



## On revealing the effect of alkaline lignin and ammonium polyphosphate additives on fire retardant properties of sustainable zein-based composites



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### ARTICLE INFO

#### Article history:

Received 5 August 2016

Received in revised form

23 September 2016

Accepted 1 October 2016

Available online 5 October 2016

#### Keywords:

Vegetable proteins

Composite

Fire behavior

Lignin

### ABSTRACT

The paper deals with the evaluation of the efficacy of both ammonium polyphosphate, APP, and alkaline lignin, AL, as suitable additives for the development of innovative and sustainable composites based on thermo-plasticized zein, TPZ. The chemical and physical interactions which occur between AL and APP and the secondary structure of thermo-plasticized zein were investigated by torque analysis and FTIR spectroscopy and were exploited to rationalize macroscopic properties such as the thermal stability, fire behavior and the mechanical properties. In details the fire behavior of the composites was evaluated by both cone calorimetry and self-sustained vertical combustion tests in order to simulate different fire scenario. The results highlighted that AL intercalates both the  $\alpha$ -helix and  $\beta$ -sheets structures and thus improves the fire retardant behavior of composites in the vertical burning scenario by enabling the withdrawal effect of the film from flame due to the removal of PEG plasticizer during the burning test.

On the other side, APP enhances the fire resistance of composites exposed to pool forced combustion due to an enhanced charring effect which protects the substrate during burning. Finally the composite containing simultaneously 10 wt% APP and 3 wt% AL exhibited excellent fire resistance behavior in different fire scenario and satisfying mechanical properties with a toughness which is around 30% higher than that of pristine TPZ. Due to this peculiar combination of functional and structural properties the composite materials may be considered as potential substitutes of traditional polymeric materials in several application fields (i.e packaging, electrical components, ...).

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### 1. Introduction

Environmental concerns about “plastics” and waste management is leading the scientific and industrial interest towards advanced materials classified as sustainable or “green” materials. Biodegradable polymers and, in particular polymers obtained from renewable-resources such as the polysaccharides (e.g., starch, cellulose) and proteins (e.g. wheat gluten, zein) have been accepted as the most promising candidates for substituting petrochemical-

based polymers. They are abundant, cheap, biodegradable and both economically and environmentally sustainable [1]. Moreover these materials exhibit technological limitations such as poor melt-flow properties and shoddy structural and functional performances, i.e. mechanical properties, barrier properties, durability and fire resistance which restrict their applications [2]. As for proteins the low melt-flow is mainly due to the existence of strong inter/intra-molecular interactions between the several amino-acid of macromolecules. These interactions stabilize the secondary protein structure which often, during heating, degrades before achieving the melt flow state. In order to increase the processability of proteins, the secondary structure is commonly modified by using specific compounds, such as plasticizers that act as an internal

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lubricant, increasing the molecular mobility by substituting the protein-protein interactions with weaker protein-lubricant interactions [2]. Among the several renewable materials, the zein has attracted many scientific and industrial interests being used as thermoplastic polymers for the production of films, filament and foams [3]. Furthermore, this material is available in large amounts as by-products of agricultural and biofuel processing activities (i.e ethanol production) [4].

In the design and development of innovative composite materials it is widely requested that besides sustainability of the polymer also additives and fillers, generally used to tailor the structural and functional properties, have to be sustainable as well. As for the flame retardant properties, several kinds of additives such as hydrated salts, phosphorus compounds, graphite, carbon nanotube etc., have been commonly used as substitutes of toxic flame retardants like halogenated compounds. Verdolotti et al. [5] i.e., investigated how an high amount of sustainable inorganic filler (60 wt% of hydrated cement) chemically interconnected with polymer phase (such as polyurethane foam) [6] is able to delay the onset of thermo-oxidative degradation of polymeric phase and to improve its fire resistance without the addition of flame retardants.

However, in the recent literature there are many papers in the field of green flame retardant polymers. Intumescent system with melamine and ammonium polyphosphate (APP) was studied into a PLA matrix. The FR formulation at 30%wt. was very efficient with a reduction of peak of Heat Release Rate of 87%. With the addition of nanoparticles it was found a large synergistic effect when Cloisite 30B was used whereas multiwall carbon nanotubes acted as an antagonistic [7]. In the same biopolymer the effect of expanded graphite and organic modified montmorillonite [8] were also investigated. The authors found an improvement of thermal and mechanical properties obtained by the presence of both nanoparticles in PLA associated to the good co-dispersion and co-reinforcement. In terms of fire retardant properties it was found the best performances with the presence of both nanoparticles at 3%wt with a HB classification without drops and with char formation. With the addition of expandable graphite in PLA [9] it was possible achieve the V-0 ranking in UL-94 test with the addition of 5%wt while only with 10%wt of additive was obtained a sensibly decrease of the rate of combustion. The same authors [10] have studied also the effect of organic nanoclays in the PLA matrix and it was found that LOI index decreases in the nanocomposites also in the presence of commercial flame retardant. This effect was attributed to nanoparticles-catalysed oxidation of the gases generated at the surface of the condensed phase by thermal volatilization of the PLA matrix. Finally a large increase in the LOI index (27,2%) was found when in the PLA matrix it was added a mixture of APP and melamine with a  $\beta$ -cyclodextrin as a carbon source [11]. In the field of biocomposites synergism between phosphinate and nanometric metal oxide in a PHBV/PBAT blend [12] was found with a V-0 ranking in the UL-94 test and a value of LOI of 29.5%. Both the phosphorus and the nanofiller components participate simultaneously in the flame-retardancy mechanism: the first acting as flame inhibition in the gas phase, and the second promoting cross-linking in the solid phase.

The effect of APP in ramie fiber-reinforced PLA was considered [13] and it was found an increase in the flame retardant properties like UL-94 with V-0 ranking and LOI value of 35,6% but the presence of APP disturbed the compatibility between PLA and fibers with a decrease in mechanical properties.

The flame retardant properties of coconut fiber (CF) was investigated to reduce the content of aluminum trihydrate (ATH) required in thermoplastic starch [14]. CF induced some charring activity, slightly decreasing the fire load and burning propensity in cone calorimeter test. ATH decomposes endothermally into water

and inorganic residue. Replacing 25%wt of ATH with CF it was obtained similar flame retardant characteristics in terms of cone calorimeter data. Preparation of a multi-component structure was proven to be a successful alternative approach for balancing mechanical and fire retardancy performance in biopolymer composites. The application of layers on the surface of biopolymer in a multi-component laminate materials was found a good solution with a great reduction in the peak of HRR with a simultaneous improve of the flexural modulus [15] Finally a UV-curable system coated on bio-polyamide 10.10 [16] were recently examined with a significant decrease in the peak of HRR (–30%) but contrariwise there were a lower time to ignition and an increase of smoke production.

However, among the several compounds both phosphorous fire-retardant filler (i.e ammonium phosphorous, APP) and lignin-based compounds (i.e alkaline lignin, AL) represent a valid approach to enhancing the fire resistance of biopolymer-based materials. In fact APP as intumescent flame-retardant has been extensively investigated [17,18]; it works by building up a cross-linked residue that, during exposing to heat or fire, produces a porous carbonaceous foam. This foam acts as a barrier to prevent heat and air from entering the surface of the material [17].

Lignin is a by-product of cellulose industry which is disposed by incineration for energy recovery. Its environmental impact may be optimized by promoting its use as a fire retardant additive for polymers. Prieur et al. [19] added lignin as flame retardant in acrylonitrile-butadiene-styrene (ABS) to enhance fire resistance and observed that to achieve the highest fire performances the lignin has to be phosphorylated to obtain a more cohesive protective char. Other authors [8,9] showed that lignin, alone or in combination with ammonium polyphosphate, is a suitable fire retardant for example for polypropylene, displaying an environment friendly fire retardant mechanism based on emission-free condensed phase with fire retardant action [20,21].

Herein, the combustion and the fire behavior of biocomposites based on thermo-plasticized zein filled with flame retardants such as alkaline lignin (AL) and ammonium polyphosphate (APP) and their combination were analyzed in different fire scenario. Exhaustive chemico-physical characterization was addressed to the understanding of the effect of additives on the secondary structure of proteins by correlating it to the mechanical and combustion properties. The results showed that by compounding AL and APP in TPZ matrix it is possible to obtain composites with both satisfactory fire retardant behavior in several fire scenarios and enhanced mechanical properties. These biocomposites exhibit an optimized balance between functional and structural properties and thus may be considered as real and innovative substitutes of petrochemical-based polymers in several application fields including packaging and components for electrical systems.

## 2. Experimental section

### 2.1. Materials

Maize zein powder (code Z3625, lot number: 065K0110) and plasticizer poly(ethylene glycol), PEG (Mw = 400, code 81170) purchased from Sigma Aldrich (Italy) were used as received for the preparation of thermoplastic zein, TPZ. To improve the fire retardant behavior of TPZ, two different flame retardant compounds were used: alkaline lignin, hereafter denoted as AL, (average Mw = 28000 ca., code 370959, Sigma Aldrich, Italy) and ammonium polyphosphate hereafter denoted as APP ((NH<sub>4</sub>PO<sub>3</sub>)<sub>n</sub> Mw = 97 (number average), CAS number 68333-79-9, Tecnosintesi S.p.a, Italy).

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