Sustainable green coating for natural fibers: a flame retardant approach for pla-based composites

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SUSTAINABLE GREEN COATING FOR NATURAL FIBERS: A FLAME RETARDANT APPROACH FOR PLA-BASED COMPOSITES

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Abstract
This study presents a sustainable approach to enhance the fire resistance of natural fiber-reinforced poly(lactic acid) (PLA) composites. A bioinspired approach to functionalize the surface of flax (FF) and basalt (BF) fibers with an innovative organic-inorganic hybrid flame retardant (FR) is proposed. The fibers underwent a three-step coating method: first, ozone (O_3) pretreatment enhanced their surface reactivity by forming oxygen-containing functional groups that, in turn, enable the covalent immobilization of gallic acid (GA) units. Ultimately, inspired by the bacterial iron acquisition mechanism, iron phenylphosphonate was complexed with the phenolic groups of gallic acid units, resulting in FR-coated fibers. The coated flax and basalt fibers were used to produce PLA-based composite materials, named PLA/FF-FeP and PLA/BF-FeP, respectively. Thermogravimetric analysis (TGA) results revealed that, despite the low loading (0.1 wt% as assessed by Microwave Plasma Atomic Emission Spectroscopy - MP-AES) of the coating on the fiber surface, both composites exhibited improved thermal stability. The cone calorimetry test (CCT) highlighted an extended time to ignition (TTI), a reduced time to flame out, an 8% decrease in the peak of heat release rate (pHRR) and a 15% decrease in Fire Propagating Index (FPI) for PLA/BF-FeP. Further, the PLA/FF-FeP turned out to be smoke suppressant, showing a decrease in both total smoke release (TSR) and specific extinction area (SEA) of about 87 and, 68%, respectively.

1. Introduction

In recent years, increased awareness of environmental issues has prompted the implementation of various regulations, both locally and globally, aimed at directing industries toward reducing their environmental footprint and promoting the use of renewable materials [1,2]. In response, both industries and academic research are increasingly focusing on the development of high-performance

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materials from renewable origin. In this context, natural fiber-reinforced biopolymers have emerged as a compelling sustainable alternative to traditional synthetic fiber reinforced polymer (FRP) composites [3]. Among the polymer matrices derived from renewable feedstock, poly(lactic acid) (PLA), a biodegradable aliphatic thermoplastic polyester, has received considerable attention [4]. Due to its unique characteristics such as high stiffness and transparency [5], PLA has found applications in various fields, from packaging to fiber production and composite manufacturing [6]. Numerous studies have focused on reinforcing PLA with plant fibers to obtain composites with a favorable combination of physical and mechanical properties [7]. The growing interest in these composites arises from their valuable properties, cost-effective production, and eco-friendly nature. Consequently, there is a growing demand for PLA composites reinforced with natural fibers in various industrial sectors such as construction and automotive. However, despite their merits, significant concern with biocomposite materials regards their limited fire resistance. Indeed, such biopolymers as PLA inherently exhibit high flammability, which intensifies fire propagation, notably through the generation of extended dripping [8]. Compared to synthetic reinforcing fibers, the incorporation of natural fibers significantly exacerbates their already poor fire resistance [9]. This shortcoming is an obstacle to the widespread commercial use of biocomposites, especially in the transportation sector, where fire safety regulations are stringent [10]. Therefore, the use of flame retardants (FRs) is essential to improve the flammability resistance of biocomposites. The predominant approach involves the direct incorporation of FRs into the polymer matrix [11,12]. However, this method frequently leads to compromised mechanical properties and leaching of the FR due to the inherent low compatibility between the two components [13]. An alternative strategy involves the direct grafting of the FR onto the surface of the reinforcing fiber. This approach avoids FR leaching and mitigates the "candlewick effect" induced by the higher thermal conductivity of the fibers as compared to the polymer matrix [14]. This method finds primary application in composites reinforced with plant fibers, exploiting their functional groups to facilitate the bonding of appropriate FRs [15].

The proposed study introduces a bioinspired protocol for the surface modification of flax fiber (FF) and basalt fiber (BF) with a halogen-free phosphorus-based hybrid FR specifically tailored for flame retardant applications in PLA-based biocomposites. FF and BF fibers were selectively chosen considering their different surface reactivity properties. Ozone (O_3) was selected as a safe oxidizing agent for fiber pretreatment to enhance surface chemical reactivity by forming hydroxyl and carboxyl groups for BF and FF, respectively. The new surface functional groups were exploited for the covalent immobilization of renewable gallic acid (GA) units. Subsequently, taking inspiration from the bacterial enterobactin-mediated iron acquisition mechanism [16], iron phenylphosphonate was complexed to the GA phenolic groups. The modified fibers were thoroughly characterized using Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) and microwave plasma atomic emission spectroscopy (MP-AES). The FR-coated fibers were used as reinforcement in PLA-based composites, with fire resistance assessed through cone calorimetry tests (CCT); further, the mechanical properties were preliminarily evaluated.

2. Materials and Methods

2.1 Fiber coating

A Salinovo ozone generator, air-fed with a maximum diffusion rate of 0.5/h, was employed for fibers ozonization. 20g of fibers were placed in a 500 cm^3 ozonation chamber. The treatment lasted for a maximum of 7 hours. Gallic acid (GA) (34 g, 0.2 mol) and thionyl chloride (100 mL, 0.9 mol) were introduced into a dried single-necked flask. The reaction mixture was heated to 80 °C for 3 hours. After the reaction time, excess $SOCl_2$ was removed under vacuum. Crude galloyl chloride (36.9 g) obtained was dissolved in tert-Amyl methyl ether (TAME) (270.6 g, 2.6 mol) to yield a 12% (w/w) mixture. 30g of fibers were immersed in the mixture and stirred for 2 hours. The resulting sample was washed with H_2O and dried. 36 g of GA-functionalized fibers were mixed with 520 mL of deionized water in a beaker. 130 mL of $FeCl_3 \cdot 6H_2O$ (0.82 g, 3 mmol) aqueous solution was added. After stirring, PPA (0.96 g, 6 mmol), previously dissolved in 130 mL of H_2O, was added dropwise over 6 hours. The

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reaction proceeded at room temperature for 12 hours. The resulting iron phosphonate-coated fibers were washed with H_2O and dried [17].

2.2 Composite Manufacturing

The composites were fabricated using Brabender-like equipment (Rheocord EC, Haake Inc.) and a lab hydraulic press (Collin model P400E) to create 100 mm × 100 mm × 4 mm plates. The fibers were mixed with PLA using a micro compounder set at 60 rpm and 180 °C for 5 minutes. Subsequently, the PLA composites were compression-molded at 180 °C with a pressure profile of 2 min at 0 bar, 1 min at 5 bar, 1 min at 10 bar, and 1 min at 20 bar. The cooling down to room temperature was performed while maintaining the material at the maximum pressure of 20 bar. The fiber content was set at 20 wt%. The composite specimens suitable for tensile tests were prepared via injection molding (Haake MiniJet II Pro, Thermo Fisher Scientific) with the loading cylinder at 190 °C and the temperature mold set at 45 °C.

2.3 Characterization techniques

Fourier Transform Infrared spectra were acquired with a Bruker VERTEX 70 spectrometer equipped with an attenuated total reflectance diamond (ATR) cell. The spectra were recorded in the mid-infrared region (400-4000 cm^{-1}) collecting 128 scans, with a resolution of 4 cm^{-1}. The morphology of the fiber surface was examined with a Field Emission Scanning Electron Microscope (FE-SEM) coupled with Energy Dispersive Spectroscopy (EDAX). Micrographs were acquired on a Tescan Mira3 system at 10 kV after having sputtered the samples with chromium. Thermogravimetric analysis was performed with an SDT-Q600 thermoanalyzer (TA Instruments) in a nitrogen atmosphere (100 mL/min) with a heating rate of 10 °C/min from room temperature to 800 °C. Differential scanning calorimetry (DSC) analysis was conducted using a DSC 250 calorimeter (TA Instruments) with high-purity nitrogen flowing at 40 mL/min and heating and cooling rates of 10 °C/min. Detection of iron content on FR-coated fibers was carried out with an MP-AES 4210 instrument. Tensile tests were carried out on a Zwick/Roell Z010 universal testing machine in accordance with ISO 527-2.

The fire behavior was evaluated utilizing an oxygen consumption cone calorimeter (CCT) (Fire Testing Technology Limited FFT Cone Calorimeter model and Noselab instrument (Nova Milanese, Italy) following the ISO 5660 standard.

3. Results

3.1 FR-coated fibers characterization

The effectiveness of O_3 pretreatment in the surface functionalization of flax fibers (FF) with carboxylic groups and basalt fibers (BF) with -OH groups was checked through FT-IR analysis. Pretreated FF showed a new signal at 1731 cm^{-1} associated to carboxylic C=O stretching [18], while BF exhibited new absorptions at 3365 cm^{-1} and 1637 cm^{-1}, attributed to adsorbed water and Si-OH stretching, respectively [19]. TGA analysis of the ozonated FF indicated a marginal decrease in the lignin degradation temperature, attributed to O_3 improved reactivity toward phenols and polyphenols [20]. Pretreated BF exhibited increased weight loss between 200 and 300 °C, likely due to the depletion of surface hydroxyl groups [21]. FT-IR analysis of the fibers, following functionalization with GA units, revealed signals corresponding to O-H stretching of the phenolic ring, C-C stretching of the aromatic ring, C-O stretching, and O-H bending. These signals confirm the presence of GA units bound to the surface of both fibers [22]. The successful functionalization is further corroborated by a noticeable morphological change observed on the fiber surface, as depicted in SEM micrographs (Figure 1). In Figures 1b and 1e, the previously clean and smooth surface of the untreated fibers (Figure 1a and 1d) is replaced by a new rough layer, attributed to the immobilization of GA units. The phenolic groups of GA units were then exploited for iron phenylphosphonate complexation. SEM analysis of the resulting coated fibers (Figures 1c and 1f) revealed the occurrence of a distinct globular coating on the fiber surface. EDS analysis confirmed the presence of phosphorus (P) and iron (Fe), validating that the material adhered to the fiber was indeed iron phenylphosphonate. MP-AES analysis revealed an iron loading of 0.1 wt% on both coated fibers, indicating a reduced amount but significant complexation of Fe^{III}-gallic acid units on their surfaces. TGA analysis of FR-coated BF showed two

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distinct stages of weight loss occurring in temperature ranges of 170-270 °C and 270-400 °C, respectively. The 1.8 wt% decrease in the lower range is attributed to the decomposition of gallic acid units [23] and phenyl moiety of FR complex, while the 5.4 wt% reduction at higher temperatures is ascribed to the breakdown of C-C, C-H, and C-P bonds present in the structure of the phenylphosphonic units [24]. FR-coated FF exhibited a maximum decomposition rate temperature (T_{max}) of 309 °C, which is lower than that of untreated FF (354 °C), and a second degradation step in the temperature range from 400 °C to 520 °C. This can be attributed to the presence of the FR complex; the shift to lower T_{max} temperatures is ascribed to the degradation of gallic acid and phosphonate phenyl moieties, which degrade at about 250-260 °C. Subsequently, the iron phenylphosphonate undergoes a secondary stage of thermal degradation at temperatures above 420 °C, associated with the decomposition of the organic constituents of the coordination complex and/or dehydration of the H_2PO_4 and HPO_4 groups formed during the thermal degradation process [25].
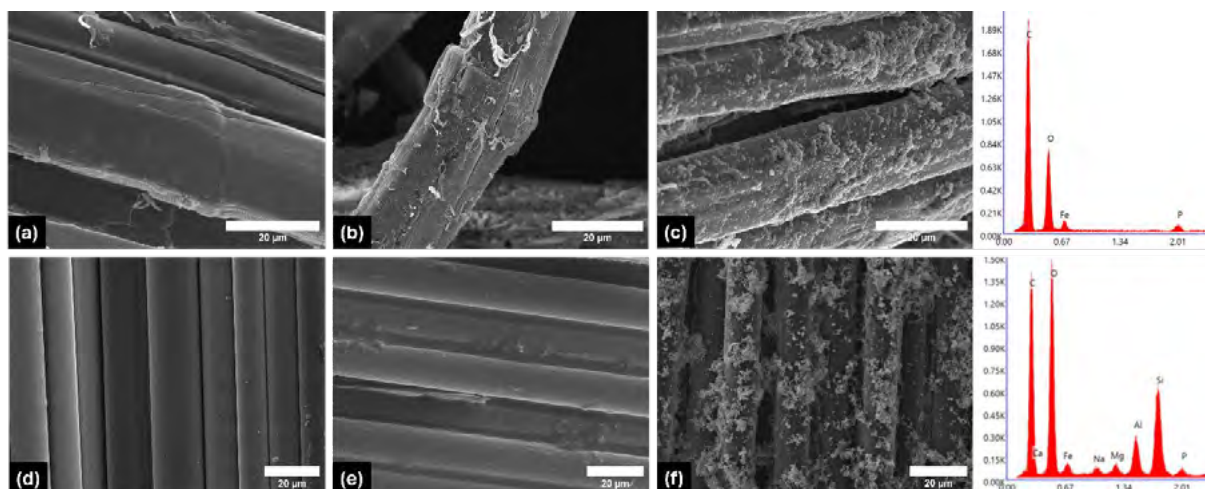

Figure 1. SEM-EDS analysis of (a) neat FF, (b) GA unit-functionalized FF, (c) FR-coated FF, (d) neat BF, (e) GA unit-functionalized BF and (f) FR-coated BF

3.2 PLA-based composites characterization

Fibers coated with the developed flame retardant (FR) complex were employed as reinforcement for fabricating PLA-based composites. Both composites reinforced with coated fibers (PLA/FF-FeP and PLA/BF-FeP) and those reinforced with uncoated fibers (PLA/FF and PLA/BF) were subjected to thermal characterization. The PLA/BF composite exhibited a temperature corresponding to 5% weight loss ($T_{5\%}$) at about 328.5 °C, a temperature for 10% weight loss ($T_{10\%}$) at approximately 338.7 °C, and a maximum decomposition temperature (T_{max}) of roughly 358.1 °C. Conversely, PLA/BF-FeP demonstrated slightly higher temperatures, with values of about 337.8 °C, 345.1 °C, and 365.6 °C for $T_{5\%}$, $T_{10\%}$, and T_{max}, respectively. A marginal increase in temperature was also observed for PLA/FF-FeP compared to PLA/FF. Specifically, PLA/FF recorded $T_{5\%}$, $T_{10\%}$, and T_{max} values at roughly 308.4 °C, 319.4 °C, and 350.9 °C, while PLA/FF-FeP showed slightly higher readings at approximately 318.8 °C, 331.3 °C, and 359.1 °C, respectively. Therefore, despite the low load on the fiber surface, the developed coating appears to be promising for improving the thermal stability of PLA composites.

DSC analysis revealed a peak of cold crystallization temperature (T_{cc}) at about 118.8 C for PLA/FF-FeP and approximately 119.8 °C for PLA/FF. Conversely, no significant differences were observed between PLA/BF and PLA/BF-FeP. To gain deeper insights into the impact of the flame retardant on the thermal properties of the composite, DSC analyses were performed by incorporating the as-synthesized iron phenylphosphonate into neat PLA at a concentration of 1 wt.% (PLA-FeP). The results revealed a reduction in T_{cc} for PLA-FeP (about 111.0 °C) compared to neat PLA (about 115.2 °C), as well as a

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significant 65% increase in the degree of crystallinity. This suggests that the FR complex promotes the nucleation phase of the PLA crystallization process.

Cone calorimetry tests were conducted on the composites to evaluate the flame-retardant properties of the developed FR coating complex. PLA/FF-FeP compared to PLA/FF exhibited a slight increase in time to ignition (TTI), a 7% reduction in the peak heat release rate (pHRR), and, most significantly, a remarkable reduction in both specific extinction area (by about 68%) and total smoke released (87%), hence highlighting the high smoke suppressant activity exerted by the treated fiber. In addition, a reduction of 15% in the Fire Propagating Index (FPI = pHRR/TTI ratio) was recorded. When comparing PLA/BF-FeP to PLA/BF, a slight increase in TTI was observed, along with reductions of 13%, 8%, and 14% in the time to flame out, pHRR, and FPI, respectively. Despite its minimal presence on the fiber surface, the designed FR coatings acted as high efficient flame retardants. Finally, some preliminary tensile tests were conducted to assess the impact of FR coating on the mechanical properties of the composites. PLA/FF-FeP and PLA/BF-FeP exhibited a 5% and 17% reduction in tensile strength, respectively, compared to PLA reinforced with the corresponding untreated fibers. This decrease may be attributed to the presence of the organic-inorganic hybrid coating, potentially acting as a stress concentrator [26]. Furthermore, the non-uniform distribution of the coating on the fiber surface might have exacerbated this effect. Conversely, PLA/FF-FeP and PLA/BF-FeP exhibited an increase in stiffness by 15% and 8%, respectively. This finding is likely to be due to the enhancement of fiber stiffness resulting from the presence of the hybrid coating, thereby leading to an increased Young's modulus for the composite. Further characterizations are needed to validate these hypotheses.

4. Conclusion

A sustainable method of coating basalt and flax fibers with an organic-inorganic hybrid flame retardant has been successfully devised. This bioinspired coating process facilitates the immobilization of iron phenylphosphonate on the fiber surface, utilizing moderate reaction temperatures and eco-friendly solvents such as TAME and H_2O. Comprehensive characterization analyses including SEM-EDS, FT-IR, TGA, and MP-AES attest to the efficacy of the coating process, confirming the successful grafting f the flame retardant onto the fiber surface.

The incorporation of these coated fibers into PLA-based composites resulted in improvements in thermal stability and flame retardancy, despite the low loading of the FR coating on the fiber surface. Cone calorimetry tests revealed such improvements as a slight increase in Time to Ignition (TTI), a 5% reduction in Peak Heat Release Rate (pHRR), and substantial decreases of 87% in Total Heat Release (THR) and 68% in Smoke Evolution Area (SEA) for PLA/FF-FEP. Similarly, PLA/BF-FeP exhibited an extended TTI, reduced flame out time, an 8% decrease in pHRR, and a 15% decrease in Fire Propagation Index (FPI) compared with neat fiber-reinforced composite.

However, PLA reinforced with FR-coated fibers showed a decrease in tensile strength compared to the counterparts reinforced with unmodified fibers, likely due to the effect of the hybrid complex that could act as a stress concentrator. Nonetheless, an increase in Young's modulus suggests a potential influence of FR coating on fiber stiffness.

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