# FIRE RETARDANT ZEIN-BASED MATERIALS

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## Abstract

Plastics find many uses in the modern-day life. Many of these polymers are derived from petroleum, a not replenish-able resource. To alleviate this problem, governments in many countries have established laws to encourage the use of recycled and/or bio-based “green” products. In this paper, the combustion behavior of a thermoplastic protein zein (TPZ) obtained from a renewable-resource and the fire retardant effect of either lignin (AL) or ammonium polyphosphate (APP) and of their combination on TPZ combustion is studied. Combustion behavior is tested on samples in vertical burning upon small flame ignition or in horizontal configuration on exposure to radiant heat source and pilot flame ignition. Addition of lignin improves the fire retardant behavior of TPZ in vertical self-sustained burning scenario and APP that in pool forced combustion, so their combination is tested to target a material with satisfactory fire retardant behavior in both scenarios.

## 1. Introduction

The growing global environmental awareness and societal concern, high rate of depletion of petroleum resources, concepts of sustainability and new environmental regulations have together triggered the search for new products compatible with the environment [1]. The biodegradable polymers and, in particular polymers obtained from renewable-resources such as the polysaccharides (ex. starch) and proteins (ex. wheat gluten, zein) has long been recognized as one of the most promising approach for substituting petrochemical-based polymers. Zein is an example of the vegetable protein used as a sources to produce thermoplastic polymers. It is found in corn endosperm and has been the object of research as well as industrial interest for its film-forming ability [2, 3].

The sustainable approach to polymer materials requires that besides sustainability of the polymer also additives and fillers (ex. lignin) generally necessary to tailor the material properties to the application (ex. protection to fire risk), be sustainable as well. Lignin from wood is a waste product of cellulose based industry. Its environmental impact could be reduced by its use as a fire retardant additive for polymers. Indeed, it is shown that used alone or in combination with ammonium polyphosphate it is a suitable fire retardant for example for polypropylene, displaying an environment friendly fire retardant mechanism based on emission-free condensed phase fire retardant action [4].

In this work, the combustion behavior of thermoplastic zein (TPZ) and the fire retardant effect of either lignin (AL) or ammonium polyphosphate (APP) and of their combination on TPZ combustion is studied .

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## 2. Materials and methods

### 2.1. Materials

Maize zein powder and plasticizer poly(ethylene glycol), PEG are used for the preparation of thermoplastic zein (TPZ). To improve the combustion behavior of TPZ, two different flame retardant compounds were used: alkaline lignin, denoted AL, and ammonium polyphosphate, denoted APP. The TPZ-AL biocomposites are prepared by using a melt mixing process [5]. The same procedure is used to produce the biocomposites with APP in place of AL and the biocomposites with both flame retardants AL and APP. After mixing, the biocomposites were compression molded at 80°C, 50 bar into sheets and slabs by a hot press (P300P, Collin, Germany). The compositions and nomenclature adopted are reported in table 1.

**Table 1.** Compositions and nomenclature of TPZ-based biocomposites.

| Samples | AL (wt%) | APP (wt%) |
|---|---|---|
| **TPZ** | - | - |
| **TPZ3AL** | 3 | - |
| **TPZ10APP** | - | 10 |
| **TPZ3AL10APP** | 3 | 10 |

### 2.2. Methods

Combustion behavior is tested on sheet samples in vertical burning upon small flame ignition or in horizontal configuration on exposure to radiant heat source and pilot flame ignition which are the two typical fire scenario used to assess reaction to fire of polymer materials. In vertical burning, films 100x50 $mm^2$ and thickness ranging between 100 and 300 µm are supported on a vertical frame and exposed to a Bunsen flame impinging on the low sheet side and the upward burning behaviour is recorded similarly to the UL 94 vertical burning test [6] measuring afterflame time following first and second 3s ignition ($t_1$ and $t_2$ respectively), total after flame time $t_{tot}=t_1+t_2$, specimen weight loss and observing whether combustion occurrs with dripping and whether the cotton underlying the burning specimen is ignited by flaming drops.

Exposure to radiant heat is carried out in the Oxygen Consumption Calorimeter (“Cone Calorimeter”) following the ISO 5660 procedure. Specimens of 100x100 $mm^2$ and thickness of 3mm are characterized with cone calorimeter at heat flux of 50 $kW/m^2$ . This equipment is the first choice for measuring heat release rate (HRR). HRR is defined as the amount of calorific energy released per unit time by a material during combustion and it is one of the fundamental fire properties to take in account in any assessment of fire hazard.

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## 3. Results and discussions

### 3.1 Forced combustion, Cone Calorimeter.

TPZ combustion behavior in the Cone Calorimeter test, shown in Figure 1, is typical of a non-charring material, showing heat release acceleration after ignition, to a maximum (100s, 865 kW/m$^2$) then slowing down upon material consumption. Addition of 3% AL to TPZ, noticeably increases time to ignition (TTI) from 10s to 50s with negligible effect on the heat release trend, reaching a peak HRR 60s after pure TPZ (160s), of 717 kW/m$^2$ which is 15% lower than TPZ. Addition of 10% APP, besides increasing TTI to 15s, it turns the heat release rate trend of TPZ to that of a charring material, leveling off 50s after ignition, showing then oscillations between 100 and 200 kW/m$^2$ that is a reduction by 80 to 90% of TPZ peak HRR. At least, addition of 3% lignin to TPZ10APP has a negligible effect on its overall HRR trend and overall combustion behavior.
In figure 2 the images of samples after cone calorimeter tests are shown. It is clear the passage from a non-charring material (TPZ) to a charring material (TPZ10APP and TPZ3AL10APP).

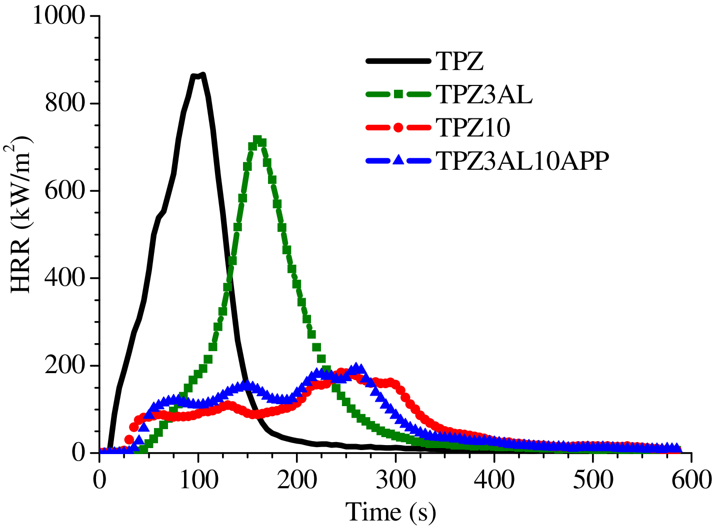

**Figure 1.** Heat Release Rate (HRR) for TPZ, TPZ3AL, TPZ10APP and TPZ3AL10APP at 50 kW/m$^2$.

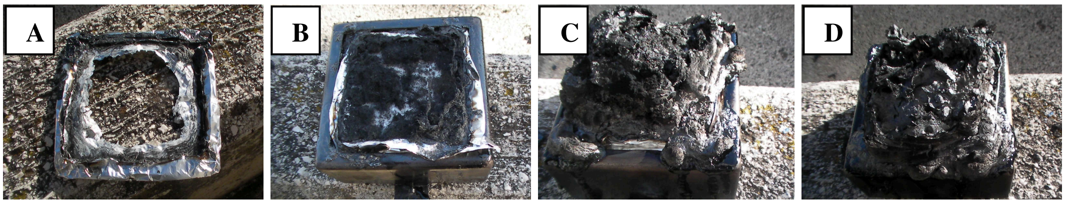

**Figure 2.** Images of samples after cone calorimeter tests: (A) TPZ, (B) TPZ3AL, (C) TPZ10APP and (D) TPZ3AL10APP.

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### 3.2 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. Although the test is carried out in slightly different conditions compared to UL 94 (3s ignition instead of 10s and width sample 50 mm instead of 13 mm) this behavior could be compared to that leading to V-2 fire retardant ranking in regular UL94 test. At end of test about 90% of TPZ is recovered, as shown in Table 2 and Figure 3.
Addition of 3% lignin to TPZ, has no remarkable effect on film withdrawal from the flame but avoids flaming combustion, so that the fire retardant ranking would raise to V-0 with reduction of sample consumption to 5%. 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. In particular, at 10% APP loading, TPZ combustion time increases, however fire retardant ranking is increased to V-1 because falling drops do not ignite the cotton underlying the burning specimen as in the case of pure TPZ.
Since addition of lignin improves the fire retardant behavior of TPZ in vertical self-sustained burning scenario and APP that in pool forced combustion, their combination is tested to target a material with satisfactory fire retardant behavior in both scenarios. The results summarized in table 2 together with those shown in Figure 1, show that 3 wt% AL and 10 wt% APP provide TPZ with most effective fire protection in both above fire scenarios

**Table 2.** Vertical combustion performance.

| Samples | $t_1$(s) | $t_2$(s) | $t_{tot}$ (s) | Cotton Ignition | Residual weight (%) |
|---|---|---|---|---|---|
| **TPZ** | - | 3 | 3 | YES | 91 |
| **TPZ3AL** | - | - | - | NO | 95 |
| **TPZ10APP** | - | 16 | 16 | NO | 86 |
| **TPZ3AL10APP** | 0/5 | 3/7 | 6/10 | NO | 91 |

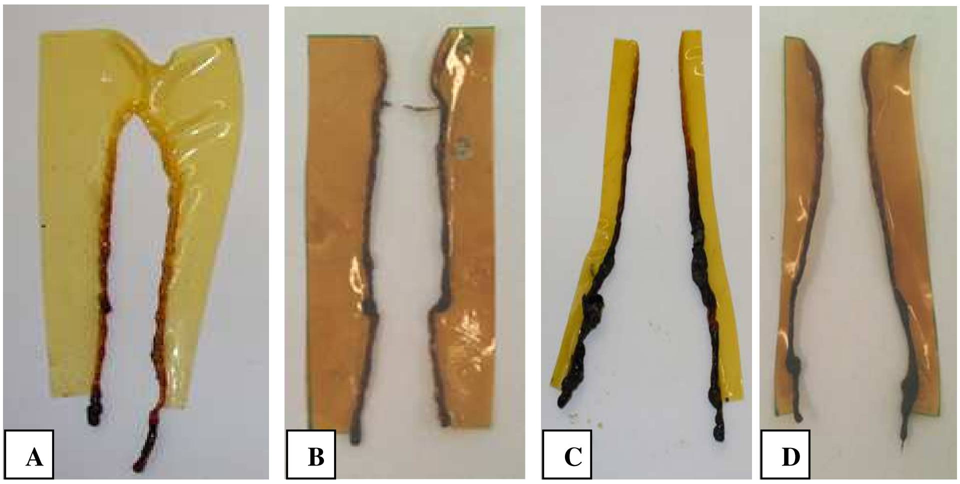

**Figure 2.** Images of samples after vertical combustion tests: (A) TPZ, (B) TPZ3AL, (C) TPZ10APP and (D) TPZ3AL10APP.

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## 4. Conclusions

The combustion behavior of thermoplastic protein zein (TPZ) and the fire retardant effect of either lignin (AL) or ammonium polyphosphate (APP) and of their combination on TPZ combustion is studied by the two typical fire scenario used to assess reaction to fire of polymer materials: vertical flammability test and a forced combustion test in horizontal configuration.

Flammability tests show, for TPZ film, a withdraw from the flame with occasional dripping of small drops. This behavior can be compared to that leading to V-2 in a traditional flammability UL 94 test. Addition of lignin to TPZ improves the fire retardant ranking to V-0, while addition of APP does not improve flammability behavior.

Cone calorimeter tests show that AL and APP both increase time to ignition of TPZ, but, while AL has a negligible effect on TPZ forced combustion behavior, APP strongly modifies it. At least, since addition of AL improves the fire retardant behavior of TPZ in vertical self-sustained burning scenario and APP that in pool forced combustion, a combination of the two (3 wt% AL and 10 wt%) has been identified to obtain a TPZ with satisfactory fire retardant behavior in both scenarios.

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