Effect of tall oil pretreatment on physical and mechanical properties of heat treated fir and beech

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ABSTRACT

Thermal treatment is an environmentally friendly process and effective to improve biological resistance as well as enhance dimensional stability of wood material. However, the mechanical properties of the wood are decreased by heat treatment, since the temperature is applied between 180 °C and 260 °C which affect the wood cell wall components. Tall oil is a major byproduct from pulp and paper industry running according to Kraft process. The water repellent and decay resistance properties of tall oil make it a valuable product in the field of wood protection.

In this study, fir and beech samples treated with tall oil at concentration of 10 % alone, also heat treated at 190 and 212 °C respectively. In addition, the combination of both tall oil and heat treatment was applied on fir and beech samples. Water uptake and tangential swelling of untreated and treated samples was measured during two weeks. From the mechanical properties, bending strength and modulus of elasticity were determined on the samples of untreated, tall oil treated, heat treated and combination of both treatments. The lowest water uptake was obtained with the fir samples treated with tall oil and heat treated in the temperature of 212 °C. Minimum tangential swelling was found to be 3.36 % in the samples of fir treated with 10 % tall oil and heat treated at 212 °C, while the control samples exhibited the maximum as 6.59 %. In the beech samples, the best result in terms of water uptake was achieved by heat treatment at 212 °C when compared to other treatments. Tall oil treated samples improved the tangential swelling in beech samples when they were exposed to heating at 190 °C as a second treatment. ASE was improved by the combination of tall oil and heat treatment at 190 °C and 212 °C in fir and beech samples. Tall oil increased the bending strength (MOR) to the fir and beech woods when combined with heat treatment at 212 °C in comparison to heat treatment alone.

Key words: tall oil / heat treatment / water uptake / bending strength

1. 1.INTRODUCTION

It is well known that heat treatment is an environmentally friendly and potential method to improve wood decay resistance and dimensional stabilization (Tjeerdsma et al. 1998; Weiland and Guyonnet 2003; Hill 2006). In the heat treatment process, initially hemicellulose is subjected to degradation, resulting in the decreasing in hydroxyl groups and the formation of O-acetyl groups, which makes the wood more hydrophobic. Therefore, heat treated wood gains improved dimensional stability because of the decrease in swelling and shrinking as a result of less water absorption (Stamm 1956; Kocaefe et al. 2008). The decrease in equilibrium moisture content was attributed to lower water absorption by wood cell wall after heat treatment due to the chemical change resulting in reduced hydroxyl groups (Jamsa and Viitaniemi 2001). Besides, cross-linking as a result of polycondensation reaction in lignin component might help the decreasing in equilibrium moisture content (Boonstra and Tjeerdsma 2006).

Repellin and Guyonnet (2005) investigated the swelling of heat treated beech by means of differential scanning calorimetry and relationships between chemical changes and the reduction of swelling, and proposed that the reduction in swelling could not only be attributed to the hemicellulose degradation but also structural modifications and chemical changes of lignin had an important role. However, mechanical properties such as shock resistance, modulus of elasticity (MOE), bending strength (MOR), compressive resistance, shear strength, and abrasion resistance are reduced in wood by heat treatment (Boonstra et al. 2007). The mechanical properties of wood is either determined by static or dynamic methods, however static bending is one of the most used to assess the strength of the wood specimens. With regard to heat treatment, static and impact bending of the wood are most affected depending on the wood species and treatment conditions (Esteves and Pereira 2009). Another nonbiocidal treatment is made by tall oil which is composed of resin acids and fatty acids, enhances the decay resistance of wood, and provides water repellency and decay resistance like heat treatment.

Hyvönen et al. (2006) investigated the water repellent efficiency of crude tall oil and tall oil-water emulsions in Scots pine sapwood. The water uptake was decreased by crude tall oil; moreover tall oil emulsions showed almost equal performance with pure tall oil for water repellent efficiency. Jermer et al. (1993) compared to the tall oil derivatives with traditional preservatives such as CCA and creosote, and found that two of the derivatives were efficient against decay in the field test when compared to preservatives.

Despite the extensive researches on heat treatment of wood, less study was conducted with tall oil treated wood. This study aimed the combine effect of tall oil and heat treatment on water uptake, tangential swelling and strength properties of wood.

2. 2.MATERIALS AND METHOD

Tall oil was provided from an industrial pulp and paper plant (OYKA) running according to kraft process. Fir and beech timbers free of defects were cut in to small sizes. The dimensions of the samples were 2x2x30 cm for strength tests and 2x2x1 cm for physical experiments such as water uptake and tangential swelling. To prepare treatment solutions, tall was dissolved in ethanol at 10 % ratio, the wood samples for mechanical test were treated with tall oil under full cell process including vacuum (0,3 mbar) and pressure (8 bar). The samples prepared for physical test were treated by vacuum process.

Heat treatment was done in an oven based on the thermowood process. Wood samples were subjected to heat treatment at 190 °C for 1.5 hours and at 212 °C for 2 hours for beech and fir, including untreated and tall oil pretreated samples.

The small size specimens, heat treated for 2 h, were immersed in liquid water for 2 weeks, measuring weight and dimensions (radial, tangential and longitudinal) for 2, 4, 6, 24, 48, 72 hours followed by 1 and 2 weeks respectively. The bending strength test was performed with Universal test device.

$$\text{Water Absorption (\%)} = \frac{W2-W1}{W1} \text{ X } 100 \qquad (1)$$

W1 weight of oven dried wood
W2 weight of wood after soaking

$$\text{Swelling (\%)} = \frac{S2-S1}{S1} \text{ X } 100 \qquad (2)$$

V1 oven-dry volume of the wood, V2 water-swollen volume of the wood

The MOR and MOE were determined according to the equations 3-4 below (N/mm2):

$$\mathrm{MOR} = \frac{3.\mathrm{Pmax.L}}{2\mathrm{bh2}} \tag{3}$$

$$\mathrm{MOE} = \frac{\Delta \mathrm{F.L3}}{\Delta \mathrm{f.4b..h3}} \tag{4}$$

where Pmax is the load at failure, ΔF is the difference in load in elastic deformation area, Δf is the bending difference in the sample, L is the span length, and b and h are the width and the height.

The mechanical properties was evaluated according to Analysis of variance (ANOVA) test at 95 % confidence level, and the was homogeneous subsets were displayed by Tukey test.

3. 3.RESULTS AND DISCUSSION

3.3.1. WPG and Mass loss

The weight percent gain (WPG) of the tall oil treated samples and mass loss of the wood after heat treatment are given in Table 1.

Table 1. WPG and mass loss of the fir and beech samples

	FIR		BEECH	
Treatments	WPG (%)	Mass loss (%)	WPG (%)	Mass loss (%)
10 % CTO	17.26(1.39)	-	7.96(0.41)	-
190 °C	-	1.60(0.13)		2.12(0.14)
212 °C	-	6.34(0.50)		9.95(0.45)
10 % CTO + 190°C	15.42(3.80)	3.59(0.80)	7.71(0.44)	3.49(0.21)
10 % CTO + 212°C	15.81(3.44)	7.81(0.76)	7.37(0.87)	10.05(0.35)

It is shown from Table 1 that WPG ranged from 15 % to 17 % for the tall oil treated fir samples. The mass loss was much higher in the fir heat treated at 212°C than those at 190 °C. Further, tall oil amount being in the samples increased the mass loss due to the heat treatment. To the beech samples, WPG was lower when compared to fir samples. This demonstrates that the fir is more permeable than beech wood. The mass loss also was greater in beech than fir because of the heat treatment. This can be attributed to the higher hemicellulose ratio in beech.

3.3.2. Water uptake

After two hours exposing to water, there was great difference between untreated fir and treated fir samples in relation to water uptake (Figure 1). The temperature of 190 °C and 212 °C alone initially showed lower uptake, but the longer exposure times (2 weeks) highly increased the absorption, and almost similar results were obtained in two weeks experiment. Crude tall oil showed slightly lower water uptake than heat treated samples at both temperatures after 2 weeks. The results indicated that pretreatment with tall oil improved the resistance to water absorption when compared to heat treatment alone. The lowest water uptake was obtained for the fir samples treated with tall oil and heat treated at the temperature of 212 °C for each duration, giving the value of 97.3 % after 2 weeks. However, water uptake was 154.1 % for heat treated woods (212 °C) without tall oil after 2 weeks. The reason of the reduced equilibrium moisture content is that means less water is absorbed by wood cell wall after heat treatment was attributed to the chemical change resulting in the decrease of hydroxyl groups (Jamsa and Viitaniemi 2001). In addition, the reduction in wood swelling was not only attributed to the degradation of hemicellulose but also to the structural modifications and chemical changes of lignin component (Repellin and Guyonnet 2005, Esteves 2009).

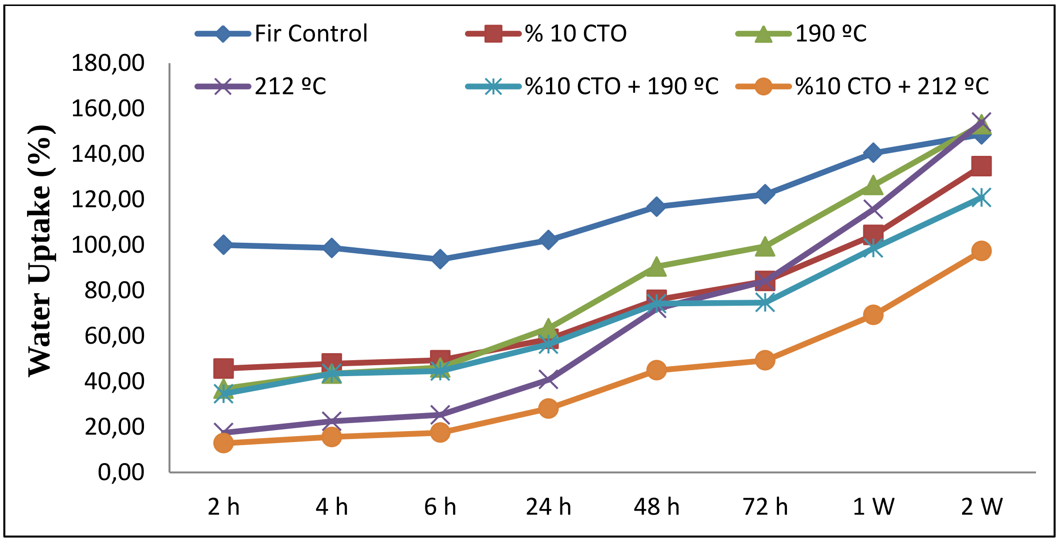

Figure 1. Water uptake of Fir wood

Figure 2 shows that the samples heat treated at 212 °C, as well as the samples treated with 10 % of CTO and the samples with 10 % CTO + 212 °C resulted in lower tangential swelling than other treatments at the final exposure period . However, the better performance of the 10 % CTO + 212 °C treatment proved that tall oil pretreatment induced the positive impact on heat treatment (212 °C) by hindering the swelling. Therefore, the lowest tangential swelling was found to be 3.36 % in the samples of fir treated with 10 % tall oil and heat treated at 212 °C, while the control samples exhibited the maximum as 6.59 % for 2 weeks experiment.

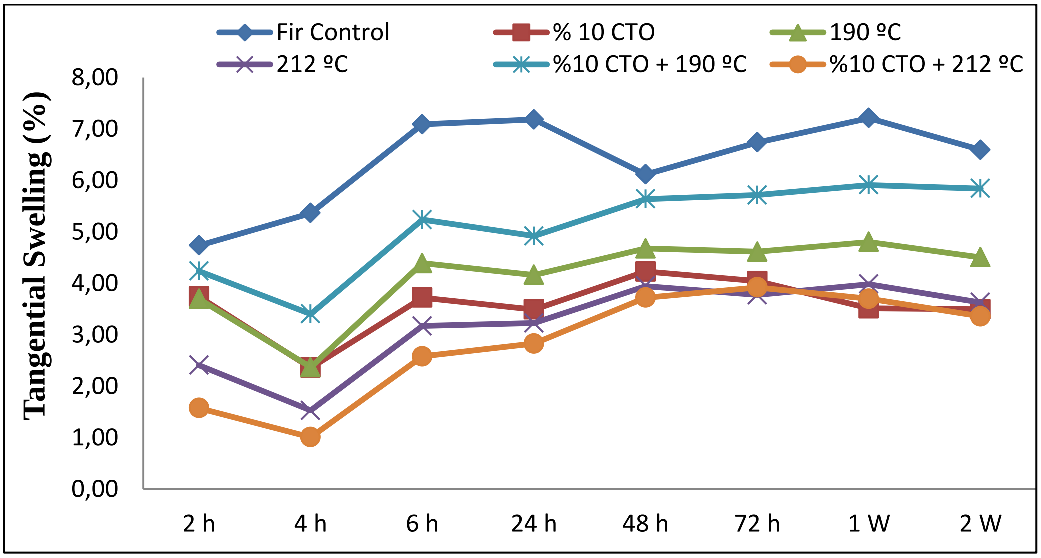

Figure 2. Tangential swelling of Fir wood

Figure 3 demonstrates that water uptake was clearly higher in untreated beech samples for short term exposure like 2, 4 and 6 h.

The best result in terms of water uptake was achieved by heat treatment at 212 °C (% 70.28) when compared to other treatments. Water uptake of heat treated samples at 190 °C (% 92.34) was higher than those heat treated at 212 °C. This indicates that the lower heat treatment is the more water uptake. The combination of tall oil and heat treatment did show resistance to water uptake when heating was operated at 212 °C in beech samples.

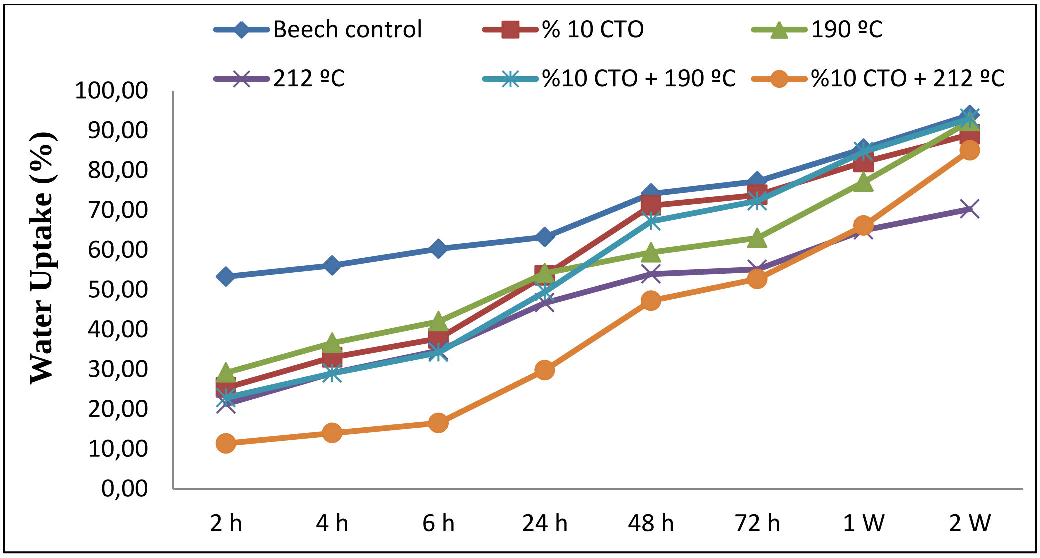

Figure 3. Water uptake of Beech wood

Figure 4 shows that swelling declined between 2 and 4 hours immersion, raised after this point up to 6 hours, and then regained stability until the end of the immersion for most of the samples. However, this trend was shown more clearly in control beech samples.

Tall oil treated samples improved the tangential swelling in beech samples when exposed to heat treatment at both temperatures (190 °C and 212 °C). The outstanding result in tangential swelling was that the great difference between heat treated samples at 190 °C and 212 °C.

As can be seen from Figure 4, heat treatment at 212 °C decreased the tangential swelling about two times less than 190 °C after 2 weeks. Minimum swelling in tangential direction was obtained with beech heat treated at 212 °C for 2 weeks soaking.

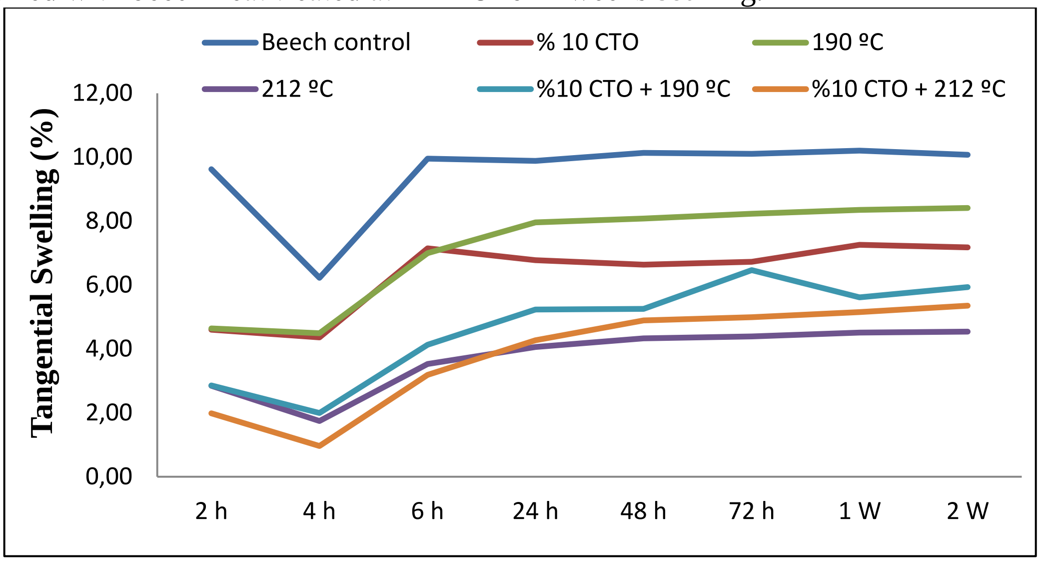

Figure 4. Tangential swelling of Beech wood

The water properties of heat treated wood were generally interpreted with regard to equilibrium moisture content and dimensional stability (ASE) in previous studies. The research on wettability of thermally modified Scots pine and spruce revealed that the lower temperatures of 170°C and 190°C increased the wettability, and high temperature of 230°C was suggested to decrease the wettability of wood (Metsä-Kortelainen and Viitanen 2012).

Dirol and Guyonnet (1993) found the radial and tangential swelling in all cases lower in heat treated woods including spruce, fir and poplar according to retification process.

3.3.3. ASE (%)

The results regarding Anti swelling efficiency as percent (ASE %) for two weeks is given for fir and beech in Figure 5 and Figure 6 respectively.

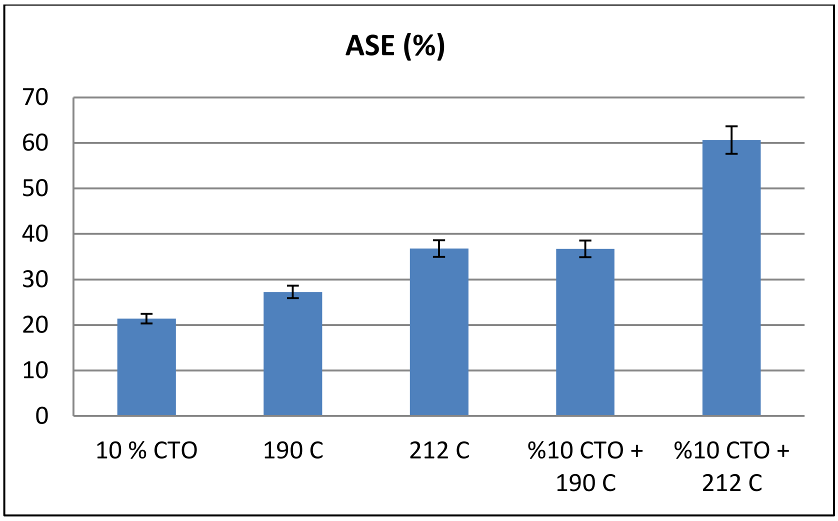

Figure 5. ASE values of treated fir samples

When compared to tall oil treatment, heat treatment at 190°C and 212°C slightly improved the ASE in fir samples. As expected, higher temperature with 212°C led to higher ASE (36.78 %) than that of 190°C (27.25 %). However, when the samples treated with tall oil before heat treatment of 190°C the ASE was found higher than that of 190°C alone, moreover equal to heat treatment at 212°C. This demonstrates the favorable effect of tall oil on ASE when combined with heat treatment. Furthermore, the increasing of temperature to 212°C after tall oil treatment yielded the highest result (60.62 %) in ASE as shown in Figure 5.

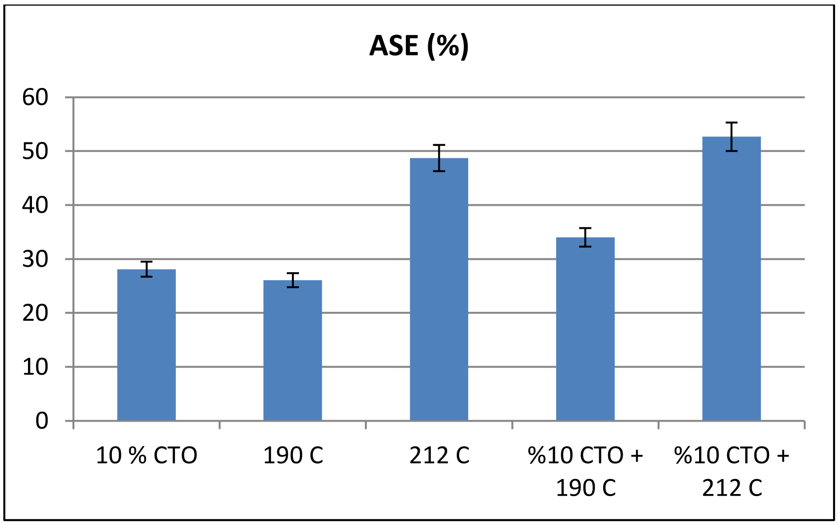

Figure 6. ASE values of treated beech samples

With respect to beech samples, there was little difference between tall oil treatment and heat treatment at 190°C in ASE values. Higher temperature increased the ASE as the same in fir. As can be clearly shown from Figure 6, tall oil pretreatment either with 190°C or 212°C improved the ASE in comparison to heat treatment alone. Giebeler (1983) decreasing in swelling ranged from 50 % to 80 % for beech, poplar, pine, spruce and birch with the heat treatments between 180°C and 200 °C in the presence of inert gas. Improvement in dimensional stability was associated with the wood species according to Militz (2002), based on the results with beech, Scots pine and radiata pine. It was also associated with the wood direction (Sailer et al. 2000). Maritime pine was heat treated in an oven during 2 to 24 hours at 170-200 °C. Dimensional stability was improved and mechanical properties were decreased by oven heat treatment more than steam heat treatment. The increase in dimensional stability is due to the equilibrium moisture content (Esteves et al. 2008). The effect of steam-heat treatment on chinese fir was investigated by Cao et al. (2012) with respect to anti-shrink efficiency and anti-swelling efficiency at temperatures ranging from 170 to 230°C, from 1 to 5 hours. The increasing in dimensional stability was found 73% for heartwood and 71% for sapwood at 230°C for 5 hours.

Rubberwood and silver oak specimens were heat treated at 210, 225, 240 °C for 1, 2, 4, 6, and 8 hours under 400 mm Hg vacuum. Thermal treatment resulted in reduction in volumetric swelling coefficient as well as increase in ASE associated with treatment severity and weight loss. The improved dimensional stability was interpreted with regard to decrease in hygroscopicity as a result of hemicellulose degradation and increase in condensed lignin interunit bonds (Srinivas and Pandey 2012).

Thermally treated Fir (Abies bornmulleriana) and hornbeam (Carpinus betulus L) were compared in terms of chemical changes and dimensional stabilization by heating 170, 190 and 210 °C for 4, 8, and 12 hours respectively. Water absorption and swelling was lowered by all heat treated samples, but higher by fir than that of hornbeam. Additionally, heat treatment at 210 °C for 12 h was found effective in improving the hygroscopicity (Aydemir et al. 2011).

3.3.4. Strength properties

Table 1.Bending strength (MOR) and modulus elasticity (MOE) of fir samples

Fir	MOR (N/mm2)	MOE (N/mm2)
Control	68.80 C (4.1)	6555.39 C (292.3)
10 % CTO	57.18 BC (8.9)	5618.85 BC (292.3)
190 °C	49.92 AB (4.7)	5173.57 ABC (721.6)
212 °C	36.26 A (8.0)	3957.72 A(487.8)
10 % CTO + 190°C	50.70 AB (14.8)	5512.78 BC (270.5)
10 % CTO + 212°C	44.58 AB (5.6)	4548.21 AB (643.2)

* The capital letters indicates the homogeneous subsets

Table 1 indicates that control samples of fir resulted in the highest value in MOR when compared to tall oil and heat treated samples. Tall oil treatment reduced the bending strength to some extent. However, heat treatment at 190 °C and 212 °C significantly lowered the bending strength in the wood samples than those of control. Korkut (2007) reported that the mechanical properties were affected by heat treatment even at the temperatures below 200 °C. For instance, heat treatment between 120 and 180 °C reduced the mechanical properties of fir with the increasing in temperature and treatment time. The mechanical properties differ in wood species after heat treatment. Boonstra (2007) found small reductions (3 %) in bending strength of heat treated Scots pine, whereas higher (31 %) in heat treated Norway spruce.

In addition, no significant difference was found between tall oil pretreatment before heat treatment (190 °C) and heat treatment alone with 190 °C. However, pretreatment with tall oil provided positive impact by increasing the bending strength after heating at 212°C. As can be seen from Table 1, MOE values of the tall oil and heat treated samples were lower than control samples. Of all the treatments, the highest MOE was obtained by control fir which was in accordance with the strength value of the control. These results also proved that bending strength and modulus of elasticity in fir samples was adversely effected by tall oil treatment as well as heat treatment. But, tall oil combination with heat treatment at 190 °C or 212 °C led to better results than only heat treatment in relation to MOE.

Table 2. Bending strength (MOR) and modulus elasticity (MOE) of beech samples

Beech	MOR (N/mm2)	MOE (N/mm2)
Control	103.85 DE (9.61)	7305.9 AB (905.71)
% 10 CTO	110.02 E (9.62)	7464.7 AB (1604.09)
190 °C	91.41 CD (7.24)	7143.0 AB (257.86)
212 °C	50.50 A (3.58)	6042.5 A (22.99)
%10 CTO + 190°C	85.57 C (6.33)	7901.5 B (399.72)
%10 CTO + 212°C	69.78 B (4.19)	7223.0 AB (540.17)

* The capital letters indicates the homogeneous subsets

As for the beech samples, tall oil slightly increased the bending strength, while heat treatments (190 °C and 212 °C) decreased it when compared to the control samples (Table 2). The MOR was much lower in the samples exposed to 212 °C. Poncsak et al. (2006) examined the effect of high temperature on the mechanical properties of birch. From the mechanical properties MOR decreased with increasing treatment temperature, especially above 200°C in which the hardness increased slightly. Tall oil pretreatment with heat treatment (190 °C) lowered to MOR than only heat treatment at 190 °C. When the beech was treated with both tall oil and heat treatment at 212°C, the strength value was higher than heat treatment (212°C) alone. This indicates that the effect of tall oil before heating (212°C) was positive in relation to MOR. Slight increasing in MOE was shown in beech samples when treated with tall oil at 10 % concentration. This suggests that tall oil treatment had no adverse effect on the strength properties of beech wood.

However, the rising temperature affected negatively the modulus elasticity in heat treated samples (190 °C and 212°C) in comparison to control and tall oil treated samples. Effect of heat treatment on aspen samples was reported by Kocaefe et al. (2007) in terms of hardness, modulus of elasticity and modulus of rupture. MOE was increased by increasing temperature which led to decrease in MOR, and temperature above 160 °C reduced the hardness. Kamdem et al. (2002) observed the MOR and MOE reduction in spruce 8 % and 11 %, in beech 40 % and 20 % respectively when exposed to heat treatment between 200 °C and 260 °C. Two-step heat treatment was studied by Tjeerdsma et al. (1998), found the decreasing MOR 3 % in beech and 20 % in Scots pine. In the present study, results indicated that treated samples had lower mechanical properties compared to the control samples. In addition, increase in temperature reduced the mechanical properties.

It is concluded from the experiments regarding strength properties of fir and beech, tall oil can be used before heat treatment in the case of 212°C to enhance mechanical properties, and this combination might also show synergistic effect on biological durability.

4. CONCLUSIONS

Tall oil pretreatment (10 %) and subsequently heat treatment at 212°C was found efficient in reduce the water uptake and tangential swelling. Tall oil treatment at 10 % ratio seems promising, indicating better performance than heat treatment at 190°C and 212°C for fir samples regarding water uptake. Pretreatment with tall oil followed by heat treatment either with 190°C or 212°C improved the ASE when compared to heat treatment alone.

Tall oil treatment alone showed better interaction in beech samples regarding MOR and MOE when compared to control samples. The rising temperature reduced the MOR higher in beech, and less in fir samples. In all cases, fir and beech woods heat treated at 212°C displayed lower strength properties than other treatments. Further experiments should be done on the samples treated with tall oil and heat in terms of other mechanical properties.

REFERENCES

Aydemir, D.; Gunduz, G.; Altuntas¸ E.; Ertas, M.; Turgut, S. H.; Alma, M.H. (2011): Investigating changes in the chemical constituents and dimensional stability of heat-treated hornbeam and uludag fir wood. BioResources 6(2):1308–1321

Boonstra, M. J.; Tjeerdsma, B. F. (2006); Chemical analysis of heat treated softwoods. Holz als Roh- und Werkstoff 64: 204-211.

Boonstra, M.J.; Van acker, J.; Kegel, E. (2007); Strength properties of thermally modified softwoods and its relation to polymeric structural wood constituents. Ann For Sci 64:679–690

Cao, Y.; Lu, J.; Huang, R.; Jiang, J. (2012): Increased dimensional stability of Chinese fir through steam-heat treatment. Eur J Wood Prod 70: 441–444.

Dirol, D.; Guyonnet, R. (1993): The improvement of wood durability by retification process (1993) IRG/WP 93-40015

Esteves, B.M.; Domingos, I.J.; Pereira, H.M. (2008): Pine wood modification by heat treatment in air.BioResource 3(1): 142-154

Esteves, B.; Pereira, H. (2009): Wood modification by heat treatment: a review. BioResources 4(1):370–404

Giebeler, E. (1983): Dimensionsstabilisierung von Holz durch eine Feucht/Wa¨rme/Druck Behandlung. Holz Roh- Werkstoff 41:87–94

Hill, C.A.S. (2006): Wood modification: chemical, thermal and other processes. Wiley, Chichester

Hyvönen, A.; Piltonen, P.; Niinimäki, J. (2006): Tall oil/water-emulsions as water repellents for scots pine sapwood. Holz als Roh und Werkstoff, 64, 68–73

Jämsä, S.; Viitaniemi, P. (2001): Heat treatment of wood- Better durability without chemicals, In: Proceedings of special seminar held in Antibes, France, 68p.

Jermer, J.; Bergman, Ö.; Nilsson, T. (1993): Fungus cellar and field tests with tall oil derivatives. Final report after 11 years' testing. The international research group on wood preservation, document no. IRG/WP 93-30007. Stockholm. 7 p.

Korkut, S. (2008): The effects of heat treatment on some technological properties in Uludag fir (Abies bornmuellerinana Mattf.) wood. Build. Environ. 2008;43:422–428.

Kamdem, D.P.; Pizzi, A.; Jermannaud, A. (2002): Durability of heat-treated wood. Holz Roh- Werkst 60:1–6

Kocaefe, D.; Chaudry, B.; Poncsak, S.; Bouazara, M.; Pichette, A. (2007): Thermogravimetric study of high temperature treatment of aspen: effect of treatment parameters on weight loss and mechanical properties. J Mater Sci 42:854–866

Kocaefe, D.; Poncsak, S.; Doré, G.; Younsi, R. (2008): Effect of heat treatment on the wettability of white ash and soft maple by water. Holz Roh- Werkst 66:355–361

Lyon, F.; Thevenon, M.F.; Imamura, Y.; Gril, J.; Pizzi, A. (2007): Development of boron/linseed oil combination treatment as a low-toxic wood protection: evaluation of boron fixation and resistance to termites according to Japanese and European standards. The international research group on wood protection. Document no. IRG/WP 07-30448. Stockholm

Metsä-kortelainen, S.; and Viitanen, H. (2012): Wettability of sapwood and heartwood of thermally modified Norway spruce and Scots pine. European Journal of Wood and Wood Products, 70(1), 135-139.

Militz, H. (2002): Thermal treatment of wood: European processes and their background. The International Research Group on Wood Preservation, Document no. IRG/WP 02-40241

Poncsak, S.; Kocaefe, D.; Bouazara, M.; Pichette, A. (2006): Effect of high temperature treatment on the mechanical properties of birch (Betula papyrifera). Wood Sci Technol 40:647–663

Repellin, V.; Guyonnet, R. (2005): Evaluation of heat-treated wood swelling by differential scanning calorimetry in relation to chemical composition. Holzforschung 59:28-34

Sailer, M.; Rapp, A.O.; Leithoff, H. (2000): Improved resistance of Scots pine and spruce by application of an oil-heat treatment. IRG/WP 00-40162

Srinivas, K.; Pandey, K.K. (2012): Effect of heat treatment on color changes, dimensional stability and mechanical properties of wood. J Wood Chem Technol 32:304–316

Stamm, A.J. (1956): Thermal Degradation of Wood and Cellulose. Ind Eng Chem 48:413–417

Tjeerdsma, B.F; Boonstra, M.; Pizzi, A.; Tekely, P.; Militz, H. (1998): Characterisation of thermally modified wood: molecular reasons for wood performance improvement. Holz Roh Werkst 56:149–153

Weiland, J.J.; Guyonnet, R. (2003): Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy. Holz Roh Werkst 61:216–220.