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AUTOADHESION OF LAMINATED BOARDS FROM SCOTS PINE VENEERS: EFFECT OF OXIDATIVE PRETREATMENT

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Abstract

This paper presents results from studies on the pre-treatment of veneers from Scots pine using hydrogen peroxide and a ferrous catalyst followed by pressing at 220, 230, and 240°C. The treatment gave boards that did not delaminate when exposed to water followed by drying of room temperature, whereas boards without a pre-treatment delaminated. The press-plate temperature did not influence the extent of delamination, but the thickness swelling was lower at higher press temperature. Analysis of extracts from the oxidative pre-treated and hot-pressed surface material using UV-spectroscopy was compared with analysis of bondlines from water-stable laminated boards from beech.

Key words: *delamination; extractives; LVL; hot-pressing; hydrogen peroxide; water stability.*

INTRODUCTION

European regulations regarding formaldehyde containing adhesives used in wood boards make it interesting to develop alterrnative bonding methods in such products. It is well known that wet conditions can be used for manufacturing hardboards such as Masonite-board without or with only small amounts of adhesive. However, to be able to form boards under drier conditions without adhesives, activation or stronger pressing conditions may be necessary. Technologies for self-bonding veneer without any binder or chemical activation prior to pressing were introduced in Germany in the 1940s by Runkel and Jost (1948) and in the US by Boehm (1951). A method has been developed in our laboratory to produce self-bonded laminated boards from beech veneers at lower moisture contents by pressing at temperatures higher than 200°C (Cristescu et al. 2006, 2008), and properties such as the shear strength of the board were strongly related to the temperature and pressure applied.

By treating wood with oxidants, it has been found that boards can be bounded without synthetic adhesives (Johns 1977, Stofko and Zavarin 1977). It was speculated that lignin was the main contributor to the auto-adhesion observed. Activation of lignin was the target when using peroxidases and other oxidases for the auto-adhesive bonding of wood fibres into boards (Felby et al. 1997, Kharazipour et al. 1998). Later, a method for producing boards from wood particles and fibres without using synthetic binders such as urea-formaldehyde was developed (Karlsson and Westermark 2002, Karlsson et al. 2006). The method involves the pre-treatment of wood particles or fibres using hydrogen peroxide and ferrous sulfate as catalyst under relatively dry conditions followed by hot pressing at temperatures of 170-200°C. This gave boards with a considerably greater resistance to swelling in water than without the pre-treatment. It was found that the leaching of treated wood particles with water left particles with almost no bondability when hot-pressed. Interestingly, the re-addition of leachate followed by drying to a suitable moisture content gave particles in which bondability was to a large extent recreated. This indicated that most of the bondability is related to the formation of extractives by the oxidative treatment and that long-lived bonding groups are more important for the formation of bonds in the material.

OBJECTIVE

Together with Norway spruce, Scots pine is the dominant softwood in the Nordic countries and there is a great interest in finding new applications for such materials. Preliminary results from the hot-pressing of veneers of softwood into laminated boards without adhesive suggests that bonds between the layers in such a product need to be improved, and the effect of pre-treating of veneers using hydrogen peroxide to produce self-bonded laminated boards from Scots pine has here been studied.

MATERIALS AND METHODS

Rotary-cut veneers with dimensions of 140x70x3.25mm (LxWxT) from Scots pine were treated by spraying an aqueous-solution of ferrous sulphate (0.1% odw) followed by 0.5% hydrogen peroxide. The veneers were conditioned at 20°C and 60% R_H (MC 10%), and two veneers were pressed with their treated sides against each other in a hot press. Press conditions for self-bonded laminated boards have been presented, and the conditions for forming board stable under dry conditions were chosen, based on results from pressing untreated veneers (Cristescu et al. 2015). Boards were pressed at 2.6MPa for 170s and finally at 0.5MPa for 30s. Press plate temperature of 220, 230, and 240°C were used and three boards of each condition, making a total of (3x3x2)=18 boards, were prepared.

A cycling test was carried out in which boards were immersed in water overnight and then dried to constant weight in a laboratory atmosphere. This procedure was repeated twice. The extent of delamination was evaluated and documented. The thickness reduction after hot pressing (TRP) was estimated. Thickness swelling (TS) and water uptake (WA) during 24h were determined, and the thickness increase after drying the samples which had been immersed in water for 24h (TIWD) was also determined. These values are calculated as:

$$TRP = \frac{T_{initial} - T_{dry}}{T_{initial}} \quad [\%] \tag{1}$$

$$TS = \frac{T_{wet} - T_{dry}}{T_{dry}} \quad [\%] \tag{2}$$

$$WA = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad [\%] \tag{4}$$

$$TIWD = \frac{T_{driedwet} - T_{dry}}{T_{dry}} \quad [\%] \tag{5}$$

where:
$T_{initial}$ - the total thickness of two veneers before pressing
T_{dry} - the thickness of the laminated board,
T_{wet} - the thickness of the laminated board after soaking in water for 24h
$T_{driedwet}$ - the thickness after drying of laminated board that had been soaked in water for 24h
m_{wet} - the mass of the water-soaked board
m_{dry} - the mass of board before soaking.

UV-spectrophotometry

50mg of isolated surface material was extracted with 2ml water using an ultrasonic bath for 1h. After centrifugation, 0.5ml of the solution was diluted with water in a 10ml flask. The remaining solution was dried and extracted with methanol in a similar manner. After dilution of 0.5ml of the methanol solution with water to 10ml, the solutions were analysed by UV-spectrophotometry.

The solution was treated with excess of $NaBH_4$ twice for two days and analysed.

UV-difference spectra were obtained from the neutral and an alkaline solution. 0.5ml of the extracts were diluted with water and 1M NaOH until pH 12 was reached in a volume of 10ml.

RESULTS AND DISCUSSION

Veneers of Scots pine were treated with or without hydrogen peroxide and ferrous catalyst and then hot-pressed at three press plate temperatures (220, 230 and 240°C).

Swelling and shrinking forces acting on the bond-line between the veneers under wet conditions were studied by immersing boards in water and then drying them in air. Most of the boards

without any oxidative pre-treatment were found to be unstable and to delaminate in water, and the board stability in water was not influenced by the press-plate temperature. It might be of interest to study whether more stable boards could be prepared by increasing press parameters such as the pressure and temperature.
Fig. 1 show boards where the bonding surfaces in the board were pre-treated with hydrogen peroxide and iron-catalyst before hot pressing, and most of the boards could withstand the forces acting during swelling and shrinking. In only a few cases was slight delamination noticed. The press-plate temperature had no great influence on the wet strength of the bond-line of the laminated boards, no change in delamination was observed after performing another two swelling-shrinking cycles.

220°C

230°C

240°C

240°C

Fig. 1.
Effect of swelling and drying of boards in which the veneers had been treated with hydrogen peroxide and ferrous sulphate catalyst before hot-pressing

The influence of press temperature on the interaction of water with boards from oxidative pre-treated veneers was further investigated. Water uptake in the board was found to decrease with increasing press-plate temperature (Table 1). The uptake of water also led to swelling of the material, but the thickness swelling was lower with a higher press temperature (Table 1). The increase in thickness after drying of wetted samples followed a similar pattern; with a higher press temperature, the residual thickness was smaller. The lower uptake of water and reduced swelling suggest that the water-resistant bonds between the wood components are more prominent after compression at higher temperatures. The lower swelling indicates that these bonds hinder the penetration of water into the board and into the wood cell wall.

Table 1

Swelling and water uptake of oxidised boards from Scots pine after hot pressing. Standard deviation in brackets

Press-plate temperature (°C)	Water uptake (%)	Thickness swelling (%)	Thickness increase after drying (%)
220	75.9 (2.1)	27.8 (1.4)	17.7 (1.3)
230	70.3 (7.0)	21.9 (3.1)	12.5 (4.1)
240	64.1 (4.0)	20.2 (2.3)	9.1 (2.4)

It is interesting to note that thickness reduction (TR) and density were fairly similar for the boards after pressing (Table 2) even though their stability in water was different as shown in Table 1.

Table 2

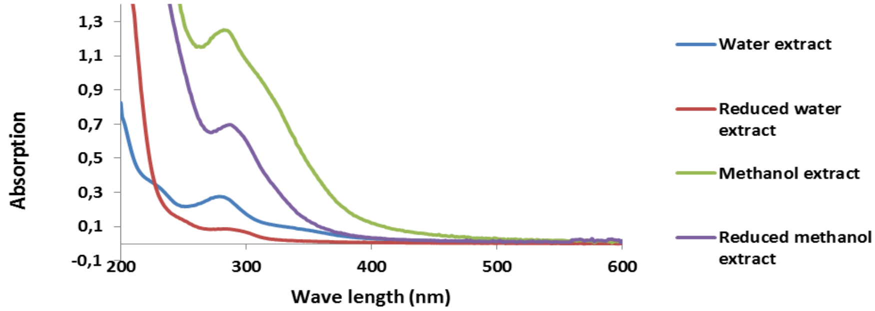
Thickness reduction (TR) in boards of Scots pine as a result of hot pressing. Standard deviation in brackets

Press plate temperature (°C)	Density after pressing (mm)		Thickness reduction (%)	
	Un-treated	Pre-treated	Un-treated	Pre-treated
220	777 (20)	741 (41)	39.9 (0.5)	39.6 (1.7)
230	743 (67)	741 (46)	38.3 (6.1)	40.2 (2,2)
240	792 (32)	743 (64)	40.8 (4.1)	41.7 (6.3)

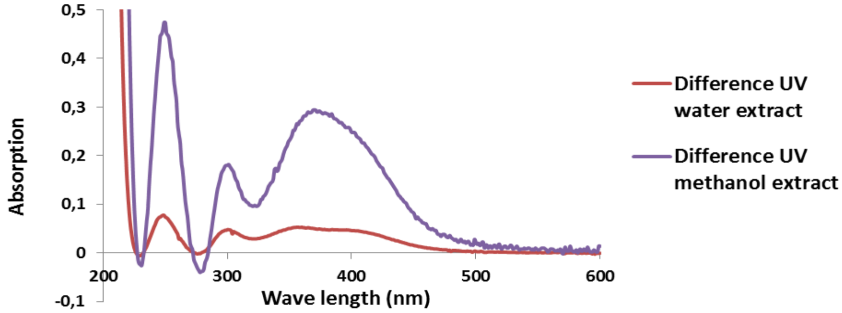
One sample has a much darker appearance than the other boards in Fig. 1 because its outer surface had also been treated with hydrogen peroxide and iron catalyst before hot-pressing. Scraping with a knife could remove this coloured and thin surface layer, and it was further extracted with water followed by methanol, as was reported in an earlier paper (Karlsson et al. 2012). The methanol fraction was more coloured than the fraction extracted in water, but coloured solid wood material remained after the extractions as was also reported when other thermally modified wood was extracted in a similar way (Karlsson et al. 2012). To investigate what the coloured material consist, possible precursors for such a coloured layer were sought in the water and methanol extracts.

The extracts were diluted with water 10 times and studied by UV-spectrometry. The UV-absorption at 280nm of the methanol solution was stronger than that of the aqueous solution (Fig. 2a). After reduction with sodium borohydride, the colour of the diluted extracts diminished. The treatment also led to a reduction in the UV-absorption at 280nm in the water extract by more than 50% (Fig. 2a). Aldehydes are reduced to alcohols by treatment with $NaBH_4$ and furfurals lose their absorption at 280nm. It is therefore likely that structures containing furfurals may contribute to the absorption at 280nm. Furfurals have been found in extracts from isolated bond-lines of laminated boards of beech (Cristescu and Karlsson 2013). A large reduction in the UV-absorption at 280nm was also observed when methanol extract was treated with sodium borohydride (Fig. 2a).

Difference UV-absorption spectra of alkaline and neutral solutions have been used to study phenols in industrial lignins (Wexler 1964). However, care should be taken as the specific absorption coefficients are not known in detail. Nevertheless, difference UV-absorption spectra for water and methanol indicated that the methanol extract contained more phenolic compounds (absorption at 250nm) than the aqueous extract (Fig. 2b). The presence of phenolics of both unconjugated (absorbing around 300nm) and conjugated types (absorbing at 350nm or higher wave lengths) was indicated. Such results also have been reported for aqueous extracts from isolated bond-lines of veneers from laminated beech boards (Cristescu and Karlsson 2013). This is interesting, since the extent of oxidative reactions should be much less in the latter case. Similarities in the bonding mechanism involving both phenols and furfurals are suggested by the present data, but further studies on the solid part of bond-line need to be undertaken before any final conclusions can be drawn.



a)



b)

Fig. 2.
UV-spectrometry curves for: a) UV-absorption of diluted water and methanol extract and of corresponding extract reduced with $NaBH_4$ from colored surface material of boards pre-treated with hydogen peroxide, and b) difference UV-absorption of diluted alkaline and neutral solutions of aqeuous as well as of methanol extract

The bending strength of the oxidative pre-treated boards was studied. The bending strength was higher for boards oxidised with hydrogen peroxide than without. No clear relation of bending strength with press-plate temperature was observed (Fig. 3).

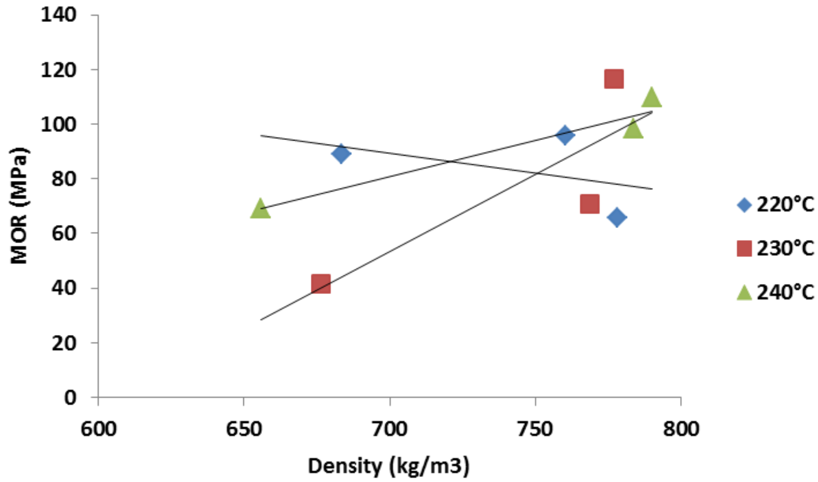


Fig. 3.
Bending strength (MOR) of boards pretreated with hydrogen peroxide and the influence of press-plate temperature

CONCLUSIONS

The results show that by treating the surface of veneers from Scots pine with small amounts of hydrogen peroxide, more water-stable laminated boards could be formed by hot pressing. Increasing the press plate temperature, reduced the water uptake and swelling of the board in water.

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REFERENCES

Boehm RB (1951) Process of making a plywood product. US Patent No. 2557071.

Cristescu C (2006) Bonding laminated veneers with heat and pressure only. Proceedings of the 2nd International Conference on Environmentally-Compatible Forest Products "Ecowood", 20-22 September, Porto, Portugal, pp. 339-348.

Cristescu C (2008) Bonding veneers using only heat and pressure. Focus on bending and shear strength. Licentiate thesis (Luleå: Luleå University of Technology).

Cristescu C, Karlsson O (2013) Changes in content of furfurals and phenols in self-bonded laminated boards. BioResources 8(3):4056-4071.

Cristescu C, Sandberg D, Ekevad M, Karlsson O (2015) Influence of pressing parameters on mechanical and physical properties of self-bonded laminated beech boards. Wood Material Science & Engineering 10(2):205-214.

Felby C, Pedersen LS, Nielsen BR (1997) Enhanced auto-adhesion of wood fibers using phenol oxidase. Holzforschung 51(3):281-286.

Johns WE (1977) Peroxyacetic acid bonding of wood. Forest Products Journal 27(1):17-23.

Karlsson O, Yang Q, Sehlstedt-Persson M, Morén T (2012) Heat treatments of high temperature dried Norway spruce boards: Saccharides and furfurals in sapwood surfaces. BioResources 7(2):2284-2299.

Karlsson O, Westermark U, Backlund U, Halvarsson S (2006) Environmentally friendly process for high density fibreboards. Nordic-Baltic Network in Wood Material Science and Engineering (WSE) Conference in Stockholm, Sweden, Oct 30-31, p. 8.

Karlsson O, Westermark U (2002) Resin-free particleboard by oxidation of wood. Proceedings of 6th Pacific Rim Bio-Based Composites Symposium & Workshop on the Chemical Modification of Cellulosics in Portland, Oregon, USA, Nov 10-13.

Kharazipour A, Bergmann K, Nonninger K, Ludemann, HD (1998) Properties of fibre boards obtained by activation of the middle lamella lignin of wood fibers with peroxidase and H_2O_2 before conventional pressing. Journal of Adhesion and Technology 12(19):1045-1053.

Runkel R, Jost J (1948) Verfahren und Vorrichtung zur Herstellung von Formungen aus Holz, Holzabfällen oder verholzten Pflanzenteilen unter Druck, bei höheren Temperaturen. (Method and apparatus for the production of mouldings from wood, wood waste or vegetable origin under fibres under pressure at elevated temperatures.) German Patent No. DE841055.

Stofko J, Zavarin E (1977) Method of bonding solid lignocellulosic material and resulting product. US Patent No. 4007312.

Wexler AS (1964) Characterization of lignosulfonates by ultraviolet spectrometry. Direct and Difference Spectrograms Analytical Chemistry 36(1):213-221.