

Flame Retardance of Insolubilized Silica Inside of Wood Material

Ivan Šimkovic,¹ Helena Martvoňová,² Desana Maníková,² Ondrej Grexa²

¹*Institute of Chemistry, Slovak Academy of Sciences, 84238 Bratislava, Slovakia*

²*State Forest Products Research Institute, 83330 Bratislava, Slovakia*

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ABSTRACT: Beech wood boards were studied with a cone calorimeter. As the specific density of these materials is greater, the total amounts of CO and CO₂ produced were bigger than values measured on spruce specimens. Also, the shape of the heat release rate (HRR) curve was different as its second peak was bigger than the one observed on spruce wood. It was shown that impregnation of wood with water solutions of H₃BO₃ resulted in decreased HRR values with increasing acid concentrations. Mass loss and CO and CO₂ production rates also decrease in the same way. Impregnation with water-soluble NaOH-silica resulted in improved data, when compared to untreated specimens, but were not better than those obtained with H₃BO₃. Simple mixing of both fire retardants gave no improvement, nor was the

two-step impregnation with drying effective after the first step. When the second step-treatment with acid was followed without drying after impregnation with NaOH-silica in the first step, then improvement was evident. This is explained by precipitation of the silica content inside the material when the NaOH was neutralized with H₃BO₃, which could penetrate inside when the material was not dried before the second step. The improvement resulted in lower smoke production and longer times to ignition. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1948–1952, 2005

Key words: degradation; flame retardance; wood; silica; cone calorimeter

INTRODUCTION

Synthetic polymers and wood-inorganic composites containing silicates were studied as materials with improved flammability.^{1–3} There are commercial products on the market for mechanical engineering or food conservation applications, which could be used also for wood specimen impregnation. They are water soluble (SiO₂)_x oligomers alkalized with NaOH to improve the solubility. In our previous studies, we have used magnesium hydroxide, aluminum hydroxide, polyphosphate, diammonium hydrogen phosphate, monoammonium phosphate, sodium thiosulfate, and metabisulfite impregnated on beech plywood, particleboards, and spruce wood specimens.^{4–6} It was demonstrated that water-soluble components could be insolubilized by acidification after being impregnated into the wood cell walls.⁶ In the present work, we have used beech wood specimens to compare the results with spruce materials. For impregnation, boric acid and water-soluble alkaline silicates were used. The goal was to find out how the impregnation with “water glass” (WG) could improve flammability properties and characteristics studied under the cone calo-

rimeter conditions and if similar insolubilization phenomena could be observed by combination of the two additives.

EXPERIMENTAL

Materials

Beech boards (100 × 100 × 15 mm) were impregnated with 1, 2, 4, or 6% water solutions of H₃BO₃ or 10% H₃BO₃/6.5% NaOH for 100 h at room temperature (23°C) and air-dried to constant weight. A similar procedure was applied for water-soluble silicate (WG; 1300 g/L density; pH 11.5; Laro, Slovak Republic) impregnation at 25, 50, and 100% concentrations. For sample 10 (Table I) a solution containing 3% of WG and 1% of H₃BO₃ was used, while for sample 11 after drying to constant weight the second step was applied using 2% H₃BO₃. On sample 12 there was no drying after the first step impregnation with 25% WG, and the sample was immediately treated with 5% H₃BO₃ solution in the second step.

Instrumentation

The materials were tested on the cone calorimeter, by the procedure defined by the ISO 5660 standard method. The tests were done at horizontal orientation. Prior to the testing, the samples were conditioned at

Correspondence to: I. Šimkovic (chemsimk@savba.sk).

TABLE I
The Uptake of Chemicals in Samples Treated with Fire Retardants (FR)

Sample	Uptake of FR [% of original mass]	
	First step	Second step
Unmodified (1)	—	—
1% H ₃ BO ₃ impregnated (2)	0.62	—
2% H ₃ BO ₃ impregnated (3)	11.79	—
4% H ₃ BO ₃ impregnated (4)	3.61	—
6% H ₃ BO ₃ impregnated (5)	4.35	—
10% H ₃ BO ₃ /6.5% NaOH impregnated (6)	12.61	—
100% WG impregnated (7)	7.13	—
50% WG impregnated (8)	8.52	—
25% WG impregnated (9)	2.93	—
1% H ₃ BO ₃ /3% WG impregnation (10)	4.00	—
50% WG impregnation (11)	5.68	0.35 ^a
25% WG impregnation (12)	—	4.27 ^b

^a 2% H₃BO₃ impregnation.

^b 5% H₃BO₃ impregnation without drying after first step.

RH 55% and temperature 23°C for two weeks. All the samples were tested at 50 kW/m², and the edge frame was used for all tests.

RESULTS AND DISCUSSION

Effect of H₃BO₃ impregnation

Unmodified beech wood when analyzed on the cone calorimeter gave a bigger average value of HRR (Tables I and II, sample 1), in comparison to spruce

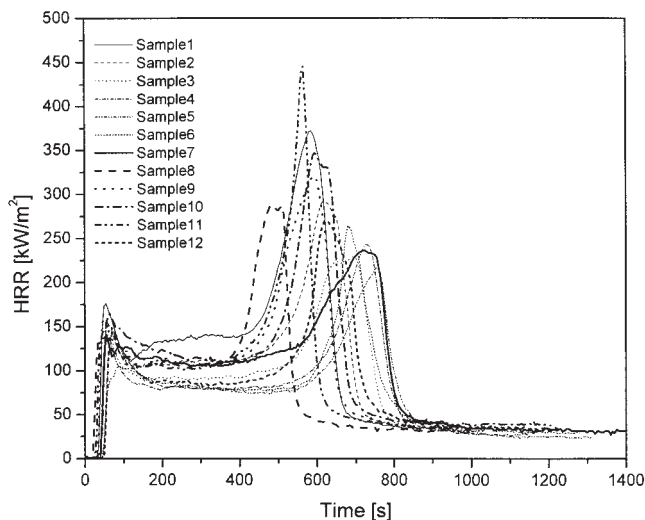


Figure 1 Heat release rates of the samples. Numbering of samples in legend is in relation to Table I.

board.⁶ The shape of the curve is also different, having the second peak more than double the first peak (Fig. 1), while the peak maxima of the two peaks were equal for spruce wood. This is probably due to different content and composition of hemicelluloses and lignin in the used wood species. The effective heat of combustion (EHC) and total heat release (THR) values are only 84 and 57% of the values measured on spruce specimens, while mass loss rate (MLR) and mass lost (ML) values are 204 and 116% of the spruce data. Specific extinction area (SEA) is smaller, while the CO

TABLE II
Average Values of Cone Calorimeter Data on Impregnation of Samples 1–9

Sample	1 ^a	2 ^b	3 ^c	4 ^d	5 ^e	6 ^f	7 ^g	8 ^h	9 ⁱ
Heat release rate [kW/m ²]	177	145	121	108	103	106	140	143	153
Effective heat of combustion [MJ/kg]	10.4	9.9	9.5	9.0	8.9	8.0	10.5	9.5	9.4
Total heat release [MJ/m ²]	45.5	41.5	38.5	36.8	38.6	34.0	48.2	33.1	40.8
Mass loss rate × 1000 [g/s]	161	126	111	104	103	116	118	137	143
Mass lost [%]	79.52	78.68	73.44	72.99	74.03	73.60	81.58	77.12	78.01
Specific extinction area [m ² /kg]	32	14	11	7	9	17	43	49	48
CO production rate × 10 ⁵ [g/s]	53.7	14.5	17.9	13.5	17.8	29.2	32.8	46.0	41.4
Total CO × 10 ² [g]	57.5	63.6	38.1	68.6	111.5	51.6	143.7	66.4	49.1
Total CO ₂ [g]	97.8	94.5	79.3	79.0	82.7	83.8	108.9	74.3	91.4
CO ₂ production rate × 100 [g/s]	15	13	10	10	9	10	12	13	14
CO ₂ yield × 100 [kg/kg]	100	102	92	91	91	85	103	92	95
Time to ignition [s]	33	41	40	41	48	46	41	26	30

^a Unmodified beech board.

^b Modified with 1% H₃BO₃.

^c Modified with 2% H₃BO₃.

^d Modified with 4% H₃BO₃.

^e Modified with 6% H₃BO₃.

^f Modified with 10% H₃BO₃/6.5% NaOH.

^g Modified with 100% WG.

^h Modified with 50% WG.

ⁱ Modified with 25% WG.

and CO₂ values are bigger on beech boards. As the dimensions of both specimens were identical, the different results might be due to bigger specific density of the beech material. Interestingly, although on both specimens more CO₂ than CO is produced, on beech the total CO value is about two orders of magnitude bigger.

Impregnation with 1% H₃BO₃ (sample 2) resulted in decrease of HRR as well as EHC and THR. All three parameters gradually decreased as the concentration of H₃BO₃ in solution increased up to 6% (samples 3 to 5). According to the fire retardant (FR) uptake (Table I), the biggest value was obtained at 2% concentration. Combination of 10% H₃BO₃ and 6.5% NaOH (sample 6) resulted in a slightly bigger value of HRR than on sample 5, while EHC and THR are smaller. This might be due to the fact that the amount of impregnated salts is close to the maximal amount that could be diffused into the material (Table I). With increasing concentration of H₃BO₃, the second peak of the HRR curve (Fig. 1) is decreasing. The curve with maximal H₃BO₃ uptake (sample 3) had the second peak split into two equal peaks. On samples 4 and 5, this maximum is postponed to later times of combustion. For sample 6, although the FR uptake is maximal, the second peak appears earlier with bigger maximal value than on sample 3. The retardation effect observed on samples 3 and 5, where THR was reduced by 15%, seems to be more convenient due to lower FR uptake than on sample 6 where 25% reduction of THR was achieved.

MLR decreased with increasing concentration of used H₃BO₃. Similar trends are observed for values of ML and SEA. The CO production rate decreased dramatically when impregnated with 1% H₃BO₃ (sample 2) in comparison to the unmodified material, while it remained similar when higher concentrations of H₃BO₃ were used due to smaller uptake. Total CO and CO₂ productions were not positively affected with increasing H₃BO₃ concentration. On sample 6, although 10% of H₃BO₃ could be solubilized at 6.5% NaOH concentration, the obtained CO and CO₂ results are confusing. This is probably due to partial consumption of H₃BO₃ with NaOH.

Effect of WG impregnation

With WG the obtained data were better than on unmodified wood (samples 7–9), and with dilution of the solution the HRR values increased, while THR gave the lowest value at 50% dilution (sample 8). This is due to the maximal FR uptake at this concentration (Table I). The second maximum of the HRR curve (Fig. 1, sample 7) was dramatically lowered at the original WG concentration. With dilution it increased and appeared earlier (samples 8 and 9). MLR values were smaller than on unmodified material and were increasing with the dilution of WG. ML values were

TABLE III
Average Values of Cone Calorimeter Data on H₃BO₃/WG Impregnation

Sample	10 ^a	11 ^b	12 ^c
Heat release rate [kW/m ²]	160	149	122
Effective heat of combustion [MJ/kg]	10.4	9.2	8.8
Total heat release [MJ/m ²]	43.3	36.5	35.8
Mass loss rate × 1000 [g/s]	135	142	121
Mass lost [%]	82.2	73.0	73.8
Specific extinction area [m ² /kg]	35.7	31.2	12.6
CO production rate × 10 ⁵ [g/s]	27.3	48.2	2.9
Total CO × 10 ² [g]	71.3	49.2	59.2
Total CO ₂ [g]	99.76	88.41	80.35
CO ₂ production rate × 100 [g/s]	14	14	11
CO ₂ yield × 100 [kg/kg]	101	96	85
Time of ignition [s]	41	26	55

^a Impregnation with 1% H₃BO₃/3% WG.

^b Impregnation with 50% WG/2% H₃BO₃.

^c Impregnation with 25% WG/5% H₃BO₃.

close to those of the unmodified material. SEA values for all three samples were bigger than on all previous samples. Also, the CO and CO₂ values were bigger than on H₃BO₃-treated samples.

The combination of 1% H₃BO₃/3% WG (Table III, sample 10) resulted in bigger FR uptake than with 25% WG impregnation (sample 9). The heat values were smaller than those of unmodified samples as well as both maxima of the HRR curve. This indicates that there is no synergistic effect of the H₃BO₃/WG system at the ratio used with sample 10, probably due to the fact that NaOH in the solution reacted with the present H₃BO₃ and part of the WG was precipitated before it could diffuse into the wood material. When the specimen were impregnated in two steps, separated with drying, WG was eluted in the second step and also part of H₃BO₃ was neutralized, which resulted in smaller FR uptake than obtained on all other samples (Table I, sample 11). The measured average data on this sample were better than on unmodified material as well as on samples 9 and 10, although the second maximum on the HRR curve was the biggest from all studied samples. This shows the effectiveness of the H₃BO₃-Na₃BO₃ combination with excess of acid as FR. When the sample was not dried after the first step, impregnation with 25% WG and subsequent impregnation with 5% H₃BO₃ in the second step (sample 12), the FR uptake was bigger than on sample 9, when only 25% WG solution was used. The measured data are better than on samples 9–11. This indicates that some improvement took place, probably due to the H₃BO₃, which could neutralize some NaOH and cause precipitation of (SiO₂)_x inside the material and then it could not be eluted from inside the wood cell walls. The second maximum on the HRR curve was smaller than on samples 10 and 11 and close to sample 2, when 1% H₃BO₃ was used. On sample 11 after drying, the

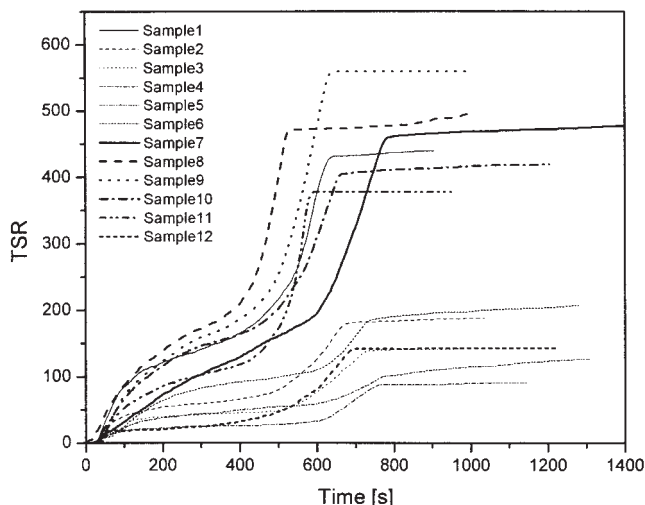


Figure 2 Total smoke release of the samples. Numbering of samples in legend is in relation to Table I.

diffusion process probably could not take place and most of the FR introduced in the first step was washed with 2% H_3BO_3 . When 5% H_3BO_3 was used on sample 12, the diffusion could proceed in unsealed cell walls and precipitation of $(SiO_2)_x$ due to NaOH neutralization could take place.

Time to ignition

The beech specimen gave longer time to ignition (Table II) than unmodified spruce boards.⁶ Most of the impregnated samples had longer times, which indicates a positive flame retardance effect in contrary with $Na_2S_2O_3$ or $Na_2S_2O_5$ impregnated materials.⁶ The smallest value was measured on 50% WG (samples 8 and 11), while the longest time was measured on the 25% WG/5% H_3BO_3 two-step-impregnated sample 12. Sample 5 impregnated with 6% H_3BO_3 gave the second biggest value. This confirms fair properties of those two specimens and the improvement effect on sample 12. According to this parameter, the flame resistance decreases in the following sequence of samples: $12 > 5 > 6 > 7 = 10 = 4 > 3 > 1 > 9 > 11 = 8 > 11$.

Total smoke release effect

In Figure 2 there are the total smoke release (TSR) curves, showing the same two-step trend on the beech material as was observed on the spruce boards.⁶ The smallest effect was observed on sample 4, impregnated with 4% H_3BO_3 solution, followed by the specimen impregnated with 6% H_3BO_3 . As expected also, sample 12 impregnated in two steps showed low smoke release data with a slightly bigger second step of TSR than the previous two samples. The close shape of the curve of sample 12 was observed on the sample

modified with 2% H_3BO_3 (sample 3). The next two curves with similar shape were samples impregnated with 1% H_3BO_3 (sample 2) and sample 6 impregnated with 10% H_3BO_3 /6.5% NaOH. The remaining six samples belong to the second group, with a lot of smoke produced in both steps. Sample 8 gave the biggest first step, while sample 9 has the curve with the most distinguished second step. This parameter also confirms the trends and shows that during the first 300 s the curves of samples 4 and 12 are overlapping. At the second step of smoke formation, the curves of samples 3 and 12 are close, which might be due to the fact that they contain similar amounts of additive.

Mass loss of specimens

As seen from Figure 3, most of the modified samples exhibited smaller loss of mass with time than the unmodified sample. Only sample 8 impregnated with 50% WG gave a dramatically bigger loss of mass with time. The smallest loss of mass was observed on the sample impregnated with 6% boric acid (sample 5). The differences started to be evident after 400 s, and at 800 s the residues were between 20 and 30% of the starting mass, with the lowest value for the unmodified sample. Sample 12 at the end of the process gave about the same residue as sample 5.

When the data are plotted as MLR versus time, the curves are similar to HRR curves, indicating the relation between these parameters.¹ It was confirmed that the second peak is related to the effect of the thickness of the specimens.⁷ Also, CO and CO_2 production rate versus time have the same shape, proving the relation between the parameters.

CONCLUSIONS

Beech wood boards gave bigger HRR values than observed on spruce specimens. Impregnation with

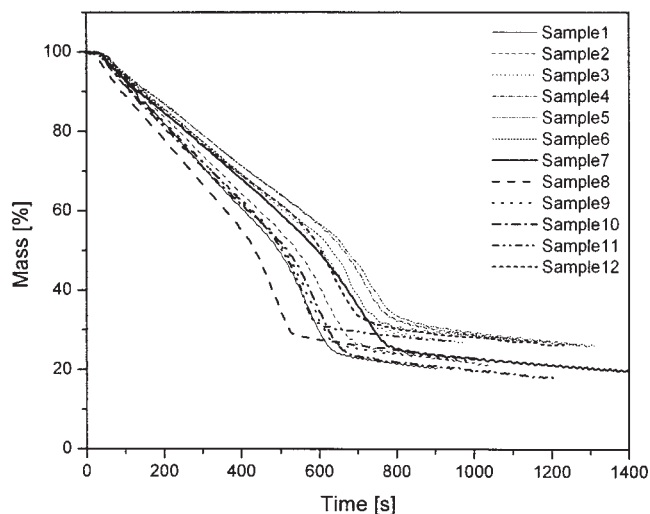


Figure 3 Mass release of the samples. Numbering of samples in legend is in relation to Table I.

H₃BO₃ resulted in gradual decrease of the parameter. The impregnation with WG resulted in less effective protection. The combination of both FR gave an improvement, when the acidic step was the second without drying between individual steps. This could be explained by precipitation of impregnated (SiO₂)_x inside the material due to neutralization of the present NaOH with H₃BO₃. While the total CO amount increased for H₃BO₃ treatment, on WG-modified samples the trend was not clear and CO₂ production decreased for both types of FR. The TSR and ML curves as well as time to ignition data confirm the improved properties of the FR combination.

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