML* (%)**	15.8	13.7	14.4	15.6	5.7	0.1	1.6	10.7	3.1	21.6	49.0	19.1	15.2
***EMC* (%)**	5.2	5.9	5.9	5.3	6.0	9.2	8.1	6.1	7.2			5.7	5.4

batch n°	#14	#15	#16	#17	#18	#19	#20	#21	#22	#23	#24	#25	#26
***t* (h)**	0.2	2.1	0.5	2.2	1.5	0.5	1.1	1.1	1.1	1.1	1.1	1.1	1.1
***T* (°C)**	240	240	240	240	240	240	212	200	195	180	175	165	155
***p* (mbar)**	1000	1000	1000	250	250	250	250	250	250	250	250	250	250
***ML* (%)**	9.8	17.2	11.6	17.8	14.0	11.2	4.6	2.7	1.5	0.8	0.5	0.4	0.2
***EMC* (%)**	5.1		5.3	6.1	5.5	5.9	6.5	7.5	8.5	8.7	9.2	9.8	9.8

batch n°	#27	#28	#29	#30	#31	#32	#33	#34	#35	#36	#37	#38
***t* (h)**	1.1	1.1	2.2	4.3	0.0	6.4	6.1	6.4	4.7	13.0	6.0	4.8
***T* (°C)**	150	220	212	212	212	212	195	175	212	175	240	220
***p* (mbar)**	250	250	250	250	250	250	250	250	100	250	250	1000
***ML* (%)**	0.3	7.8	7.8	9.3	1.6	12.1	4.1	1.5	10.5	2.1	24.8	12.8
***EMC* (%)**	9.7	5.9	5.9	5.2	8.0	6.1	5.9	8.4	6.3	8.0		5.8

Thermal Treatment

The thermal treatment was performed in the thermo-vacuum prototype plant previously described by Sandak *et al*. (2015a). Conductive instead of convective heating was used by means of electrically heated aluminum plates. The ventilation was disabled in this experiment, so that the test chamber acted only as a sealing system of the vacuum, allowing a continual low oxygen concentration.

Each modification process consisted of two phases, wood drying (at 100 °C under vacuum for 20 min) and a specific thermal treatment. The treatment consisted of a heating stage with a constant temperature (*T*) and a defined duration (*t*). Heating and cooling ramps during the thermal treatment phase were kept constant at 60 °C/h. The process variables controlled within the experiment included temperature (*T*), time (*t*), and pressure (*p*). As shown in Table 1, a total of 38 batch processes with various treatment conditions (*T* ranging from 150 to 240 °C, *t* from 0.5 to 22.5 h, as well as *p* of 100, 250, and 1000 mbar) were performed. The batch specific values of *T*, *t* and *p* were selected on the basis of previous studies on other wood species (Allegretti *et al.* 2012) and dedicated pilot tests. The overall aim was to investigate combined effects of the main parameters covering in the whole functional range of processor. The experimental tests were implemented randomly in order to minimize the effect of any systematic errors related to sequencing, instrumentation and processor. The batch #31 had no constant *T* stage ($t = 0$).

Sample Characterization

The material was analyzed before and after each treatment to determine the modification of selected physical and chemical wood properties induced by the process.

Physical properties

Mass loss was determined according to Eq. 1 by weighing each sample before the treatment (m_0) and immediately after (m_{tr}), assuring that the wood was oven-dried (0% moisture content). The equilibrium moisture content *EMC* of treated and non-treated samples was calculated on specimens conditioned at a relative humidity (RH) of 65% and 20 °C, according to the ISO 13061-1 (2014) standard, following Eq. 2.

$$ML = \frac{m_{tr} - m_0}{m_0} \cdot 100\% \quad (1)$$

$$EMC = \frac{m_c - m_0}{m_0} \cdot 100\% \quad (2)$$

where m_c is the mass of the conditioned wood (g), and m_0 is the mass of anhydrous wood (g).

Mechanical properties

Because an international standard for the mechanical testing of veneers is currently not available, the bending strength was determined according to the method proposed by Castro *et al.* (2014; 2016), based on EN 310 (1994).

Test pieces (20 × 80 × 2.5 mm^3 width × length × thickness, respectively) were conditioned in a climatic chamber (20 ± 2 °C and 65 ± 5% RH) until they reached a constant mass. Longitudinal strength (modulus of rupture, *MOR*) was determined through three-point static bending with a span of 70 mm using a horizontal Hounsfield tensiometer (Tensiometer Ltd, Croydon, England) suitable for small-sized samples (100 daN load cell).

The moving rate of the loading head was 5 mm/min up to the test piece rupture, resulting in a total test time between 90 and 120 s.

Colour measurement

A MicroFlash 200D portable spectrophotometer (DataColor Int,, Lawrenceville, USA), suitable for direct determination of the *CIE L*a*b** colour coordinates according to ISO 11664-4 (2008) was used for the measurement over a 18 mm diameter spot with a standard light source D65 and an observer angle of 10°.

Each sample was measured 10 times on varying positions over the surface. The standard deviation of colour measurement was considered an indicator of the texture variability of the material.

FT-NIR measurement

A VECTOR 22-N Fourier transform near infrared spectrometer (Bruker Optics GmbH, Ettlingen, Germany) equipped with the fibre-optic probe was used for spectra collection. The spectral range was between 4000 and 12000 cm^{-1}. The spectral resolution of the spectrometer was set to 8 cm^{-1}. The spectral wave number interval was 3.85 cm^{-1} with zero-filling = 2. Each spectrum was computed as an average of 32 successive scans to minimize the measurement error. Measurements were performed in an air-conditioned laboratory, five times on each sample. Bruker Optics OPUS 7.0 software was used for spectra collection, pre-processing, and data mining. Spectra interpretation was performed according to Schwanninger *et al.* (2011). The list of assigned bands is summarized in Table 2.

Table 2. NIR Band Assignment (According to Schwanninger *et al.* 2011)

band nr	Wavenumber (cm^{-1})	Band Assignment
1	4198	C–H deformation in holocellulose
2	4280	C–H stretching + C–H deformation in cellulose
3	4404	C–H_2 stretching + C–H_2 deformation in cellulose
4	4620	O–H stretching + C–H deformation in cellulose
5	4890	O–H stretching + C–H deformation in cellulose
6	5219	O–H stretching + O–H deformation in water
7	5464	O–H + C–H stretching semi- or crystalline regions in cellulose
8	5587	C–H stretching (first overtone) semi- or crystalline regions in cellulose
9	5800	C–H stretching (first overtone) furanose/pyranose due to hemicelluloses
10	5883	C–H stretching (first overtone) aliphatic
11	5935	C–H stretching (first overtone) aromatic skeletal sue to lignin
12	5980	C–H stretching (first overtone) aromatic skeletal sue to lignin
13	6287	O–H stretching (first overtone) crystalline regions in cellulose
14	6450	O–H stretching crystalline regions in cellulose
15	6722	O–H stretching semi-crystalline regions in cellulose
16	6785	O–H stretching amorphous and crystalline regions in cellulose
17	7008	O–H stretching amorphous regions in cellulose
18	7309	C–H stretching aliphatic
19	7418	C–H stretching aliphatic

NIR spectral data evaluation for process quality control

Understanding of the wood thermal degradation mechanisms, thermal treatment process modelling, resulting product quality prediction, and production quality control are of great importance for both research and industry. Several analytical techniques and scientific methods were adopted for that purpose, with near infrared spectroscopy being a promising alternative (Willems *et al*. 2015; Candelier *et al*. 2016).

For the needs of this research, principal component analysis (PCA), identity test (IT), and partial least squares (PLS) were applied.

Principle components analysis is a powerful method for the de-correlation of highly correlated data, and to reduce the multidimensional data set to lower dimensions. It searches for unique properties of signals (spectra) and separates sets of input data into groups of peculiar similarities. The measure of the geometrical overlap of such groups is the selectivity coefficient (*S*) calculated as follows (Eq. 3),

$$S = \frac{D}{T_1 + T_2} \quad (3)$$

where D is the distance between the average spectra, and T_1 and T_2 are the threshold values computed for compared groups 1 and 2, thus indicating the group homogeneity. Accordingly, selectivity $S < 1$ means that both groups are overlapping, $S = 1$ signifies that clusters are in contact, and $S > 1$ indicates both clusters being separated.

The identity test is a statistical method used for the determination of the affinity of unknown spectra/sample. The algorithm compares the unidentified spectrum with other reference spectra having a well-defined source. The result is the spectral distance, called hit quality (*HQ*). A smaller spectral distance indicates a better spectra match. Therefore, the *HQ* for identical spectra is equal to zero. The resulting *HQ* of each comparison is weighted against the threshold *Tr*. The threshold is an indicator assuring the proper spectra identification and is related to the scatter of the source data used for setting the identity test. As a result of the identity test there are three possibilities of unknown spectra identification (Opus Spectroscopy Software 2006):

- Case 1: the spectra is identified as one of the modelled classes (*HQ* < *Tr* for one class)
- Case 2: the spectra is identified as none of the modelled classes (*HQ* > *Tr* for all classes)
- Case 3: the spectra is identified as probably belonging to more than one modelled classes, therefore not unique identification is possible (*HQ* < *Tr* for more than one class).

Partial Least Squares is a common chemometric technique allowing the quantitative prediction of sample properties on the basis of NIR spectra. The method requires an intensive calibration where spectra are regressed against the set of reference variables to be predicted. It is extremely important to validate the PLS model after calibration. Depending on the number of available samples/cases, two validation strategies are possible: cross-validation or test-set validation. The second approach was implemented in this research, assuming 67% of measured spectra were used for calibration and 33% were for validation.

The coefficient of determination (R^2), the root-mean square error of prediction (*RMSEP*), and the ratio of standard error of prediction to sample standard deviation (*RPD*) are indicators of the PLS model quality. A high value of R^2 and small value of *RMSEP* indicates excellent PLS models. An *RPD* > 2.5 means that the models are suitable for screening, an *RPD* > 5.0 for quality control, and an *RPD* > 8.0 for applied research (AACC 1999).

RESULTS AND DISCUSSION

Mass Loss

The *ML* reflects the thermal modification process intensity and also the resulting material properties. The *ML* varied from 0% (batch #27: T = 150 °C, t = 1 h, p = 250 mbar) to 48% (batch #11: T = 240 °C, t = 22 h, p = 250 mbar). As expected, *ML* depended mainly on T and t. Different coupled process parameters of T and t gave the same *ML*. For example, an equivalent *ML* of ~8% could be achieved with 212 °C and 2.2 h or with 220 °C and 1.1 h. Surprisingly, p had no real influence on. The change in *ML* as a function of T and t can be modelled by means of a 3D regression function (Eq. 4) and is shown in Fig. 1. The shape of the function revealed the characteristic asymptotic dependence for treatment time t and the exponential dependence upon the treatment temperature T,

$$ML(T,t) = \left(a - b \cdot c^{t}\right) \cdot \left(\exp\frac{T - T_{cr}}{k} - 1\right) \quad (4)$$

where a, b, c and k are function parameters and T_{cr} is the critical temperature at which the mass loss starts to occur.

The function optimized parameters (r^2 = 0.98) for p = 250 mbar were a = 0.039, b = -0.033, c = 0.962, and k = 33. The estimated T_{cr} was 140 °C.

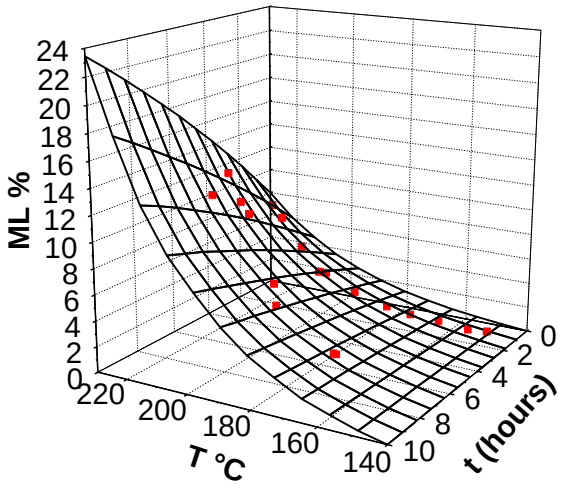

Fig. 1. 3D model regressing mass loss *ML vs.* treatment temperature (*T*) and time (*t*) (note: red points corresponds to experimental data)

It should be emphasized that *ML* is commonly accepted as a main indicator quantifying the thermal treatment process intensity (Willems *et al.* 2015). For practical reasons, all the following statistical models are referred to *ML* and not to the primary processes parameters (*T* and *t*).

Colour

As expected, the heat treatment process affected wood colour by uniformly darkening the sample volume. The absolute values of corresponding ΔL^* and ΔE^* were similar in each batch, indicating that the greatest part of the colour variation was caused by lightness loss. Similar results were reported by Gonzáles-Peña and Hale (2009), Salca *et al.* (2016), and Bekhta and Niemz (2003). The relationship between ΔL^* and *ML* is plotted in Fig. 2a. The darkening trend of the wood at increasing *ML* was similar to the trend reported by Ferrari *et al.* (2013) for other species. The regression model of $\Delta L^* = f(ML)$ for thermally modified polar veneers is presented in Eq. 5. The set of optimal values of constants that fit to the experimented samples as determined numerically were $a = 62$, $k = 0.034$, and $y_0 = -1$.

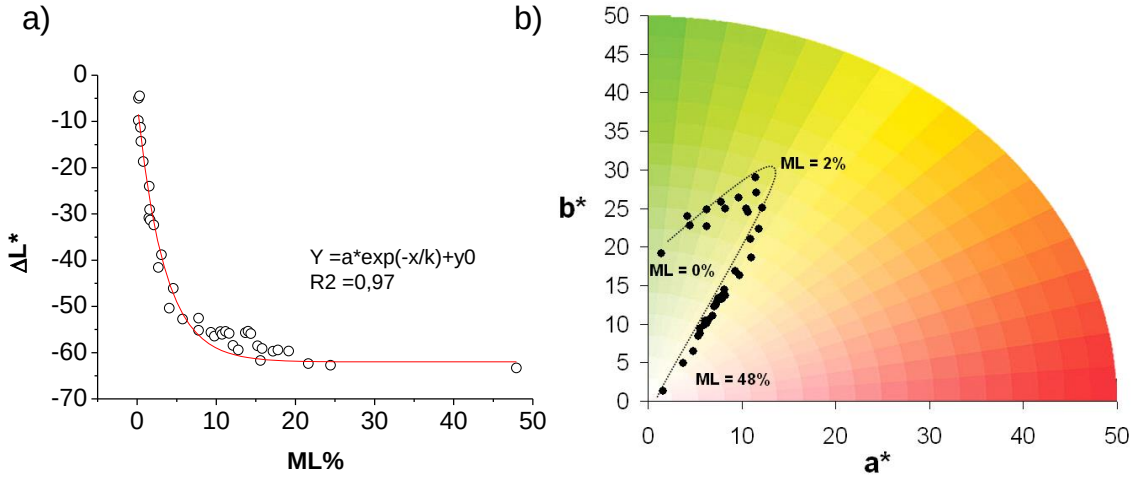

Fig. 2. The relation between colour change *CIE ΔL** and mass loss *ML* of thermally modified poplar veneers (a) and progress of colour coordinates *CIE a** and *CIE b** changes along the mass loss increase (b)

$$CIE\Delta L^*(ML) = a \cdot \exp\left(\frac{-ML}{k}\right) + y_0 \quad (5)$$

Even if the greatest part of the colour change was due to ΔL^*, the trend of colour coordinates a^* and b^* followed a specific pattern, as shown in Fig. 2b. The hue (*h*) (Eq. 6) decreased along the *ML* increase, indicating that the colour turns from yellow to red. The saturation C^* (colour intensity, as expressed in Eq. 7) increased with *ML* and reached a peak at *ML* = ~2 (Fig. 3), and subsequently continuously decreased.

$$h = \arctan\left(\frac{b^*}{a^*}\right) \quad (6)$$

$$C^* = \sqrt{CIEa^{*2} + CIEb^{*2}} \quad (7)$$

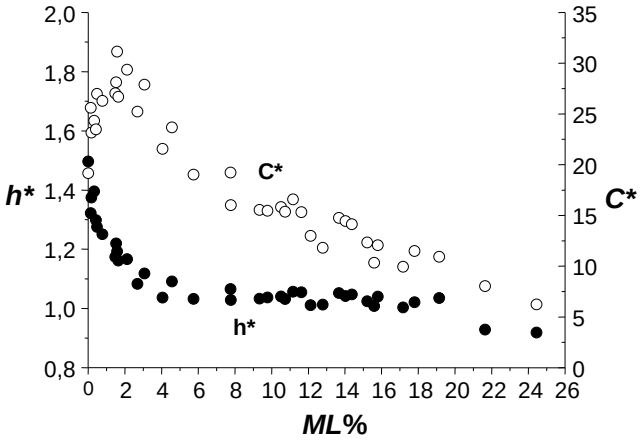

Fig. 3. Changes to hue (h^*) and colour saturation (C^*) with the progress of the *ML*

This turning point occurred in a *T* range between 190 and 210 °C. An analogous trend was previously observed for rubberwood and silver oak treated in a vacuum at 480 mbar in the range of *T* = 210 to 240 °C and *t* = 1 to 8 h, by Srinivas and Pandey (2012) and by Schnabel *et al.* (2007). Heat treatments of low and medium intensities increased the *a** value. The *a** value remained unchanged using a heat treatment of strong intensity. The *b** value increased slightly due to low heat treatment, and when high temperatures were applied the *b** value decreased.

Mechanical Properties

The *MOR* of the treated samples varied in the range between 37 and 65 MPa. Therefore, the reduction of mechanical resistance due to the thermal modification as related to the untreated sample (*MOR* = 62 MPa) reached 70% in the worst case.

The *MOR* was more correlated with the wood density ρ (r^2 = 0.7) than with the *ML* (r^2 = 0.58), as shown in Fig. 4.

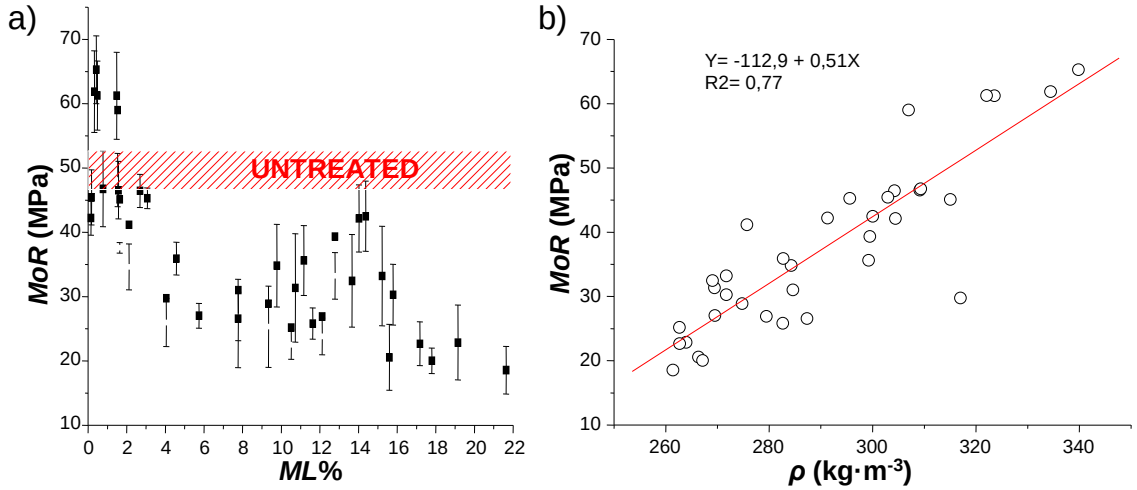

Fig. 4. The relationship between mechanical strength *MOR* and mass loss *ML* (a), and *MOR* and density ρ (kg/m^3) (b), of poplar wood samples treated thermally

The direct correlation between ρ and *ML* was weak (r^2 = 0.53). For that reason, a multiple regression model (Eq. 8) demonstrated the best relationship between the mechanical properties of modified wood *MOR vs.* its density and *ML*. The optimal values of the constants for the investigated samples were a = -84.54, b = 390.9, and c = -2.723, with the determination coefficient of the model r^2 = 0.81.

$$MOR(\rho, ML) = a + b \cdot \rho + \ln(ML) \quad (8)$$

Equilibrium Moisture Content

The *EMC* of the thermally modified wood ranged from 5.1% to 9.8%, while the *EMC* of untreated wood was 11.2% ± 0.7%. The extent of such reduction depends on the treatment temperature and time. A decrease in the *EMC* is related to the chemical modifications (and degradation) of wooden polymers.

Exposure of wood to sufficiently high temperature leads to a reduced *EMC* that is mainly attributed to the chemical changes of hemicelluloses (Willems 2015). Previous experiments on the thermo-hydro treatment of birch veneers showed that increased process temperature and time resulted in hydrophobization of veneers, as indicated by decreasing *EMC* and increasing contact angle values (Grinins *et al.* 2016). Decreasing the moisture uptake was linked to the drop of water storage capacity in modified wood (Bak and Németh 2012). This was an effect of the reduction of the accessibility of the hydroxyl groups of wood carbohydrates, the degradation of hemicelluloses, and their conversion to less hygroscopic furan-based polymers, as well as polycondensation and crosslinking of lignin (Sandberg *et al*. 2013)

Hence, the change of the moisture content (ΔEMC) closely correlated with *ML* as shown in Fig. 5. The relationship can be expressed as an exponential function (Eq. 9), where optimal values of the constants determined on the base of experimental results are a = 0.370 and k = 0.027.

$$EMC = a \cdot \exp\left(\frac{-ML}{k}\right) + y_0 \quad (9)$$

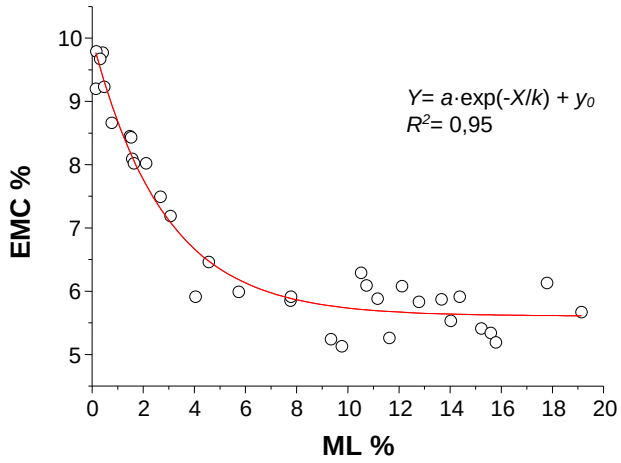

Fig. 5. The relationship between EMC and ML due to the thermal treatment of poplar wood veneers

FT-NIR Spectroscopy

Figure 6 presents part of the second derivative of an averaged near infrared spectra as measured on the surface of veneers treated in both mild (150 to 210 °C) and higher temperatures (> 210 °C). The variation in absorption was clearly associated with the treatment temperature.

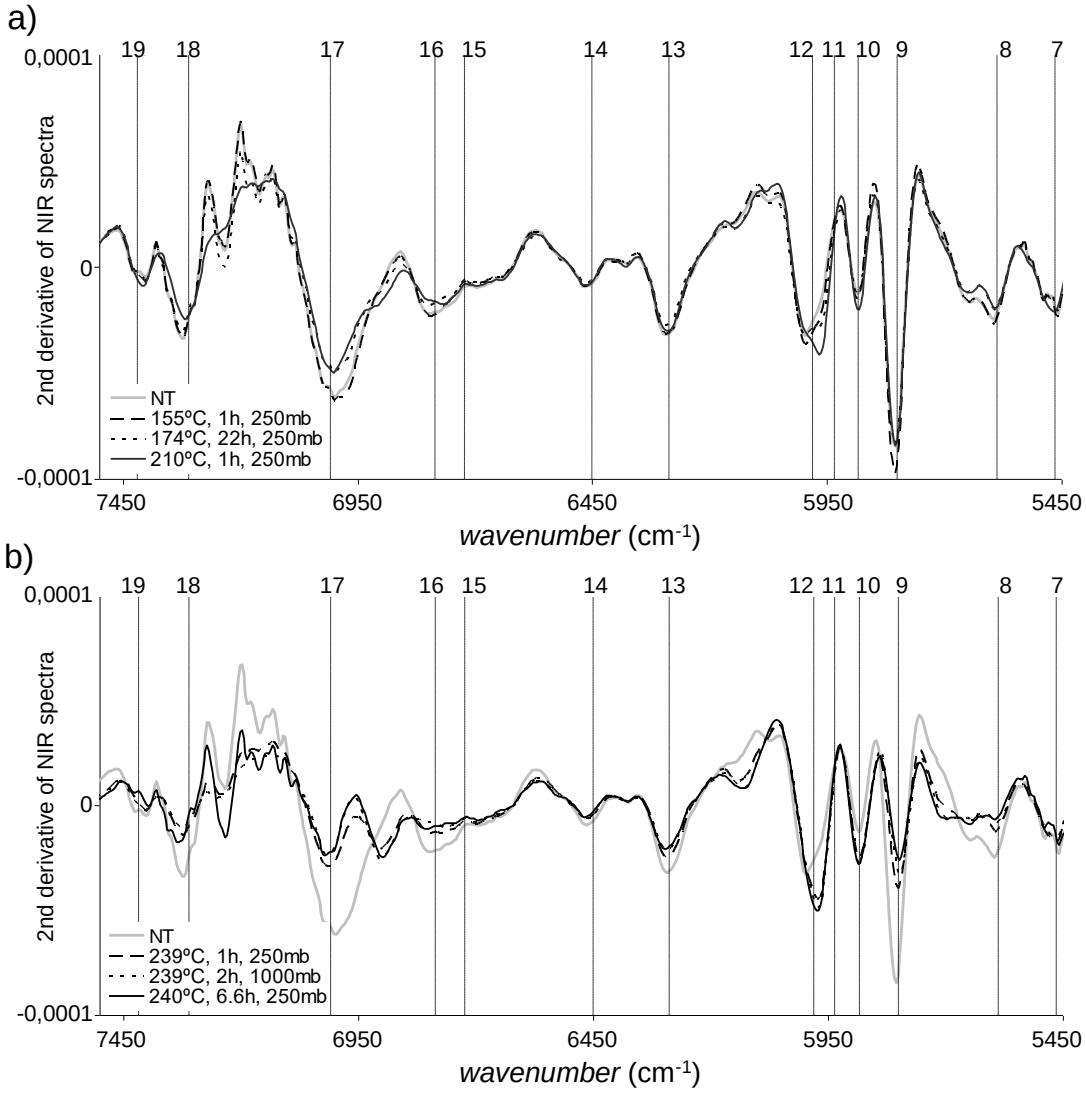

Fig. 6. The second derivative of the NIR spectra of veneers treated at mild (a) and high temperatures (b)

Relatively low temperatures affected amorphous carbohydrates (band 17) and, with the increase in temperature, the degradation of crystalline cellulose was more evident (bands 13 and 16). Mild treatment (155 °C, 1 h in 250 mbar) of batch #26 barely affected chemical properties of the veneers, apart from a slight change in their hygroscopic properties (changes to band 6 related to O–H stretching plus O–H deformation in water [spectra not shown]). The combination of chemical constituent degradation (mainly hemicelluloses) and the migration/removal of extractives, low molecular weight sugars, and aminoacids, is associated with the colour changes of thermally treated wood (Akgül and Korkut 2012).

Figure 7 presents an example of PCA performed on the NIR spectra of veneers treated with various process parameters. All groups were clearly separated; even those untreated samples are clustered close to samples treated with relatively low intensity (batches #27 and #24), as shown in Fig. 7a. Both treatments were performed for only 1 h at mild temperatures of 149 °C and 174 °C, respectively. Veneers treated at slightly higher temperatures (174 °C and 175 °C from batches #9 and #36) were clustered close to each other. The difference between both treatments was their durations corresponding to 22 and 12 h, respectively. Samples from the batch #6 (150 °C at the long treatment time of 12 h) were also well separated, indicating chemical differentiation due to thermal treatment.

A similar analysis was performed on batches with high temperatures (Fig. 7b). In this case, spectra of most batches were evidently separated. Only veneers from batch #22, even if treated at the high temperature T = 193 °C, appeared close to the non-treated wood cluster. The wood was, however, treated only for a short time (1 h). It was therefore assumed that the chemical composition did not change noticeably, which was then confirmed by a relatively low mass loss (1%) of batch #22.

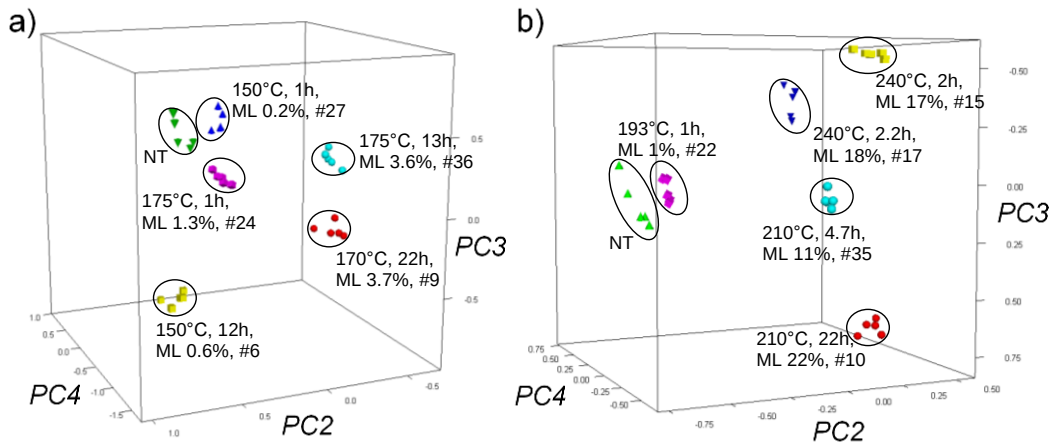

Fig. 7. Principal components analysis performed on the NIR spectra: batches with mild temperature treatments (a), and batches with high temperature treatments (b)

Quality Control Approach for Thermo-Vacuum Production of Poplar Veneers

Evaluation of the NIR spectra as well as PCA allowed direct comparison of the effects of varying thermal treatment process parameters on the material properties and chemical composition of poplar veneers. It was evident that such changes were recorded in the near infrared spectrum and might be linked to the product quality. A series of tools were therefore developed for the assessment of the thermo-vacuum process by means of NIR spectroscopy.

Selectivity test

The analysis of selectivity indexes can be applied for quantifying direct geometrical overlap of the sample groups.

Table 3 presents an example of selectivity indexes S calculated for thermally treated veneers at both mild and high temperatures.

Table 3. Selectivity Index Calculated on the Basis of Principal Components Presented in Fig. 7

	Mild Treatment Temperature							High Treatment Temperature						
***T* (°C)**		150	175	170	150	170			193	210	240	210	240
***t* (hours)**		1	1	13	12	22			1	4.07	2.02	22	2
***p* (mbar)**		250	250	250	250	250			250	100	250	250	100
batch	**NT**	**#27**	**#24**	**#36**	**#6**	**#9**		**NT**	**#22**	**#35**	**#17**	**#10**	**#15**
NT	-	**0.76**	1.05	1.33	1.49	1.99	**NT**	-	**0.58**	2.08	3.02	4.18	4.40
#27	**0.76**	-	1.45	1.28	2.90	3.14	**#22**	**0.58**	-	0.15	0.17	≥5	≥5
#24	1.05	1.45	-	1.57	1.32	2.84	**#35**	2.08	0.15	-	0.13	≥5	≥5
#36	1.33	1.28	1.57	-	2.64	1.42	**#17**	3.02	4.06	0.13	-	4.28	1.14
#6	1.79	2.90	2.32	2.64	-	2.85	**#10**	4.18	≥5	≥5	4.28	-	≥5
#9	1.99	3.14	2.84	1.42	2.85	-	**#15**	4.40	≥5	≥5	1.14	≥5	-

There was a clear statistical separation between clusters in almost all presented cases because $S > 1$. The unique exception was the overlapping of samples #27 (for mild temperature treatments) and #22 (for high temperature treatments) with non-treated samples. In both cases thermal treatment was applied for only 1 h and apparently did not noticeably affect the chemical composition of the wood.

Identity test

The practical use of the selectivity test might be in the application of previously developed models for the discrimination of veneer samples with unknown treatment history. The averaged spectrum of the veneers from the two batches #32 and #6 were assumed as unknown samples and were compared with the reference batches defined within the identity test. In the case of #32, the spectra were not recognized as belonging to any of the reference batches and therefore no classification was possible ($HQ > Tr$ for all reference groups). Nevertheless, the NIR spectra of samples from batch #6 were correctly classified ($HQ < Tr$) and identified as "batch #6".

Partial Least Squares

Partial least squares are a suitable numerical tool for the development of quantitative models that has good predictive power while reducing noise and maximizing extracted information (Danvind 2002). Thus PLS are often used for the computation of regressions linking near infrared spectra and reference values corresponding to different wood properties. Prediction models of the *ML* and *EMC* were developed within this research to enable the NIR system to directly predict treated material properties and to assure optimal product quality. Reference values for both properties were implemented in the chemometric software toolbox. High values of the determination coefficients ($R^2 > 0.96$ and $R^2 > 0.97$ for *EMC* and *ML*, respectively) as well as $RPD = 5.18$ for *EMC* and $RPD = 9.12$ for *ML*, confirmed the superior performance of the PLS models. Figure 8 presents the regression of the predicted *versus* the measured values of *ML* and *EMC*. Prediction errors of validation models based on NIR spectra were relatively small: $RMSEP_{ML} = 0.97\%$ and $RMSEP_{EMC} = 0.30\%$. NIR was therefore confirmed as an effective technique capable of predicting wood physical properties *ML* and *EMC*, both considered the most reliable indicators of the modified wood quality.

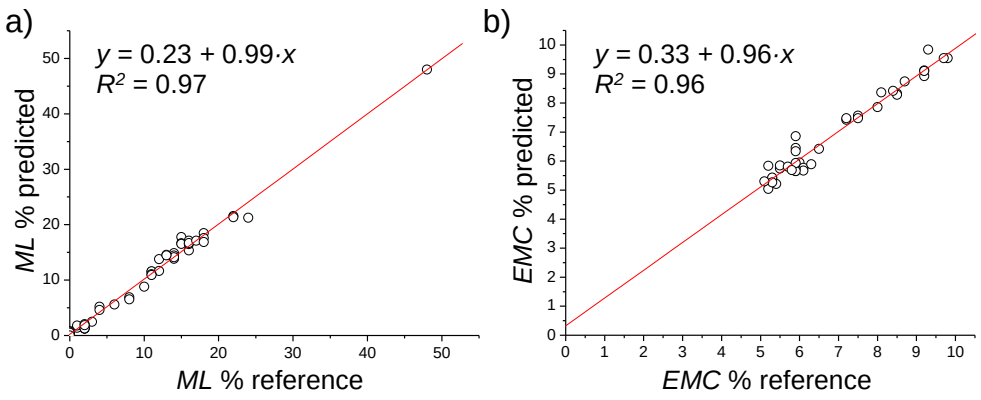

Fig. 8. NIR predicted *versus* measured values of *ML* (a) and *EMC* (b) of thermally modified veneers

CONCLUSIONS

1. Thermal treatment under vacuum conditions was tested as an innovative process for up-grading value and technological properties of the important wood species - poplar. Treated veneers differed noticeably depending on the thermal modification conditions and the process intensity.
2. The balanced combination of the process parameters enabled the production of modified poplar veneers with mild degradation, improved hygroscopic and stability properties, and controlled colour change.
3. The darkening of poplar veneers and reduction of poplar's mechanical strength was observed when increasing the treatment time and increasing process intensity. Mass loss was closely correlated, with the decrease of equilibrium moisture content being a result of chemical changes in wooden polymers.
4. Multivariate data analysis and chemometric modelling of near infrared spectra were proposed for evaluating the effects of treatment process parameters on the selected properties of poplar veneers. They allowed the understanding of the process mechanism as well as degradation kinetics and might be used for the selection and monitoring of optimal process parameters.
5. As a fast and non-destructive technique, NIR was effectively used to predict mass loss and equilibrium moisture content, both of which are considered the most reliable indicators of the wood modification advancement. Prediction errors of PLS models based on FT-NIR spectra were relatively small, 0.97% and 0.30% in case of ML and EMC, respectively. The corresponding coefficients of determination were $R^2 > 0.96$ in both cases.
6. Preliminary results supported the assumption that presented PLS models were suitable for the quality control of thermally treated veneers by vacuum system.

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