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ORIGINAL

Fire performance and leach resistance of pine wood impregnated with guanyl-urea phosphate/boric acid and a melamine-formaldehyde resin

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Abstract

Scots pine (*Pinus sylvestris* L.) wood impregnated with guanyl-urea phosphate/boric acid and a melamine-formaldehyde resin exhibited considerably increased resistance to leaching, while sustaining superior fire retardancy as tested by the limiting oxygen index (LOI) method. It was found that guanyl-urea phosphate has been well trapped in the wood structure by the cured resin network as evidenced by FTIR spectroscopy. Markedly, weight percentage gain (WPG) losses of fire retardant as low as 7.4% were achieved after excessive leaching of treated wood (EN 84). This was attributed to the effect of melamine-formaldehyde resin. Overall, this type of treatment could be a reliable method for producing fire-resistant pine wood for exterior uses.

1 Introduction

Water soluble guanyl-urea phosphate (GUP) with boric acid (BA) has been proved to be an effective system for producing fire-retardant (FR) treated wood (Gao et al. 2006). However, neither GUP nor BA adhere strongly with the wood polymers and normally leach out during natural weathering (LeVan and Tran 1990; Mantanis 2002).

Thus, such fire-retardant treated (FRT) wood is only suitable for interior use if no further protection is applied. One simple method that can reduce the loss of the water-soluble fire retardants (FRs) is a post surface treatment such as painting. However, this type of FRT wood does not maintain long-term exterior usage due to the fact that FRs migrate to the surface along with the water movement within the wood (Wang et al. 2006; Kawarasaki et al. 2018).

Nevertheless, if the FRs can be fixed within the wood, a steady fire-retarding property should be retained even during exterior use. It was found that wood modified with melamine-formaldehyde (MF) resin can probably provide increased dimensional stability (Inoue et al. 1993), thermal stability (Deka et al. 2002), and to some extent, improved combustion behaviour (Xie et al. 2016). The use of leach-resistant FRs incorporating resins in the wood has been reviewed in the past (LeVan 1984; Östman et al. 2001). However, to the best of the authors` knowledge, direct blending of both water-soluble FRs like GUP and boric acid, and MF resin for decreasing the leaching of fire retardants from FRT wood has not been published previously.

Therefore, the purpose of this research work was to evaluate the fire performance of Scots pine wood treated with a combined GUP/BA system and MF resin, aiming at increasing FRT wood's resistance to leaching. The hydrophobic property of cured MF resin is expected to encapsulate the FR within the wood structure, thus preventing the leaching of the fire retardant.

2 Materials and methods

2.1 Materials

Scots pine (*Pinus sylvestris* L.) sapwood specimens, free of defects, originating from northern Sweden and measuring $10\times10\times150$ mm^3 (T × R × L), with air density of 0.48 g/cm^3, were oven dried at 103 °C for 48 h. The specimens were then conditioned in a chamber at 20 °C and 65% relative humidity

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(RH). The final moisture content (MC) of the wood specimens was around 11%.

Guanyl-urea phosphate was obtained from Fisher Scientific, Sweden. ACS-grade boric acid was purchased from Merck, Germany. Melamine-formaldehyde (MF) resin in water-based solution was obtained from NTL Chemical Consulting (Thessaloniki, Greece). MF resin contained 50% of melamine-formaldehyde prepolymer, < 15% of melamine content, and approximately 35% of water.

2.2 FR treatments

Preparation of each FR solution for the wood impregnation was performed by dissolving GUP/BA (in a weight ratio of 7:3) in deionised water, prior to pouring it slowly into the MF resin solution under continuous stirring. Different amounts of MF resin were added to the GUP/BA solution. The FR treatments applied in this work are analytically shown in Table 1.

Fully immersed specimens were impregnated using a full-cell pressure process in the laboratory, i.e. 30 min of vacuum at 20 mbar, followed by 15 bar pressure for 1 h. Following that, the treated specimens were heated in an oven at 103 °C for 48 h, before measuring the dry mass (m_0). Then, the specimens were climatised in a conditioning chamber (20 °C/65% RH) for one week, prior to further analysis. Ten replicates were used for each treatment. Weight percentage gain (WPG) after impregnation with FR, for each wood specimen, was calculated using Eq. 1.

$$\mathrm{WPG}(\%) = 100 \times (m_i - m_0)/m_0 \tag{1}$$

2.3 Characterisation

2.3.1 Accelerating ageing (EN 84)

Leaching tests were carried out in five replicates according to standard EN 84 (1997). All specimens were immersed in water in a polypropylene container, applying 20 min vacuum in a desiccator and replacing the water ten times, during the 14-day leaching period. The leached specimens were then oven-dried at 103 °C, before measuring the dry mass. The water from each leaching test was collected for FTIR analysis.

2.3.2 Fourier transform infrared spectroscopy (FTIR)

PerkinElmer FTIR spectrometer, Frontier equipped with UATR Diamond/ZnSe ATR (Single Reflection) was used over the wavenumber range of 4000−650 cm^{-1} with 4 scans at a resolution of 4 cm^{-1}, to investigate the chemical characteristics of the leached water collected from the leaching tests (EN 84). Each leached water fraction was first evaporated in a fume hood, prior to the analysis of the solid residues.

2.3.3 Limiting oxygen index (LOI)

Fire tests of both unleached and leached FR treated wood specimens were carried out (five replicates for each run) using the well-known limiting oxygen index (LOI) test in accordance with ISO 4589-2 (2006). This method enabled the evaluation of the influence of various FR formulations and the impact of leaching on the fire performance of treated pine wood in a small scale (White 1979). It is normally measured by passing a mixture of oxygen and nitrogen over a burning wood specimen until a critical level of oxygen is reached, which corresponds to the LOI value. Typically, LOI values of 20–25% are measured for untreated wood specimens (White 1979). A higher LOI value indicates enhanced fire retarding performance.

2.4 Statistical analysis

Results from the FR treatments were analysed using a computerised statistical program to perform an analysis of variance (ANOVA), and by carrying out the Duncan test at a $P \leq 0.05$ confidence level.

3 Results and discussion

Figure 1shows the results of weight percentage gain (WPG) of FRT wood specimens, without leaching and after excessive leaching, following the standard EN 84. In addition, the percentages of WPG losses of FRT wood, after water leaching, for the treatments with 10-0MF, 10-10MF, 10-20MF and 10-30MF solutions are shown in Table 2.

As expected, increasing additions of MF resin in GUP/BA FR systems, namely 10-10MF, 10-20MF and 10-30MF

Table 1 FR treatments used in this work

Denotation	10-0MF	10-10MF	10-20MF	10-30MF	0-30MF
	10% GUP/BA + 0 wt% MF resin	10% GUP/BA + 10 wt% MF resin	10% GUP/BA + 20 wt% MF resin	10% GUP/BA + 30 wt% MF resin	0% GUP/BA + 30 wt% MF resin

resulted in much higher WPGs, i.e. 22.9%, 36.7% and 44.8%, respectively (Fig. 1).

As a matter of fact, wood specimens treated with the FR system 10-0MF, which had no MF resin, underwent a full depletion of the FR after leaching, i.e. 104.8%. This implies that GUP/BA itself did not adhere sufficiently within the wood and was fully extracted after excessive leaching.

In addition, it was observed that the higher the MF resin addition in the FR, the lower the WPG losses after leaching (Table 2). This indicates that the presence of melamine-formaldehyde resin in GUP/BA, as cured, enabled higher retention of the FR in the wood structure, even after leaching with water (EN 84). Characteristically, with the FR system 10-30MF, the WPG loss of FR after leaching was only 7.4%, that is from WPG 44.8% to WPG 41.5% (Fig. 1, Table 2).

To assess the fire performance of FRT pine wood, LOI values were determined both for unleached and leached specimens. In Fig. 2, the LOI values attained are depicted in detail. Evidently, wood treated with 10 wt% GUP/BA (10-0MF), after leaching, exhibited the same LOI (approx. 25%) as untreated wood. To understand the effect of water leaching, clearly with the FR treatment 10-0MF, the unleached wood samples showed LOI of 80.9%, while the leached ones only 25.2% (Fig. 2). This is a hint that GUP/BA itself (i.e. 10-0MF) was not fixed within the wood and very easily extracted (Fig. 1).

On the other hand, the addition of MF resin in the fire retardant GUP/BA was critical. Indeed, even after leaching, much higher LOI values, that is, higher fire performance of FRT wood was achieved after adding 10 wt% and 20 wt% MF resin to GUP/BA, i.e. the mean LOI values increased to 57.3% and 56.8%, respectively (Fig. 2). Further, the LOI

Table 2 WPG losses of FR treated wood after water leaching (EN 84)

	FR treatments			
	10-0MF	10-10MF	10-20MF	10-30MF
WPG loss (%)	104.8 (0.6)*	27.9 (1.4)	7.9 (1.0)	7.4 (0.3)

*Standard deviation in parentheses

value obtained for leached wood treated with 10-30MF solution was 66.3%, which was statistically the highest of all.

The synergetic effect of GUP and BA in enhancing the fire performance of wood has been reported by Gao et al. (2006). High flame retardancy, in terms of LOI, was also verified in this study, for Scots pine wood treated with these chemicals. Take note, still after extensive water leaching, the LOI of pine wood impregnated with GUP/BA and MF resin was clearly quite higher than that obtained in wood treated with only MF resin, i.e. treatment 0-30MF (LOI: 41.4%).

Moreover, lower WPG losses and higher FR resistance of treated wood, even after excessive leaching, was achieved following the addition of 10 to 30 wt% MF resin to the GUP/BA solution (10-10MF, 10-20MF, 10-30MF). Consequently, the effect of MF addition on increasing the resistance to water leaching was found to be statistically very significant.

To investigate the chemical compounds that leached out from the wood impregnated with MF/GUP/BA systems, leached water fractions were evaporated and the solid residues were analysed using the FTIR technique.

The spectrum of leached water (from the 4th day of extraction) of pine wood treated with 10-30MF solution is presented in Fig. 3. Markedly, all the spectra of leached water collected from the different treatments (10-10MF,

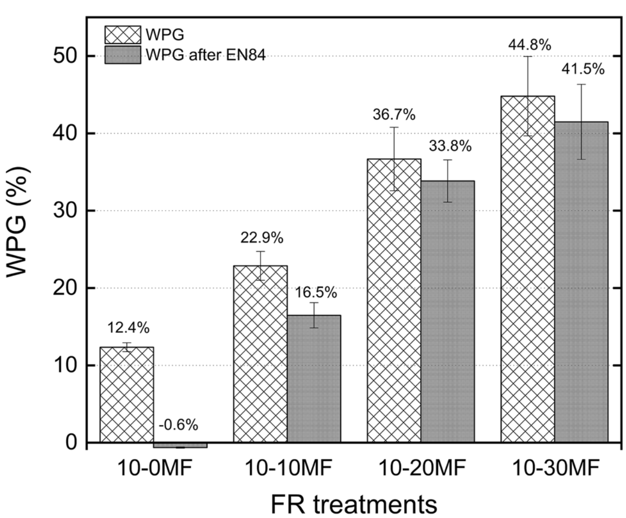

Fig. 1 Weight percentage gain (WPG) of FRT pine wood before and after leaching

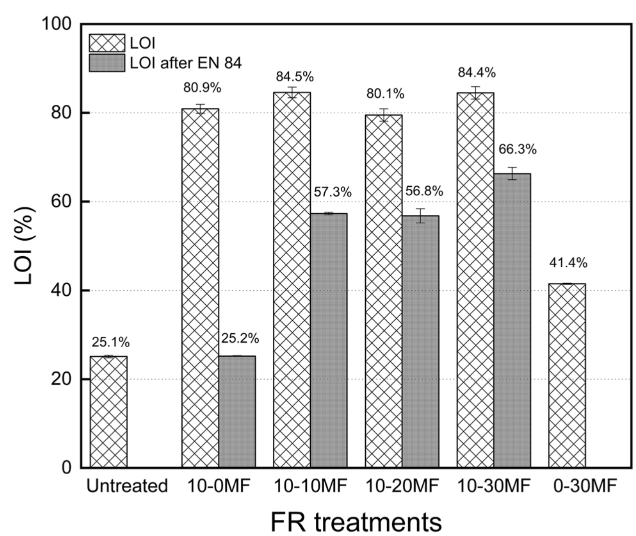

Fig. 2 Limiting oxygen index (LOI) values of unleached and leached FRT pine wood

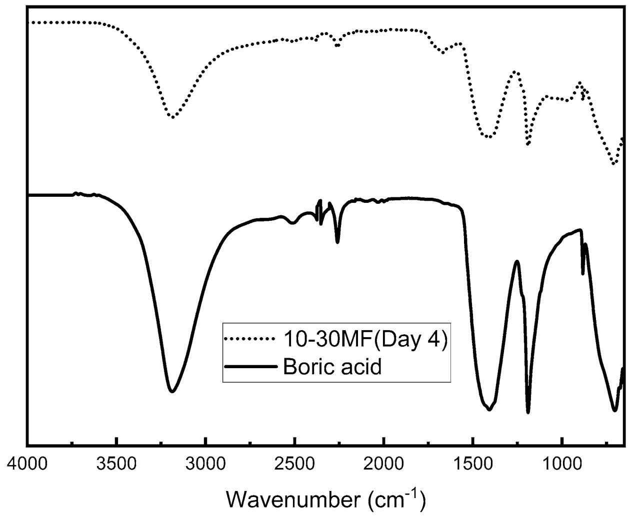

Fig. 3 FTIR spectrum of leached water (dotted line) from 10-30MF treated pine wood vs. the spectrum of pure boric acid (solid line)

10-20MF, 10-30MF) exhibited a similar trend to that in Fig. 3. This spectrum was compared with that of pure boric acid, and it became apparent that leached water was mainly composed of boric acid.

It was also noted that the wave number of 810 cm^{-1} (triazine ring bending vibration of MF resin) as cited by Merline et al. (2013), as well as that of 1700 cm^{-1} which is related to GUP (Wang et al. 2006), was not clearly revealed in the spectrum, as shown in Fig. 3. This implies that both GUP and MF stayed captured within the wood structure, possibly in the lumen, during leaching. A possible explanation may be that nitrogen phosphate salt, such as GUP, perhaps, can be encapsulated by the hydrophobic MF polymeric structure (Wang et al. 2015). As a consequence, it prevents GUP from being leached out of such FRT wood.

4 Conclusion

The resistance to leaching of Scots pine wood treated with GUP/BA can be considerably increased, while retaining superior fire retardancy, by the incorporation of a melamine-formaldehyde resin into the FR solution. It is known that water leaching, according to EN 84, is a drastic method to examine the retention of chemicals within the wood structure after impregnation. The results of the work have implied that the strategy of combining a melamine-formaldehyde resin and water-soluble GUP/BA is an effective approach for alleviating the excessive leaching of FRs, such as GUP, during weathering of FR treated pine wood. Actually, a WPG loss of FR lower than 8% was accomplished with the use of 20 wt% and 30 wt% MF in GUP/BA, most likely by encapsulating the FR within the cured polymeric MF network (possibly in the lumen).

Noticeably, even after leaching, LOI values of 57.3%, 56.8% and 66.3% were obtained for pine wood treated with the FR solutions 10-10MF, 10-20MF and 10-30MF, respectively. Overall, it is suggested that such FR treatment can be a reliable method for producing FRT pine wood for outdoor applications.

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