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EFFECTS OF PLASMA SURFACE TREATMENT ON BENDING STRENGTH AND MODULUS OF ELASTICITY OF BEECH AND POPLAR PLYWOOD

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ABSTRACT

This is a study on the effect of plasma treatment with different gases and plasma intensity on the bending strength and modulus of elasticity of plywood manufactured from beech and poplar. Oxygen (O_2) and ammonia (NH_3) plasma were applied on the veneer sheets; two plasma intensities were applied on the veneers with 150 and 300 W in the plasma chamber during one minute. Phenol formaldehyde resin was applied on one surfaces of each veneer with approx. 160 g/m^2. Bending strength and modulus of elasticity were determined according to EN 310.The effects of plasma surface treatment on chemical structure of the panels were determined with FTIR-ATR analysis. Bending strength of all tested panels slightly and partly increased without statistical significance when applying oxygen plasma. The effect of ammonia plasma treatment on bending strength and was determined by the wood species and the plasma intensity, and it was not uniform. Modulus of elasticity of the panels with oxygen plasma treatment showed in most cases improvement, whereas ammonia plasma pretreated veneers caused lower values compared to the control panels.

Keywords: *Fagus orientalis,* IR spectra, mechanical properties, plasma treatments, *Populus deltoides*, veneers.

INTRODUCTION

In recent years, the plasma modification process has been used to modify the surfaces of wood and wood based materials in order to enhance surface properties of the wood component and mechanical strength of the wood based materials (Aydin and Demirkir 2010, Acda *et al.* 2012, Demirkir *et al.* 2014).Plasma treatment is used to improve bonding properties of many materials such as wood based products by altering the surface properties and chemical structure of the wooden components. Bond quality as one of the most important parameters in wood based panels depends on the intermolecular attraction between the adhesive and the wood components.

Plasma treatment contributes to improve the attraction between them by generating polar functional groups such as carboxyl (-COOH) and hydroxyl (-OH) on the surface of the wood (Mortavazi and Nosonovsky 2012). Plasma consists of atoms, ions, molecules, free radicals, electrons, and metastable species (Podgorski *et al.* 2000).Different gas species can be used in plasmas in order to obtain the desired surface properties, by influencing the interactions between the gas and the solid surface depending upon the nature of the gas species used in plasma. Some gas species can change the surfaces hydrophobic, whereas other ones create hydrophilic surfaces (Mortavazi and Nosonovsky 2012). One of the most popular gas species used in plasma influencing wood surfaces is oxygen, with target to improve adhesion (Acda *et al.* 2012; Aydin and Demirkir 2010). Oxygen plasma has also been used for cleaning different areas such as micro electro mechanical systems (Berman and Krim 2012). Literature contains some studies about the effects of plasma treatment with different gas species on adhesion properties (Wolkenhauer *et al.* 2009), contact angle (Aydin and Demirkir 2010), wettability and bond

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quality of wood based and other composite materials (Kim *et al.* 2009).

Bonding quality of wood composites affects various mechanical properties such as bending strength (MOR) and modulus of elasticity (MOE) as important parameters when determining the application areas of the composites. Therefore clarification of possible effects of plasma treatment on MOR and MOE of wood based panels is requested before use in wood panel industry. Acda *et al.* (2012) stated that plasma modification results in to the formation of hydroxyl, carboxyl, aldehyde, and other polar functional groups effecting surface polarity. These effects not only depend from gas species, but also from the wood species used in the study reported here. In literature, it is hard to find a study describe the effects of plasma with different gas species and intensity on MOR and MOE of wood based materials from different wood species.

The study reported here investigated the effect of plasma treatment with different gases and plasma intensity on the MOR and the MOE of plywood panels manufactured from different wood species.

MATERIALS AND METHOD

Beech (*Fagus orientalis Lipsky*) and poplar (*Populus deltoides*) logs with 45 cm diameter were obtained from the region near the border of Turkey-Georgia, and from the Trabzon region, resp. The beech logs were steamed for 20 h before veneer production; poplar logs were peeled freshly. Rotary cut veneers with dimensions of 400 x 400 x 2 mm were manufactured from these logs. The veneer sheets were oven-dried in a veneer dryer at 200 °C until 3-5% moisture content.

Plasma Treatment on the Veneers

Plasma treatment applied on beech veneers was achieved by a Diener Nano LF type plasma treatment apparatus, manufactured by Diener Electronic GmbH (Germany) and equipped with a plasma chamber for dimensions up to 400mm by 400 mm. First vacuum was applied with a rotation pump to below 40 Pa, and then oxygen (O_2) and ammonia (NH_3)were introduced with about 80-150 Pa pressure with flow rate of 0,0009 m^3/h. Two plasma intensities(150 and 300 W in the plasma chamber)were applied on the veneers during one minute. The panels of control group, non-plasma, were manufactured from the veneers which were not applied plasma treatment in order to determine the effect of plasma.

Manufacturing of Plywood Panels

Phenol formaldehyde (PF) resin supplied from POLISAN A.S with non-volatile content of 47% was used for plywood manufacturing as adhesive without addition of filler and hardener. The adhesive mixture was applied on one surface of each of the veneers with approx. 160 g/m^2. First of all, the veneers were laid up in cross-laminated layers, with the grain of the face layers were oriented parallel to the long dimension of the panels. Then, the hot press time and temperature were 5 min and 140°C, respectively. Press pressures were 0,8 MPa for poplar and 1,2 MPa for beech panels, respectively. Three layered plywood panels with two replicates were manufactured from each wood species. Test samples were conditioned to achieve equilibrium moisture content at 20°C temperature and 65% relative humidity prior to testing. Bending strength and modulus of elasticity (MOE) of the plywood panels were investigated according to EN310 (general use).Fifteen specimens for each group were tested in order to determine the bending strength and MOE. The test specimens were rectangular with width b, (50 ± 1 mm) and the length 20 times the nominal thickness (t) plus 50 mm as stated in standard EN 310 (1993). Ultimately, the test specimen was set between the supports with the center point under the load as shown in Figure 1. The deflection of the mid-span as depicted in Figure 1 was measured and the load-deflection curves were plotted.

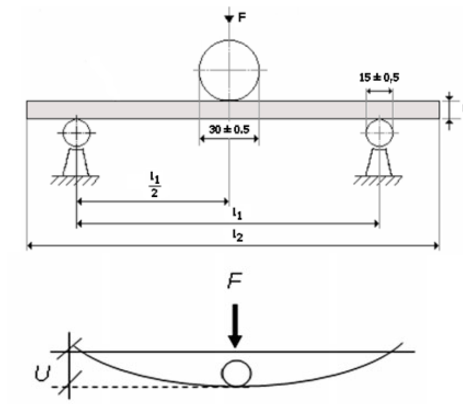

Figure 1. Bending test setup and measurement of deflection (U) according to EN 310 (Fun and Jumaat 2013).

The modulus of elasticity (MOE) of each test pieces is calculated as follows:

$$E = \frac{(F_2 - F_1)\ x\ l_1^3}{4\ x\ b\ x\ t^3\ x\ (U_2 - U_1)} N / mm^2 \qquad (1)$$

where

l_1 l_1 is the distance (mm) between the centres of two supports (mm),
b is the width (mm) of the test pieces,
t is the thickness (mm) of the test pieces,
(F_2 - F_1) is the increment of load on the straight line portion of the load–deflection curve, F_1 is approximately 10 % and F_2 is approximately 40 % of the maximum load Fmax (U_2 - U_1) is the increment of deflection corresponding to (F_2 - F_1) in load–deflection curve.

The FT-IR spectra were obtained by a Perkin-Elmer Spectrum on FT-IR instrument with a Universal ATR Diamond/ZnSe crystal with one reflection.

RESULTS AND DISCUSSION

The effect of the plasma treatment on the mechanical properties of the plywood panels (MOR and MOE) depends on wood species, gas type and plasma intensity. The results of Student-Newman-Keuls test at 99% confidence level for MOR of the panels are shown in Table 1.

Table 1. Results of Student-Newman-Keuls test at 99% confidence level for MOR Results.

Properties	Factors		LS Mean	Homogenous Groups*
150 Watt	Wood Species			
		Beech	122,81	a
		Poplar	82,86	b
	Plasma			
		Non-plasma	102,62	a
		Oxygen	104,78	a
		Ammonia	101,01	a
300 Watt	Wood Species			
		Beech	122,6	a
		Poplar	83,74	b
	Plasma			
		Non-plasma	102,62	a
		Oxygen	106,52	a
		Ammonia	100,36	a
Beech	Gas			
		Control	120,66	a
		Oxygen	126,06	a
		Ammonia	121,39	a
	Intensity			
		Non-plasma	120,66	a
		150	123,88	a
		300	123,56	a
Poplar	Gas			
		Control	84,57	a
		Oxygen	85,79	a
		Ammonia	80,07	a
	Intensity			
		Non-plasma	84,57	a
		150	82,54	a
		300	83,32	a

* Different letters denote a statistically significant difference

Figure 2 shows the effect of plasma process on bending strength of the plywood panels according to wood species. The bending strength of all plywood panels has increased with oxygen plasma in comparison with the control panels. Seki *et al.* (2009) reported that interfacial adhesion for jute fiber/polyethylene composites increased after oxygen plasma treatment. Wolkenhauer *et al.* (2009) also found an increase of adhesion properties of some wood species after plasma treatment. The increase in mechanical panel properties after O_2 plasma treatment as reported here seems to be the effect of improved adhesive bonding quality and adhesion properties. There exists a linear correlation between the oxygen plasma intensity and the bending strength of the panels. The introduction of oxygen containing functional groups to the surface of polymer materials during oxygen plasma treatment has been demonstrated by former study (Chen *et al.* 2008). It is thought that the oxygen-based polar species could generate oxygen-containing functional groups on the surface of veneers, which may contribute to adhesion leading to increase MOR. Karahan *et al.* (2007) also stated that the effectiveness of the plasma process was improved with increased plasma intensity due to higher quantity of ionized gas.

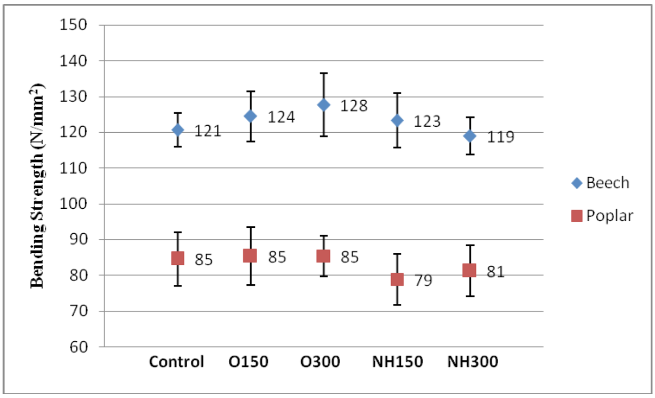

Figure 2. Bending strength (MOR) of the test panels.

On the other hand, the effect of ammonia plasma treatment influences bending strength of plywood according to wood species and plasma intensity. The bending strength of beech plywood panels has improved with ammonia plasma at 150 W, but it decreased at 300 W (Figure 2). Contrary, the bending strength of plywood panels decreased when ammonia plasma treatment took place. This might be the consequence of formation of different functional groups in the various wood species induced by the plasma process. Podgorski *et al.* (2000) reported that bonding shear strength decreased after ammonia plasma treatment. This can be also the explanation for lower MOR, because bending strength strongly depends on shear resistance between the wooden elements (Marra 1992). MOE shows slightly different behavior to MOR when plasma treatment was applied before preparing the plywood panels. Table 2 shows the results of Student-Newman-Keuls test at 99% confidence level for MOE of the panels. As can be seen from Table 2, MOE of the panels after ammonia plasma treatment are in most cases lower compared to the control panels, but the difference is not statistically significant. Ammonia penetrates the cellulose structure readily and causes swelling of the wood structure (Unger *et al.* 2001), hence this slightly reduces MOE of the panels. Lewin (2007) reported that the elongation of wood fiber decreased in tensile mode after ammonia treatment.

Table 2. Results of Student-Newman-Keuls test at 99% confidence level for MOE Results.

Properties	Factors		LS Mean	Homogenous Groups*
150 Watt	Wood Species			
		Beech	11378,61	a
		Poplar	8869,1	b
	Plasma			
		Non-plasma	9889,13	a
		Oxygen	10753,6	b
		Ammonia	9728,83	a
300 Watt	Wood Species			
		Beech	11251,76	a
		Poplar	8794,52	b
	Plasma			
		Non-plasma	9889,13	ab
		Oxygen	10438,7	b
		Ammonia	9741,58	a
Beech	Gas			
		Control	11275,71	a
		Oxygen	11534,93	a
		Ammonia	11134,92	a
	Intensity			
		Non-plasma	11275,71	a
		150	11430,07	a
		300	11239,8	a
Poplar	Gas			
		Control	8502,56	a
		Oxygen	9657,36	b
		Ammonia	8335,49	a
	Intensity			
		Non-plasma	8502,56	a
		150	9052,35	a
		300	8940,49	a

* Different letters denote a statistically significant difference

Figure 3 shows the MOE of the panels improved remarkably with oxygen plasma. Zhou *et al.* (2013) found that the boards with oxygen plasma treated enzymatic hydrolysis lignin exhibited satisfactory MOE results. At the lower intensity MOE increased with oxygen plasma treatment, but decreased again when the plasma intensity has been doubled (Figure 3). This might be the effect of the decrease of DP due to glycolysis. However, Table 2 shows the decreasing is not statistically significant.

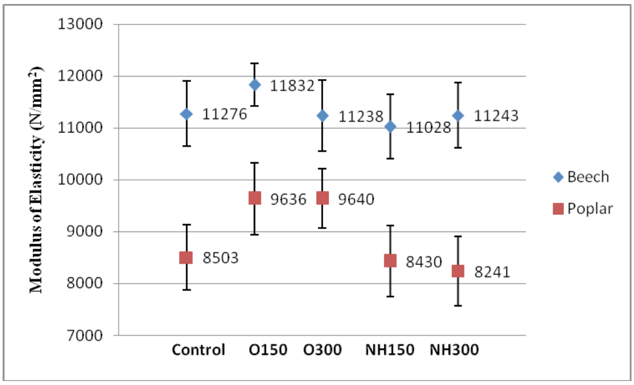

Figure 3. Modulus of elasticity (MOE) of the test panels.

It is known that the modulus of elasticity depends on degree of polymerization (DP) of cellulose in wooden materials. The higher degree of polymerization of cellulose causes the more flexible wood (Hon and Shiraishi 2001, Fan *et al.* 1987). Oxygen plasma at 150 W caused the formation of carboxyl, but still without decreasing DP; thiscan induce improved adhesion due to higher proportion of polar site at the cellulose molecules at the veneer surface. With increased plasma intensity, cleavage of the carbohydrate rings can occur, hence reducing DP and finally causing reduced flexibility. The expected reaction between the cellulose and oxygen under the conditions of the plasma treatment is shown in Figure 4.

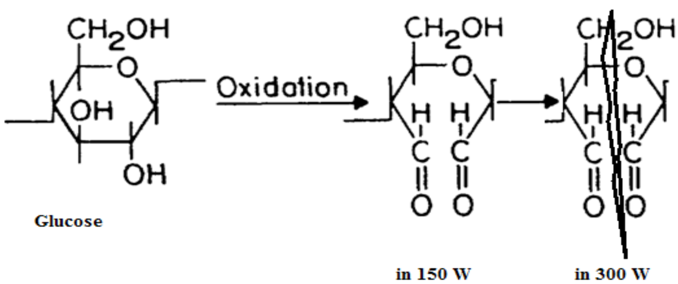

Figure 4. Expected reaction between cellulose and oxygen at two different plasma intensities.

IR spectra of test groups were obtained by FT-IR-ATR (Fourier transform infrared attenuated total reflectance) technique to determine the effects of plasma treatment on functional groups located on the surfaces of veneer specimens. Although similar spectra were obtained for control and plasma treated test groups,peak at *1,740 cm^{-1} increased after O_2 plasma treatment for all groups as can be seen from Figure 5 .This peak is the characteristic for non-conjugated carbonyl group, which arises due to C=O stretch. This could be attributed the formation of oxidized species rich in hydroxyl, carbonyl, carboxyl groups and phenoxy radicals which explain the increase in the *1,740 cm^{-1} intensity after plasma treatment.

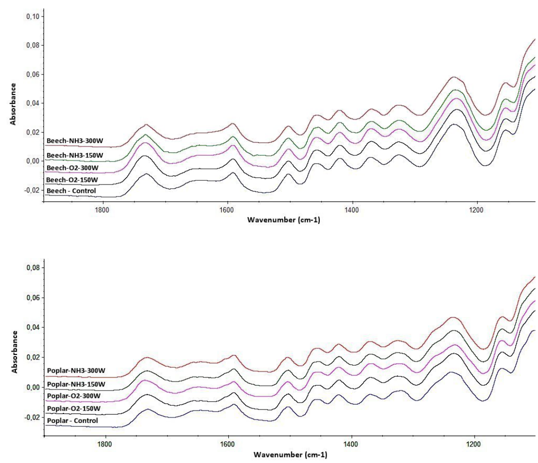

Figure 5. IR spectra of control and plasma treated samples.

With oxygen plasma treatment, various polar groups such as –C–OH, –C=O, –COOH and $–CO_2$ introduce on the treated surface (Seki *et al.* 2009). Free radicals created by low pressure gas plasma may have four major effects on the surfaces. Each major effect is always present to some degree; however, one effect may be favored over another, depending on substrate chemistry, reactor design, gas chemistry, and processing conditions.

It was concluded in a study conducted on plasma treated wood surfaces that an increase was found in polar groups such as C–O and C=O and a decrease in non-polar groups such as C–C and C–H after plasma treatment (Wolkenhauer *et al.* 2009).

CONCLUSIONS

The effect of plasma treatment with different gases and plasma intensity on the bending strength (MOR) and modulus of elasticity (MOE) of plywood panels was investigated.

Generally, MOR of all plywood panels increased with oxygen plasma compared to control panels. For the ammonia plasma treatment no clear changes were found; at lower intensity. The MOR of beech plywood panels has improved with ammonia plasma at 150 W, but it is decreased when the power has been increased to 300 W.

MOE increased with oxygen plasma for beech at the lower intensity and for poplar at both intensities; however, ammonia plasma treatment in all cases showed decrease in MOE.

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