

EFFECTS OF THE CHEMICAL TREATMENT
CONDITIONS OF THE NARROW-LEAVED ASH
(*FRAXINUS ANGUSTIFOLIA* VAHL. SSP. *PANNONICA* SOO
& SIMON) ON THE LAP SHEAR STRENGTH

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ABSTRACT

The effect of chemical treatment on wood tissue leads to changes in the chemical composition of wood, thereby changing its wetability and its chemical reactivity with adhesive. In this study, wood samples of narrow-leaved ash (*Fraxinus angustifolia* Vahl. ssp. *Pannonica* Soo & Simon) were treated with water and with the aqueous solutions of acetic acid and sodium carbonate at the temperatures of 100 and 120°C, and for a period of 60 min. The addition of acetic acid and sodium carbonate was 0.03, 0.06 and 0.09 g·g⁻¹ dry matter of wood. The effects of the applied treatments on the lap shear strength were evaluated by the standard test method using urea-formaldehyde adhesive. The entire sample series treated with the sodium carbonate have shown the significant increase of the shear strength when compared to the control sample series (17.5 to 49.6 %). In addition, the increase of the shear strength corresponded to the increase in the concentration of the sodium carbonate solution. On the other side, the acetic acid and the water treatments have not caused any significant changes to the shear strength of the samples. The increase in the concentration of the acetic acid solution has showed a tendency to decrease the shear strength, but this effect could not be confirmed statistically. Finally, the results of the shear strength for all the treated sample series have not been significantly affected by the applied temperature.

KEYWORDS: Pretreatment, narrow-leaved ash, shear strength, urea-formaldehyde resin.

INTRODUCTION

The significant research activities towards the application of pretreatments in processing of wood raw material have been evident during last few decades. The treatments change the original chemical structure of wood, which may be used to improve certain properties of wood material or to improve its hydrolysis, together with optimizing the utilization of wood (Mosier et al. 2005). Type of the applied treatment and its conditions may lead to various effects such as: partial removal of lignin and hemicelluloses (Mosier et al. 2005), decrease of crystallinity and polycondensation degree of cellulose (Rojo et al. 2013), removal of acetyl groups from hemicelluloses (Hosseinai et al. 2011a, b, Xue et al. 2007) etc.

Different chemicals in the form of oxidants, alkalis, acids and salts, may be used as a pretreatment reagents in order to modify chemical structure of lignocellulose materials. However, there is a selectivity of the applied reagents towards certain types of chemical reactions, i.e. specific chemical bonds in lignin-carbohydrate matrix (Zhang and Lynd 2004, Al-Dajani and Tschirner 2008; Yoon and Heiningen 2008, Mittal 2006, Mosier et al. 2005; Hendriks and Zeeman 2009). Changes in the chemical composition of wood, caused by the pretreatment, reflect on the changes of mechanical, physical, thermal and biological properties of original material (Hill 2006). In addition, pretreatments affect the changes in the adhesion properties of wood and the adhesive bond strength (Šernek et al. 2007).

Because of the complexity of the wood structure, both on the cellular and the chemical levels, the interaction between wood and the adhesive presents a very complex process. The adhesion process involves mechanical interlocking as well as chemical interaction between the adhesive and the wood as an adherent (Frihart 2006). During bond formation, the adhesive wets the surface and penetrates into the lumens, and sometimes through the cell walls (Johnson and Kamke 1992) which provides the mechanical interlocking (Packham 2003). There are many factors which controls the wetting of the surface and the penetration. They may include relative surface energy of the adhesive and the substrate, compatibility between adhesive and wood, equilibrium contact angle, adhesive viscosity, bonding temperature, specific pressure (Frihart 2005a). The appropriate degree of adhesive penetration, which greatly depends on the diameter of cell lumens and on the porosity and permeability of wood, is related to the presence of the extractives (Frihart 2006), and has a special importance for a quality of an adhesive bond (Frihart 2005a).

Chemical aspect of the adhesion considers close interaction between adhesive and wood, through formation of London dispersion forces, Van der Waals forces, dipole-dipole interaction and hydrogen bonds (Frihart 2006). Some of the important factors of the chemical aspect of adhesion are the chemical composition of wood, diameter of cellulose fibers, ratio and dispersion of lignin and hemicelluloses (Frihart 2006), but also the presence of the carboxyl and ester groups, as a potential sites for the chemical bond formation (Frihart 2005a). Some of those factors may be affected during chemical treatments, thus changing the properties of wood important for the adhesion.

Hemicelluloses are considered as a wood component responsible for hydrogen bond formation with the adhesive (River et al. 1991, Salehuddin 1970, Frihart 2005b). The water extraction of hemicelluloses decreases the accessible OH groups, which as a result has the following effects: increase in the hydrophobic character of the sample, decrease of water adsorption and increase of dimensional stability of the treated wood samples, and decrease of the surface energy (Zhang et al. 2011, Hosseinai et al. 2011a, b). Besides, decrease in the number of accessible OH groups, the potential sites for bond formation (River et al. 1991), also decreases the number of realized bonds between wood and the adhesive. In addition, the removal of acetyl groups and extractives

changes the pH value of wood, which also affects the adhesive curing behavior.

Studies on the acid treatments are usually aimed to optimize the hydrolytic degradation of wood, used as a raw material for bio-ethanol production. Hence, there is much less interest in the research of the influence of those treatments on the physical and mechanical properties of wood (Taherzadeh and Karimi 2007; Jacobsen and Wyman 2000; Kumar et al. 2009; Mosier et al. 2005). However, with suitable processing parameters it is possible to obtain lower degradation of treated samples, and with improvements of certain wood properties for further processing (McConnell et al. 2011). Li et al. (2011) have determined that the water sorption and the thickness swelling of MDF panels made from the fibers treated with oxalic acid are less than for the MDF panels made from non-treated and water treated fibers, due to the partial removal of hemicelluloses; but the mechanical properties of the former panel have worsen. Winandy et al. (2008) have explained the decrease in mechanical properties of the wood-plastic composites made of fibers treated with oxalic acid by lower compatibility of treated wood fibers with UF adhesive after the extraction of hemicelluloses. An additional cause on lower mechanical properties of treated wood is the lower density of the treated samples, which is the result of the mass loss in wood during treatment (Kellog and Ifju 1962; Blankenhorn et al. 1989).

During treatments at high pH values, and in regard to the treatment conditions and characteristics of the lignocellulosic material itself, the numerous processes take place, such as: peeling reactions with formation of the alkali-stable end groups, hydrolytic degradation of glycoside bonds, cleavage of acetyl groups, decomposition and dissolving of non-degradable polysaccharides, decomposition of ester bonds between lignin and hemicelluloses (Gaspar et al. 2007, Fengel and Wegener 1984, Zhao et al. 2008). The treatments with NaOH solutions of different concentrations have been studying the most. Such treatments lead to the limited intercrystalline swelling and to the changes of parameters of cellulose crystal lattice in original sample (Rojo et al. 2013). Higher alkali concentrations and high processing temperatures result in significant delignification of fibers, which leads to the weakening and damaging of fibers (Wang et al. 2007; Xue et al. 2007; Rojo et al. 2013). Due to the significant changes in structure and composition of wood, the treatments with alkaline solutions impose significant changes on the mechanical and physical properties of wood.

In this study, the narrow-leaved ash wood samples were treated with different concentrations of reagent solutions and at different temperatures. The water, the acetic acid and the sodium carbonate were selected as the reagents. Tests of the tensile shear strength were performed in order to evaluate the effects of the treatments on the lap joints bonded with urea-formaldehyde resin.

MATERIAL AND METHODS

The following materials were used in this research:

- **Narrow-leaved Ash** (*Fraxinus angustifolia* Vahl. ssp. *Pannonica* Soo & Simon), the 72 years old tree, was sampled from the Morovic area in the Republic of Serbia.
- **Sodium carbonate anhydrous** (Na_2CO_3) (99.9 %) AnalaR NORMAPUR (Belgium).
- **Acetic acid (glacial)** (CH_3COOH) (99.5 %) Zorka Pharma - Hemija d.o.o. (Serbia).
- **Ureaformaldehyde (UF) resin** "Lendur 730F" was obtained from the Nafta Petrochem (Lendava, Slovenia) with following characteristics: solid mass 65.07 %, viscosity 453 mPa·s, pH value 8.6, gel time (20 % NH_4Cl , 100°C) 41 s.
- **Ammonium sulphate** p.a. ($(\text{NH}_4)_2\text{SO}_4$), was used as the hardener (Zorka Pharma – Hemija

d.o.o., Serbia). The addition of hardener was 3 % in regard to the adhesive dry mass.

- **Wood panel samples** (5 x 20 x 150 mm, at tangential, radial and axial direction, respectively) were taken from the log at 5 different height zones. The panel samples were sorted into 15 test series: The 14 treatment series and one control series. Each test series consisted of 13 pairs of panel samples, representing the equal distribution of pairs throughout the log. Additional number of 30 wood panel samples was taken for the determination of moisture content by laboratory gravimetric method. The moisture content of wood samples was 10.34 ± 0.2648 %.

Treatments were performed in the glycol heater with 6 rotating autoclaves, with the following parameters: duration of treatment was 60 min; treatment temperatures were 100 and 120°C; the ratio of liquid to dry wood was 5:1 (the water already present in the air dried samples was taken into account for the calculation). The addition of Na_2CO_3 and CH_3COOH was 0.03, 0.06 and 0.09 $\text{g}\cdot\text{g}^{-1}$ wood dry mass.

After the treatment, the autoclaves were cooled in the water bath until reaching the ambient temperature. Wood panel samples were washed with distilled water upon reaching the neutral pH value and consequently air dried and conditioned at $20 \pm 2^\circ\text{C}$ and at the relative humidity of 65 %, according to EN 205 2003. Finally, the mass loss was determined for all of the treated samples.

Bonding of samples was carried out with the UF adhesive mixes prepared by addition of 3 % (by resin mass) of ammonium sulphate as a hardener and distilled water which added to the hardener in order to achieve 54.45 % of dry content in UF adhesive. The adhesive mixes were applied by a rubber roller onto one surface of the two wood panels to be bonded ($200 \text{ g}\cdot\text{m}^{-2}$). Five joint samples were pressed simultaneously in a hydraulic press at 120°C and 1 MPa for 13 minutes. Bonded test samples were conditioned at $20 \pm 2^\circ\text{C}$ and 65 ± 5 %, according to the requirements of EN 205 2003.

The tensile shear tests were conducted on a hydraulic test machine (ZWICK, Germany) with a measuring scale of 50 kN at a testing speed of $10 \text{ mm}\cdot\text{min}^{-1}$ in tensile mode. The shear area ($20 \times 10 \text{ mm}$) was examined to determine the proportion of wood failure and the thickness of the wood layer in the wood failure. Statistical analysis was performed with single factor ANOVA test, at the confidence level of 95 %.

RESULTS AND DISCUSSION

All of the applied treatments have caused the mass loss of the panel samples (Tab. 1). The effects of the temperature and the concentration of reagent's aqueous solutions on the mass loss of panel samples were evident for both, the acetic acid and the sodium carbonate treatments. At the treatment temperature of 100°C, the increase of the acetic acid addition (from 0.03 to 0.09 $\text{g}\cdot\text{g}^{-1}$) affects the decrease in the wood mass loss of the samples (from 0.98 to 0.67 %). The acetic acid treatments at 120°C have showed higher mass loss, but with the maximal value of 2.15 % at the acetic acid addition of 0.06 $\text{g}\cdot\text{g}^{-1}$. The highest wood mass loss at both treatment temperatures was recorded for the samples treated with sodium carbonate solution. The earlier studies of water treatment (Zhang et al. 2011) and the oxalic acid and its derivatives Li et al. (2011) also have showed that the higher treatment temperatures lead to the higher loss in wood mass. However, the water treatment has showed very little influence of the treatment temperatures on the mass loss of panel samples.

Tab. 1: Mass loss of treated panel samples.

Mass loss (%)			
Temperature			
	Addition, (g.g ⁻¹)*	100°C	120°C
Water	/	0.90 ± 0.2265	0.92 ± 0.3826
CH ₃ COOH	0.03	0.98 ± 0.3518	1.02 ± 0.3956
	0.06	0.83 ± 0.3130	2.15 ± 1.0035
	0.09	0.67 ± 0.2671	1.18 ± 1.2450
Na ₂ CO ₃	0.03	1.41 ± 0.3380	1.91 ± 0.6088
	0.06	1.95 ± 0.5525	2.51 ± 0.7365
	0.09	1.58 ± 0.3360	3.48 ± 0.7190

*g CH₃COOH or Na₂CO₃ /g oven dry wood.

Tensile shear strength in the lap joint

The mean shear strength of the samples treated with water, at both temperatures, do not differ significantly (8.34 and 8.28 N.mm⁻²), and they are very close to the mean shear strength of the control sample series of 8.87 N.mm⁻² (Fig. 1a). The similar behavior can be noticed with the samples treated with the acetic acid (Fig. 2a).

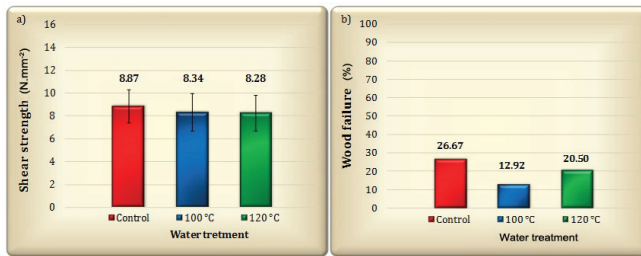


Fig. 1: The tensile shear strength of lap joint a) and the wood failure b) of the control series and the sample series treated with water at 100 and 120°C.

Having in mind that the chemical composition of wood has significant impact on the formation of adhesive bond, especially in the aspect of accessibility of the OH groups (River et al. 1991; Frihart 2006), it is expected that the changes in wood resulted from the treatments will consequently change the adhesion properties of treated wood. However, on the basis of the presented results, it could be noticed that the water treatment and the treatment with acetic acid solution have not significantly changed the adhesion properties of the wood panels of narrow-leaved ash, since the mean shear strength values between the control series and the vast majority of the sample series treated with water and acetic acid did not show the significant difference (Tab. 2). The exception is the series of the samples treated with 0.09 g.g⁻¹ of acetic acid and at the 100°C. Its mean value of the shear strength of 7.56 N.mm⁻² was significantly lower the mean shear strength of control series (8.87 N.mm⁻²) and from the mean values of other treated sample series. Testing the properties of beech wood after the hydrothermal treatment, Mirzaei et al. (2012) have noticed the decrease in the bond strength between the beech wood and the urea-formaldehyde adhesive, which corresponds to the slightly lower values of shear strength of the samples treated with water and with acetic acid, found in this work. Tjeerdsma and Militz (2005) have explained the decrease in the shear strength in the adhesive joint after the hydrothermal treatment of wood through the

decrease in the number of hydroxyl groups, as potential sites for bonding formation between the wood and the adhesive, due to extraction of hemicelluloses (Zhang et al. 2011, Hosseinaei et al. 2011 a). In addition, Winandy et al. (2008) found in its work that the formation of the adhesive bond has been influenced decreased compatibility of treated wood fibers and UF adhesive due to the extraction of hemicelluloses during the oxalic acid treatment.

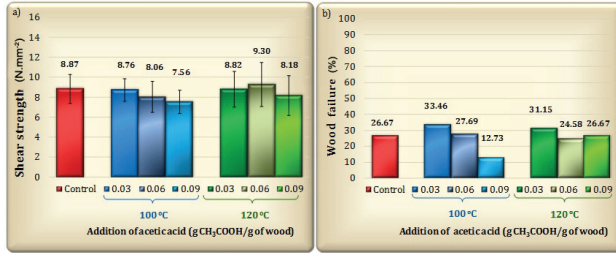


Fig. 2: The tensile shear strength of lap joint a) and the wood failure b) of the control series and the sample series treated with acetic acid at 100 and 120°C.

On the other hand, the mean values of the shear strength in lap joint of all sample series treated with the sodium carbonate solution (10.42 - 13.27 N.mm⁻²) were significantly higher in comparison to the control series and the series of samples treated with the acetic acid solution (Fig. 3a).

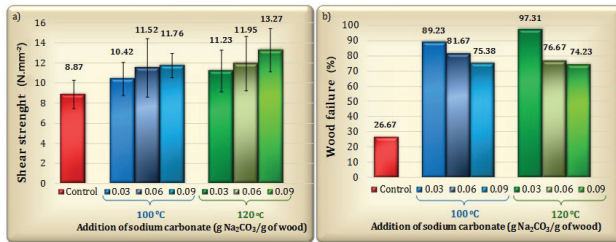


Fig. 3: The tensile shear strength of lap joint a) and the wood failure b) of the control series and the sample series treated with sodium carbonate at 100 and 120°C.

Higher mean values of the shear strength of the samples treated with sodium carbonate might be the consequence of the increased number of OH groups at the surface of the microfibrils due to the penetration of sodium ions into the cellulose structure, which results in the increase of the specific surface of cellulose fibers and hence greater effective surface available for chemical reactions (Rojo et al. 2013), and probably leads to an increase in the portion of amorphous region in treated samples. In alkaline conditions, the hydrolytic cleavage of acetyl groups in hemicelluloses and their substitution with OH groups is common (Stevanović-Janežić 1993; Dumitriu 2005), which may have enabled better chemical interaction between the samples treated with sodium carbonate and the UF adhesive. Besides, it can be assumed that the increased porosity and permeability of the treated samples has improved the adhesive penetration into wood tissue, and hence brought to the increase of the mechanical adhesion in those samples. In that aspect, the higher mass loss of these samples (Tab. 1) could have been the indicator of the higher shear strength values (Fig. 3a).

Tab. 2: Statistical comparison of the control and the treated sample groups (ANOVA.)

Treatment temperatures	100°C			120°C		
	F	P-value	F crit	F	P-value	F crit
Control/ Water	0.7084	0.4090	4.3009	0.7964	0.3833	4.3808
Control /0.03 g CH ₃ COOH /g o.d.w.*	0.0423	0.8390	4.3009	0.0042	0.9490	4.3009
Control /0.06 g CH ₃ COOH /g o.d.w.*	1.7351	0.2007	4.2793	0.3064	0.5854	4.3009
Control /0.09 g CH ₃ COOH /g o.d.w.*	5.4785**	0.0292	4.3247	0.7755	0.3895	4.3808
Control /0.03 g Na ₂ CO ₃ /g o.d.w.*	6.3327**	0.0193	4.2793	10.7907**	0.0032	4.2793
Control /0.06 g Na ₂ CO ₃ /g o.d.w.*	8.1951**	0.0089	4.2793	12.1477**	0.0021	4.3009
Control /0.09 g Na ₂ CO ₃ /g o.d.w.*	30.3519**	1.331E-05	4.2793	35.3714**	4.603E-06	4.2793

* oven dry wood

**denotes a statistically significant difference at the confidence level of 95 %.

Estimated portion of wood failure

Results of the failure surface analysis for the water treated samples show that the failure in wood occurred in less proportion (12.92 % at 100°C, and 20.50 % at 120°C) then with the control series. Contrary, other researchers have noticed a decrease in the mechanical properties of the water treated samples, which they addressed to the closer contact formation between cellulose and lignin after decomposition of hemicelluloses (Hosseinaei et al. 2011 b, Gündüz et al. 2009; Kocaefe et al. 2010).

The Fig. 2b shows that the wood failure of the samples treated with acetic acid do not differ significantly from the control series. However, the samples treated with the 0.09 g.g⁻¹ of acetic acid at 100°C had significantly lower failure surface in wood (12.73 %) in comparison to the control series, which is in accordance with the lowest shear strength (7.56 N.mm⁻²) obtained for this sample series in regard to all of the other sample series used in this research.

Wood failure surface of the samples treated with sodium carbonate have reached the range of 74.23 up to 97.31 %, hence 3 - 4 times more in regard to the control sample series. Such results suggests that the mechanical adhesion have increased in those samples, which is in accordance with the findings of Mihulja and Bogner (2007) that the high portion of wood failure indicate the high bond strength. In the same aspect, it could be assumed that the wood is the weakest link in this adhesive system, which may be the consequence of decrease in its mechanical properties due to the partial degradation of wood during the treatment. River et al. (1991) suggests that the wood failure decreases with the increase in wood density, and hence in its strength, while the Hill (2006) suggests that due to the degradation of hemicelluloses, the wood becomes brittle and stiff, and hence easy to break. Besides, Kellog and Ifju (1962), as well as Blankenhorn et al. (1989) suggests that the decrease in mechanical properties of wood may be the consequence of the mass loss during treatments, which was higher for the samples treated with sodium carbonate in regard to the other sample series.

Influence of the treatment temperature

For the most sample series, the change in the treatment temperature from 100 to 120°C did not have significant influence on the mean values of the shear strength, which is confirmed by the statistical analysis (Tab. 3). The changes of the shear strength affected by treatment temperature are the most expressed for the sample series treated with acetic acid, but they are still not statistically different. Additionally, statistical analysis shows that the treatment temperature (100 and 120°C) do not affect the shear strength of the samples treated with sodium carbonate solution, except for the samples treated with the sodium carbonate addition of 0.09 g.g⁻¹.

Tab. 3: Statistic comparison of the sample groups treated with solutions of the same concentrations at different temperatures (ANOVA).

Between groups		F	P-value	F crit
Water	100°C/120°C	0.0091	0.9249	4.3248
0.03 g CH ₃ COOH/g o.d.w.*	100°C/120°C	0.0106	0.9188	4.3009
0.06 g CH ₃ COOH/g o.d.w.*	100°C/120°C	2.4419	0.1318	4.2793
0.09 g CH ₃ COOH/g o.d.w.*	100°C/120°C	0.6707	0.4235	4.4139
0.03 g Na ₂ CO ₃ /g o.d.w.*	100°C/120°C	1.1948	0.2852	4.2597
0.06 g Na ₂ CO ₃ /g o.d.w.*	100°C/120°C	0.1412	0.7105	4.2793
0.09 g Na ₂ CO ₃ /g o.d.w.*	100°C/120°C	4.8561**	0.0374	4.2597

* oven dry wood

**denotes a statistically significant difference at the confidence level of 95 %.

Influence of the reagent concentration

In order to evaluate the influence of the concentration of applied treatment reagent, the statistical analysis of the significance of the shear strength values have been performed for the sample series treated with solutions of different concentrations at the same treatment temperatures. The results are shown in the Tab. 4.

Tab. 4: Statistic comparison of the sample groups treated with solutions of different concentrations at the same temperatures (ANOVA).

Treatment temperatures	100°C			120°C		
	F	P-value	F crit	F	P-value	F crit
0.03/0.06 g/g (CH ₃ COOH)	1.5129	0.2311	4.2793	0.3125	0.5818	4.3009
0.06/0.09 g/g (CH ₃ COOH)	0.7275	0.4029	4.3009	1.2796	0.2720	4.3808
0.03/0.09 g/g (CH ₃ COOH)	5.7957*	0.0253	4.3248	0.5365	0.4728	4.3808
0.03/0.06 g/g (Na ₂ CO ₃)	1.4114	0.2464	4.2597	0.5641	0.4602	4.2793
0.06/0.09 g/g (Na ₂ CO ₃)	0.0748	0.7868	4.2597	1.8414	0.1880	4.2793
0.03/0.09 g/g (Na ₂ CO ₃)	5.6397*	0.0259	4.2597	6.0596*	0.0214	4.2597

*denotes a statistically significant difference at the confidence level of 95 %.

Observing the influence of the concentration of treatment solution, shown on the Fig. 2, it could be noticed that at the same treatment temperature the shear strength decreases with the increase in the concentration of the acetic acid from 3 up to 9 %. Contrary, the increase in the concentration of sodium carbonate solution, the shear strength of the treated samples also increases, but with simultaneous decrease in the wood failure surface (Fig. 3). However, the statistical results given in the Tab. 4 shows that there is no significant difference in the shear strength values between the sample series treated with different concentration of reagent solutions at the same temperature, except between the samples series treated with the addition of 0.03 and 0.09 g.g⁻¹ of acetic acid at 100°C, and between the samples series treated with the addition of 0.03 and 0.09 g.g⁻¹ of sodium carbonate at both treatment temperatures.

CONCLUSIONS

Based on the results presented in this work, the following conclusions may be drawn:

- Treatments with water and with acetic acid solutions (0.03, 0.06 and 0.09 g.g⁻¹) for both of the applied temperatures (100 and 120°C) have not changed significantly the shear strength of the narrow-leaved ash samples. Only the samples treated with the 0.09 g.g⁻¹ of acetic acid at the 100°C have showed significantly lower shear strength in comparison to the control (non-treated) series.
- Treatments with sodium carbonate solutions (0.03, 0.06 and 0.09 g.g⁻¹) for both of the applied temperatures (100 and 120°C) have increased the shear strength of the narrow-leaved ash samples significantly. In comparison to the control series, this increase in shear strength was in the range from 17.5 - 49.6 %.
- In addition, the increase in concentration of sodium carbonate from 0.03 to 0.09 g.g⁻¹, and the increase in temperature from 100 to 120°C had a positive effect on the quality of the adhesion between the treated narrow-leaved ash samples and the UF adhesive.
- Treatments with water and with the acetic acid solutions did not affect the wood failure in the most cases. However, water treatment at 100°C resulted in the 51.6 % lower wood failure surface in regard to the control series. Also, a treatment with the acetic acid of 0.09 g.g⁻¹ and at the temperature of 100°C has decreased the wood failure surface for 52.3 %, which corresponded to the low adhesive bond strength (7.56 N.mm⁻²).
- The significant increase of the shear strength of the samples treated with sodium carbonate have been consequently followed with the 3 - 4 times increase in the wood failure surface in regard to the control series. The high strength of the adhesive bonds formed between these samples and the UF adhesive, suggests that the wood is the weakest link in this adhesion chain, which may be indication of decrease in the mechanical properties of the samples treated with sodium carbonate solutions.

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