Effect of Combined Fire- and Bio-Protective Coatings on the Thermal Degradation of Spruce Wood: Insights from Radiant Heat and Simultaneous Thermal Analysis

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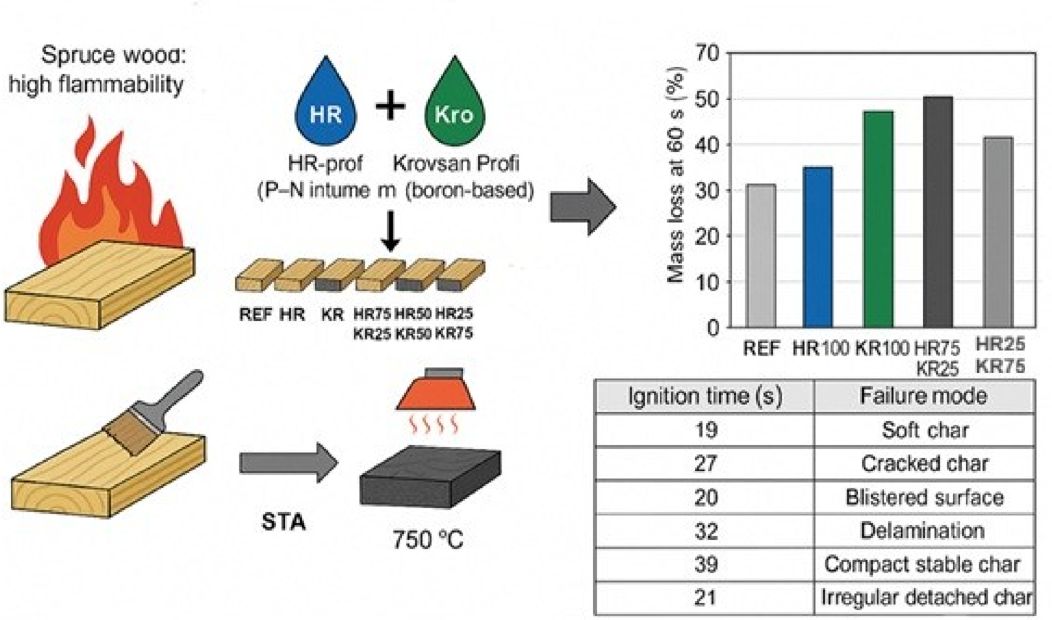
GRAPHICAL ABSTRACT



Ignition time (s)	Failure mode
19	Soft char
27	Cracked char
20	Blistered surface
32	Delamination
39	Compact stable char
21	Irregular detached char

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Iveta Mitterová, Andrea Majlingová,* and Viktória Barna

The influence of two commercial fire-retardant formulations, HR Prof and Krovsan, and their mixtures on the thermal behavior and fire resistance of spruce wood was evaluated by simultaneous thermal analysis STA (namely TG/DTG/DSC) and radiant-heat exposure. The untreated wood exhibited the typical three-stage degradation of lignocellulosic material with a maximum mass-loss rate near 265 °C. All treated specimens showed delayed decomposition, reduced oxidation rate, and markedly higher residual mass at 700 °C. A strong correlation was found between thermogravimetric residue and the mass retained after radiant-heat testing, confirming that improved performance resulted from condensed-phase stabilization. Phosphorus–nitrogen components of HR Prof promoted early dehydration and intumescence, while boron–copper species in Krovsan reinforced the carbonized layer and limited oxidation at elevated temperature. The balanced mixture (50 HR – 50 KR) provided the most effective protection, combining early char formation with long-term stability. The synergistic action of HR Prof and Krovsan thus offers an efficient and environmentally acceptable strategy for enhancing the fire safety of spruce wood.

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Keywords: Boron-based coating; Fire-retardant coating; HR Prof; Krovsan; Mass loss; Norway spruce; Radiant heat exposure; Wood thermal degradation; Simultaneous thermal analysis (STA)

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INTRODUCTION

Wood-based construction products such as cross-laminated timber (CLT) are experiencing rapid market growth because they store biogenic carbon, have low embodied energy, and enable fast off-site manufacturing (Brandner *et al.* 2016). Europe's CLT production capacity rose from 0.4 million m^3 in 2012 to over 2.5 million m^3 in 2024, with mid-rise residential and educational buildings being prominent application sectors (Liu and Fischer 2022; Nazrun *et al.* 2025). Despite these advantages, wood is a combustible material whose thermal degradation releases flammable volatiles, leading to rapid flame spread, high heat-release rate (HRR), and structural charring (Babrauskas 2005; Lowden and Hull 2013). Large-compartment fire experiments have shown that delamination of CLT layers can trigger secondary flash-over events and extend the duration of post-flashover fires (Liu and Fischer 2022). Consequently, building codes in many jurisdictions require combustible members that remain exposed to achieve Euroclass B or better fire reaction ratings, which are unattainable for untreated softwoods such as Norway spruce (lat. *Picea abies*) (EN 13501-1 2018; Mitrenga *et al.* 2025).

Strategies for Improving the Fire Performance of Wood

Fire-retardant (FR) technologies for wood can be broadly divided into (i) bulk impregnation with water-soluble salts, (ii) surface coatings that intumesce or form inorganic barriers, and (iii) emerging nano- and bio-based hybrid treatments, such as layer-by-layer (LbL) deposited chitosan–ammonium polyphosphate systems, graphene oxide, or nanoclay-enhanced coatings, and sol–gel silica/titania protective layers that provide simultaneous fire, moisture, and UV resistance (Hull and Stec 2008; Xie *et al.* 2010; Yan *et al.* 2022; Yuan *et al.* 2025).. Water-soluble salts, typically phosphates, borates, sulphates or silicones, enhance char formation and dilute the combustible gas phase but suffer from leaching under humid or exterior service conditions (Kartal *et al.* 2010). Intumescent coatings based on phosphorus–nitrogen chemistry are currently the most commercially important solution for interior applications: upon heating, the acid source (*e.g.*, ammonium polyphosphate) catalyzes dehydration of a carbon source (*e.g.*, pentaerythritol) while a blowing agent (*e.g.*, melamine) expands the melt into a multicellular char that insulates the underlying wood, reducing the peak HRR by 40 to 70% in cone-calorimetry at loadings of 200 to 400 g m^{-2} (Gu *et al.* 2007; Lu *et al.* 2024).

In addition to fire resistance, the long-term durability of wood depends on protection against biological agents such as fungi and insects, typically achieved using boron-based preservatives (Reinprecht 2016).

Role of Treatment Concentration

A critical parameter controlling performance is the chemical retention or coating add-on. Brahmia *et al.* (2020) found a monotonic reduction in total heat evolved when impregnation retentions of a PEG-400/phosphate/borate system were increased from 5 to 20 wt.% in Scots pine and poplar. In contrast, Nussbaum (1988) reported diminishing returns above 5 kg m^{-3} of phosphate–borate for spruce, noting that excessive acid content accelerated strength loss at elevated temperature. Jiang *et al.* (2015) achieved a Limiting Oxygen Index (LOI) of 78% for poplar veneers with a 28 wt.% pentaerythritol/ urea/phosphoric-acid treatment but observed 3% thickness swelling after four wet–dry cycles, illustrating the trade-off between fire performance and dimensional stability. Optimizing concentration is therefore essential to satisfy both fire and mechanical requirements.

Synergistic and Multifunctional Approaches

Boron compounds, which are widely used for biodeterioration control, can also act as FR synergists by forming boron–oxygen–carbon networks that reinforce the phosphorus-rich char generated by intumescent systems (Doğan and Bayramlı 2011). Lloyd and Manning (1995) documented up to a 30% reduction in mass-loss rate when wood previously impregnated with borax was coated with an ammonium-polyphosphate paint. Similar synergistic effects have been confirmed in polymer composites where borates strengthen intumescent phosphorus systems, leading to improved char yield and delayed decomposition (Yan *et al.* 2022). Recent nano-enabled formulations further improve efficacy at low add-on. Layer-by-layer (LbL) deposited chitosan/ammonium-polyphosphate/graphene-oxide assemblies have raised the LOI of poplar from 22% to 42% with an areal weight below 5 mg/cm² and retained 90% of their performance after 24 h water immersion (Yan *et al.* 2022). Nanoclay, layered double hydroxide (LDH), and nano-SiO_2/TiO_2 sol–gel top coats create tortuous diffusion paths for gases while providing UV stability and abrasion resistance (Kiliaris and Papaspyrides 2010; Xie *et al.* 2010). Such multifunctional coatings address not only fire safety but also moisture, ultraviolet, and biological degradation in a single layer.

Regulatory and Environmental Context

Regulatory pressure further drives the transition toward halogen-free, durable FR systems. The European Chemicals Agency (ECHA) proposed an EU-wide restriction on several aromatic brominated flame retardants in December 2024, citing persistence and potential endocrine activity (ECHA 2024). Sustainable procurement guidelines now favor products whose fire-protection efficacy is maintained after accelerated ageing and whose additives do not interfere with end-of-life recycling. Consequently, there is a strong incentive to develop integrated fire- and bio-protective coatings that meet durability criteria at minimal chemical loading.

Aim of the Present Study

- Against this backdrop of increasing use of combustible timber elements in construction (Lowden and Hull 2013; Liu and Fischer 2022; Mitrenga *et al.* 2025), the present work evaluated the fire-retardant performance of a commercial phosphorus–nitrogen intumescent coating (HR Prof), a boron-based preservative (Krovsan Profi), and their mixtures at a fixed total add-on (300 g/m²) on Norway spruce wood. Radiant-heat mass-loss testing was employed to assess practical fire performance, while simultaneous thermal analysis (STA, namely TGA/DTG/DSC) provided mechanistic insight into thermal decomposition and char stabilization (Babrauskas 2005; Schindler *et al.* 2002; Yan *et al.* 2022). By combining these approaches, the study examined the synergistic potential of phosphorus–boron systems and their relevance for multifunctional, durable, and environmentally acceptable wood protection systems.

EXPERIMENTAL

The experimental work focused on evaluating the influence of commercial fire-retardant formulations on the thermal behavior and oxidative stability of spruce wood. Particular attention was given to the interaction between HR Prof and Krovsan (KR) fire retardants. The two formulations were combined in different ratios to determine potential synergistic effects on thermal degradation and char formation.

To assess these phenomena, simultaneous thermal analysis STA was used to monitor mass loss, reaction rates, and heat flow under oxidative conditions.

Untreated spruce wood (REF) was analyzed in parallel to serve as a reference for natural lignocellulosic decomposition.

This approach enabled a comparative evaluation of the temperature-dependent decomposition steps, heat effects, and char-forming tendencies of the treated and untreated materials.

Materials

Clear, defect-free Norway spruce (lat. *Picea abies* L.) lumber was sourced from a commercial mill in Slovakia. Samples were conditioned to a moisture content of 12 ± 1% at 20 ± 2 °C and 65 ± 5% RH, according to EN 13238 (2020). Final sample dimensions were 50 mm (L) × 40 mm (R) × 10 mm (T), which are representative of small-scale structural panels.

Two commercial formulations of fire-retardant and preservative systems were tested:

- HR Prof (HR): a commercial water-based intumescent fire-retardant coating containing phosphorus–nitrogen active components. According to the manufacturer's technical data sheet, the formulation contains approximately 18 to 22 wt.% phosphorus (P) and 8 to 12 wt.% nitrogen (N) in the form of ammonium polyphosphate and melamine derivatives. These components act as the acid source and blowing agent, respectively, promoting early dehydration and intumescent char formation during heating. (Holz Prof OÜ, Tallinn, Estonia)
- Krovsan (KR): a commercial water-borne biocidal wood preservative based on boron salts and copper compounds. The formulation contains approximately 3 to 5 wt.% boron (B), mainly in the form of borates, and 0.2 to 0.5 wt.% copper (Cu) as auxiliary biocidal and stabilization agents. Boron contributes to char stabilization and oxidation inhibition at elevated temperatures, while copper enhances biological resistance.(Chemolak a.s., Slovakia)

Experimental Design

Mixtures of HR Prof and Krovsan were prepared in mass ratios of 100% HR (HR100), 100% KR (KR100), 75% HR to 25% KR (HR75KR25), 50% HR to 50% KR (HR50KR50), and 25% HR to 75% KR (HR25KR75), while untreated spruce wood served as the reference sample (REF). The selected volumetric ratios (25/75, 50/50, and 75/25) were chosen to systematically investigate potential synergistic or antagonistic effects between the intumescent (HR Prof) and boron-based (Krovsan) components. Symmetric mixture steps of 25% increments are commonly used in coating optimization studies because they allow identification of nonlinear or threshold effects in char formation, ignition behavior, and mass-loss response while keeping the total add-on constant. These three ratios therefore represent a balanced and experimentally tractable design that captures the transition from HR-dominated to KR-dominated behavior.

Application Protocol

All formulations were mixed in-house immediately before application to ensure homogeneity. Each sample was brush-coated on all faces with two uniform layers applied 24 h apart. Total dry add-on was controlled to 300 ± 10 g/m² using a high-precision balance (0.01 g resolution). Coated samples were reconditioned for seven days under controlled conditions of 20 ± 2 °C and 65 ± 5% relative humidity before testing. Visual inspection ensured full coverage and the absence of defects such as pooling or brush streaks.

Radiant Heat Test Procedure

Thermal degradation was assessed using a horizontal radiant heat exposure setup adapted from cone calorimetry principles for small-scale mass-loss evaluation, following the methodology reported in previous comparative fire-performance studies on coated wood (Gu *et al.* 2007; Brahmia *et al.* 2020). A 1 kW full-trough ceramic infrared emitter (Repa Germany, 245 × 35 × 60 mm) was mounted 30 ± 2 mm above the wide face of the horizontal sample. The emitter surface reached 750 ± 20 °C, delivering an average radiant heat flux of approximately 25 kW/m² to the sample surface.

Each sample was placed on a non-combustible ceramic fiber platform and weighed to the nearest 0.01 g before exposure. The mass was logged in real-time using a calibrated Sartorius Basic Plus balance connected to data acquisition software (LabVIEW 2022).

Logging frequency was set to 10 s intervals. The test continued until self-extinguishment, complete surface charring, or a maximum duration of 600 s.

Fire Performance Evaluation Metrics

Key indicators recorded included:

- Cumulative mass loss (%): relative to initial dry mass.
- Ignition time (s): visually determined from the first appearance of sustained flaming.
- Visual failure modes: including surface cracking, bubbling, and coating detachment.

Post-test samples were photographed under ambient conditions, and selected samples were cross-sectioned to inspect char layer thickness.

Statistical and Analytical Methods

Data were analyzed using MATLAB R2024a (MathWorks Inc., Natick, MA, USA). One-way ANOVA was used to assess the effect of treatment group on mass loss and ignition time. Tukey's HSD post-hoc tests ($\alpha = 0.05$) were performed to determine statistically significant pairwise differences. Assumptions of normality and homoscedasticity were verified using the Shapiro–Wilk and Levene's tests, respectively. Error bars in figures represent standard deviations. Repeatability was ensured by testing five replicate samples per group (n = 5), consistent with standard practice for small-scale fire testing (Nussbaum 1988; Gu *et al.* 2007).

For each treatment group (REF, HR100, KR100, HR75KR25, HR50KR50, and HR25KR75), five independent replicate specimens ($n = 5$) were tested in the radiant heat exposure experiments to ensure statistical reliability. For simultaneous thermal analysis (STA), three replicate measurements ($n = 3$) were performed for each formulation using separately prepared surface flakes. The reported values represent mean values, and the associated variability is expressed as standard deviation.

Simultaneous Thermal Analysis STA

Thermal decomposition behavior was further examined using simultaneous thermal analysis STA, which combines thermogravimetry (TGA), first derivative (DTG), and differential scanning calorimetry (DSC). Small flakes were scraped from the coated surfaces of REF, HR100, KR100, HR75KR25, HR50KR50, and HR25KR75 samples.

Thermal degradation and oxidation behavior were analyzed using a NETZSCH STA 509 Classic simultaneous TG/DTG/DSC analyzer. Approximately 20 ± 1 mg of each sample was placed in an open Al_2O_3 crucible and heated from 30 to 700 °C at a 10 °C $\cdot min^{-1}$ rate under an $O_2/N_2/N_2$ atmosphere (oxidative mode). Calibration was performed with indium and alumina standards to ensure accuracy.

TG curves were used to determine the onset temperature (1% mass loss) and residual mass at 700 °C. The DTG signal identified the maximum decomposition temperature (T_{max}) and the corresponding mass-loss rate, while DSC data revealed exothermic and endothermic transitions related to oxidative decomposition, charring, and late-stage oxidation.

Key STA outputs included:

- Onset temperature of decomposition (T_{onset})
- Maximum degradation rate temperature (T_{max}, DTG)

- Maximum DTG value (wt.%/min)
- Residual mass (%) at 700 °C

All raw TG, DTG, and DSC datasets were exported from Proteus software as CSV files and processed in Python using custom scripts to ensure consistent parameter extraction. DSC baselines were corrected by linear fitting in the 150 to 220 °C region, and enthalpy changes (ΔH, $J \cdot g^{-1}$) were calculated by integrating the baseline-corrected heat-flow curves. TG onsets, DTG peaks, and DSC maxima were identified algorithmically from smoothed datasets (five-point moving average). All temperature parameters were reproducible within ±3 °C, and enthalpy values within ±5%.

The calculated values are summarized in Tables 1 through 4, and representative TG–DTG–DSC curves for each composition are presented in Figs. 5 through 10. Those are presented in Results and Discussion. The STA values were compared across formulations to identify differences in de-composition pathways and char-forming ability. Results were cross-referenced with radiant-heat performance to establish mechanistic correlations.

RESULTS AND DISCUSSION

This section presents the results of radiant heat exposure and simultaneous thermal analysis STA of spruce samples treated with different fire-retardant formulations. The study assessed the influence of formulation type and composition on ignition resistance, mass loss, decomposition behavior, and visual degradation. Quantitative data were supported by statistical analysis and physical inspection of post-burn samples. Each key indicator, ignition time, cumulative mass loss, rate of degradation, char morphology, and thermal decomposition pathway, was evaluated across all six experimental groups.

Ignition and Early Decomposition Behavior

All untreated reference samples (REF) ignited within 17 to 21 s of exposure, with visible flaming and vigorous mass loss. In contrast, the HR50KR50 and HR75KR25 groups exhibited delayed ignition (mean times of 39 s and 32 s, respectively), while HR100 ignited at 27 s on average. KR100 and HR25KR75 ignited quickly (20 to 23 s) but also displayed blistering and coating delamination within the first 60 s. Delayed ignition in the HR50KR50 mixture was attributed to the combined effects of phosphorus–nitrogen intumescence and borate-induced char promotion. Phosphorus-containing compounds catalyze dehydration of cellulose, generating an early protective carbonaceous layer that limits the evolution of flammable volatiles, while melamine-based nitrogen components release inert gases that dilute combustible pyrolysis products. Simultaneously, borates from Krovsan promote cross-linking and glassy char formation, increasing the thermal stability of the protective layer. These combined mechanisms slow heat penetration into the wood, thereby delaying ignition and reducing early mass loss.

Cumulative Mass Loss

Figure 1 illustrates the cumulative mass loss curves for all six groups. The results highlight the synergistic effect of the combined phosphorus–nitrogen and borate system in suppressing thermal degradation. After 60 s of radiant heating, the untreated REF samples lost 4.77 ± 0.21% of their initial mass. HR100 and KR100 exhibited high mass losses of 51.32 ± 1.42% and 59.17 ± 1.65%, respectively. Mixtures containing both HR and KR provided significantly better performance, with HR50KR50 showing the lowest mass loss

(1.92 ± 0.12%). HR75KR25 and HR25KR75 exhibited intermediate results (41.20 ± 1.55% and 63.31 ± 1.84%, respectively).

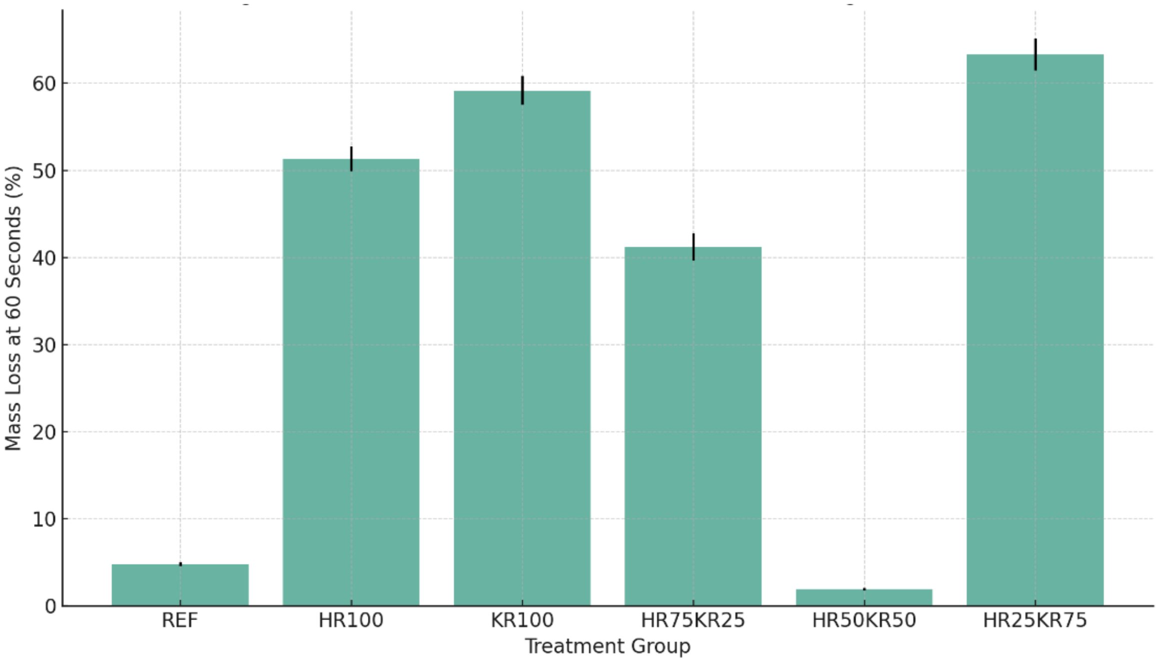


Fig. 1. Mass loss at 60 seconds for spruce samples treated with various fire-retardant formulations under radiant heat exposure (750 °C, ~25 kW·m^{-2}). Error bars represent ±1 SD (n = 5)

A one-way ANOVA confirmed that treatment group had a statistically significant effect on mass loss at 60 s ($F = 188.3$, $p < 0.001$). Tukey's HSD test grouped HR50KR50 as statistically distinct ($p < 0.05$) from all other treatments, indicating a synergistic interaction.

Time-resolved Degradation Kinetics

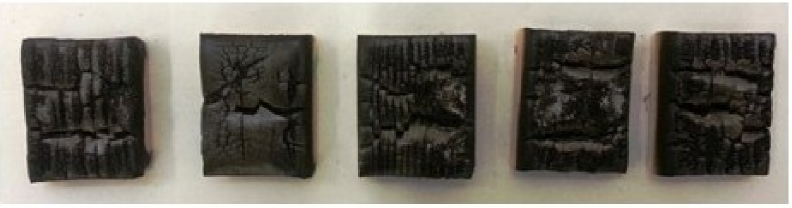
The untreated and KR-treated samples showed steep linear mass loss between 20 to 80 s, indicating active pyrolysis. In contrast, HR100 and HR75KR25 displayed an initial lag followed by a gentler slope, consistent with intumescent char build-up. HR50KR50 uniquely exhibited an initial plateau phase (0 to 40 s) with negligible mass loss, confirming early barrier formation. An analogous effect is evident in the DTG curves (Fig. 3), where the maximum mass-loss rate was markedly suppressed.

Visual Damage and Char Integrity

Post-exposure photographs (Fig. 2) revealed that HR100 samples formed a foamed char layer but showed deep longitudinal cracking, exposing unprotected wood beneath. KR100 samples blistered and lost coating adhesion. HR50KR50 retained full surface coverage with minimal cracking and a dense, compact char structure. HR25KR75 developed irregular char and partial surface detachment. The HR50KR50 samples formed a continuous and compact char layer with an estimated thickness of approximately 1.2 mm, confirming effective thermal shielding of the underlying wood.

REF

HR 100



KR100

HR75KR25

HR50KR50

HR25KR75

Fig. 2. Post-exposure photographs of spruce samples after radiant heat testing, showing differences in char morphology and surface integrity

Summary of Key Fire Performance Metrics

Table 1 summarizes ignition time, mass loss at 60 s, and dominant visual failure mode across all treatments. HR50KR50 consistently outperformed other groups in all parameters. The untreated reference (REF) displayed the shortest time to ignition (≈19 s) and moderate early mass loss (≈4.8%), confirming the high flammability of spruce. Pure Krovsan (KR100) provided negligible ignition delay and actually promoted rapid blistering, resulting in the highest mass loss (>59%). Pure HR Prof (HR100) delayed ignition by ~45% relative to REF but lost structural integrity after intumescence, leading to >51% mass loss. The synergistic 50/50 mixture (HR50KR50) markedly outperformed all other treatments: ignition was delayed by more than 110% compared to REF, and mass loss was reduced by ≈60× relative to HR100 and ≈30× relative to REF. The intermediate mixtures HR75KR25 and HR25KR75 demonstrated partial benefits but suffered either cracking or delamination, indicating sub-optimal stoichiometry. Overall, the data underline the importance of balancing phosphorus–nitrogen and borate constituents to achieve both extended ignition time and minimal thermal degradation. When considered alongside STA data, the HR50KR50 mixture emerges as the only formulation achieving synergy across both radiant-heat exposure and controlled thermal decomposition tests.

Table 1. Fire Performance Metrics of Coated and Uncoated Spruce Samples

Treatment	Ignition Time (s)	Mass Loss at 60 s (%)	Dominant Failure Mode
REF	18.6 ± 1.5	4.77 ± 0.21	Rapid ignition; soft char
HR100	27.2 ± 1.9	51.32 ± 1.42	Foamed char; longitudinal cracks
KR100	20.1 ± 2.0	59.17 ± 1.65	Blistered surface; coating loss
HR75KR25	32.0 ± 1.7	41.20 ± 1.55	Char with delamination
HR50KR50	39.4 ± 2.2	1.92 ± 0.12	Compact, stable char; no cracking
HR25KR75	21.5 ± 1.8	63.31 ± 1.84	Irregular char; coating detached
Notes: mean ± SD; *n* = 5			

Simultaneous Thermal Analysis STA

Thermal analysis revealed clear differences in the decomposition behavior of spruce wood treated with HR Prof and Krovsan compared with untreated reference wood. The reference (REF) sample displayed the typical three-step profile of lignocellulosic materials: an initial mass loss below 120 °C related to moisture evaporation, a main decomposition between 200 and 380 °C associated with hemicellulose and cellulose degradation, and a slower oxidation above 500 °C attributed to lignin. The TG/DTG/DSC curves of the untreated wood are presented in Fig. 3, showing a distinct DTG maximum near 265 °C and a strong DSC exothermic peak at 289 °C. This pattern corresponds to oxidative decomposition and combustion of cellulose and hemicellulose.

The kinetic parameters derived from STA provide essential insight into how the treated spruce wood will respond under real fire conditions, particularly during the early heating stage when ignition and flame spread are governed by thermal decomposition pathways. An increase in the onset temperature of degradation (T_{onset}) indicates delayed generation of combustible volatiles, which corresponds to an extended pre-ignition phase under an external heat flux. Similarly, a shift of the maximum mass-loss rate (T_{max}) to higher temperatures and a reduction in the DTG peak intensity reflect slower volatilization and diminished release of heat-producing decomposition products. These effects directly relate to lower flame intensity and reduced risk of flashover. Furthermore, higher char residue at elevated temperatures signifies that the treatments promote a cohesive, thermally stable carbonaceous layer that restricts oxygen diffusion and heat transfer to the underlying wood substrate. Together, these kinetic–thermal characteristics allow STA to serve as a predictive tool for assessing macroscopic fire performance, offering a mechanistic basis for explaining the ignition delay, reduced mass loss, and improved thermal shielding observed during the radiant heat exposure tests. All samples treated with HR Prof and Krovsan exhibited modified thermal behavior compared with REF. The TG and DTG curves shifted toward higher temperatures, indicating delayed mass loss and improved stability. The decomposition was less intense, and the amount of solid residue at 700 °C increased, confirming the formation of thermally stable char.

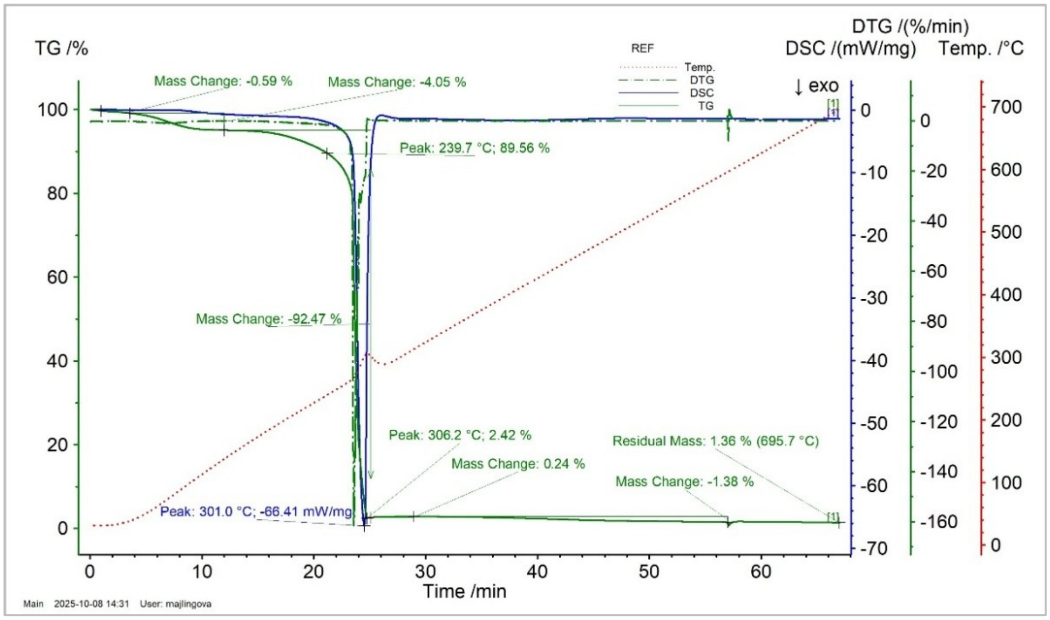


Fig. 3. TG–DTG–DSC curves of untreated spruce wood (REF)

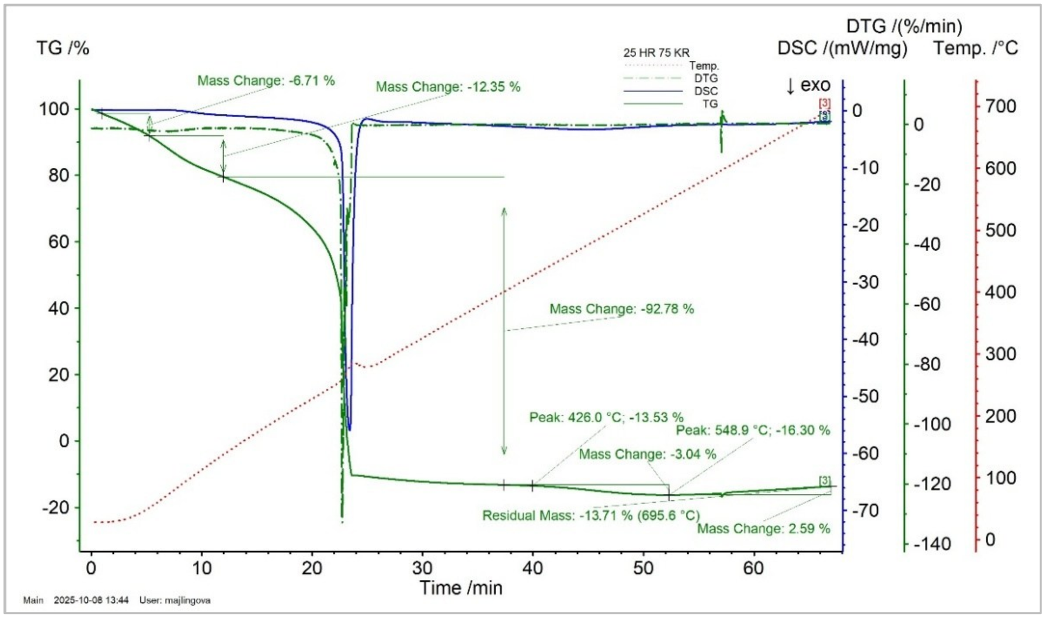


Fig. 4. TG–DTG–DSC curves of spruce wood treated with 25% HR Prof and 75% Krovsan (HR25KR75)

Representative TG/DTG/DSC curves of the treated samples are shown in Figs. 4 through 8. The figures are arranged according to increasing HR Prof content. The 25 HR – 75 KR formulation (Fig. 4) retained a decomposition profile similar to the reference but shifted *T_{max}* to 258 °C.

Increasing the HR Prof fraction (50 HR – 50 KR; Fig. 5) produced the sharpest DTG peak (T_{max} ≈ 275 °C) and the highest decomposition rate, suggesting a dominant single-step process.

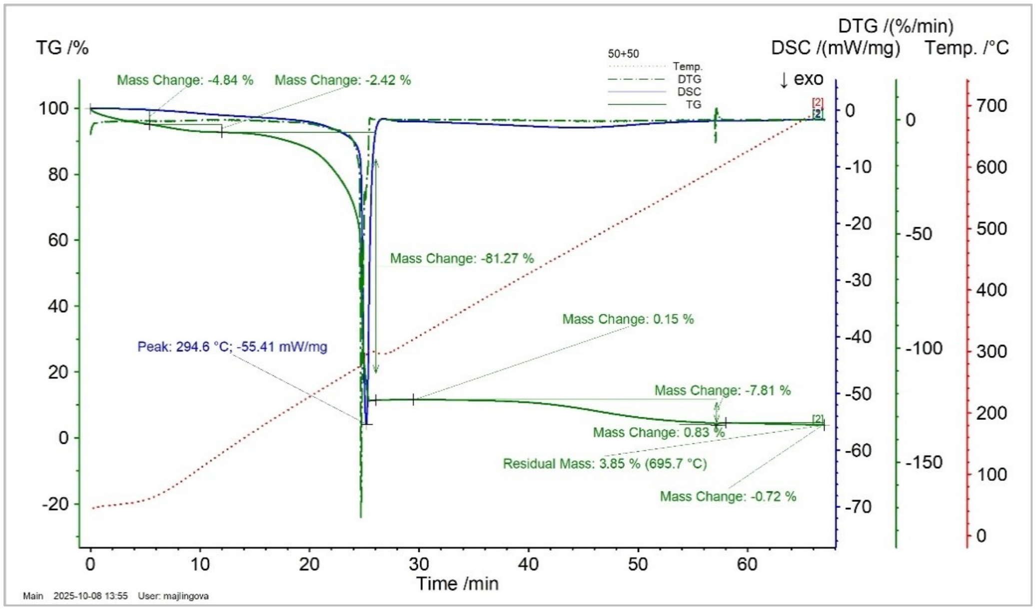


Fig. 5. TG–DTG–DSC curves of spruce wood treated with 50% HR Prof and 50% Krovsan (HR50KR50)

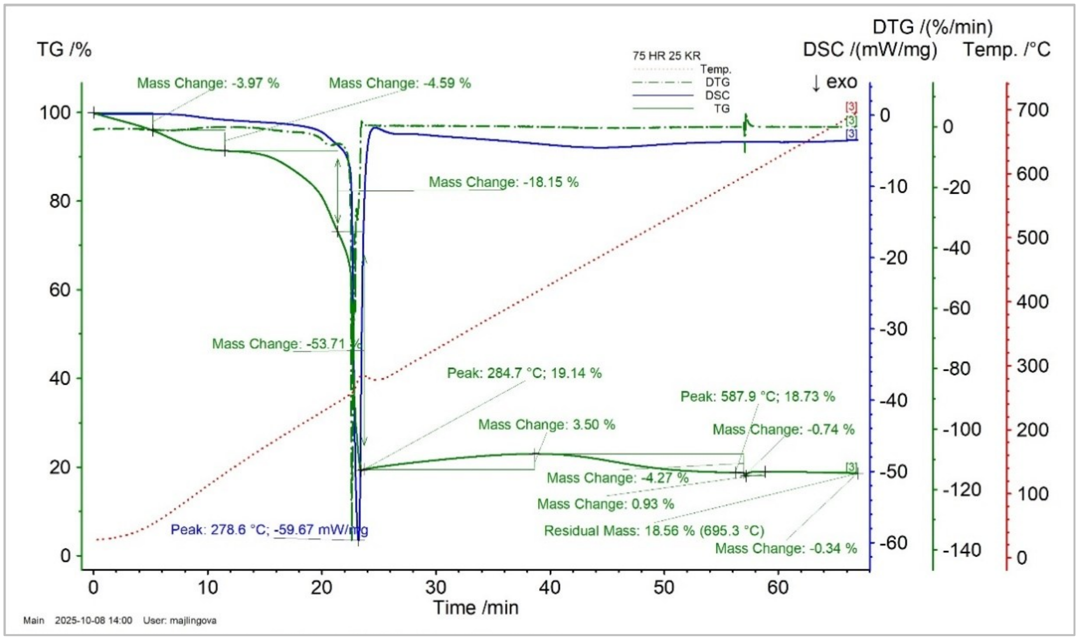


Fig. 6. TG–DTG–DSC curves of spruce wood treated with 75% HR Prof and 25% Krovsan (HR75KR25)

The HR Prof-rich systems (Figs. 6 and 7) decomposed slightly earlier (≈260 °C) but left the largest char yields, while the Krovsan-only formulation (Fig. 8) decomposed at higher temperature (≈280 °C) and released the most heat, reflecting oxidation of aromatic lignin and metal–borate species.

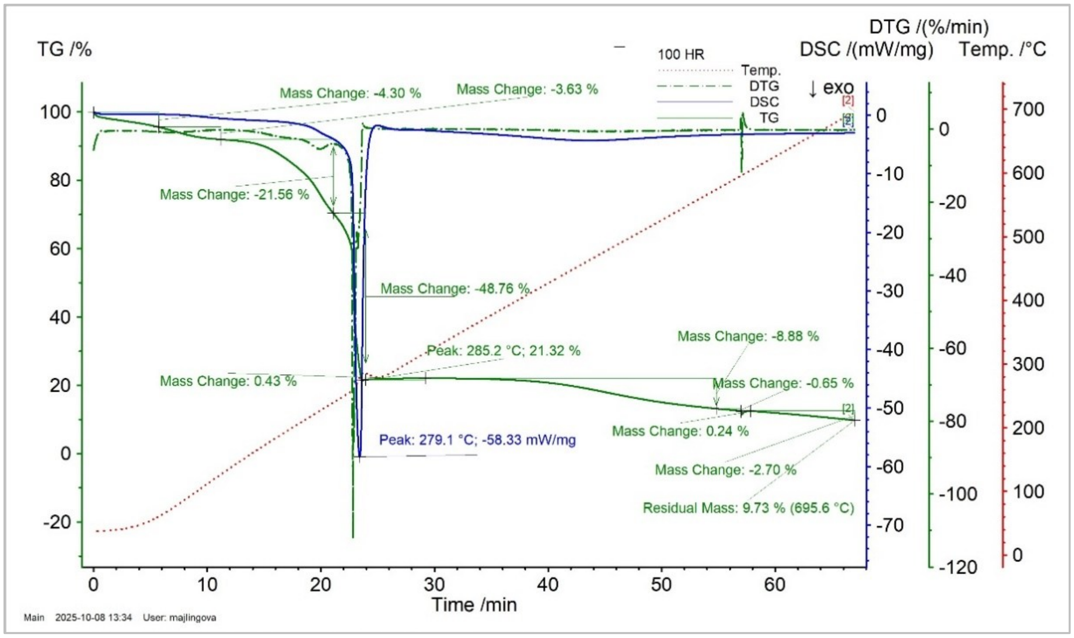


Fig. 7. TG–DTG–DSC curves of sample HR 100

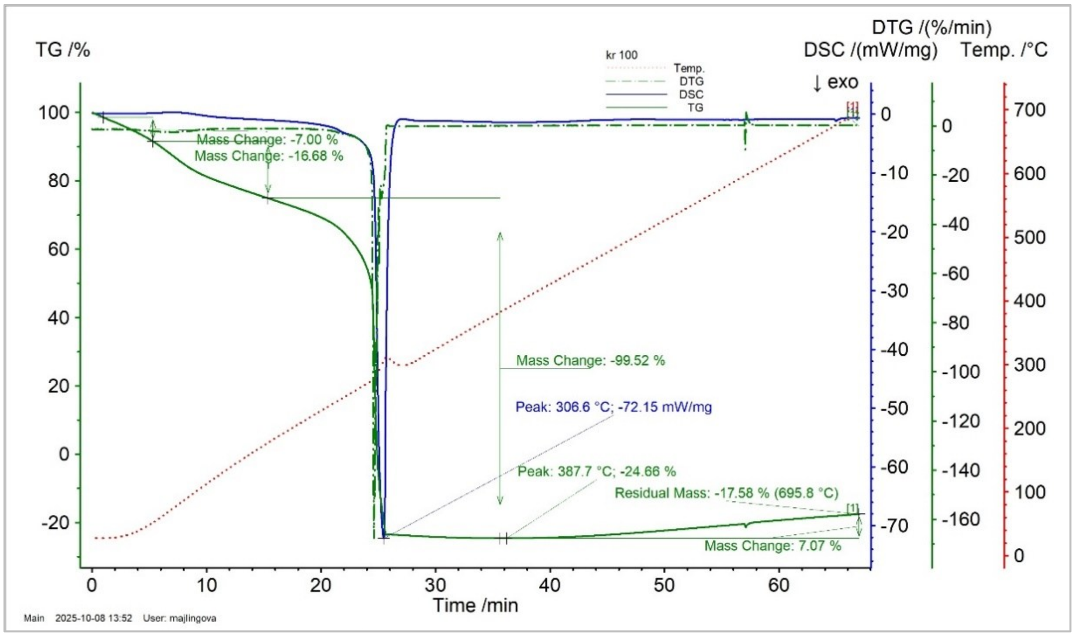


Fig. 8. TG–DTG–DSC curves of sample KR 100

A summary of the characteristic STA parameters for all formulations is provided in Table 2. The onset temperatures (T_{onset}) ranged from 240 to 290 °C, and T_{max} shifted from 310 °C for Krovsan to 350 °C for the 50 HR – 50 KR mixture. Samples with higher HR Prof content showed lower decomposition rates but produced more residue, consistent with phosphorus- and boron-driven charring reactions. The DSC data confirm these effects: the main exothermic events occurred between 300 and 340 °C, while secondary endothermic transitions above 500 °C corresponded to char oxidation and structural rearrangement. The lower heat-release intensity for HR Prof-containing systems supports their function as condensed-phase fire retardants.

Table 2. Key STA Parameters of Coated and Uncoated Spruce Wood Samples

Treatment	T_{onset} (°C)	T_{max}, DTG (°C)	Max DTG (wt.% min⁻¹)	Residue 700 °C (%)	DSC main event (°C, type)
REF	280	340	–6.5	12	330 (exo, cellulose)
HR 25 – KR 75	250	320	–5.6	17	305 (exo / endo)
HR 50 – KR 50	290	350	–3.1	30	340 (exo, stabilized)
HR 75 – KR 25	270	330	–4.5	20	320 (exo, char formation)
HR 100	260	315	–4.8	18	300 (exo, intumescence)
KR 100	240	310	–7.2	15	295 (endo, dehydration)

Notes: T_{onset} = 5% mass loss; T_{max}, DTG = maximum decomposition temperature; residue determined at 700 °C; DSC event = dominant heat-flow transition.

The STA parameters summarized in Table 2 show a clear relationship between the thermogravimetric characteristics and the fire-exposure performance. Samples that exhibited higher onset and maximum decomposition temperatures and greater residue at 700 °C also showed lower total mass losses during radiant-heat testing. For instance, the 50 HR – 50 KR composition, which retained approximately 30% char in STA, maintained more than 40% of its original mass after radiant exposure, while the untreated reference (REF) left only 12% char and less than one-third of its initial mass. This strong proportionality confirms that laboratory thermal-analysis parameters reliably predict the macroscopic fire-retardant efficiency of the treated wood.

The observed trends highlight the complementary actions of HR Prof and Krovsan. Phosphorus and nitrogen components in HR Prof catalyze early dehydration and promote the formation of a foamed, intumescent carbon layer. Simultaneously, boron and copper species from Krovsan act as glass-forming and oxidation-inhibiting agents that strengthen this layer at higher temperatures. As a result, HR Prof-rich mixtures generate thicker, more thermally stable chars, whereas Krovsan-rich formulations delay decomposition and reduce oxidation rate. The balanced mixture (50 HR – 50 KR) combines both effects—rapid initial charring and strong structural stabilization—resulting in the most effective overall protection.

The DSC curves further support this interpretation. All treated samples exhibited smaller exothermic peaks between 300 and 340 °C compared with REF, indicating that a portion of the heat normally released during cellulose oxidation was instead consumed by char stabilization. Endothermic shoulders above 500 °C reflect the rearrangement and slow oxidation of residual carbon. Such redistribution of heat flow corresponds to diminished flammability and improved condensed-phase resistance, consistent with the reduced mass losses observed during external heat exposure. In summary, the combined TG–DTG–DSC and radiant-heat results demonstrate a synergistic mechanism between the two commercial fire-retardant formulations.

Although advanced fire-protection strategies such as nano-enabled coatings, bio-based flame retardants, and combined thermo-chemical modification treatments have demonstrated superior performance in laboratory-scale studies, the present work intentionally focused on commercially available and readily applicable formulations. These systems represent practical solutions for immediate use in wood protection without the need for complex synthesis routes or specialized processing. While a direct quantitative comparison with such advanced approaches was outside the scope of this study, the trends observed in ignition delay, mass-loss suppression, and enhanced char formation are consistent with those reported for more sophisticated systems in the literature. This confirms that even conventional phosphorus–nitrogen and boron-based treatments, when properly combined, can deliver substantial fire-performance improvements that are highly relevant for real construction practice.

HR Prof initiates dehydration and intumescence in the early heating stage, while Krovsan contributes boron- and copper-based stabilization at higher temperatures. Together, they delay the release of combustible volatiles, enhance char cohesion, and increase the final residue yield. The HR Prof–Krovsan system therefore provides a dual protective action, chemical and physical, that markedly improves the thermal stability and fire resistance of spruce wood.

CONCLUSIONS

1. Thermal analysis and fire-exposure testing demonstrated that both HR Prof and Krovsan significantly enhance the thermal stability and fire resistance of spruce wood.
2. The combined treatment reduced mass-loss rate, delayed decomposition, and increased the formation of thermally stable carbonaceous residues.
3. A strong correlation was observed between the thermogravimetric (TG) residue at 700 °C and the mass retained after radiant-heat exposure, confirming that the fire performance is governed by condensed-phase protection.
4. Phosphorus and nitrogen species from HR Prof promote dehydration and intumescent char formation, while boron and copper compounds from Krovsan stabilize the resulting carbon layer and inhibit oxidation at elevated temperatures.
5. The synergistic action of both formulations leads to lower heat release, slower degradation kinetics, and enhanced char cohesion.
6. Among the tested mixtures, the 50 HR – 50 KR composition exhibited the most balanced performance, combining early intumescence with durable char stability.
7. Overall, the HR Prof–Krovsan system provides an effective, environmentally acceptable dual-mechanism fire-retardant treatment for improving the safety and thermal endurance of spruce wood.

Although the present study clearly demonstrates the beneficial effects of combined phosphorus–nitrogen and boron-based treatments on the thermal stability and fire resistance of spruce wood, long-term durability under real service conditions was not evaluated. Future work should therefore include accelerated climatic ageing, water-leaching resistance, and outdoor exposure to assess the long-term effectiveness of the coatings. In addition, smoke production and the release of potentially toxic combustion products should be investigated using advanced fire testing methods to further verify the environmental and health safety of the developed systems for real construction applications.

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Conflict of Interest

The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Use of Generative AI

Authors used AI tools (ChatGPT 5) in the preparation of graphical abstract and collation of references.

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