



Phosphorous compounds as flame retardants for polybutylene succinate/flax biocomposite: Additive versus reactive route



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ABSTRACT

This paper investigates the effect of three phosphorous compounds on the thermal and fire behavior of PBS/flax biocomposites: ammonium polyphosphate (APP), dihydrogen ammonium phosphate (DAP) and phosphoric acid (PA). A comparison of the additive and reactive routes for the fireproofing of biocomposites is investigated by TGA, PCFC and cone calorimetry.

The incorporation by additive route of APP, DAP and PA in biocomposites leads to the charring effect of flax fibers due to the phosphorylation and the dehydration of the cellulose, (the main component of flax fibers). PA leads to a lower condensed phase action compared to APP and DAP. PBS hot hydrolysis is also highlighted due to the presence of phosphorous compounds in the matrix. In the reactive route, DAP and PA are grafted onto flax fibers. The first temperature of degradation, assigned to flax degradation, is progressively shifted to lower temperature with increasing grafting rate while the amount of residue is also enhanced. Using this route, no PBS hydrolysis occurs. The proximity of the phosphorous compound with the flax fibers allows the formation of a strong char at lower phosphorus content. This char residue acts as a protective layer that limits gas and heat transfer, allowing the decrease of pHRR and MARHE.

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1. Introduction

During the last years, the use of biocomposites (biopolymers reinforced by natural fibers) in sectors such as building, transportation or electrical equipment has generated a great interest [1]. This kind of materials offers many advantages like low cost, low density, low abrasiveness during processing or renewable origin, that make them a credible alternative to traditional glass fiber composites. However, the poor compatibility between fibers and matrix [2], the thermal and fire sensitivity [3–5] still limit their use in the above-mentioned applications. Thus, the improvement of the reaction to fire of biocomposites represents a stimulating challenge.

Until now, a limited number of papers has been published on flame retardancy of biocomposites. Most of them are dedicated to materials using polylactic acid (PLA) as matrix. Some researchers have brought out the interest of nanoparticles like expandable graphite [6], multi-walled carbon nanotubes or sepiolite nanoclays [7] as fire retardant agent (FR). But the most commonly

employed FRs in biocomposites remain the phosphorous compounds [8–11]. These FRs could be used either by direct incorporation into polymer matrix during the process or by impregnation or grafting onto natural fibers. Schartel et al. [6] studied the incorporation of APP in PP/flax biocomposites. They delivered a comprehensive characterization of the fire response for forced flaming combustion. Matkó et al. [9] also observed the effect of APP in PP/wood flake. In this study, the influence of the interface between the matrix and wood flakes was evidenced. The surface modification of the wood flakes by alcoxysilane improves the compatibility, but also the thermal stability of the biocomposite.

Several authors have demonstrated the interest to modify natural fiber surface using phosphorous compounds [8,10,11]. Shumao et al. [8] used APP as FR in PLA/ramie composite. APP was either directly added in the PLA matrix or deposited onto the ramie surface. The authors showed that the targeted action of APP on the fibers may inhibit mass transfer in the combustion zone and thus improves the fire behavior of the composite. However UL94 rating could not be changed due to a too low APP loading, contrary to direct incorporation in the matrix. The best results were obtained by combining both strategies. Chen et al. [11] have compared APP and microencapsulated APP (MAPP) as flame retardant in PLA/

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ramie biocomposites. The objective of their work was to study the fire behavior of these biocomposites after UV irradiation and hydrothermal aging. The combined use of MAPP in the matrix and deposited onto the fibers leads to the best aging resistance since UL94 rating decreases only from V0 to V1 after 21 days exposure. This result was attributed to the good dispersion of MAPP in the matrix and to the good interaction between ramie and MAPP. Since APP is almost insoluble, other forms of ammonium phosphate have been used to achieve grafting onto natural fibers. Suardana et al. studied the grafting of diammonium phosphate onto coir and jute fibers in a PLA matrix. They observed that the burning rate of biocomposite was decreased with increasing phosphate grafting rate [10].

In a previous work [4], we studied the fire behavior of polybutylene succinate (PBS) reinforced by various natural fibers. PBS was chosen as emerging biopolymer for which monomers from renewable resources are now available [12]. Moreover PBS exhibits interesting mechanical properties close to those of polyolefins and can be processed at low temperature (120 °C) [13], avoiding fiber thermal degradation [14,15]. In this paper, it was highlighted that, during combustion and above a certain amount of lignocellulosic fibers, a residue constituted by the skeleton of fibers is formed. This residue induces a controlled release of decomposition products and thus a relatively low heat release rate. Furthermore, it was evidenced that the barrier action of this residue could be greatly enhanced by addition of APP in the PBS matrix. The presence of APP leads to the formation of a strong char resulting from the dehydration of the natural fibers under the action of phosphoric acid. However, APP induces also a hot hydrolysis of PBS. Based on these observations, it was decided to investigate fiber surface modification as an alternative to the incorporation of FR in the matrix.

The present study focuses on the fire behavior of flame retarded PBS/flax fibers biocomposites. The objective of the paper is to investigate the flame retardant action of three phosphorous compounds that have been commonly used for cellulose fibers or textiles [16,17]: ammonium polyphosphate (APP), dihydrogen ammonium phosphate (DAP), and phosphoric acid (PA). A comparison between the additive route (incorporation of FR in the matrix) and the reactive route (grafting onto fiber surface) was attempted. Thermal and fire properties have been characterized by TGA, PCFC and cone calorimeter.

2. Experimental

2.1. Materials

Flax fibers (Fibras-S6D) were purchased from Fibres Recherche et Développement (FRD[®]). Dihydrogen ammonium phosphate (DAP-Prolabo), phosphoric acid (PA-Panreac) and ammonium polyphosphate (APP-Exolit AP 423-Clariant) were used as flame retardant agents. DAP and PA were also used as fiber surface treatment agents. The poly(1,4-butanediol succinate) (PBS film grade 1903F-Xinfu Pharm) was used as matrix.

2.2. Fibers treatments

2.2.1. Pretreatment of the flax fibers

Before chemical modification with the phosphorous compound, the flax fibers (Tfl) were pretreated with ethanol to remove waxes and pectin which ensure the cohesion of the flax beam [18].

In a reactor equipped with a condenser, 50 g of flax fibers and 1 L of ethanol were introduced. The mixture was heated under reflux

Table 1
Designation of the biocomposites.

Designation	Sample	PBS (wt%)	APP (wt%)	DAP (wt%)	PA (wt%)	Tfl ^a (wt%)
FTfl	Tfl-xDAP ^a Tfl-yPA ^a			x	y	100-x 100-y
PBS-Tfl	PBS + Tfl	70				30
PBS-FTfl (reactive)	PBS + Tfl-xDAP ^a PBS + Tfl-yPA ^a	70		30x	30y	30(1-x) 30(1-y)
FPBS-Tfl (additive)	PBS + Tfl + 3DAP PBS + Tfl + 3PA PBS + Tfl + 3APP PBS + Tfl + 5APP PBS + Tfl + 10APP PBS + Tfl + 15APP	68.5 68.5 68.5 65 60 55	3 3 3 5 10 15			28.5 28.5 28.5 30 30 30

^a x and y are = 2.5; 5; 7.5; 10 wt%.

for 5 h with mechanical stirring. The liquid phase was eliminated and the flax fibers were dried at room temperature.

2.2.2. Chemical modification of the flax fibers

In a reactor equipped with a condenser, 45, 46.2, 47.5 and 48.7 g of pretreated flax fibers with 5.0, 3.8, 2.5 and 1.3 g of the treatment agent (for treatment at 10%, 7.5%, 5% and 2.5%) were introduced, respectively. 1 L of ethanol was added. The mixture was heated under reflux for 5 h with mechanical stirring. The liquid phase was eliminated and the flax fibers were washed three times with ethanol and dried at room temperature. The natural fibers without fire retardant treatment were designated as Tfl and those functionalized with DAP or PA were designated as FTfl.

2.3. Composite preparation

2.3.1. Processing of the flame retardant biocomposites

The biocomposites were obtained by mixing PBS pellets and (functionalized or unfunctionalized) natural fibers in a Haake Rheomix internal mixer (100 rpm at 110 °C). PBS was firstly introduced in the chamber of an internal mixer and mixed for 2.5 min until a constant torque was obtained. For the FPBS-Tfl systems (biocomposites fire retarded by additive route), the flame retardant agent was firstly added and mixed with the matrix for 2min. Then for all formulations, the fibers (Tfl or FTfl) were added progressively during 9min. After the final fiber addition, the mixing was extended for 2 min. The total time of blending was around 15min. Biocomposites compositions and designations are given Table 1.

All materials were compression molded at 110 bars into 100 × 100 × 4 mm³ square sheets weighing around 50 g.

The process retained to prepare biocomposites comprising PBS and flax fibers brings out two different routes; an additive route for which the flame retardant agent (DAP, PA or APP) is added in the melted PBS and flax fibers (Tfl) are further added. The biocomposite

Table 2
TGA values of PBS + Tfl and FPBS-Tfl.

Samples	T _{deg} (1st) (°C)	T _{deg} (2nd) (°C)	Res ₆₀₀ (%)	Phosphorus content (%) ^a
PBS + Tfl	376.4	401.2	7.0	0
PBS + Tfl + 3DAP	309.5	393.7	8.7	2.7
PBS + Tfl + 3PA	259.1	376.3	11.7	3.2
PBS + Tfl + 3APP	276.8	379.3	11.7	3.2
PBS + Tfl + 5APP	288.6	378.9	15.5	5.3
PBS + Tfl + 10APP	288.6	357.6	20.0	10.6
PBS + Tfl + 15APP	276.4	333.1	13.3	16.0

^a The phosphorus content was calculated from the content of phosphorus on the treatment agents. This is the theoretical value. This value is relative to the fiber content.

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