

Wastewater phosphorus enriched algae as a sustainable flame retardant in polylactide

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ABSTRACT

Revolutionizing our polymer industry for adaption to a sustainable carbon circular economy has become one of today's most demanding challenges. Exploiting renewable resources to replace fossil-fuel-based plastics with biopolymers such as poly(lactic acid) (PLA) is inevitable while using waste streams as a raw material resource at least is promising. When it comes to using PLA as technical polymer, its high flammability must be addressed by flame retardants compatible with the thermoplastic processing of PLA and its compostability. This study proposes microalgae enriched with phosphorus from wastewater (P-Algae) as an elegant way towards a kind of sustainable organophosphorus flame retardant. The concept is demonstrated by investigating the processing, pyrolysis, flammability, and fire behavior of PLA/P-Algae, while varying the P-Algae content and comparing P-Algae with four alternative bio-fillers (phosphorylated lignin, biochar, thermally treated sewage sludge, and metal phytate) with different P-contents as meaningful benchmarks.

1. Introduction

Biopolymers, a promising alternative to conventional plastics, are being integrated into industrial production as their improved properties and expanding applications have come to rival those of petrochemical polymers. Their innate biodegradability sets them apart, offering diverse end-of-life possibilities like recycling into raw materials [1–3]. When it comes to replacing technical polymers, fiber reinforcement and flame retardancy become key issues. The proposed biocomposites consist of distinct biopolymer / natural fiber / ecologically friendly flame-retardant combinations [4]. For instance, Gallo et al. showed that the addition of aluminum trihydrate and coconut fibers to thermoplastic starch manifests synergistic effects resulting in improved fire performance [5]; other studies demonstrated the synergistic flame retardancy of aluminum diethylphosphinate and nanosized metal oxides in poly(3-hydroxy-butyrate-co-3-hydroxyvalerate)/poly(butylene adipate-co-terephthalate) / natural fiber biocomposites [6,7]. PLA in particular stands out amid environmental challenges, as it boasts a reduced carbon footprint, non-toxic degradation, and safe packaging potential. While PLA is used in a wide range of applications, the need to

address flammability risks remains critical when it comes to applications that demand flame-retardant technical polymers. Improving the thermal stability, mechanical properties, and flame retardancy of PLA or PLA/natural fiber composites without decreasing their molar mass during processing is essential [8–13].

Bio-based flame retardants have garnered significant interest as a solution to enhance the flame resistance of PLA materials [14–16]. With growing demand for sustainability and environmentally friendly alternatives, researchers and manufacturers have been exploring various bio-based additives to mitigate the flammability risks associated with PLA. These bio-based flame retardants are derived from renewable resources such as natural fibers, proteins, starches, and plant extracts [17, 18]. The advantage of using bio-based flame retardants is twofold. First, they offer a sustainable alternative to conventional flame retardants, which are often derived from non-renewable fossil resources. Second, bio-based flame retardants can contribute to the overall biodegradability of PLA materials. The inclusion of bio-based additives ensures that the flame-retardant properties do not compromise the environmentally friendly nature of PLA [19–21].

Lignin is composed of phenolic, hydroxyl and carbonyl functional

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groups [22]. The phosphorylation of lignin (P-Lignin) involves the introduction of phosphate groups into the complex polymer structure of P-Lignin molecules. By incorporating phosphate groups, the solubility, reactivity, and compatibility of P-Lignin with other materials can be enhanced, paving the way for innovative and sustainable composite materials with enhanced performance characteristics [23,24]. Lignin has a high proportion of aromatics in its structure, which is also responsible for its high thermal stability and charring potential [25]. During burning, P-Lignin shows a high char yield, which suggests its use as flame retardant or flame-retardant adjuvant for thermoplastics and thermosets.

Biochar can be used as an additive to bio-based polymer composites. Its properties have been shown to also improve mechanical properties and flame retardancy when used at appropriate levels in the composite [26].

Phytic acid is a naturally occurring compound in many plant-based foods. Its salts have shown to be useful as a flame retardant due to the chemical structure of phytic acid, which contains 28 wt.% phosphorus. Phytic acid phytates are considered as alternative “green” phosphorus-based flame retardants [27,28]. The phosphate groups act as char promoters. Decomposition facilitates the dehydration of the carbon source, crosslinking, and graphitization, and leads to the formation of a stable protective layer as well. This protective layer acts as a barrier between the flame and the pyrolyzing material, providing a reliable heat shield [21,27,29].

The utilization of algae as fillers would be highly valuable. Algae offer a vast and inexpensive potential for serving as fillers in polymer-matrix composites. However, there is a significant lack of knowledge regarding the properties of composites filled with algae. Algae biomass is rich in hydrosoluble polysaccharides, which contain high levels of proteins, and minerals that can act as effective flame retardants [30]. Currently, several researchers are using algae biomass to develop biodegradable plastics. Examples of such compounds include PLA (polylactic acid), PHA (polyhydroxyalkanoates), PHB (polyhydroxybutyrate), PE (polyethylene), PVC (polyvinyl chloride), starch, and cellulose-based polymers [31,32]. Bulota and Budtova conducted a study in which they synthesized biocomposites of PLA (polylactic acid) mixed with red, brown, or green algae [33]. They observed that as the concentration of algae in the composites increased the mechanical properties deteriorated. The study also showed that the particle size of the algae has an effect on the mechanical properties of the composites, with larger particles having better mechanical properties. Algae-based fillers can also help reduce the carbon footprint of products, as algae absorb carbon dioxide as they grow, helping to mitigate climate change [32]. Harnessing the natural properties of algae and combining them with advanced materials can pave the way to green, safer, and more resilient products.

Building upon previous successful results from using bio-fillers in PLA [34–36] as well as renewable bio-fillers exploiting waste streams [37–40], the present study aimed to delve into the potential of utilizing microalgae enriched with phosphorus cultivated in wastewater (P-Algae) as a flame retardant in PLA biocomposites. Using wastewater as a resource for phosphorus is not only a very sustainable route in terms of the critical raw material phosphorus, but also contributes to the removal of phosphorus from wastewater, one of the current challenges in environmental protection. P-Algae were incorporated into PLA matrices at different concentrations to assess their efficacy in enhancing flame retardancy. Furthermore, these P-Algae-based biocomposites were compared with biocomposites containing alternative, eco-friendly flame retardants as meaningful benchmarks, such as P-Lignin as an alternative for a renewable P-enriched waste product, biochar (Biochar) as an alternative biowaste, thermally treated sewage sludge (TTSludge) as an alternative for P-removal from wastewater, and zinc phytate (ZnPhyt) as an alternative for a renewable P-containing biomaterial. Comprehensive characterization encompassed flame retardant performance, thermal stability, response to small flame, and molar mass

changes of the matrix during processing. The findings elucidate the efficacy of P-Algae and of other eco-friendly alternatives in PLA biocomposites. The P-Algae employed in this investigation not only serve as exemplary contributors to exploiting renewable resources in a sustainable way, but also to waste management in terms of the critical raw material phosphorus. Thus, this innovative study opens the door for further research and applications.

2. Materials and methods

2.1. Materials

The commercial injection molding grade PLA granulates (MVR of 23 cm³/10 min at 190 °C and a bulk density of 1.24 g/cm³) were provided by Tecnar GmbH, Germany. Based on data from the provider, tensile modulus of PLA is 3500 MPa (ISO 527), tensile strength 63 MPa (ISO 527) and hardness Shore A – 99.

Phytic acid (50 % in H₂O) was purchased from Sigma Aldrich. ZnSO₄·7H₂O (purity 99.5 %) and NaOH (purity 98 %) were obtained from Chemsolute, Th. Geyer GmbH & Co. KG, Germany. Phosphorus enriched algae *Desmodesmus* sp. (P-Algae) were provided by Constructor University Bremen. P-Lignin was provided by Fraunhofer LBF in Darmstadt. TTSludge was provided by another research project at the Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin. Biochar fillers were provided by Ruhr Lab GmbH, Gelsenkirchen Deutschland.

Zinc phytate synthesis: Due to the strong chelation ability of phosphate groups present in phytic acid, metal complexes can be formed easily. For this study, zinc salt of phytic acid (ZnPhyt) was synthesized according to the method reported by Cheng et al. [41]. 0.06 mmol (17.25 g) of ZnSO₄·7H₂O was dissolved in 200 mL distilled water and added to a three-neck flask with magnetic stirring. Then 0.01 mmol (13.2 g) of phytic acid was separately dissolved in 200 mL distilled water and added dropwise to the flask. The pH of the mixture was adjusted to 7 – 8 by addition of 0.1 mol/L NaOH. The mixture was stirred continuously at 80 °C for 2 h. The products were filtered using vacuum suction and washed three times with deionized water. The obtained ZnPhyt (white solid) was dried in a vacuum oven at 60 °C for 24 h to remove any excess water. The average particle size was 0.11 mm.

Algae cultivation: Phosphorus enriched *Desmodesmus* sp. cultures were produced at the Greenhouse facility of the Oceanlab at Constructor University Bremen. The *Desmodesmus* strain used was isolated from a German municipal sewage plant in Fulda, Hesse. Industrial wastewater was created by adding NH₄Cl, KH₂PO₄, MgSO₄, A5 micro-nutrients, Fe-EDTA, and Na₂CO₃ pH buffer to tap water (N and P levels of the tap water were below 0.05 mg/L) was used as a cultivation medium for algae growth, as it contains a high nutrient concentration [42]. The wastewater used was pre-treated by an anaerobic membrane bioreactor (AnMBR) to remove organic carbon content from the wastewater. *Desmodesmus* species were maintained in Bold’s Basal Medium and grown in the AnMBR-treated wastewater in 2 L photobioreactors (PBR). Cultures were grown at 24 ± 1 °C and illuminated by fluorescent tube lights (L 58 W/840, OSRAM, Germany). This stock culture was eventually used to treat the secondary AnMBR wastewater continuously in a 1000 L pilot scale photobioreactor to generate the biomass for enrichment [42].

Phosphorus enrichment: After the cultivation process was completed, the biomass was stored in cubic containers at 4 °C in complete darkness, and the pH was maintained at 7.8. After continuing the same process for 7 days, the cells were starved of phosphorus and kept without sunlight for 3 days. After 3 days the cells were exposed to sunlight and fed with KH₂PO₄ (5 mg/L of P) to force luxury uptake. After 6 h of exposure to sunlight and excess P, the biomass was harvested using an industrial centrifuge (Delaval, Germany). The average particle size was 0.5 mm.

Biochar was obtained from cocoa shells, which are agricultural waste. The shell was converted into biochar by the process of pyrolysis

and reduction as per the information provided by the supplier. The whole process was done for 26 days; first pyrolysis was performed at a control temperature of 450 °C. After that the entire biomass was reduced at a control temperature of 815 °C. During this time the system was operated continuously. The sample was prepared according to the DIN 51,701–3 standard (2006). The average particle size was 3.5 mm.

P-Lignin: The phosphorylation of lignin involves introducing phosphate groups onto the monomers of lignin by reacting phosphorylating agents like phosphorus pentoxide (P_2O_5) [24,43] with the hydroxyl groups present [44]. Kraft lignin (2 kg) was dissolved in THF (7.5 L). Once the P-Lignin was fully dissolved, phosphorus pentoxide P_2O_5 added at room temperature. Then the solution was heated for 8 h in a solvent reflux system. After 8 h the mixture was cooled down and distilled water was added to convert unreacted phosphorus pentoxide into phosphoric acid. Then THF was evaporated in a rotary evaporator at 40 °C. The collected phosphorylated P-Lignin was filtered, washed, and dried at 75 °C under reduced pressure. The average particle size was 0.8 mm.

The TTSludge was obtained from a wastewater treatment plant and treated thermally at 1800 °C using a chamber furnace [45]. The sewage sludge was treated at around 900 °C under reducing conditions and through the addition of sodium compounds ($NaHCO_3$, Na_2CO_3 or Na_2SO_4). The average particle size was 30 μ m.

2.2. Preparation of the composites

The compounding of biocomposites was done using an Xplore MC 15 HT twin screw micro compounder (chamber capacity: 15 mL). The rotation velocity of 75 rpm was applied for a compounding cycle of 6 min and the temperature range from 190 to 200 °C. The PLA granulates and the additives used were dried overnight in a vacuum oven at 50 °C before processing. The temperature of the chamber and the melt as well as the torque were monitored simultaneously. When the torque reached a minimum value during compounding cycle, it meant that the polymer pellets and additives were mixed homogeneously and ready for collection. The polymeric mixture was then collected and pelletized via an electric cutter. The combination of the composites in terms of weight percentages is shown in Table 1. The total mass of biocomposites produced was about 250–300 gs. Considering that one can apply a maximum of 10 gs of substance, it was needed 25–30 cycles. Each time, the amounts of matrix and filler were measured and mixed only in the mixer.

For the preparation of the limiting oxygen index (LOI) and UL 94 test specimens, an injection molding tool (Xplore micro injection mold IM 12) was used. The melt was operated at 200 °C. The molding process was carried out using the following parameters: $T_{mould} = 30$ °C, injection force = 18 kN, forming pressure $P = 8$ bar and cooling time $t = 10$ s. The size of the samples obtained from the mold was 80 mm x 10 mm x 4 mm.

Hot press compression molding: The calculated weight of polymer granulates required to obtain the cone calorimeter test specimen, plates 100 mm x 100 mm x 4 mm in size, were poured into the aluminum

compression frame of the same size. The frame was located between two metal plates. The molding process was carried out at 200 °C. The first compression process was carried out for 5 min at a low pressure of 200 N, and the second for 5 min at a high pressure of 500 kN. Then the mold and samples were cooled down with the built-in water circulating cooling system under the same pressure at a cooling rate of 10 K/min. The sample sheets were then removed from the mold.

2.3. Characterization

The phosphorus content of bio-based fillers was analyzed through elemental analysis performed by Mikroanalytisches Labor Kolbe, Germany.

FTIR spectrum were acquired using a Vertex70 spectrometer (Bruker Optics, Germany) in the range between 400 and 4000 cm^{-1} , with a resolution of 0.4 cm^{-1} .

Thermogravimetry (TGA) measurements were performed on a TG 209 F1 Iris (Netzsch Instruments, Germany), in which a 10 mg cryo-milled sample was treated under inert atmosphere with a nitrogen gas flow of 30 mL/min and a heating rate of 10 K/min in a temperature range from 30 to 900 °C.

The Size Exclusion Chromatography (SEC) was equipped with a refractive index detector and 3 Phenogel columns (1×10^5 Å; 1×10^3 Å; 1×100 Å, each 5 μ m; 7.8×300 mm). Samples were dissolved in $CHCl_3$ (2–3 mg/mL); 100 μ L of solution was injected at a flow rate of 1 mL/min. Calibration was done using polystyrene standards ranging from 580 to 9.15×10^5 g/mol. The calibration curve of polystyrene was used as a reference to calculate the molar masses of the biocomposites.

The Pyrolysis Combustion Flow Calorimeter (PCFC) (ASTM D7309, Fire Testing Technologies Ltd, UK) was used as a tool to analyze the volatile products at a constant rate of 1 K/s and in a temperature range between 100 °C and 750 °C. To analyze the volatile products yielded by 5 mg of powdered material subjected to anaerobic pyrolysis, the material was combusted at 900 °C in a gas mixture consisting of a nitrogen flow of 80 mL/min and an oxygen flow of 20 mL/min.

Cone calorimeter experiments were performed using a dual cone calorimeter from Fire Testing Technology, UK, equipped with a spark igniter, according to ISO 5660. Specimens 100 mm x 100 mm x 4 mm in size were examined in a horizontal position with an external heat flux of 50 kW/m^2 and a distance between the cone heater and the sample surface of 35 mm to give the materials some space for intumescence without substantially changing the area of uniform heat flux [46]. Three measurements were taken of each type of material.

The materials' reaction to a small flame was tested by oxygen index or LOI according to ISO 4589–2 using an apparatus from FTT (East Grinstead, UK). UL 94 tests were carried out according to the IEC 60,695–11–10 standard in a flame chamber from FTT. The sample size for all materials was 80 mm x 10 mm x 4 mm. All materials were pre-conditioned for at least 48 h at 23 °C and 50 % R.H. Since the specimens were somewhat short, the linear burning rate was calculated using a burning length of 55 mm rather than 75 mm in horizontal burning tests.

3. Results and discussion

3.1. Elemental analysis

Elemental analysis was performed on the bio-based fillers to quantify the phosphorus content. The results of the analysis showed the following phosphorus contents displayed in Table 2.

The variation in phosphorus content between different materials, including P-Algae, P-Lignin, Biochar, TTSludge, and ZnPhyt, provides valuable insights into the elemental composition and potential applications of these materials. P-Algae, composed of primarily photosynthetic organisms, have the lowest phosphorus content of the materials studied. This is due to their natural growth and metabolic processes, which typically prioritize the assimilation of other essential nutrients

Table 1

Composites' formulation with different flame retardants in weight percentage.

Sample	PLA	P-Algae	P-Lignin	Biochar	TTSludge	ZnPhyt
PLA	100					
PLA_P-Algae ₅ %	95	5				
PLA_P-Algae ₁₀ %	90	10				
PLA_P-Algae _{12.5} %	87.5	12.5				
PLA_P-Algae ₂₀ %	80	20				
PLA_P-Lignin ₁₀ %	90		10			
PLA_Biochar ₁₀ %	90			10		
PLA_TTSludge ₁₀ %	90				10	
PLA_ZnPhyt ₁₀ %	90					10

Table 2
Phosphorus content of bio-based fillers.

Bio-Based Fillers	Phosphorus content (wt.%)
P-Algae	0.88 ± 0.01
P-Lignin	3.09 ± 0.01
Biochar	5.00 ± 0.01
TTSludge	5.34 ± 0.02
ZnPhyt	12.73 ± 0.01

such as nitrogen and carbon. The relatively low phosphorus content in P-Algae is consistent with their ecological role in nutrient cycling and their ecological niche. The phosphorus content of P-Lignin is reported to be in line with the expected amount provided by the supplier. Lignin, as a complex and rigid polymeric compound, is typically extracted from plant materials, so that the phosphorus content in P-Lignin is consistent with the source material and production process. The phosphorus content in biochar is explained by the presence of phosphorus pentoxide, a compound confirmed by the supplier's research. This suggests that biochar may act as a carrier for phosphorus, making it potentially useful for applications in agriculture or soil remediation where controlled release of phosphorus is desired. TTSludge is developed to be used as fertilizer, since in EU it is forbidden to use sewage sludge. It contains slightly more phosphorus than biochar. This difference is due to the high organic matter and nutrient content of sludge. Organic matter can bind and retain phosphorus, while the presence of nutrients in sludge, such as residual organic matter and microbial byproducts, can contribute to a higher phosphorus content. This is particularly relevant in the context of wastewater treatment, where sewage sludge is a byproduct rich in organic matter and nutrients. The highest phosphorus content is observed in ZnPhyt, which is expected due to the known composition of phytic acid. Phytic acid contains approximately 28 wt.% phosphorus,

and ZnPhyt is a zinc salt of phytic acid. This high phosphorus content in ZnPhyt makes it a valuable source of phosphorus for various applications, including as a nutrient source or fertilizer.

SEC analysis: The observed sensitivity of PLA to moisture has been a topic of significant interest due to its potential impact on molar mass. The inherent hydrophilicity of PLA makes it susceptible to moisture absorption, resulting in reduced molar mass, which affects its overall performance in diverse applications. However, PLA is not only affected by hydrolysis, but is also very sensitive to active additives such as FR in terms of re-esterification. In the case of PLA, the filler's interaction with the polymer matrix triggers the re-esterification of PLA chains [47]. To investigate the interaction of bio-based fillers with the PLA matrix, size exclusion chromatography (SEC) was performed. SEC is a powerful analytical technique that allows the molar mass distribution in a polymer sample to be determined. In this study, we focused on composites containing 10 wt.% of the filler and explored the effects of different concentrations of P-Algae in PLA matrices.

The results presented in Fig. 1A highlight the filler's impact on the molar mass distribution of PLA composites. Shifts in molar mass distribution curves suggest potential interactions between the filler and PLA chains. Fig. 1A shows that the smallest decrease in molar mass is for the composite containing TTSludge as FR. The next is P-Algae, followed by ZnPhyt and P-Lignin. The highest decrease in molar mass is observed for the sample containing biochar. These results support the observations made during the preparation of the material. PLA with biochar, after preparation, was completely brittle and not suitable for further processing. In Fig. 1B, SEC results for PLA composites with varying P-Algae concentrations reveal systematically adjusting P-Algae content in PLA matrices. We aimed to elucidate how filler content influences PLA molar mass, crucial for optimizing PLA-based composite formulations. Fig. 1B shows that PLA composites with 5 wt.% P-Algae filler exhibit a molar

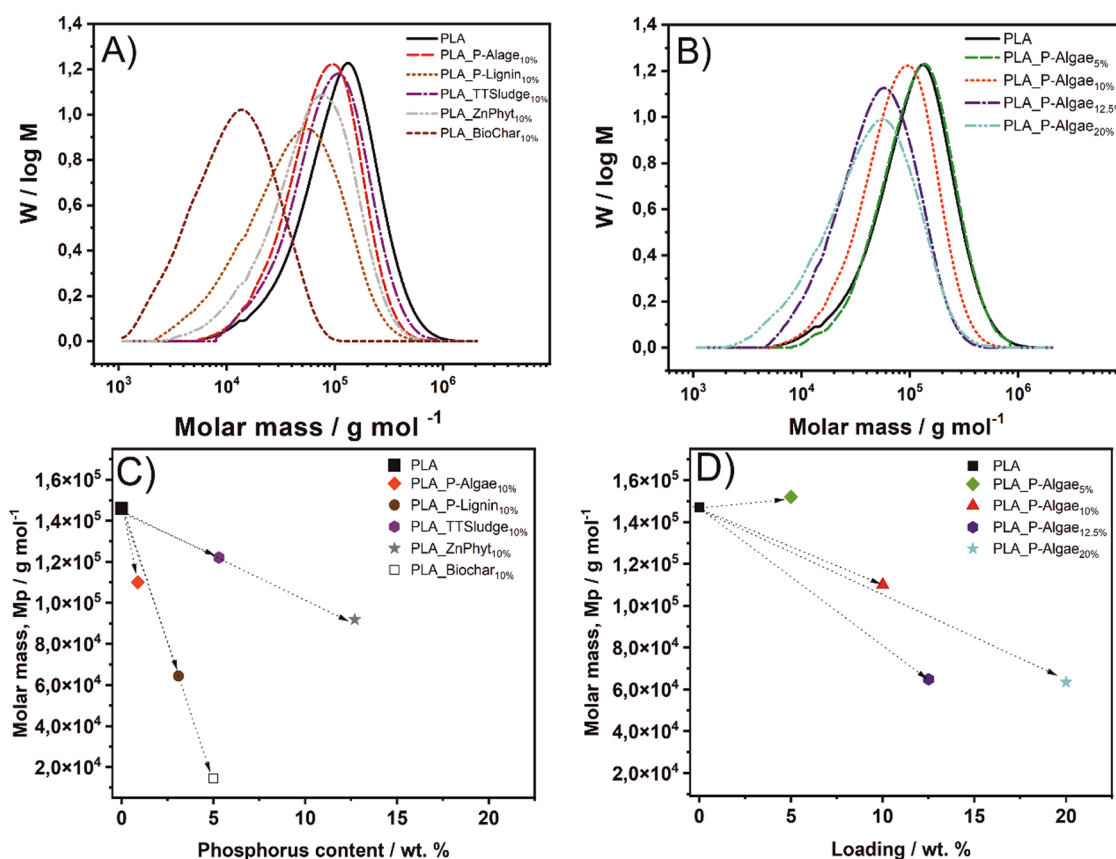


Fig. 1. SEC plots of PLA and PLA-based composites with (A) 10 wt.% filler (B) different P-Algae concentrations. Comparison of changes in molar mass (C) as a function of phosphorus content and (D) loading of P-Algae in the composite.

mass similar to untreated PLA. This observation holds potential for maintaining structural integrity and performance in PLA-based materials while incorporating sustainable bio-fillers. Some biocomposites in our study led to reduced PLA molar mass, indicating filler-PLA chain interactions causing structural modifications. Table 3 presents the molar mass distributions for various PLA composites, demonstrating degradation induced by different fillers.

The presence of biochar strongly affected the physical and mechanical properties of the resulting composite, as evidenced by the molten polymeric composite's water-like consistency and brittleness. These observations were helpful to exclude further examinations of PLA-biochar composite.

FTIR analysis: The infrared (IR) spectrum of PLA reveals distinct bands that provide information about the molecular structure of this biodegradable polymer. One of the most prominent features in the IR spectrum of PLA is the strong characteristic band at 1747 cm^{-1} . This peak is indicative of the stretching vibration of the carbonyl group (C=O) present in the ester linkage of PLA, while the appearance of two additional peaks, one at 1180 cm^{-1} , corresponding to the stretching vibration of the C—O bond, and another at 1080 cm^{-1} , represent the stretching vibration of the C—O—C bond. The -CH_3 and -CH stretching vibrations are observed at 2997 cm^{-1} and 2945 cm^{-1} , respectively. In addition to stretching vibrations, the IR shows asymmetric and symmetric bending frequencies for -CH_3 groups. These bands are observed at 1452 cm^{-1} and 1377 cm^{-1} , respectively. Examining the fingerprint region of the IR spectrum, two prominent bands, attributed to the C—C stretching vibration, are observed at 867 cm^{-1} and 755 cm^{-1} [48]. The FTIR spectra of the PLA and its biocomposites are shown in Fig. 2.

The IR spectrum of P-Algae—filled PLA shows a small broad peak at 3280 cm^{-1} attributed to N—H and O—H vibrations arising from amides or alcohol groups found in proteins. In addition, a shoulder at 2867 cm^{-1} is observed, corresponding to the C—H stretching frequencies of aliphatic molecules [48]. The PLA composite with 10 wt.% P-Lignin filler shows a broad peak at 3400 cm^{-1} , indicative of OH group vibrations present in both the aliphatic and aromatic chains of P-Lignin. A small shoulder at 2867 cm^{-1} corresponds to C—H stretching vibrations of the aliphatic backbone, highlighting the integration of P-Lignin into the polymer matrix [35]. Furthermore, the appearance of peaks at 1594 and 1508 cm^{-1} indicates the significant influence of aromatic ring vibrations originating from phenylpropane units within the P-Lignin structure. The PLA biocomposites with metal phytate filler show distinctive IR features, including one small, broad peak at 3400 cm^{-1} and another at 1639 cm^{-1} . The peak at 3400 cm^{-1} corresponds to stretching vibrations of the OH group, which can be associated with the presence of water molecules interacting with the metal phytate. The peak at 1639 cm^{-1} is attributed to the bending vibrations of these OH groups, providing evidence of hydrogen bonding or interactions within the composite. In the case of biocomposites containing TTSludge, two additional bands appear in the IR spectrum. The bands at 2916 and 2850 cm^{-1} correspond to aliphatic C—H stretching vibrations, indicating the presence of hydrocarbons within the organic matter of the TTSludge.

Table 3

Molar mass distributions of processed PLA and PLA-based biocomposites.

Sample	M_n (g mol $^{-1}$)	M_w (g mol $^{-1}$)	M_p (g mol $^{-1}$)
PLA	7.42×10^4	1.47×10^5	1.47×10^5
PLA_P-Algae _{5%}	8.32×10^4	1.49×10^5	1.51×10^5
PLA_P-Algae _{10%}	5.63×10^4	1.00×10^5	1.10×10^5
PLA_P-Algae _{12.5%}	3.55×10^4	6.67×10^4	6.48×10^4
PLA_P-Algae _{20%}	2.62×10^4	6.30×10^4	6.34×10^4
PLA_TTSludge _{10%}	6.34×10^4	1.18×10^5	1.22×10^5
PLA_ZnPhyt _{10%}	3.91×10^4	8.53×10^4	9.18×10^4
PLA_P-Lignin _{10%}	2.44×10^4	6.25×10^4	6.43×10^4
PLA_Biochar _{10%}	7.80×10^3	1.60×10^4	1.44×10^4

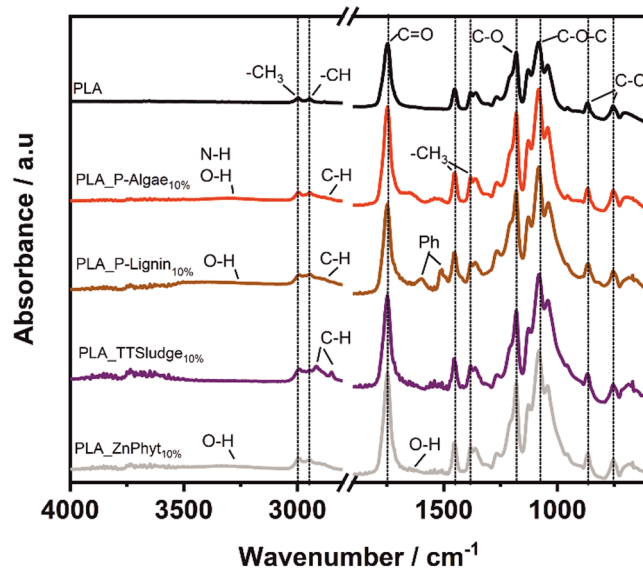


Fig. 2. FTIR spectra of PLA and its composites.

3.2. Pyrolysis

Thermogravimetric analysis was carried out under inert conditions to investigate the pyrolysis of the biocomposites. The beginning of thermal decomposition was determined by monitoring the temperature at which 5 wt.% (T_5) of mass was lost, and the maximum mass loss (T_{max}) was used as the characteristic decomposition temperature. The results obtained are summarized in Table 4.

Fig. 3A shows a comparison of the thermal decomposition and mass loss rates of biocomposites loaded with 10 wt.% fillers, and Fig. 3B of the different P-Algae concentrations in PLA. The results show that the addition of different bio-based fillers to PLA affected its thermal stability. PLA decomposes at $370\text{ }^\circ\text{C}$, while the addition of fillers to PLA decreases the thermal stability of PLA and shifts the beginning of decomposition (T_5) and (T_{max}) to lower temperatures (Fig. 3A). The addition of P-Algae changed the decomposition temperature of PLA. With 5 wt.% filler the decomposition peak occurred $4\text{ }^\circ\text{C}$ earlier, and this effect increased systematically up to $26\text{ }^\circ\text{C}$ with increasing P-Algae content. Fig. 3(B) shows a comparison of the mass loss and DTG (mass loss rate) curves for P-Algae-based biocomposites. It is observed that the addition of P-Algae systematically reduced the mass loss rate in the main decomposition step. The increase in char residue at $800\text{ }^\circ\text{C}$ is close to linearity, indicating the charring potential of P-Algae. Fig. 3B shows the

Table 4

Summary of the decomposition steps observed for PLA and its composites.

Sample	T_5 / $^\circ\text{C}$	T_{max} / $^\circ\text{C}$	ML $_{max}$ / wt. %	Residue ($800\text{ }^\circ\text{C}$) / wt. %	
				Measured	Calculated
PLA	342 ± 1	370 ± 1	94.5 ± 0.1	0.5 ± 0.1	0
PLA_P-Algae _{5%}	329 ± 1	366 ± 1	93.6 ± 0.1	1.4 ± 0.4	1.6
PLA_P-Algae _{10%}	306 ± 1	360 ± 1	92.7 ± 1.2	3.2 ± 0.1	2.8
PLA_P-Algae _{12.5%}	318 ± 1	350 ± 1	94.2 ± 0.5	3.5 ± 0.1	3.4
PLA_P-Algae _{20%}	288 ± 1	344 ± 1	88.4 ± 0.3	6.6 ± 0.1	5.2
PLA_P-Lignin _{10%}	312 ± 3	369 ± 1	84.1 ± 0.1	10.3 ± 0.5	5.8
PLA_TTSludge _{10%}	288 ± 3	329 ± 3	88.0 ± 0.5	7.0 ± 0.5	10.2
PLA_ZnPhyt _{10%}	337 ± 1	369 ± 1	86.6 ± 0.1	8.4 ± 0.2	8.5

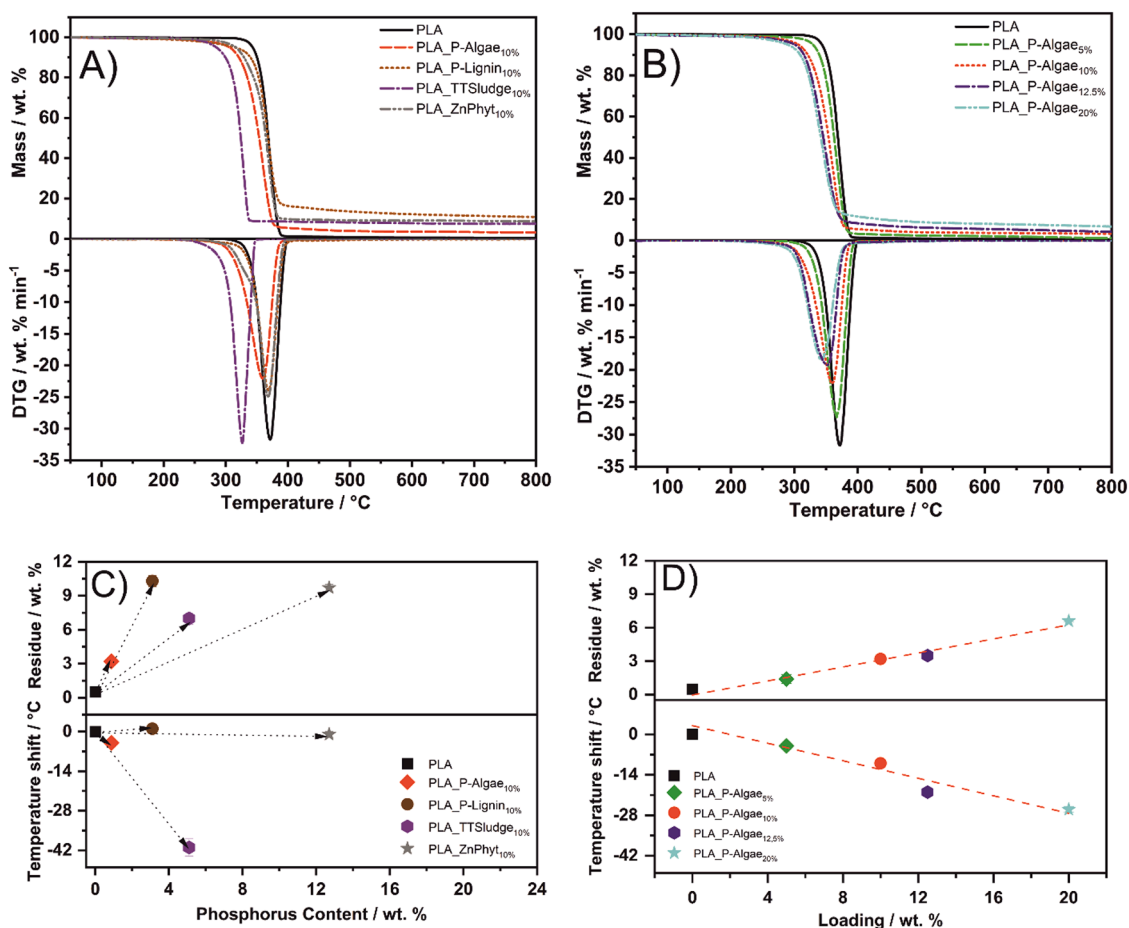


Fig. 3. Mass loss and DTG curves for PLA and its composites (A) 10 wt.% with different fillers and (B) different concentrations of P-Algae; temperatures shift at T_{\max} and residue in weight percent as a function of (C) phosphorus content in fillers and (D) P-Algae loading.

temperature shift for T_5 %, i.e., the start of decomposition. A maximum shift of -54 °C is observed at 20 wt.%, indicating that the P-Algae tend to decrease the thermal stability of the PLA matrix. The reduced thermal stability is due to the proteins, lipids, and carbohydrates, which have a lower thermal resistance than pure PLA [49].

The influence of various fillers on the thermal stability and decomposition characteristics of PLA matrices was compared systematically (Fig. 3C). P-Lignin and ZnPhyt demonstrated decomposition temperatures (T_{\max}) nearly identical to PLA, suggesting comparable thermal behavior. For the biocomposite containing ZnPhyt, the onset of decomposition occurred at 337 °C, corresponding to the decomposition of the ZnPhyt compound. The addition of ZnPhyt to the PLA matrix, due to the high phosphorus content, resulted in a greater charring tendency. The biocomposite incorporating P-Lignin exhibited a decomposition temperature akin to PLA. However, this composite displayed a higher char yield than anticipated, indicating interactions between the PLA matrix and P-Lignin. The composite with TTSludge exhibited the poorest thermal stability, manifesting a higher mass loss rate during the main decomposition step than pure PLA. The observed lower char yield, not consistent with superposition principles, suggested additional interactions between the PLA matrix and TTSludge filler during decomposition. Despite the inert nature of phosphorus within the TTSludge, it failed to impart thermal stability or promote char formation in the PLA matrix. Fig. 3C shows changes in maximum temperature (T_{\max}) and residue in wt.% as a function of P-content in fillers. The increase in residue, the decrease in thermal decomposition temperature—or in other words, the interaction between biofiller and PLA decomposition—seems to be hardly affected by the P-content. We conclude that not the amount of phosphates is important, but their reactivity.

Fig. 3D shows the increase in residue and the changes in T_{\max} as a function of P-Algae loading in PLA matrix. There is a straightforward linear dependency of residue amount and concentration of P-Algae, as well as of the temperature shift.

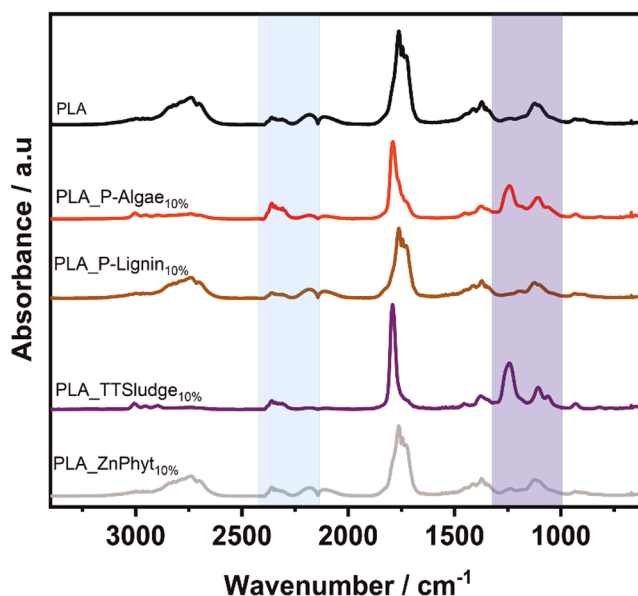


Fig. 4. FTIR spectra of evolved gaseous products at T_{\max} for PLA and its composites.

Fig. 4 shows a comparison of evolved gaseous products from the thermal decomposition of PLA and PLA-based biocomposites.

The interplay during decomposition influenced thermodynamic stability and reactivity, causing variations in onset temperatures and decomposition rates. Changes in evolved gas composition resulted in distinctive FTIR spectra modifications. Two material systems produced similar gases as PLA during pyrolysis. Fillers minimally altered PLA's primary decomposition, with differences in CO and CO₂ peak intensities. P-Algae-filled biocomposites exhibited somewhat reduced CO and hydrocarbon peaks, a tendency to elevated CO₂ intensity, and distinctive signals indicating hydrocarbons and phosphorus enriched components. P-Lignin-based composites showed decreased water, CO, and CO₂ peaks, suggesting reduced aliphatic ether compounds in volatile products. The spectra at max degradation temperature remained largely unchanged for P-Lignin-based biocomposites. In the biocomposite with metal phytate filler, similar gaseous products to PLA were observed, with a notable reduction in CO peak intensity, while CO₂ remained unchanged. A new band at 1250 cm⁻¹ indicates the presence of ν_{as} (P=O) from phytate groups. The TTSludge-filled biocomposite exhibited reduced CO, CO₂, and hydrocarbon intensities during the main decomposition step, accompanied by peaks at 1247 and 1066 cm⁻¹ from esters and sulfoxide S=O in the organic matter. A shift in carbonyl compound peaks was also noted.

The investigation of the thermal stability of biocomposites through microcalorimetry using PCFC provided valuable insights into their combustion potential. Three measurements were taken for each material, and then the average was drawn from them. Fig. 5 shows the comparison of heat release rate (HRR) curves for PLA and its composites as well as changes in the peak heat release rate (PHRR) for different phosphorus content and different P-Algae loading in PLA composites.

Single, representative curves are shown in the graph. Table 5 summarizes key results obtained from the experiments, comparing them to TGA and elucidating the impact of various bio-based fillers on the total heat evolved. The measurements were well reproducible, as indicated by the very low uncertainty.

Fig. 5. (D) Represents phenomenon of leveling off the PHRR value with increment of filler loading, also known in the literature [50].

First, the char yield as well as the peak of the release rates obtained from PCFC corresponded well with the results in TGA. The inclusion of all bio-based fillers consistently resulted in a downward trend in the total heat evolved. This reduction in heat release rate translated to diminished Heat Release Capacity (HRC), indicating an overall decrease in fire load and enhanced fire safety characteristics. Analyzing the HRR curves for bio-based composites (Fig. 5), those with 10 wt.% loaded fillers were compared. The composite with P-Algae and P-Lignin filler exhibited the lowest HRC. This reduction was attributed to a slower rate

Table 5

Summary of results obtained from PCFC determinations of PLA-based biocomposites.

Sample	Residue (wt.%)	HRC (J/gK)	THE (kJ/g)	Tmax (°C)
PLA	0.4 ± 0.1	484 ± 4	17.5 ± 0.1	389.8 ± 2.1
PLA_P-Algae ₅ %	1.5 ± 0.8	432 ± 7	16.6 ± 0.4	387.7 ± 0.4
PLA_P-Algae ₁₀ %	3.0 ± 0.1	363 ± 1	16.7 ± 0.1	383.3 ± 0.3
PLA_P-Algae _{12.5} %	3.2 ± 0.3	314 ± 5	15.8 ± 0.1	377.0 ± 0.2
PLA_P-Algae ₂₀ %	5.4 ± 0.2	289 ± 6	16.3 ± 0.3	376.2 ± 6.8
PLA_P-Lignin ₁₀ %	10.7 ± 0.1	368 ± 1	14.6 ± 0.1	392.9 ± 0.1
PLA_TTSludge ₁₀ %	6.8 ± 0.1	445 ± 4.5	16.1 ± 0.1	366.0 ± 0.7
PLA_ZnPhyt ₁₀ %	8.3 ± 0.1	428 ± 0	15.9 ± 0.1	390.9 ± 0.9

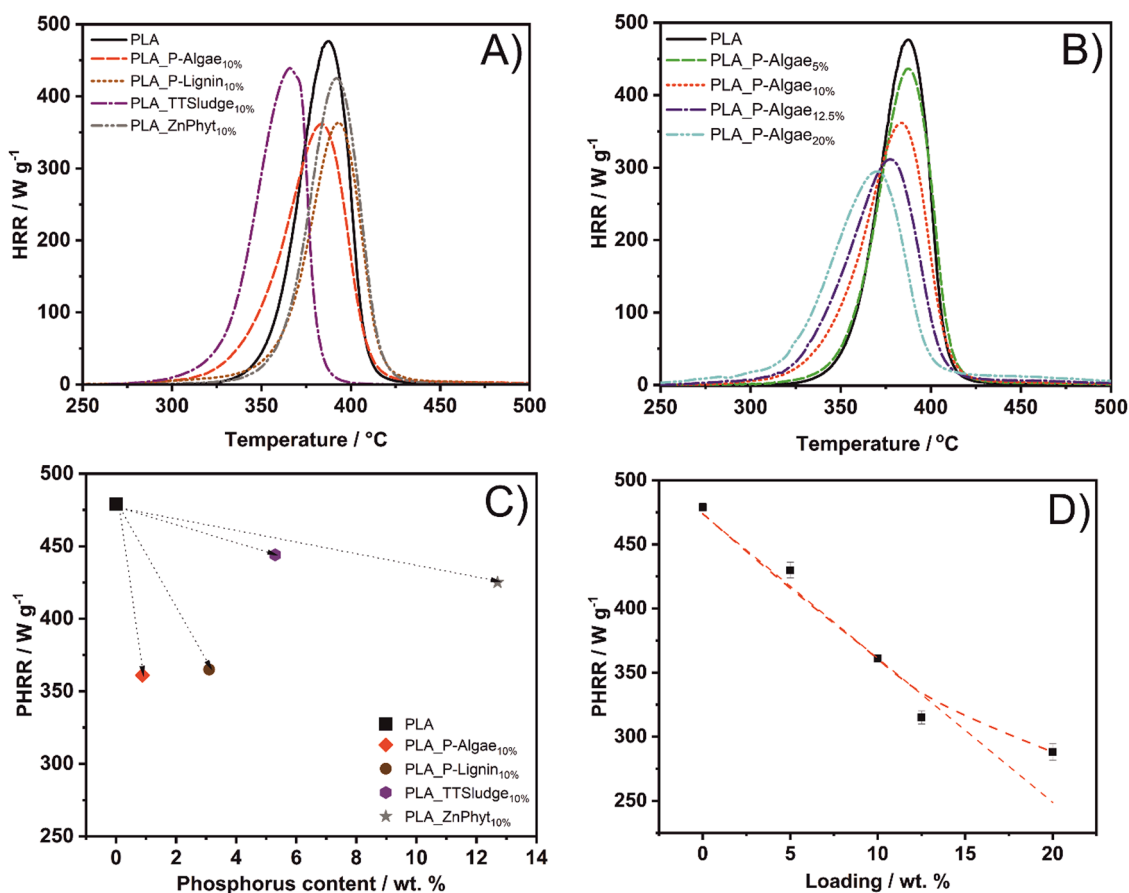


Fig. 5. Heat release rate curve of PLA and its composites with different (A) fillers at 10 wt.% loading; (B) P-Algae concentrations. Change in PHRR of PLA and its composites with (C) 10 wt.% fillers as a function of phosphorus content in fillers; (D) different P-Algae concentrations as a function of filler loading.

of material decomposition, leading to a decreased release rate of combustible volatiles, in line with the TGA results indicating a decrease in the rate of mass loss. In contrast, the biocomposite with TTSludge showed the lowest reduction in HRR, followed by the biocomposite with ZnPhyt. The diminished reduction in HRR and Total Heat Evolved (THE) was linked to fuel dilution effects by fillers and the presence of incombustible volatiles. The inclusion of P-Algae filler notably enhanced char yield compared to pure PLA, correlating with a minor decrease in the THE, attributed primarily to increased residue formation. The introduction of P-Algae resulted in the substitution of some evolved gases from PLA by other pyrolysis products possessing a lower effective heat of combustion. The composite with 20 wt.% P-Algae filler demonstrated the lowest HRC and PHRR, showcasing a nearly linear reduction, suggesting a fuel replacement effect. All of the obtained biocomposites show decomposition temperatures lower than pure PLA, which is a result of the addition of natural fillers to the polymer. DTG and PCFC analysis showed a correlation between the concentration of P-Algae in the polymer and the reduction in maximum mass loss rate and PHRR, respectively. The greater the addition of P-Algae, the lower the PHRR and peak appearance temperature of the resulting composite. Comparing these results on pyrolysis to other benchmarks, similar results were observable for materials containing P-Lignin, which increased the char yield significantly.

3.3. Fire behavior

The cone calorimeter investigation provided valuable insights into the fire behavior of PLA-based biocomposites under forced flaming fire conditions. The discussion focuses on the impact of different bio-based fillers on key parameters such as Peak Heat Release Rate (PHRR),

Total Heat Released (THR), apparent Effective Heat of Combustion (EHC), and Maximum Average Rate of Heat Emission (MARHE). Fig. 6 visualizes the obtained data. The experimental data gathered in Table 6 show some of the most important parameters that were obtained from cone calorimeter determination of biocomposites. The low uncertainty indicated a high reproducibility achieved by well compounded materials and well prepared specimens.

The addition of fillers at a 10 wt.% concentration was observed to decrease the time to ignition compared to pure PLA. This phenomenon was attributed to the earlier decomposition of biocomposites, and fillers observed in TGA, as well as to changes in heat absorption and convective thermal conduction in the molten surface layer. Fig. 5A shows the HRR results obtained for PLA and its biocomposites of the same wt.% but different fillers. The most apparent change in flame behavior is exhibited by the samples with 10 wt.% TTSludge and P-Lignin — with the first exhibiting a higher PHRR than PLA and the second a lower PHRR. In the case of the TTSludge-filled biocomposite, an increase of 21 % in PHRR occurred, and for the P-Lignin a decrease of 37 %. P-Algae and ZnPhyt are characterized by a similar decline in PHRR, with the P-Algae-based biocomposite showing a slightly reduced value for this parameter. A decrease in PHRR might be caused by charring, resulting in an effective protective layer in composites. The TTSludge material burned intensely and extinguished more quickly, consuming all the fuel, whereas the P-Lignin material showed longer and less intense burning, resulting in a longer burning time. THR analysis revealed that the least heat, and over the longest time, was released from the material containing P-Lignin, while the fastest and largest heat release occurred for the composite with TTSludge, which corresponds with TTSludge's decreasing effect on PLA in TGA. Similar but slightly lower values are observed for the PLA/ZnPhyt. The reason for the good flame retardancy effect in the P-Lignin

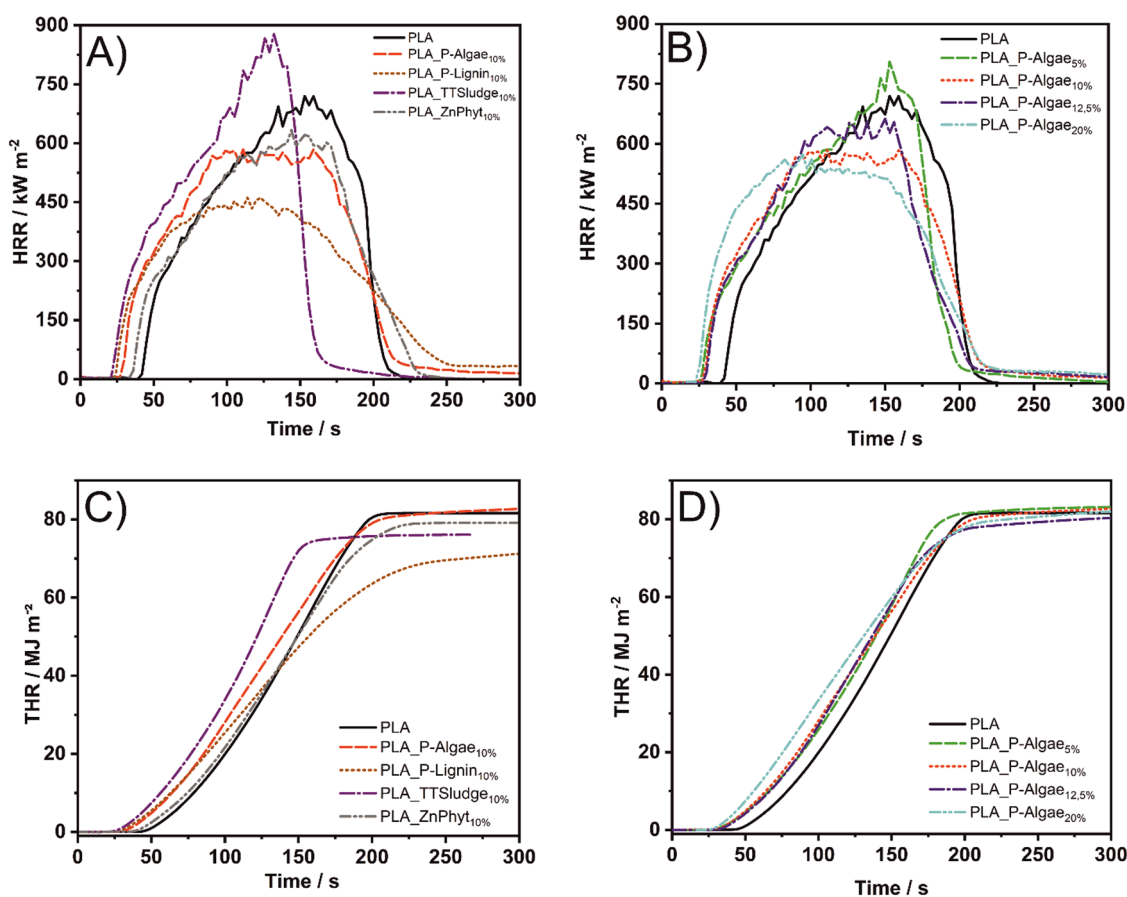


Fig. 6. Cone calorimeter plots for PLA and its composites with (A) different fillers (B) different P-Algae loading. Comparison of THR for PLA and its composites with (C) different fillers and (D) different P-Algae loading corresponding to cone calorimeter plots.

Table 6
Cone calorimeter values obtained experimentally for PLA and its composites.

Sample	t_{ig} (s)	PHRR (kW/m ²)	THE (MJ/m ²)	EHC (MJ/Kg)	Residue (wt.%)	TSP (m ²)	MARHE (kW/ m ²)
PLA	39 ± 1	736 ± 23	81.5 ± 0.5	17.6 ± 0.01	0 ± 0	0.2 ± 0.1	406 ± 2
PLA_P-Algae ₅ %	24 ± 1	791 ± 19	83.0 ± 1.2	18.0 ± 0.3	2 ± 1	0.2 ± 0.1	433 ± 1
PLA_P-Algae ₁₀ %	31 ± 6	584 ± 1	80.5 ± 0.5	18.1 ± 0.1	4 ± 1	0.7 ± 0.1	390 ± 17
PLA_P-Algae _{12.5} %	26 ± 7	697 ± 6	81.0 ± 1.1	17.6 ± 0.2	4 ± 1	1.3 ± 0.1	400 ± 6
PLA_P-Algae ₂₀ %	23 ± 1	562 ± 16	80.0 ± 0.1	18.2 ± 0.2	6 ± 1	1.9 ± 0.1	417 ± 40
PLA_P-Lignin ₁₀ %	23 ± 2	467 ± 9	69.5 ± 0.6	17.0 ± 0.5	10 ± 1	0.9 ± 0.1	328 ± 6
PLA_TTSludge ₁₀ %	20 ± 1	893 ± 23	75.0 ± 0.1	17.5 ± 0.2	9 ± 1	0.1 ± 0.1	491 ± 16
PLA_ZnPhyt ₁₀ %	38 ± 1	605 ± 2	77.5 ± 0.5	17.6 ± 0.6	9 ± 1	0.7 ± 0.1	418 ± 11

composite may be the slow release of phosphorus compounds from the decomposing P-Lignin. The combination of the release of phosphorus radicals scavenged OH and H radicals in the gas phase, and the carbonaceous char layer improved heat insulation, further reducing the pyrolyzing rate of the substrate.

Loading of the PLA with more than 5 wt.% P-Algae led to an improvement in the material's fire performance. The material containing 20 wt.% of P-Algae in PLA was characterized by the greatest decrease in PHRR, of about 27 % compared to pure PLA. The shape of the HRR curves became plateau-like, and the peak at the end of the HRR curve vanished. All PLA/Algae composites show a very similar worsening in the time to ignition. Similar THR values were observed for all PLA/Algae composites within the uncertainty margin of the THR of PLA. The fire behavior in the cone calorimeter showed similar results for P-Algae and P-Lignin biocomposites. In general, a reduction in measures such as PHRR, THE and EHC was observed, while PLA/P-Lignin exhibited the highest char yield and most efficient protective layer, followed by P-Algae.

3.4. Reaction to small flame: LOI and UL 94

The LOI is a widely employed bench scale method for assessing the flame retardancy of materials by determining the minimum oxygen concentration necessary to sustain combustion. The UL 94 measurement determines the tendency of the material to either spread the flame or extinguish once the sample has been ignited. Table 7 shows the collected LOI values, and the results obtained in the UL 94 tests.

The LOI value of pure PLA was determined to be 23.2 vol%. The LOI values obtained for biocomposites did not exhibit a significant increase compared to neat PLA. In fact, samples with TTSludge, P-Lignin and low P-Algae loading displayed LOI values below 23.2 vol%, suggesting a potential decrease in flame resistance due to increased viscosity reducing any retreat effect [51,52]. Although P-Lignin composites have shown better performance in previous measurements, here they unfortunately failed, in some contrast to expectations. This performance in LOI is attributed to the absence of effective flame inhibition or char formation in these biocomposites. Efficient flame inhibition or char formation is crucial in preventing the continuous flaming of a material. Biocomposites containing P-Algae and metal phytate salt showed higher LOI values, implying more effective flame retardancy. The success of these materials stems from their enhanced interaction with the polymer

Table 7
Fire testing of PLA and its composites via LOI and UL 94 investigations.

Sample	LOI (vol% O ₂)	UL 94 (mm/s)
PLA	23.2 ± 0.2	30.6 ± 1.8
PLA_P-Algae ₅ %	22.1 ± 0.2	31.4 ± 1.0
PLA_P-Algae ₁₀ %	25.1 ± 0.2	V-2
PLA_P-Algae _{12.5} %	24.6 ± 0.2	V-2
PLA_P-Algae ₂₀ %	24.6 ± 0.2	V-2
PLA_P-Lignin ₁₀ %	21.0 ± 0.2	14.4 ± 1.0
PLA_TTSludge ₁₀ %	22.7 ± 0.2	34.3 ± 1.0
PLA_ZnPhyt ₁₀ %	24.4 ± 0.2	V-2

matrix, facilitated release of phosphorus radicals, and consistent, dense charring during combustion. Notably, the P-Algae composites exhibit a significant increase in the LOI value. Among these, the composite containing 10 wt.% filler stands out with the most impressive performance. Moreover, all composites exhibit higher LOI values compared to PLA and those incorporating alternative flame retardants, highlighting their fire-retardant properties. Therefore, the best composite of the above mentioned is one containing between 10 and 12.5 wt.% of P-Algae in PLA. This reduction in flammability is indicative of the multifaceted nature of flame retardancy, where factors such as char formation, interaction with the polymer matrix, and chemical composition all play crucial roles. The enhanced LOI values for these biocomposites suggest that the presence of P-Algae and ZnPhyt contributed significantly to improving flame resistance. Fig. 7A illustrates the correlation of LOI and phosphorus content for different fillers, and 7B the P-Algae concentrations in PLA composites. It is interesting to note that the material containing the least phosphorus showed the greatest increase in LOI values. At the same time, the material with the most phosphorus—ZnPhyt—was the second. There is no linear relationship between phosphorus content and an increase in the LOI value. Neither do LOI values for different P-Algae concentrations in the composite exhibit a linear relationship. The 5 wt.% Algae PLA composite underperforms, as was indicated by the PHRR in the cone calorimeter, whereas 10 wt.% is the best; 10, 12.5 and 20 wt.% may mark a plateau close to LOI = 25 vol%.

The results presented in Table 7 quantify the linear burning rate (mm/min) at which the flame spreads over the sample. The UL 94 vertical test, which is the most difficult for flammable polymeric materials, showed that composites containing P-Lignin, TTSludge and 5 wt.% P-Algae did not meet the vertical test criteria. The TTSludge-filled composites exhibited the highest flame spread rate, surpassing even PLA. Thus, the results for PLA/TTSludge are very consistent, showing that it acted as a catalyst, resulting in enhanced pyrolysis and vigorous burning with intense dripping. Biocomposites containing 10 wt.% of ZnPhyt and 10, 12.5 and 20 wt.% of P-Algae passed the vertical test with a V-2 rating. The UL 94 performance and LOI are consistent. During the test flaming drips were observed; however, the charring behavior of these materials limited heat transfer and volatile release.

In response to a small flame, the addition of P-Algae resulted in an increasing LOI, with the best result for 10 wt.% P-Algae, which achieved 25.1 vol% as compared to PLA which managed 23.2 vol%. The UL 94 test allowed this material to be classified as V2. The best of the benchmarks with respect to LOI and UL 94 was the material containing ZnPhyt, with an LOI similar to P-Algae—containing biocomposites; this material passed the UL 94 classification test as V2 as well. Whereas P-Lignin and P-Algae showed superior flame retardant performance in the cone calorimeter, the LOI analysis and UL 94 test showed that biocomposites containing P-Algae and ZnPhyt improved flame-retardant properties best among the materials tested. All the investigated materials contain phosphorus in the form of phosphates; the amount differs by more than an order of magnitude, with P-Algae containing the smallest amount of phosphorus. Also, the performance of the benchmarks does not show a dependency on the P-content. It is concluded that the P-content does not determine the flame retardancy, but perhaps its

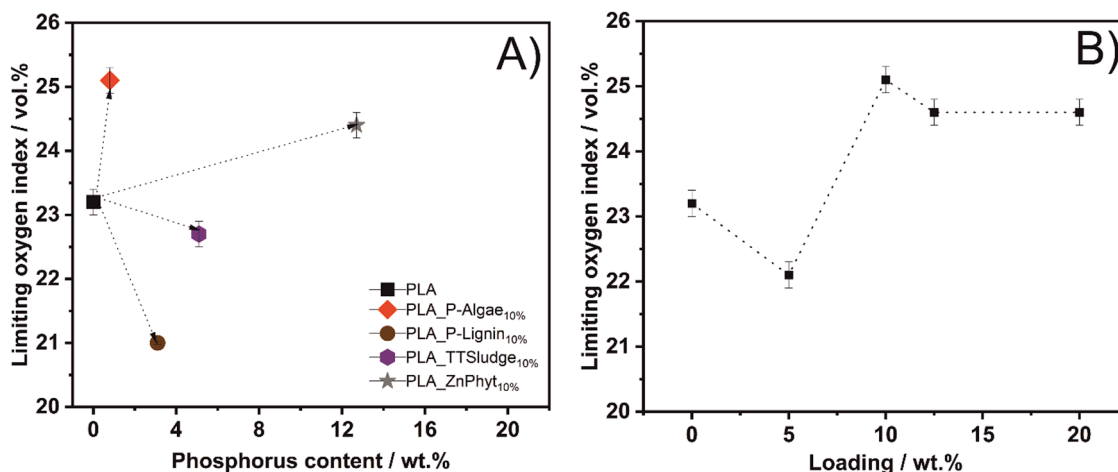


Fig. 7. LOI values of (A) PLA with 10 wt.% fillers as a function of phosphorus content in fillers and (B) PLA with different P-Algae concentrations in composites as a function of loading.

reactivity does.

4. Conclusions

This study proposes the use of P-algae for sustainable, flame-retardant PLA biocomposites. The use of wastewater as a resource addresses phosphorus scarcity and wastewater treatment needs. Biocomposites with different amounts of P-Algae between 0 and 20 wt.% were investigated. Addition of 10 wt.% P-algae resulted in the best flame retardancy effect compared to P-lignin and biochar, without significantly altering the biocomposite properties. The potential of P-Algae is underlined by the comparison with meaningful benchmarks. This research paves the way for further investigation of wastewater P-enriched algae as the most promising sustainable flame retardants.

CRedit authorship contribution statement

Mateusz Dudziak: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. **Riya Bhatia:** Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **Rohit Dey:** Writing – review & editing, Methodology, Investigation, Data curation. **Jana Falkenhagen:** Writing – review & editing, Methodology, Investigation, Data curation. **Matthias S. Ullrich:** Writing – review & editing, Supervision, Conceptualization. **Claudia Thomsen:** Writing – review & editing, Supervision, Conceptualization. **Bernhard Schartel:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing 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.

Data availability

Data will be made available on request.

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