

## THE EFFECT OF CHEMICAL TREATMENT OF WOOD VENEER SURFACES ON THEIR BONDABILITY

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### ABSTRACT

In this study, the chemical treatment of veneer surfaces was applied for minimizing surface inactivation and enhancing the bondability of wood veneers. The effect of different type of activating agents (hydrogen peroxide, aluminium persulfate, acetic acid, and sodium carbonate), their concentration (1%, 2% and 3%) and their amount (10, 20 and 30 g/m<sup>2</sup>) on the physical and mechanical properties of veneer surface and veneer-based products (especially plywood) made using treated veneers, was examined through laboratory tests. The results of this study revealed that chemical treatment of veneer surfaces increased their bondability. It was found that the samples of plywood panels made using treated veneers had higher shear strength than those of the control samples made using non-treated veneers.

**Keywords:** activating agents, birch veneer, formaldehyde free, bondability, surface activation treatment.

### INTRODUCTION

The manufacture of veneer-based products (plywood, LVL) involves many different processes; one of the most essential is the adhesive bonding of veneer sheets. Moreover, manufacturing processes including peeling and drying can essentially change physical and chemical surface properties of veneer. The interaction between liquid adhesive and the veneer surface depends, first of all, on the properties of the applied adhesive and conditions of the veneer surface. The strength of the adhesive bond is intimately associated with the surface and sub-surface properties of veneer. In order to achieve optimum adhesion between substrate and adhesive a clean solid surface is required. However, veneer surface is subjected to self-contamination that according to BACK (1991) is a result of a natural surface inactivation process where low-molecular wood extractives migrate to the surface.

In the production of veneer-based products a significant area of new wood surface is created in a short period of time. But, in many cases, the time between creating a new surface and adhesive spreading is too long. Within this period of time, freshly cut wood surfaces undergo a transformation termed surface inactivation. Wood surface inactivation is a surface phenomenon resulting in the loss of bonding ability (CHRISTIANSEN 1991). Therefore, quality preparation of the surface is extremely important. The existing technique of manufacturing plywood does not provide the preparation of veneer surface before glue application, although such operation could have an essential influence on the

reduction of the glue spread and on the improvement of the plywood performance (BEKHTA *et al.* 2009, BEKHTA *et al.* 2012, BEKHTA and MARUTZKY 2007).

Mechanical pre-treatments such as sanding and planing (AYDIN 2004) or densification by cold rolling (BEKHTA *et al.* 2009) or densification by hot pre-pressing (BEKHTA and MARUTZKY 2007, BEKHTA *et al.* 2012) can be applied to modify the surface characteristics that improve glue bonding of wood. In order to improve bonding ability, wettability and to reactivate wood surfaces for glue-wood bonds, some chemical pre-treatments are widely applied to wood surfaces (BELFAS *et al.* 1993, GARDNER and ELDER 1988). In most instances, surface activation has been accomplished through the use of various oxidizing agents, such as hydrogen peroxide (PHILIPPOU *et al.* 1982), nitric acid (JOHNS *et al.* 1978), sodium hydroxide (YOUNG *et al.* 1985), and others. Surface activation treatment of wood using hydrogen peroxide, nitric acid, and sodium hydroxide was examined by GARDNER and ELDER (1988) to assess its effect on the gel time of phenol-formaldehyde resin. They showed that surface activated treated wood decreases the gel time of phenol-formaldehyde resin with hydrogen peroxide treatment having the greatest effect followed by nitric acid and sodium hydroxide treatments. SUBRAMANIAN *et al.* (1982) were found that nitric acid oxidation of wood resulted in the formation of carboxylic acid covalently bonded to the wood. The results of CHAPMAN and JENKIN (1986) showed that panel (fiberboard, particleboard, and plywood) pressing times could be reduced by 30%, and in some cases better resin cure permitted a reduction in binder level when hydrogen peroxide was used in combination with phenol-formaldehyde, urea-formaldehyde, and tannin-formaldehyde resin-adhesives. MIRSKI *et al.* 2011 analysed the potential to shorten pressing time or reduce pressing temperature for plywood resinated with alcohol- and ester-modified PF resin resulting in the manufacture of plywood with good properties even at a pressing temperature reduced by 20 °C or pressing time shortened to 150 s.

In accordance with this chemical pre-treatment, the functional groups present on the wood surface are modified so that they can react and bond with the functional groups more effectively in the adhesive. Hereby, the surface of wood should be cleaned just before bonding in order to remove all foreign substances that interfere with bonding. CHRISTIANSEN (1994) summarised the mechanisms responsible for changes of wood surfaces that may influence the physical and bonding properties of wood: 1) migration of hydrophobic extractives during drying, 2) oxidation, 3) closure of micro-voids in the wood surface which reduces adhesive penetration, 4) acidity or reactivity of extractives affecting cure of adhesives, 5) molecular reorientation of functional groups at the surface.

The objectives of this research were: (a) to develop and understand how various activating agents affect the surface properties (such as hydrogen ion concentration (pH) and wettability) of wood veneers; (b) to understand the influence of activated veneer surface on the bondability of the adhesive bond between veneer and polymeric materials and hence plywood performance; (c) to establish the relationships between surface properties of activated veneer and plywood.

## MATERIAL AND METHODS

Rotary cut veneer sheets of birch (*Betula verrucosa* Ehrh.) with dimensions of 500 mm by 500 mm and with thickness of 1.5 mm and conditioned to moisture content of 6% were chosen for the experiments. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), aluminium persulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), acetic acid (CH<sub>3</sub>COOH), and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) were examined for veneer surface activation treatments. Three levels of the concentration solution of 1%, 2%,

and 3% of activating agents were studied. Surface activation was accomplished by spraying the activating agent with consumption of 10, 20 and 30 g/m<sup>2</sup> on the veneer surfaces before glue application. Surface activity of treated veneers was evaluated by measuring the hydrogen ion concentration (pH) and contact angle. Three and thirty replicates for pH and contact angle tests respectively were used.

In addition, five-layer experimental plywood panels were manufactured from veneers with treated and non-treated surfaces using commercial phenol-formaldehyde glue resin with a solid content of 42% and viscosity Ford 4/20 of 120 s at following pressing factors: pressure of 1.8 MPa, temperature of 135 °C, and time of 6 resp. 8 and 10 min. The glue spread was 150 g/m<sup>2</sup> based on the wet mass. For each treatment, the shear strength of plywood panels was measured according to EN 314-1. Twelve replicates were used.

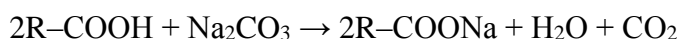
## RESEARCH RESULTS

The pH values of veneer surface treated with different activating agents are presented in Table 1. Solutions (2% and 3%) of aluminum sulfate and acetic acid reduces the pH of wood surface; but 1% solutions have almost no influence on the changing of the acidity of wood surface. The use of 2% and 3% solutions of sodium carbonate provides an opportunity to an increase of the acidity of wood surface. However, the use of 1% solution of sodium carbonate is ineffective, as well as in the case of aluminum sulfate and acetic acid.

Hydrogen peroxide can lead to the decrease in surface acidity due to the accumulation of carboxyl groups under the oxidation of wood components. However, the used peroxide solution still had a low pH value due to the presence of stabilizers in it. This led to the decrease in the pH of the surface under the treatment by hydrogen peroxide solution.

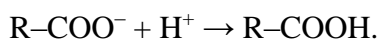
The little impact of 1% solutions on an acidity of wood surface is caused by some buffer capacity of wood components. That is, the wood components can interact with the substances used for the treatment of wood, reducing their concentration in the solution and consequently the activation ability of the solution.

In particular, the concentration of sodium carbonate may decrease due to the reactions with free fatty, resin and uronic acids of wood:



where R are the remnants of fatty, resin and uronic acids.

Ions of hydrogen which are generated under hydrolysis of aluminum sulphate and dissociation of acetic acid, cause acidity of their solutions and can interact with anions of uronic acids:



The results also revealed that the surface activation treatment of veneer improved both surface properties of veneer and mechanical properties of plywood panels. Surface activated treated veneer decreases the contact angle (Table 2) and increases the shear strength (Fig.1) of plywood panels with hydrogen peroxide treatment having the greatest effect followed by acetic acid, and sodium carbonate, and aluminium persulfate treatment. Contact angle of treated veneer surface had up to 36% improved values as compared for those of non-treated samples. That is, the surface activation of veneer increases the bondability of wood. Consumption of activating agents had greater influence on surface contact angle than concentration solution. Increasing concentration solution from 1% to

3% results to the reduction pH of veneer surface for all activating agents except sodium carbonate, for which the pH is increased. MATUANA *et al.* (1998) using four different coupling agents to treat the wood veneer also showed that coupling treatment helped improve the compatibility at the interface. In the study (LU and WU 2005), the morphology of water droplets on wood veneer with different coupling agents was investigated. The study showed that coupling agent type, molecular structure, and retention greatly influenced the wetting behaviour of the modified wood surfaces and wood-polymer interface.

**Tab. 1 pH values for birch veneer surface treated by different activating agents.**

Activating agent	H <sub>2</sub> O <sub>2</sub>								
Concentration solution, % (pH of solution)	1 (pH=6.46)			2 (pH=5.10)			3 (pH=3.24)		
Consumption, g/m <sup>2</sup>	10	20	30	10	20	30	10	20	30
pH of veneer surface	6.85	6.75	6.64	6.52	6.41	6.32	6.24	6.01	5.93
Activating agent	CH <sub>3</sub> COOH								
Concentration solution, % (pH of solution)	1 (pH=2.74)			2 (pH=2.53)			3 (pH=2.39)		
Consumption, g/m <sup>2</sup>	10	20	30	10	20	30	10	20	30
pH of veneer surface	6.32	6.21	6.08	5.91	5.79	5.72	5.69	5.46	5.33
Activating agent	Na <sub>2</sub> CO <sub>3</sub>								
Concentration solution, % (pH of solution)	1 (pH=7.60)			2 (pH=7.55)			3 (pH=7.51)		
Consumption, g/m <sup>2</sup>	10	20	30	10	20	30	10	20	30
pH of veneer surface	6.80	7.08	7.15	7.78	8.20	8.36	8.15	8.20	8.21
Activating agent	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>								
Concentration solution, % (pH of solution)	1 (pH=2.85)			2 (pH=2.24)			3 (pH=1.99)		
Consumption, g/m <sup>2</sup>	10	20	30	10	20	30	10	20	30
pH of veneer surface	6.53	6.41	6.27	6.35	6.22	5.92	6.13	5.93	5.85

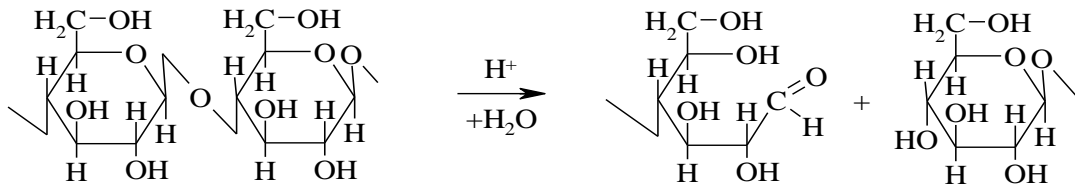
\*pH of non-treated veneer surface 6.40

**Tab. 2 Contact angle values for different activating agents.**

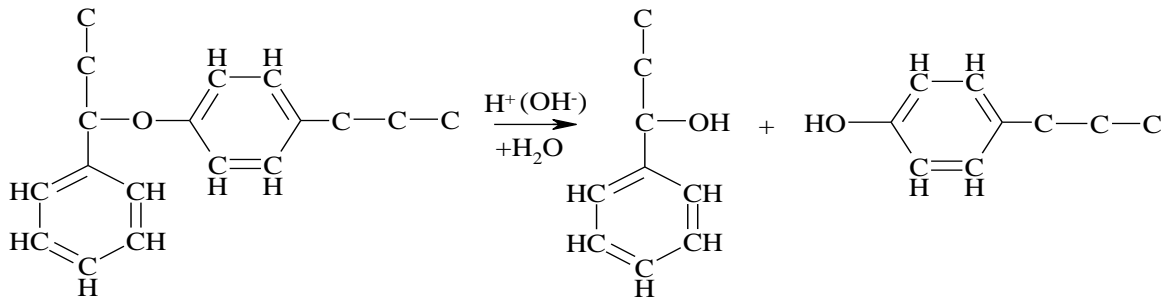
Concentration solution [%]	Consumption [g/m <sup>2</sup> ]	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH	Na <sub>2</sub> CO <sub>3</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
		Contact angle			
1	10	48.4 (1.3)*	47.1 (2.8)	47.4 (2.7)	48.2 (2.9)
	20	40.9 (2.7)	42.2 (3.7)	37.9 (3.3)	41.0 (2.5)
	30	36.4 (2.1)	37.5 (2.8)	35.3 (2.0)	36.5 (1.7)
2	10	45.9 (3.5)	46.0 (3.8)	47.3 (2.7)	46.9 (1.9)
	20	40.4 (3.2)	40.7 (2.5)	40.3 (2.5)	39.7 (2.4)
	30	35.3 (2.2)	36.8 (0.6)	36.0 (1.8)	35.4 (1.6)
3	10	45.7 (2.9)	45.1 (3.4)	47.9 (1.7)	46.3 (2.8)
	20	38.6 (2.3)	38.1 (2.3)	38.7 (1.9)	39.3 (2.4)
	30	35.2 (2.0)	36.1 (1.4)	35.3 (3.2)	35.4 (1.6)

\*Values in parenthesis are standard deviations. Contact angle for non-treated veneer surface 53.5.

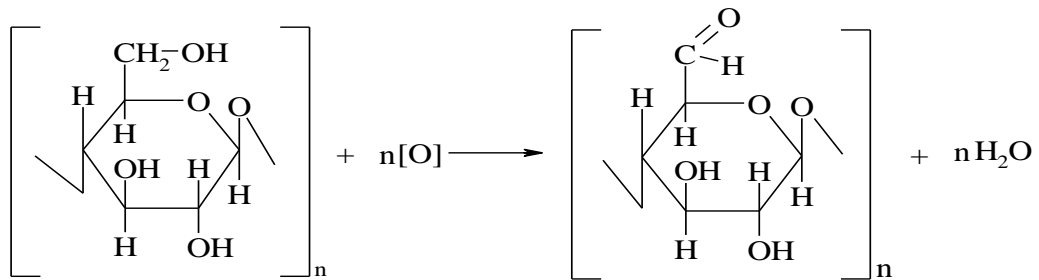
Activation effect of acidic and alkaline aqueous solutions is based on the catalyzed hydrolysis reaction of basic chemical components of wood: cellulose, hemicellulose and lignin. The molecular weight of cellulose decreases during its hydrolysis owing to the breaking of glycoside bonds (PAVASARS *et al.* 2009); as a result, there is an additional reactive carbonyl group:



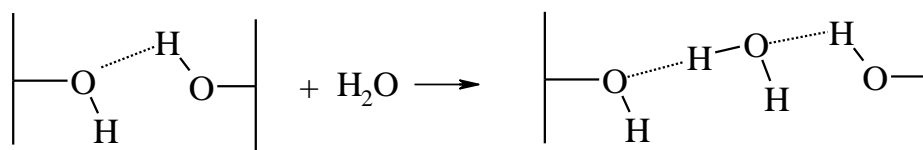
Hydrolysis of lignin occurs in the alkaline and acidic environment (GUPALO 1993). The molecular weight of lignin during hydrolysis is reduced because of breaking the essential connections between the links and additional reactive (OH) groups are generated under the scheme:



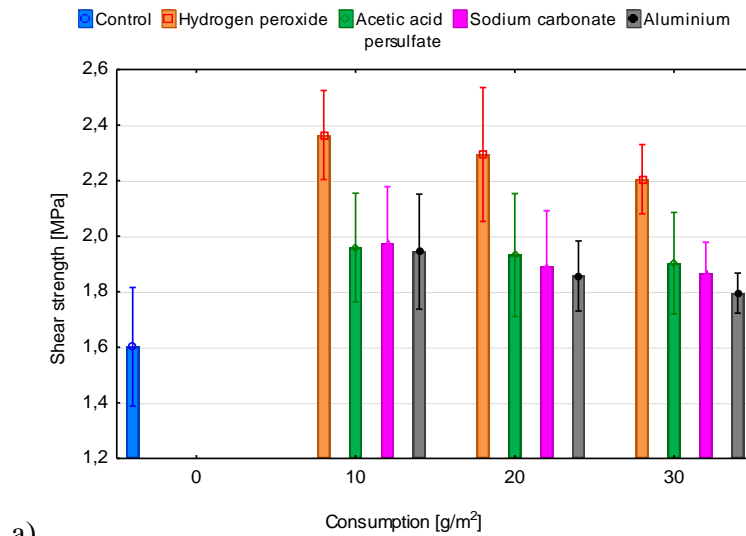
The number of polar groups and reaction centers on the wood surface increases because of such surface treatment. This contributes to an efficient intermolecular interactions as well as the formation of strong chemical bonds between the molecules of adhesive and molecules of the main components of wood for all investigated activating agents. This action is further enhanced by the stitching of macromolecules of wood and glue for radical mechanism (OMORI and DENCE 1981, PETIGARA *et al.* 2002). The accumulation of carbonyl groups occurs on the wood surface treated by hydrogen peroxide, through oxidation of carbohydrates:



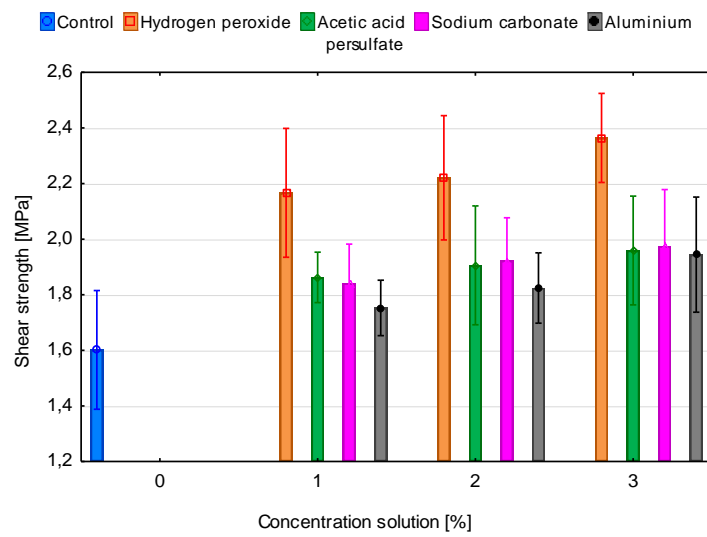
Changes in the surface properties of wood treated by the solutions of activating agents are caused not only by the changes of chemical structure of the main components of wood, and largely by the changes in their supramolecular structure, due to the penetration of water molecules between the cellulose macromolecules in the surface layers of cellulose fibrils (MATUSIEVICH 2010):



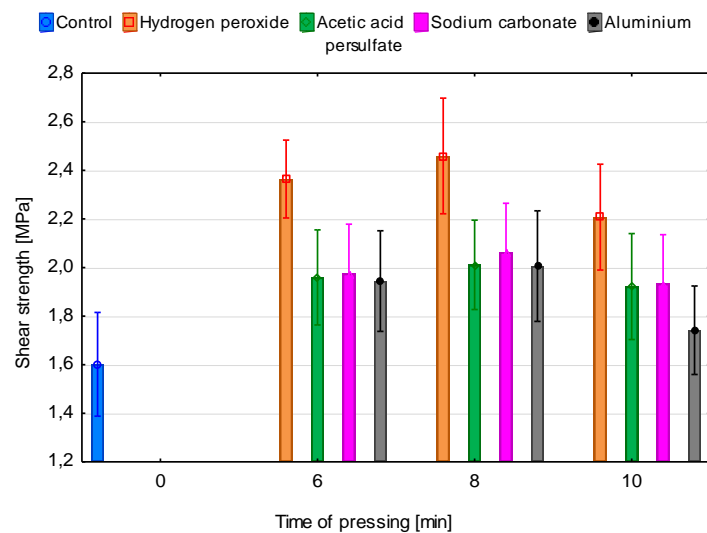
This leads to a decrease in the degree of crystallinity of cellulose, but hydroxyl groups which are involved in the formation of hydrogen bonds between cellulose macromolecules are released to form hydrogen bonds with the molecules of the adhesive.



a)



b)



c)

**Fig.1 Shear strength of plywood samples depending of activating agents and on consumption (a) for concentration solution of 3% and time of pressing 6 min; concentration solution (b) for consumption of 10 g/m<sup>2</sup> and time of pressing 6 min; time of pressing (c) for concentration solution of 3% and consumption of 10 g/m<sup>2</sup>.**

Thus, surface activation can markedly improve the bondability of veneer, as evidenced by higher values (1.7–2.4 MPa) of shear strength of plywood compared to the non-treated surface (1.6 MPa). Though, the increasing of the consumption of activating agents from 10 g/m<sup>2</sup> to 30 g/m<sup>2</sup> results even to a slight reduction by 3-7% in shear strength. This can be explained by increased moisture content of treated veneer and thus increased the probability of adhesive bonds failure under the effect of the excess pressure of gas-vapor mixture during pressing. The raising concentration solution of activating agents from 1% to 3%, on the contrary, leads to increase by 6–9% in shear strength. This may be cause by an increase in the reaction of activating agents with the veneer surface, producing a greater number of functional groups on the surface veneer that may react with the phenol-formaldehyde resin (GARDNER and ELDER 1988). The highest shear strength of the panels were found for those panels made using veneer treated with 3% solution of hydrogen peroxide at 10 g/m<sup>2</sup> consumption. These samples had 1.5 times higher shear strength values than those of the control panels.

## CONCLUSIONS

Chemical treatment of veneer surfaces improved both surface properties of veneer and mechanical properties of plywood panels made using treated veneer. The wettability of treated veneer surfaces improved due to decreased contact angle values. Contact angle decreased after chemical treatment of veneer surfaces by all investigated activating agents. The chemical treatment of veneer surfaces by hydrogen peroxide had the greatest positive effect on the shear strength of plywood samples followed the treatment by acetic acid, and sodium carbonate, and aluminium persulfate. It was not found a direct correlations between pH, contact angle and shear strength of plywood. Based on the findings of this work such treatment process could have potential to be used as alternative method to enhance properties of the plywood panels.

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