

Bio-sourced flame retardant systems for polymers: the influence of chemical modification of giant reed on thermal stability and flammability of PA11

Kamila Sałasińska¹ · Zaida Ortega² · Magdalena Jurczyk-Kowalska¹ · Marcin Borowicz³ · Michał Misiak¹ · Daria Rutkowska¹ · Kamila Strycharz¹ · Tomasz Cygan¹ · Joanna Paciorek-Sadowska³ · Mateusz Barczewski⁴

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Abstract

As part of the research, bio-sourced flame retardant systems (FRs) containing raw and chemically modified plants were investigated. This work proposes the combination of melamine phosphate (MP) and giant reed (R) biomass as FRs for bio-based polyamide 11 (PA11). The influence of chemical modification on plant components' chemical structure was determined using analytical methods. Next, the materials with 20 mass% of the flame retardant systems were obtained by twin-screw extrusion and injection or compression molding, with a fixed MP/R ratio of 3:1. The materials were comprehensively characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and thermal analysis (DSC, TGA). Moreover, research techniques, including pyrolysis combustion flow calorimeter (PCFC) and cone calorimetry, were employed to establish the impact of FRs on the flammability of the polymer. The composition containing NaOH-treated reed showed a reduced heat release capacity, which shifted from 866 J g⁻¹ K⁻¹ for neat PA11 to 580 J g⁻¹ K⁻¹ for PA11/15MP5RN. In turn, the lowest total heat evolved and smoke emission was noted for FRs with reed after boric acid treatment.

Keywords Flame retardant \cdot Thermal analysis \cdot Pyrolysis combustion flow calorimetry \cdot Cone calorimetry \cdot Plant component

Introduction

Besides mechanical strength and durability, the polymer's fire performance is critical to plastic products' useability. Fire retardancy, especially relevant in aerospace and defense, electrical and electronics, transportation, and building industries, can be improved by chemical modification of the

Kamila Sałasińska kamila.salasinska@pw.edu.pl

- ¹ Faculty of Materials Science and Engineering, Warsaw University of Technology, Wołoska 141, 02-507 Warsaw, Poland
- ² Departamento de Ingeniería de Procesos, Universidad de Las Palmas de Gran Canaria, Campus Universitario de Tafira Baja, 35017 Las Palmas de Gran Canaria, Spain
- ³ Department of Chemistry and Technology of Polyurethanes, Kazimierz Wielki University, J. K. Chodkiewicza 30, 85-064 Bydgoszcz, Poland
- ⁴ Institute of Materials Technologies, Poznan University of Technology, Piotrowo 3, 61-138 Poznan, Poland

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polymer structure or physical modification by using additives with various mechanisms of action. Unfortunately, such solutions are more and more expensive and often characterized by insufficient sustainability. Legal regulations, rapidly rising prices, and shortages of raw materials caused by the global economic and political situation, as well as the devastation of the natural environment, stimulate the search for novel sustainable solutions in the fire retardants (FRs) area. Phosphorus FRs react with the cellulose hydroxyl groups by esterifying and enhancing their effectiveness in char formation, which is beneficial for a bio-sourced fire retardant search [1–7].

The synergistic effect of systems consisting of phosphorus FR and plant materials, confirmed by preliminary research results [8–10], shows the possibility of prospective research activities in this field. The plant flame retardancy potential is in the chemical structure and possible interaction with polymer decomposition products with FR, which are susceptible to phosphorylation. Due to the presence of polar groups such as carboxylic acids and high concentrations of hydroxyl groups, the structure of lignocellulose components is appropriate for improving the effectiveness of phosphorus flame retardants [2]. Implementing appropriately transformed plant materials interacting with commercially available FRs will define a new generation of highly efficient, sustainable FR systems with reduced environmental impact.

Alkali (mainly NaOH) treatment has been shown to increase the thermal stability of plant materials by partially removing hemicellulose [9, 10]. This modification can also block some of the hydroxyl groups in the cellulose (specifically in the glucopyranose ring), reducing the formation of flammable gas and thus increasing time to ignition and reducing heat release rate (HRR) of modified with its use polymer [10]. The treatment with phosphoric acid can effectively reduce the release of levoglucosenone, reducing the flammability of the cellulose [11]; for instance, the incorporation of 20 mass% phosphorylated microcrystalline cellulose into a polylactide (PLA) resulted in a slight decrease of the peak heat release rate (pHRR) concerning neat PLA and to the achievement of V-0 rating in the UL 94 test [12]. Similarly, the treatment of wood flour with boric acid has also been demonstrated to increase the degradation temperatures, making the material suitable to be introduced into a polyamide matrix, incorporating boron compounds into the biomass and shifting from cellulose I to cellulose II, which is more prone to char formation [13]. These authors concluded that, although the modification with boric acid resulted in a lower temperature of maximum degradation, the thermal degradation rate of borated wood flour decreased, and the rate of char formation increased, which is an indicator of the significant effect of boric acid on the fire retardancy of lignocellulose.

The core research hypothesis is that properly processed biomass enables the design and increase of the effectiveness of FR systems in polymer fire retardancy. The major challenge is correctly selecting the most suitable raw resources and identifying the optimal sequence of chemical modifications of plant components before mixing with the FR and polymer. This research work focuses on the use of giant reed (*Arundo donax* L.), a promising crop for biorefineries due to its fast growth under stress conditions, with insufficient quality waters and soils, able to restore polluted ground and reduce soil loss in damaged areas [14]. This plant has also been shown to be attractive for obtaining composite materials with good mechanical and thermal properties and with interesting features related to polymer stabilization during processing [15–18]. However, its behavior with polyamide has not been studied so far, nor has the performance of obtained composites on flammability testing. Therefore, this work comprehensively analyzes the behavior of materials obtained by combining reed biomass subjected to different chemical modifications to produce a green flame retardant system tailored to PA11 features.

Experimental

Materials

Bio-based polyamide 11 (PA11), with trade name Rilsan BMN O TLD NATURAL (density 1.03 g/cm³, $MVR_{235 \ ^\circC; \ 2.16 \ kg}$ 30 cm³/10 min), was applied for the investigation. As a flame retardant, melamine phosphate (MP) Exflam MP from Grolman, with P and N content min. 12% and 36–38%, respectively, and D50 < 10 μ m, was used. Reed was obtained from the aerial parts (culms and leaves) of giant reed plants (Arundo donax L.), naturally growing in Gran Canaria (Spain). The material was chopped and processed twice in a Retsch SM 300 cutting mill with a 10 mm screen. Once ground, it was washed with water, dried with forced air in Retsch TG 200, and then sieved in Retsch AS 200 Control device to remove clustered particles. The MP/R ratio in the system was 3:1 and the total amount of FR systems incorporated in PA11 compositions was 20 mass%.

The biomass was chemically modified following wellknown straightforward procedures. The objective of such treatments was to increase the fillers' thermal stability and add selected functional groups onto their surface, which might have a beneficial effect on their later performance. Therefore, five different modifications were performed and are summarized in Table 1.

After the treatments, the materials were washed to remove chemical residues until a neutral pH was obtained and then dried for 24 h at 105 °C in a forced-air stove.

Table 1 Chemical treatments applied to lignocellulosic component

Modification	Reagent	Conditions
NaOH	NaOH 1 N	1 h, room temperature, 25 g biomass/l
BA	Boric acid 5% (w/w)	2 h, room temperature, 25 g biomass/l
MA	Maleic anhydride 2% (w/w)	24 h, room temperature, 25 g biomass/l
APTES	(3-Aminopropyl) triethoxysilane 5% (w/w)	Ethanol/water 80/20 (in volume), 50 °C, 30 min
NaOH + APTES	NaOH 1 N+5% APTES (w/w)	NaOH + drying + APTES

Sample preparation

The samples were prepared by mixing PA11, flame retardant, and reed (Table 2) using the laboratory twin-screw extruder HAAKE MINILAB from Thermo Fisher Scientific. Before processing, the PA11 was dried for about 24 h at 60 °C. The extrusion process was performed twice with the following parameters: barrel temperature 210 °C, screws speed 50 rpm. Then, the materials were cooled down and pelletized. To obtain samples for mechanical investigation, the pellets were injection molded using a HAAKE Mini Jet Piston Injection Molding System from Thermo Fisher Scientific, while for the flammability tests, a hydraulic press Hydraulische Werkstattpresse WPP 50 E from Unicraft was applied. The injection molding process parameters were as follows: cylinder temperature 230 °C, mold temperature 70 °C, injection pressure 90 MPa, holding pressure 75 MPa, injection time 10 s, and holding time 8 s. The compression molding of the granulate on a hydraulic press was carried out at 215 °C for 10 min at a pressure force of 10 MPa. Then, the temperature decreased to 130 °C, after which the plate was removed from the heating mold.

Sample characterization

For the lignocellulose component, before and after chemical treatments, humidity, ashes content, extractives in ethanol and water, petroleum ether, cellulose, hemicellulose, and lignin were determined. The lignin content was assessed using the Klason method [19], which combines hydrolysis with H_2SO_4 . Holocellulose content was obtained by the gravimetric method described by Browning et al. [20], in which acetic acid and sodium chlorite produce the delignification of the sample. Total cellulose content was obtained from the holocellulose using the protocol presented in the ANSI/ASTM 1977b standard [21]. Finally, hemicellulose was calculated as holocellulose minus cellulose contents. Extractive content was determined following NREL/TP-510–42619 [22], which

 Table 2
 The list of samples includes the material formulation and type of plant modification

Sample	Modification	PA11	MP	R
		mass%		
PA11	_	100	_	_
PA11/15MP5R	-	80	15	5
PA11/15MP5RN	NaOH	80	15	5
PA11/15MP5RB	BA	80	15	5
PA11/15MP5RM	MA	80	15	5
PA11/15MP5RA	APTES	80	15	5
PA11/15MP5RNA	NaOH + APTES	80	15	5

consists of two subsequent extraction processes with water and ethanol. As the materials prepared with these lignocellulosic components will undergo fire behavior tests, fat content was also determined by performing another extraction step with petroleum, as explained in the protocol. For all these tests, three replicas from three different batches were used. Results are expressed as average values with standard deviations.

The Fourier-transform infrared spectroscopy (FTIR) measurements were carried out using a Perkin Elmer spectrometer in a mode of attenuated total reflectance (ATR) from 4000 to 500 cm⁻¹. A resolution of 4 cm⁻¹ was chosen, showing an average of 64 scans in each spectrum.

The morphology of plant particles and samples was observed using a scanning electron microscope SU-8000 from HITACHI at an accelerating voltage of 5.0 kV. The samples were mounted on carbon tape and coated with a 10 nm thin film of gold, using a low vacuum coater EM ACE200 from Leica.

Differential scanning calorimetry (DSC) was performed to specify the changes in the thermal behavior of PA11 using a Netzsch 204 F1 Phoenix apparatus. 5.0 ± 0.2 mg specimens were subjected to double heating/cooling (from -50to 240 °C) at a rate of 10 °C·min⁻¹ under nitrogen flow.

The thermal stability was assessed by thermogravimetric analysis (TGA) using the Netzsch TG F1 Libra apparatus. 10 ± 0.5 mg samples were placed in Al₂O₃ crucibles and tested under nitrogen or air. The analysis was performed in the temperature range of 25–900 °C, and the heating rate was 10 °C min⁻¹.

Flammability was examined using a pyrolysis combustion flow calorimeter (PCFC) from Fire Testing Technology, according to ASTM D7309. The samples were pyrolyzed with a heating rate of 1 °C s⁻¹, and the gas stream mixed with oxygen entered a combustor, where, at 900 °C, products were completely oxidized. The sample mass was 2 ± 0.5 mg, and the results were averaged from three runs.

Cone calorimeter measurements, performed on the Fire Testing Technology apparatus following the ISO 5660–1 and ISO 5660–2 procedures, were used to assess the burning behavior of investigated materials. The horizontally oriented samples were irradiated at a heat flux of 35 kW m⁻², and an electric spark ignited the pyrolysis products. An optical system with a silicon photodiode and a helium–neon laser provided a continuous survey of smoke. The residues after burning were photographed using a digital camera.

The gases exhausted from the TG analyzer were investigated by the FTIR method in a Perkin Elmer Spectrum 2 spectrophotometer. The spectra were collected continuously throughout the entire heating cycle from 30 to 900 °C, and airflow of 10 mL min⁻¹. The transfer line and measurement cell were set at 270 °C, with a 70 mL min⁻¹ gas flow.

Results and discussion

Characteristics of plant component

Table 3 shows the chemical composition of the *Arundo*derived materials used in this work before and after the chemical modification. APTES-treated materials are not included in the table as this procedure is aimed to graft the silane groups onto the biomass and not to perform any modification on the composition of the materials; the results of this approach are more likely to be observed in the thermogravimetric study [23]. The composition of the untreated reed is within the range obtained by other authors, namely 20–30% lignin, about 35–45% cellulose, and hemicellulose [15, 24–26], while ashes are found to be 2–5.5% [15, 27, 28].

Water extractives for reed (without the washing stage) are about 10%, while ethanol ones are lower and reached 2%, which is related mainly to chlorophyll compounds. After the treatments, extractive content is almost negligible, as they are transferred into the treating liquor; therefore, these results are not introduced in Table 3.

The most labile compound turned out to be hemicellulose. Hemicellulose can be hydrolyzed by NaOH [29], similar to the work [30], where about 60% of the content was hydrolyzed. As a result of the decrease in hemicellulose content, the treated plant showed a significant increase in cellulose, with almost no affection for the lignin content. The modification by MA or BA did not significantly affect the composition, although a slight reduction in hemicellulose was also found. Moreover, several authors have reported an increase in cellulose crystallinity, with cellulose I shifting to cellulose II as a consequence of NaOH treatment [31], which may affect the char formation during pyrolysis, as crystalline cellulose is less prone to the production of char, being the formation of levoglucosan a preferential route during its decomposition [11]. On the other hand, the increased cellulose II content would benefit char formation [13]. The ashes content is also reduced due to the dissolution of inorganic salts in the water used for the treatment; however, the series treated with baric acid provides a higher content, possibly due to the attachment of boron compounds into the lignocellulose.

Figure 1 shows the recorded spectra for all samples assessed. Typical bands for lignocellulosic materials can be observed, namely:

- Broadband at 3000–3700 cm⁻¹, assigned to O–H stretching, was reduced possibly due to the reduction in the hemicellulose content and is related to the lower hydrophilicity of the treated samples.
- The double absorption bands at 2918 and 2850 cm⁻¹, attributed mainly to C–H aliphatic groups in hemicellulose [28], were also decreased in intensity and importance (narrower peak) due to the treatments and the reduced hemicellulose content.
- The sharp peak at about 1720 cm⁻¹, related to C=O stretching in lignin and hemicellulose [32, 33], is reduced in intensity and disappears for NaOH-treated materials because of the reduction in hemicellulose ratio.
- Reduced intensity at 1640 cm⁻¹ is attributed to lower absorbed water (also found in composition tests). The area under this peak is also directly related to higher amorphous phase content [34], and the reduced intensity found here can be a reflex of an increased crystallinity of the treated samples.
- Increased intensity absorption bands are found for boric acid-treated samples between 1400 and 1240 cm⁻¹, which is related to boric compound attachment, mainly



Fig. 1 FTIR spectra for reed before and after chemical modification

 Table 3
 Results from composition analysis for the lignocellulose materials (in mass%)

Sample	Humidity	Ashes	Lipids	Water extractives	Ethanol extractives	Kraft lignin	Cellulose	Hemicellulose
Raw reed	3.70 ± 0.14	4.00 ± 0.28	1.70 ± 0.57	1.45 ± 0.92	3.10 ± 0.71	24.35 ± 1.77	40.95 ± 0.07	42.60 ± 0.42
Reed NaOH	5.25 ± 0.32	3.40 ± 0.55	NA	NA	NA	20.00 ± 1.19	71.17 ± 4.71	18.64 ± 2.92
Reed MA	3.48 ± 0.07	1.90 ± 0.67	NA	NA	NA	24.50 ± 2.39	57.44 ± 1.38	32.38 ± 1.09
Reed BA	4.68 ± 0.26	8.00 ± 0.43	NA	NA	NA	24.00 ± 0.61	49.41 ± 5.15	40.53 ± 4.90



related to the esterification of compounds in the biomass to form B-O-B and B-O-C [13].

(c)

Fig. 2 SEM images of reed before and after chemical modification: non-modified (a), NaOH (b), BA (c), APTES (d)

• A broad, intense peak found at 1022 cm⁻¹ is observed for all the samples, which is attributed to C=O stretching ring vibration in cellulose [35].

_SU8000 5.0 kV 8.0 mm × 200 LM(L

The FTIR results align with those obtained from the chemical composition analyses, as a hemicellulose content reduction was observed, especially for NaOH-treated samples. No particular differences are found in the spectra for the samples after APTES treatment, apart from a minimal change at approximately 750 cm⁻¹, related to C–Si vibration [36], either for those pretreated with the alkali neither for the untreated ones, suggesting that a different approach should be followed to attach the silane groups onto the lignocellulose surface effectively. The typical bands for NH₂ groups in APTES, expected to appear at approximately 1560 cm⁻¹ [37], are absent for all samples.



(d)

00 5.0 kV 8.0 mm × 200 LM

Fig. 3 FTIR spectra of polyamide and PA11 with developed FR systems

Fig. 4 SEM images of PA11 (a), PA11/15MP5R (b), PA11/15MP5RN (c), PA11/15MP5RB (d), PA11/15MP5RM (e), PA11/15MP5RA (f), and PA11/15MP5RNA (g)



The morphology of the particles subjected to mechanical grinding and chemical modifications was assessed based on SEM images, and representative ones are shown in Fig. 2.

Despite different treatments, the reed particles were similar in size and shape. In all cases, particles of various sizes with



Fig. 5 DSC curves measured for PA11 and its composites

Table 4 Thermal parameters obtained by DSC

Sample	T _c /°C	T _m , °C	X _c /% *
PA11	163.7	182.1; 189.5	32.0
PA11/15MP5R	162.5	181.7; 189.7	32.9
PA11/15MP5RN	163.7	182.0; 189.3	32.4
PA11/15MP5RB	163.5	182.1; 189.4	28.8
PA11/15MP5RM	164.1	182.1; 189.7	34.3
PA11/15MP5RA	163.9	182.5; 189.4	35.9
PA11/15MP5RNA	164.0	183.0; 189.5	30.3

^{*} X_c = $\Delta H_m/(\Delta H_{M100\%} \cdot (1 - \Phi))$, ΔH_m —melting enthalpy; $\Delta H_{m100\%}$ for PA11 = 200 J g⁻¹ [31],

 Φ —mass fraction of the additives

porous structures and developed surfaces can be observed. Moreover, the elongated particles predominated.

Evaluation of the properties and structure of PA11 with flame retardant systems

Chemical structure

FTIR-ATR was also performed on pure polyamide and its compositions with FR systems. As observed in Fig. 3, typical bands for PA11 are observed, especially standing out the bands for N-H stretching (3300 cm⁻¹), CH₂ asymmetric and symmetric stretching (2919 cm⁻¹ and 2850 cm⁻¹, respectively), C=O stretching from amide I (1634 cm⁻¹), N-H bending and C-N stretching in amide II (1540 cm⁻¹) and CH_2 asymmetrical bending (1460 cm⁻¹). Apart from those, some weaker bands are observed at 3080 cm⁻¹ from NH. N-H deformation (1436 cm⁻¹), NH-O stretching in amide III (1223 cm⁻¹), CH₃ rocking (1120 cm⁻¹), C-C(O) stretching in amide IV (957 cm⁻¹), and CH₂ rocking and C=O deformation (720 cm⁻¹) [38–40]. According to the spectra obtained, the only evidence of the presence of the melamine phosphate or the reed fillers is observed in the appearance of weak absorption bands at about 3400 cm⁻¹ (evidenced as a shoulder of the peak at 3300 cm⁻¹) from O-H stretching in biomass and MP, as well as the higher intensity of the bands at about 1100 cm^{-1} , related to C=O stretching in cellulose and to the P-O bond in P-OH, from MP [41]. Only the samples immersed in APTES do not show the shoulder mentioned at about 3300 cm^{-1} , which might indicate a higher interaction between the polymer and the fillers.



Fig. 6 TGA results for PA11 and PA with bio-sourced FR systems; TG (a) and DTG (b) curves

Table 5 The results from TG analysis									
Sample	Т _{5%} , °С	DTG1, °C; % min ⁻¹	DTG2, °C; % min ⁻¹	DTG3, °C; % min ⁻¹	DTG4, °C; % min ⁻¹	DTG5, °C; % min ⁻¹	Residue at nitrogen, %	Residue in air, %	
PA11	383	_	_	-	435; 27.90	469; 4.82	0.6	0.8	
PA11/15MP5R	327	253; 0.52	322; 0.71	375; 4.85	402; 21.02	432; 8.13	8.3	3.1	
PA11/15MP5RN	327	258; 0.37	314; 0.79	374; 5.11	403; 21.92	432; 6.16	7.2	4.4	
PA11/15MP5RB	327	266; 0.54	323; 1.01	378; 8.36	403; 21.65	430; 5.57	7.3	4.7	
PA11/15MP5RM	337	258; 0.31	323; 0.90	377; 7.39	403; 21.05	431; 6.07	7.5	4.7	
PA11/15MP5RA	338	258; 0.32	326; 0.82	369; 3.84	401; 25.55	435; 4.62	5.7	4.2	
PA11/15MP5RNA	328	255; 0.42	321; 0.80	379; 6.57	402; 21.50	432; 7.27	7.6	5.1	



Fig. 7 PCFC results for PA11 and PA with bio-sourced FR systems

Microstructure

Microstructure was assessed using SEM, and images of the fracture surface of the polymer and PA11 with flame retardant systems are shown in Fig. 4. Unmodified PA11 shows the features of a typical semicrystalline fracture with a developed surface [42]. In turn, the images of polymers with flame retardant systems revealed the presence of components in the whole volume of materials; however, it is visible that the plant component particles have a more varied and usually larger size. Some agglomerates, as well as pores, can also be observed. The occurrence of pull-out holes resulted from the removal of flame retardant component particles, suggesting limited adhesion between them and the polymer. Moreover, a few stages of the manufacturing process did not result in a noticeable presence of pores caused by the thermal decomposition of flame retardants or evaporation of water and low

Sample	T _{pHRR} /°C	pHRR/W g ⁻¹	THR/kJ g ⁻¹	HRC/J $g^{-1} K^{-1}$
PA11	446 ± 1	904 ± 24	32 ± 1	866 ± 20
PA11/15MP5R	418 ± 1	648 ± 36	27 ± 1	649 ± 38
PA11/15MP5RN	416 ± 2	595 ± 21	27 ± 1	580 ± 16
PA11/15MP5RB	419 ± 2	714 ± 43	28 ± 1	695 ± 53
PA11/15MP5RM	420 ± 1	649 ± 65	30 ± 1	657 ± 68
PA11/15MP5RA	420 ± 1	752 ± 48	27 ± 1	760 ± 50
PA11/15MP5RNA	418 ± 2	591 ± 18	28 ± 2	598 ± 18

 Table 7
 The results from cone calorimetry analysis

Table 6 The results from P

analysis

Sample	TTI/s	pHRR/ kW m ⁻²	MARHE/ kW m ⁻²	THE/ MJ m ⁻²	EHC/ MJ kg ⁻¹	SEA/ m ² kg ⁻¹
PA11	41±5	746±19	327±31	83±12	33 ± 3	324 ± 55
PA11/15MP5R	41 <u>+</u> 1	611 ± 44	329 ± 19	85 ± 7	29 ± 1	211 ± 10
PA11/15MP5RN	42 ± 1	686 ± 10	357 ± 8	88 ± 11	29 ± 1	277 ± 44
PA11/15MP5RB	49±6	717 ± 5	322 ± 10	69 ± 6	26 ± 2	193 ± 37
PA11/15MP5RM	45 ± 1	607 ± 1	351 ± 5	95±7	29 ± 2	279 ± 33
PA11/15MP5RA	44 ± 1	627 ± 8	336±6	84 ± 2	30 ± 2	222 ± 32
PA11/15MP5RNA	46 ± 5	606 ± 3	339 ± 9	88 ± 0	28 ± 1	246 ± 36



Fig.8 Representative heat release rate curves of PA11 and PA with bio-sourced FR systems

molecular mass substances from treated reed. This structure analysis aligns with our former process-oriented degradation studies of PA11 and its composites [42].

Thermal analyses

Figure 5 presents curves obtained for unmodified PA11 and polyamide with FR systems, and Table 4 provides detailed data on characteristic values of phase transitions determined using differential scanning calorimetry.

For all material series considered based on PA11, an overlapping double melting peak was observed during the second heating cycle. The double melting effect is due to crystal reorganization during the relatively slow heating used in the DSC test ($10 \ ^{\circ}C \ min^{-1}$) [43] and the crystallization

of selected grade of polyamide matrix in at least two crystallographic forms [44, 45]. This effect suggests that reed and MP did not exhibit nucleation ability influencing the polymorphic behavior of PA11. Determined based on melting enthalpy crystallinity of all tested material series is at a similar level except one containing filler modified with boric acid. In the case of PA11/15MP5RB, a slight decrease in crystallinity was observed concerning both PA11 and the reference sample containing an unmodified plant. Similar effects were noted in other works for thermoplastic semicrystalline composites with filler modified by BA [13, 46]. Zhang et al. [13] described changes in the crystal structure of polyamide 6 filled with wood flour treated by BA and explained this effect by a limited trans-crystallization effect after treatment. The DSC results also showed low vulnerability of PA11 to heterogeneous nucleation. Moreover, considering the constant concentration of MP in the polymer and the application of procedures that lead to a change in the plant filler structure induced by chemical modification, it can be concluded that MP does not demonstrate additional nucleating ability toward PA11. The observed lack of changes in crystallization and melting temperatures suggests that the surface treatment of reed with different methods with simultaneously incorporated MP does not significantly affect the polymer's crystallization process and final structure. This information can be regarded as beneficial from the point of control of the technological process of shaping the final properties of the products.

Figure 6 displays the curves of mass loss (TG) and derivatives as a temperature function (DTG), while the obtained data are summarized in Table 5. The analyses were performed in nitrogen and air to determine the residue yield in the presence of oxygen.

Fig. 9 Photographs of residue after burning tests





Fig. 10 Gram-Schmidt profiles for PA11 and the materials with FRs

The polymer's onset degradation temperature, corresponding to 5% mass loss, was 383 °C, while for samples with FR a reduction due to the use of flame retardant components was observed [47]. The most intense degradation, related to the polymer's decomposition, appeared above 400 °C and presented two stages. The additional steps corresponding to the degradation of components of FR systems can be observed. In the case of plant components, hemicellulose, lignin, and cellulose decomposition occurred at 250-290 °C, 350-390 °C, and 190-450 °C, respectively. Moreover, the sublimation of melamine, which takes place at about 350 °C, but volatilization starts at a lower temperature, allowing for the swollen layer's continuous formation [1, 6], was noticed. Applying a multi-component FR system led to peaks shifting toward lower temperatures and their overlap. The change in decomposition rates in each stage led to a much higher residue yield than unmodified polymer, regardless of the analysis conditions (nitrogen or air). Chemical modification of the plant component favors residue formation, especially for analyses performed in the presence of an oxidant.

Pyrolysis combustion flow calorimetry

Pyrolysis combustion flow calorimetry allows for evaluating small samples by imitating the processes that appear during burning without maintaining a flame [48]. The course of the heat release rate (HRR) is presented in Fig. 7, and Table 6 shows the process parameters.

The HRR curves for the unmodified polymer and PA with bio-based flame retardant systems have a similar pattern, although the presence of the second peak is more visible in samples with FR systems. Moreover, similar to TG analysis, the pHRR in the PA with FR appears earlier and corresponds to a temperature of about 30 degrees lower. A decrease in pHRR compared to PA11 was achieved for all samples with FR; however, the lowest value was determined for PA11/15MP5RN and PA11/15MP5RNA (reduction by approx. 35%). Moreover, the heat release capacity (HRC), one of the most approved indicators for assessing the fire hazard of materials [49], was also reduced. HRC of PA11 was 866 J g⁻¹ K⁻¹, while for PA11/15MP5RN reached 580 J g^{-1} K⁻¹. This suggests that alkali treatment was the most effective of all used modifications of the plant component. The samples with NaOH + APTES modified reed show similar results, confirming that the silane compound was not well attached to the surface and, therefore, is not providing any effect. In turn, the lowest total heat release (THR) was recorded for systems with R, RN, and RA; however, a reduction was observed for all materials with FRs, probably due to replacing some parts of the polymer with less flammable components.

Cone calorimetry

Burning behavior was evaluated using a cone calorimetry investigation, and the average values of key parameters obtained from the tests are given in Table 7. Figure 8 shows representative heat release rates (HRR) vs. time curves as a critical parameter determined during the CC measurement by oxygen consumption. In the case of unmodified PA, the HRR curve is characterized by one distinct peak with a maximum value at the end of burning. The introduction of flame retardant systems caused the flattening of the curves and the occurrence of an additional peak at the beginning of the test. For samples with FR, the second peak yielded the maximum heat release rate (pHRR), which, depending on the modification, varied from 606 to 717 kW m⁻². The lack of a characteristic plateau between the peaks [50] and insufficient residue (Fig. 9) does not confirm that the systems worked effectively in the combustion zone.

All tested materials ignited after 40 s, and the highest time to ignition (TTI) was recorded for the system with reed after modification with boric acid. PA11/15MP5RB also recorded the highest pHRR; however, based on the pHRR value, a noticeable effect of the applied modifications on the HRR was not observed. Similarly, no significant differences were recorded in the case of the maximum average rate of heat emission (MARHE), allowing flame spread evaluation. The obtained values were similar to each other and the result obtained for polyamide (Table 7). Noteworthy differences were noted in the case of total heat evolved (THE), corresponding to the total heat released at the end of flame combustion. Maleic anhydride caused an increase in THE, while the boric acid reduced the parameter by 17%. The reduction typically follows from incomplete combustion as an effect of char forming or reduced combustion efficiency [51], and the



Fig. 11 Spectra collected during the thermal oxidation of the PA11 (a), samples with (b) MP and reed, and c MP and NaOH-treated reed



Fig.12 Spectra collected at different moments of the assay for PA11/15MP5R $% \left({{{\rm{A}}} \right)$

accompanying decrease in the effective heat of combustion (EHC) suggests increased activity in the gas phase. Soluble sodium borates, as well as combinations of borate and boric acid, are known flame retard for cellulose and polymers containing hydroxyl groups. The mode of action is a combination of forming a glassy inorganic layer (B_2O_3), charring (formation of borate esters), and releasing water, which acts as a heat sink, fuel diluent, and blowing agent [1]. The gas phase activity is also visible in smoke emission, assessed by specific extinction area (SEA). A significant reduction of the parameter value below 200 m² kg⁻¹ was observed only for PA11/15MP5RB.

Analysis of evolved gas products during thermal decomposition

Exhaust gases from TG were continuously analyzed via infrared spectroscopy, and Fig. 10 shows the Gram-Schmidt profile for the samples investigated. For the neat polyamide, a main peak, with the highest intensity of about 460 °C, related to lactams, nitriles, and unsaturated hydrocarbons, with a secondary release of low molecular mass compounds [52], can be observed. The use of FRs caused a shift of decomposition toward lower temperatures, as already mentioned, and a change in intensity.

As can be seen in Fig. 11, the obtained spectra corresponded to the degradation of the polymer, visible related to C-H vibration in CH₃ and =CH₂ stretching in alkenes [52] found between 2800 and 3000 cm⁻¹, together with some weaker bands at 1700 and 1500 cm⁻¹, attributed to C=O in ketones and C=C-C in aromatic groups [53]. Moreover, traces of ammonia from polyamide decomposition can be seen under 1000 cm⁻¹. Absorption bands found at 580 °C are associated with the transient char decomposition and the release of additional volatile products, including carbon dioxide and low molecular mass hydrocarbons, visible in the spectra in the weak bands close to 3000 and in between 2400 and 2200 cm⁻¹ [4, 54]. From Figs. 3, 12 b and c, showing the spectra from the thermal degradation of PA11/15MP5R and PA11/15MP5RN, the main differences are found in the temperature of degradation and the release of volatile components (from MP) at lower temperature than the PA degradation.

In the case of all samples with FRs, new spectra at about 390 °C were collected. The absorption bands at 3550, 3475, 1600, 1450, and 800 cm⁻¹ [47] indicate the melamine released during the decomposition of MP, as shown in Fig. 12. The spectra obtained for MP and untreated reed in the different temperatures gradually reduce when the PA starts degradation while increasing the amount for NH₃ release (about 1000 cm⁻¹). In higher temperatures, only CO₂ emission was obtained, especially for APTES-treated reed, which indicates more intense char formation, as evidenced by the higher yields of residue.

Conclusions

The main goal of the research was to assess an effective flame retardant system containing biomass. The influence of various chemical treatments of the filler on the possibility of achieving synergistic interaction with a commercial flame retardant on bio-based polyamide compositions was verified by examining its thermal properties and fire performance. Using plant waste and phosphorus flame retardants resulted in an additive effect, contributing to the reduction of heat release rate and smoke emission compared to neat polyamide. Depending on the modification methods, differences in the mechanism of action of FR systems were observed. The most promising results were obtained after alkali and boric acid treatment.

The research confirmed the potential of plants as components of effective systems with synthetic flame retardants, reducing their negative impact on the environment by limiting their quantity and increasing their effectiveness. The applied chemical modification improved the efficacy of the plant component in the developed flame retardant system. This was due to changes in the chemical structure of plants, including changes in the proportion of components containing hydroxyl groups from less (hemicellulose) to more thermally stable (cellulose) ones, as well as the addition of chemical substances, such as the attachment of boron to lignocellulose.

This study supplemented the ongoing research on the use of thermally modified lignocellulose as a component of flame retardant systems, a promising pathway for developing flame retardant systems based on natural biomaterials. Acknowledgements This study was supported by the National Centre for Research and Development of Poland under project LIDER13/0095/2022 "Innovative use of lignocellulosic material as a component of the flame retardant system of polymer products for electrical industry and electromobility." LICEM project (EIS 2021 33), funded through Consejería de Economía, Conocimiento y Empleo del Gobierno de Canarias, Fondo Europeo de Desarrollo Regional. Canarias Avanza con Europa.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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