

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

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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 α -helix and β -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 10wt% APP and 3wt% 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,...).

Keywords: vegetable proteins, composite, fire behavior, lignin

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, ie. 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 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 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 to 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 sensible 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 β -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 endothermically 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 ((NH₄PO₃)_n Mw=97 (number average), CAS number 68333-79-9, Tecnosintesi S.p.a, Italy).

2.2 TPZ-based Composites Preparation

The TPZ-based composites with lignin additives were prepared by using a melt mixing process, as described in reference [22]. Briefly, AL was first added to PEG and magnetically stirred in a beaker at room temperature for 3 minutes in order to allow a good dispersion of lignin particles. Zein powder was manually mixed with the dispersion of AL in PEG, and then the resulting mixture was fed in a twin counter rotating internal mixer (Rheomix 600 and PolyLab QC, respectively, Haake, Germany) operating at 70°C and 50 rpm for 10 min. For the zein thermoplasticization the amount of PEG was 25wt% of the overall system consisting of zein and PEG. Torque and temperature of the melted phase were recorded during the mixing process to monitor the thermoplasticization process. The same procedure was adopted for the preparation of the biocomposites with APP as well as for the ternary biocomposites containing simultaneously AL and APP fillers. The obtained composites have been denoted as TPZ_xAL_yAPP, with *x* and *y* to indicate the final weight percentage of AL and APP with respect to the thermoplasticized zein (i.e the system consisting of zein and PEG), respectively. After mixing, pristine TPZ and the biocomposites were compressed by using a press (P300P, Collin, Germany) operating at 80°C and 50 bar in order to produce sheets and slabs specimens. The compositions of the several samples are reported in Table 1.

Table 1: Compositions of TPZ-based composites.

Sample	AL (wt%)	APP (wt%)
TPZ	-	-
TPZ3AL	3	-
TPZ10AL	10	-
TPZ10APP	-	10
TPZ30APP	-	30
TPZ3AL10APP	3	10
TPZ3AL30APP	3	30
TPZ10AL10APP	10	10
TPZ10AL30APP	10	30

2.3 TPZ-based Composites Characterization

Knowledge of chemical interactions which take place between AL and APP additives and TPZ matrix is a key issue for the understanding of the macro-scale behavior of biocomposites. These interactions were investigated by FTIR measurements. In details FT-IR spectra for APP, APP/PEG mixture, APP/PEG/AL mixture and TPZ films as well as TPZ-based composites were collected in ATR mode by using a Nicolet apparatus (Thermo Scientific, Italy) from 4000 to 600 cm^{-1} with a wavenumber resolution of 4 cm^{-1} for 64 scans. The spectra of composites were baseline corrected by following the Wellner method and ensuring the zero-level at 1800 cm^{-1} [23]. The spectra were also normalized to the intensity of the Amide II band at 1480 cm^{-1} [23,24]. To evaluate the effect of the several additives (PEG and PEG/APP and PEG/AL mixtures) on the zein protein structure, the absorption of the amide I band in the range 1800-1600 cm^{-1} was deconvoluted by using OriginPro 8.0 software [22-25]. In particular the broad protein Amide I band consists of two components centered around 1658-1648 cm^{-1} and 1630-1620 cm^{-1} assigned to the ordered phases α -helix and β -sheet respectively, and a further band centered around 1665-1675 cm^{-1} ascribed to the disordered phases, β -turns [22,24].

Thermal degradation investigation was performed by using TA Instruments thermal analyzer SDT2960 (New Castle, USA) under nitrogen and air flowing at 20 cm³/min. The samples were heated from 30 up to 1000°C by applying a heating rate of 10°C/min.

Tensile properties of the TPZ-based composites were tested at room temperature according to ASTM standard D1708-02 by using a 4204 Universal Testing Machine (Instron, USA) with a load cell of 1kN and at displacement rate of 10mm/min. Samples were preconditioned at relative humidity (RH) of 50% for at least 48 h before testing. Force and elongation were recorded during extension to evaluate Young's modulus, tensile strength, elongation at break and toughness. The mechanical properties have been reported as average values of five samples tested for each composition.

Combustion behavior was tested on sheet samples in both vertical burning upon small flame ignition and in horizontal configuration on exposure to radiant heat source and pilot flame ignition. These are the two typical fire scenario used to assess reaction to fire of polymer materials. In vertical burning, films 100x50 mm² and thickness ranging between 100 and 300 μm were supported on a vertical frame and exposed to a Bunsen flame impinging on the low sheet side. The upward burning behavior was recorded similarly to the UL 94 vertical burning test [26] by measuring the flame time following the first and second ignition (t_1 and t_2 respectively), the total flame time t_{tot} equal to the sum of t_1 and t_2 and the specimen weight loss. Furthermore it was recorded whether combustion occurred with dripping and the cotton underlying the burning specimen were ignited by flaming drops.

Exposure to radiant heat was carried out in the Oxygen Consumption Calorimeter Fire Testing Technology, FFT dual cone calorimeter model, by following the ISO 5660 procedure. Specimens of 100x100 mm² and thickness of 3mm, previously conditioned to constant mass at 23°C and 50% HR, were exposed to an external heat flux of 50 kW/m² while the heat release rate, HRR was measured. HRR is defined as the amount of calorific energy released per unit time by a material during combustion and it represents the key fire property to take in account in any assessment of fire hazard. Additional parameters as ignition time and total heat released (THR), weight loss, were also monitored during tests.

3. Results and discussions

3.1 Torque data analysis

Figure 1 shows the evolution of torque during the thermal mixing of the several components used for the preparation of TPZ-based composites. Typically, the torque curves obtained during

thermoplasticization of proteins are characterized by an initial “induction time”, which is function of wettability of the protein by the plasticizer [27], followed by a steep increase of the torque up to a maximum value. Afterwards the torque decreases to a stationary value (plateau) which indicates the occurring of protein thermo-plasticization [2, 3, 28]. In this paper, all composite systems containing AL and/or APP, as well as the pristine TPZ exhibit the presence of maximum of the torque after an induction time whose entity depends on the formulation (i.e from a few seconds for pristine TPZ to several minutes for the composites systems). After plasticization, the value of the torque is somewhat constant and is not observed any evidence of effects ascribed to plasticizer loss, crosslinking or degradation. The thermo-plasticization is a complex process and depends on the presence of low molecular weight compounds able to plasticize the supramolecular structure of proteins. In particular, due to the combined effect of temperature and mechanical shear the plasticizer interacts with the protein macromolecules and diffuses within the ordered domains (i.e α -helix and β -sheets domains) present in the secondary structure of proteins by denaturing the protein up to achieving disentangled macromolecules. In this scenario, the presence of additional compounds that affect the wettability and so the diffusion of the plasticizer into the ordered domains of protein structure can induce an accelerating or slow-downing of the whole thermoplasticization process.

From torque data, it is possible to observe that the presence of AL, as compared to TPZ, slightly slows down the thermoplasticization process whereas increase the torque requested to get plasticization and the torque level at the plateau. Therefore, AL in these concentrations doesn't modify the wettability of the protein by the PEG and acts as interactive filler for the TPZ, as reported by Oliviero et al.[22]. On the other side, the presence of APP, alone or in combination with the AL brings significant delaying in the thermoplasticization process which occurs at higher value of maximum torque. As shown in the images reported in Figure 1, the composite mixture with 10wt% APP appears after 5 minutes of thermal-mixing yet as a crude blend. Only in correspondence of the maximum torque value, it is completely thermo-plasticized and assumes the classical “cream” aspect. The observed delay may be tentatively ascribed, in this case, to the formation of larger adducts between APP and PEG which hinder the diffusion of plasticizer into the zein secondary structures, increasing the time requested for the zein thermoplasticization. Similar behavior were observed by Pommet et al [29] who noted that the plasticizers with higher molecular weight influenced the “induction time” of thermoplasticization.

Moreover a complete rationalization of the phenomena which occur during thermoplasticization is reported in the following section by considering the chemical modifications which occur during the thermal-mixing.

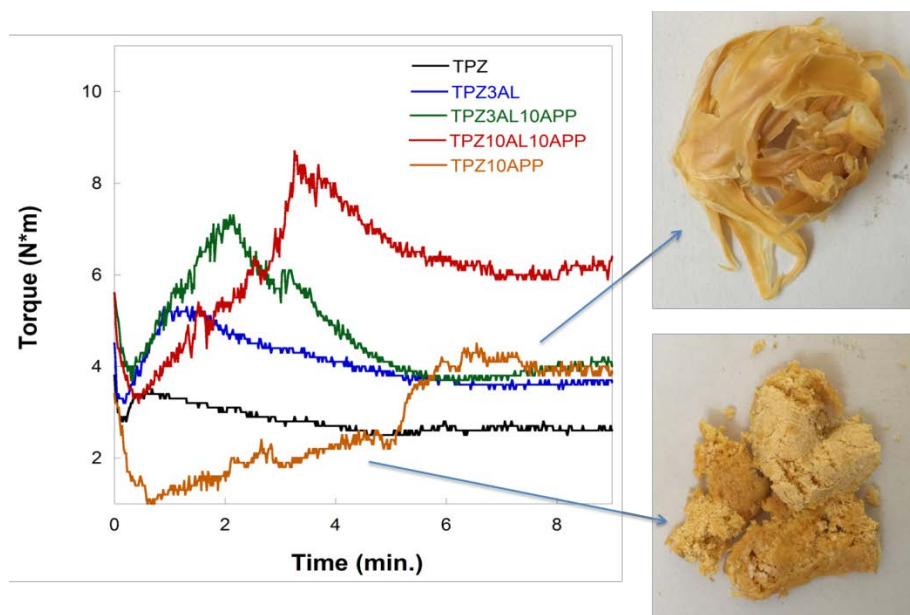


Figure 1: Torque evolution during mixing process of TPZ-based composites.

3.2. Chemical characterization

Figure 2 shows the FTIR spectra of APP, PEG and APP/PEG mixture (30/70 wt/wt). The APP/PEG mixture has been obtained by blending at 80°C the single components and simulating the real process adopted for the preparation of composites. In Table 2 are listed the assignments of vibration bands for all the materials. FTIR spectrum of APP shows a distinct absorption band at around 1256 cm^{-1} due to the symmetric vibration of P=O, at 1020 cm^{-1} related to the PO_3 and PO_2 asymmetric stretching vibrations, at 1075 cm^{-1} and 890 cm^{-1} due to the symmetric and asymmetric stretching of P-O respectively, and around 802 cm^{-1} due to the P-O-P asymmetric stretching [30,31]. After mixing with PEG at 80°C, the absorbance bands of APP change significantly above all in the spectral region 1200-1600 cm^{-1} . It is worth noting that the additive spectrum of APP/PEG mixture is not simply the “weighted” sum of PEG and APP spectra which can be obtained by taking into account that in the mixture APP is around the 30wt% and PEG is around the 70wt% (see Figure S1 in the Supporting Information). This confirms that significant interactions take place between APP and PEG which bring to substantial modifications of the FTIR spectrum of the resulting mixture, as compared to the spectra of single components. Due to the chemical interactions, the APP/PEG

mixture behaves as constituted by a “single adduct” which hinders the diffusion of PEG in the ordered structures of protein and delays the plasticization of protein with respect to the other systems.

As for the AL/PEG mixture (11/89 wt/wt), the FTIR analysis (spectra not reported for brevity) does not show any chemical interactions taking place between the two components. PEG is available to interact with zein structure during the melt mixing process and thus the effect of the PEG/AL mixture on the plasticization, even though delayed, is similar to that shown by PEG. Figure 3 show deconvoluted FTIR spectra of selected thermo-plasticized systems (TPZ, TPZ10APP and TPZ3AL) in the region of Amide I, the FTIR data in terms of wavenumber, band area and the band area ratio for the different conformations are summarized in Table 3. The spectra showed that both AL and APP additives affected the secondary structure of TPZ at different extent. In particular, in addition to the peak correlated to AL at 1740 cm^{-1} , the spectrum of Al-based composite showed that the intensity of ordered structures (α -helix and β -sheet) reduces as compared to the TPZ; on the other side, the β -sheet absorbance band completely disappeared. Simultaneously the intensity of the disordered conformation (β -turns) increased and shifted towards high wavenumber. These spectral modifications, as widely described by Oliviero et al [22,32], are ascribed to the strong hydrogen bonding generated between the functional groups of AL (i.e. SH and OH groups) and the functional groups of zein protein (ie. NH and OH groups) that modified the sovramolecular structure of native zein (see FT-IR spectrum in the Supporting Information) [22]. Conversely the APP addition affected only marginally the secondary structure of protein and the ordered conformations as well as their relative ratio does not change significantly as compared to the pristine TPZ.

The infrared results allow to justifying the previously discussed outcomes obtained from the torque data analysis and give further insights in the complex interactions which establish between the secondary protein structure and the single components of the composites. In conclusion the AL does not interact with PEG during thermal mixing but is able to affect significantly the secondary protein structure by inserting competitively with PEG macromolecules inside the order proteins structures (as schematized in Scheme 1, route b)). On the other side the APP is able to interact with PEG but does not affect the secondary structure of protein (as schematized in Scheme 1, route c)), which after thermoplasticization results to be very similar to that of pristine TPZ (as schematized in Scheme 1, route a)).

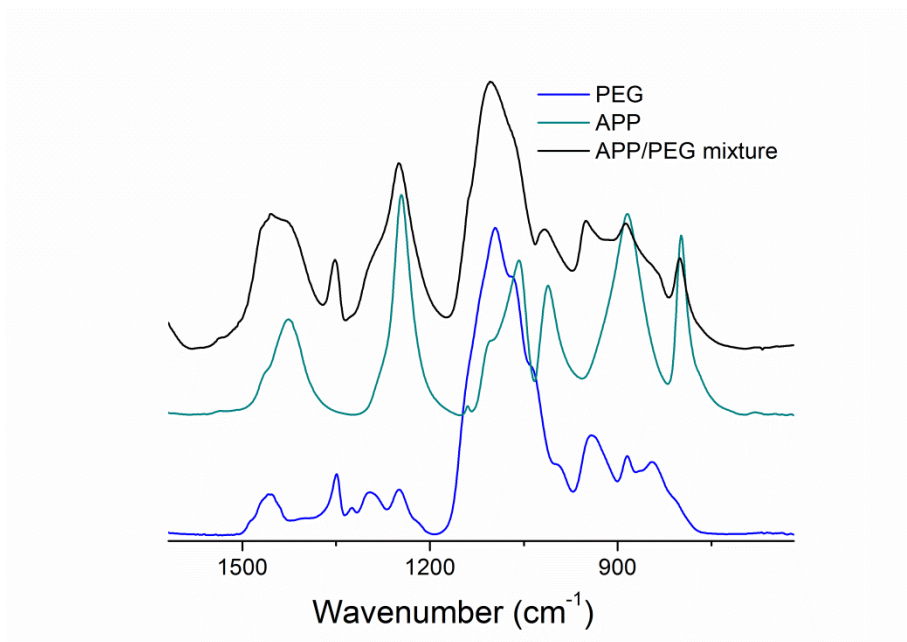


Figure 2: FTIR spectra of PEG, APP and APP/PEG (30/70wt/wt) mixture.

Table 2: The experimental assignments of characteristic IR absorption bands of analyzed systems

Wavenumber, cm^{-1}	Band Assignments
880	P-O-P (APP)
1020	PO_2 and PO_3 (APP)
1028-1079	Ether -O- (AL)
1075	P-O (APP)
1094	C-O- stretching (PEG)
1120-1147	C-H aromatic in S units* and in plane deformation (AL)
1210-1220	C-C and C-O (AL)
1256	P=O (APP)
1265	G* ring and C=O ring (AL)
1343	C-H bending (PEG)
1425-1459	(R)-O- CH_3 groups (AL)
1430	(P)O-H (APP)
1456 and 1280	O-H bending (PEG)
1520-1615	C-H vibration of the aromatic ring (AL)
1720-1740	C=O (AL)
3100 and 3168	NH_4^+ asy str (APP)
3410-3460	O-H in phenolic and aliphatic structures (AL)
3445	O-H (H-bonded) (PEG)
3500-3200	O-H (H-bonded) (APP)

*The lignin network is mainly composed of ring guaiacyl (G) moieties and of a low content of syringyl (S) units [33].

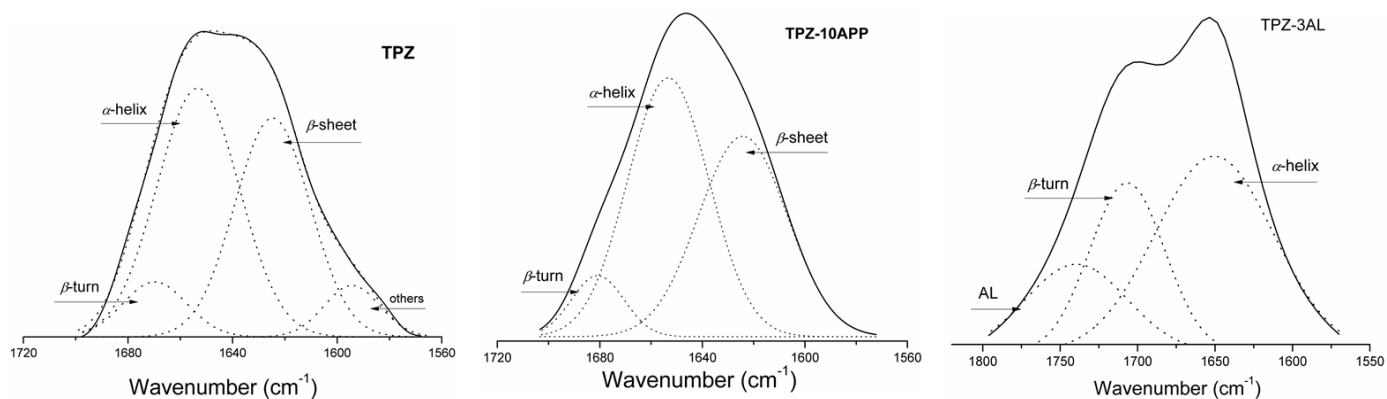
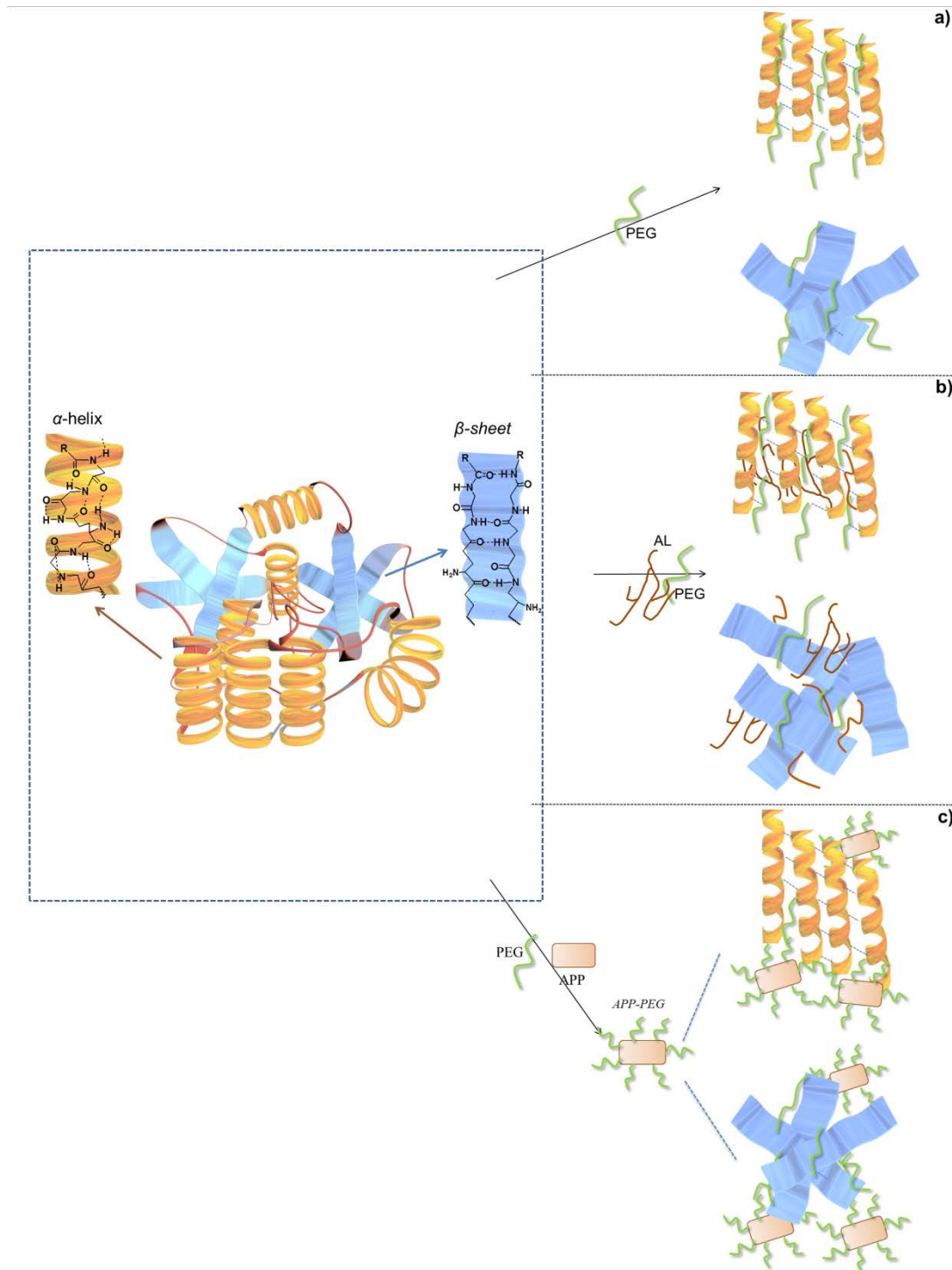
**Figure 3:** FTIR spectra of deconvoluted TPZ, and TPZ-10APP and TPZ-3AL films.

Table 3: FTIR data

Sample	β -sheet		α -helix		β -turns		others		R^{\S} ($A_{(\alpha\text{-helix}+\beta\text{-sheet})}/A_{\beta\text{-turns}}$)
	λ (cm ⁻¹)	A*(%)	λ (cm ⁻¹)	A*(%)	λ (cm ⁻¹)	A*(%)	λ (cm ⁻¹)	A*(%)	
TPZ	1624	38	1653	47	1669	8	1594	7	10.62
TPZ-10APP	1624	42	1653	50	1680	8	-	-	11.5
TPZ-3AL	-	-	1650	58	1705	25	1740	17	2.32

*A: area; § area ratio



Scheme 1: Schematic representation of the secondary structure of zein protein after thermoplasticization. The insertion of a) PEG and b) PEG and AL between the α -helix and β -sheets modifies the protein secondary structure. c) The APP additive interacting with PEG reduces its plasticizing effect and the secondary structure of protein is not affected.

3.3. Thermogravimetry analysis

Figure 4 shows the thermogravimetry curves of TPZ, AL and APP alongside with the curve of TPZ3AL10APP composite, collected both in nitrogen and air flow. The respective weight losses at 450 and 900°C are reported in Table 4. During heating up to 200°C, TPZ and AL show an initial weight loss equal to around 10wt% which is likely due to water and volatile impurities. A further heating brings a weight loss of about 70wt% for the TPZ in the range 250-450°C in both nitrogen and in air. This loss is due to the overlapping of two processes with maximum weight loss rate at 330 and 400°C and at 330 and 430°C in nitrogen and air respectively. At temperatures higher than 450°C the TPZ is quite stable in nitrogen, showing a slow weight loss due to the volatilization with a residue of 8wt% at 900°C; whereas in air the TPZ thermal degradation residue is oxidized to complete volatilization between 450 and 650°C [32]. As for AL, above 200°C the material undergoes a two steps degradation process on heating in nitrogen. The first step (200-450°C, max. rate 400°C) takes place with 40% weight loss, producing a residue which undergoes a slow, continuous thermal volatilization second step with a residue of about 30wt% at 900°C. In air the thermal degradation consists of two steps: thermal degradation of AL and oxidation of the resulting degradation products, resulting in a weight loss covering a broad range of temperatures (200-650°C) with maximum rate at 500°C and complete volatilization [33], as in the case of TPZ. Also APP thermal volatilization occurs in two steps both in nitrogen and air conditions. In the first step (300-400°C, 16wt% weight loss, Table 3), water and ammonia are evolved with formation of a crosslinked polyphosphoric acid-phosphoramidate structure. In the range 600-700°C, this material undergoes a sharp weight loss leaving a residue (22wt% in nitrogen, 10wt% in air, Table 3) which is stable in both atmospheres upon heating up to 900°C [34].

Finally the composite material containing 3wt% AL and 10wt% APP shows degradation processes both in air and nitrogen which are very similar to those exhibited by TPZ material. However the two thermal degradation steps, present in the region 200-450°C, are slightly anticipated with respect to those of TPZ.

A simple evidence of chemical interactions taking place between the several components within the composites, can be obtained by comparing the experimental TGA data for the system TPZ3AL10APP with those calculated by assuming additive behavior on the basis of data for single component. In Table 4 this comparison is made at 450°C and 900°C. Taking into account the experimental error, the most evident calculated-experimental weight loss difference is found at 450°C in air (experimental 32wt% to be compared with the calculated 26wt%) and at 900°C both in

nitrogen and in air (22wt% and 5wt% to be compared with 11wt% and <1wt% respectively). This shows that the residues of the degradation process of TPZ3AL10APP at 450 and 900°C, due to the interactions established between the components as confirmed by FTIR spectroscopy, are much more thermally stable than those obtained from pristine TPZ and single components. Obviously the thermal stability of the residues may be ascribed to the complex interactions established between the several components such as PEG, AL, APP and the zein matrix and their effect on the secondary structure of proteins as previously discussed. As far as flammability is concerned, the presence of residues with enhanced thermal stability at around 450°C, which correspond to the thermal regime of materials during exposure to flame, may strongly contribute to reduce heat transfer from flame to burning polymer. In fact it may likely act as a thermal shield lowering thus the combustion rate.

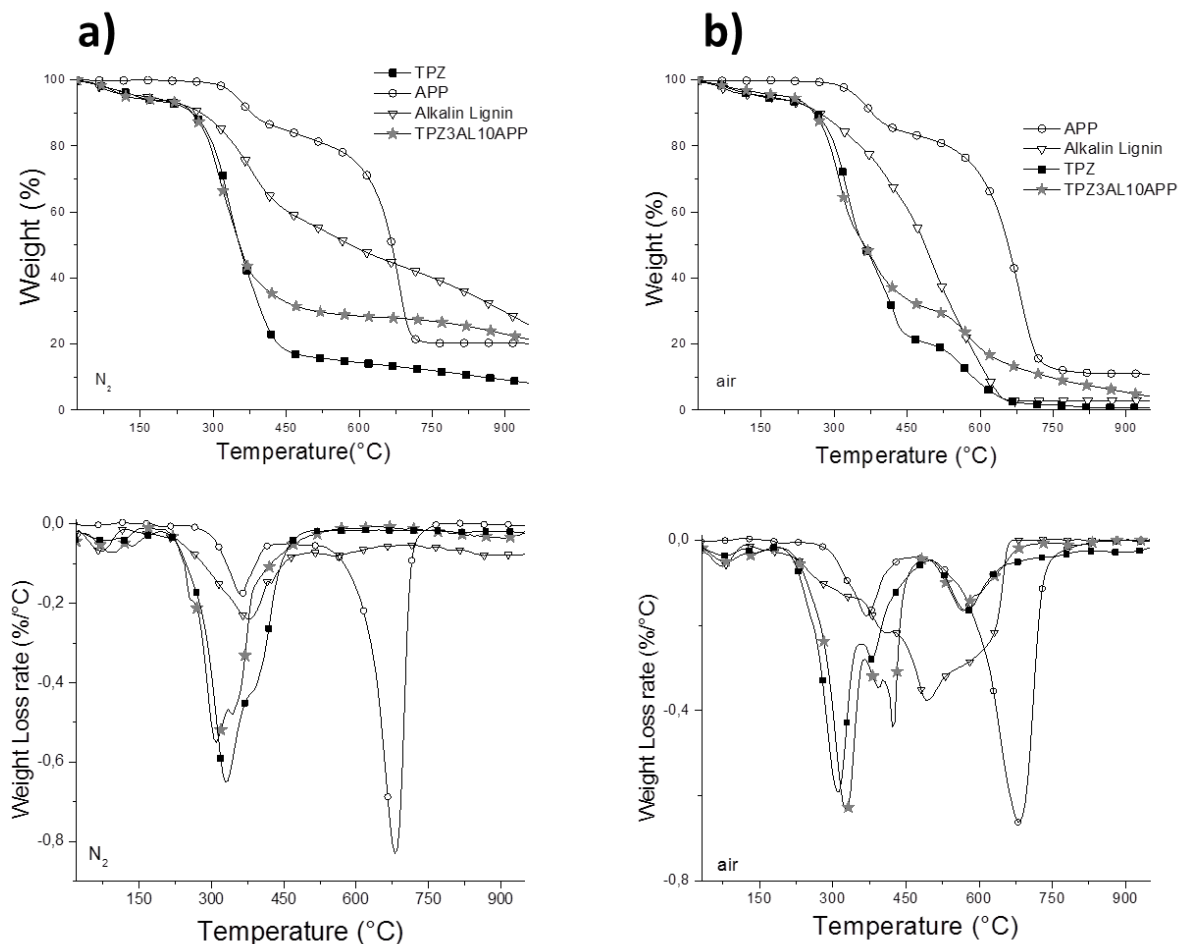


Figure 4: Thermogravimetry data in a) nitrogen and b) air atmosphere of TPZ, AL, APP and composite films TPZ3AL10APP.

Table 4: TGA weight residues

<i>Weight residues at 450°C (%wt)</i>				
Conditions	TPZ	AL	APP	TPZ3AL3APP*
Nitrogen	18	60	84	30 (35)
Air	23	62	83	32(26)

<i>Weight residues at 900°C (%wt)</i>				
Conditions	TPZ	AL	APP	TPZ3AL3APP*
Nitrogen	10	30	22	22 (11)
Air	0	0	10	5 (<1)

*In brackets calculated values based on additive behavior

3.4. Combustion behavior

3.4.1. Forced combustion, Cone Calorimetry

TPZ combustion behavior in the Cone Calorimeter test, shown in Figure 5a, is typical of a non-charring material, showing heat release acceleration up to a maximum (90s, 865 kW/m²) and then slowing down upon material consumption. Combustion is likely to occur mostly in equilibrium anaerobic conditions between ignition and flaming out, at a temperature not larger than 450°C since the residue at the end of combustion (200s, 18wt%, Figure 5b) is comparable to that obtained in nitrogen TGA at that temperature (Figure 4a). On air exposure, the residue after flame out is quite stable and its temperature does not exceed 550°C because of its weight loss occurs at a low rate; at higher temperature fast oxidation to volatiles is shown to occur by TGA in Figure 4b and the residue left at end of experiment of about 6wt%. The total heat released at end of combustion (200s) amounts to 72 MJ/m² for combustion of about 85wt % of TPZ. Addition of 3wt% AL to TPZ, noticeably increases time to ignition from 10s to 50s (Figure 5a) with negligible effect on the heat release trend, reaching a HRR peak after around 160s (i.e 70s after pure TPZ) equal to about 717 kW/m² which is approximately 15% lower than that of TPZ. A comparable decrease is also observed in the weight loss (Figure 5b) and THR (Figure 5c). This is in agreement with lower weight loss and production of combustible volatiles from lignin as compared to TPZ shown by TGA analysis (Figure 4a). After flame out (300s), the TPZ3AL combustion residue behaves as that of TPZ, reaching temperatures below complete oxidation (550°C). A similar behavior (data not shown here) was found for the composite with 10wt% AL. Addition of 10wt% APP turns the heat release rate trend of TPZ to that of a charring material, leveling off at about 50s after ignition,

showing then oscillations between 100 and 200 kW/m² equal to a reduction by 80 to 90% of TPZ's peak HRR. Combustion stops after about 400s when the THR and the weight loss level off respectively at 35MJ/m² and 35wt% of original weight. Thus, in the presence of APP, the heat released by the combustion of APP based composite is reduced by 50wt% and the material volatilized, by 43wt%. On the other hand, TGA of APP based composite under nitrogen (data not shown here) shows an additive behavior in the temperature range 300-450°C in which the thermal degradation feeding the flame in the cone calorimeter generally occurs, which would predict a 75wt% calculated weight loss at end of combustion, instead of experimental 55wt%. Therefore, it appears that in the forced cone calorimeter where compared to the TGA analysis realizes the combustion of a more massive sample, an interaction takes place between polyphosphoric acid deriving from APP ammonia elimination at 300-400°C and TPZ reactive OH and NH₂ groups. This interaction strongly reduces the combustion rate of TPZ and the burned amount. This behavior reminds that of intumescent fire retardant compositions based on APP/Polyhydroxy and amine compounds such as pentaerythritol and melamine [34-35] in which chemical dehydration and charring reactions are promoted on heating, producing a foamed char on the surface of the polymer which shields it from the action of the flame. Addition of 3% lignin to TPZ10APP has a negligible effect on its overall HRR trend and overall combustion behavior. These results show that lignin and APP both increase time to ignition of TPZ but while lignin has a negligible effect on TPZ forced combustion behavior, APP strongly modifies it, improving the fire performances as effect of charring reactions which produce a foamed materials able to protect the substrates.

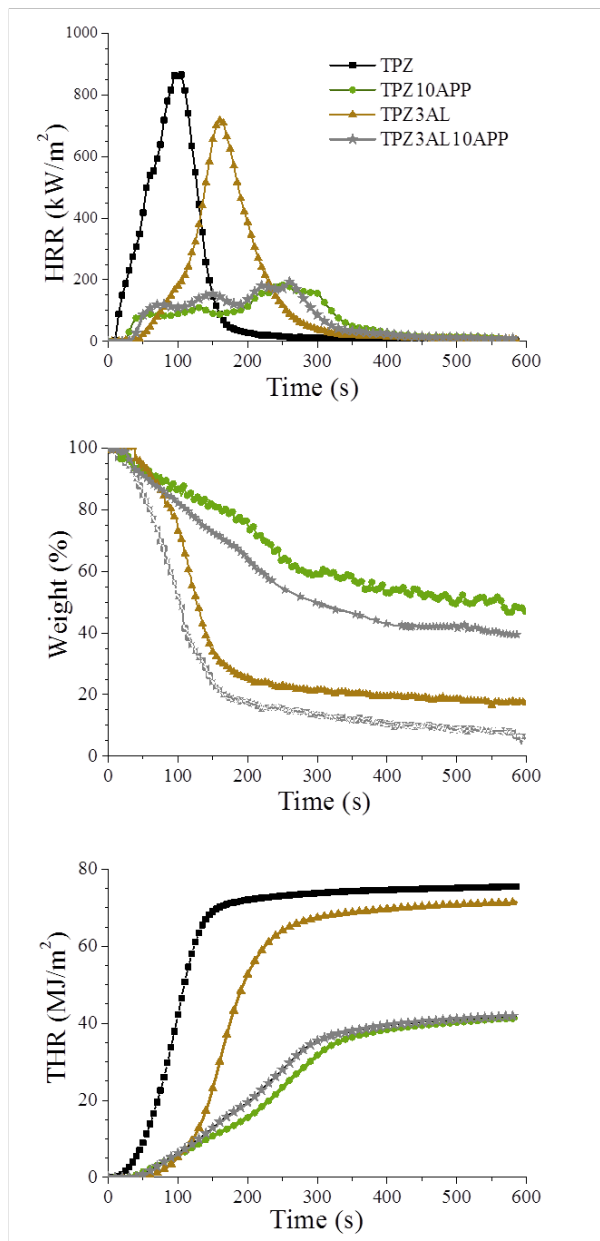


Figure 5. a) Heat Release Rate, b) Weigh Loss and c) Total Heat Release for TPZ, TPZ3AL, TPZ10APP and TPZ3AL10APP materials

3.4.2. Self-sustained vertical combustion test

Exposure of TPZ film to a flame of a small burner for 3s, makes the film rapidly withdraw from the flame with occasional dripping of one or two flaming small drops (Figure 6a). Although the test is carried out in slightly different conditions compared to UL 94 (3s ignition instead of 5s and width sample 50 mm instead of 13.5 mm) this behavior could be compared to that leading to V-2-like fire

retardant ranking in regular UL94 test. At end of test about 90 % of TPZ is recovered, as shown in Table 5.

The thermal shrinking-based fire retardant mechanism displayed by TPZ, has also been found for example in PE films added with a thermal radical initiator and it was named “run away” effect [36] whose molecular mechanism has not yet been identified. In the case of TPZ it is possible that the degradation-volatilization of the plasticizer, which takes place during the sample heating induced by the ignition flame, brings back the supramolecular arrangement of the secondary protein structure to the initial stage, corresponding to that of native zein powder. This may happen with consequent macroscopic shrinking and withdrawing of film from the flame. This mechanism is confirmed by comparing the spectra of native zein, TPZ and TPZ-post burning treatment (see Figure S2 in the Supporting Information). The secondary structure of protein, just around the burning area, appears significantly similar to that of native zein (i.e zein powder). This is ascribed to the volatilization of PEG plasticizer as consequence of the burning process and the re-establishing of the native secondary structure of the zein with the re-formation of the initial inter and intra-molecular interactions with consequent relaxations of the protein macromolecules. This mechanism brings to some movements of the films.

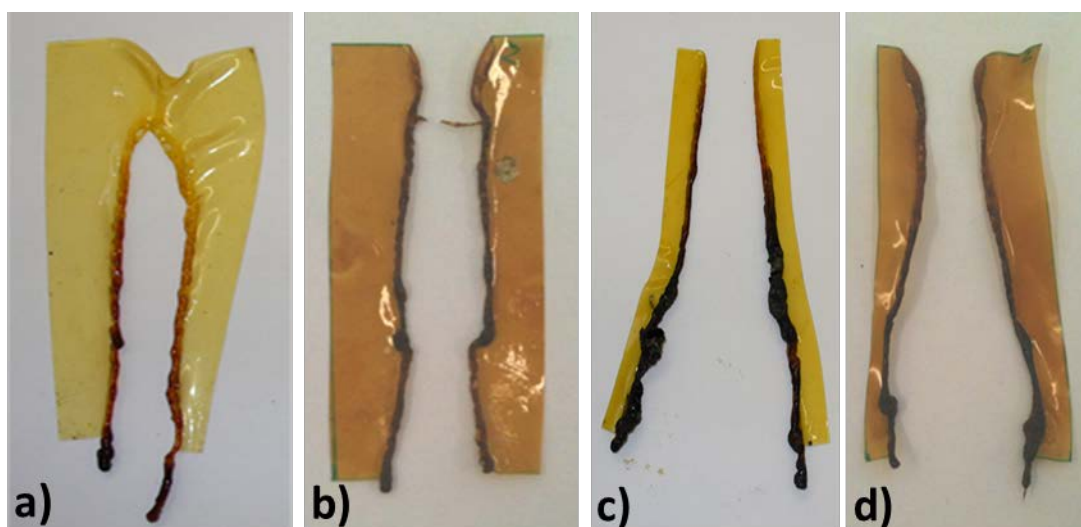


Figure 6: Vertical burnt specimens of a) TPZ, b) TPZ3AL, c) TPZ10APP and d) TPZ3AL10APP materials

Table 5. Vertical combustion performance

Sample	t ₁ [s]	t ₂ [s]	t _{tot} [s]	Cotton ignition	Residual weight [%]
TPZ	/	3	3	YES	91
TPZ3AL	/	/	/	NO	95
TPZ10APP	/	16	16	NO	86
TPZ30APP	/	4	4	YES	89
TPZ3AL10APP	0-5	3-7	6-10	NO	91

Addition of 3wt% of lignin to TPZ, has some remarkable effects on film withdrawal from the flame and avoids flaming combustion, so that the fire retardant ranking would raise to V-0-like with reduction of sample consumption to 5wt%. Further addition of lignin to 10wt% doesn't have additional effects.

APP moderately lowers the shrinking trend of TPZ and avoids flaming combustion on first flame exposure, whereas it promotes flaming and heavy dripping at the second one, depending on concentration. At 10wt% APP loading, TPZ combustion time increases; however fire retardant ranking is increased to V-1-like because falling drops do not ignite the cotton underlying the burning specimen as in the case of pure TPZ. Whereas, at 30wt% APP concentration the combustion time decreases, owing to extensive flaming dripping which lowers the ranking to V-2-like level. The contrasting fire retardant effects of lignin and APP in vertical burning, are the result of their effect on the supramolecular structure of the TPZ which governs its withdrawal from the flame. In particular, thermal decomposition of lignin which is inserted within the zein secondary ordered domains together with volatilization of PEG, may give way to a larger zein molecular shrinking packing than in the case of APP with consequent significant withdrawal from the flame. In conclusion, since the addition of lignin improves the fire retardant behavior of TPZ in vertical self-sustained burning scenario and APP that in pool forced combustion, the TPZ-based composites containing both additives have also been tested. The results reported in Table 5 alongside with those

shown in Figure 5, show that 3wt% lignin and 10wt% APP provide TPZ with most effective fire protection in both above fire scenarios.

3.4. Mechanical properties

The effects of AL and/or APP on elastic modulus and tensile strength for the pristine TPZ and TPZ-based composites are shown, respectively, in Figure 7a and 7b. The elongations at break measured during tensile tests and the toughness obtained by the area under the stress-strain curves are presented in Table 6. The elastic modulus and the tensile strength increased with AL content, and a significant improvement was observed, even, at 3%wt. Conversely, the percentage elongation at break values showed a slight decrease as the AL content increased. These mechanical insights are attributed to the formation of the strong hydrogen bonding between the some functional groups of aminoacids of the zein (i.e -C=O, -OH, -NH groups) and the functional groups (i.e -OH and -SH groups) of AL [22,32]. At higher filler content, 10wt%, the AL can be instead simply considered as a reinforcing filler for TPZ. The addition of APP decreased the tensile strength, but increased the stiffness of all TPZ-based composites. Similar results have been reported by Bocz et al. [37] for flax fiber reinforced PLA/TPS biocomposites flame retarded with multifunctional additive system. As seen from Table 5, the toughness increased drastically up to 5.5 MJ/mm³, which corresponds to an increment of 60% compared to pristine TPZ, when the content of AL is 10wt%. The toughness of the TPZ-based composites decreased, instead, after the addition of APP. The greater the content of APP, the greater the decrease of composites toughness. However, when the content of APP is of 10wt%, the biocomposites containing AL still exhibit good mechanical properties and can have practical utility. In particular the system TPZ3AL10APP exhibits a toughness which is around 30% higher than that of pristine TPZ.

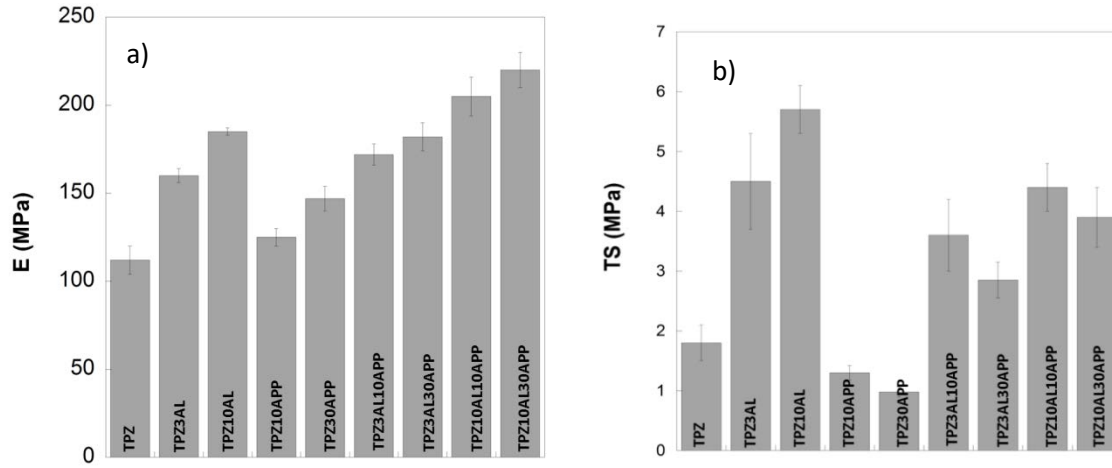


Figure 7. a) Young's modulus and b) Tensile strength of TPZ-based composites.

Table 6: Elongation at break and toughness of TPZ-based composites (standard deviation in bracket).

Sample	Elongation at break, %	Toughness, MJ/mm ³
TPZ	180 (11)	2.84 (0.17)
TPZ3AL	90 (10.3)	4.01 (0.21)
TPZ10AL	130 (8.3)	5.55 (0.14)
TPZ10APP	160 (12)	2.52 (0.18)
TPZ30APP	135 (7.6)	1.4 (0.10)
TPZ3AL10APP	85 (6.2)	3.75 (0.15)
TPZ3AL30APP	79 (5.8)	2.9 (0.10)
TPZ10AL10APP	125 (13)	3.94 (0.16)
TPZ10AL30APP	119 (9.7)	3.4(0.2)

Conclusions

The study deals with the preparation and characterization of innovative composites based on biopolymer as protein from renewable sources and additives such as APP and AL which exhibit improved mechanical properties as well as the resistance to fire in different scenario. The results confirm that APP and AL have a key role to targeting the properties of the resulting composites above all with respect to the fire behavior. In particular the lignin filler improves the fire retardant behavior of TPZ in vertical self-sustained burning scenario due to the volatilization of PEG and the simultaneous degradation of lignin which imparts a severe shrinking of the zein structure with consequent withdrawal of the film from the flame. On the other side APP improves the fire retardant behavior of composites exposed to pool forced combustion. This is due to the prominent charring effect of the inorganic filler. Therefore, the combination of the two selected fillers was proposed as valid approach to design and produce a material with satisfactory fire retardant behavior in both scenarios. The formulations have been optimized to maximize also the mechanical properties. In particular, the best results were obtained for a biocomposites containing 10wt% APP and 3wt% AL, which exhibit improved stiffness and tensile strength coupled with a satisfying toughness.

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