Effects of Thermal Modification on Physical and Mechanical Properties of Douglas-Fir Heartwood

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The flexural properties, mass losses, and moisture behavior of thermally modified Douglas-fir pretreated with boron or glycerol were examined. Pretreatments were associated with slight, but not significant, reductions in modulus of rupture (MOR) and modulus of elasticity (MOE) of Douglas-fir at different thermal treatment levels. Boron pretreatment had the greatest effect on MOR. MOR of non-pretreated and boron-treated samples increased slightly at the initial stage of thermal treatment and then decreased with rising temperature and time. The MOR of glycerol-treated samples decreased with increasing temperature and time. The thermal treatments employed had no significant effect on MOE. Both temperature and pretreatments improved anti-swell efficiency. Further studies are underway to characterize the nature of the chemical changes associated with the thermal modification process.

Keywords: Douglas-fir; Thermal modification; Anti-swelling efficiency; Equilibrium moisture content; Boron; Glycerol

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INTRODUCTION

Conventional preservative treatments have a well-deserved reputation for markedly extending the useful life of a variety of wood products; however, some wood users object to the use of preservatives and seek "non-chemical" methods for protecting wood. A number of approaches have emerged for this purpose under the broader title of wood modification including furfurylation (Esteves *et al*. 2011), acetylation (Popescu *et al.* 2014), and thermal treatment (Poncsák *et al*. 2006; Lekounougou and Kocaefe 2014). Each has merits under certain applications and there is evidence of increasing use of these technologies for wood protection in Europe.

Thermal treatment has drawn substantial commercial interest in Europe because it is relatively simple to apply and has the potential to enhance some wood properties, including dimensional stability and durability without the addition of chemicals (Poncsák *et al*. 2006; Esteves *et al*. 2008; Calonego *et al*. 2010; Lekounougou and Kocaefe 2014). Most thermal modification processes employ temperatures between 160 and 250 ^{o}C, usually above 200 ^{o}C depending on the wood species and the desired material properties. Hemicelluloses start to degrade first, resulting in reduction of OH bonds and formation of O-acetyl groups. These modified hemicelluloses then crosslink with lignin, rendering the wood more hydrophobic. These changes decrease swelling and shrinkage of wood, thereby improving dimensional stability (Kocaefe *et al.* 2008)

Thermal treatment is not a new process; it has been used for decades to alter the color on some hardwood species, but its use to enhance the durability of woods represents

a new application for this technology. There are a number of thermal treatment methods including relatively simple heating in an oven, heating between oil heated plates, and finally heating in vessels in the absence of oxygen (Militz 2002). Heat treatments have generally developed to navigate the fine line between altering wood/moisture relationships and inducing substantial structural damage. The majority of thermal treatments have been employed on low-durability woods such as spruce (*Picea abies* (L.) H. Karst.) or Scots pine (*Pinus sylvestris* L.). Attempts to use thermal modification to improve the durability of a U.S. hard pine, ponderosa pine (*Pinus ponderosa* Dougl. Ex Laws.), for use in windows and door frames were less successful (Vidrine *et al*. 2007).

One approach that might prove useful for improving the prospects for thermal modification would be to employ this process to enhance the durability of a wood that already had some inherent resistance to degradation and while incorporating pre-treatments that have the potential to further enhance durability. The heartwood of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) is classified as moderately durable and can provide reasonable performance when used out of direct soil contact (USDA 2010). The heartwood of this species is generally resistant to impregnation, and developing methods for enhancing the durability of this material might provide new applications that meet the needs for those concerned about using conventional biocides for wood protection. Douglas-fir tends to be susceptible to damage when heated in the green state, and many specifications limit maximum heating times and temperatures for this species (AWPA 2012). The effect of elevated temperatures on the properties of dry Douglas-fir; however, appear to be less substantial, suggesting that this species might be suitable for thermal modification.

The potential for pretreatment prior to thermal modification has been explored with both boron and glycerol. Boron is a well-known fungicide, but it also has the potential to modify the effects of heating on other wood properties. Glycerol appears to accelerate thermal degradation, resulting in reactions between hemicellulose and lignin at much lower temperatures (Yan *et al*. 2011). This might allow for thermal modification processes to occur more rapidly at lower temperatures, thereby improving the economic viability of the process and reducing the risk of negative effects on wood properties.

The potential for using thermal modification with or without pretreatments to improve the durability of Douglas-fir was evaluated in a series of trials examining the effects of heating on color, flexural properties, wood/moisture relationships, and resistance to mold fungi, decay fungi, and termites. This report examines the effects of thermal modification on flexural properties, mass loss, and moisture behavior.

EXPERIMENTAL

Materials

Kiln dried Douglas-fir (*Pseudotsuga menziesii*) heartwood lumber (50 mm by 125 mm by 2.4 m long) was obtained locally. The boards were free of visible defects such as large checks, stain, or decay.

Methods

The lumber was cut into clear 12 by 12 by 200 mm long beams for flexural testing or 50 by 75 by 125 mm long blocks for moisture behavior assessment that were oven dried

(65 °C) and weighed. Fifteen beams and five blocks were each randomly allocated to 30 treatment groups.

Ten groups received no-pretreatment, ten groups were dipped in 10% disodium octaborate tetrahydrate (DOT) to produce a loading of 0.56% wt/wt boric acid equivalent basis (pH=8.3), and ten groups were vacuum-treated with 20% glycerol. Boron was evaluated for its potential to provide supplemental insect and fungal resistance to the thermally modified woods, while glycerol was evaluated for its ability to accelerate the thermal modification process.

The boron-treated specimens were stored wet for 28 days at 5 °C under non-drying conditions to allow the boron to become more evenly distributed in the wood. The samples were then air-dried and then finally oven dried (65 °C). Glycerol-treated beams were weighed after treatment to determine uptake (average glycerol uptake was 147% by weight) before being allowed to air-dry.

The beams in a given pre-treatment group were then wrapped in foil to limit oxygen access before being subjected to heating to 160, 180, or 200 °C for 2, 4, or 6 h in an oven. After cooling, the beams were weighed to determine mass loss as a result of heating, then conditioned to constant weight at 23 °C and 65% relative humidity. Each treatment was replicated on 15 beams and 5 blocks. The samples were weighed after treatment to determine the effects of the various heating regimes on mass loss.

The beams were then tested to failure in third point loading according to procedures described in ASTM Standard D143 (ASTM, 2011) using a loading speed of 2 mm/minute. Load and deflection were continuously recorded, and the resulting curves were used to calculate modulus of elasticity (MOE) and modulus of rupture (MOR) for each beam.

The oven-dried blocks were weighed (nearest 0.1 g), and their dimensions were measured before they were conditioned at 90% RH and 30 °C for 2 weeks. The blocks were reweighed and measured before they were conditioned at 30% RH and 30 °C for 2 weeks. The blocks were again weighed and measured. This process of exposure under the two temperature/relative humidity followed by weighing and measurement was repeated one more time. The weights were used to calculate equilibrium moisture content (EMC) under a given RH condition.

Anti-swelling or shrinkage efficiency (ASE) were calculated using the volumes of samples after exposure to a given moisture level as follows,

$$ASE = \frac{VS_c - VS_t}{VS_c} \times 100 \ \% \quad (1)$$

where VS_c is the percentage of volumetric change (swelling or shrinking) of untreated controls as they move from one moisture condition to the next and VS_t is the same factor for the various treated samples.

Anti-swelling or shrinkage efficiency were determined after each exposure at 90% RH or 30% RH and 30 °C. Samples were exposed to two cycles of 90% RH and 30% RH in each cycle, but only data from the first cycle are shown because the trends were similar for the two cycles.

The data for mass loss, flexural properties and swelling/shrinkage were each subjected to Analyses of Variance (α=0.05) to determine the effects of pre-treatment, heating time and heating temperature on properties. Individual means were then examined using Tukey's Multiple Comparisons Test at α=0.05.

RESULTS AND DISCUSSION

Mass Loss of Thermal Treated Wood

Combinations of pretreatment and thermal modification produced significant reductions in mass based upon pretreatment (P=0.015), temperature (P=0.000), or time (P=0.004). Mass losses were lowest in boron-treated samples compared to non-pretreated and glycerol-treated samples at each thermal treatment level (Fig.1). Mass losses tended to increase with increasing thermal modification temperature or treatment time, which was consistent with previous reports (Poncsák *et al.* 2006; Esteves *et al.* 2008). The highest mass losses (4.16%) were found on glycerol-treated samples heated at 200 ºC for 6 h. As expected, mass loss was negatively correlated with MOR for each of the pre-treatments (Fig. 2) (r^2 between 0.71 and 0.84). The effect was greatest on boron-pretreated samples and lowest on the glycerol-treated samples. These results indicate that pre-treatments have the potential to influence the effects of thermal modification on wood properties. These results merit further study to determine the mechanisms by which these pre-treatments affect the thermal modification process.

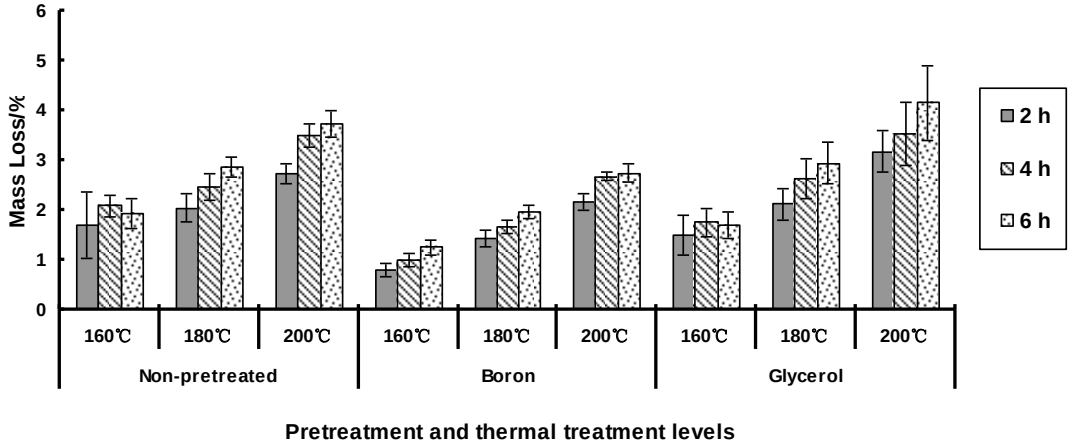

Fig. 1. Effect of combinations of glycerol and boron treatments and thermal modification on mass loss of Douglas-fir beams

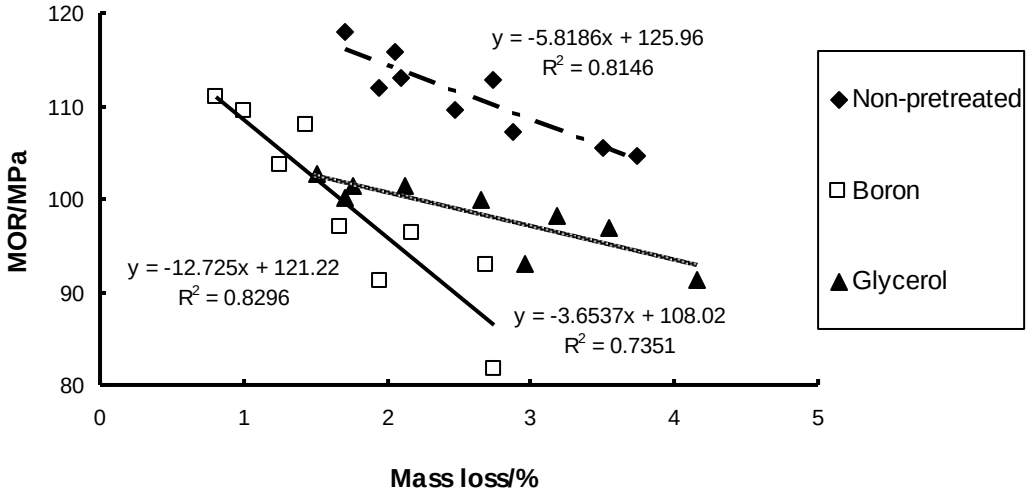

Fig. 2. Relationship between mass loss and MOR of non-pretreated, boron-treated and glycerol-treated wood subjected to different levels of thermal treatment

Effects of Thermal Modification on MOR

Pre-treatment with boron or glycerol, treatment temperature, and treatment time all significantly affected MOR of the wood (P=0.01, 0.044, and 0.015, respectively); however, the variations within individual treatments were often high (Table 1). MOR of samples treated with boron or glycerol prior to thermal exposure both declined compared to the non-pretreated samples. Boron samples heated for 6 h at 200 ºC experienced the greatest losses in MOR. The losses associated with boron were consistent with previous studies of fire retardant treated wood (Lebow and Winandy 1999; Winandy 2001). The strength losses associated with glycerol pretreatment were also consistent with previous reports (Yan *et al.* 2011).

MORs tended to decline with increasing treatment time and temperature in a pattern that was consistent with previous studies (Boonstra *et al.* 2007; Ding *et al.* 2011; Lekounougou and Kocaefe 2014); however, the effects were only significant with boron-treated samples heated at 200 ºC for 4 or 6 h. Interestingly, MOR increased slightly in boron-treated and non-pretreated samples heated for 2 h at 160 ºC, but then declined. Similar results were obtained by Kubojima *et al.* (2000), who found that the bending strength increased at the initial stage of the heat treatment and then later decreased. This phenomenon was attributed to the ordering and rearranging of the more amorphous cellulose due to the thermal motion of molecules within a certain temperature range. While the results were interesting, the lack of significant negative effects on MOR was promising for the use of thermal modification on Douglas-fir.

Effect of Thermal Modification on MOE

Pre-treatments, treatment temperature, and treatment time had no significant effects on MOE (P=0.07, 0.373, and 0.145, respectively) (Table 1). MOE should be more susceptible to thermal modification since these processes initially affect the hemicelluloses that are considered to more important in stiffness. While there were overall differences in MOE, pre-treatment and thermal modification were only significantly different from non-thermally treated samples in a few cases, including boron pre-treatment coupled with thermal modification at 200 ºC for 4 or 6 h. As noted earlier, boron has been associated with some losses in properties when the wood is subsequently exposed to elevated temperatures; however, the results generally indicate that pre-treatments and thermal modification did not adversely affect MOE and suggests that these processes might be useful for improving other properties of Douglas-fir such as dimensional stability, decay resistance, or color.

Effects of Heating on Moisture Behavior

The degrees of shrinkage or swelling serve as indirect measures of the effects of heating on the hydrophilic nature of the lignocellulosic matrix. Processes that disrupt the hydroxyls, either *via* removal or cross-linking between polymer chains should reduce the hydrophilic nature of wood. Thermal modification should induce these changes and the effects might be expected to increase with either higher temperatures or prolonger heating periods.

Table 1. Effects of Pretreatment Followed by Thermal Modification on Flexural Properties of Douglas-Fir Beams[a]

Treatment	Temp (°C)	Mean MOR (MPa)				Mean MOE (GPa)			
		No thermal treatment	2 h	4 h	6 h	No thermal treatment	2 h	4 h	6 h
None	-	115.6 (5.8) ab	-	-	-	12.7(0.9) bc	-	-	-
	160		118.1(8.3)a	113.0(12.3)ab	112.1(12.0)abc		12.7(1.6)a	12.4 (1.9)a	12.1 (1.8)a
	180		115.9(18.9)abc	109.7(16.5)abcdef	107.3(11.8)abcdef		12.5(1.3)a	12.2 (1.3)a	11.9 (1.2)a
	200		113.0(6.5)abcd	105.6(6.1) abcdef	104.8(9.0) abcdef		12.5(0.2)a	11.9 (0.5)a	11.9 (0.8)a
Boron	-	109.0(7.6) bcdefg	-	-	-	11.6 (1.1) c	-	-	-
	160		111.0(16.5)abcde	109.5(18.7)abcdefgh	103.6(15.4)cdefgh		12.6(1.4)a	12.6 (2.4)a	12.4 (1.9)a
	180		108.0(11.9)abcdef	97.0(5.3) bcdefgh	91.1(5.9)efgh		12.3(2.2)b	12.2(0.8)bc	11.6 (0.9)c
	200		96.4(6.2) abcdefg	93.0 (7.9)fgh	81.8(8.6)h		12.1(0.9)bc	12.0 (1.0)bc	10.7 (1.7)c
Glycerol	-	112.8(8.1) abcdefg	-	-	-	12.4(0.5) bc	-	-	-
	160		102.8(9.8)abcdefg	101.5(11.5)abcdefg	100.3(10.8)bcdefgh		12.7(1.6)bc	12.5 (1.3)bc	12.5 (1.0)bc
	180		101.4(8.6)abcdefg	100.1(9.1)abcdefgh	93.2(11.0) bcdefgh		12.3(0.8)bc	12.2 (1.0)bc	12.0 (1.0)bc
	200		98.3(9.1)abcdefgh	97.0 (6.0)defgh	91.5 (8.4)gh		12.1(1.1)bc	12.0 (0.6)bc	11.9 (0.7)bc

[a] Values represent means of 15 replicates per treatment, while figures in parentheses represent one standard deviation. Values followed by the same letter(s) do not differ significantly by Tukey's Multiple Comparisons test at α=0.05.

Anti-swelling and shrinkage of samples not subjected to a pretreatment both followed similar trends, with heating time having little effect on either property at 160 ºC, but with a slight trend towards increasing ASE with temperatures above that level. The effect was more noticeable with shrinkage than with swelling (Fig. 3). Pretreatment and temperature both significantly affected ASE values in the first exposures to 90 and 30% relative humidity (p=0.0021, 0.002 for pretreatment and 0.001, 0.023 for temperature, respectively). Heating time had no significant effect on ASE at either the 90 or 30% RH exposure (p=0.172 and 0.132, respectively). Boron or glycerol pretreatment were both associated with significantly enhanced ASE values, and this effect continued over 2 moisture cycles. As with the non-pretreatment samples, there was a definite trend upward in ASE values with temperature and heating period, but the differences were only significant for temperature for the first moisture cycle (P=0.001 and 0.023, respectively). Glycerol pretreatment seemed to have the greatest effect on ASE values, and the effect seemed to increase with both temperature and heating times. As noted, glycerol should accelerate the effects of thermal modification, and this was especially evident in the shrinkage data. It was interesting to note that glycerol pre-treated samples also tended to have higher equilibrium moisture contents when subjected to the 90% RH conditions. One possible explanation for the increased EMC values coupled with improved ASE values would be that residual glycerol in the cell lumens was sorbing moisture (Fig. 4). This would result in mass gains without concurrent changes in wood dimensions. Boron pretreated samples also had improved ASE values, but without any changes in EMC values compared with the non-pretreated controls.

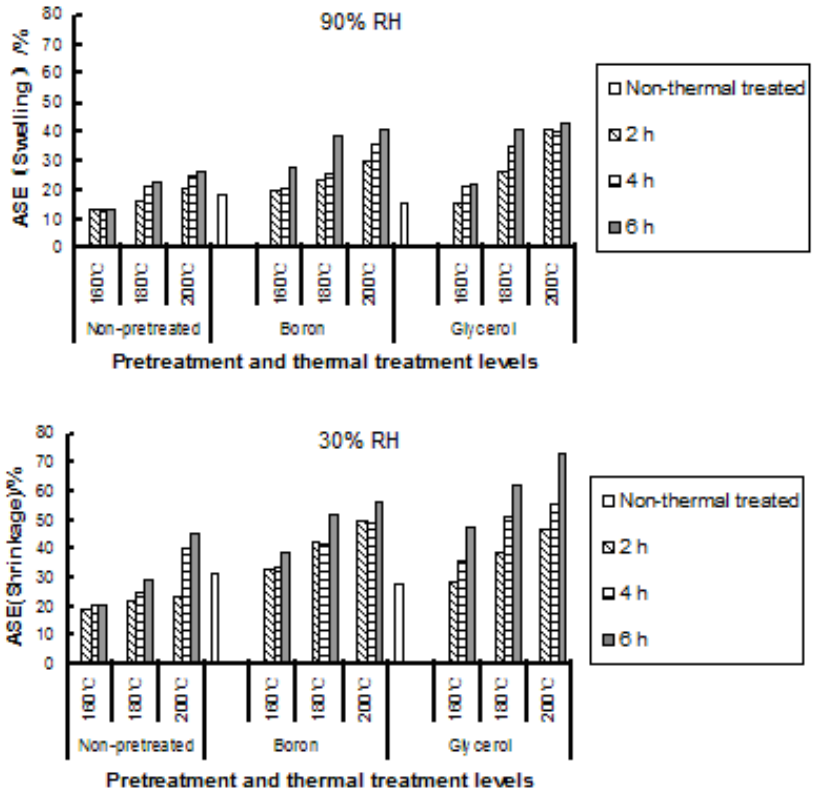

Fig. 3. Effect of combinations of pre-treatment and thermal modification under varying temperatures and heating times on shrinkage and swelling of Douglas-fir heartwood blocks exposed to 90 % RH or 30 % RH at 30 ºC

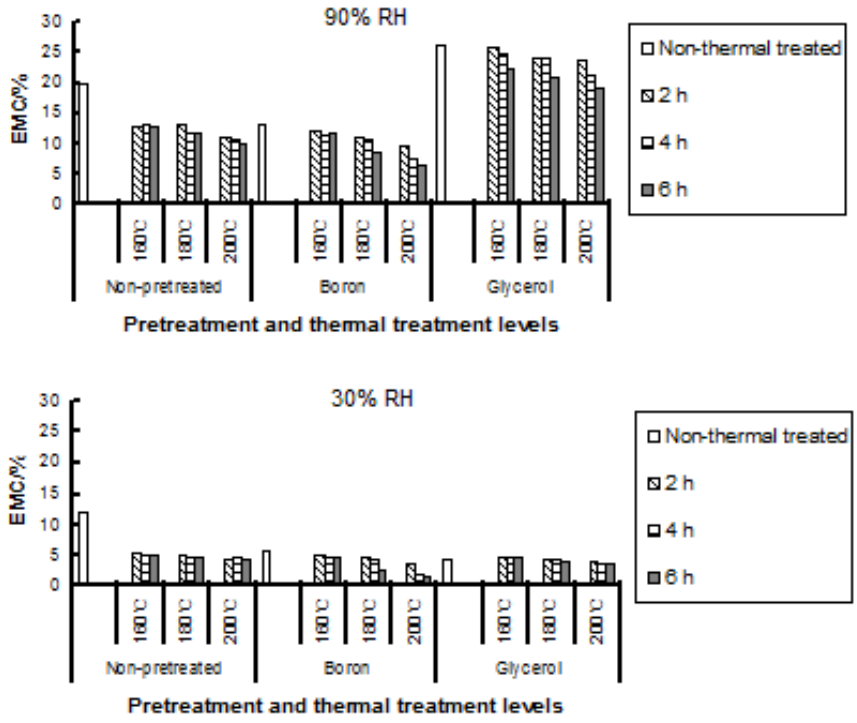

Fig. 4. Effect of combinations of pre-treatment and thermal modification under varying temperatures and heating times on equilibrium moisture contents of Douglas-fir heartwood blocks exposed to 90 % RH or 30 % RH at 30 °C

One interesting observation was the tendency for ASE values to decline slightly for shrinkage in boron- and glycerol-pretreated samples in the second cycle while EMC values remained the same. It is unclear why values would vary for this property, and further studies are underway to better understand the potential changes in the lignocellulose matrix that were associated with the pre-treatments.

CONCLUSIONS

1. Thermal modification at various temperatures and times did not significantly affect MOR or MOE, while pre-treatments with glycerol or boron were associated with slight, but significant effects.
2. Thermal treatment significantly affected shrinkage and swelling, with glycerol pretreatment having the greatest effect on ASE. Glycerol-pretreated samples also had higher EMC values when the samples were subjected to 90% RH conditions. Boron pretreatment improved ASE without any changes in EMC.
3. The results suggest that thermal modification might be useful for improving other properties of Douglas-fir heartwood without negatively affecting flexural properties.

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