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SHEAR STRENGTH OF HEAT TREATED PINE WOOD (*Pinus nigra*) WITH SOME STRUCTURAL ADHESIVES

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Abstract

The shear strength of heat treated wood with adhesives would significantly increase the range of applications for this material, although heat treatment can affect the ability of adhesives to bond the wood. The aim of this study was to evaluate the influence of heat treatment on the shear strength of some structural adhesives. Shear strength of untreated and heat-treated pine (*Pinus nigra*) wood bonded with phenol-formaldehyde (PH), melamine-urea-formaldehyde (MUF), melamine-formaldehyde (MF), polyurethane (PUR) and urea-formaldehyde (UF) adhesives was studied. An industrial heat treatment method (ThermoWood) was used. Pine timbers were thermally modified for 2 hours at 212 ºC. Laminated samples having two lamellas were prepared from untreated and heat-treated pine for the shear strength test. The results of the tests showed that the ThermoWood can be bonded with these structural adhesives but shear strength of ThermoWood pine was less than that of untreated pine. The heat treatment affected the shear strength, negatively. No considerable difference was observed between the adhesives used to bond heat treated wood although the least affected adhesive was UF.

Keywords: Adhesive, wood, shear strength, heat treatment

1. Introduction

Increasing environmental pressure appeared in the last years in many European countries leading to important changes in the field of wood preservation, particularly regarding biocide toxicity promoting the non-biocidal alternatives. Among these alternatives, wood heat treatment by mild pyrolysis has been intensively investigated leading to the development of several industrial processes in Europe [1, 2].

Heat treated wood is exposed to a maximum temperatures of between 160°C and 260°C. The presence of oxygen at these temperatures would cause severe losses in the mechanical properties of wood, so different process conditions (nitrogen, steam, oil or intact vacuum) have been used in order to reduce the oxygen content in the reactor atmosphere [1,3]. The wood samples investigated in this study were thermally modified in an industrial-scale heat treatment process, "ThermoWood Process", was developed at the Technical Research Centre of Finland (VTT) in the early 90's. The ThermoWood process is based on heating the wood material for a few hours at high temperatures above 180 °C under normal pressure while protecting it with water vapour [4]. Water vapour protects the wood from burning and cracking, and it also affect the chemical changes taking place in wood [5].

During heat treatment, considerable changes in the chemical composition of wood occur, including the degradation of the hemicelluloses, cellulose and lignin [2, 6]. As a consequence of chemical changes in wood's structure the physical properties of wood are also modified. The main targets for industrial heat-treatment are increased biological durability, enhanced weather resistance and decreased shrinking and swelling of wood. Also, lower equilibrium moisture content, darkened colour and increased thermal insulation are welcome changes in the wood properties during heat-treatment. On the other hand, as a result of heat-treatment, mechanical properties of wood decrease in relation of the level of heat-treatment [7,8]. The degree and intensity of modifications and/or reactions during heat treatment depend on several factors such as the state of the wood specimens, the level of temperature load, the prevailing atmosphere and the duration of the treatment [9].

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The heat treatment process is tailored for different applications, mostly for purposes where wood is exposed to weathering and variations in moisture content, for example, exterior, cladding and garden furniture. One interior application is a floor material. The use of heat-treated wood is not recommended when it is in contact with the ground or used in load bearing constructions [10]. The bonding of heat treated wood with adhesives would significantly increase the range of applications for this material, although heat treatment can affect the ability of adhesives to bond the wood [11]. Heat treatment can be expected to cause significant changes related to adhesion, which makes it necessary to adapt the bonding process [3]. Heat treatments result in wettability changes associated with a decrease of hygroscopicity and equilibrium moisture content of wood, which could favourably modify the reactivity of organic reagents sensitive to moisture [8, 12, 13]. This might hinder waterborne adhesives from adequately wetting the surface and alter the distribution of the adhesive on the wood surface and the penetration of the adhesive into the porous wood structure [3].

The pH value of wood is another factor which could affect the bonding process. Heat treatment results in a decrease of pH due to production of acetic and formic acids [14]. Changes of the pH value of the wood surface might retard or accelerate the curing of adhesives, depending on the type of adhesive used for bonding [3]. Increase in acidity in wood after heat treatment, might neutralize the alkaline hardeners used for phenol-recorcinol formaldehyde resins and hinder the adhesive hardening. On the other hand, a low pH of the wood surface could accelerate the chemical reactions of acid catalyzed amino resins: urea-formaldehyde and melamine formaldehyde [15].

With increasing use of heat treated wood for exterior and interior applications, the concerns about bonding performance of heat treated wood bonded with various adhesives such as phenol–formaldehyde (PF) resin, melamine–formaldehyde (MF) resins, urea-formaldehyde (UF) or polyurethane (PU) has increased. The aim of this study was to evaluate the effect of heat treatment on the shear strength of the structural adhesives which used widely in woodworking industry.

2. Material and Method

2.1 Materials

10 Pine (Pinus nigra) planks 32×125 mm in cross section and 4 m long) were obtained from Nova ThermoWood in Gerede. The planks have approximately an initial moisture content of 50%-60%. Prior to heat treatment the each plank were cut into two 2 m long pieces from the middle because the thermally modified and untreated samples were from the same planks. Then, the one half of these planks which were used for control samples were dried in industrially drying-kiln at approximately at a temperature of 70 ºC to a moisture content of 11%-15%. The other half of these planks were subject to ThermoWood heat treatment process.

The phenol formaldehyde (PH), melamine-urea-formaldehyde (MUF), melamine formaldehyde (MF), polyurethane (PUR) and urea-formaldehyde (UF) adhesives were used as adhesives. The ready-to-use PH, MF, MUF, PUR and UF adhesives were supplied from GENTAŞ and POLİSAN, producer firms in Turkey and their characteristics are given in Table 1.

Table.1. Characteristics of adhesives used

Adhesives	Density (20 ºC) (g/cm^3)	pH (20 ºC)	Viscosity (20 ºC) (cPs)	Solid (2 h, 120 ºC) (%)
PF	1.20	11.0	300	47.06
3%MUF	1.24	9.0	400	55.00
%20	1.28	9.2	600	64.90
MUF	1.23	9.15	50	55.2
MF	1.11	7.0	5500	100
PUR	1.22	7.5	100	55
UF				

2.1.1 Heat Treatment of Wood (ThermoWood)

The heat–treatment was applied according to method described in Finnish ThermoWood Handbook (ThermoWood Handbook 2003). The Thermo-Wood process involves three distinct process stages: 1. warming up stage, 2. drying stage, and 3. cooling and conditioning stage. The warming up stage is to heat and pre-dry lumber. The temperature in the kiln is raised rapidly and a large amount of steam is generated. At the beginning of the drying stage, the temperature is increased steadily and the timber is dried intensively. At a certain point of the drying stage when the moisture content of the lumber reaches nearly 0%, the temperature is raised rapidly to a range of 185 °C to 215 °C depending on the applications of the treated products. Wood is kept at this temperature for 2–3 h. In cooling and conditioning phase, the temperature of the wood is lowered to 80 °C to 90 °C using water spray system. Conditioning is carried out to moisten the heat-treated wood and bring its moisture content to 4%–7%.
Pine was heat treated at about 212 °C under steam. The total time of the heat treatment was 113 h and the duration time at this high temperature was 2h. The heat treatment operation was carried out quite slowly, because the initial moisture of the planks were high and due to this there was not a big risk of drying cracks. After heat treatment only the planks that were free of defects were selected for further testing.

2.2 Moisture Content and pH Determination

The native (untreated control) and heat-treated boards were then into lamellas and conditioned in a standard climate with 65% relative humidity (RH) and at a temperature of 20 °C. The MC of the specimens was determined by the gravimetric method. The MC of the untreated and heat treated lamellas prior to bonding were 11.7% and 6.8%, respectively. The pH value was evaluated by using extraction method 20 g of wood was ground into small particles and soaked in 160 g of distilled water for 24 hours. The extract was filtered and analyzed with a pH meter. The pH of the untreated and heat treated lamellas were 5.08 and 4.53 respectively.

2.3 Specimen preparation and property testing

The lamellas were planed to a thickness of 5 mm, bonded together into small samples. The adhesive was applied at the rate of about 180-200 g/m^2 on single bonding surface of the lamellas (single glue line) as recommended by the manufacturer. Glues were spread uniformly on the veneers by manually hand brushing. The press pressure, temperature and duration were applied as 1.2 N/mm^2, 120 ºC and 15 min for PF, MUF, MF and UF adhesives and 1.2 N/mm^2, 22 ºC and 90 min for PUR, respectively. In total, 120 samples were bonded (2 groups of wood, 6 adhesives, and 10 duplicates). The samples were tested after being conditioned for 3 weeks at 20±2 °C and 65±3 % relative humidity.
The measurement of shear strength was carried out in a Zwick/Roel Z50 universal testing machine, according to BS EN 205 (2003) and TS EN 12765 (2004) [16,17]. The loading speed was 5 mm/min. The loading was carried out until a break or separation occurred on the surface of the test samples. The shear strength (σk) was calculated using the observed load (Fmax) and bonding surface of sample (A, mm^2) according to the following formula (1):

$$\sigma_k = \frac{F_{\max}}{A} = \frac{F_{\max}}{ab}\left(N.mm^{-2}\right) \quad (1)$$

where a is the width of the glued surface (10 mm) and b is the length of glued surface (20 mm).

3. Result and Discussion

Measured equilibrium moisture content (EMC) and density values of untreated and heat treated samples prior to shear test are given in Table 2.

Table 2. The EMC and density values of untreated and heat treated samples prior to shear test

Adhesives	Untreated control		Heat treated	
	Density	EMC[a]	Density	EMC[a]
PUR	0.513	9.1	0.448	5.5
MF	0.507	8.3	0.479	5.3
FF	0.501	8.2	0.484	5.5
MUF%3	0.504	8.2	0.453	5.9
MUF%20	0.511	8.1	0.447	5.4
UF	0.514	8.5	0.484	5.3

[a] EMC, equilibrium moisture content

Heat treatment caused a decrease in the EMC and density of samples. The availability and/or accessibility of the free hydroxyl groups of the wood carbohydrates play an important role in the process of water adsorption and desorption. The heat treatment changes chemical structure of wood, especially hydroxyl groups. Hence, reduction of water absorption after heat treatment is most probably due to depolymerisation of the carbohydrates and especially hemicelluloses, resulting in a reduction of the total amount of hydroxyl groups, including the free hydroxyl groups [18]. Therefore the EMC of the heat treated pine is less than untreated pine. Due to heat treatment and thermal degradation, wood losses its mass [7]. This causes a decrease in density of wood.
The shear strength values of the heat-treated and untreated pine samples bonded with the adhesives and decrease in the shear strength values with the heat-treatment are shown in Table 3.

Table. 3. Shear strength of untreated and the heat-treated pine

Adhesives	Control	St.Dev.	Heat-Treated	St.Dev.	Decrease %
PUR	6.36	1.13	3.41	0.44	-46
MF	5.74	1.21	3.34	0.81	-42
PF	6.07	1.14	3.73	0.82	-39
MUF%3	6.33	0.59	3.30	0.38	-48
MUF%20	6.15	0.60	3.24	0.56	-47
UF	5.84	1.33	4.58	1.04	-22

The heat-treatment affected the bond line negatively (Table 4). The shear strength of all adhesives was decreased by the heat-treatment. The decrease of shear strength after heat-treatment can be explained by considering the combination of some facts. Heat treatment can alter the distribution of the adhesive on the wood surface and its penetration into the porous wood structure because the wood, generally hydrophilic, became hydrophobic after heat treatment [19]. Also, the wettability of wood with water is decreased after heat treatment [20, 21], mainly because the surface of the heat-treated wood is hydrophobic, less polar and significant repellent to water. This might hinder waterborne adhesives from adequately wetting the surface [3]. Heat treatment reduces the pH of wood. The increase in wood acidity is due to the formation of acetic acid liberated from the hemicelluloses, which further catalyses carbohydrates cleavage causing a reduction of degree of polymerization of the carbohydrates [9, 14, 18]. According to the results of this study, the heat treatment reduced the pH of pine from 5.08 to 4.53. Changes in pH affect the hardening process of adhesives depending on the adhesive type. Low pH conditions might neutralize of the alkaline hardener for PF. Decrease of pH might accelerate the condensation reactions of amino resins. This accelerated condensation hinders the penetration of the adhesive in to wood. According to the results of this study it has been said that the heat-treatment decreased the pH of wood slightly, therefore the shear strength of adhesives was not affected considerably by decrease of pH.

Table 4. Results of Multi Variance Analyses

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	200.996679	11	18.272	17.116	0.000
Intercept	2810.464613	1	2810.465	2632.606	0.000
Process	184.559247	1	184.559	172.880	0.000
Adhesive	5.107717874	5	1.022	0.957	0.448
Process * Adhesive	11.32971409	5	2.266	2.123	0.068
Error	115.2964719	108	1.068		
Total	3126.757764	120			

The heat treatment of wood can change its surface properties and the changes might causes difficulties in the adhesion of adhesives and painting colours. One reason in difficulties in wood surface processing is that low-molecular weight wood extractives such as fatty acids, fats and waxes migrate to the surface of the heat-treated wood, thus interfering with the absorption process [22, 23]. Fats and waxes of pine moved during the heat treatment along the radial parenchyma cells onto the edges of the sapwood [10]. These extractives might affect the adhesion of bond line.

The highest decrease was observed in shear strength of about 47-48% in samples bonded with MUF adhesives (Table 3). Decrease in shear strength of 46% and 42% was observed in samples bonded with PUR and MF adhesives, respectively. The decrease in samples bonded with PF was obtained as 39%. The lowest decrease (22%) was obtained in samples bonded with UF adhesive.

The data were further analyzed using an analysis of variance and followed by Duncan test at the 95% confidence level. According to the results, there was no statistically significant difference between the shear strength of the adhesives in untreated control samples. For heat treated samples there was not also significant difference between the shear strength of the adhesives except the UF adhesive. This is indication that heat treatment decreases the shear strength of wood itself. It is well-known that heat treatment reduces strength properties of wood.

Sernek et al. (2007) reported a decrease in shear strength of 13% for spruce bonded with PF and UF, each by heat treatment at 210 °C for 2 hours. In another study Sernek et al. (2008) reported that shear strength was 6.28 N/mm^2 for untreated spruce bonded with MUF and 4.86 N/mm^2 for heat treated spruce and a decrease of 23%. The decreases occurred with heat treatment in our study in pine were relatively high. But these results are not comparable properly because of variation in heat treatment method and especially wood species used in these studies.

4. Conclusions

The results of the tests carried out in this study revealed that the heat treatment reduced the equilibrium moisture of content, density and shear strength of pine bonded with PF, PUR, MF, MUF and UF adhesives. All the adhesives bonding performance was affected negatively by the heat treatment. The highest decrease in shear strength was observed in samples bonded with MUF adhesives. UF adhesive gave the highest shear strength for the heat treated pine. Because there was no statistically significant difference between the adhesives, all of them can be used for bonding the heat treated wood. PF adhesive can be preferred in exterior application because of its relatively low cost according to the other exterior grade adhesives. PUR adhesive can be preferred in exterior application for assembly purpose due to its easy to use. In addition, in interior application UF adhesive can be used for its higher shear strength and low cost.

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