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The combined effects of boron and oil heat treatment on beech and Scots pine wood properties. Part 1: Boron leaching, thermogravimetric analysis, and chemical composition

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Abstract The aim of the study was to screen any possible synergistic effect available with combination of plant oils and boron compounds to decrease boron leaching and improve thermal degradation of wood by means of dual treatment. In order to reduce the leachability of boron compounds, sapwood of beech and Scots pine samples were treated with oils to create a hydrophobic layer on the wood cells that may prevent water uptake. Increase (%) of boron retained in double-treated samples after leaching was approximately 20% compared to boron-treated samples without oil. The most promising results on boron leaching obtained in the case of using waste and sunflower oil. Thermogravimetric residues were increased by the higher loading of boron compounds in double-treated samples. Spectra of FTIR-Photoacoustic spectrometer showed some deformation of lignin and cellulose followed by degradation of hemicelluloses of treated wood samples due to heat effect at 160 °C.

Introduction

As one of the main components of many fire retardant formulations, boron has a long history in wood technology [1]. Boron compounds are also used as low-toxicity preservatives that are effective against most wood attacking organisms, are inexpensive, colorless, odorless, and are non-corrosive [2]. With the introduction of the Biocidal Product Directive 98/8/EC [3], several traditional wood preservatives have had to be removed from the market, and as a result, boron-based formulations have gained popularity and are now one of the strongest alternatives in the field of wood preservation [4, 5]. Thus, many researchers working on wood preservation have focused on boron compounds [6]. Among the boron compounds of interest, boric acid (BA) and borax are the most widely used and studied. Other boron containing compounds are also of interest in wood technology. One such is an agricultural product known as Tarim-Bor trade name developed by the National Boron Research Institute of Turkey (BOREN) for agricultural purposes. Although there have been some limited studies on the application of this compound in wood treatment [7], there remains little information about its efficacy.

Despite the many advantages of boron compounds they have limited utility in outdoor applications; their high solubility in water ensures that they are easily leached from impregnated wood without some form of additional protection [2]. There are a number of approaches to reducing boron leaching from treated wood [6]; however, despite extensive research there is as yet no commercially viable solution to this problem. Of the approaches to reducing boron leaching, one of the most promising is to use agents that render the wood hydrophobic thereby inhibiting water absorption and subsequent leaching. In this respect, vegetable oils could prove viable, by creating a hydrophobic layer on the surface of the wood cells, hindering water uptake.

Vegetable oils such as palm, soybean, rapeseed, sunflower, and coconut oil are good candidates; they are

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non-toxic and relatively inexpensive. Unsaturated oils can oxidize when exposed to atmospheric oxygen leading to the formation of a protective layer on the surface of the wood [8, 9]. The improvement in water repellency during oil treatment is not only dependent on the oil type and its properties, but also upon the oil treatment temperature, processing time, and the amount of oil retained in the wood. Higher treatment temperatures, extended process times and greater oil retention promote water repellency [10]. In recent years, a simple bi-oleothermal process has been developed that leads to a greater impregnation of wood by vegetable oil [11, 12]. High-retention values and deep penetration of oil into the wood are needed in order to provide good long-term performance [9, 13].

Alone, impregnation with vegetable oil is insufficient to impart adequate biological decay resistance and indeed the treatment may increase wood's propensity to burn. Laboratory decay resistance and termite tests have shown that the mechanical barrier imparted by oil treatment appears to be insufficient to protect wood against all wood decay fungi and termite attack [11, 14], whilst in a single-flame source test, oil treated samples have been shown to burn easily according to EN 13501 [12]. Combining boron treatment with vegetable oils has the potential not only to improve the decay resistance of wood but also to improve its fire resistance. Moreover, vegetable oils have the potential to "lock" boron into wood and thereby reduce leaching. This approach, exploiting the synergistic effects of the two forms of treatment has already shown some potential. Impregnation with BA and tall oil derivates, linseed oil, soybean oil, and rapeseed oil has demonstrated promise in the protection of wood against fungi and termite attack [11, 14].

The results of a study to assess the efficacy of an oil heat treatment process employing various vegetable oils in preventing leaching from wood previously impregnated with selected boron compounds (BA, borax, and an agricultural boron compound) are reported herein. Furthermore, the results of an investigation into the thermal stability and chemical structure of the oil heat-treated–boron-impregnated wood are presented. In Part II of this series, the water absorption characteristics, compression strength, color changes, and decay resistance of the oil heat-treated–boron-impregnated wood will be reported.

Materials and methods

Specimens 30 × 30 × 15 mm (R, T, L) were machined from the sapwood of Scots pine (*Pinus sylvestris*) and beech (*Fagus orientalis*) logs obtained from Gumushane and Macka located in the North-East Black Sea region of Turkey. Before impregnation, the specimens were conditioned at 65% relative humidity and 20 °C for 2 weeks to a moisture content of around 12%.

Boric acid, Borax decahydrate (BX), and an agricultural boron compound (TB) were obtained from BOREN, Ankara, Turkey. For the impregnation procedure, aqueous solutions of the compounds having concentrations of 1, 2, and 5% (w/v) were prepared using distilled water at 20 °C.

Six different vegetable oils were used to treat the samples. Nut oil, sunflower oil, soybean oil, canola oil, and corn oil were provided by the Ordu Oil Company, Turkey, whilst used (waste) vegetable oil was obtained from various fast food restaurants in Trabzon, Turkey. The Iodine value of the oils was determined according to TS 4961 EN ISO 3961 [15].

Impregnation with boron compounds

The specimens were first vacuum impregnated with the boron solutions at 760 mmHg for 60 min at 20 °C. Following this, the specimens remained immersed in the solutions for 60 min at atmospheric pressure. The boron retention level of the specimens (R in kg/m^3) was calculated according to Eq. 1. The treated specimens were subsequently conditioned for 2 weeks at 20 °C and 65% relative humidity.

$$R = \left[\frac{G \cdot C}{V}\right] \cdot 10, \tag{1}$$

where G is the sample weight after impregnation—sample weight before impregnation (g); C is the concentration (%); and V is the sample volume (cm^3).

Oil heat treatment

Oil heat treatment was carried out in a two-stage process as described in by Lyon et al. [11] and Podgorski et al. [12]. Selected boron treated and untreated wood specimens were first placed in an oil bath containing oil at ambient temperature and the temperature raised to 160 °C at a rate of 5 °C/min. Once the target temperature had been reached, the temperature was held constant for 30 min, following which the specimens were quickly moved to a second oil bath containing oil at room temperature where they remained immersed for a further 30 min. The specimens were not placed directly into hot oil at 160 °C so as to prevent crack formation in the transverse sections.

Oil retention values (R_o in kg/m^3) were also calculated by the following equation on the basis of the initial volume (V_0) for each specimen [16],

$$R_0 = \frac{(W_1 - W_0)}{V_0}, \tag{2}$$

where W_0 is the initial oven dry weight, and W_1 is the weight of specimen after oil heat treatment.

Leaching test

Leaching test was conducted according to AWPA E11-97 [17] without stirring. Specimens were first impregnated with distilled water under vacuum for 20 min. After 6, 24, and 48 h and thereafter at 48-h intervals, the leaching water was removed and replaced with an equal amount of fresh distilled water. Leaching was carried out for a total of 14 days.

Boron analysis

The boron content of both leached and unleached wood samples was measured using Inductively Coupled Plasma (ICP) analysis, using an ICP spectrometer (ICP-AES, Spectro Genesis). Specimens for ICP analysis were prepared from Scots pine and beech wood treated with boron only and those treated with boron and subsequently oil heat treated. Sample preparation was according to AWPA A7-93 [18]. Wood samples for the ICP analysis, as well as for thermogravimetric analysis (TGA) and infra-red spectroscopy, were prepared by grinding in a Wiley mill with a mesh size of 0.5 mm (IKA MF10, IKA-Werke, Staufen, Germany) followed by oven drying at 103 ± 2 °C. Two grams of ground wood was weighed to the nearest 0.01 g and placed in a 100 mL flask. Nitric acid (65%) was then added to the flask, which was placed on a hot plate. After the evolution of brown fumes had ceased, hydrogen peroxide (30%) was added dropwise to clear the solution. After cooling, the contents in the flask were filtered through Whatman #4 filter paper and were diluted with distilled water for measurement. For each treatment, four replicate samples were ground and analyzed.

Thermogravimetric analysis

Only specimens oil heat treated with waste oil and sunflower oil and their combinations with the boron compounds BA, BX, and TB were analyzed as these had shown the greatest boron retention following leaching. TGA was carried out using a Perkin-Elmer TGA-7 thermogravimetric analyzer. The analysis was run under nitrogen at a purge rate of 50 mL/min. About 10 mg of unleached sample material was heated from 35 to 800 °C at a rate of 10 °C/min. Mass loss as a function of temperature and time was recorded. In addition, samples treated with 5% BA, and its oil combinations were also analyzed in order to understand if other oils had a different effect on the thermal decomposition.

FTIR analysis

FTIR spectra were obtained from powdered treated wood samples using a Bio-Rad 6000 spectrometer equipped with a MTEC 300 Photoacoustic detector (Bio-Rad, Digilab, MA). Before the measurements, the PA cell was purged with helium. The spectra were collected in the wavenumber region of 400–4,000 cm^{-1}, with a spectral resolution of 8 cm^{-1}. Two accumulated spectra for every sample with 300 scans were analyzed. FTIR spectra were obtained from specimens treated with waste oil, sunflower oil, and their boron combinations as well as from samples treated with 5% BA and its oil combinations.

Results and discussion

Boron and oil retention values in oil heat-treated pine and beech

The initial boron and oil retention values of the oil heat-treated pine and beech wood specimens are shown in Table 1. As expected, high retentions were obtained with Scots pine due to the good penetrability of this species.

In order to provide good long-term performance, deep penetration of the oil into the wood is required, which in turn demands high-retention values [9, 13]. Approximately, 550 $\mathrm{kg/m^3}$ oil retention was observed in the pine samples, whereas for beech the value was approximately 390 $\mathrm{kg/m^3}$. There were no noteworthy differences in the oil retention value between the oil types, nor was any significant effect from the different boron concentrations observed. In both species, the retention of samples that had been impregnated with vegetable oil following boron treatment was similar to that of samples that had only been oil treated; boron impregnation before the oil treatment did not seem to affect the success of oil heat treatment.

Boron retention following leaching

Figures 1, 2, and 3 show the percentage of boron remaining (relative to un-leached specimens treated at the same boron concentration and without oil heat treatment) in oil heat treated and untreated pine and beech wood following leaching for 336 h in distilled water.

As may be seen, in samples that had not been oil heat treated nearly all the boron has been removed during leaching. In all cases, oil heat treatment reduced the level of boron leaching compared to samples that had not been oil treated. The type of oil had an impact on boron leaching. Lyon et al. [11] also reported that the type of oil was an important factor in boron retention in wood during leaching. They found that linseed oil seemed to be more efficient than soybean oil, and much better than rapeseed oil in preventing leaching. Regardless of the boron compound and its concentration, waste oil and sunflower oil seemed more effective in preventing leaching than the other oils studied. This could be explained by the different

Table 1 The retention (kg/m^3) of specimens

Treatment groups		Retentions (kg/m^3)						
		Boron	Nut oil	Waste oil	Soybean oil	Corn oil	Sunflower oil	Canola oil
1%BA	Pine	5.8 (0.12)[a]	550.1 (28.1)	557 (44.5)	566.5 (22.4)	547.8 (13.6)	560.6 (31.6)	548 (29.8)
	Beech	4.3 (0.19)	392.2 (17.1)	395.3 (18.2)	402.5 (24.9)	359.4 (22.8)	396 (23.1)	392.9 (18.1)
2%BA	Pine	11.8 (0.24)	585.6 (24.1)	476.7 (32.4)	576.8 (31.4)	487.2 (34.7)	559.7 (10.7)	561.6 (28.6)
	Beech	8.8 (0.25)	424.5 (18.1)	412.6 (23.6)	422.3 (23.3)	408.9 (22.9)	417.6 (20.6)	409.8 (13.3)
5%BA	Pine	36.5 (0.95)	544.5 (9)	495.3 (37.1)	554.7 (24.1)	503.3 (30)	602.6 (25.8)	610.8 (23.8)
	Beech	29.1 (1.07)	424 (12.6)	401.3 (24.7)	404.3 (29.3)	395.2 (36.3)	401.9 (33.9)	429.8 (31.8)
1%TB	Pine	6.2 (0.12)	516.2 (20.2)	514 (14.8)	558.4 (26.2)	515 (29.1)	550.1 (58.1)	565.8 (30.5)
	Beech	5 (0.45)	370.3 (21.8)	354.9 (32.6)	401 (31.9)	363.6 (19.8)	401.9 (19.1)	381 (29.5)
2%TB	Pine	12.9 (0.35)	485.4 (29.4)	507 (38.4)	501.8 (27.6)	510 (38.1)	524.1 (46.6)	522.6 (44.4)
	Beech	11.4 (0.46)	396.9 (30.4)	393.7 (28.5)	388.1 (26.2)	400.9 (11.7)	398 (32.6)	404.7 (10.4)
5%TB	Pine	30.7 (1.57)	574.3 (11.8)	564.3 (29)	526 (16.8)	478.4 (17.7)	568 (27.8)	579 (19.3)
	Beech	21.4 (0.60)	382.9 (16.1)	381.5 (24.1)	385.9 (29.8)	383.8 (30.8)	382.9 (24.3)	383.3 (20.5)
1%BX	Pine	5 (0.07)	490.3 (23.1)	461 (22.7)	534.5 (25.1)	498 (23.1)	535.1 (17.1)	538.5 (37.2)
	Beech	4.5 (0.16)	347.9 (20.5)	381.6 (17.8)	368.7 (29.9)	368.9 (14.3)	391.5 (25.1)	369 (16.8)
2%BX	Pine	11.7 (0.22)	522.8 (25.2)	451 (23.4)	469.5 (16.1)	484 (18.4)	514.7 (19.3)	509 (40.8)
	Beech	8.3 (0.17)	398.4 (18.4)	331.3 (9)	365.6 (24.3)	337.3 (19.9)	384.1 (36.3)	372 (22.2)
5%BX	Pine	34.8 (1.08)	500.9 (35.1)	451.6 (15.7)	560.9 (9.9)	473.9 (21.2)	539.9 (55.7)	530.5 (16.2)
	Beech	22.6 (0.50)	377.4 (35.1)	346.6 (27.9)	370.9 (28)	362.4 (13.3)	374.2 (34.1)	368.5 (28.6)
–	Pine	–	573.8 (13.9)	510 (26.2)	571.3 (23.4)	458.1 (27.6)	549.5 (24.2)	505.6 (29.8)
	Beech	–	376.7 (28.9)	361.5 (18.4)	347.6 (21.7)	330 (26.9)	370 (17.5)	353.1 (17.4)

[a] Values in parentheses are standard deviations

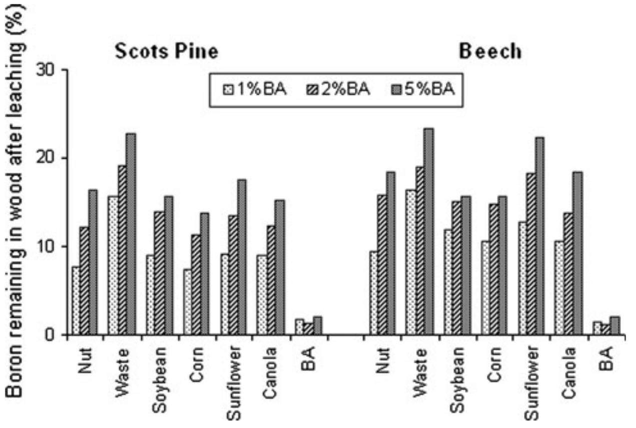

Fig. 1 Boron remaining (%) in BA + oil-treated wood specimens after leaching 336 h in distilled water

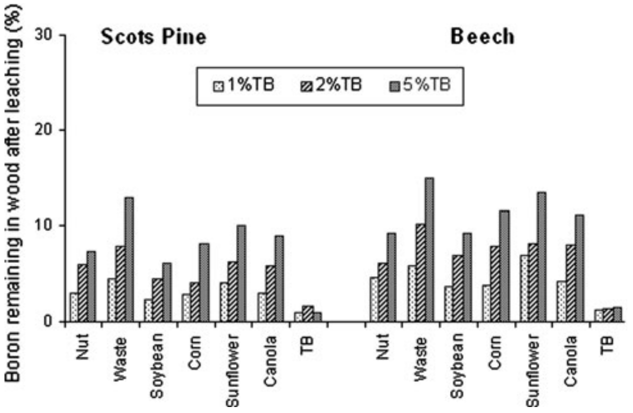

Fig. 2 Boron remaining (%) in TB + oil-treated wood specimens after leaching 336 h in distilled water

penetration rates of oils during the impregnation, and the drying properties of oils when exposed to air. The drying characteristics of oils may have an effect on the creation a hydrophobic layer on the wood cells, preventing water uptake. The degree of unsaturation in oils determines its drying characteristics and can be found by adding iodine (I_2). High iodine values (>140) are typical for drying oils and low ones (<125) of non drying oils, with the iodine values of semi-drying oils lying between two [13]. The iodine value of nut oil is 90 and this means that the oil does not dry or form a film even on lengthy exposure to air. Corn, soybean, and canola oils are semi-drying oils, having iodine values of 124, 129, and 126, respectively. These oils oxidize and polymerize slowly over time. The sunflower and waste oil used in this study have slightly higher iodine values than other oils at 140 and 135, respectively, and they are a little faster drying and form an elastic film when exposed to air. The boron content in the

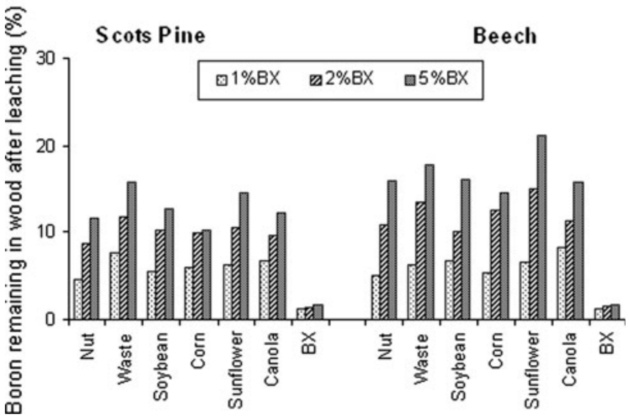

Fig. 3 Boron remaining (%) in BX + oil-treated wood specimens after leaching 336 h in distilled water

5%BA + oil-treated pine samples was approximately 15–23% after leaching. In the case of beech, this ratio was 15–26% (Fig. 1). TB is easily dissolved in water; the solubility rate of TB in water at room temperature is more than three times greater than that of BA and borax [19]. For this reason, TB + oil-treated pine and beech samples showed relatively low-boron retention after leaching. At a boron concentration of 5% TB, retention was from 6 to 13% in the case of pine and from 9 to 17% in beech, depending upon the oil type (Fig. 2). The 5%BX + oil treatment improved boron retention in wood, with pine showing 11–16% retention and beech 15–22% retention (Fig. 3). The boron remaining in wood after leaching increased with an increase in the initial boron concentration.

Thermogravimetric analysis

Figures 4 and 5 show the weight of treated and untreated pine and beech wood (expressed as a percentage of the original weight) with respect to temperature, respectively.

The decrease in sample weight in the 100–120 °C region is most probably due to the loss of water from the conditioned wood samples. A sharp decrease in weight between 300 and around 450 °C is most likely associated with the decomposition of carbohydrates, starting with hemicellulose at around 200 °C or even lower [20, 21]. The samples treated with boron only decomposed earlier than the samples that had been treated with a combination of the boron compounds and waste oil heat treatment. At temperatures above about 400 °C the rate of weight loss slowed down considerably until the test finished. The residue after the test can be supposed to contain a high proportion of charcoal from lignin decomposition [20]. The treatment of wood with boron compounds resulted in increased weight loss at lower temperatures but a decreased weight loss at higher temperatures. BA-treated wood lost considerably more weight than the combined oil and BA samples at a temperature lower than 165 °C (Figs. 4a and 5a). Since no significant chemical reactions are thought to take place in untreated wood at this low temperature, we can deduce that BA may have catalyzed the dehydration of wood. This contention is also supported by Wang et al. [1]. LeVan and Tran [22] mentioned the char-forming catalytic effect of borax and BA, and this effect has subsequently been shown to occur [1, 21, 23]. It is commonly accepted that the fire retardant mechanism of boron compounds is a physical mechanism achieved by the formation of a coating or protective layer on the surface of wood at high temperatures [1]. An increased amount of char could provide additional surface insulation and also inhibit volatilization of the wood beneath during exposure [23].

The percentage residual weights of wood treated with the different boron compounds and oils pyrolyzed at 800 °C under nitrogen are shown in Tables 2 and 3. No significant differences in the weight of the residues was observed between the three different boron compounds, although the BX-treated pine samples showed a bit lower residue weight, followed by the BA-treated samples. The weight of residue from TB-treated samples was slightly higher than the others. These small differences might have arisen from the chemical composition and function of the compounds.

As expected, the degradation rate was lower when the amount of boron was higher. The greater amount of residue left by the higher BA loading in wood may indicate that BA reduces the volatiles lost through combustion. On the other hand, with higher chemical loading, there was an increased amount of residue suggesting that more material remained as solid rather than being lost as volatiles during combustion [23]. The residue weight of the controls diminished continuously with increasing temperature up to around 650–700 °C; thereafter, there was no residue, the wood having been totally degraded.

In the case of the boron and waste oil-treated samples, a sharp decrease in weight was observed up to around 450 °C, and thereafter, it remained stable, whereas the weight loss of the control samples continued to decrease after this point. These samples pyrolized at a much higher temperature than the ones treated with boron only. BA, TB, and BX impregnation before oil treatment yielded considerably more residue weight than samples treated with oil alone. Figures 4a and 5a indicate that final weight loss of the wood samples occurred in the following order: 5%BA < 2%BA < 1%BA < 5%BA + waste oil < 2%BA + waste oil < 1%BA + waste oil < waste oil < control. TB (Figs. 4b and 5b) and BX (Figs. 4c and 5c) and their combinations showed same order of weight losses as BA. Boron + oil-treated samples showed less residual weight than those treated with boron only.

The thermal behavior of sunflower oil-treated samples was also investigated. When compared with the waste

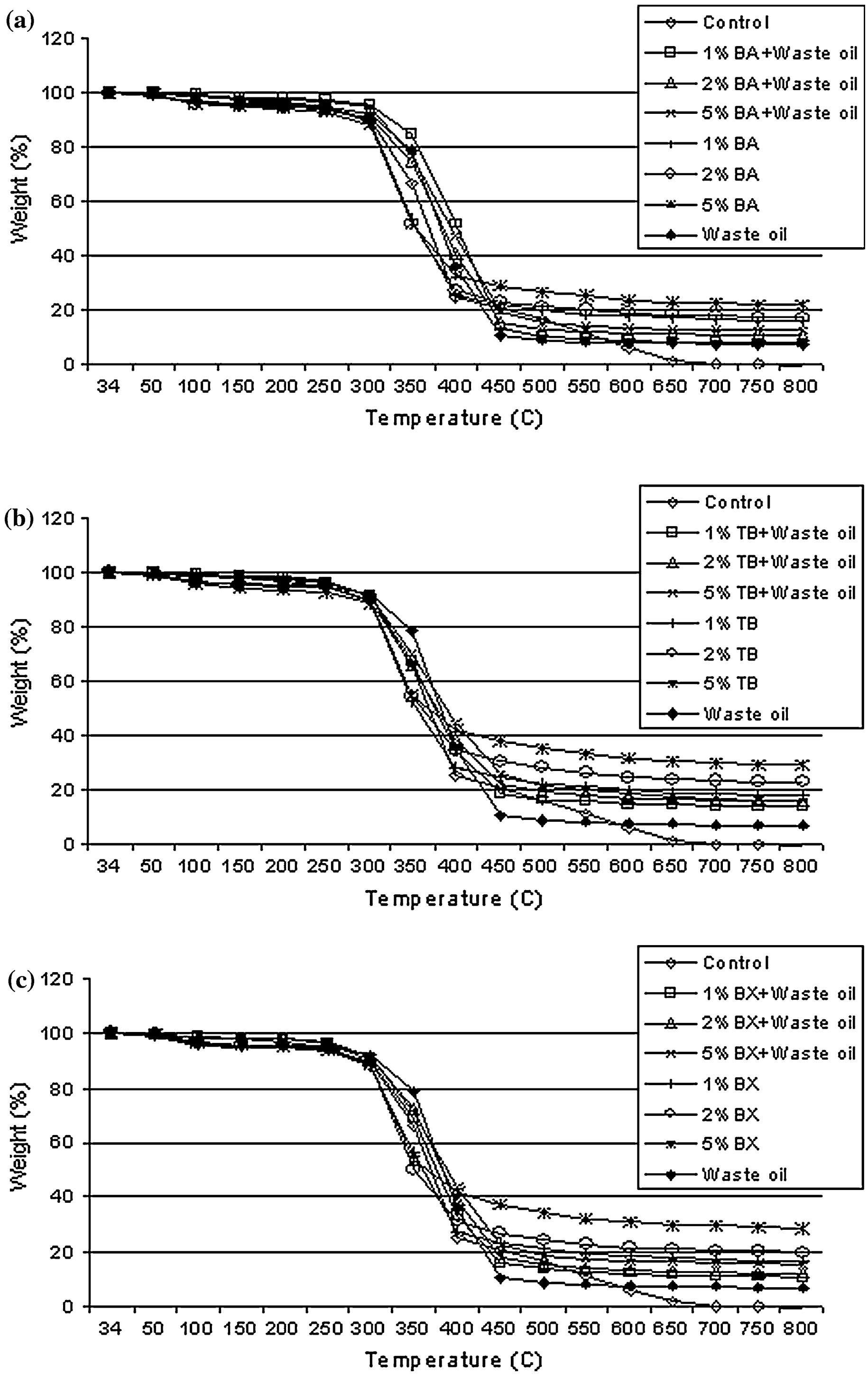

Fig. 4 TGA curves of pine specimens treated with boron compounds and waste oil (**a** BA + waste oil; **b** TB + waste oil; **c** BX + waste oil)

oil-treated samples, both oils showed similar thermal decomposition behavior. Some difference would have been expected, since the waste oil had been used many times before, and therefore, it might be expected that its chemical structure would be different to that of the other vegetable oils. This observation needs further investigation especially with respect to the chemical analysis of waste oil. As can be seen from Table 3, the residual weight of wood did not change significantly with the type of oil. The six types of oil used in this study gave nearly the same residual weight.

FTIR analysis

The FTIR-PAS spectra of boron compounds + waste oil-treated samples showed compositional changes in the wood

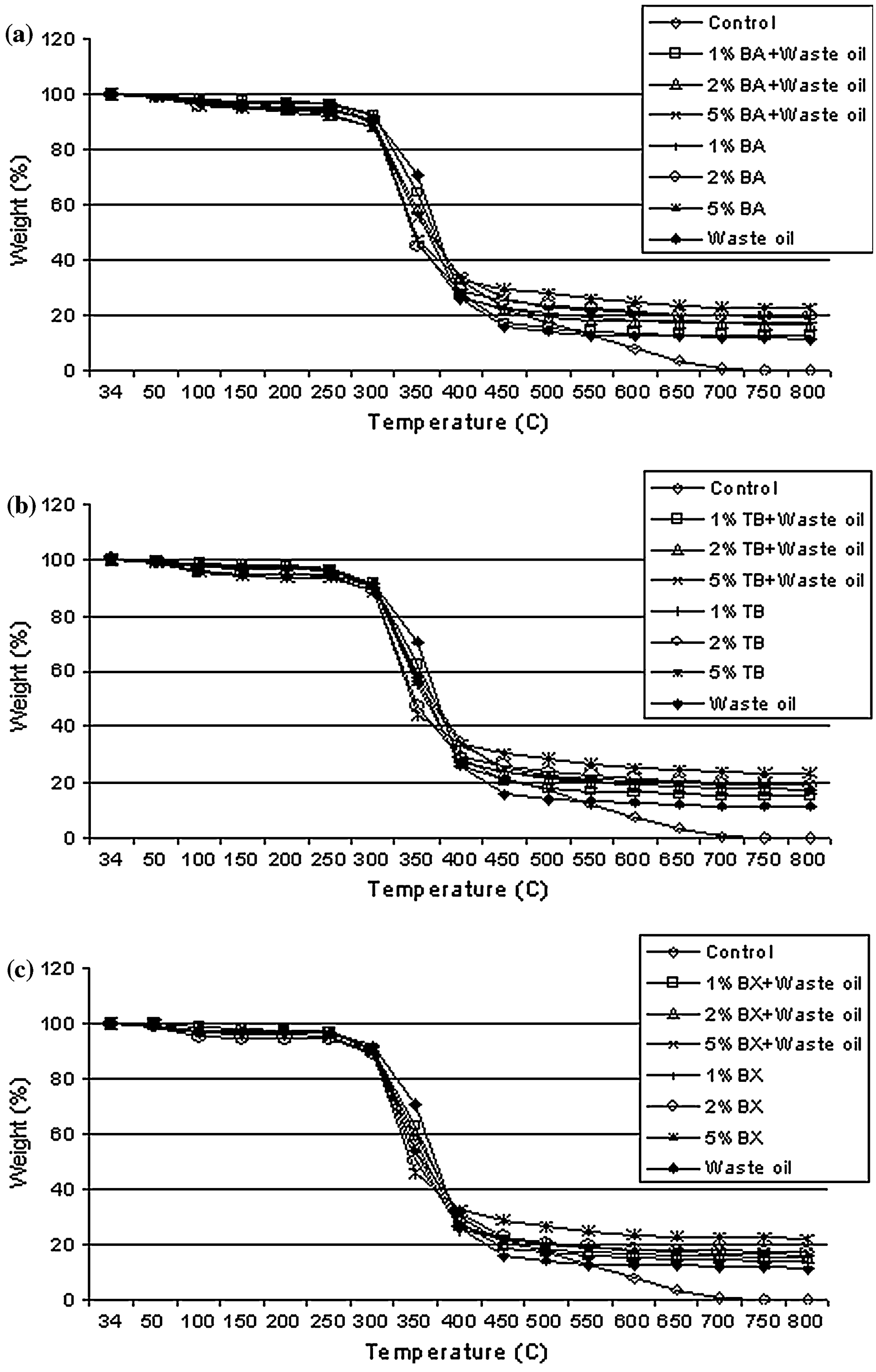

Fig. 5 TGA curves of beech specimens treated with boron compounds and waste oil (**a** BA + waste oil; **b** TB + waste oil; **c** BX + waste oil)

matrix. The assignments of the characteristic IR absorption peaks in wood are listed in Table 4.

FTIR-PAS spectra of boron + waste oil and oil only treated samples showed similar changes in wood structure; however, there were some changes suggesting that thermal degradation of the wood components had taken place (Fig. 6). Heat treatment causes significant transformation in the chemical composition. Chemical modification and degradation of wood components take place through dehydration, hydrolysis, oxidation, decarboxylation, and transglycosylation, and wood becomes less hydroscopic [24].

In the case of pine, the carbonyl absorption peak (1) at 1,734 cm^{-1} increased compared to the controls. This was possibly caused by the degradation of hemicelluloses. Kocaefe et al. [24] reported that the carbonyl absorption peak decreased with increasing heat treatment temperatures

Table 2 The residual weight of wood treated with boron compounds and waste/sunflower oil at 800 °C in nitrogen by TGA (%)

Boron comp. and conc.	Wood species	Boron	Waste oil	Sunflower oil
1%BA	Pine	16.01	7.53	7.58
	Beech	16.82	12.35	14.92
2%BA	Pine	17.09	10.33	8.47
	Beech	19.20	16.36	16.25
5%BA	Pine	21.55	12.37	12.58
	Beech	22.36	19.4	18.30
1%TB	Pine	18.06	13.82	12.68
	Beech	17.62	14.90	16.22
2%TB	Pine	22.68	16.05	15.36
	Beech	19.25	17.61	17.70
5%TB	Pine	29.08	15.90	16.54
	Beech	23.24	19	21.87
1%BX	Pine	17	10.74	11.17
	Beech	16.01	14.07	14.43
2%BX	Pine	19.90	12.29	11.14
	Beech	16.82	15.28	15.38
5%BX	Pine	28.5	15.27	15.29
	Beech	21.88	16.94	18.86
–	Pine	–	6.95	6.86
	Beech	–	11.39	11.28

Table 3 The residual weight of wood treated with 5%BA and oils at 800 °C in nitrogen by TGA (%)

Treatment groups	Wood species	Residual weight (%)
5%BA + nut oil	Pine	11.21
	Beech	17.23
5%BA + waste oil	Pine	12.37
	Beech	19.4
5%BA + soybean oil	Pine	12.44
	Beech	17.51
5%BA + corn oil	Pine	13.95
	Beech	17.61
5%BA + sunflower oil	Pine	12.58
	Beech	18.29
5%BA + canola oil	Pine	12.15
	Beech	17.43

Table 4 Assignments of absorption IR spectra bands in wood [27, 29]

Peak number	Wavenumber (cm^{-1})	Assignments and remarks
1	1,734	C=O stretching in xylan
2	1,590	C=C in aromatic ring in lignin
3	1,505	C=C in aromatic ring in lignin
4	1,450	CH_3 deformation in lignin and CH_2 bending in xylan
5	1,420	CH_2 scissor vibration in cellulose
6	1,370	CH_2 bending in cellulose and hemicellulose
7	1,320	CH_2 wagging vibration in cellulose
8	1,270	Guaiacyl nuclei in lignin
9	1,230	Syringyl nuclei in lignin and C–O in xylan
10	1,157	C–O–C asymmetric band in cellulose and hemicellulose
11	1,056	C–O stretching in cellulose and hemicellulose
12	890	C1 group frequency in cellulose and hemicellulose

from 160 to 230 °C. The temporary increase in this band can be related to the formation of degradation byproducts such as carboxyl acids during treatment. These acids can decrease the degree of polymerization of the hemicelluloses by catalyzing their hydrolysis [24]. Nuopponen et al. [25] stated that broadening of the carbonyl absorption region to 1,630–1,800 cm^{-1} at high temperatures indicated that new extractable carbonyl and carbonyl compounds were formed, originating from hemicelluloses. Tjeerdsma and Militz [26] determined an increase in the specific ester carbonyl peak at 1,740 cm^{-1} in heat-treated wood due to newly formed carbonyl groups.

There was a smaller weakening of the band at a wavenumber of 1,590 (2) and 1,505 cm^{-1} (3) (benzene ring stretching in lignin) for pine and beech. These changes provide evidence of the modification of lignin. The peak at 1,505 cm^{-1} indicates splitting of the aliphatic side chains in lignin and cross-linking formation by condensation reactions of lignin. New cross linking in the lignin network can decrease water absorption and can consequently lead to a reduction in the shrinkage and swelling of wood [24]. The band at 1,450 cm^{-1} (4) is related to CH_3 deformation in lignin and CH_2 bending in xylan [27]. The C–H peak changed slightly for pine but it did not change for beech. In fact, thermal treatment does not cause any change in C–H bonds. However, the number of C–H groups can decrease slightly because of their presence in volatile components which leave the surface, which can be partially replaced by those migrating toward the surface from the inside of the wood sample [24]. These volatile components such as terpenes, fatty acids, etc., are more prevalent in softwoods than in hardwoods [28]. This might be one of the possible reasons for the absence of similar changes in the C–H peak in beech.

There was a small decrease in the peak at 1,420 cm^{-1} (5), related to the CH_2 vibration of the aromatic structures and CH_2 in carbohydrates [29]. A slight weakening at 1,370 cm^{-1} (6) and 1,320 cm^{-1} (7) was seen in beech

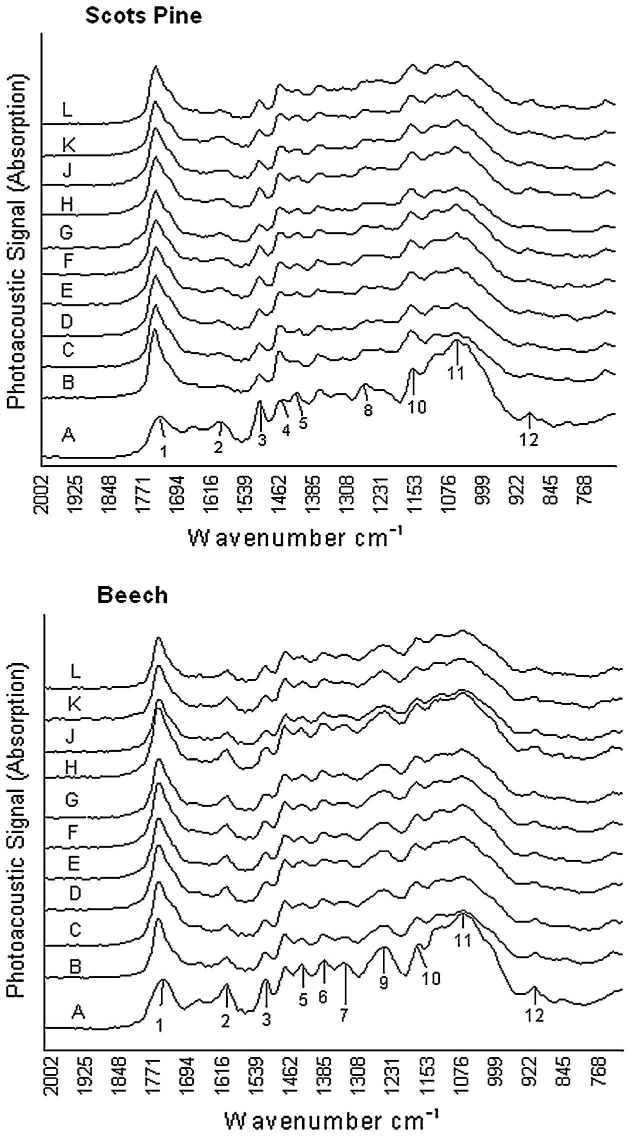

Fig. 6 FTIR-PA spectra of control and boron compounds + waste oil treated specimens. *A* control; *B* 1% BA + waste oil; *C* 2% BA + waste oil; *D* 5% BA + waste oil; *E* 1% TB + waste oil; *F* 2% TB + waste oil; *G* 5% TB + waste oil; *H* 1% BX + waste oil; *J* 2% BX + waste oil; *K* 5% BX + waste oil; *L* waste oil

samples, corresponding to the OH plane bending. A reduction in the number of free hydroxyl groups accessible to water makes wood more hydrophobic [24]. There was also a weakening of the band at 1,270 cm^{-1} (8) for pine and 1,230 cm^{-1} (9) for beech (guaiacyl nuclei in lignin). This is the characteristic peak of C–O stretching vibrations in lignin and hemicelluloses. The intensity of these bands decreases as the guaiacyl structures are modified during heat treatment at high temperatures [25, 30].

The peaks at wavenumbers of 1,157 cm^{-1} (10) and 1,056 cm^{-1} (11) showed slight changes. The cellulose skeleton vibrations including the C–O–C bridge stretching signals occurring at 1,168 cm^{-1}. These changes may be caused by the degradation of hemicelluloses. This is in agreement with the findings of previous studies by Salmen et al. [31]. The asymmetric ring stretching band of cellulose at 895 cm^{-1} (12) started to diminish in the treated samples. The band at 898 cm^{-1} is characteristic of the C1–H group vibration of cellulose and hemicelluloses [25, 27]. This reduction in the peak can be caused by thermal degradation (depolymerization) of the hemicelluloses [24, 32]. Of the structural components, hemicelluloses are the most vulnerable to thermal degradation. The degradation rate of hemicelluloses has been reported to be four times higher at 150 °C than that of wood and α-cellulose [33]. In this study, the hemicelluloses of wood samples treated with oil at 160 °C were shown to have been deformed and degraded.

Combined boron and oil treatment in beech samples showed smaller and weaker changes in the peaks shown in Fig. 6 suggesting that less modification of the wood components had taken place than in treated pine samples. The probable reason for this might be attributed to the different retention ratios and to the anatomical structure as well as differences in the hemicellulose content between the two species. The type of boron compound and the level of boron concentration did not cause important changes in the chemical structure of the samples.

Samples with sunflower oil, waste oil, and their boron combinations showed similar intensities of specific bonds and functional groups within the wood structure. Neither the boron compounds nor the oils are fixed to the wood structure, so significant chemical interaction between the wood components and oils would be expected. Changes in the intensity of the functional groups in the FTIR spectra were due to heat treatment at 160 °C not due to oils or boron compounds. In this respect all oils showed a similar tendency in FTIR spectra.

Conclusions

Vegetable oils have been shown to decrease the leaching rate of boron compounds from wood, with the best performance being obtained with waste and sunflower oils. The TB used in this study was more susceptible to leaching but resulted in higher residual weight following pyrolysis than the other boron compounds studied. TB could be used for wood preservation in indoor applications, in addition to its utilization in agricultural applications. A high level of oil absorption is required for good protection as well as the ability of the oil to dry and so form a protective layer. However, high-retention levels increase the weight of the wood, and this may make it impractical and uneconomic to use. Further work is needed to minimize oil uptake in without loosing the capacity to prevent boron leaching.

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