THE EFFECTS OF NATURAL WEATHERING ON THE PROPERTIES OF HEAT-TREATED ALDER WOOD

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The objective of this study was to investigate the effect of natural weathering in ground contact on biological resistance, modulus of rupture, and color stability of heat-treated alder wood. Chemical composition of weathered wood was also studied by FTIR-ATR spectra. Wood stakes were heated at 150, 180, and 200°C for periods of 2, 6, and 10 hours, and the stakes were subsequently exposed to natural weathering and decay in a field area located in the north of Turkey for 3 years. The decay index of heat-treated stakes was lower than that of the controls. The weight loss prevention ratio had an increasing tendency with increasing treatment temperature and length of time. Depending on the treatment parameters, heat treatment reduced the modulus of rupture by up to 50%; however decay caused by soil micro-organisms gave rise to a greater loss of modulus of rupture than heat. Weathering processes caused remarkable color changes in the samples. FTIR-ATR spectra showed significant deformations and degradations in wood components, especially in the hemicelluloses of heat-treated samples. Degradation of hemicelluloses increased with an increase in heat temperature and exposure time.

Keywords: Alder wood; Field test; Heat treatment; Natural weathering; FTIR-ATR

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INTRODUCTION

Weathering is a general term used to define the slow decomposition of materials subjected to the weather (Williams 2005). Natural weathering modifies the molecular structure of wood because of a complex combination of chemical, mechanical, biological, and light-induced changes that occur simultaneously and affect each other (Feist 1992).

During the course of an outdoor weathering process, the original wood surfaces become rough as the grain rises, the wood checks, and the checks grow into large cracks; grain may loosen, and boards cup and warp and pull away from fasteners. The roughened surface changes in color, gathers dirt and mildew, and may become unsightly (Feist and Hon 1984). The change in wood color occurs with photochemical reactions and their effects of ultraviolet and visible light (Williams 2005). A loss in strength is associated with light-induced depolymerization of lignin and cell wall constituents and to the subsequent breakdown of wood microstructure. Heat may not be as critical a factor as UV light or water, but as the temperature increases, the rate of photochemical and oxidative reactions increases (Feist and Hon 1984).

Feist and Hon (1984) stated that "Weathering is not to the confused with decay, which results from decay organisms (fungi) acting in the presence of excess moisture and air for an extended period of time. Under suitable conditions for the development of decay, wood can deteriorate rapidly and the results are far different than that observed for natural outdoor weathering." Many researchers have examined weathering of wood in the outdoors since it exposes wood to a number of abiotic and biotic agents (Opoku 2007). However, there is a gap of evaluation of weathering performance in ground contact. Natural durability of wood is determined by the European standard EN 252 for stakes in ground contact. In soil bed and/or field test methods, partial burial of a stake with exposure to the micro-organisms, to half its length, is a more realistic simulation of ground contact exposure (Baines 1984; EN-252 1989). The other half of the stake above the ground zone provides a test of exposure to weathering conditions. Therefore it may be possible to evaluate the stakes as both weathered and decayed, and stakes may be assessed visually, by examining for checking, by chemical and color analysis of wood surface on the ground zone, or by measuring the weight loss caused by micro-organisms in the soil or loss in mechanical strength.

Thermal treatment is an effective method to improve the dimensional stability and biological durability of natural wood. Heat-treated wood products can be used for an extensive range of applications such as garden fences, sauna furnishing, window frames, cladding, decking, and exterior joinery. One of the most important effects gained by a heat treatment of wood is reduced wood hygroscopicity. The other two main advantages of heat-treated wood are enhanced resistance to biodegradation and improved dimensional stability (Boonstra 2008). Thermally modified wood has drawn a great deal of attention, as being one of the wood protective treatments without using any harmful chemicals, so thermal treatment can be considered an ecological alternative to the impregnation of wood (Wikberg 2004). However, some undesired side effects, such as loss of strength and increased brittleness of the treated wood are the main barriers limiting many commercial applications of heat-treated timber (Boonstra 2008). There are various methods of thermal treatment of wood. The main differences between these methods are based on the wood species, process conditions, and the treatment equipment (Boonstra 2008). High temperature and long durations during the heat treatment process cause severe decrease of mechanical properties (Yildiz, 2002). The rate of thermal degradation is also affected by the surrounding atmosphere, especially regarding the presence or absence of oxygen. It is demonstrated that thermal degradation in the presence of oxygen is more rapid than that in an oxygen-free atmosphere (Mitchell 1998).

Despite the availability of several studies on artificial weathering of thermally modified wood, there remains little information about natural weathering and durability of heat-treated wood. A field test method can be used for both determining the protective effectiveness against to attack by micro-organisms in the soil, in particular fungi, and testing the natural weathering of wood in ground contact.

The objective of this study was to investigate the influence of weathering on color stability and chemical changes occurring in the surface structure of heat-treated alder wood. Biological effectiveness was evaluated by a grading system to determine the extent of attack of stakes caused by micro-organisms. Furthermore, modulus of rupture test was performed due to a suspicion of extensive rot attack and degradation by weathering conditions on the wood structure.

EXPERIMENTAL

Materials

Stakes 20 x 20 x 300 mm (tangential x radial x longitudinal) were machined and sanded from the sapwood of alder (*Alnus glutinosa* L.) logs obtained from Trabzon located in the North-East Black Sea region of Turkey. Before heat treatment, the stakes were conditioned at 65% relative humidity and 20 ºC for two weeks to a moisture content of 12%. For each treatment ten replicate stakes were used.

Methods

Heat treatment was applied on the test stakes in an oven, controlling the temperature with ± 1ºC sensitivity. The temperature raised to 150 ºC, 180 ºC, and 200 ºC at a rate of 10 ºC / min. Once the target temperature had been reached, the temperature was held constant for 2, 6, and 10 h, under atmospheric pressure and in the presence of air, without any humidity and/or gas (Yildiz 2002).

The stakes were then exposed to natural weathering and decay testing in ground contact for 3 years in Carsamba-Samsun, located in the north of Turkey. In this study "natural weathering" term was used in the meaning of the test procedure in which stakes were exposed to both weathering agents and soil organisms. The field area exhibits favorable conditions for degradation of wood. The treated and untreated stakes were inserted randomly to half of their length in the soil. Stakes were inspected in the same month twice a year (Yildiz et al. 2010), and assessed visually according to EN-252 (1989) and AWPA-E7 (1993). The report of the weather conditions of this area during the weathering period for 3 years was obtained from Samsun Regional Directorate of Meteorology. After the exposure time of weathering and decay testing, the stakes were cleaned, oven dried, and weighed, and then weight loss was calculated. Weight loss of wood was calculated according to Equation 1.

$$\textit{Weight loss of wood (\%)} = [\, (m_0 - m_d) / m_0 \,] \times 100 \qquad (1)$$

where m_0 is the dry weight prior to test, and m_d is the dry weight after the test.

The results were statistically analyzed by univariate analysis of variance (ANOVA), and significant differences in weight losses between the temperature and time were classified by the Duncan test.

Modulus of rupture (MOR) was determined by 3-point bending according to the Turkish Standard (TS 2474 (1976)) in a Universal Testing Machine. Loading was done at the tangential direction of the stakes. The distance between the centers of the two supports was 240 mm free span, and the crosshead speed was 1.1 mm/min.

Color measurements were carried out using a Minolta CM-2600d spectrocolor-imeter, equipped with an integrating sphere (Hunter 2008). Measurements were made over a 8 mm diameter spot with 10° observer angle. Four replicate measurements on each stakes were recorded. The L^*, a^*, and b^* color coordinates were measured on the tangential face of the stakes at the air zone. These values were used to calculate the total color change (ΔE^*) as a function of the treatments applied to the wood stakes according to Eq.2. A low ΔE^* value corresponds to a low color change or a stable color (Aydin et al. 2006).

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (2)$$

where ΔL^*, Δa^*, and Δb^* are the changes in value between before and after treatment.

Biological effectiveness of heat treatment for in-ground use was determined by the Index of decay (*ID*) criteria based on the EN 252 (1989) and AWPA-E7 (1993) standards. The rating system for decay is shown in Table 1.

Table 1. Rating System for Decay (EN 252-89 standard)

Condition	Rating of decay	Index of decay
Sound - no decay	0	0
Slight decay	1	25
Moderate decay	2	50
Severe decay	3	75
Very severe decay	4	100

The FT-IR spectra were recorded with a PerkinElmer Spectrum 100 with a Universal ATR sampling accessory. Four accumulated spectra with a resolution of 4 cm^{-1} were obtained from the top portion of stakes exposed to weathering. FTIR and color measurements were done on the south-facing portion of tangential surface.

RESULTS AND DISCUSSION

The average weight loss (%), statistical test results, and weight loss prevention ratios (%) of heat-treated and weathered stakes after three years of exposure on field are summarized in Table 2. Weight loss prevention ratio (%) can be defined as the ability of decreasing weight losses of heat treated samples compared to that of controls.

As can be seen in Table 2, the average weight losses after the field test were reduced at elevated temperatures and with increasing length of treatment. Hence, weight loss prevention ratios were higher in heat-treated stakes than weathered control stakes. Heat treatment at 200 ºC and 180 ºC for 10 h showed best performance against to bio-degradation. There were no statistically significant differences between the temperatures of 180 ºC and 200 °C and the durations of 6 and 10 hours. Accordingly, it can be stated that heat-treatment at various elevated temperatures and periods may prevent the rate of weight loss resulting from decay. However, the weight loss resulting from the heat treatment itself was also considered. In this study, weight losses on account of heat treatment were between a range of 1.6-3.8%; 4.4-9.8%, and 4.9-12.2% for heat-treated stakes at 150, 180, and 200 ºC, respectively. Fengel (1966) recorded that "during the heating of spruce wood for 24 h, a weight loss is 0.8 % at 120 °C and it is increased up to 15.5 % at 200 °C". In the study of Fengel and Wegener (1989), heat treatment of beech wood with an increasing temperature of 5 °C per minute resulted in a weight loss of 8.1 % at 150 °C and 9.8 % at 200 °C. Bruno et al. (2008) reported that "weight loss increased with treatment time and temperature". Alen et al. (2002) studied the weight loss of heat treated spruce at temperatures between 180 °C and 225 °C during 4 to 8 hours and found 1.5 % weight loss at 180 °C for 4h and 12.5 % at 225 °C for 6h.

Table 2. Weight Loss Amounts (%) and Statistical Test Results for Weathered Samples

Temperature (°C)	Treatment Time (h)	Average Weight Loss (%)	Weight loss prevention ratios (%)	Temperature (°C)	HG **
Control		46.1 (5.3)*	-	Control	c
150	2	36.9 (9.7)	+20.0	150	b
	6	24.5 (14.9)	+47.0	180	a
	10	23.0 (0.1)	+50.1	200	a
180	2	28.6 (12.8)	+38.0	Time (h)	HG
	6	9.8 (3.2)	+78.9	Control	c
	10	3.8 (0.8)	+91.7	2	b
200	2	23.5 (6.0)	+49.0	6	a
	6	8.9 (1.1)	+80.8	10	a
	10	4.4 (1.3)	+90.4		

*Values in parentheses are standard deviations
**HG: Homogeneous groups Different letters (a-c) indicate significant difference by Duncan's homogeneity test, P<0.05

Despite the fact that the heat treatment was conducted in the presence of air, the weight losses ranged from 1.6 to 12.2%. However, the weight losses in the same stakes after weathering and decaying varied within the range 3.8 to 36.9% (Table 2). Especially at low treatment temperatures, the weight loss caused by soil organisms was much more than that of the weight loss caused by heat treatment itself. On the other hand, heat treatment of alder wood at higher temperatures increased its durability against the deterioration agents in the field test. Similar results have been obtained by other researchers. Scheiding et al. (2005) reported that commercially heat treated wood samples demonstrated good natural resistance against wood destroying fungi. Welzbacher et al. (2005) found significant resistance against to soft-rotting micro-fungi with oil-heat-treated spruce samples.

Table 3 shows the changes in MOR caused by the heat treatment and natural weathering. The MOR of heat-treated stakes generally exhibited a decrease with increasing treatment time and temperature (Table 3). Decreasing ratios of bending strength after heat treatment were in a range of 5.4 to 6.5%; 9.1 to 31.2%, and 17.6 to 54.9% for heat-treated stakes at 150, 180, and 200 ºC, respectively. The most dramatic reductions were observed in the variations of 180°C-10h (32%), 200°C-6h (34%), and 200°C-10h (55%). Decreasing ratios at 150°C were judged to be tolerable. These reductions in MOR are consistent with other studies (Viitaniemi 1997; Kubojima et al. 2000; Bengtsson et al. 2002; Johansson and Moren 2006; Bruno et al. 2008). The reductions in the strength properties can be attributed to the rate of thermal destruction and losses of some substances after heat treatments (Rusche 1973). According to the Kotilainen (2000) the decrease in strength properties is mainly due to the depolymerization reactions of wood polymers. Additionally, heat treatment in the air medium causes more reductions in strength properties than heat treatment carried out in an inert gas medium such as nitrogen. The thermal degradation of wood heated in the presence of oxygen is more rapid than that of wood heated in an oxygen free atmosphere. The presence of oxygen during hydrolysis forms acids. Thus, the combined process of hydrolysis and oxidation contribute to the thermal degradation of wood (Mitchell 1988). Kubojima et al. (2000) also reported similar decreases on bending strength of heat treated wood in air medium.

Table 3. MOR Values of the Samples after Heat Treatment and Weathering

Temperature (°C)	Treatment Time (h)	Heat-treated Average MOR (kp/cm²)	Change (%)	Heat-treated and weathered Average MOR (kp/cm²)	Change* (%)
Control		755 (18.3)	-	66 (19.1)	-
150	2	716 (27.6)	-5.4	236 (25.4)	- 67.0
	6	730 (17.4)	-3.3	211 (20.6)	-71.1
	10	706 (47.5)	-6.5	133 (12.4)	-81.2
180	2	686 (16.6)	-9.1	298 (8.2)	-56.6
	6	603 (47.6)	-20.1	204 (29.5)	-66.2
	10	514 (49.1)	-31.9	182 (12.7)	-64.6
200	2	622 (46.5)	-17.6	147 (10.9)	-76.4
	6	498 (18.2)	-34.0	121 (11.7)	-75.7
	10	340 (31.5)	-54.9	200 (26.8)	-41.2

* Decreasing ratios of bending strength values compared to the heated samples.

After the three years of field exposure, decreasing ratios of bending strength values compared to the heated stakes are also shown in Table 3. The decreasing ratios of bending strength were between 67.0-81.2%; 56.6-64.6%, and 41.2-76.4% for heat-treated stakes at 150, 180 and 200 ºC, respectively. The strength losses in control-weathered stakes were higher than those of heat-treated and weathered samples resulted from the heat treatment effect. The main factor on reduction of MOR in controls could be explained by high weight loss caused by micro-organisms attack. The decay rating of controls was ranked as "4" means very severe decay (Table 7). Minimum strength loss was obtained from the stakes heated at 200°C for 10 h.

Heat treatment affected the MOR values positively under outdoor conditions. However, the total effect of two different factors (heat treatment and field test) caused serious reductions in MOR compared to the control groups (untreated and unexposed to weathering). Long-term exposure of the heat-treated stakes to outside conditions caused more effective degradation of bending strength values. When such stakes were compared to the weathered control group, the positive effect of the heat treatment was seen clearly in all outdoor variations (Table 3).

The effects of climatic parameters on weathering process were evaluated according to the some climatic data obtained from Samsun Regional Directorate of Meteorology for 3 years (Table 4). According to Table 4 it can be said that both the humidity and the temperature increased especially during the summer season. However, the temperatures did not reach high values even in summer months. Autumn rainfall (mm) tended to increase. The number of rainy days (>10mm/day) was maximum in November. July and August were the cloudiest months. The snowiest days were in February. Soil temperature was quite reasonable even in winter. In general, Samsun has a typical Black Sea climate with high rainfall. Summers are warm and humid, whereas winters are cool and damp. Snowfall is quite common between the months of December and April. Under these climatic conditions, the low MOR values and degradation of surfaces observed in the control stakes were as an expected. However, as reported before, decay plays an important role in strength losses.

Table 4. Average of Climatic Parameters in Field Area during Weathering for 3 years

Climatic parameters	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Average Temp. (°C)	8.8	6.5	6.9	10.4	15.6	20.3	23.5	24.5	20.3	16.7	12.0	9.3
Average Humudity (%)	68.4	69.7	76.3	78.7	81.3	75.3	76.1	76.0	78.2	73.8	73.2	65.2
Average rainfall (mm)	58.4	54.9	93.8	77.9	48.5	44.0	27.0	54.2	66.8	105.7	104.1	76.3
Number of rainy days (>10mm/d)	2.0	0.7	3.3	2.7	1.0	1.7	-	1.3	3.0	3.0	3.7	1.7
Number of cloudy days	23.7	20.3	15.0	16.7	20.7	22.3	24.0	24.0	23.3	20.7	18.0	19.0
Number of stormy days	3.7	2.7	0.7	0.7	-	-	0.3	-	0.3	0.3	0.7	1.0
Number of snowy days	1.3	6.3	4.0	1.3	-	-	-	-	-	-	-	1.3
Number of days covered by snow	-	1.7	0.7	0.7	-	-	-	-	-	-	-	1.0
Max. snow depth (cm)	-	3.0	1.7	3.3	-	-	-	-	-	-	-	3.7
Soil temp. (an average of 10 cm)	7.4	6.7	8.5	13.5	19.9	25.3	28.8	29.4	23.3	17.8	11.7	8.0

Feist (1990) reported that wood weathering has been ascribed to a complex set of chemical changes occur on wood surface due to solar radiation (UV, visible, and IR light), moisture (dew, rain, snow, and humidity), temperature, and oxygen. In addition to these environmental factors, the presence of atmospheric pollutants such as sulfur dioxide, nitrogen dioxide, and ozone also affect main wood components. The total effects of these factors could be provoked the reduction rate of MOR beside decay. According to the some researchers a loss in strength properties can be related to light-induced depolymerization of lignin and cell wall components and to the subsequent breakdown of wood microstructure (Raczkowski 1980; Feist and Hon 1984).

Tables 5 and 6 show the effects of heating and weathering on the color properties of alder wood stakes, respectively. Generally the discoloration, as represented by ΔL^*, Δa^*, and Δb^*, became greater with increasing duration of treatments. Moreover, the negative values of lightness (ΔL^*) and chromaticity coordinates (Δa^* and Δb^*) indicate that the surfaces of the stakes were getting darker. The darkening color can be attributed to the increased temperature and duration of heat treatment. Sundqvist (2002) reported that "color of wood darkens as a result of different oxidative and/or hydrolytic discoloring reactions taking place in wood during the heat treatment. Darkening of wood is usually more intense with increasing treatment time and temperature (Sundqvist 2002).

Table 5. Effect of Heat Treatment on CIE L*a*b* Color Properties of Alder Wood Samples

Temperature (°C)	Treatment Time(h)	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*
Control*		66.39	10.12	21.81	-	-	-	-
150	2	65.39	8.42	18.20	-1.3	-1.7	- 3.8	4.4
	6	61.41	7.71	16.73	-5.4	-2.5	-5.5	8.1
	10	56.69	6.96	17.96	-11.5	-3.7	- 4.0	12.8
180	2	48.48	9.72	19.79	-18.8	-1.3	-3.0	19.1
	6	39.23	9.77	16.09	-27.6	-2.2	-5.9	28.3
	10	35.57	7.39	11.29	-31.2	-3.2	-11.1	33.3
200	2	44.94	9.17	18.64	-22.4	-2.2	-4.0	22.8
	6	38.42	8.82	13.93	-29.7	-2.0	-9.0	31.1
	10	33.40	6.64	9.31	-34.7	-3.9	-12.7	37.2
* Unheated control samples								

Table 6. Effect of Natural Weathering on CIE L*A*B* Color Properties of Alder Wood Samples

Temperature (°C)	Treatment Time(h)	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*
Control*		35,70	8,02	21,89	30,7	2,1	-0,1	30,8
150	2	42,02	9,78	25,90	23,4	- 1,4	-7,7	24,6
	6	35,60	10,22	27,75	25,8	- 2,5	-11,0	28,2
	10	33,15	10,01	27,29	23,5	- 3,1	- 9,3	25,5
180	2	29,55	10,33	27,79	18,9	-0,6	- 8,0	20,6
	6	28,16	10,88	28,65	11,1	-1,1	- 12,6	16,8
	10	23,25	10,84	25,90	12,3	-3,5	-14,6	19,4
200	2	25,44	11,82	27,44	19,5	-2,7	- 8,8	21,6
	6	20,54	11,01	26,70	17,9	-2,2	-12,8	22,1
	10	17,23	9,19	19,90	16,2	-2,6	-10,6	19,5
* Unheated control samples exposed to natural weathering								

The lightness values of heat-treated wood stakes (Table 5) were almost two times higher than the results of weathered stakes (Table 6). This result can be attributed to an increased degree of surface oxidation of the weathered stakes (Laurent and Kamdem 2002). The ΔL^* generally decreased with increasing treatment time and temperature in weathered stakes. According to the Feist and Hon (1984) when wood is subjected to the outdoors conditions or in artificial UV light for a short period, changes in brightness and color are readily observed. Ayadi et al. (2003) found that the light-induced decomposition of wood is observed mainly due to the some photochemical reactions occurring in lignin. Temiz et al. (2005) reported that depolymerization of the lignin on the exposed surface may also render the surface darker. In addition, Bourgois et al. (1991) noted an effect of hemicellulose on the change in color with heat treatment. Therefore, it is thought that the decrement of L^* of light-irradiated wood with thermal treatment is due to not only lignin or lignin derivatives but also to hemicelluloses decomposition (Mitsui et al. 2004).

After heat treatment, the overall color change (ΔE^*) increased with increasing treatment time and temperature. A low ΔE^* corresponds to a low color change or a stable color. Therefore, it can be said that heat treatment increased the changes in the original wood color. Similar results were reported by Ayadi et al. (2003). As can be seen in Table 6, there was a decreasing tendency on color changes in heat treated and weathered stakes compared to the weathered control stakes. This decreasing tendency was much clearer at elevated treatment temperatures and durations. Heat treatment at 180 °C and 200 °C much more delayed the color changes against to weathering factors than heat treatment at 150 °C. The weathering factors can be responsible for high color changes in weathered control stakes. The cause of these findings can be explained as follows: Chemical reactions in wood during weathering cause changes in wood color. As rain leaches the brown decomposition products of lignin, a silver-gray layer consisting of a disorderly arrangement of loosely matted fibers develops over the brown layer. The original color of wood changes to gray when wood exposed to the sun in climates (Feist and Hon 1984). However, another mechanism of surface graying of weathered wood – fungal action – usually predominates, particularly in the presence of moisture (Feist and Hon 1984). Microorganisms may also produce dark-colored spores and mycelia, which can induce a dark gray, blotchy, and unsightly appearance of some weathered wood. All wood surfaces will eventually turn gray when exposed to sun and rain (Feist 1992). Exposure of wood to UV light is known to be mainly responsible for the degradation and discoloration of the wood surface in natural weathering (Nuopponen et al. 2004).

During the weathering and decay testing, each stake was visually inspected for the level of decay. The evaluation rating from 0 to 4 and decay index are described in Table 7. Stakes treated at 150 °C - 2h / 6h / 10h, and 180 °C-2h were generally more sensitive to different wood decaying factors. In these stakes, a significant decay was observed in the wood to an apparent depth of 3 to 5 mm over a wide surface. There were some small holes through in the stakes. A decay depth of 2 to 3 mm was observed in all around the stakes treated at 180 °C-6h / 10h and 200°C - 2 h / 6h. Especially in spots, there were deeper attacks (3 to 4 mm). Treatment at 200 °C for 10 h which has the highest temperatures and the longest treatment time was recorded as the best treatment conditions. There were some perceptible changes on wood stakes, but they were very limited.

As can be seen from Table 7, the lowest decay index (*ID*) value (30%) was obtained in the stakes treated at 200°C for 10 hours. In a research paper about durability of thermally modified timber, the term of durability factor was developed for evaluation of heat treated wood samples in field tests. In accordance with EN 252 (1989), durability factors were determined as follows (Welzbacher and Rapp 2007):

$$Durability\ factor = Decay\ rate_{control} / Decay\ rate_{tested\ samples} \qquad (3)$$

Table 7. Decay Rating of Samples Exposed to Field Test for Three Years by Visual Inspection and Index of Decay (ID)

Temperature (°C)	Treatment Time(h)	Grading	Index of decay(ID)
Control		4.0	100
150	2	3.7	92.5
	6	3.4	85
	10	3.2	80
180	2	3.0	75
	6	2.4	60
	10	2.0	50
200	2	2.2	55
	6	2.1	52.5
	10	1.2	30

Accordingly, as a result of thermal modification, the obtained durability classes ranged from 1 “durable” to 4 “non-durable” in our study. The stakes treated at 150ºC for 2, 6, and 10 h were classified as non-durable; the stakes treated at 180ºC for 2, 6, and 10 h, and 200ºC for 2 and 6 h were classified as slightly durable; and the stakes treated at 200ºC for 10 h were assigned as durable. The results indicated that heat-treated wood is more resistant against to natural deterioration agents than untreated wood. Similar results were obtained in some studies applied various heat treatment techniques. Scheiding et al. (2005) reported that the durability classes of heat-treated wood species ranged from non-durable to durable.

Ayadi et al. (2003) suggested that the modified structure of lignin and new phenolic moieties were responsible for the improved durability of heat-treated and weathered wood. In other studies, rot resistance was related to decomposition of wood components (Viitaniemi et al. 1997), lower equilibrium moisture content (Buro 1954), and formation of some toxic degradation products (Kamdem et al. 2000). In thermally treated wood, a process that reduces hemicellulose content, such reduction has been demonstrated to have a significant impact on the biological resistance of wood (Buro 1954), since the hemicelluloses are the most important carbon source of such fungi (Nuopponen 2005). Prolonged thermal treatment duration and increased temperature have been reported to enhance fungal resistance of wood (Buro 1954; Nuopponen 2005). Nuopponen et al. (2004) reported that heated wood is more resistant to biodegradative effects in outdoor conditions.

The highest *ID* value was obtained from the control group. It was observed that there was very severe microorganisms attack over all the circumference of the control stakes at the ground line zone or below. Additionally, there were very large cracks and erosions on the upper part of the stakes. Outdoor factors such as light, moisture, heat, oxygen, and pollutants degrade unprotected wood exposed to outdoor conditions (Nuopponen et al. 2004).

The FTIR-ATR spectra of heat treated and untreated samples before and after weathering are shown in Figs. 1-3. The assignments of the characteristic IR absorption peaks in wood samples are listed in Table 8.

Table 8. Assignments of Absorption IR Spectral Bands in Wood (Temiz 2005; Ximenes and Evans 2006; Temiz et al. 2007)

Wavenumber cm^{-1}	Assignments and remarks
1720-1740	C=O stretching in xylan
1645-1660	C=O stretching, C=C stretching, H-O-H deformation
1595±5	C=C in aromatic ring in lignin
1510±5	C=C in aromatic ring in lignin
1465±5	CH_3 deformation in lignin and CH_2 bending in xylan
1425±5	CH_2 scissor vibration in cellulose
1370±5	CH_2 bending in cellulose and hemicellulose
1315±5	CH_2 wagging vibration in cellulose
1234±5	Syringyl nuclei in lignin and C-O in xylan
1156±5	C-O-C asymmetric band in cellulose and hemicellulose
1100	O-H association band in cellulose and hemicellulose
1031	C-O stretching in cellulose and hemicellulose
894	C1 group frequency in cellulose and hemicellulose

Heat treatment causes significant transformation in the chemical composition of wood during heat treatment process. Wood components are degraded and modified through reactions such as dehydration, hydrolysis, oxidation, decarboxylation, and transglycosylation (Kocaefe et al. 2008).

The carbonyl absorption peak at 1720-1740 cm^{-1} decreased on the heat treated samples compared to the un-weathered controls. This was probably caused by the degradation of hemicelluloses. The change of this peak confirms the cleavage of the acetyl side chains in hemicelluloses (Kocaefe et al. 2008). The carbonyl absorption region at 1630 to 1800 cm^{-1} at high temperatures showed that new extractable carbonyl and carbonyl compounds were formed, originating from hemicelluloses (Nuoppenen et al. 2004). The carbonyl absorption peak decreased with increasing heat treatment temperatures and durations. This effect was clearer in samples treated at 180 and 200ºC. These findings of decreased intensity at 1733 cm^{-1} with increasing treatment temperature are in consistent with the heat treatment studies carried out by Tjeerdsma and Militz (2005) and Kocaefe et al. (2008). Weaker peaks resulting from contributions of xylan, especially at 1735cm^{-1}, were seen in heat-treated samples by Salmen et al. (2008). The band at 1649 cm^{-1} is related to C=O stretching of the aromatic structures. There was a smaller weakening at this band according to similar findings by Temiz et al. (2007). However it increased in weathered control samples compared to un-weathered controls.

Chemical degradation of weathered controls was clearly seen in the figures. High degradation may be related to orientation which measurements were carried on. FTIR measurements were done on the south facing portion of wood surface, and sunlight of this direction is higher than other orientations.

As expected, weathering process caused more reductions in the range 1720 to 1740 cm^{-1} than heat treatment in all treatment temperatures and durations, suggesting that there was decreasing photo-oxidation of wood surface after sunlight irradiation. Weathered samples showed remarkable decreases at this peak compared to un-weathered control samples. The band at 1743 cm^{-1} originates from the C=O stretching vibration of the acetyl groups of galactoglucomannan, and it is a sign of cleavage of acetyl groups during weathering (Nuoppenen et al. 2004). Nuoppenen et al. (2004) extensively reviewed the decrease at this band after heating and weathering. Temiz et al. (2007) reported a decrease on the carbonyl absorption band at 1710 to 1745cm^{-1} in weathered samples with an explanation of leaching the carbonyl content formed by UV degradation due to water applied on the sample surfaces.

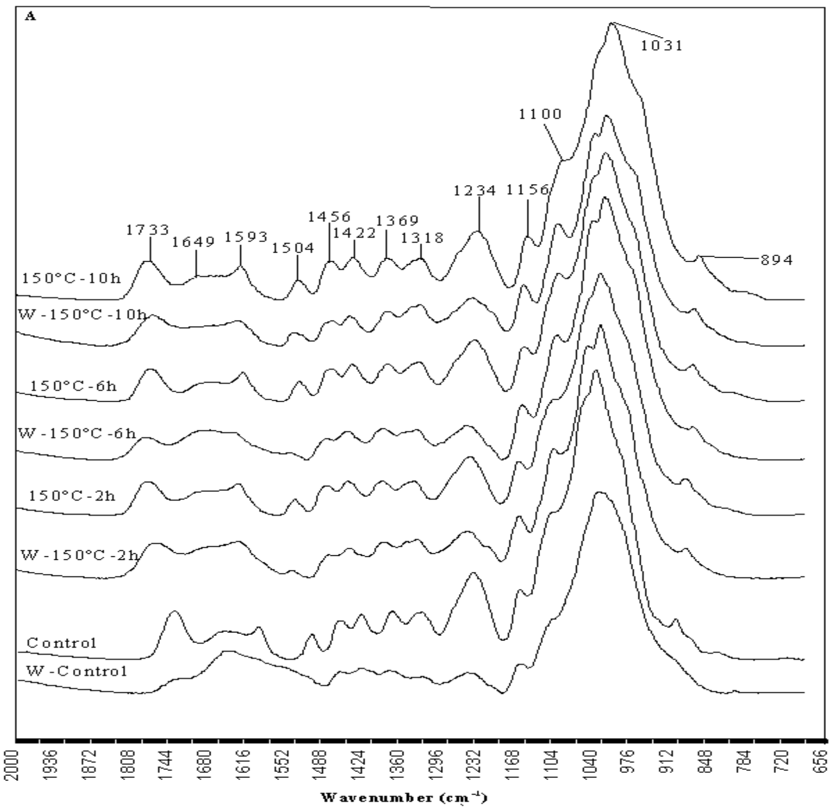

Fig. 1. The FTIR-ATR spectra of heat treated at 150ºC and untreated samples before and after weathering

Samples heated at 200 ºC for 6-10h and then weathered showed not too much reduction in at 1735 cm^{-1} compared to heated and un-weathered samples. Heat treatment at 200 ºC for 6-10 h can be expected to protect wood components against to environmental conditions such as UV, water, fungi etc. In Table 7, the decay rating of the samples exposed to field testing was better than that of others. However the strength losses in these treatment variations were greater than other treatment variations. This result is consistent with higher degradation extents of hemicelluloses after treatment at higher temperatures and longer durations.

The absorption peaks at 1156, 1100, 1031, and 894 cm^{-1} showed slight changes. The cellulose skeleton vibrations including the C-O-C bridge stretching signals occurring at this area. These changes were supposed to be caused by the degradation of hemicelluloses. This is in agreement with the findings of a previous study by Salmen et al. (2008). The asymmetric ring stretching band of cellulose at 894 cm^{-1} started to decrease in the treated samples. The band at 894 cm^{-1} is characteristic of the C1-H group vibration of cellulose and hemicelluloses (Nuopponen et al. 2004; Ximenes and Evans 2006). Thermal degradation of the hemicelluloses could cause a reduction at this peak (Colom et al. 2003; Kocaefe et al. 2008). Hemicelluloses are the most vulnerable to thermal degradation among the other wood components (Nuopponen 2005). In this study, the hemicelluloses and celluloses of wood samples exposed to heat treatment were shown to have been deformed and degraded. In weathered samples the reduction at these peaks was higher than heated samples.

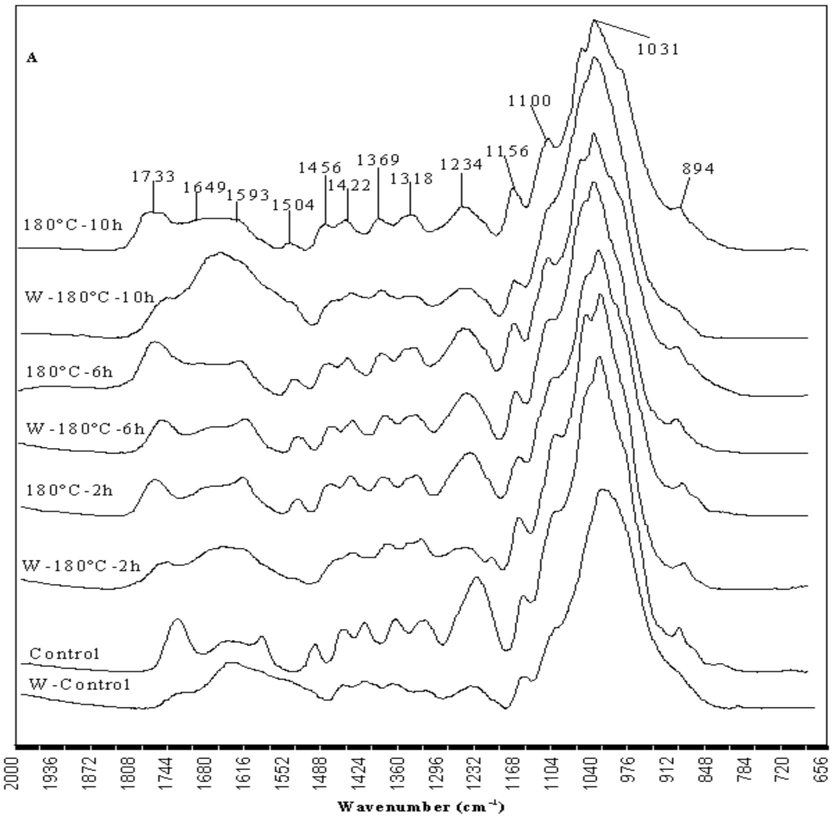

Fig. 2. The FTIR-ATR spectra of heat treated at 180ºC and untreated samples before and after weathering

The absorbance bands at 1593, 1504 cm^{1} (benzene ring stretching in lignin), and 1456 cm^{-1} (CH_3 deformation in lignin and CH_2 bending in xylan) were slightly changed by heat treatment. However in weathered samples significant differences at 1504 cm^{1} were obtained. The reduction indicates lignin modification, especially degradation of lignin, occurred during weathering (Nuopponen et al. 2004). The reduction in this band was decreased by increasing temperature and durations of treatment in weathered samples.

It has been known that lignin in the heat-treated wood is cross-linked. Therefore, a modified structure of lignin in heat treated samples could partly inhibit UV-light-induced free-radical reactions and formation of low molecular weight degradation products. Higher dimensional stability of the heat-treated wood that reduces the effect of moisture content in outdoor weather conditions may be another reason for this (Nuopponen et al. 2004). In addition to these changes, the absorbance at 1234 cm^{-1} (C=O stretching in xylan, and syringyl nuclei in lignin) in heated samples also showed weakening. These changes suggested that thermal treatment modified hemicelluloses as well as lignin. This peak indicates the cleavage of acetyl groups in the hemicelluloses which form carbonic acids and degradation of lignin during weathering (Nuopponen et al. 2004; Kocaefe et al. 2008).

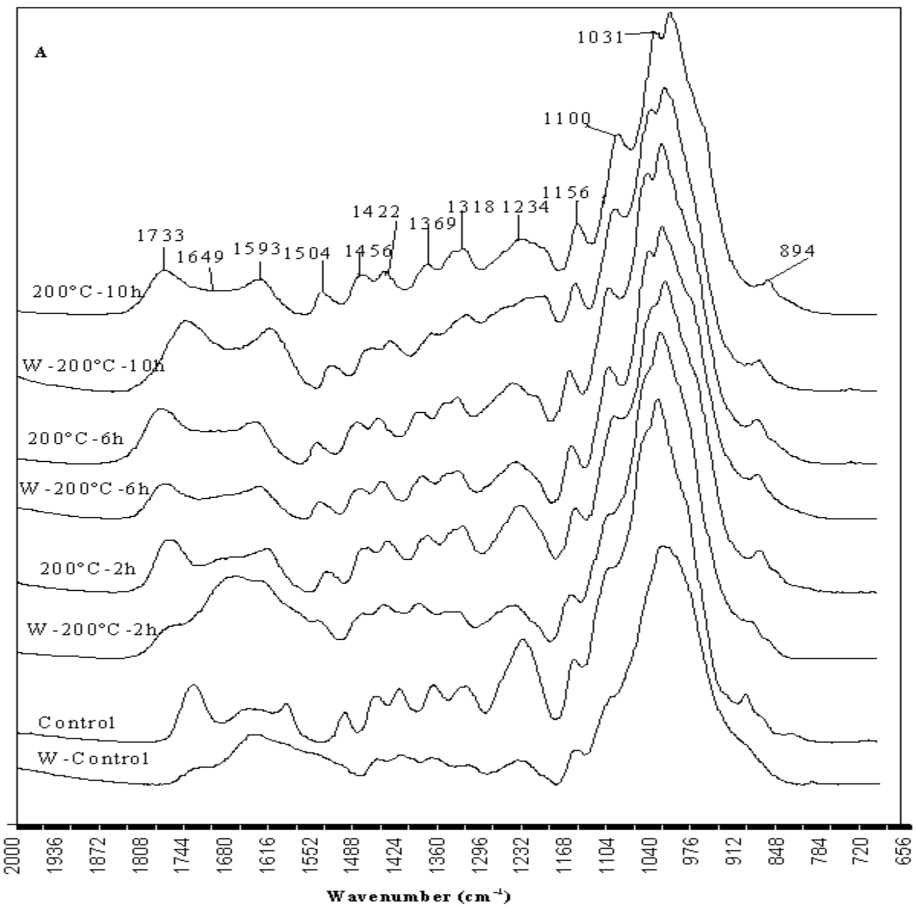

Fig. 3. The FTIR-ATR spectra of heat treated at 200ºC and untreated samples before and after weathering

There was a small decrease with increasing temperature and durations of heat treatment in the peak at 1422 cm^{-1}, related to the CH_2 vibration of the aromatic structures and CH_2 in carbohydrates (Kocaefe et al. 2008). A slight weakening at 1369 cm^{-1} and 1318 cm^{-1} was also seen in heat treated samples, corresponding to the OH plane bending.

Wood becomes more hydrophobic due to a reduction in the free hydroxyl groups (Kocaefe et al. 2008). Similar decreases at this peak were also observed by Yildiz and Gumuskaya (2007) for heat treated beech and spruce due to increase in crystalline structure. The reduction of the peaks corresponding to the cellulose component in weathered samples was more than in heated samples. This result indicates that the structure of the cellulose polymer was degraded to an important extent after weathering.

CONCLUSIONS

1. Heat treatment at elevated temperature and duration reduced weight losses resulting from weathering and microorganisms attack. The lowest *ID* value (30%) was obtained in the stakes treated at 200°C for 10 hours.
2. After the heat treatment, it was observed that MOR was reduced by up to 50% compared with untreated wood. At the end of the 3 years, the MOR of decayed stakes was clearly lower than that of heat treated stakes.
3. Color changes (ΔE^*) of the stakes ranged between 4 and 37 after heat treatment. Depending on treatment temperature and durations, original wood color went from dark brown to blackish. Heat treatments delayed/decreased the rate of color change caused by weathering factors but did not completely prevent it.
4. All the test results showed that the most advantageous treatment condition, in many aspects, was 200 °C-10 hours. If better weather and decay resistance is necessary, the temperatures chosen for the heat treatment process should be at least 200 °C. In addition, it is advisable to take into consideration decreases in strength at high temperatures in some usage areas where strength properties are important. On the other hand, heat-treated wood does not fully protect wood in the ground contact. So, it is recommended to use heat treated wood with protective coatings or painting in these usages.
5. Significant deformations and degradations in wood components, especially in hemicelluloses, of heat treated samples due to heat effect were observed by FTIR spectra. Degradation of hemicelluloses increased with an increase in heating temperature and exposure time. However, heat treatment at 200 ºC for 6-10 h protected wood components against environmental conditions.

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REFERENCES CITED

Alen, R., Kotilainen, R., and Zaman, A. (2002). "Thermomechanical behavior of Norway spruce (*Picea abi*es) at 180-225 °C," *Wood Science and Technology* 36, 163-171.

American Wood-Preservers' Association. (1993)."Standard method of evaluating wood preservatives by field tests with stakes,"AWPA-E7, P.O. Box 5690, Granbury, TX 76049, USA.

Ayadi, N., Lejeune, F., Charrier, F., Charrier, B., and Merlin, A. (2003). "Color stability of heat treated wood during artificial weathering," *Holz als Roh- und Werkstoff* 61, 221-226.

Aydın, I., Çolakoğlu, G., and Hızıroğlu, S. (2006). "Surface characteristics of spruce veneers and shear strength of plywood as a function of log temperature in peeling," *Process International J. Solids and Structures* 43, 6140-6147.

Baines, E.F. (1984). "Preservative evaluation using a soil bed and static bending strength to major performance," *AWPA* 67-79.

Bengtsson, C., Jermer, J., and Brem, F. (2002). "Bending strength of heat-treated spruce and pine timber," *The International Research Group on Wood Preservation 33rd Annual Meeting*. IRG/WP 02-40242, 14-17 May, Cardiff, U.K.

Boonstra, M. J. (2008). "A two-stage thermal modification of Wood," Ph.D. Thesis, Ghent University, Belgium.

Bourgois, P. J., Janin, G., and Guyonnet, R. (1991). "La mesure de couleur. Une méthode d'optimisation des transfomations chimiques du bois thermolys," *Holzforschung* 45, 377-382.

Bruno, M. E., Domingos, I. J., and Pereira, H. M. (2008). "Pine wood modification by heat treatment in air," *BioResources* 3, 142-154.

Buro, A. (1954). "Die Wirkung von Hitzebehandlungen auf die Pilzeresistenz von Kiefern- und Buchenholz," *Holz Roh Werkstoff* 12, 297-304.

Colom, X., Carrillo, Nogues, F., and Garriga, P. (2003). "Structural analysis of photodegraded wood by means of FTIR spectroscopy," *Polymer Degradation and Stability* 80, 543-549.

European Committee for Standardization. (1989). "Field test method for determining the relative protective effectiveness of a wood preservative in ground contact," EN 252, Brussels, Belgium.

Feist, W. C. (1990). "Outdoor wood weathering and protection, archaeological wood, properties, chemistry and preservation," Rowell, R. (ed.), Advances in Chemistry Series No. 225. Washington DC: American Chemical Society; Chapter 11, 263-298,

Feist, W. C. (1992). "Natural weathering of wood and its control by water-repellent preservatives," *American Painting Contractor* 69, 18-25.

Feist, W. C., and Hon, D. N. (1984). "Chemistry of weathering and protection," In: *The Chemistry of Solid Wood,* Rowell, R. M. (ed.), Advances in Chemistry Ser. 207, Washington DC: American Chemical Society; 401-451.

Fengel, D. (1966). "On the changes of the wood and its components within the temperature range up to 200 ºC-Part III: Thermally and mechanically caused structural changes in spruce wood," *Holz Roh-und Werkstoff* 24, 529-536.

Fengel, D., and Wegener, G. (1989). *Wood, Chemistry, Ultrastructure, Reactions*, Walter de Gruyter and Co, Berlin, New York, pp. 613.

Hunter Associates Laboratory. (2008). "CIEL* a*b* color scale. Applications note-Insight on Color," *HenterLab* 8(7), 1-4.

Johansson, D., and Morén, T. (2006). "The potential of colour measurement for strength prediction of thermally treated wood," *Holz als Roh- und Werkstoff* 64, 104-110.

Kamdem, D. P., Pizzi, A., and Triboulot, M.C. (2000). “Heat-treated timber: Potentially toxic byproducts presence and extent of wood cell wall degradation,” *Holz als Roh- und Werkstoff* 58, 253-257.

Kocaefe, D., Poncsak, S., and Boluk, Y. (2008). “Effect of thermal treatment on the chemical composition and mechanical properties of birch and aspen,” *BioResources* 3, 517-537.

Kotilainen, R. (2000). “Chemical changes in wood during heating at 150-260°C,” Ph.D. Thesis, Jyväskylä University, Finland.

Kubojima, Y., Okano, T., and Ohta, M. (2000). “Bending strength and toughness of heat treated wood,” *Wood Science* 46, 8-15.

Laurent, M. M., and Kamdem, D. (2002). “Accelerated ultraviolet weathering of pvc/wood-flour composites,” *Polymer Engineering and Science* 42, 1657-1666.

Mitchell, P.H. (1988). “Irreversible property changes of small loblolly pine specimens heated in air, nitrogen, or oxygen,” *Wood and Fiber Science* 20, 320-335.

Mitsui, K., Murata, A., and Tolvaj, L. (2004). “Changes in the properties of light-irradiated wood with heat treatment: Part 3. Monitoring by DRIFT spectroscopy,” *Holz als Roh-und Werkstoff* 62,164-168.

Nuopponen, M., Wikberg, H., Vuorinen, T., Maunu, S. L., Jämsä, S., and Viitaniemi, P. (2004). “Heat-treated softwood exposed to weathering,” *J. Applied Polymer Science* 91, 2128-2134.

Nuopponen, M. (2005). “FT-IR and UV Raman spectroscopic studies on thermal modification of scots pine wood and its extractable compounds,” Ph.D. Thesis, Helsinki University of Technology, Espoo.

Opoku, Y.F. (2007). “An investigation into the suitability of selected lesser utilized Ghanaian hardwoods for use as outdoor furniture and decking,” M.Sci Thesis, Brunel University, Uxbridge, United Kingtom.

Raczkowski, I. (1980). “Seasonal effects of atmospheric corrosion of spruce microsection,” *Holz als Roh und Werkstoff* 38, 231-234.

Rusche, H. (1973). “Thermal degradation of wood at temperatures up to 200 °C –Part I: Strength properties of dried wood after heat treatment,” *Holz als Roh-und. Werkstoff* 31, 273-281.

Salmen, L., Possler, H., Stevanic, J. S., and Stanzl-Tschegg, S. E. (2008). “Analysis of thermally treated wood samples using dynamic FTIR-spectroscopy,” *Holzforschung* 62, 676-678.

Scheiding, W., Kruse, K., Plaschkies, K., and Weib, B. (2005). “Thermally modified wood (TMW) for, playground toys: Investigations on 13 industrial manufactured products,” *The Second European Conference on Wood Modification*, 6-7 October, Göttingen, Germany.

Sundqvist, B. (2002). “Color response of Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*) and Birch (*Betula pubescens*) subjected to heat treatment in capillary phase,” *Holz als Roh- und Werkstoff* 60, 106-114.

Temiz, A., Yildiz, U. C., Aydın, İ., Eikenes, M., Alfredsen, G., and Çolakoğlu, G. (2005). “Surface roughness and color characteristics of wood treated with preservatives after accelerated weathering test,” *Applied Surface Science* 1, 35-42.

Temiz, A. (2005). "The effect of simulated weathering on preservative treated wood," Ph.D Thesis, Karadeniz Technical University, Trabzon, Turkey.

Temiz, A., Terziev, N., Eikenes, M., and Hafren, J. (2007). "Effect of accelerated weathering on surface chemistry of modified wood," *Applied Surface Science* 253, 5355-5362.

Tjeerdsma, B. F., and Militz, H. (2005). "Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood," *Holz als Roh- und Werkstoff* 63, 102-111.

Turkish Standard. (1976). "Wood-determination of ultimate strength in static bending," TS 2474, Ankara.

Viitaneimi, P. (1997). "Thermowood – Modified wood for improved performance," In: Proceedings of Wood the Ecological Material. *The 4th Eurowood Symposium*, Sep 22–23, Trätek rapport 9709084, pp. 67-69, Stockholm, Sweden.

Viitaniemi, P., Jämsä, S., Ek, P., and Viitanen, H. (1997). "Method for improving biodegradation resistance and dimensional stability of cellulosic products," *Pat*., US 5,678-324.

Welzbacher, C. R, Rapp, A. O., Haller, P., and Wehsener, J. (2005). "Biological and mechanical properties of densified and thermally modified Norway spruce," *The Second European Conference on Wood Modification*, 6-7 October, Göttingen, Germany.

Welzbacher, C. R., and Rapp, A. O. (2007). "Durability of thermally modified timber from industrial-scale processes in different use classes: Results from laboratory and field tests," *Wood Material Science and Engineering* 2, 4-14.

Wikberg, H. (2004). "Advanced solid state NMR spectroscopic techniques in the study of thermally modified wood," Ph.D. Thesis, Faculty of Science of the University of Helsinki, Finland.

Williams, R.S. (2005). *Handbook of Wood Chemistry and Wood Composites*, *Weathering of Wood*, Rowell, R. M. (ed.), Taylor and Francis Group, CRC Press, New York, pp. 139-185.

Ximenes, F. A., and Evans, P. D. (2006). "Protection of wood using oxy-aluminum compounds," *Forest Products Journal* 56, 116-122.

Yildiz, S. (2002). "Physical, mechanical, technologic and chemical properties of *Fagus orientalis* and *Picea orientalis* wood treated by heating," Ph.D. Thesis, Institute of Natural Sciences, Karadeniz Technical University, Trabzon, Turkey, 264 p.

Yildiz, S., and Gumuskaya, E. (2007). "The effects of thermal modification on crystalline structure of cellulose in soft and hardwood," *Building and Environment* 42, 62-67.

Yildiz, S., Yildiz, Ü.C., and Dizman, E. (2010). "The effects of natural weathering on the properties of heat treated alder wood," *The International Research Group on Wood Preservation 41st Annual Meeting*. IRG/WP 10-40484, 9-13 May, Biarritz, France.

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