Thermal modification of poplar veneers in vacuum conditions

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ABSTRACT

Poplar wood has the potential to be used for many purposes, since is one of the most economical species, ease to process, has low density and uniform light colour. However one of the main problems noticed during industrial manufacturing and further use of the derived products is the high hygroscopicity of the material. Vacuum thermal treatment is proposed here for improvement of dimensional stability, decrease of hygroscopicity and colour changing of poplar veneers used for plywood manufacturing.

38 batch processes with a range of treatment conditions were performed. Samples were characterized considering their appearance (colour), physical (mass loss and equilibrium moisture content) and chemical properties (near infrared spectra). All measured veneers characteristics differ with the thermal modification process, even if trends and kinetics of changes varied between parameters. Selected chemometric techniques: Principal Component Analysis (PCA) and Partial Least Squares (PLS) were used for data evaluation. PCA allowed direct comparison of the effect of process parameters on chemical composition of poplar veneers. PLS prove potential of near infrared spectroscopy for development of robust prediction models for mass loss and equilibrium moisture content. Such methodology might be helpful for development of on-line process control and for further optimization of the thermal treatment of poplar veneers at industrial scale.

INTRODUCTION

Poplar is a fast growing species, widespread in plantations with rotation period of 5 to 20 years, economically important for several industrial and ecological purposes. In Europe poplar plantations cover about 940.000 hectares and approximately 90% of their production is used for manufacturing of plywood, sawn timber, pulpwood, fuelwood and biomass for energy (Nervo *et al*. 2011). One of the main problems noticed during industrial manufacturing and further use of the derived products is the high hygroscopicity of the wood material. Poplar plywood tends to deform with the adsorption of moisture (Murata *et al*. 2013).

Thermally modified wood (TMW) is an example of wooden products that follow the trend of substitution of traditional resources with novel of improved characteristics. According to CEN/TS 15679:2007 TMW is defined as a timber in which the chemical composition of constitutive woody polymers and wood physical properties are modified by the exposure to high temperatures (usually from 160 to 230°C) in conditions of reduced oxygen availability. Wood modified in that way possesses superior durability against decay and weathering, enhanced dimensional stability, constant colour, reduced thermal conductivity and lowered equilibrium moisture content.

Several researchers reported the advantages of thermal treatment of veneers used for improvement of dimensional stability, decrease of their hygroscopicity and colour changing (Bak and Németh 2012, Zdravković *et al*. 2013, Lovrić *et al*. 2014, Goli *et al*. 2015). However wooden surfaces exposed to high temperature can experience surface inactivation and consequently can cause adhesion problems during plywood manufacturing (Ayrilmis and Winandy 2009). The thermo-vacuum process is an alternative technology for thermal modification of wood where reduction of oxygen concentration inside the reactor, necessary to avoid wood combustion, is obtained by applying vacuum. Absence of volatiles and water vapour being the result of their continuous removal by vacuum pump, ensures a lower rate of wood mass loss (ML), assures high energy efficiency, less corrosion and lower reduction of mechanical properties comparing to alternative treatment technologies (Allegretti *at al*. 2012).

Fourier Transform Near Infrared Spectroscopy (FT-NIR) is a technique capable of 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). Spectroscopy often serves for development of Partial Least Squares (PLS) models based on NIR spectra for indicators of thermal modification advancement: mass loss (ML) and equilibrium moisture content (EMC). Promising results obtained previously by Esteves and Pereira 2008 and Sandak *et al*. 2015 suggest possibility of spectroscopy utilisation for quality control of thermally treated wood.

The research presented here is an attempt for detailed characterization and evaluation of poplar veneers modified in vacuum conditions. The goal of this work was to evaluate the influence of temperatures, time and pressure on principal indicators of thermal modification process such as ML and EMC of investigated material. The other scope was to develop PLS models that might be used for quality control of treated veneers in industrial scale production.

EXPERIMENTAL

Samples preparation

Rotary-cut veneer sheets of Poplar clone 'I-214' (*Populus ×canadensis* Moench) were used for preparation of experimental samples. One sheet of plywood was prepared for each treatment. The veneers were cut to dimensions 360 mm x 150 mm x 2.5 mm and were characterized both before and after vacuum thermal treatment.

Thermal treatment

The thermal treatment has been performed in prototype plant described previously by Sandak *et al*. (2015). Aluminium plates heated electrically which produce a heating of the conducting type were used. Heating and cooling ramp were kept constant at 60°C/h. The ventilation was disabled so that the test chamber only acts as a sealing system of the vacuum. Each modification process consists of three phases; 1) wood drying, 2) thermal treatment and 3) wood conditioning. In one case (batch #31) the process after reaching the maximum temperature was stopped and the thermal treatment phase was omitted. The treatment time value, presented in Table 1, is equal to 0 in this case. Experimental set-up and example of samples are presented on Figure 1.

a) b)

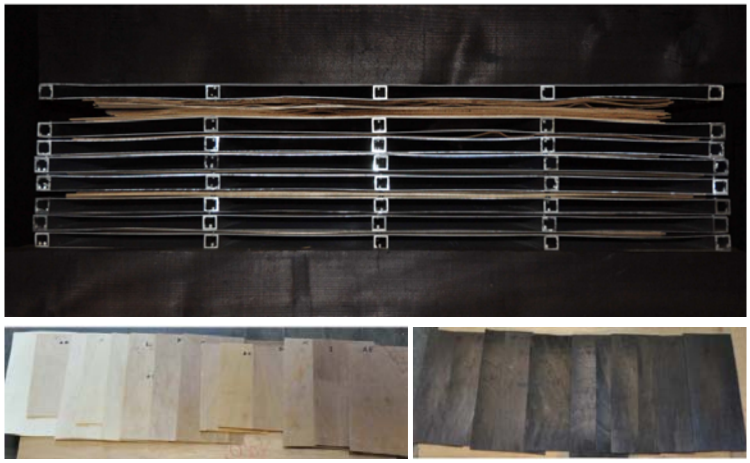

Figure 1: Veneers treatment set-up (a) and experimental samples after thermal treatment (b)

Totally 38 batch processes with various treatment conditions (temperature ranging from 150°C to 240°C, pressure: 100, 250 or 1000 mbar and duration from 0.5 to 22.5 hours) were performed (Table 1).

Table 1: Combinations of the performed tests

batch number	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**#10**	**#11**	**#12**	**#13**
T max [ºC]	240	238	238	238	195	150	174	192	174	213	240	253	239
time [hours]	1.5	1.5	1.5	1.5	6.1	12.4	6.4	22.2	22.5	22.2	22.3	1.1	1
pressure [mbar]	1000	250	100	1000	1000	250	1000	250	250	250	250	250	1000
batch number	**#14**	**#15**	**#16**	**#17**	**#18**	**#19**	**#20**	**#21**	**#22**	**#23**	**#24**	**#25**	**#26**
T max [ºC]	239	239	238	241	239	239	212	203	194	182	174	165	155
time [hours]	0.5	2.12	0.24	2.22	1.07	0.5	1.08	1.1	1.07	1.07	1.07	1.07	1.07
pressure [mbar]	1000	1000	1000	250	250	250	250	250	250	250	250	250	250
batch number	**#27**	**#28**	**#29**	**#30**	**#31**	**#32**	**#33**	**#34**	**#35**	**#36**	**#37**	**#38**	
T max [ºC]	149	223	213	213	211	213	194	173	214	175	240	217	
time [hours]	1.07	1.07	2.24	4.3	0	6.42	6.1	6.4	4.7	12.9	6.6	4.8	
pressure [mbar]	250	250	250	250	250	250	250	250	100	250	250	1000	

Samples characterization

The resulting material was analyzed before and after each treatment in order to determine the modifications rate on physical/chemical wood properties induced by the process.

Physical properties

Mass loss (ML) was determined by weighting each sample before the treatment and immediately after it, assuring the wood was absolutely dry (0% moisture content). The Equilibrium Moisture Content (EMC) was calculated according to the ISO 3130 standard for treated and untreated samples.

Colour measurement

MicroFlash 200D spectrophotometer (DataColor Int), suitable for direct determination of the CIE L*a*b* colour coordinates was used for the measurement over an 18 mm diameter spot with a standard light source D65 and an observation angle of 10°.
Each sample has been measured in 10 zones. The standard deviation of such measurement was considered as an indicator of the instrument reliability and texture variability of the material.

NIR measurement

Fourier transform near infrared spectrometer VECTOR 22-N (Bruker Optics GmbH, Ettlingen, Germany) equipped with the fibre-optic probe was used for spectra collection. The spectral range measured was between 4000cm^{-1} and 12000cm^{-1}. The spectral resolution of the spectrometer was set to 8cm^{-1}. The spectral wave number interval was 3.85 cm^{-1} with zero-filling = 2. Each spectrum has been computed as an average of 32 successive scans in order to minimize the measurement error. FT-NIR measurements were performed in air-conditioned laboratory (20°C, 65%RH), five times on each sample. OPUS 7.0 (Bruker Optics GmBH), software was used for spectra collection, pre-processing and data mining. QUANT2 module was applied for chemometric data evaluation.

RESULTS AND DISCUSSION

As expected, heat treatment affected the wood colour; the wood becomes darker uniformly all over the piece. Figure 2 present changes to lightness of samples treated in similar conditions (≈ 210ºC and 250mbar) for various periods (up to 22 hours). It is clearly visible that the drop of L* is correlated with thermal treatment duration. Only samples from batches #29 and #30, which were treated for 2.2 and 4.3 hours have similar ΔL. Analogous trend are also present for other treatments configurations. The changes of colour are due to combination of degradation of chemical constituents (mainly hemicelluloses) and migration or removal of extractives, low molecular weight sugars and aminoacids (Akgül and Korkut 2012).

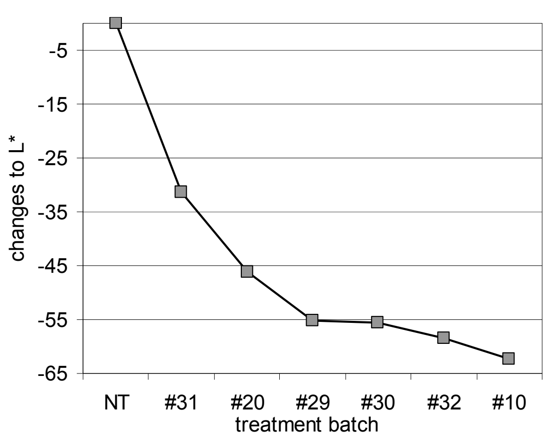

Figure 2: Changes of L* of veneers treated in ≈ 210ºC and 250mbar for different time duration

Treated wood has significantly lower EMC compare to untreated wood. Decreasing of the moisture uptake is due to the decreasing of its water storage capacity (Bak and Németh 2012). It is an effect of reduction of accessibility of hydroxyl groups of wood carbohydrates, degradation of hemicelluloses and their conversion to less hygroscopic

furan-based polymers and polycondensation and crosslinking of lignin (Sandberg *et al*. 2013). The EMC decrease depends on the treatment temperature time and pressure. Thermal treatment influence also mass loss, which according to Ferrari *et al*. 2013 may be a reliable indicator of the wood modification advancement. ML is closely correlated with decrease of EMC and leads to reduction of wood density. It is a result of polymers degradation and its evaporation during the heat treatment process. The mass losses in investigated samples vary from 0% (in case of veneers treated in 150°C for 1 hour, 250 mbar) to 48% in case of long treatment (22h) in high temperature (240°C) and 250 mbar. Same treatment parameters (240°C, 250 mbar) but shorter time (6,6h) resulted 24% of mass loss. Similar effect (22% of ML) was obtained in slightly lower temperature (213°C), however with longer treatment (22h).
Figure 3 presents an example of Principal Component Analysis performed on NIR spectra of veneers treated with various process parameters. It is clearly visible that all groups are clearly separated; however, untreated samples are cluster close to samples treated in relatively low temperature (batch #26). This group includes also samples after low temperature treatment, however conducted for long period (batch #9, 22h). Veneers treated in temperature above 200ºC are clustered together with exception of veneers treated in 240ºC for 6.6 hours (batch #37). PCA allowed in this case direct comparison of the effect of process parameters on chemical composition of poplar veneers.

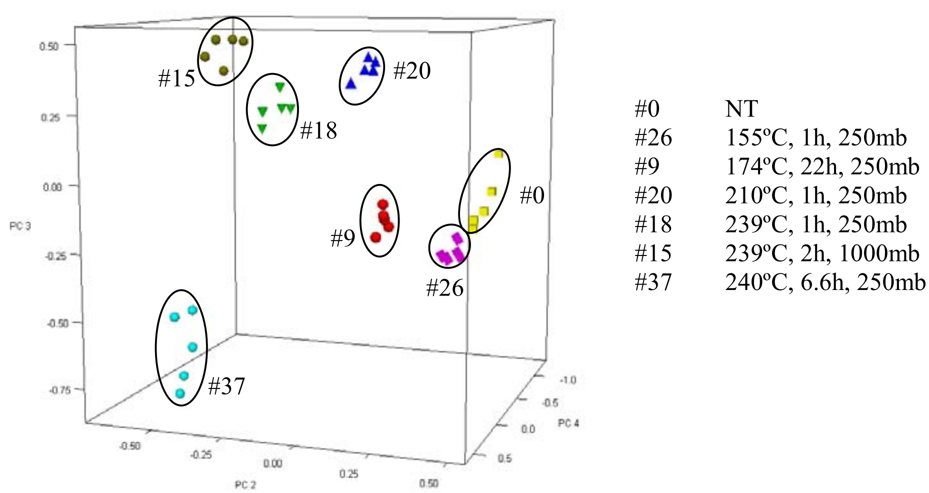

Figure 3: Example of PCA analysis performed on NIR spectra

Partial Least Squares (PLS) can be used to create models with good predictive power, avoiding noise and maximising information (Danvind 2002), therefore are often used for computation of regression models linking near infrared spectra and reference values corresponding to diverse wood properties. Prediction models of the ML and EMC were developed within this research. Mass loss and equilibrium moisture content values were implemented in to the QUANT2 software module as the reference variables. Each model was characterized by the coefficient of determination (R^2), root mean square error of cross-validation (*RMSECV*), residual prediction deviation (*RPD*), bias (the average difference between the instrumentally measured values and the reference values) and rank (number of principal components used). High values of the determination coefficients ($R^2 > 0.96$ for both parameters) and *RPD* = 5.15 for ML and *RPD* = 5.26 for EMC respectively, confirm superior performance of the PLS (Alves *et al.* 2012). Figure 4 presents regression of the predicted versus measured values of ML.

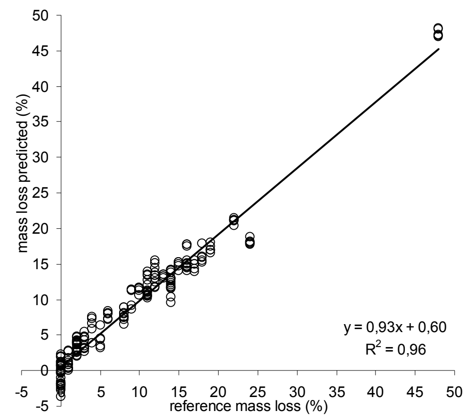

Figure 4: PLS predicted versus measured values of ML of thermally modified veneers.

CONCLUSIONS

Accurate characterization of the final product quality after wood thermal treatment is still of a great concern for both producers and consumers. All measured veneers characteristics differ with the thermal modification process, even if trends and kinetics of changes varied among parameters. Multivariate data analysis and chemometric modelling allowed understanding of the process mechanism and its kinetics and might be used for selection of optimal process parameters. NIR as a fast and non-destructive technique was effectively used to predict selected wood physical properties, considered as reliable indicators of the wood modification advancement. Prediction errors of validation models based on FT-NIR spectra were relatively small (1.8% and 0.29% in case of ML and EMC respectively). The corresponding coefficients of determination were $R^2 > 0.96$ in both cases. Preliminary results support the assumption that PLS model of NIR spectra are suitable for quality control of vacuum thermally treated veneers and might be used at industrial scale in case of further implementation toward on-line process control.

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