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Effects of phosphorus-nitrogen containing flame retardants on the compostability of poly(lactic acid)

Kata E. Decsov [a,*], Bettina Ötvös [a], Lívia Lengyel [a], Dániel Gere [b], Dóra Fecske [c], Anna Petróczy [c], Béla Iván [c], Viktória Feigl [d], Mónika Molnár [d], Katalin Bocz [a]

[a] Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., Budapest H-1111, Hungary
[b] Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3., Budapest H-1111, Hungary
[c] Polymer Chemistry and Physics Research Group, Institute of Materials and Environmental Chemistry, HUN-REN Research Centre for Natural Sciences, Magyar Tudósok Körútja 2, Budapest H-1117, Hungary
[d] Department of Applied Biotechnology and Food Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., Budapest H-1111, Hungary

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ABSTRACT

Poly(lactic acid) (PLA), a versatile bio-based polyester, is valued for its industrial compostability. However, the incorporation of flame retardants (FRs) can alter its degradation behavior. In this study, PLA composites containing 15% of commonly used phosphorus- and nitrogen containing flame retardants—ammonium polyphosphate (APP), microencapsulated ammonium polyphosphate (MC-APP), and melamine polyphosphate (MPP)—were prepared and subjected to controlled aerobic composting to evaluate their disintegration and degradation behavior. Post-composting analyses using gel permeation chromatography, Fourier-transform infrared spectroscopy, thermogravimetric analysis, and differential scanning calorimetry revealed that the additives influenced the degradation kinetics but did not compromise compostability. All flame retarded PLA composites achieved complete disintegration within 21–28 days under industrial composting conditions. APP was found to leach out rapidly under composting conditions, resulting in only marginal effects on the biodegradation process, whereas the less hydrolysis-sensitive MC-APP and MPP particles were found to slightly accelerate the bio-fragmentation of the PLA's molecular chains.

Ecotoxicological evaluation of the compost, using *Sinapis alba* (white mustard) root elongation as an indicator, showed that the phytotoxicity of the examined polyphosphate flame retardants is influenced not only by their chemical structure but primarily by their solubility. Based on the EC_{20} values, the mature compost derived from flame-retarded PLA composites is expected to exhibit only limited adverse effects on compost quality under industrial composting conditions.

Overall, the results demonstrate that PLA composites containing polyphosphate-type flame retardants maintain industrial compostability, with only minor differences in degradation rate, mechanism, and compost quality compared to neat PLA.

1. Introduction

Plastics are among the most widely used materials today, with global annual production reaching approximately 400 million tons, and this figure is expected to continue rising [1]. Their versatility and low cost have made them indispensable across multiple industries. However, the rapid growth in plastic use has raised significant environmental concerns, particularly regarding end-of-life management [1]. Accumulation of plastic waste underscores the urgent need for sustainable materials, effective recycling, and waste management strategies.

In this context, biopolymers have gained increasing attention as sustainable alternatives to conventional plastics. Among them, poly (lactic acid) (PLA) is the most commonly used biopolymer: it is bio-based, as it can be produced from agricultural waste, and

* Corresponding author.
E-mail address: decsov.kata@vbk.bme.hu (K.E. Decsov).

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biodegradable under appropriate conditions. PLA's biodegradability is particularly advantageous in applications such as disposable packaging, compostable bags and utensils, and agricultural products like mulch films and plant pots, where reducing environmental impact is a key concern. At the same time, PLA is highly versatile and is increasingly used in technical fields such as the mobility sector, electronic devices, and construction materials [2–4], where its biodegradability apparently does not provide functional benefits. In these cases, the incorporation of fillers and additives, such as flame retardants, is necessary to meet performance and safety requirements. While these components are intended to remain functional during use, the inherent biodegradability of PLA may still be emphasized to minimize environmental persistence after disposal.

Phosphorus-nitrogen (P-N) containing compounds, primarily employed in intumescent flame retardant (IFR) systems, are widely used to enhance the flame retardancy of PLA [5]. In these systems, combustion leads to the formation of a carbonaceous foam layer, which inhibits the transfer of combustible gases and heat between the condensed phase and the flame [5]. In PLA composites, IFRs are typically incorporated at loadings of 10–30 wt% [6,7]. Ammonium polyphosphate (APP) and melamine polyphosphate (MPP) are commonly used IFRs, as they can simultaneously act as an acid source and a blowing agent, and possess high phosphorus content [8]. APP is often applied in a microencapsulated form to improve its compatibility with polymers and reduce water absorption, thereby enhancing its efficiency as a flame retardant [9]. Moreover, the encapsulating shell can serve as a carbonizing agent, enabling the creation of a "3-in-1" IFR system [10]. Clay minerals such as montmorillonite (MMT) and sepiolite (SEP) show synergistic effects when combined with P-N flame retardants [11–13]. At low filler contents (<3 wt%), significant anti-dripping behavior and enhanced char formation are achieved [14]. Owing to their availability and balanced flame-retardant performance, these materials are increasingly employed in a variety of PLA-based flame-retardant systems [15–17].

Flame retardants (FRs) influence a wide range of properties in polymer composites, including mechanical performance, thermal stability [18], and biodegradability [19,20]. The investigation of these properties is essential in material development, as it ensures that the effects of additives are fully understood and properly addressed. Disintegration of plastics under various conditions (sediment, seawater, compost, soil, sludge, or landfill) is generally simply assessed by monitoring the size reduction or weight loss over time [21], while biodegradation caused by biological activity is typically evaluated based on the production of CO_2 and CH_4 or the consumption of O_2 [22]. However, combining these approaches with other analytical techniques—such as gel permeation chromatography (GPC) [23,24], thermogravimetric analysis (TGA) [25], differential scanning calorimetry (DSC) [26], and Fourier-transform infrared spectroscopy (FTIR) [27]—provides a more comprehensive understanding of the degradation processes, as these methods allow for the assessment of decomposition as well as compositional and structural changes.

The effect of FRs on the biodegradability of PLA is a complex and relatively underexplored area. While certain flame retardants can inhibit PLA's biodegradation, others—particularly bio-based compounds—may promote or accelerate it. *Qiu* et al. investigated the influence of bio-derived flame retardants on the degradation behavior of PLA. Specifically, the incorporation of LC-PA/TA [28], synthesized from phytic acid (PA), L-citrulline (LC), and tannic acid (TA), as well as PA@CHTM [29], composed of chitosan microspheres (CHTM) and PA forming a core–shell structure, was found to significantly accelerate the degradation rate of PLA under outdoor soil conditions.

Although the degradation behavior of flame-retardant-containing PLA products is strongly influenced by experimental conditions, to date, no studies have attempted to simulate relevant industrial composting conditions. Furthermore, the fate of different flame retardants during composting and their potential toxicity to the resulting compost remain unclear, raising questions about the safety and quality of compost produced from these materials.

In this study, the degradability of PLA containing commonly used phosphorus and nitrogen-containing flame retardants is investigated, aiming to understand how these additives influence degradation behavior under relevant composting conditions. Moreover, the fate of the flame retardants and their potential impact on the safety and quality of the resulting compost are also addressed. The insights gained from this work are expected to guide the development of PLA-based materials that achieve an optimal balance between performance, safety, and environmental sustainability.

2. Materials and methods

2.1. Materials

PLA composite systems were prepared using Ingeo™ Biopolymer 3052D (PLA, NatureWorks LLC, U.S.) along with additives including chain extender (CE, Joncryl ADR-4468, BASF SE, Germany), and bentonite-type montmorillonite (MMT, CLOISITE® 116, BYK Additives, Germany). The used flame retardants were neat ammonium polyphosphate (APP, Exolit® AP422, P content 31.0–32.0 wt%, N content 14.0-15.0 wt%) and melamine resin microencapsulated APP (MC-APP, Exolit® AP462, P content 29.0-31.0 wt%, N content 15.0–17.0 wt%) supplied by Clariant GmbH (Switzerland), and melamine polyphosphate (MPP, Budit® 341, P content 12.0–14.0 wt%, N content of 42.0-44.5 wt %) from Chemische Fabrik Budenheim KG (Germany). Tetrahydrofuran (THF, ≥99.5%, Molar Chemicals Ltd., Halásztelek, Hungary) was used for GPC measurements without further purification.

For comparative purposes, three types of reference samples were used: virgin PLA hot-pressed from pellets (PLA-V), PLA extruded without any additive (PLA-E), and PLA extruded with the co-additives (MMT and CE) without any flame retardants (PLA-SE). The PLA-SE sample served as a critical reference point for assessing the effect of flame retardants in systems where co-additives were also present, enabling a clearer evaluation of additive interactions in the flame-retardant PLA composites. The PLA-E sample was the reference point for evaluating the effects of the co-additives, while PLA-V was a reference for the effects of thermal degradation that may occur during the extrusion. The composition of the manufactured samples is presented in Table 1.

2.2. Sample preparation

2.2.1. Extrusion

Prior to processing, both the PLA and the flame retardant additives were dried at 80°C. Compounding was carried out using an LTE 26-44 twin-screw extruder (Labtech Engineering, Thailand) featuring a modular screw design, a screw diameter of 26 mm, and a length-to-diameter (L/D) ratio of 44:1. The applied temperature profile along the extruder barrel was set to 160/160/165/165/170/170/175/175/180/180°C, and the screw speed was maintained at 80 rpm. Prior to feeding, the PLA and additives were pre-homogenized to ensure uniform dispersion. The resulting extrudate was pelletized using an LZ-120/VS (Labtech Engineering Co., Ltd., Thailand) strand pelletizer.

Table 1
The composition of the PLA samples.

Sample name	PLA [%]	MMT [%]	CE [%]	FR [%]
PLA-V	100.00	-	-	-
PLA-E	100.00	-	-	-
PLA-SE	98.25	1.50	0.25	-
PLA/APP	83.25	1.50	0.25	15.00
PLA/MC-APP	83.25	1.50	0.25	15.00
PLA/MPP	83.25	1.50	0.25	15.00

2.2.2. Compression moulding

The pellets were compressed into sheets at 180°C under a pressure of 100 bar using a P 200 E (COLLIN Lab GmbH, Germany) heated hydraulic press. For the fire tests, 130 × 130 × 3 mm^3 samples were prepared, while for composting, the pellets or compounded granules were placed into a 120 × 120 × 0.5 mm^3 steel mould. The obtained sheets were then cut to the required dimensions according to the specific test requirements.

2.3. Testing methods

2.3.1. Flammability tests

Test specimens used for flammability tests measured 100 mm in length, 10 mm in width, and 3 mm in thickness. The Limiting Oxygen Index (LOI) test was conducted per ASTM D2863 on an FTT0077 device (Fire Testing Technology, U.K.). The UL 94 flammability tests followed the ASTM D635 and D3801 standards, including horizontal and vertical configurations.

2.3.2. Composting

The compost medium composition and treatment regimen of the materials were based on the ISO 20200:2023 standard. The composting reactors were polypropylene boxes (300 × 200 × 100 mm^3) with lids and pre-drilled 5 mm diameter holes on both sides to ensure adequate aeration. The composting was performed at 58°C in a DN-63 ventilated drying cabinet (Baxter International Inc., U.S.).

Six test specimens (25 × 25 mm^2) of each composition (detailed in Table 1) were buried approximately 1 cm deep in the compost of each container. Over the course of 4 weeks, photographs were taken of a reference specimen embedded in the compost throughout the entire period. Also, samples of composted PLA were taken at regular intervals for subsequent analysis. After removal from the compost, the samples were gently wiped with ethanol to remove any residual compost material. The cleaned samples were left at room temperature to dry before measurements for at least 48 hours.

2.3.3. Gel permeation chromatography

The gel permeation chromatography (GPC) measurements were performed using a system consisting of a Waters 515 HPLC pump (Waters Co., Milford, MA, USA), a guard column, a column set composed of Waters Styragel HR1, HR3, and HR4 columns (Waters Co., Milford, MA, USA), a Jetstream II Plus thermostat, and an Agilent 1260 Infinity differential refractive index detector (Agilent Technologies, Santa Clara, CA, USA). Analyses were conducted in tetrahydrofuran (THF) at a flow rate of 0.3 mL/min and a temperature of 35°C. The chromatograms were evaluated with PSS WinGPC software applying a calibration based on narrow molecular weight distribution polystyrene standards.

The control and composted PLA samples were dissolved in THF overnight at room temperature, followed by 2 hours of heating at 50°C. After cooling, all solutions were filtered through a 0.45 µm filter. For the PLA/MPP samples, which remained highly opalescent even after heating, the solutions were first filtered through a 1.2 µm syringe filter and then through a 0.45 µm filter. In all cases, the resulting solutions were homogeneous and transparent, with a slightly yellowish color of the solutions for samples composted for several days.

2.3.4. Infrared spectroscopy (FTIR)

Fourier-transform infrared (FTIR) spectroscopy was used to analyze the chemical composition of the composted PLA samples qualitatively. The spectra were recorded using a Tensor 37 FTIR spectrometer (Bruker Corporation, U.S.) in transmission (TR) mode, as well as in attenuated total reflectance (ATR) mode with a Specac Golden Gate ATR accessory.

To ensure the comparability of spectra over time and between samples, baseline correction was made, particularly below 1800 cm^{-1}, where drift may occur. Following this, normalization was performed using a stable internal reference band, the methylene (CH_2) deformation vibration around 1454 cm^{-1}, which has been shown to remain relatively constant during degradation [30,31].

2.3.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed to examine the thermal behaviour of the samples. A TA Instruments Q5000 TGA (Waters Corporation, U.S.) system was used. The measurements were conducted in a nitrogen atmosphere (25 mL/min). Approximately 10 mg of each sample, and the temperature range was set from 50 to 800°C, with a heating rate of 10°C/min.

2.3.6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to determine the thermal transitions of the samples. Measurements were performed with a DSC 3+ instrument (Mettler Toledo, Switzerland). Approximately 10 mg of each sample was measured in an open 100 µl aluminium crucible. The thermal program consisted of three cycles: first heating from 25 to 200°C at 10°C/min, cooling from 200 to 25°C at 2°C/min, and a second heating from 25 to 200°C at 10°C/min. Data were evaluated using STAR^e Evaluation Software (Mettler Toledo, Switzerland). From the recorded heat flow data, the glass transition and melting temperatures were determined, and the degree of crystallinity of the PLA samples was calculated, considering the melting enthalpy, cold crystallization enthalpy, the theoretical melting enthalpy of 100% crystalline PLA [32], and the mass fraction of additives.

2.3.7. Ecotoxicity test (plant growth inhibition)

Sinapis alba (white mustard) is a sensitive test plant whose growth is inhibited in the presence of toxic contaminants, making it suitable for the assessment of soil and water pollution. The applied test procedure was based on the Hungarian standards HS 21976-17:1993 [33] corresponds to a simplified terrestrial plant growth inhibition assay comparable to ISO 11269-1 (Seedling emergence and growth test) [34]. Toxic effects were evaluated based on root elongation inhibition.

The base compost medium described in Section 2.3.2 was allowed to mature for 10 days prior to testing. After maturation, the compost material was air-dried at room temperature to a constant mass and homogenized. The three types of flame-retardant (FR) additives were incorporated into the dried compost at nominal concentrations of 3,000, 7,500, 15,000, and 30,000 ppm (w/w, dry matter basis). Compost without added FR served as the reference medium.

The lowest test concentration (3,000 ppm) was selected based on the FR loading (15%) of the PLA sheets and the estimated polymer amount introduced during the composting experiments, calculated from the dry mass of compost and the mass of polymer sheets added. The upper concentration was derived from the maximum polymer content permitted by composting standards combined with a worst-case additive content of 30 wt% within the polymer matrix. This calculation resulted in a theoretical maximum FR concentration of approximately 30,000 ppm in the compost, which was therefore included to ensure adequate bracketing of the EC_{20} and EC_{50} values, which represent the effective concentrations causing 20% and 50% inhibition of the measured endpoint relative to the control, respectively.

Due to the possible hydrolytic degradation of the FR additives over time, two experimental exposure scenarios were investigated. In the first test series (*fresh*), ecotoxicity was assessed using compost samples containing freshly incorporated FR additives. In the second test series (*mature*), the FR-amended compost was subjected to additional composting conditions for two weeks prior to testing in order to allow partial degradation and transformation of the additives. After this degradation period, the compost samples were used for the ecotoxicity assay under identical conditions.

For the ecotoxicity assessment, the compost samples were air-dried to constant mass, ground, and sieved, then 5.0 g portions of the additive-containing and reference compost were placed into glass Petri dishes (90 mm diameter) and evenly distributed. The compost was

moistened with 12 mL of boiled tap water. *Sinapis alba* seeds (20 seeds per dish) were placed uniformly on the compost surface. The Petri dishes were wrapped in aluminium foil to exclude light and incubated at 22°C for 72 h under dark conditions. Each treatment and the reference compost were tested in three replicates.

After the incubation period, the root lengths of individual seedlings were measured using a ruler. Root elongation inhibition was evaluated based on root length measurements and was expressed as a percentage relative to the untreated control according to the following equation:

$$I = \frac{C - S}{C} \times 100$$

where I is the inhibition of root growth expressed as a percentage, C is the mean root length of seedlings grown on the control (additive-free compost matter), and S is the mean root length of seedlings grown on the treated compost. A sigmoidal dose-response regression model using a logistic function was fitted to the concentration–response data using OriginPro (OriginPro, Version 2026, OriginLab Corporation, Northampton, MA, USA), and EC_{20} and EC_{50} values were derived from the fitted model.

3. Results and discussion

The influence of three commonly used P-N flame retardants—APP, MC-APP, and MPP—at an identical loading of 15% was investigated with respect to the fire retardancy performance and degradation characteristics of PLA under industrial composting conditions, as well as their implications for compost quality and environmental safety. In addition, the effects of melt processing and the presence of co-additives were also evaluated by analyzing suitable PLA reference materials.

3.1. Flammability testing of flame retarded PLA composites

The influence of the P-N flame retardants on the flammability characteristics of PLA was evaluated using LOI measurements and UL 94 flammability tests, respectively. The results are summarised in Table 2. The LOI value of the virgin PLA composite (PLA-V) decreased from 23% to 22% after melt processing, likely due to molecular degradation during thermomechanical treatment, but increased back to 23% upon the addition of CE and MMT co-additives, both of which are expected to increase the melt viscosity [35,36]. Considering the UL 94 testing results, all PLA references are HB-rated in the absence of flame-retardant additives; however, the extrusion process and the presence of CE and MMT additives slightly reduced the horizontal flame-spread rate.

At a 15% loading, among the flame retarded samples, PLA/MC-APP yielded the highest LOI value of 34.5%. This performance was further accompanied by a V-0 classification according to the UL 94 test. The PLA composites with 15% APP or MPP reached V-2 rating due to flaming drops of molten material that ignited the cotton below the specimens. MPP was slightly less effective than APP in reducing flammability and increasing LOI of PLA, which is associated with its lower phosphorus content and comparatively weaker condensed-phase char-forming activity [37]. Although PLA/APP and PLA/MC-APP exhibit similar LOI values, MC-APP provided a superior, V-0 UL 94 rating due to its nitrogen-containing melamine resin shell, which promotes more effective intumescent char formation and self-extinguishing behaviour during the dynamic vertical burn test.

Table 2
LOI and UL 94 results of the samples.

Sample name	LOI [%]	UL 94 classification
PLA-V	23.0	HB (v_f=29.7 mm/min)
PLA-E	22.0	HB (v_f= 26.1 mm/min)
PLA-SE	23.0	HB (v_f=23.1 mm/min)
PLA/APP	33.0	V-2
PLA/MC-APP	34.5	V-0
PLA/MPP	29.0	V-2

3.2. Investigation of the degradation behaviour of PLA during composting

In this first part, the analysis results of the PLA-V sample are presented to give an understanding of the processes occurring during composting.

3.2.1. GPC

The GPC chromatograms presented in Fig. 1 illustrate the molecular weight evolution of PLA during industrial composting over a period of 0 to 25 days. Corresponding results, such as number average molecular weights (M_n), peak molecular weight (M_p), and dispersity ($Đ$), are summarised in Table S1 of the supplementary appendix. The initial, non-composted sample (day 0) exhibits a relatively broad elution peak at lower elution volumes, corresponding to a high number average molecular weight (M_n=106,300 g/mol) polymer. After 4 and 7 days of composting, the chromatograms progressively shift toward higher elution volumes, indicating a pronounced reduction in molecular weight due to abiotic hydrolytic chain scission.

At the beginning of the composting process, the molecular weight distribution broadens and the main peak shifts to higher elution volumes, reflecting ongoing polymer degradation and the formation of lower molecular weight fractions. From approximately day 14 onward, the chromatograms largely overlap, dominated by peaks at high elution volumes, suggesting extensive depolymerization and convergence to a low molecular weight region of 3,500–4,500 g/mol. Minor shoulders and tailing observed at later stages indicate the presence of low molecular weight oligomers and heterogeneous fragments. According to the literature [38,39], PLA macromolecules in the 10,000–20,000 g/mol range become susceptible to microbial degradation, being converted into carbon dioxide, water, and humus. Accordingly, biotic fragmentation of PLA is assumed to begin around day 7, while mineralization — microbial consumption of low molecular weight oligomers — dominates by day 14.

Overall, the GPC results demonstrate rapid molecular weight reduction of PLA during the early stages of industrial composting, followed by a plateau phase at longer composting times, consistent with advanced polymer breakdown under composting conditions [23,24].

3.2.2. FTIR spectroscopy

The degradation of PLA under composting conditions proceeds through distinct stages, each marked by characteristic changes in the IR spectra recorded in ATR mode. As it is presented in Fig. 2, in the early phase (e.g., days 0–7), the intensity of the carbonyl stretching band near 1753 cm^{-1} tends to decrease, reflecting chain scission and the onset of hydrolytic fragmentation. This process leads to a breakdown of the ester backbone and the formation of shorter chains, which is accompanied by a broadening or splitting of the carbonyl region as new oxygen-containing functional groups emerge [31,40].

In the subsequent stage (approximately days 11–14), a new absorption emerges around 1600 cm^{-1}, attributed to the formation of carboxylate end groups. This change has been associated with microbial activity, where lactic acid and its oligomers on the polymer surface are metabolized by microorganisms, leaving behind ionized carboxyl groups at the ends of the polymer chains [26,27]. This spectral evolution signifies the transition from purely chemical degradation to microbially driven processes.

Later in the degradation timeline (days 18–25), further changes become evident: a pronounced increase in the free hydroxyl band near 3274 cm^{-1} [41], and the appearance of new bands around 1635 and 1543 cm^{-1}, characteristic of amide I and aminde II vibrations of proteins, which indicates the presence of microbial proteins and enzymes on the polymer surface [41]. The emergence of the broad band in the 3100–3300 cm^{-1} region, associated with O-H and N-H stretching

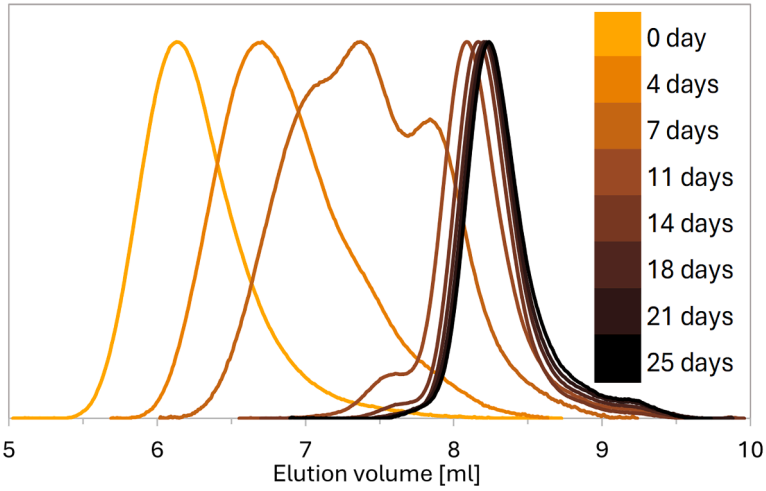

Fig. 1. GPC chromatograms of the reference PLA-V sample as a function of composting time.

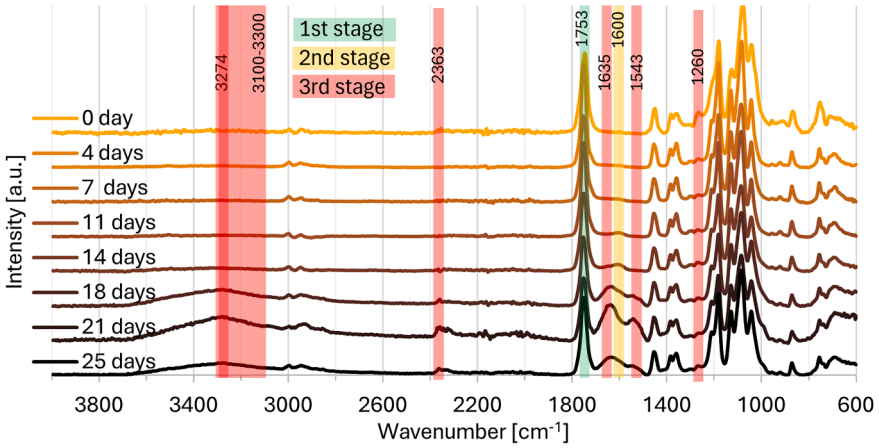

Fig. 2. ATR-FTIR spectra of the PLA-V sample over composting time.

vibrations, further supports the formation of a microbial biofilm on the sample surface [41]. These features collectively suggest advanced stages of biodegradation, including mineralization. Additionally, the emergence of a band near 2363 cm^{-1} can be linked to CO_2 evolution, supporting the conclusion that microbial activity has led to significant mineral byproduct formation [27].

The structural evolution of PLA during the composting process is illustrated schematically in Fig. 3. According to the FTIR spectroscopic results, the analysed reference PLA-V sample underwent composting degradation in accordance with previously reported literature, both in terms of behaviour and duration [39].

3.2.3. TGA and DSC analyses

The thermal properties of PLA undergo significant changes during composting as a result of hydrolytic degradation and microbial activity [25]. Fig. 4a presents the evolution of the TGA and dTG curves of the virgin PLA-V sample over the composting period, while corresponding data are given in Table S2 of the supplementay appendix. During the

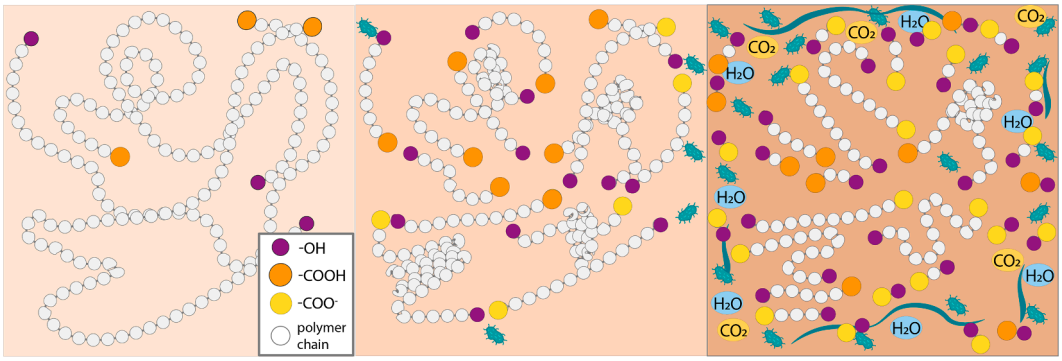

Fig. 3. Schematic representation of the degradation processes.

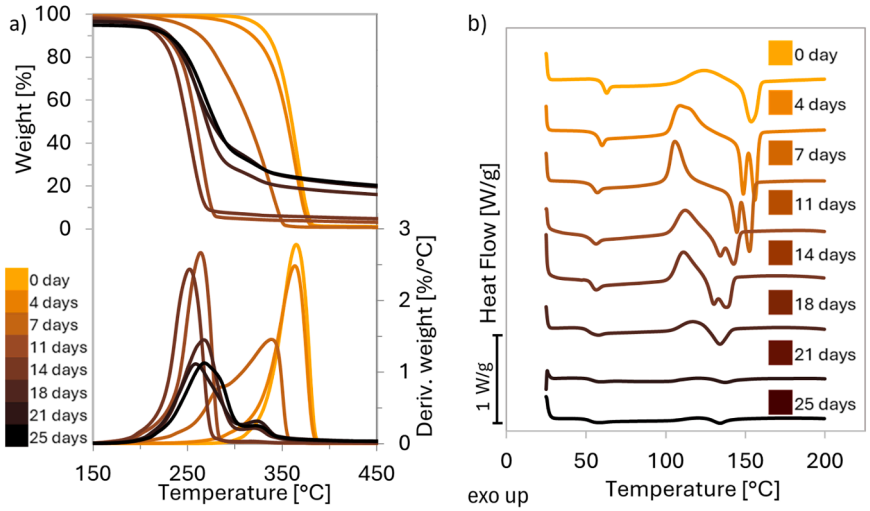

Fig. 4. (a) TGA and dTG curves; and (b) DSC curves of the PLA reference (PLA-V) material over composting time.

first 14 days, the decomposition temperature gradually decreases, indicating pronounced chain scission caused by hydrolytic degradation and bio-fragmentation. By day 18, a noticeable increase in the residual mass is observed, suggesting the onset of mineralization, which is associated with the formation of biomass by microbial action.

The evolution of the second-heating DSC curves of the PLA-V sample with increasing decomposition time is presented in Fig. 4b. The multiple melting peaks observed during 4–18 days of composting are attributed to the presence of distinct crystalline structures or lamellae with varying perfection [42]. As degradation progresses, both cold crystallization and melting temperatures decrease compared to their initial values, reflecting molecular weight reduction and structural disintegration of the polymer chains [43]. The disappearance of crystallization and melting peaks by 21 days of decomposition reflects the breakdown of PLA into smaller molecules and the consequent loss of crystalline structure.

3.3. Compostability of flame retarded PLA composites

In this second part, the influence of melt-processing and the incorporation of P-N flame retardants on the compostability and degradation behavior of PLA are presented, with complementary evaluation of the ecotoxicological impact of the resulting compost.

3.3.1. Determination of the degree of disintegration of flame retarded PLA composites under composting conditions

Photographs illustrating the physical disintegration of PLA composite sheet samples over the 28-day composting period are presented in Fig. 5. The last samples were taken at day 25; after that, there were no collectable samples present. According to ASTM D6400 [44] and ISO 20200:2023 [45], a plastic product is considered to have demonstrated satisfactory disintegration if, after 12 weeks in a controlled composting test, no more than 10% of its original dry weight remains on a 2 mm sieve. This criterion was met by all the studied PLA composites within 4 weeks. Therefore, all the studied flame-retarded PLA (FR-PLA) composites containing 15% of a polyphosphate-type additive can be considered compostable under industrial aerobic composting conditions. Depending on the composition, only minor differences in disintegration time (ranging from 21 to 28 days) were observed. Compared to virgin PLA (PLA-V), the addition of MPP appeared to slightly delay the physical breakdown of PLA into smaller fragments (Fig. 5).

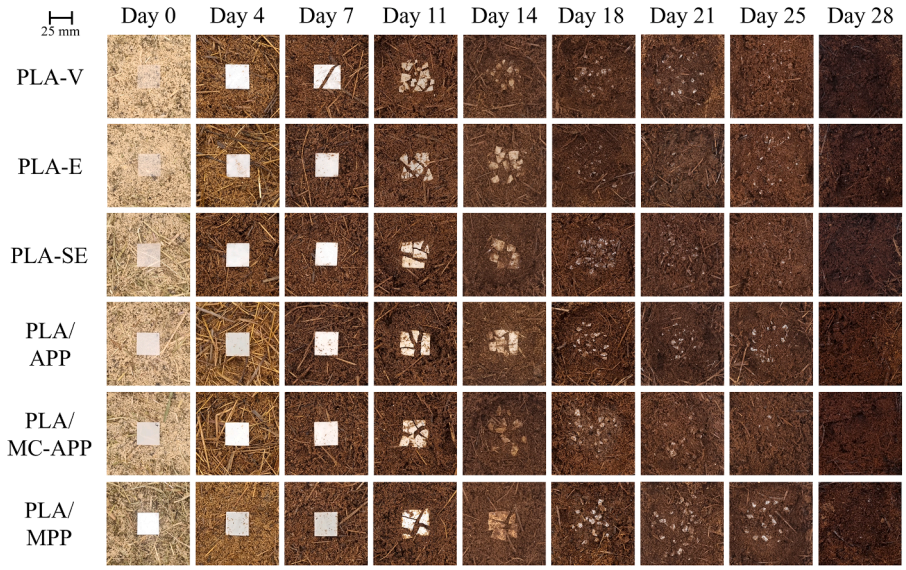

Fig. 5. Photos of the composted PLA samples over time.

3.3.2. Effect of processing on PLA's degradation

Fig. 6 shows the evolution of the number average molecular weight (M_n) of the three PLA reference materials during industrial composting over 25 days. Additional data are given in the Supplementary (Table S1). For each formulation, the '0 day' GPC measurement corresponds to the sample taken immediately after processing and prior to composting. PLA-V (hot-pressed virgin PLA) serves as the baseline for evaluating processing-induced molecular changes. All three PLA materials exhibit a rapid decrease in M_n during the early stages of composting, reflecting the expected molecular weight reduction due to significant hydrolytic chain scission. PLA-V starts with an M_n of 106,300 g/mol and shows a sharp decline within the first 11 days to 4,700 g/mol. PLA-E follows a similar trend, starting from an M_n of 105,400 g/mol to 4,900 g/mol, suggesting that melt-processing only marginally increases susceptibility to degradation. PLA-SE, containing co-additives, has the highest initial M_n of 112,800 g/mol and shows the slowest initial decrease, indicating that the crosslinks introduced by the used CE temporarily retard hydrolysis of the polymer chains. After approximately 18 days, the M_n values of all three materials converge to a low molecular weight plateau around 4,000 g/mol (Table S1), indicating extensive depolymerization and formation of oligomeric species.

The effects of extrusion processing and the addition of CE and MMT on the time-dependent evolution of the thermal characteristics of flame-retardant-free PLA samples were investigated using TGA analysis. The temperature of maximum degradation rate (T_{max}) and the residual mass at 500°C are compared as a function of composting time for the three reference samples in Fig. 7a and 7b, respectively. Accordingly, three stages of degradation can be identified [46,47]: hydrolysis-induced chain scission (0–7 days); bio-fragmentation (7–14 days), and mineralisation (14–28 days).

The temperature of maximum degradation rate (T_{max}) is initially slightly lower for the extrusion-processed reference (PLA-E), which is likely due to processing-induced degradation of the material. The PLA-SE sample yielded a higher residual mass over the composting period, which can be attributed to the presence of MMT. The MMT promotes charring of PLA and consequently increases the amount of inorganic residue [48]. The apparent increase in TGA residual mass observed after 14 days of composting (Fig. 7b), at which point PLA has already degraded to low-molecular-weight fragments (as seen in Fig. 6), is not associated with PLA decomposition products but is instead attributed to microbial biomass embedded within the softening PLA fragments (which become inseparable at advanced stages of degradation), as well as to small quantities of compost residues adhering to the surface.

Nevertheless, no noticeable shifts in the degradation stages were observed between the analysed reference samples. Hereinafter, PLA-SE, containing the same co-additives and manufactured under identical processing conditions, will be used as the reference for evaluating the performance of the flame-retarded PLA composites.

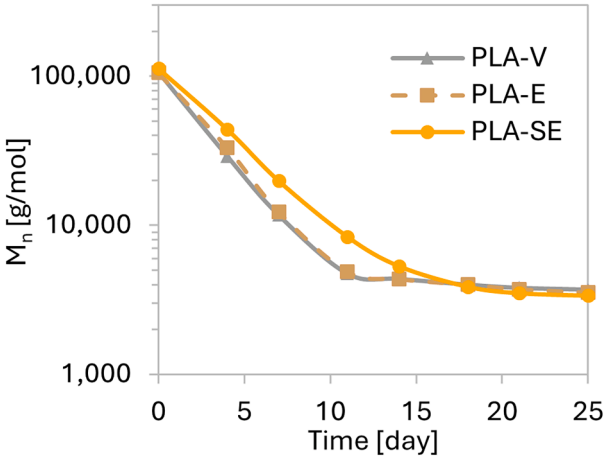

Fig. 6. Evolution of the number average molecular weight (M_n) of the reference materials over composting time.

3.3.3. GPC analysis of the composted FR-PLA samples

The evolution of the M_n of the flame-retardant-containing PLA composites during composting is presented in Fig. 8a. In the early stage of composting, all formulations show a rapid decrease in M_n, indicating intense chain scission driven by hydrolytic degradation. After approximately 14 days, the degradation rate slows, and M_n gradually decreases to about 3,000–4,000 g/mol by day 18–21, where it begins to level off. Overall, the degradation trends are similar for all formulations. Minor differences are observed during the intermediate stage (around days 7–14), where PLA/APP retains slightly higher M_n values compared to PLA/MC-APP and PLA/MPP. This indicates that chain scission of PLA proceeds somewhat faster in the presence of MC-APP and MPP, while APP does not cause any noticeable change compared to the reference sample (PLA-SE).

Fig. 8b presents the molecular weight distribution of PLA-SE and the flame-retardant containing PLA composites after 7 days of composting. All samples display a predominantly multimodal distribution centered in the mid-to-high molecular weight range (10^4–10^5 g/mol), indicating that, despite significant degradation, a considerable fraction of polymer chains remains within this range after one week. However, distinct differences are apparent in the low-molecular-weight region. The reference sample (PLA-SE) and PLA/APP show a comparable, relatively symmetric, and narrower distribution, suggesting more uniform bulk hydrolysis, suggesting that APP does not noticeably accelerate early-stage degradation under the investigated conditions. In contrast, PLA/MC-APP and PLA/MPP exhibit broader distributions with noticeable shoulders extending toward lower molecular weights (10^3–10^4 g/mol). This behaviour indicates enhanced chain scission and increased formation of oligomeric fragments, reflecting a less homogeneous degradation process.

Based on the GPC results, MC-APP and MPP appear to promote earlier or more heterogeneous fragmentation, possibly due to localized acidic effects during hydrolysis. Nevertheless, by the end of the composting period, all samples converged to similar molecular weight values. It can be concluded that the presence of the investigated phosphorus- and nitrogen-containing flame retardants does not significantly alter the long-term molecular weight reduction behaviour of PLA under industrial composting conditions.

3.3.4. TGA analysis of the composted FR-PLA samples

The effect of phosphorus- and nitrogen-containing flame retardants on the degradation process was monitored through changes in thermal characteristics obtained from TGA analyses over the composting period. The temperature corresponding to the maximum degradation rate and the residual mass at 500°C as a function of composting time are presented in Fig. 9a and b, respectively. As seen in Fig. 9a, the decrease of T_{max} occurs somewhat later for the FR containing PLA composites, around 11-14 days, compared to the reference PLA-SE sample. Based on the GPC results presented in Fig. 8, the change in T_{max} is not primarily due to variations in molecular weight but rather to char formation from the polyphosphate-type flame retardants during TGA, which acts as a protective barrier and effectively stabilizes the polymer against further high-temperature decomposition.

The char-promoting effect of the used polyphosphate-type FRs is also indicated by the noticeable residue (13–15%) inherently formed from the FR-containing PLA composites (Fig. 9b). The decreasing amount of charred residue over the first 14 days indicates a reduction in phosphorus-containing species, suggesting the leaching or decomposition of the used P-N flame retardant additives under composting conditions. By day 14, an increase in residual mass is observed, suggesting the onset of mineralization associated with biomass formation through

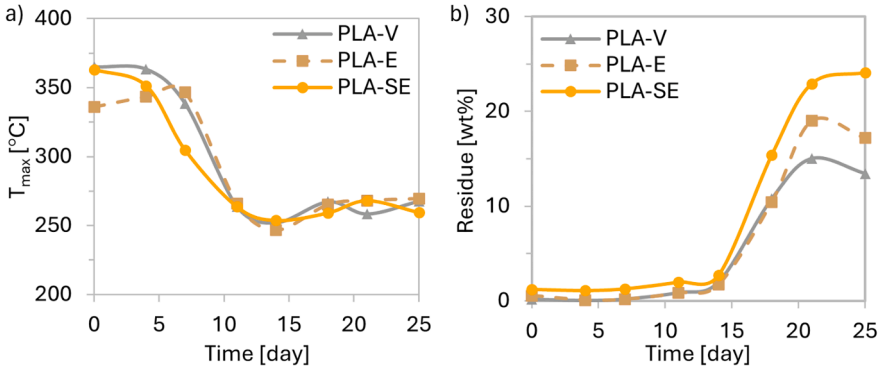

Fig. 7. TGA results of the composted reference materials; a) temperature of the maximal degradation speed (T_{max}); b) residue of the samples at 500°C.

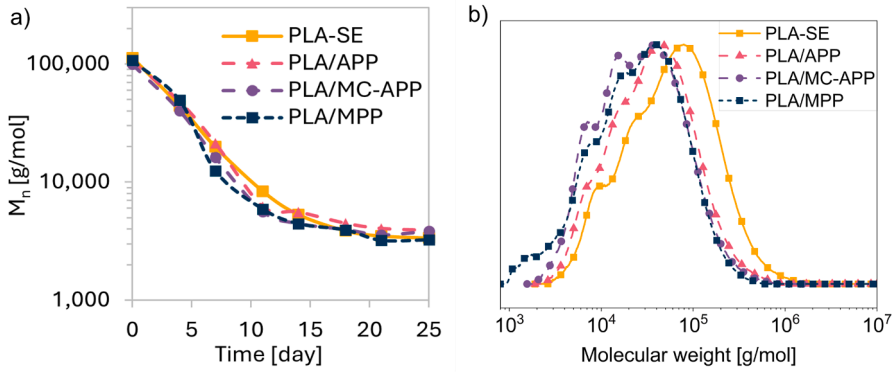

Fig. 8. (a) Evolution of M_n of the flame retardant-containing PLA composites over composting time and (b) Molecular weight distribution at day 7 of the PLA composites.

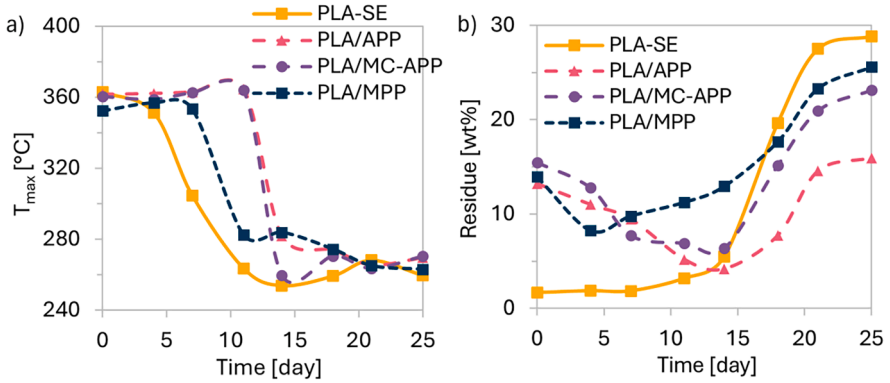

Fig. 9. (a) Temperature of the maximal degradation speed (T_{max}), and (b) the residue at 500°C of the TGA measurements of the composted FR PLA samples.

microbial activity, similarly to the results of others [39,49,50]. This process is most pronounced in the FR-free reference sample. It is presumed that the decomposition products of the polyphosphates increase soil acidity, which in turn reduces microbial activity.

3.3.5. *DSC analysis of the composted FR-PLA samples*

The changes in the transition temperatures and crystallinity of the FR-containing composites over the composting period are presented in Fig. 10 and Fig. 11, respectively. As can be seen in Fig. 10, the transition temperatures show similar trends across the different PLA-based formulations throughout the composting period. Considering the melting temperature ($T_{melting}$) (Fig. 10a), the three stages of biodegradation [51] can be clearly distinguished. The first stage, occurring between 0 and 7 days, involves hydrolytic chain cleavage, where the polymer chains begin to break down through hydrolysis. Following this, between 7 and 14 days, bio-fragmentation takes place, which is influenced by both abiotic factors, such as temperature and moisture, and biotic factors like microbial activity. Finally, after 14 days, the process of mineralization occurs, during which the fragmented polymers are further broken down and converted into inorganic substances like carbon dioxide, water, and biomass by microorganisms. The glass transition temperature (T_g) of the samples shows a progressive decrease during degradation (Fig. 10b), dropping by approximately 10°C after 14 days. This decline reflects the reduction of the amorphous phase and an increase in chain mobility, which can be attributed to molecular weight reduction as well as the potential plasticizing effect of degradation byproducts, such as lactic

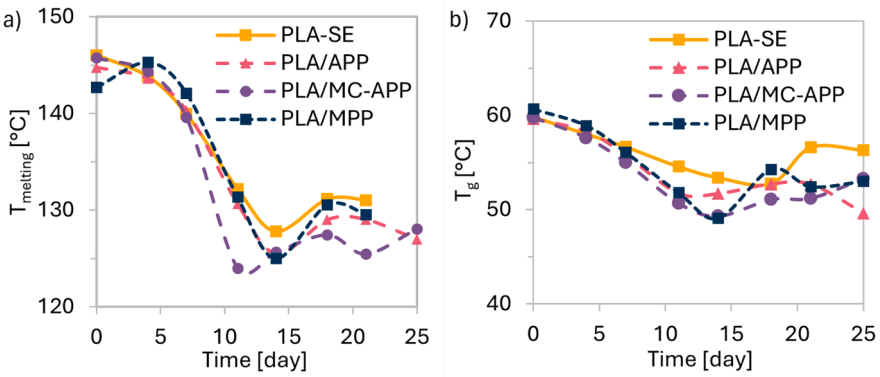

Fig. 10. (a) Melting- and (b) glass transition temperatures from the 2nd heating cycle of the DSC measurements of the FR PLA samples.

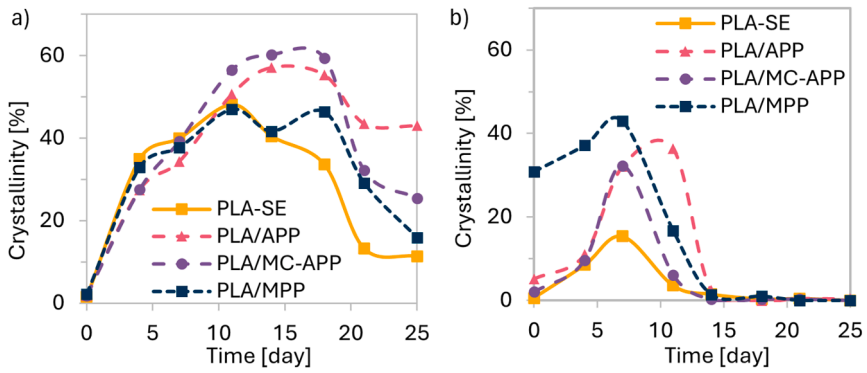

Fig. 11. Crystallinity values from the heating DSC cycles of the FR samples obtained from (a) 1st cycle, and (b) 2nd cycle.

acid oligomers [26].

As shown in Fig. 11a, the crystallinity of the initially almost fully amorphous PLA composites rapidly reaches the 27–30% level by the 4th day of composting and further continues to rise. The PLA/APP and PLA/MC-APP samples reached 60% crystallinity by the 18th day, while the other samples (PLA-SE, PLA/MPP) reached the maximum crystallinity value at approximately 50%. This sharp increase in crystalline fraction results from the selective degradation of the amorphous regions, which are more accessible to hydrolytic and microbial attack [52]. As these amorphous regions are the first to degrade, the relative proportion of more resistant crystalline regions increases [53]. The subsequent decline in measured crystallinity after about 18 days reflects the onset of structural breakdown within the crystalline domains themselves and the progression toward mineralization.

A noticeable decline in crystallinity after the 7th day, as determined from the second DSC heating cycle (Fig. 11b), suggests that the biofragmentation process progressively penetrates the crystalline domains as well. In this stage, the degradation no longer affects only the more accessible amorphous regions but also disrupts the intermolecular interactions within the crystalline lattice. This structural "erosion" of the crystalline phase becomes evident only upon the second heating cycle, where the reduced capacity for recrystallization reflects the ongoing chain scission and molecular weight decrease. These findings are in good agreement with the TGA results, which show a concomitant reduction in thermal stability starting from day 7. Based on the crystalline fractions determined from the second heating cycle, a nucleating effect of MPP particles can be assumed. In summary, the DSC results indicate that the polyphosphate-type flame retardants used do not significantly affect the structural changes of PLA during composting.

3.3.6. FTIR spectroscopy of the composted FR-PLA samples

The characteristic degradation stages – namely, hydrolytic fragmentation, microbial scission, and eventual mineralization – are identifiable in the FR-containing PLA composites through distinct changes observed in the ATR-FTIR spectra (Supplementary Figs. S1-6) collected from the composite surfaces. The timing and progression of these stages only slightly varied depending on the sample composition.

Nevertheless, because ATR-FTIR primarily probes surface chemistry, the bulk composition of the composites, particularly in the presence of FR additives, was further investigated using transmission-mode FTIR (TR-FTIR) with KBr pellets. Fig. 12 shows the changes in the fingerprint region (1600–400 cm^{-1}) of the TR-FTIR spectra of FR-containing PLA composites over the course of the first 14 days of composting. The broader absorption bands (e.g., the pronounced broadening of the C-O stretching band around 1000–1200 cm^{-1}) observed in the TR-FTIR spectra likely result from particle size effects and enhanced light scattering within the KBr pellet. Analysing the spectra, it was found that the intensity of the vibrational bands corresponding to the polyphosphate flame retardants, such as the P-O-P bending vibration at 802 cm^{-1} and 780 cm^{-1} in APP and MPP respectively, and the symmetric deformation vibration of P=O in PO_4^{3-} at around 480 cm^{-1} [54,55], gradually decrease over time and even disappear by the 14th day of composting. It was therefore concluded that the flame retardants themselves undergo hydrolysis and degradation under composting conditions. This conclusion is consistent with the assumption drawn from the evolution of TGA residues (Fig. 9b).

3.3.7. Ecotoxicity assessment of the additives in the compost media

Fig. 13 presents the effect of FR additives at different concentrations on the root elongation of *Sinapis alba* plant seedlings in the different compost media, comparing freshly incorporated additives (Fig. 13a)

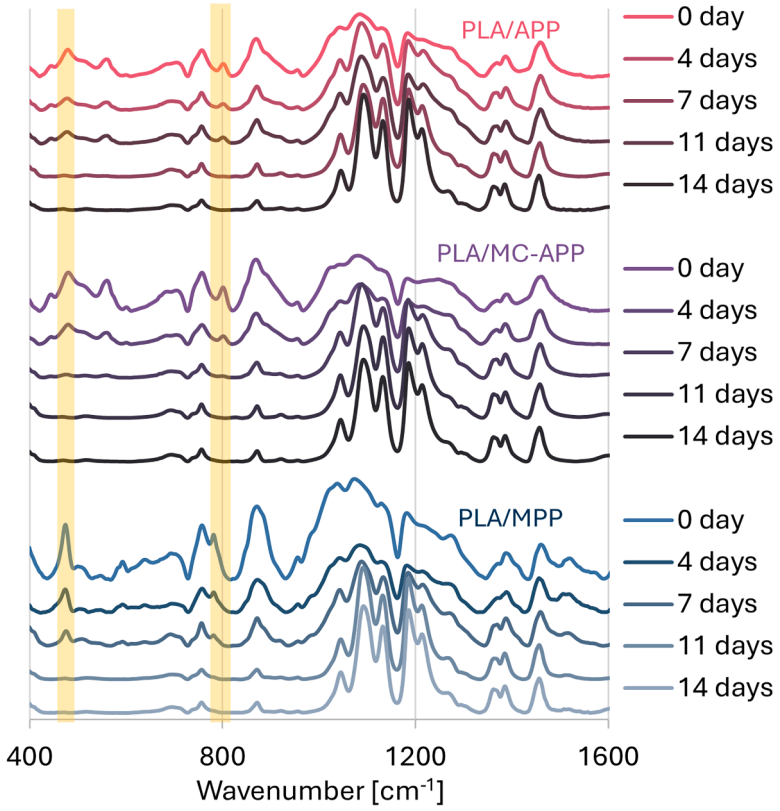

Fig. 12. TR-FTIR spectra of FR-containing PLA composites over the course of the first 14 days of composting. PLA/APP, PLA/MC-APP, and PLA/MPP.

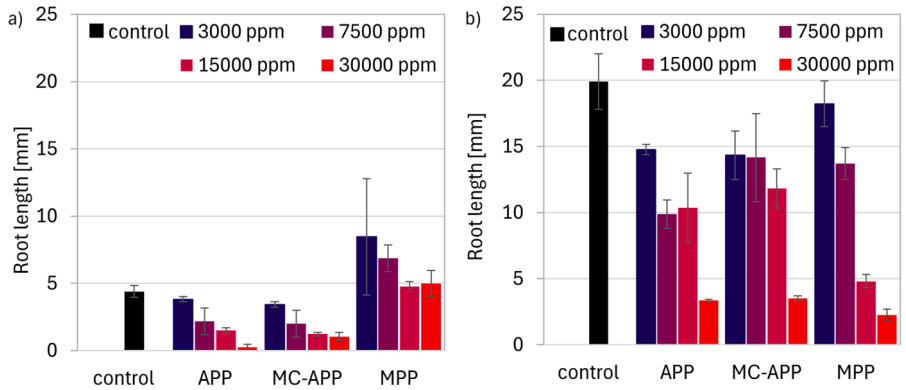

Fig. 13. Root elongation of *S. alba* in compost medium: (a) with freshly incorporated FR additives, and (b) with FR additives matured for two weeks.

with those matured for two weeks (Fig. 13 b). In the non-treated control compost, root growth was moderate before further maturation (around 4–5 mm), but increased to approximately 20 mm after the two-week ageing period. This indicates that the compost medium becomes more supportive for plant growth over time, likely due to the breakdown of phytotoxic compounds and improved nutrient availability during maturation. After maturation, almost all treatments demonstrated noticeable improvement in root growth, except MPP at the higher concentrations of 15,000 and 30,000 ppm, compared with the corresponding fresh samples.

Before maturation, root length decreased progressively with increasing concentrations of both APP and MC-APP. At 3,000 ppm, APP was comparable to the control, while MC-APP showed slightly stronger (22%) inhibition, indicating minimal phytotoxicity at this level. However, at the highest concentrations (30,000 ppm), root development was strongly inhibited (~75–85% reduction vs. control), with both APP- and MC-APP-treated seedlings showing very short roots. This pattern demonstrates a clear dose-dependent phytotoxic effect of both APP and MC-APP, with the two additives exerting broadly comparable inhibitory effects at the same nominal concentration, likely arising from high ionic strength or osmotic stress induced by polyphosphate salts [56,57]. Thus, the chemical modification of APP into MC-APP did not lead to a consistent increase or decrease in phytotoxicity under the tested conditions.

In contrast, MPP-treated seedlings showed a different response when freshly incorporated into the compost. At lower concentrations (3,000 and 7,500 ppm), root growth was comparable to or exceeded that of the untreated control. Even at higher concentrations (15,000–30,000 ppm), root growth remained ~2–3 times longer than in equivalent APP or MC-APP treatments, indicating substantially lower phytotoxic effect. This pattern likely reflects the lower solubility of MPP, which limits its availability in the growth medium and reduces stress on the seedlings,

while slowly released phosphate species may provide a gradual nutrient benefit. This is supported by the maturation results: these advantages largely disappeared, and at concentrations above 7,500 ppm, MPP showed more severe inhibition than APP or MC-APP.

The EC_{20} and EC_{50} values determined for the three tested FR additives in both freshly incorporated and matured form are summarised in Table 3. As shown, the EC_{20} and EC_{50} values for APP and MC-APP approximately doubled after prolonged residence time in the compost matrix. This means that higher concentrations were required to induce the same level of inhibition in *S. alba* root growth, indicating a reduction in ecotoxicological impact with ageing. This can be attributed to the progressive compost stabilization during maturation, where humification, hydrolysis, microbial activity, and physicochemical transformations decrease additive bioavailability. Mature organic matter better binds toxic constituents, while labile compounds degrade or dissipate. To our knowledge, this is the first report of polyphosphate FR's ecotoxicity in compost media; prior studies examined these compounds only in aqueous solution and focused on single formulations [58–60].

In contrast, an opposite effect was observed for MPP. In fresh compost, MPP exhibited a stimulatory (nutrient-like) effect on the root growth even at the highest tested concentration (30,000 ppm). However, in mature compost, a low-effect concentration (EC_{20}) of 5,500 ppm was determined, indicating the onset of phytotoxicity. This aligns with MPP's low water solubility: limited dissolution restricts fresh bioavailability, but composting conditions promote hydrolytic degradation, releasing more soluble products that become inhibitory.

Overall, the results of the ecotoxicity tests highlight that both the chemical composition and solubility of the used P-N flame retardant additives play crucial roles in their phytotoxicity, with potential implications for their safe application in industrial composting. Mature EC_{20} values of the investigated FR additives determined in mature compost are close to or higher than the concentration (3,000 ppm) of flame retardants present in the composting experiment with flame-retarded PLA composites. This indicates that the levels applied during composting were below the threshold required to induce a 20% inhibition of *S. alba* root growth. Thus, only limited inhibitory effects on compost biota and quality can be expected, particularly in mature compost.

4. Conclusions

Under simulated industrial composting conditions, the degradation of both additive-free and flame-retarded PLA composites was effectively monitored using GPC, TGA, DSC, and FTIR spectroscopic methods; furthermore, the effect of the additives on the compost was assessed through plant growth inhibition tests.

The results indicate that PLA composites modified with commonly used P-N flame retardants such as APP, MC-APP, and MPP can be considered compostable under industrial aerobic composting conditions. Depending on their composition, only minor differences were observed in the physical disintegration time (25–28 days) of the analyzed composites.

However, the presence of polyphosphate-type flame retardants influenced the degradation behaviour of PLA, particularly affecting the onset and duration of the decomposition phases. GPC analyses revealed that the presence of MC-APP and MPP particles slightly increased the susceptibility of PLA to hydrolytic and microbial attack, while APP did not markedly accelerate early-stage degradation. Residual mass analysis and the time-related progression of FTIR spectra indicated that the applied polyphosphate-type flame retardants degraded and possibly leached out during the early stages of the composting process.

The ecotoxicity assessment of the compost media, based on *S. alba* root elongation, indicated that the phytotoxic effects of the tested P-N flame retardants are influenced by both their chemical composition and water solubility. As the EC_{20} values determined in mature compost were at or above the applied concentration (3,000 ppm) used in the PLA composting experiment, the matured compost media are expected to exhibit at most limited to moderate ecotoxic effects under the investigated industrial composting conditions.

Table 3
EC_{20} and EC_{50} values of the fresh and mature additive containing compost materials.

	APP	MC-APP	MPP
EC_{20} fresh	3643 ± 369	2095 ± 588	-*
EC_{50} fresh	7879 ± 448	7953 ± 1026	-*
EC_{20} mature	2151 ± 757	3838 ± 1411	5504 ± 465
EC_{50} mature	9412 ± 1469	13674 ± 2612	9979 ± 494

* MPP exhibited not an inhibitory, but a stimulatory effect in the tested range

Overall, the phosphorus- and nitrogen-containing flame retardants examined in this study provided both effective fire safety performance and sustainable degradability to PLA composites. Their incorporation enables the development of fire-safe, PLA-based biocomposite systems that are fully compatible with the principles of the circular economy.

CRediT authorship contribution statement

Kata E. Decsov: Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Bettina Ötvös:** Writing – review & editing, Investigation, Formal analysis. **Lívia Lengyel:** Writing – original draft, Investigation, Formal analysis. **Dániel Gere:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization. **Dóra Fecske:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Anna Petróczy:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Béla Iván:** Writing – review & editing, Methodology, Investigation, Data curation. **Viktória Feigl:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Mónika Molnár:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Katalin Bocz:** Writing – original draft, Validation, Supervision, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Kata E Decsov reports financial support was provided by Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund. Katalin Bocz reports financial support was provided by Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund. Viktória Feigl reports financial support was provided by Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund. Mónika Molnár reports financial support was provided by Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund. Bettina Ötvös reports financial support was provided by National Research Development and Innovation Fund of the Ministry of Culture and Innovation and the Budapest University of Technology and Economics. Dániel Gere reports financial support was provided by Hungarian Academy of Sciences. If there are other authors, they 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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2026.112085.

Data availability

Data will be made available on request.

References

[1] B.P.S. Gautam, A. Qureshi, A. Gwasikoti, V. Kumar, M. Gondwal, Global scenario of plastic production, consumption, and waste generation and their impacts on environment and human health. Advanced Strategies for Biodegradation of Plastic Polymers, Springer Nature Switzerland, Cham, 2024, pp. 1–34, https://doi.org/10.1007/978-3-031-55661-6_1.

[2] R. Aguirresarobe, I. Calafel, S. Villanueva, A. Sanchez, A. Agirre, I. Sukia, A. Esnaola, A. Saralegi, Development of flame-retardant polylactic acid formulations for additive manufacturing, Polymers 16 (2024) 1030, https://doi.org/10.3390/polym16081030 (Basel).

[3] Y. Yang, L. Haurie, D.Y. Wang, Bio-based materials for fire-retardant application in construction products: a review, J. Therm. Anal. Calorim. 147 (2022) 6563–6582, https://doi.org/10.1007/s10973-021-11009-5.

[4] H. Ridard, J. Duvigneau, T. Mayer-Gall, W. Ali, F.R. Wurm, Biobased flame-retardant polylactic acid foams through lignin-based nanocarriers encapsulating deoxyribonucleic acid, ACS Sustain. Chem. Eng. 12 (2024) 14866–14878, https://doi.org/10.1021/acssuschemeng.4c05886.

[5] G. Fontaine, S. Bourbigot, Intumescent polylactide: a nonflammable material, J. Appl. Polym. Sci. 113 (2009) 3860–3865, https://doi.org/10.1002/app.30379.

[6] B. Tawiah, B. Yu, B. Fei, Advances in flame retardant poly(lactic acid), Polymers 10 (2018) 876, https://doi.org/10.3390/polym10080876 (Basel).

[7] T.T. Nguyen Thanh, Z. Yusifov, B. Tóth, K. Bocz, P. Márton, Z. Hórvölgyi, G. Marosi, B. Szolnoki, Preparation and characterization of microencapsulated ammonium polyphosphate with polyurethane shell and its flame retardance in polypropylene, Fire 7 (2024), https://doi.org/10.3390/fire7030097.

[8] J. Alongi, Z. Han, S. Bourbigot, Intumescence: tradition versus novelty. A comprehensive review, Prog. Polym. Sci. 51 (2014) 28–73, https://doi.org/10.1016/j.progpolymsci.2015.04.010.

[9] L. Liu, Y. Zhang, L. Li, Z. Wang, Microencapsulated ammonium polyphosphate with epoxy resin shell: preparation, characterization, and application in EP system, Polym. Adv. Technol. 22 (2011) 2403–2408, https://doi.org/10.1002/pat.1776.

[10] S. Peil, R. Mouhoubi, R. Streekstra, H. Ridard, L. Veith, W. Ali, T. Mayer-Gall, J. Duvigneau, F.R. Wurm, Encapsulation of ammonium polyphosphate in lignin nanocontainers enhances dispersion and flame retardancy in polylactic acid foams, ACS Appl. Polym. Mater. 6 (2024) 6096–6107, https://doi.org/10.1021/acsapm.4c00787.

[11] S. Li, H. Yuan, T. Yu, W. Yuan, J. Ren, Flame-retardancy and anti-dripping effects of intumescent flame retardant incorporating montmorillonite on poly(lactic acid), Polym. Adv. Technol. 20 (2009) 1114–1120, https://doi.org/10.1002/pat.1372.

[12] N.A. Isitman, C. Kaynak, Nanostructure of montmorillonite barrier layers: a new insight into the mechanism of flammability reduction in polymer nanocomposites, Polym. Degrad. Stab. 96 (2011) 2284–2289, https://doi.org/10.1016/j.polymdegradstab.2011.09.021.

[13] G. Tang, D. Deng, J. Chen, K. Zhou, H. Zhang, X. Huang, Z. Zhou, The influence of organo-modified sepiolite on the flame-retardant and thermal properties of intumescent flame-retardant polylactide composites, J. Therm. Anal. Calorim. 130 (2017) 763–772, https://doi.org/10.1007/s10973-017-6425-y.

[14] T.T. Nguyen Thanh, B. Szolnoki, D. Vadas, M. Nacsa, G. Marosi, K. Bocz, Effect of clay minerals on the flame retardancy of polylactic acid/ammonium polyphosphate system, J. Therm. Anal. Calorim. 148 (2023) 293–304, https://doi.org/10.1007/s10973-022-11712-x.

[15] D. Vadas, T. Igricz, J. Sarazin, S. Bourbigot, G. Marosi, K. Bocz, Flame retardancy of microcellular poly(lactic acid) foams prepared by supercritical CO2-assisted extrusion, Polym. Degrad. Stab. 153 (2018) 100–108, https://doi.org/10.1016/j.polymdegradstab.2018.04.021.

[16] K. Bocz, M. Domonkos, T. Igricz, Á. Kmetty, T. Bárány, G. Marosi, Flame retarded self-reinforced poly(lactic acid) composites of outstanding impact resistance, Compos. Part A Appl. Sci. Manuf. 70 (2015) 27–34, https://doi.org/10.1016/j.compositesa.2014.12.005.

[17] Y. Guo, C.C. Chang, M.A. Cuiffo, Y. Xue, X. Zuo, S. Pack, L. Zhang, S. He, E. Weil, M.H. Rafailovich, Engineering flame retardant biodegradable polymer nanocomposites and their application in 3D printing, Polym. Degrad. Stab. 137 (2017) 205–215, https://doi.org/10.1016/j.polymdegradstab.2017.01.019.

[18] W.S. Chow, E.L. Teoh, J. Karger-Kocsis, Flame retarded poly(lactic acid): a review, Express Polym. Lett. 12 (2018) 396–417, https://doi.org/10.3144/expresspolymlett.2018.34.

[19] M. Maqsood, G. Seide, Biodegradable flame retardants for biodegradable polymer, Biomolecules 10 (2020) 1–23, https://doi.org/10.3390/biom10071038.

[20] X.M. Yang, S. Qiu, A. Yusuf, J. Sun, Z. Zhai, J. Zhao, G.Z. Yin, Recent advances in flame retardant and mechanical properties of polylactic acid: a review, Int. J. Biol. Macromol. 243 (2023) 125050, https://doi.org/10.1016/j.ijbiomac.2023.125050.

[21] S.V. Afshar, A. Boldrin, T.F. Astrup, A.E. Daugaard, N.B. Hartmann, Degradation of biodegradable plastics in waste management systems and the open environment: a critical review, J. Clean. Prod. 434 (2024) 140000, https://doi.org/10.1016/j.jclepro.2023.140000.

[22] P.A. Withana, X. Yuan, D. Im, Y. Choi, M.S. Bank, C.S.K. Lin, S.Y. Hwang, Y.S. Ok, Biodegradable plastics in soils: sources, degradation, and effects, Environ. Sci. Process. Impacts 27 (2025) 3321–3343, https://doi.org/10.1039/D4EM00754A.

[23] E. Trofimchuk, V. Ostrikova, O. Ivanova, M. Moskvina, A. Plutalova, T. Grokhovskaya, A. Shchelushkina, A. Efimov, E. Chernikova, S. Zhang, V. Mironov, Degradation of structurally modified polylactide under the controlled composting of food waste, Polymers 15 (2023) 4017, https://doi.org/10.3390/polym15194017 (Basel).

[24] V. Mironov, E. Trofimchuk, A. Plutalova, Degradation of high concentrations of commercial polylactide packaging on food waste composting in pilot-scale test, Bioresour. Technol. 410 (2024) 131288, https://doi.org/10.1016/j.biortech.2024.131288.

[25] M.P. Arrieta, J. López, E. Rayón, A. Jiménez, Disintegrability under composting conditions of plasticized PLA–PHB blends, Polym. Degrad. Stab. 108 (2014) 307–318, https://doi.org/10.1016/j.polymdegradstab.2014.01.034.

[26] E. Fortunati, I. Armentano, A. Iannoni, M. Barbale, S. Zaccheo, M. Scavone, L. Visai, J.M. Kenny, New multifunctional poly(lactide acid) composites: mechanical, antibacterial, and degradation properties, J. Appl. Polym. Sci. 124 (2012) 87–98, https://doi.org/10.1002/app.35039.

[27] F. Khabbaz, S. Karlsson, A.C. Albertsson, Py-GC/MS an effective technique to characterizing of degradation mechanism of poly (L-lactide) in the different environment, J. Appl. Polym. Sci. 78 (2000) 2369–2378, https://doi.org/10.1002/1097-4628(20001220)78:13<2369::AID-APP140>3.0.CO;2-N.

[28] S. Qiu, Y. Li, P. Qi, D. Meng, J. Sun, H. Li, Z. Cui, X. Gu, S. Zhang, Improving the flame retardancy and accelerating the degradation of poly (lactic acid) in soil by introducing fully bio-based additives, Int. J. Biol. Macromol. 193 (2021) 44–52, https://doi.org/10.1016/j.ijbiomac.2021.10.119.

[29] Y. Li, S. Qiu, J. Sun, Y. Ren, S. Wang, X. Wang, W. Wang, H. Li, B. Fei, X. Gu, S. Zhang, A new strategy to prepare fully bio-based poly(lactic acid) composite with high flame retardancy, UV resistance, and rapid degradation in soil, Chem. Eng. J. 428 (2022) 131979, https://doi.org/10.1016/j.cej.2021.131979.

[30] N.S.Q.S. Amorin, G. Rosa, J.F. Alves, S.P.C. Gonçalves, S.M.M. Franchetti, G.J. M. Fechine, Study of thermodegradation and thermostabilization of poly(lactide acid) using subsequent extrusion cycles, J. Appl. Polym. Sci. 131 (2014), https://doi.org/10.1002/app.40023.

[31] N.T. Dintcheva, S. Al-Malaika, E. Morici, R. Arrigo, Thermo-oxidative stabilization of poly(lactic acid)-based nanocomposites through the incorporation of clay with in-built antioxidant activity, J. Appl. Polym. Sci. 134 (2017), https://doi.org/10.1002/app.44974.

[32] E.W. Fischer, H.J. Sterzel, G. Wegner, Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions, Kolloid-Z. Z. Polym. 251 (1973) 980–990, https://doi.org/10.1007/BF01498927.

[33] HS 21976-17:1993, Investigation of Hard Waste Of Settlements. Seedling Plant Test, Hungarian Standard Association, Budapest. In Hungarian, 1993.

[34] ISO 11269-1:2012 Soil quality — Determination of the effects of pollutants on soil flora Part 1: Method for the measurement of inhibition of root growth, 2012.

[35] B. Li, J. Li, S. Huang, S. Qin, N. Liu, Design of novel Polylactide composite films with improved gas barrier and mechanical properties using epoxy chain extender-grafted organic montmorillonite, J. Polym. Sci. 61 (2023) 1572–1583, https://doi.org/10.1002/pol.20230022.

[36] A.L.P. de L. Freitas, L.R. Tonini Filho, P.S. Calvão, A.M.C. de Souza, Effect of montmorillonite and chain extender on rheological, morphological and biodegradation behavior of PLA/PBAT blends, Polym. Test. 62 (2017) 189–195, https://doi.org/10.1016/j.polymertesting.2017.06.030.

[37] M.R. Ricciardi, V. Antonucci, M. Zarrelli, M. Giordano, Fire behavior and smoke emission of phosphate–based inorganic fire-retarded polyester resin, Fire Mater. 36 (2012) 203–215, https://doi.org/10.1002/fam.1101.

[38] E. Fortunati, F. Luzi, D. Puglia, F. Dominici, C. Santulli, J.M. Kenny, L. Torre, Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves, Eur. Polym. J. 56 (2014) 77–91, https://doi.org/10.1016/j.eurpolymj.2014.03.030.

[39] J. Lunt, Large-scale production, properties and commercial applications of polylactic acid polymers, Polym. Degrad. Stab. 59 (1998) 145–152, https://doi.org/10.1016/S0141-3910(97)00148-1.

[40] A. Leonés, L. Peponi, M. Lieblich, R. Benavente, S. Fiori, In vitro degradation of plasticized PLA electrospun fiber mats: morphological, thermal and crystalline evolution, Polymers 12 (2020) 1–18, https://doi.org/10.3390/polym12122975 (Basel).

[41] M. Sedničková, S. Pekařová, P. Kucharczyk, J. Bočkaj, I. Janigová, A. Kleinová, D. Jochec-Mošková, L. Omaníková, D. Perďochová, M. Koutný, V. Sedlařík, P. Alexy, I. Chodák, Changes of physical properties of PLA-based blends during

early stage of biodegradation in compost, Int. J. Biol. Macromol. 113 (2018) 434–442, https://doi.org/10.1016/j.ijbiomac.2018.02.078.
[42] M. Yasuniwa, K. Sakamo, Y. Ono, W. Kawahara, Melting behavior of poly(l-lactic acid): X-ray and DSC analyses of the melting process, Polymer 49 (2008) 1943–1951, https://doi.org/10.1016/j.polymer.2008.02.034 (Guildf).
[43] S. Saeidlou, M.A. Huneault, H. Li, C.B. Park, Poly(lactic acid) crystallization, Prog. Polym. Sci. 37 (2012) 1657–1677, https://doi.org/10.1016/j.progpolymsci.2012.07.005.
[44] ASTM International, ASTM D6400-21 - specification for labeling of plastics designed to be aerobically composted in municipal or industrial facilities, 2021. 10.1520/D6400-21.
[45] ISO 20200:2023 Plastics — Determination of the degree of disintegration of plastic materials under composting conditions in a laboratory-scale test, 2023.
[46] P. Stloukal, S. Pekařová, A. Kalendova, H. Mattausch, S. Laske, C. Holzer, L. Chitu, S. Bodner, G. Maier, M. Slouf, M. Koutny, Kinetics and mechanism of the biodegradation of PLA/clay nanocomposites during thermophilic phase of composting process, Waste Manag. 42 (2015) 31–40, https://doi.org/10.1016/j.wasman.2015.04.006.
[47] R.J. Mueller, Biological degradation of synthetic polyesters-Enzymes as potential catalysts for polyester recycling, Process Biochem. 41 (2006) 2124–2128, https://doi.org/10.1016/j.procbio.2006.05.018.
[48] G. Fontaine, A. Gallos, S. Bourbigot, Role of montmorillonite for enhancing fire retardancy of intumescent PLA, Fire Saf. Sci. 11 (2014) 808–820, https://doi.org/10.3801/IAFSS.FSS.11-808.
[49] G. Kale, R. Auras, S.P. Singh, Comparison of the degradability of poly(lactide) packages in composting and ambient exposure conditions, Packag. Technol. Sci. 20 (2007) 49–70, https://doi.org/10.1002/pts.742.
[50] M.L. Iglesias-Montes, M. Soccio, F. Luzi, D. Puglia, M. Gazzano, N. Lotti, L. B. Manfredi, V.P. Cyras, Evaluation of the factors affecting the disintegration under a composting process of poly(lactic acid)/Poly(3-hydroxybutyrate) (PLA/PHB) blends, Polymers 13 (2021) 3171, https://doi.org/10.3390/polym13183171 (Basel).
[51] M. Falzarano, A. Polettini, R. Pomi, A. Rossi, T. Zonfa, M.P. Bracciale, S. Gabrielli, F. Sarasini, J. Tirillò, Anaerobic biodegradation of polylactic acid-based items: a specific focus on disposable tableware products, Materials 18 (2025) 1186, https://doi.org/10.3390/ma18051186.
[52] L. Lin, M. Joe, Q.A. Dang, H.E. Park, Enhancing biodegradation of poly(lactic acid) in compost at room temperature by compounding jade particles, Polymers 17 (2025) 2037, https://doi.org/10.3390/polym17152037 (Basel).
[53] H. Tsuji, Hydrolytic degradation. Poly(Lactic Acid), Wiley, 2022, pp. 467–516, https://doi.org/10.1002/9781119767480.ch21.
[54] G. Socrates, Infrared and Raman Characteristic Group Frequencies : Tables And Charts, 3rd ed., John Wiley & Sons, Inc, Oxford, 2004.
[55] S.S. Yang, Z.B. Chen, The study on aging and degradation mechanism of ammonium polyphosphate in artificial accelerated aging, Procedia Eng. (2018) 906–910, https://doi.org/10.1016/j.proeng.2017.12.091. Elsevier Ltd.
[56] Y. Liu, N. Lai, K. Gao, F. Chen, L. Yuan, G. Mi, Ammonium Inhibits primary root growth by reducing the length of meristem and elongation zone and decreasing elemental expansion rate in the root apex in arabidopsis thaliana, PLoS One 8 (2013), https://doi.org/10.1371/journal.pone.0061031.
[57] T. Balasubramaniam, G. Shen, N. Esmaeili, H. Zhang, Plants' response mechanisms to salinity stress, Plants 12 (2023), https://doi.org/10.3390/plants12122253.
[58] National research council (US) subcommittee on flame-retardant chemicals, 12, ammonium polyphosphates, in: Toxicological Risks of Selected Flame-Retardant Chemicals, Washington (DC), 2000.
[59] U.S. EPA Design for the Environment, 2015 Update of Report on Flame Retardants Used in Flexible Polyurethane Foam: Final Report, (2015). https://www.epa.gov/saferchoice/2015-update-report-flame-retardants-used-flexible-polyurethane-foam-final-report (accessed February 26, 2026).
[60] D.Q. Brito, T.B. Piau, C. Henke-Oliveira, E.C. Oliveira-Filho, C.K. Grisolia, Ecotoxicity of fire retardants to zebrafish (danio rerio) in early life stages, J. Biot. 15 (2025) 79, https://doi.org/10.3390/jox15030079.