

**ADHESIVE BOND PERFORMANCE OF HEAT-TREATED
FIR WOOD (*ABIES BORRISSIREGIS*)**

MITANI ANDROMACHI, RAMMOU EKATERINI
TECHNOLOGICAL EDUCATIONAL INSTITUTE OF LARISSA
KARDITSA BRANCH, DEPARTMENT OF WOOD AND FURNITURE DESIGN
AND TECHNOLOGY
KARDITSA, GREECE

(RECEIVED JANUARY 2018)

ABSTRACT

The thermal treatment of wood leads to chemical, structural and natural changes in the wood components which can significantly affect the adhesive bond performance of the wood in various ways depending on the type of adhesive that is used. In the present research, fir wood (*Abies borrisiregis*) was undergone thermal treatment at 180°C, and 200°C for 3, 5 and 7 hours. Two different types of adhesives were used for the adhesive bond: polyurethane (PUR) and polyvinyl acetate PVAc. During all the wood treatment conditions, higher endurance in the bonding shear strength was noticed for the non-modified samples and the shearing strength by compression load was decreased while the thermal treatment was becoming more intense. Generally, while the PVAc bond shows better performance during the adhesion and higher modulus of rupture in comparison with the polyurethane PU after the thermal treatment of the wood.

KEYWORDS: Heat treatment, adhesive, fir wood, bonding, PVAc.

INTRODUCTION

The changes that are noticed in chemical composition of thermally modified wood lead to energy reduction on the wood surface which changes its wettability. Thus, what could be predicted is that the adhesion of the thermally modified wood with the use of polar bonding substances, spreading glues or water-diluted bonding substances is possible to lead to weak adhesive bonds. Furthermore, the separation of the wood fibers will lead to premature failure of a bond, even if the bonding area itself remains healthy. It is generally accepted that the adhesive bond performance of the wood is negatively affected by the temperature and the time of treatment (Hill 2006). However, studies have shown that the best bonding strength is achieved with milder heating treatment circumstances which use lower temperature and duration. Due to the decreased soaking, the bonding with water-diluted glues can be more difficult in comparison with the glues

without water (e.g. polyurethane). The formation of an adhesive bond involves the properties of the liquid adhesive substances and their transformation into solid ones. One of mechanisms which contribute to the bonding performance which act between the bonding substance and the wood is the wettability. Wettability affects the penetration of the glue. The factors that can affect the wettability are: the types of wood, the presence of extracts, the wood anatomy, the drying, the related moisture, the temperature and the surface roughness (Cruz et al. 2007).

The wood surface which is exposed to high temperatures during the thermal treatment is undergone inertia. The surface inertia can lead to bad quality adhesion and is considered to be a procedure which depends on the time and the temperature rise. An inert wood surface can cause detachment and generally other problems because of the wettability, the flow and the penetration of the glue. Moreover, the thermally modified wood shows slighter attraction to the water and to the moisture which is a phenomenon that leads to significant changes of the wood attitude with the most coverage procedures (paints, varnishes) or with the adhesion. The oxidation and the pyrolysis of the wood surface are real and inevitable inertial mechanisms in very high temperatures and duration. The hygroscopicity of the wood shows a period loss of the hydroxyl parts during the treatment and it is one of the bad adhesion performances of the thermally inert wood. During the thermal treatment, the natural and chemical procedures which occur on the wood surface are led to a modified surface with new characteristics. After proceeding the temperature level (160°C), the lignin plasticity is achieved which starts to affect the wood characteristics. The wettability as a property of wood is of crucial importance for its good adhesive performance (Unsal et al. 2009).

The thermally modified wood absorbs the water slowly and generally the glues based on water, such as the PVAc. This is the reason why the pressure duration of the adhesion must be increased when glues based on water are used. When glues PVAc are used, the water content in the glue must be minimized. It has been reported that the adhesive substance polyurethane (PUR) acts better with the heat treated wood. It should be taken into consideration the fact that the hardness reaction of the polyurethane demands water. The water can be absorbed either by the wood or by the air in the environment. The demanding moisture quantity depends on the glue but if the wood and the air are very dry, there is a chance of ineffective adhesion (Vladimirova 2012). In conclusion, the mechanisms which are considered to be responsible for the changes that the surface of the wood is undergone after the thermal treatment and additionally effect the bonding strength negatively are : 1) the removal of the hydrophobous extracts during the treatment 2) the oxidation 3) the closure of the small spaces pores of the wood surface reducing in this way the penetration of the adhesive substance on the wood mass 4) the oxidation and the effectiveness of the extracts which affect the hardness of the adhesive substances (Cruz et al. 2007). Moreover, the pH of the wood can affect the chemical hardness of the adhesive substance, as well. However, the matching of the pH of the wood and the pH of the adhesive substance is of major responsibility for the hardness adjustment (River et al. 1991). The knowledge of the chemical condition of a material (wood) is a useful direction in an effort to be used combined with other adhesives. Therefore, there are critical links between the pH values and the quality of the adhesive bonds as well as with the total production cost and must be considered as one of the most important factors for arranging the suitability of the raw material (Ahmand 2000).

MATERIALS AND METHODS

From the wood samples that have either undergone thermal treatment or not, boards of 2 cm thickness, 5 cm width and 40 cm length were formed. The moisture content of the samples during the adhesion was for untreated wood: 9.97%, 180°C – 3 hours: 8.55%, 180°C – 5 hours:

7.49%, 180°C – 7 hours: 6.63%, 200°C – 3 hours: 6.40%, 200°C – 5 hours: 6.55%, 200°C – 7 hours: 6.50%. After being planed and smoothed slightly with sand-paper No 220 these plates were ready for adhesion. The coating of the adhesive took place on both plates for adhesion. A special press equipped with 10 pistons of pressure for the complete control of the exerted pressure was made for conducting and applying the pressure. The pressure that was exerted was 28.83 kPa for 1 hour. The amount of the glue that was applied on the surfaces was estimated by weighing each plate separately before and soon after its coating and according to the measurements the amount of the glue that was applied on each surface was 7.6 ± 1 g which is equal to $35.1 \text{ g}\cdot\text{m}^{-2}$. Before the formation of the final specimens, the bonded plates were air –conditioned for ten days until the cure of the adhesive was completed under conditions of 20°C and 65% moisture content.

The formation of the samples which are bonded with polyurethane does not differ from the formation of the samples with PVAc except the pressure time which was 1 hour and 30 minutes. Also slight soaking of the surface was conducted. Finally, the polyurethane amount that was coated was 6.50 ± 1 g per surface which is equal with $28.125 \text{ g}\cdot\text{m}^{-2}$. The final specimens were prepared according to the International standard ISO 6238:2001 and the final shape is shown in Fig. 1.

The total length of the samples according to the standard is set at 50 mm, the width at 40 mm while the thickness is set at 40 mm on condition that the thickness of each plate was 20 mm. The bonded surface is 1600 mm^2 , while the two edges of the sample were uncovered at a length of 5 mm each.

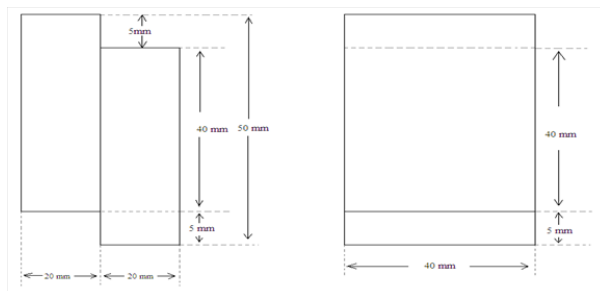


Fig. 1: The final sample format.

For the estimation of the shearing strength 15 samples were tested for each variable. The total number of samples which have been studied was 210. The samples were placed in the testing machine and pressure with speed of $8 \text{ mm}\cdot\text{min}^{-1}$ was applied until the sample broke. The strength was estimated at K_p but the final shearing strength were transformed into Newton. Finally, the modulus of rupture T was calculated according to the following equation:

$$T = \frac{F \max}{A} = \frac{F \max}{l * b}$$

where: F_{\max} - maximum load (N),
 A - the bonded area (mm^2),
 l - the length of the bonded area (mm),
 b - the width of the bonded area (mm).

Measurement of the wood pH

The pH value was measured with the hydrated method of extraction. 2 g of pulverized wood which was taken from the wood surface of the sample in depth of 0.5 ± 0.2 cm, dried in the air with dimensions of $< 420\mu\text{m}$, were mixed with 40 ml distilled water of 20°C for 24 hours. The extraction was strained to a filter and the liquid solution was dissolved to pHmeterCrisonGLP22 calibrated with solutions of 4 and 7pH.

One way analysis of variance (ANOVA) comparing the differences of values at 0.05 level was examined in order to determine the significant differences among miscellaneous heat treatment combinations on bonding strength.

RESULTS AND DISCUSSION

At Tab. 1 and Fig. 2 the modulus of rupture results are presented as well as the results of the ungluing percentage of both adhesive thermally modified samples and untreated ones. According to the results, decrease of the modulus of rupture is noticed after the thermal treatment. The more the temperature and the duration of the treatment are increased, the more the modulus of rupture is decreased. This phenomenon is noticed at both types of bond. The shearing strength reduction can be due its degradation because of the thermal treatment as well as because of its density reduction and not due to the reduction of the adhesive bond capacity. Taking the results into consideration, it seems that both adhesives do not show great differences between each other in the modulus of rupture regarding the non-modified wood but only a slight precedence of the PVAc adhesive is noted which, however, is not statistically important. Regarding the thermally modified samples it seems that polyurethane shows slighter reduction in comparison with the PVAc for the treatment at 180°C for 3 hours while in the following treatments the polyurethane shows greater reduction except the case of the 180°C for 7 hours when a slighter and insignificant difference is shown for the polyurethane adhesive. Therefore, we conclude that the PVAc adhesive has a better attitude, during the adhesion and higher modulus of rupture in comparison with the polyurethane after the thermal modification of the wood. Regarding the PVAc adhesive an increase in the detachment percentage is noticed in thermally modified wood up to 200°C for 3 hours when the reduction starts. Generally, the high percentage of detachment of a sample shows that the adhesive bond shows greater strength in comparison with the wood strength as the rupture takes place in the mass wood not in the bonded area.

The exactly opposite results were noticed for the wood failure of the polyurethane samples. Particularly, the wood failure was decreasing until the treatment at 180°C for 7 hours by the time it started increasing at 200°C for 3, 5 and 7 hours. This proves that the adhesive bond was stronger than the wood strength the more the temperature and the treatment duration was increasing. The reduction of the shearing strength after thermal treatment of wood can be explained with the change of the penetration of the adhesive, in the porous structure of the wood due to the fact that wood is generally hydrophilous before undergoing thermal treatment, while after the heat treatment it is transformed into hydrophobous (Paul et al. 2007).

Tab. 1: Modulus of rupture and wood failure of the bonded samples of two different types of adhesive before and after the thermal treatment.

Heat treatment conditions	Units	Fir wood – Shearing strength by compression loading					
		Modulus of rupture (N·mm ⁻²), Wood failure (%)					
		PVAc			PU		
		Fmax (N)	Modulus of rupture (N·mm ⁻²)	Wood failure (%)	Fmax (N)	Modulus of rupture (N·mm ⁻²)	Wood failure (%)
Untreated	X	2542	12.71	75	2507	12.53	77.85
	±s	740.5	0.37	9.40	951,6	0.47	16.25
	V	5483	0.13	88.46	9055	0.22	264.28
	s ²	0.02	0.02	0.12	0,037	0.03	0.20
180°C 3 hours	X	2039	10.19	82.85	2217	11.08	47.14
	±s	512.7	0.25	9.94	1211	0.60	13.25
	V	2628	0.06	98.90	1467	0.36	175.82
	s ²	0.02	0.02	0.12	0.05	0.05	0.28
180°C 5 hours	X	2164	10.82	84.28	2031	10.15	69.28
	±s	1101	0.55	12.22	1107	0.55	16.85
	V	1212	0.30	149.45	1227	0.30	284.06
	s ²	0.05	0.05	0.145	0.05	0.05	0.24
180°C 7 hours	X	2012	10.06	79.28	2018	10.09	66.42
	±s	639.8	0.31	14.91	599	0.29	10.08
	V	4094	0.10	222.52	3588	0.08	101.64
	s ²	0.03	0.03	0.18	0.02	0.02	0.15
200°C 3 hours	X	1986	9.93	65.71	1775	8.87	72.14
	±s	685.8	0.34	20.64	624,5	0.31	20.82
	V	4704	0.11	426.37	3900	0.09	433.51
	s ²	0,034	0.03	0.31	0.03	0.03	0.28
200°C 5 hours	X	1775	8.87	57.14	1760	8.8	80.71
	±s	951.6	0.47	13.25	578.3	0.28	13.28
	V	9057	0.22	175.82	3344	0.08	176.37
	s ²	0.053	0.05	0.23	0.03	0.03	0.16
200°C 7 hours	X	1657	8.28	65.71	1479	7.39	80.71
	±s	674.9	0.33	17.85	725.7	0.36	14.39
	V	4556	0.11	318.68	5266	0.13	207.14
	s ²	0.04	0.04	0.27	0.04	0.04	0.17

X: Average ($\pm=14$), $\pm s$: Standard deviation, V: Variance, s^2 : Variance

The reduction of its hygroscopicity has been combined with reduction of the number of the hydrophilous parts in the wood, especially the hydroxyl parts of the carbohydrates (Sahin et al. 2009). With the degradation of the carbohydrates after the thermal treatment, the concentration of the water absorbing parts of hydroxyl is reduced, resulting in the slow absorbance of the water and the absorption. The lignin plasticity and the reorganization of the lignocellulose polymeric parts of the wood can also increase the hydrophobous characteristics of the thermally modified wood. Secondly, the wettability of the wood is reduced after the thermal treatment mostly because

the surface of the thermally modified wood is hydrophobous, less polical and significantly repellent to moisture. This could prevent aqueous adhesive from substantial soaking of the surface (Serneketal 2008). Thirdly, the thermal treatment reduces the wood pH. The acidity increase is due to the formation of acetic acid which was emitted from the semi-celluloses and which catalyzes more the carbohydrates, causing reduction of the polymerism of the carbohydrates (Tjeerdsma et al. 1998, Windeisen et al 2007, Boonstra et al 2007).



Fig. 2: Sample placement in the test machine.

According to Fig. 3 which refers to the pH measuring of the modified fir wood, are duction of its value is noticed after the thermal treatment in comparison with the untreated wood. The more the temperature and the duration of the thermal treatment are increased, the more the pH value is decreased. This reduction, according to the literature, is due to the acetic acid formation which is emitted from the semi-celluloses and which catalyzes more the decomposition of the carbohydrates causing reduction of their polymerization degree (Sahin et al. 2009).

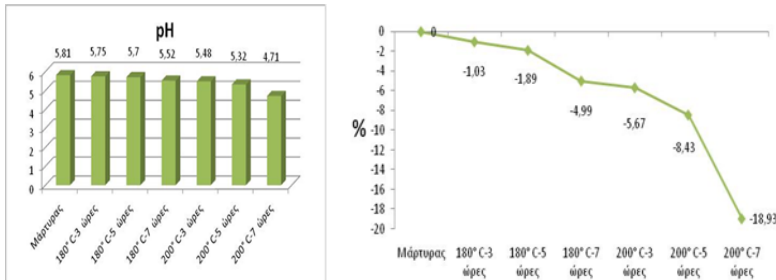


Fig. 3: Reduction percentages of the pH value after the thermal treatment.

According to the statistical analysis of the results of the thermally modified samples and of the untreated wood it seems that all the thermal treatments differ statistically in a significant way in comparison with the non-modified wood regarding both adhesives.

Ordu et al. (2013) studied the shearing strength performance on pine wood with the use of adhesive PVAc and polyurethane (PU). The thermal treatment was conducted at 100-150°C for 4 hours. The researchers mention that the temperature rise affected the adhesive bond performance positively by studding the bonded sample. Particularly, it was noticed that while the treatment temperature increased from 100 to 150°C, the adhesive performance increased at 31.51% on PVAc samples and from 28.02% on polyurethane samples.

CONCLUSIONS

Unmodified fir wood showed highest bonding strength compare to heat treated samples. The more the temperature and the duration of the treatment are increased, the more the bonding strength is decreased. Considering the two adhesives, do not show great differences between each other in the bonding performance regarding the non-modified wood but only a slight precedence of the PVAc adhesive. Therefore, the lighter thermal treatment condition should be used in order to get the highest bonding performance.

REFERENCES

1. Ahmad, M., 2000: Analysis of Calcutta bamboo for structural composite materials. Dissertation, Wood Sci. and Forest Products, VT, 210 pp.
2. Boonstra, M.J., Acker, J.V., Tjeersman, B.F., Kegel, V.E., 2007: Strength properties of thermally modified softwoods and its relation to polymeric structural wood constituents, *Ann. For. Sci.* 64: 679–690
3. Cruz, M., Martins, J., Carvalho, L., 2007: Effect of surface treatment on the bondability of pine and eucalypt with UF resins. In: Proceedings of the 5th COST E34 International Workshop. Bled-Slovenia, Pp 95-105.
4. Hill, C., 2006: Wood modification: Chemical, thermal and other processes.' John Wiley & Sons Chichester, 239 pp.
5. Ordu, M., Altinok, M., Atilgan, A., Ozalp, M., Peker, H., 2013: The effects of heat treatment on some mechanical properties of laminated black pine (*Pinus nigra*), *International journal of physical sciences* 8(19): 1029-1035.
6. Paul, W., Ohlmeyer, M., Leithoff, H., 2007: Thermal modification of OSB-strands by a one-step heat pre treatment-Influence of temperature on weight loss, hygroscopicity and improved fungal resistance, *Holz als Roh und Werkst.* 65: 57-63.
7. River, Bryan., Vick, C., Gillespie, R., 1991: Wood as an adherent. Treatise on adhesion and adhesives, Vol. 7 230 pp, NewYork, Marcel Dekker.
8. Sahin Kol, H., Özbay, G., Altun, S., 2009: Shear strength of heat-treated tali (*Erythrophleum ivorense*) and iroko (*Chlorophora excelsa*) woods, bonded with various adhesives, *BioResources* 4(4): 1545-1554.
9. Sernek, M., Boonstra, M., Pizzi, A., Despres, A., and Gerardin, P., 2008: Bonding performance of heat treated wood with structural adhesives, *Holz als Roh und Werkst.* 66(3): 173-180.
10. Tjeerdsma, B.F., Boonstra, M., Pizzi, A., Tekely, P. Militz, H., 1998: Characterisation of thermally modified wood: molecular reasons for wood performance improvement, *Holz als Roh und Werkstoff* 56: 149-153.
11. Unsal, O., Buyuksari, U., Ayrimis, N., Korkut, S., 2009. Properties of wood and wood based materials subjected to thermal treatments under various conditions. International conference: Wood science and engineering in the third millennium - ICWSE.
12. Vladimirova, E., 2013: Determination of glue joint shear strength of thermally modified pine (*Pinus silvestris*) and birch (*Betula pendula*) in comparison with the unmodified wood. 6th Innovations in forestry industry and engineering design. Yundola, November, 2013.
13. Windeisen, E., Strobel, C., Wegener, G., 2007: Chemical changes during the production of thermotreated beech wood, *Wood Science and Technology* 41(6): 523-536.

MITANI ANDROMACHI, RAMMOU EKATERINI
TECHNOLOGICAL EDUCATIONAL INSTITUTE OF LARISSA
KARDITSA BRANCH
DEPT. OF WOOD AND FURNITURE DESIGN AND TECHNOLOGY
43100 KARDITSA
GREECE
*Corresponding author: amitani@hotmail.com