**ORIGINAL ARTICLE**

# Enhancing the fire resistance properties of thermally modified *Robinia pseudoacacia* wood with natural and synthetic flame retardants: chemical characterisation and fire behaviour

Salvio Marino[1] · Milan Gaff[2,3] · Anil Kumar Sethy[4] · Gourav Kamboj[2,5] · Fatemeh Rezaei[6] · František Kačík[7] · S. Behnam Hosseini[2] · Haitao Li[8] · David Hui[9]

## Abstract

The increasing demand for wood with enhanced flame retardant characteristics in construction applications necessitates strategic interventions. This study explores the fire behaviour and chemical characterisation of *Robinia pseudoacacia* wood subjected to thermal modification and flame retardant treatments. Thermal modification was carried out at three different temperatures (160 °C, 180 °C and 240 °C). The fire properties of wood coated with Flame Gard (F), a commercial flame retardant, arabinogalactan (A), a natural flame retardant, melamine adhesive (MF) with ammonium polyphosphate (AP), nanosilica (NS), nanoclay (NC) (MF-AP-NS and MF-AP-NC) and arabinogalactan with AP, NS and NC (A-AP-NS and A-AP-NC), were assessed using cone calorimetry in terms of the weight loss rate, ignition time and heat release rate. The commercial flame retardant Flame Gard outperformed the natural and fortified flame retardants in terms of the weight loss rate, heat release rate (HRR) and ignition time ($t_{ig}$). Unmodified samples exhibited superior fire properties in terms of $t_{ig}$ and HRR compared to thermally modified samples. The peak heat release rate ($kW.m^{-2}$) and time to peak heat release rate (s) showed a moderate degree of dependency on the chemical constituents of the wood.

**Keywords** Black locust · Burning characteristics · Thermally modified wood · Flame retardant · Chemical characteristics

## Abbreviations

| | |
|---|---|
| $HRR_{180}$ | Heat release rate (180 s) |
| $HRR_{300}$ | Heat release rate (300 s) |
| pHRR | Peak heat release rate |
| tpHRR | Time taken to peak HRR |
| THR | Total heat release |
| $t_{ig}$ | Time to flame initiation |
| mr | Mass of residue after measurement |
| m''10–90% | Rate of weight loss per unit area in the main combustion phase |

✉ Milan Gaff
gaffmilan@gmail.com

1 Faculty of Forestry and Wood Sciences, Czech University of Life Sciences Prague, Kamýcká 165 00, Prague 6, Suchdol 1176, Czech Republic

2 Department of Furniture, Design and Habitat (FFWT), Mendel University in Brno, Zemědělská 1665, 613 00, Brno-Sever-Černá Pole, Czech Republic

3 Experimental Centre, Faculty of Civil Engineering, Czech Technical University in Prague, Prague 16629, Czech Republic

4 Institute of Wood Science and Technology, 18th Cross, Malleswaram, Bangalore-560003, India

5 Center for Renewable Carbon, University of Tennessee, Knoxville, TN 37996, USA

6 Department of Sustainable Bioproducts, College of Forest Resources, Mississippi State University, 201 Locksley Way, Starkville, MS 39759, USA

7 Department of Chemistry and Chemical Technologies, Faculty of Wood Sciences and Technology, Technical University in Zvolen, T. G. Masaryka 24, Zvolen 96001, Slovakia

8 College of Civil Engineering, Nanjing Forestry University, Nanjing, China

9 Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70124, USA

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| ⊿m | Weight loss |
|---|---|
| MARHE | Maximum average energy release rate |
| EHC | Efficient combustion heat |
| N | No flame retardant |
| A | Natural flame retardant (arabinogalactan) |
| F | Synthetic flame retardant |
| MF-AP-NC | Mixture of melamine formaldehyde, ammonium phosphate, and nanoclay |
| MF-AP-NS | Mixture of melamine formaldehyde, ammonium phosphate, nanosilica |
| A-AP-NC | Mixture of arabinogalactan, ammonium phosphate, and nanoclay |
| A-AP-NS | Mixture of arabinogalactan, ammonium phosphate, and nanosilica |

# 1 Introduction

Wood, as a sustainable raw material, plays a significant role in climate change mitigation by sequestering atmospheric carbon dioxide and storing it until its use. Wood plays an important role in indoor and outdoor structures. Despite its advantages in strength, versatility and high insulation rating, wood naturally has low resistance to biological attack, moisture, and fire. This is why there is high demand for tropical wood species, which are known for their natural durability. *Robinia pseudoacacia L.*, originally from North America but cultivated in Europe for over 400 years, is considered to be a promising substitute for tropical hardwoods. Black locust wood is highly valued in multiple industries due to its desirable characteristics and its ability to grow rapidly (Dünisch et al. 2010; Kačík et al. 2022).

For long-lasting outdoor applications, the heartwood of black locust is highly recommended. To mitigate the limitations of low durability, the wood is often treated thermally and chemically. The gradual heating of wood at high temperatures leads to physical and chemical changes, which in turn impacts its polymeric components (Kim et al. 2006).

Thermal modification (150–240 °C) improves the natural durability of wood (Čermák et al. 2015; Hao et al. 2018). The improvement in the fire resistance of wood after thermal modification is attributed to the reduction in hemicellulose and extractives. Despite these benefits, flame retardants are commonly applied to further enhance fire resistance. The fire safety issues associated with wood pose a disadvantage for its use as a building material. In comparison to many other inorganic materials, wood is widely recognized for its low thermal stability (Jiang et al. 2010; Hirata et al. 1991; Rowell 2005).

Various coatings, both organic and inorganic, have been used to enhance the performance and appearance of wood in order to achieve desired objectives. However, the use of certain coatings can pose significant safety risks due to the release of toxic gases. Fire resistance coatings are the preferred choice for fire protection, but their widespread application is limited due to their high cost (Gong et al. 2021). Alum and vinegar were historically used as flame retardant treatments, with inorganic salt being the most commonly used flame retardant for wood treatments (Gong et al. 2021; Lowden and Hull 2013).

Flame retardants can affect the ignition of solid materials through four mechanisms (Friedman 1998); first, they promote the formation of char, which reduces the formation of flammable gases; second, they release gases that contribute to slowing down the gaseous combustion reaction; third, they undergo endothermic decomposition, reducing the heat necessary for the combustion of the substance, and fourth, they form an insulating char layer on the surface of the combustible material. Two basic methods for improving the flame retardance of wood-based material involve impregnating them with flame retardants, or applying flame retardants as a coating (Moon and Emrick 2013; Isitman and Kaynak 2010; Naumann et al. 2012; Wang and Yang 2010). Substances such as ammonium phosphate, ammonium sulphate, zinc chloride, sodium tetra borate and boric acid are the most commonly used flame retardants. These substances aim to improve the fire properties of wood, namely to reduce weight loss, burning rate and maximum burning rate, while maintaining acceptable hygroscopicity, strength and tack of the treated wood surface (LeVan and Winandy 1990; Kol et al. 2010; Bekhta et al. 2016).

However, it should be noted that certain agents accelerate the deterioration of the wood surface; for instance, water leaching of chemicals is a crucial factor affecting the performance of retardants. Additionally, while thermal modification can improve the properties of wood, it can make also the wood more hydrophobic and affect its mechanical properties (Winandy 2013; Tribulová et al. 2017). There are various approaches to enhancing the flame retardance of wood, including the use of hybrid organic/inorganic retardants, nanoparticle suspensions and additives in commercial products. Some natural substances, such as arabinogalactan, have also demonstrated good flame retardant activity (Merk et al. 2015; Gaff et al. 2019; Popescu and Pfriem 2020). The perfect flame retardant for wood would possess several desirable attributes, including high efficiency, low toxicity, low environmental impact, durability, chemical and dimensional stability post treatment, no adverse effects on the physical and mechanical characteristics of the wood, affordability, ready availability and ease of use (Fu et al. 2017).

Many potential flame retardants can be harmful to both humans and the environment, and these products may leach from wood and lose their effectiveness. Researchers are exploring the use of carbon-based material in

flame retardants to improve performance while minimising toxicity. Pre-treatment of wood can also enhance the effectiveness of flame retardants. A thermal analysis and flammability assessment are two common approaches to evaluate the efficiency of a flame retardant on a small scale. Techniques such as differential thermal analysis, thermogravimetric analysis (TGA), cone calorimetry, lateral ignition flame spread test (LIFT), and large-scale calorimetry, are frequently employed for these purposes (Lowden and Hull 2013). While cone calorimetry provides a range of measurable flammability parameters, it is only suitable for well-ventilated fire scenarios. The flame spread on the material surface also needs to be considered when assessing fire propagation. As a result, it can be challenging to attribute the outcomes specifically to post-flashover fires or under-ventilated fires.

In recent years, thermally modified wood has gained attention due to its improved properties such as high dimensional stability, durability, and decay resistance. However, it is important to consider how thermal modification can potentially affect the fire resistance properties of wood. This study aims to examine the effect of natural and synthetic fire retardants on the combustion and chemical properties of thermally treated *Robinia pseudoacacia* wood. Although *Robinia pseudoacacia* is a highly durable wood and may not require any modification, its high shrinkage value (Pollet et al. 2012) can be a deterrent in many specialised applications. Thermal modification can certainly improve its dimensional stability besides adding to its decay resistance.

This study provides information on the burning properties, thermal degradation, and chemical composition of treated and untreated wood samples. The findings should contribute to an understanding of the potential advantages of using flame retardants to enhance the fire resistance properties of thermally modified wood products modified at different temperatures (160, 180, and 210 ºC).

# 2 Experimental procedure

## 2.1 Material

### 2.1.1 Wood

$100 \times 100 \times 20$ mm (in the axial $\times$ radial $\times$ tangential direction) *Robinia pseudoacacia* samples were conditioned in a chamber at a relative humidity of $65 \pm 3\%$ and temperature of $20 \pm 2$ °C until they reached a moisture content of about 12%. After conditioning, the test samples were divided into three groups based on the type of retardant used: natural retardants, synthetic retardants, and reference samples without any retardant treatment. Ten replicate samples were

**Table 1** Thermal modification parameters

| Parameters | Temperature (°C) | | |
| --- | --- | --- | --- |
| | 160 | 180 | 210 |
| Application of heat (hours) | 9.9 | 13.1 | 15.5 |
| Thermal modification (hours) | 3 | 3 | 3 |
| Application of cooling (hours) | 5.8 | 10.5 | 11 |
| Total modification time (hours) | 18.7 | 26.6 | 29.5 |

**Table 2** Average moisture and density of *Robinia pseudoacacia* wood

| Specimens | Unmodified (reference) | 160 | 180 | 210 °C |
| --- | --- | --- | --- | --- |
| Mass per unit volume (kg/m$^3$) | 765 (5.1) | 690 (2.0) | 660 (6.4) | 497 (5.5) |
| Moisture content (%) | 12% | | | |

*Note* Variation coefficients (CV) in percentages are shown in parentheses alongside the values

used for each treatment. The samples were thermally modified at three different temperatures (160, 180, and 210 °C). Unmodified samples were also taken as control samples.

### 2.1.2 Thermal modification

The ThermoWood® process was used to thermally modify the wood samples. The thermal modification was conducted in a heat chamber (S400/03) manufactured by L.A.C, Rajhrad, Czech Republic. The process consists of three main phases. The parameters of the thermal modification and a description of each phase for the different thermal treatment temperatures (160, 180, and 210 °C) are shown in Table 1. The average density values for the specimens of *Robinia pseudoacacia* wood are shown in Table 2.

### 2.1.3 Flame retardants

**2.1.3.1** Naturally occurring flame retardant Many flame retardants currently used contain compounds that are harmful to health and release toxic gases when burnt. Recently, extensive research has focused on the potential of biomacromolecules (e.g. DNA, proteins, and polysaccharides) as alternative flame retardants because of their biodegradable and non-toxic nature. Hemicelluloses are the second most abundant component of terrestrial lignocellulosic biomass, and they have applications in the manufacturing of various materials because of their abundance, renewability, and biodegradability. Their combination (e.g. arabinoxylan, galactomannan) with inorganic substances (e.g. nanoclay, bentonite) can provide products with excellent mechanical, fire-retardant, and barrier properties (Huang et al. 2019; Leong et al. 2021; Hosseinashrafi et al. 2023). Due to its unique structure including a high degree of branching and an unusually high content of terminating 4-O-methyl-glucuronic acid (4-OMe GlcA) residues, arabinogalac-

tan is a promising polysaccharide in the development of flame retardants. Arabinogalactan is a highly branched biopolymer consisting of arabinose and galactose monosaccharide units, often found attached to proteins, which are found on plasma membranes and in cell walls. Arabinogalactans AGs) form two main groups based on their structure: the arabino-4-galactans (1,4-β-D-galactans decorated with α-L-arabinose, α-L-Ara) are classified as type I AG and the arabino-3,6-galactans (1,3-β-D-galactan:1,6-β-D-galactan decorated with α-L-Ara) are classified as type II AG (D'Adamo 1996; Pfeifer et al. 2020; Ghosh et al. 2023; Ma and Johnson 2023).

**2.1.3.2** Synthetic flame retardant Flame Gard (Rovinka, Slovakia) is a viscous coating that dries to a transparent finish with a light-yellow tint, allowing the original wood pattern to remain visible. During combustion, the flame retardant coating undergoes thermal degradation on the protected surface, resulting in the formation of a dense, non-flammable foam layer that acts as thermal insulation. These foam layers effectively prevent fire and the transfer of heat, thereby enhancing the fire resistance properties of the wood. The fire-retardant coating is suitable for indoor applications with a relative humidity (RH) of 80% and a moisture content (MC) of 20% (Gaff et al. 2019).

In addition to Flame Gard, other chemicals such as ammonium phosphate (AP), nanosilica (NS) and nanoclay (NC) were also used as flame retardants. Four different flame retardant coating formulations, two with melamine

adhesive and two with arabinogalactan were also tested for their fire performance. Melamine adhesive from M/s Akzo Nobel, Netherlands, with a viscosity ranging from 1,500 to 9,000 mPas and a solid content of 65%, was used. The details of the formulations are as follows:

- Melamine adhesive + 15% AP + 5% NC (MF-AP-NC).
- Melamine adhesive + 15% AP + 5% NS (MF-AP-NS).
- Arabinogalactan (50% in water) + 15% AP + 5% NC (A-AP-NC).
- Arabinogalactan (50% in water) + 15% AP + 5% NS (A-AP-NS).

# 3 Methods

## 3.1 Physical properties

The density of the wood and the moisture content were evaluated according to ISO 13061-2 (2014) and ISO 13061-1 (2014), respectively.

## 3.2 Chemical analyses

For the chemical analysis, a 0.5–1.0 mm specimen was extracted with an ethanol-toluene mixture according to ASTM D1107-96 (2013). The acid-insoluble lignin content was determined using the ASTM D1106-96 (2013) method. The holocellulose content was determined with the method described by Wise (1946), while the cellulose content was determined using the Seifert (1956) method.

## 3.3 Measurement methodology - cone calorimeter

Measurements were conducted with cone calorimetry (Fig. 1) in accordance with ISO 5660-1. The samples had a square shape with dimensions of $100 \times 100$ mm and a thickness of 20 mm. Prior to the measurement, the samples were wrapped in aluminium foil on the sides and bottom. Thermal insulation made of mineral fibers served as a base. The suction speed or airflow rate was set to 0.024 $m^3 \cdot s^{-1}$. The measurement was performed in a horizontal position with the emitter positioned above the sample. An external heat of 25 $kW \cdot m^{-2}$ was applied to the samples. The oxygen content in the flue gas was recorded by the computer at 5 s intervals. The burning characteristics of the treated samples obtained by the cone calorimeter include TTI, HRR, pHRR, $T_{pHRR}$ and weight loss.
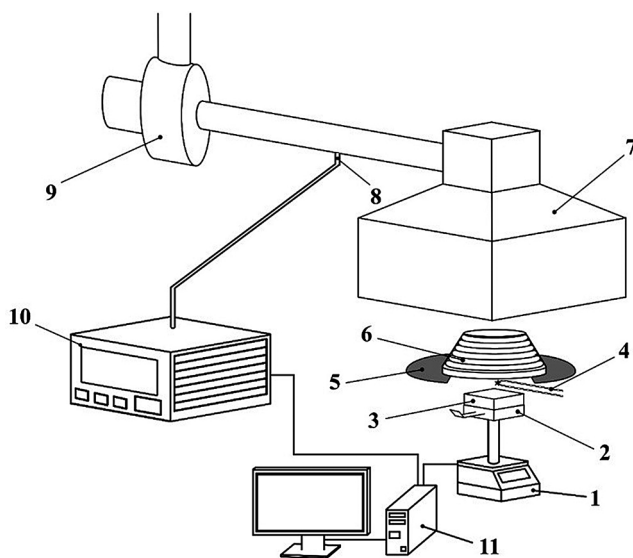


**Fig. 1** Illustration of the following components of cone calorimetry: 1 - balance, 2 - sample holder, 3 - sample, 4 - initiator, 5 - orifice, 6 - radiator, 7 - exhaust bell, 8 - flue gas sampling probe, 9 - adjustable fan, 10 - oxygen analyzer, 11 – computer

# 4 Results and discussion

Lignin is the most thermally stable wood component, and its yield increases during thermal treatment. This phenomenon is due to the formation of pseudo-lignin in condensation reactions of degradation products of lignin and polysaccharides (Hu et al. 2012; Shinde et al. 2018). Cellulose is more thermally stable than hemicelluloses because of its crystalline structure. Cellulose degradation occurs at a higher temperature than that of hemicelluloses and begins in its amorphous regions. Due to the faster degradation of hemicelluloses, the relative amount of cellulose increased up to a temperature of 240 °C. However, a significant decrease was observed above 260 °C, indicating cellulose degradation (Missio et al. 2015). Table 3 shows the average values of the chemical components of wood.

The cone calorimetric results of fire resistance coating on unmodified and thermally modified wood at an external heat flow of 25 kW·m$^{-2}$ were analyzed in terms of TTI, HRR, PHRR, ($T_{PHRR}$) and THR, and they are shown in Table 4. The results show a higher HRR at 180 and 300 kW·m$^2$, $P_{HRR}$, EHC, THR, $t_{PHRR}$ and MARHE, and weight loss is greater in unmodified wood and thermally modified wood coated with a natural fire retardant than in wood samples coated with a synthetic flame retardant.

Table 4 presents the mean values of the burning parameter and coefficient of variation (CV).

Table 5 presents the results of statistical analysis assessing the influence of thermally modified wood and flame retardants on various burning properties. This includes parameters such as test time, heat release rate ($HRR_{180}$ and $HRR_{300}$), peak heat release rate (pHRR), times to peak heat release rate (tpHRR), total heat release rate (THR), weight on permanent flame, mass loss rate (mr), change in mass per unit area (Δm) and effective heat of combustion (EHC). P values (Table 5) show that the flame retardant has a significant effect on the fire properties of wood.

**Table 3** Chemical analysis without modification and after thermal modification of black locust wood

| Temperature (°C) | Extractives (%) | Lignin (%) | Holocellulose (%) | Cellulose (%) | Hemicelluloses (%) |
|---|---|---|---|---|---|
| Without modification (reference) | 9.29 (0.82) | 25.31 (0.55) | 68.46 (0.60) | 40.50 (0.53) | 27.96 (0.70) |
| 160 | 8.71 (3.32) | 23.94 (2.14) | 67.35 (0.29) | 44.88 (0.18) | 22.47 (1.10) |
| 180 | 8.38 (2.03) | 25.23 (0.54) | 63.97 (0.25) | 47.63 (0.42) | 16.33 (2.10) |
| 210 | 7.64 (1.93) | 28.82 (0.25) | 59.30 (0.28) | 54.45 (0.51) | 4.85 (4.44) |

The results show the mean % of oven dry weight, coefficients of variation in %, $n = 4$

Figure 2a shows the rate of weight loss in thermally modified wood with (arabinogalactan-A and Flame Gard-F) and with no flame retardant. The weight loss of natural untreated wood was consistently 6 to 13% higher compared to wood modified at 160, 180, and 210 ºC. However, with the exception of samples modified at 180 º (*p value* = 0.008), no significant variation was observed in the rate of weight loss in thermally modified samples compared to unmodified samples. The weight loss rate with a natural flame retardant (arabinogalactan-A) was almost comparable to that of thermally modified wood, indicating that natural flame retardant has no significant effect on the rate of weight loss. Poor adhesion of arabinogalactan to the wood surface and imperfect layer formation led to rapid wood surface burning in the experiment, yielding similar results to untreated wood samples (Gaff et al. 2019). However, it is striking that the commercial flame retardant Flame Gard (F) outperformed the thermally modified wood and samples coated with arabinogalactan in terms of weight loss rate (Gašparík et al. 2017). The improvement in the weight loss rate after application of Flame Gard was significantly higher (*p value* ≤ 0.02).

Even though there is variability in the quality of natural products, the demand for improvement with potential natural products is growing; it was in this endeavor that we attempted to improve the properties of arabinogalactan by incorporating a traditional flame retardant such as ammonium phosphate and nanoparticles of silica and clay. A similar combination with melamine adhesive was also tested, as melamine adhesive is a good binder, and it also adds to the nitrogen content of the flame retardant, which has proven flame retardant properties. Figure 2b shows the effectiveness of the retardant (MF-AP-NC and MF-AP-NS) coating. The performance of both nanosilica (NS) and nanoclay mixture with melamine formaldehyde (MF) and ammonium phosphate (AP) was almost the same, with the exception of wood modified at 160 ºC, where NC outperformed NS. When the values of melamine-based formulations were compared to the values of only thermally modified samples (N) and samples coated with arabinogalactan (Fig. 2a), all the values were comparable, with the exception of wood thermally modified at 210 ºC; the weight loss rate was significantly reduced in samples coated with a melamine-based formulation. When compared to Flame Gard, all the melamine-based formulations were still inferior, with the exception of wood thermally modified at 210 ºC and coated with an NS-based melamine formulation, where the values were comparable (*p value = 0.22*). The results pertaining to the arabinogalactan formulation (A-AP-NC and A-AP-NS) are shown in Fig. 2c. A-AP-NC coating only significantly improved unmodified samples (*p value = 0.002*), whereas the values were comparable in other samples. The performance of Flame Gard was once again significantly better

**Table 4** Burning properties of wood with and without modification

| Variables | | Burning properties | | | | | |
|---|---|---|---|---|---|---|---|
| Flame retardant | Thermal modification (°C) | $t_{ig}$(s) | $HRR_{180}$(kW·m$^{-2}$) | $HRR_{300}$(kW·m$^{-2}$) | pHRR (kW·m$^{-2}$) | $t_{pHRR}$ (s) | THR (MJ·m$^{-2}$) |
| No flame retardant | Unmodified (reference) | 73.8 (7.8) | 32.5 (34.5) | 61.4 (14.8) | 124.5 (7.1) | 1304.2 (35.4) | 163.6 (4.0) |
| | 160 | 74.0 (6.1) | 31.5 (35.7) | 57.9 (19.2) | 145.8 (6.4) | 1319.0 (26.4) | 185.0 (6.5) |
| | 180 | 72.8 (1.5) | 51.4 (37.1) | 71.0 (7.2) | 113.5 (26.0) | 1010.2 (54.6) | 144.4 (27.1) |
| | 210 | 71.6 (2.1) | 48.2 (16.0) | 78.2 (13.0) | 132.7 (15.0) | 954.4 (42.5) | 176.6 (11.2) |
| Synthetic flame retardant | Unmodified (reference) | 52.2 (7.6) | 23.0 (33.5) | 42.6 (13.6) | 88.1 (7.3) | 925.2 (36.0) | 114.2 (3.6) |
| | 160 | 51.9 (6.8) | 22.0 (35.3) | 40.7 (19.5) | 102.9 (7.2) | 928.7 (28.4) | 131.0 (6.7) |
| | 180 | 50.8 (2.9) | 35.9 (38.2) | 50.1 (7.3) | 78.9 (25.0) | 713.9 (54.8) | 100.4 (26.1) |
| | 210 | 50.0 (2.6) | 33.6 (16.8) | 54.9 (13.1) | 94.1 (15.3) | 663.4 (42.9) | 122.8 (11.5) |
| Natural flame retardant | Unmodified (reference) | 67.0 (7.6) | 29.5 (33.7) | 55.7 (14.9) | 112.5 (7.1) | 1169.9 (34.9) | 147.6 (4.8) |
| | 160 | 66.7 (6.5) | 28.3 (35.3) | 53.4 (19.1) | 134.4 (7.5) | 1192.5 (27.9) | 166.9 (7.8) |
| | 180 | 68.2 (4.0) | 47.8 (34.3) | 65.0 (6.4) | 104.4 (27.7) | 916.6 (54.6) | 129.8 (25.4) |
| | 210 | 64.3 (2.4) | 43.3 (16.6) | 70.9 (13.0) | 120.4 (13.9) | 889.6 (46.6) | 158.7 (12.0) |
| **Variables** | | **Burning properties** | | | | | | |
| **Flame retardant** | **Thermal modification (°C)** | **Weight on permanent flame g** | $m_r$(g) | $m''_{10\text{-}90\%}$(g·m$^{-2}$·s$^{-1}$) | $m''$ (g·m$^{-2}$·s$^{-1}$) | Δm (g·m$^{-2}$) | **MARHE (kW·m$^{-2}$)** | **EHC (MJ·kg$^{-1}$)** |
| No flame retardant | Unmodified (reference) | 151.2 (4.8) | 55.0 (11.5) | 6.0 (5.2) | 5.7 (5.8) | 9868.8 (5.8) | 91.0 (4.0) | 16.6 (4.7) |
| | 160 | 143.3 (1.7) | 54.5 (1.9) | 6.2 (3.3) | 5.8 (2.7) | 10054.2 (2.6) | 102.9 (6.5) | 18.4 (4.8) |
| | 180 | 125.7 (15.4) | 58.0 (6.8) | 5.5 (5.4) | 5.2 (5.5) | 7655.6 (26.2) | 80.3 (27.0) | 18.8 (3.6) |
| | 210 | 130.6 (10.9) | 49.4 (11.8) | 5.7 (10.0) | 5.3 (10.2) | 9183.4 (10.5) | 98.3 (11.1) | 19.2 (3.1) |
| Synthetic flame retardant | Unmodified (reference) | 105.1 (4.5) | 38.5 (13.0) | 4.2 (5.9) | 4.0 (5.4) | 6927.4 (7.2) | 64.4 (4.1) | 11.8 (5.5) |
| | 160 | 100.1 (2.8) | 38.5 (2.6) | 4.4 (3.8) | 4.1 (4.0) | 7023.1 (3.8) | 72.3 (6.3) | 12.9 (6.7) |
| | 180 | 87.4 (15.9) | 40.4 (6.9) | 3.9 (3.6) | 3.6 (5.0) | 5292.4 (25.0) | 56.0 (28.2) | 13.1 (4.5) |
| | 210 | 90.8 (11.0) | 34.5 (12.6) | 4.1 (10.1) | 3.7 (11.0) | 6433.9 (12.2) | 68.5 (11.0) | 13.4 (4.0) |
| Natural flame retardant | Unmodified (reference) | 136.8 (3.4) | 49.9 (11.1) | 5.4 (7.3) | 5.2 (6.3) | 8866.9 (7.9) | 80.7 (4.1) | 14.7 (6.3) |
| | 160 | 129.3 (1.4) | 49.1 (1.3) | 5.5 (4.9) | 5.3 (6.3) | 9142.1 (2.9) | 93.2 (6.5) | 16.5 (6.2) |
| | 180 | 115.8 (17.5) | 54.3 (6.9) | 5.0 (4.6) | 4.9 (9.4) | 6917.5 (26.8) | 75.9 (30.9) | 17.3 (7.8) |
| | 210 | 117.3 (11.6) | 44.4 (12.4) | 5.2 (10.7) | 4.8 (11.6) | 8387.5 (11.1) | 87.2 (11.2) | 17.0 (6.1) |

Coefficients of variation (CV)% values are in parentheses

than that of A-AP-NC and A-AP-NS. Between melamine and arabinogalactan formulations, the performance of the melamine-based formulation was comparatively superior in terms of the weight loss rate; this can be attributed to the presence of nitrogen in the melamine molecule.

Figure 3 shows the effect of thermal modification and flame retardant coatings on the ignition time ($t_{ig}$). The ignition time of Flame Gard was significantly better (*p value < 0.002*), and its performance on unmodified wood was the best compared to only thermally modified samples (N) and samples coated with arabinogalactan (Fig. 3a). The ignition times of Flame Gard-coated samples were about 1.8–2.3 times higher than in thermally modified samples (N) and samples coated with arabinogalactan. Figure 3b and c shows the performance of melamine-based and arabinogalactan-based formulations on the $t_{ig}$, respectively. No significant difference was observed in either of these formulations in terms of improvement in the $t_{ig}$. It should be noted that the $t_{ig}$ in unmodified samples with all types of treatment was comparatively better than that of thermally modified wood;

**Table 5** Statistical analysis of the influence of thermal modification and flame retardants on burning properties

Significance level P

| | Intercept | Temperature (°C) | Flame retardant | Temperature (°C) *Flame retardant |
|---|---|---|---|---|
| Test time (s) | *** | NS | *** | NS |
| $HRR_{180}$ (kW·m$^{-2}$) | *** | *** | *** | NS |
| $HRR_{300}$ (kW·m$^{-2}$) | *** | *** | *** | NS |
| pHRR (kW·m$^{-2}$) | *** | *** | *** | NS |
| $t_{pHRR}$ (s) | *** | NS | *** | NS |
| THR (MJ·m$^{-2}$) | *** | *** | *** | NS |
| Weight on permanent flame (g) | *** | *** | *** | NS |
| $m_r$ (g) | *** | *** | *** | NS |
| $\Delta m$ (g·m$^{-2}$) | *** | *** | *** | NS |
| $m''$ (g.m$^{-2}$·s$^{-1}$) | *** | *** | *** | NS |
| $m''_{10-90\%}$ (g.m$^{-2}$·s$^{-1}$) | *** | *** | *** | NS |
| MARHE (kW·m$^{-2}$) | *** | *** | *** | NS |
| EHC (MJ·kg$^{-1}$) | *** | *** | *** | NS |

NS – not significant, *** - significant, the level of significance was set at $P < 0.05$

this can be attributed to the higher equilibrium moisture content of unmodified wood compared to thermally modified wood. Higher moisture content consumes more energy for evaporation, thereby leaving less energy for ignition, and this in turn delays the ignition time.

The cone calorimetry test employs the principle of $O_2$ combustion, evaluating the material performance. Among the crucial parameters measured, the heat release rate (HRR) is the most important, as it signifies the intensity of the fire (Fig. 4). Figure 4a illustrates the effect of thermal modification and a flame retardant coating on the heat release rate (kW/m$^2$) after 180 s. A visual analysis showed that Flame Gard (F) significantly reduces the HRR in comparison to the only thermally modified wood (N) and wood coated with arabinogalactan (A). The average HRR of Flame Gard-coated samples was in the range of 19–37 kW/m$^2$, depending on the modification temperature, while in samples only thermally modified and samples coated with arabinogalactan it was in the range of 70–93 kW/m$^2$. The HRR of Flame Gard-coated samples was about 2.5–3.7 times lower than that of thermally modified samples (N) and samples coated with arabinogalactan. As in the case of ignition time, the HRR of unmodified samples, irrespective of treatment, was the lowest compared to thermally modified samples; this is due to the higher equilibrium moisture content of unmodified wood. Figure 4b and c show the performance of melamine-based and arabinogalactan-based formulations on the HRR, respectively. No significant difference was observed in either of these formulations in terms of improvement in the HRR. The results are in line with the results reported in the literature (Lowden and Hull 2013; Marney et al. 2008; Jiang et al. 2014).

Figure 5 shows the effect of thermal modification and flame retardant coating on the heat release rate (kW/m$^2$) after 300s. The HRR results after 300 s were similar to those observed after 180s. Flame Gard (F) significantly reduced the HRR (Fig. 4a) in comparison to thermally modified samples (N) and samples coated with arabinogalactan (A). The average HRR of Flame Gard-coated samples was in the range of 18–37 kW/m$^2$, depending on the modification temperature, whereas in thermally modified samples and samples coated with arabinogalactan, it ranged between 60 and 84 kW/m$^2$. The HRR of Flame Gard-coated samples was about 2.3–3.3 times lower than that of thermally modified samples (N) and samples coated with arabinogalactan. Figure 5b and c show the performance of melamine-based and arabinogalactan-based formulations on the HRR after 300s, respectively. No significant difference was found in either of these formulations in terms of improvement in the HRR.

The results of the Spearman correlation indicate the extent of the relationship between the fire properties and chemical components of wood (Table 6). The peak heat release rate, pHRR (kW.m$^{-2}$) and time to peak heat release rate, tpHRR (s) showed a moderate degree of dependence ranging from −52 to 47%, whereas there was no significant correlation between chemical components for other fire characteristics.

## 5 Conclusion

This study investigated the efficacy of natural (arabinogalactan) and synthetic flame retardants, Flame Gard (F), melamine adhesive with ammonium polyphosphate, nanosilica (MF-AP-NS and MF-AP-NC) and arabinogalactan with ammonium polyphosphate and nanosilica (A-AP-NS and A-AP-NC) on the burning characteristics of *Robinia pseudoacacia* wood thermally modified at temperatures of 160, 180, and 210 ºC. The salient findings of this study are as follows:

- Commercial flame retardant Flame Gard (F) outperformed thermally modified samples and samples coated with arabinogalactan in terms of the weight loss rate, ignition time and heat release rate.
- The performance of Flame Gard was significantly better than that of A-AP-NC and A-AP-NS in terms of the weight loss rate, ignition time heat release rate.
- Melamine-based formulations were still inferior, with the exception of wood thermally modified at 210 ºC and coated with an NS-based melamine formulation, where the values were comparable to those of Flame Gard-coated samples.
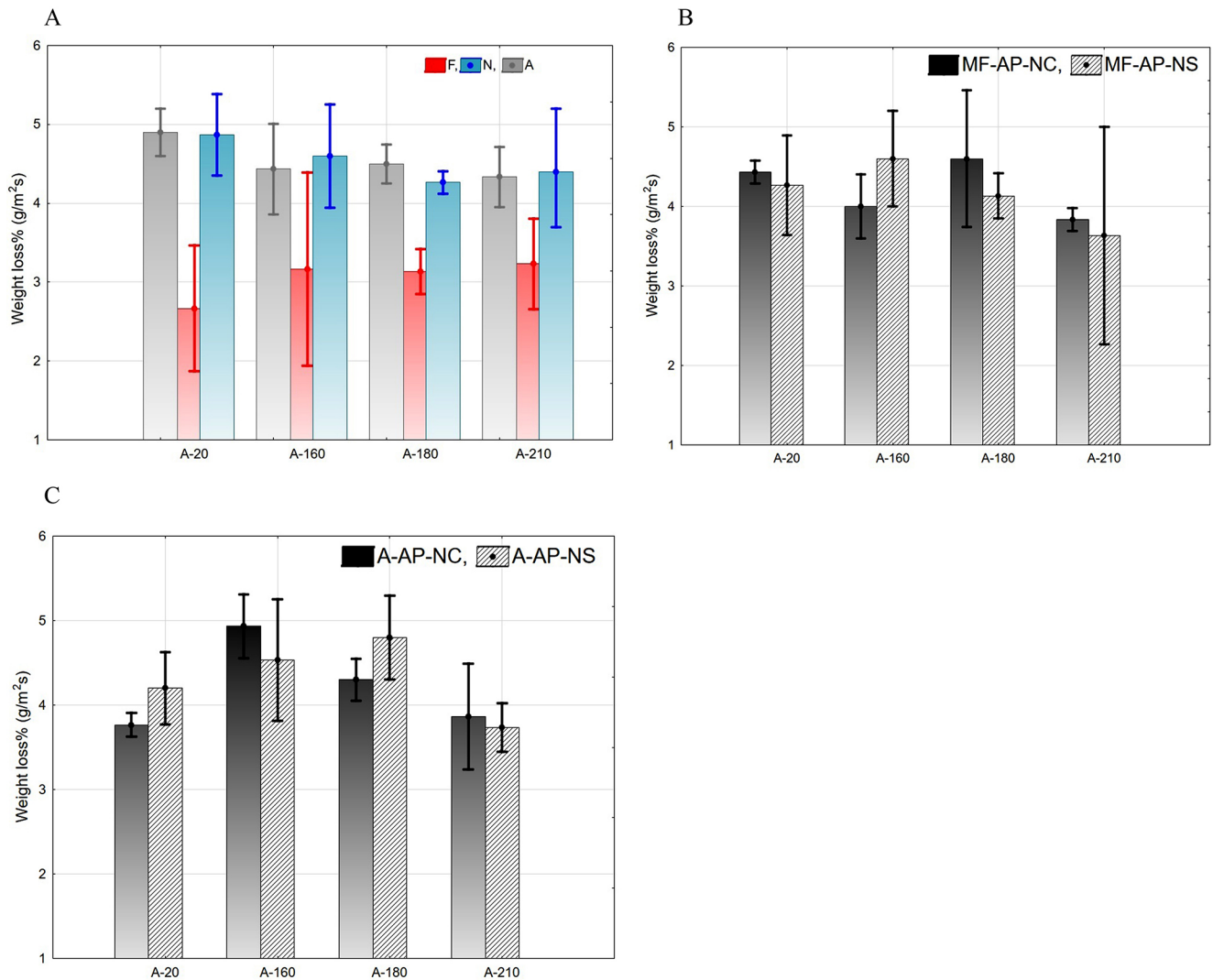
**Fig. 2** The effect of (**a**) Flame Gard (F), No flame retardant (N), and Arabinogalactan (A) as well as thermal modification (160, 180, and 210 °C) on the weight loss rate; (**b**) mixture of melamine formaldehyde, ammonium phosphate, nanoclay (MF-AP-NC), and mixture of melamine formaldehyde, ammonium phosphate, nanosilica (MF-AP-NS) as well as thermal modification (160, 180, and 210 °C) on the weight loss rate; (**c**) mixture of arabinogalactan, ammonium phosphate, nanoclay (A-AP-NC), and Mixture of arabinogalactan, ammonium phosphate, nanosilica (A-AP-NS) as well as thermal modification (160, 180, and 210 °C) on the weight loss rate

- Between melamine and arabinogalactan formulations, the performance of melamine-based formulations was comparatively superior in terms of the weight loss rate.
- The ignition time and heat release rate of unmodified samples with all types of treatments were comparatively better than in thermally modified wood.
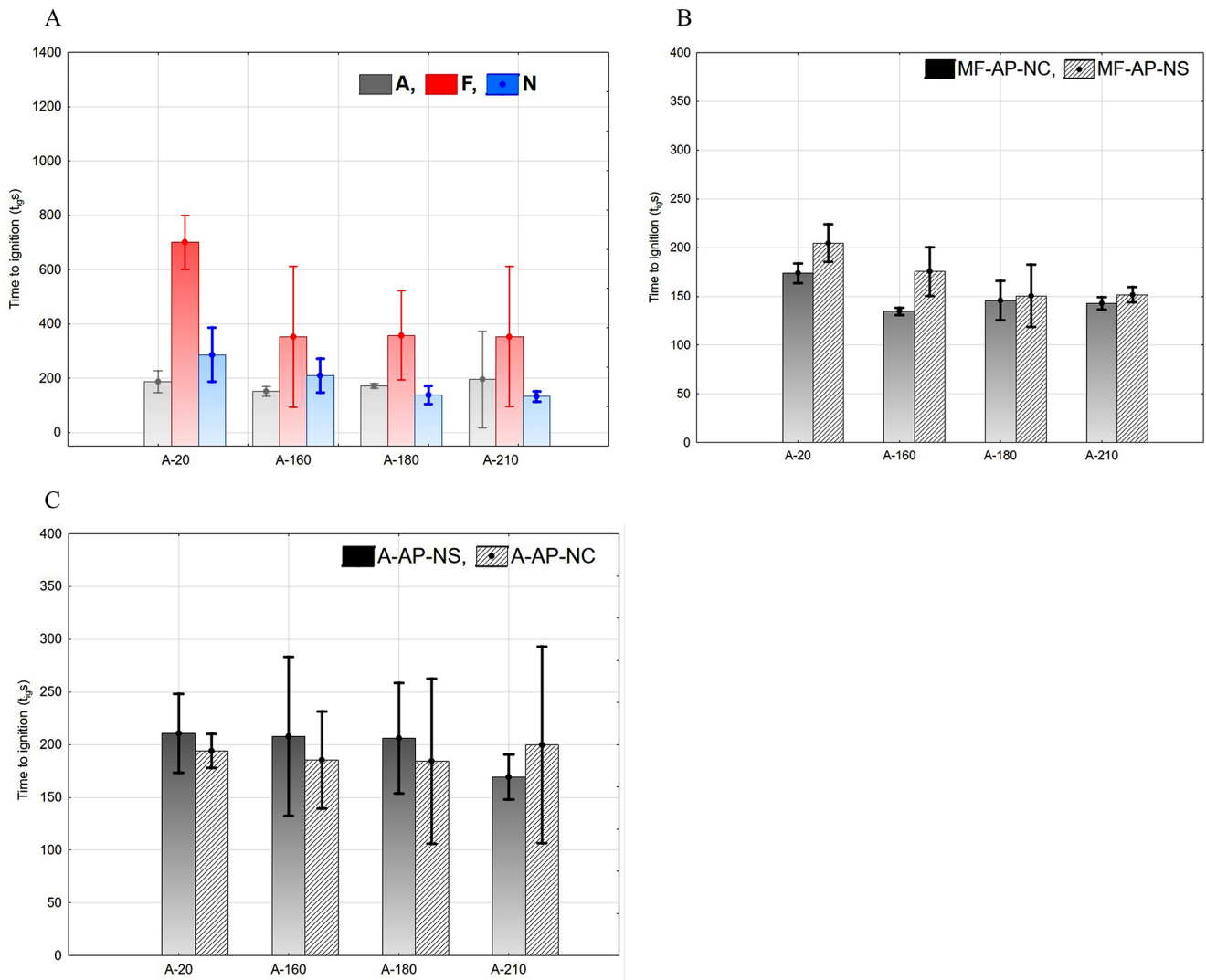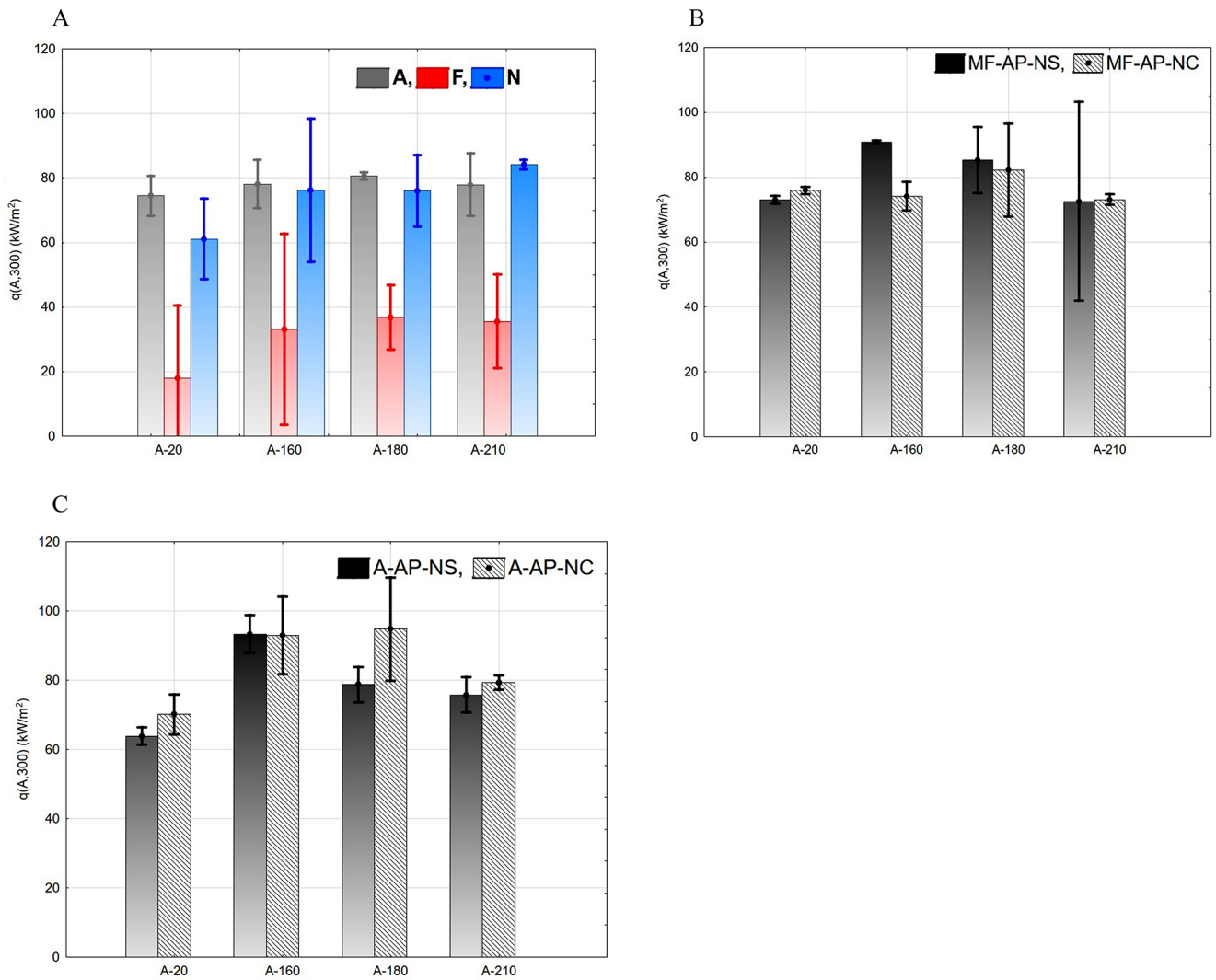
**Fig. 3** The effect of (**a**) Arabinogalactan (A), Flame Gard (F), and No flame retardant (N) as well as thermal modification (160, 180, and 210 °C) on ignition time ($t_{ig}$); (**b**) mixture of melamine formaldehyde, ammonium phosphate, nanoclay (MF-AP-NC), and mixture of melamine formaldehyde, ammonium phosphate, nanosilica (MF-AP-NS) as well as thermal modification (160, 180, and 210 °C) on ignition time ($t_{ig}$); (**c**) mixture of arabinogalactan, ammonium phosphate, nanosilica (A-AP-NS), and mixture of arabinogalactan, ammonium phosphate, nanoclay (A-AP-NC) as well as thermal modification (160, 180, and 210 °C) on ignition time ($t_{ig}$)

A



B



C
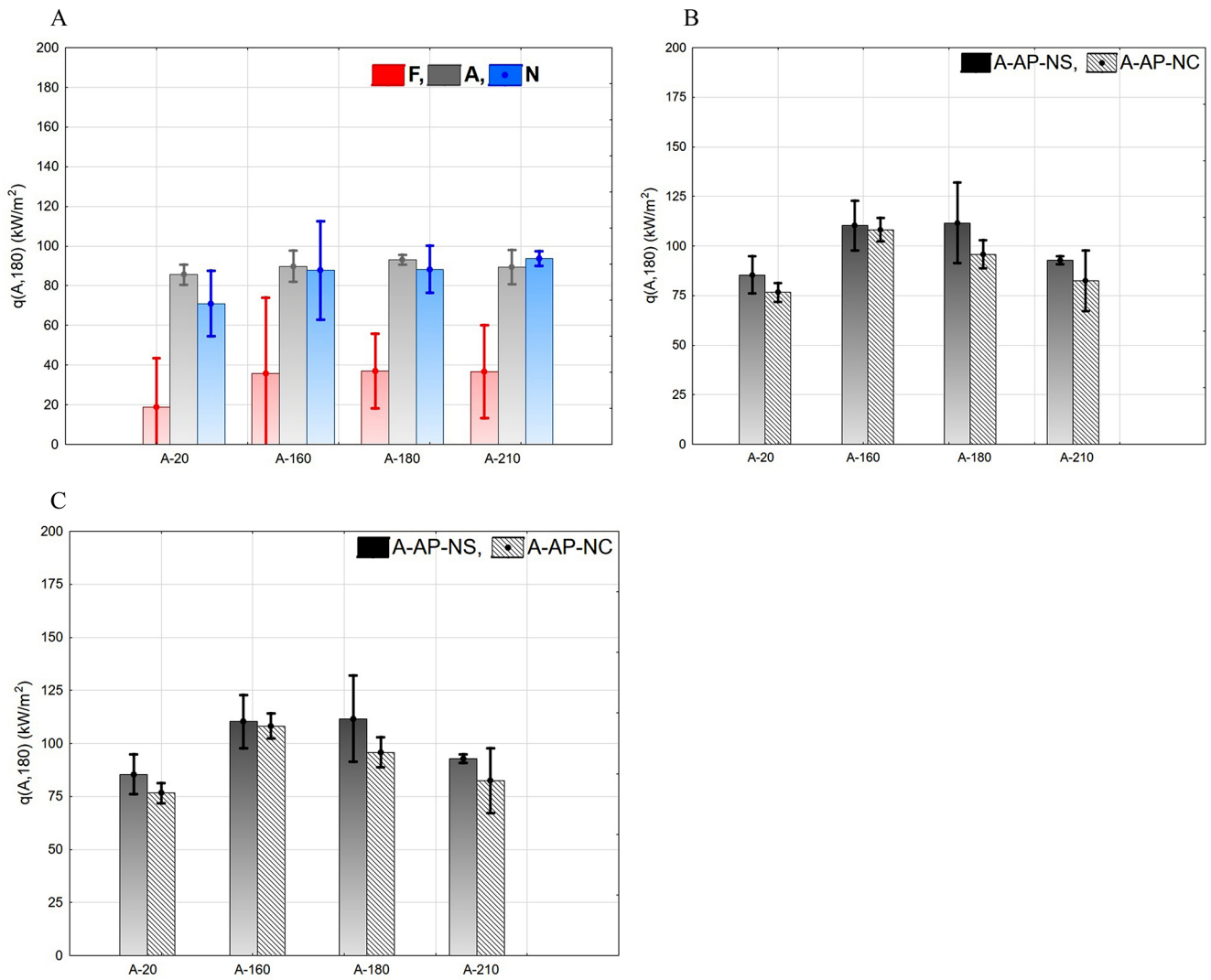


**Fig. 4** The effect of (**a**) Flame Gard (F), Arabinogalactan (A), and No flame retardant (N) as well as thermal modification (160, 180, and 210 °C) on the heat release rate (HRR) after 180 s; (**b**) mixture of melamine formaldehyde, ammonium phosphate, nanosilica (MF-AP-NS), and mixture of melamine formaldehyde, ammonium phosphate, nanoclay (MF-AP-NC) as well as thermal modification (160, 180, and 210 °C) on the heat release rate (HRR) after 180 s; (**c**) mixture of arabinogalactan, ammonium phosphate, nanosilica (A-AP-NS), and mixture of arabinogalactan, ammonium phosphate, nanoclay (A-AP-NC) as well as thermal modification (160, 180, and 210 °C) on the heat release rate (HRR) after 180 s

A



B



C



**Fig. 5** The effect of (**a**) Arabinogalactan (A), Flame Gard (F), and No flame retardant (N) as well as thermal modification (160, 180, and 210 °C) on the heat release rate (HRR) after 300 s; (**b**) mixture of melamine formaldehyde, ammonium phosphate, nanosilica (MF-AP-NS), and mixture of melamine formaldehyde, ammonium phosphate, nanoclay (MF-AP-NC) as well as thermal modification (160, 180, and 210 °C) on the heat release rate (HRR) after 300 s; (**c**) mixture of arabinogalactan, ammonium phosphate, nanosilica (A-AP-NS), and mixture of arabinogalactan, ammonium phosphate, nanoclay (A-AP-NC) as well as thermal modification (160, 180, and 210 °C) on the heat release rate (HRR) after 300 s

**Table 6** Correlation analysis evaluating the interaction between chemical components and reaction to fire characteristics and flammability

|  | Extractives (%) | Lignin (%) | Holocellulose (%) | Cellulose (%) | Hemicelluloses (%) |
|---|---|---|---|---|---|
| $t_{ig}$ (s) | 10 | -8 | 9 | -9 | 9 |
| $HRR_{180}$ (kW.m$^{-2}$) | -39 | 34 | -46 | 42 | -44 |
| $HRR_{300}$ (kW.m$^{-2}$) | -46 | 47 | -52 | 46 | -49 |
| pHRR (kW.m$^{-2}$) | 3 | -6 | 6 | 1 | 2 |
| $t_{pHRR}$ (s) | 38 | -26 | 34 | -30 | 32 |
| THR (MJ.m$^{-2}$) | 0 | 2 | 1 | 4 | -2 |
| Weight at flame (g) | 35 | -19 | 32 | -32 | 32 |
| $m_r$ (g) | 21 | -27 | 21 | -21 | 21 |
| $\Delta m$ (g.m$^{-2}$) | 23 | -8 | 22 | -18 | 20 |
| $m''$ (g.m$^{-2}$s$^{-1}$) | 21 | -18 | 23 | -20 | 21 |
| $m''_{10-90\%}$ (g.m$^{-2}$s$^{-1}$) | 14 | -10 | 16 | -13 | 15 |
| MARHE (kW.m$^{-2}$) | 0 | 1 | 1 | 4 | -2 |
| EHC (MJ.kg$^{-1}$) | -30 | 13 | -27 | 29 | -28 |

**Author contributions** All authors contributed to the study conception and design. Material preparation, data collection and analysis were preformed by SM, MG, and AKS. The first draft of the manuscript was written by MG and all authors commented on previous versions of the manuscript. All author authors read and approved the final manuscript.

**Data availability** No datasets were generated or analysed during the current study.

## Declarations

**Competing interests** The authors declare no competing interests.

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