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Sustainable Flame-Retardant Flax Fabrics by Engineered Layer-by-Layer Surface Functionalization with Phytic Acid and Polyethylenimine

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Abstract. New generation of mission-oriented fabrics meets advanced requirements; such as electrical conductivity, flame retardancy, and anti-bacterial properties. However, sustainability concerns still are on-demand in fabrication of multi-functional fabrics. In this work, we used a bio-based phosphorus molecule (phytic acid, PA) to reinforce flax fabrics against flame via layer-by-layer consecutive surface modification. First, the flax fabric was treated with PA. Then, polyethylenimine (PEI) was localized above it to create negative charges, and finally PA was deposited as top-layer. Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), and inductively-coupled plasma atomic emission spectrometry (ICP-AES) proved successful chemical treatment. Pyrolysis-combustion flow calorimetry (PCFC) showed significant drop by about 77% in the peak of heat release rate (pHRR) from 215 W/g for untreated to 50 W/g for treated flax fabric. Likewise, the total heat release (THR) decreased by more than three times from 11 to 3.2 kJ/g. Mechanical behavior of the treated flax fabric was completely different from untreated flax fabrics, changing from almost highly-strengthened behavior with short elongation at break to a rubber-like behavior with significantly higher elongation at break. Surface friction resistance was

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also improved, such that the abrasion resistance of the modified fabrics increased up to 30,000 rub cycles without rupture.

Keywords: Flax fibers, Flame retardant, Sustainability, Biobased flame retardant, Textile

1. Introduction

Development of smart and functional fibers, textiles, and fabrics has taken a speedy rate of progress just over the past decade, such that a wide range of applications are proposed and realized. For instance, textile industry has introduced and commercialized textiles as triboelectric nanogenerators for smart fabrics [1]. Modern fabrics are multidisciplinary, designed for wearable electronics [2], respiratory cloth masks [3], functional masks to combat COVID-19 [4], and even as wound dressing or artificial skin [5]. By increasing interests in multi-functional textiles and fabrics, safety and health considerations have also received more attention. Flame retardancy is a performance feature of functional textiles and fabrics [6]. In this regard, different sorts of flame retardants have been examined, among which are phosphorus-containing [7, 8], nitrogen-rich [9], and amino acid based [10] flame retardants. Moreover, fabrics should be environmental friendly and meet advanced technological circumstances.

Sustainable materials are receiving more attention in design and implementation of green production and consumption protocols [11, 12]. Development of sustainable flame-retardant textiles and fabrics has accordingly been developing fast to meet both environmental and safety requirements. Cotton and wool were quite widely under investigation to explore the potential of different kinds of green flame retardants. For instance, Zhang et al. [13] developed biomass-assisted flame retardants for cotton fabrics and ascribed the acceptable value of limiting oxygen index (LOI) of ≈ 27 to the char-forming character of the used flame retardant. Wang et al. [14] used a phosphorus-nitrogen flame retardant for cotton fabrics and used LOI and cone calorimetry for analysis. The char-forming flame retardant significantly improved flame retardancy, confirmed by a significant drop in the value of peak heat release rate (pHRR) from 144.23 to 11.64 kW/m² and considerable increase in LOI from 18 to 29%. The use of inherently phosphorus-rich phytic acid (up to ≈ 28 percent by wt.%) received a particular attention in fabrication of flame retardant fabrics [15]. Some researchers also attempted to mechanistically explain the efficiency of phytic acid as a biodegradable flame retardant for cotton fabrics [16].

Layer-by-layer assembly of coatings onto the surface of fabrics brings about the possibility of developing all-in-one fabrics. Xue et al. [17] integrated superhydrophobicity, conductivity, and flame retardancy in one package to develop multi-task cotton fabrics applying carbon nanotubes. Liu et al. [18] used layer-by-layer assembly to prepare products in which phytic acid and egg white protein were combined to phosphorus and nitrogen for development of sustainable cellulosic fabrics. Fang et al. [19] blended polyester with cotton to prepare layer-by-layer assembled fabrics reinforced with chitosan and phytic acid and claimed achieving a dual-face flame retardant acting in condensed phase and at the same time as a

catalyst leading to LOI rise from 20 to 29.2%. Such investigations are mainly reported for cotton, while other members of fabrics family with higher impotence from technological, biomedical, and military requirement angles have been the subject of a few investigations.

Flax fabric is an attractive natural material, but it is highly flammable. Several reports have addressed treatment of flax fibers/fabrics with different chemicals such as tetraethoxysilane (TEOS), diethylphosphatoethyltriethoxysilane (DEPTES), and (3-aminopropyl) triethoxysilane (APTES) [20], polydopamine [21], and extracellular polymeric substances [22] to improve flame retardancy. In a previous work, we a non-biobased flame retardant of ammonium polyphosphate (APP) and a conductive polyaniline to modify flax fabric and succeed to obtain bifunctional (flame retardant and electrical conductive) flax fabrics [23]. Herein, to achieve a fully biobased flame-retardant fabric, we used a biobased phosphorus molecule (phytic acid) to treat flax fabrics via layer-by-layer method. The chemical treatment of flax fabrics was characterized using Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), and inductively coupled plasma atomic emission spectrometry (ICP-AES). The flammability behavior of samples was investigated using pyrolysis combustion flow calorimetry (PCFC), and vertical burning test. Tensolab 2512A/2512C electromechanical tensile tester was used with pneumatic clamps and 5 kN load cell. The abrasion test and mass lost was done with the NU Martindale Abrasion and Pilling Tester.

2. Materials and Methods

Details on materials used in preparation of sustainable flame-retardant flax fabrics (S1.1), surface treatment (S1.2) and characterization methods (S1.3) are provided in Supplementary Information (SI). In brief, flax fabrics were modified with phytic acid sodium salt (PA) and polyethyleneimine (PEI) in via layer-by-layer assembly, followed by grafting phosphorus group (Fig. 1). Hydroxylation of flax fabrics was carried out in a two-stage method [24]. The pre-treated flax fabrics were mixed with PA solution followed by immersion into cationic PEI solution under controlled time and temperature [23, 25, 26]. In this manner, four samples, namely Flax fabric, Flax fabric/PA, Flax fabric/PA/PEI, and Flax fabric/PA/PEI/PA were prepared in correspondence to untreated flax fabric, flax fabric modified with PA, flax fabric coated with PA and PEI, and eventually flax fabric coated with PA, PEI and PA, respectively. Tables S1 and S2 in SI provide additional information.

Characterization techniques were including Fourier-transform infrared (FTIR) spectroscopy to characterize the modification of flax fabric after each step of modification, energy dispersive X-ray spectroscopy (XRD) to determine the effective percentage of phosphorus, scanning electron microscopy (SEM) to observe the surface modification of fabric before and after treatment, equipped with element mappings to evaluate elemental composition, thermogravimetric analysis (TGA) to study the effect of treatment on the thermal stability of fabrics and char residue yield, and pyrolysis-combustion flow calorimetry (PCFC) [27] to evaluate the

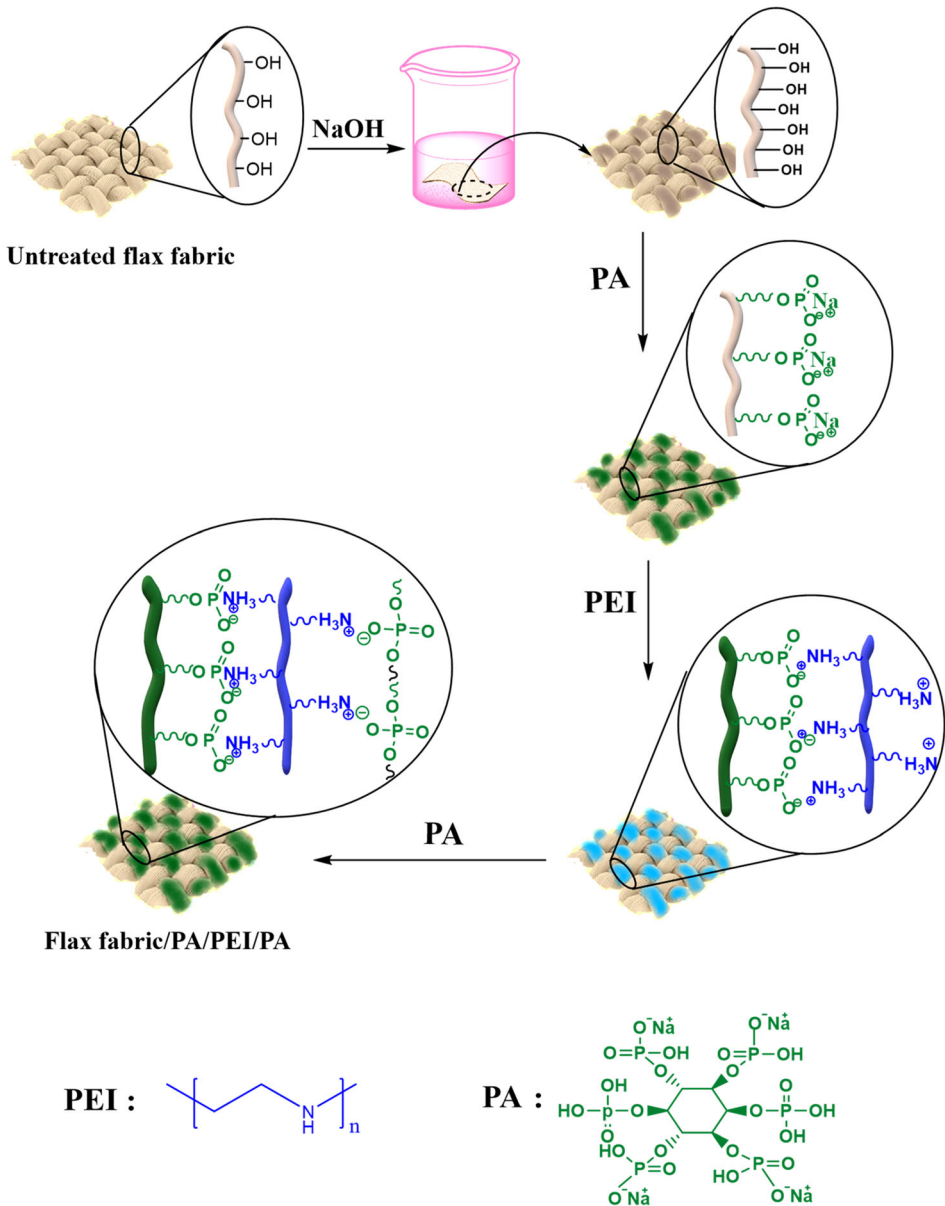


Figure 1. Layer-by-layer surface functionalization of flax fabrics by PA/PEI/PA arrangement. The layer of PEI sandwiched in between layers of PA via electrostatic forces, hydrogen bonds and van der Waals interactions.

flammability of samples. Detailed PCFC testing procedure can be found elsewhere [28]. The heat release rate (HRR), the total heat release (THR), the peak of heat release rate (pHRR), the char yield and the heat of complete combustion (HCC) were accordingly recorded and compared for samples. To evaluate the flame propagation behavior, a simple burning test was also carried out by application of a Bunsen burner on the bottom of the vertical sample, at room temperature under a laboratory fume hood. After the apparition of flame, the burner moved up in order to observe the flame behavior of samples. The digital videos were recorded, and selected images were also extracted. Tensile test was carried out to assess the mechanical strength variation under the influence of surface treatment. See S1.3 in SI for details.

3. Results and Discussion

3.1. Surface Chemistry Evaluation

FTIR analysis proved successful surface modification and layer-by-layer coating deposition onto flax fabrics (Fig. 2). Detailed peak analysis is provided in Table S3 in the section S2 in the SI. In brief, OH, C-H, CH₂, C-OH, C-O-C, C-C, C-OH, and C-H banded were detected in unsaturated flax fabrics [29]. In FTIR spectrum of flax fabric/PA/PEI/PA NH₂, OH, C-N, P = O, P-O, C-O-P and P-O in HPO₃ were detected [30, 31]. Attachment of PA and PEI to flax fabric surface was according confirmed.

3.2. Morphology of Treated Flax Fabrics

Figure 3 shows the surface of flax fabric before and after treatment obtained by scanning electron microscopy (SEM). These images clearly show the effect of treatment and coating, especially for PA/PEI/PA sample, on the surface of fabric, Fig. 3c. Energy dispersive X-ray spectrometry (EDX) analysis was also used to monitor the phosphorus presence. Figure 4 shows the flax fibers after modification by PA/PEI/PA. The phosphorus was detected on the surface of fibers. Nevertheless, phosphorus was not observed in the fiber cross-section, evidencing that it did not migrate into the fibers bulk but remains at their surface. The phosphorus content was measured using inductively coupled plasma atomic emission spectrometry (ICP-AES). After chemical modification with phytic acid, the phosphorus content is 1.7 (\pm 0.3) wt.%. The last step allows depositing a huge amount of phosphorus (3.4 \pm 0.1 wt.%).

3.3. Tensile Measurements

The tensile test was conducted on flax fabric and flax fabric/PA/PEI/PA samples to evaluate the effect of chemical treatment on the mechanical properties. Figure 5 compares the tensile stress-strain curves of non-modified and modified fabrics. The results of tensile tests demonstrated a large difference between the tensile behavior of the aforementioned samples. The non-treated fabric required a total load of 20 \pm 0.8 N/mm (almost two-fold higher than that of treated one). On the

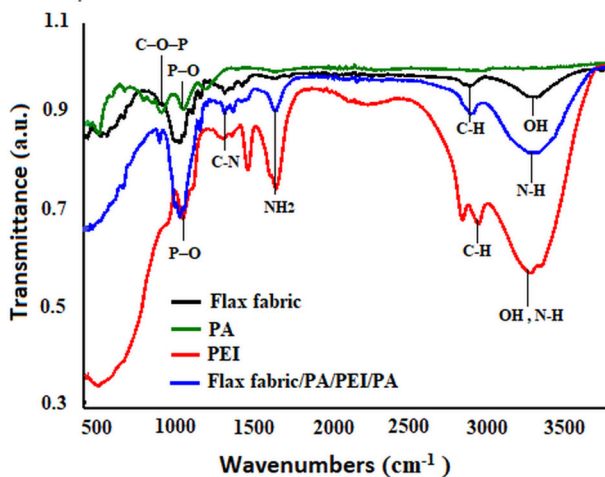


Figure 2. Fourier-transform infrared (FTIR) spectroscopy of flax fabric and flax fabric coated with different layers.

other hand, the elongation at break of the treated fabric was 12 ± 2.1 , almost five times higher than the non-treated fabric, Fig. 5. Notably, the fabric underwent shrinkage of $\approx 20\%$ in the warp and weft direction after treatment (the surface density becomes 377 g/m^2 and the yarn linear density becomes 1570 dtex). This can also be seen in the SEM images in Fig. 2. This increase in the fabric weight is due to the fabric shrinkage, which is equal to 100 g/m^2 , roots in the additive chemical present around 25%.

3.4. Abrasion Test

The abrasion test using the Martindale Method was conducted on flax fabric and flax fabric/PA/PEI/PA samples as a function of number of cycles to assess possibility of rupture of fabrics. The results presented in Fig. 6 demonstrate that the resistance to abrasion was 50% higher for treated flax fabric/PA/PEI/PA compared to untreated flax fabric, such that the treated material resisted until 30,000 rubs (cycles) for flax fabric/PA/PEI/PA, while the non-treated fabric resisted only until 20,000 rubs (cycles). The mass loss after the abrasion was 24% for flax fabric, but only 12% for flax fabric/PA/PEI/PA. The flax fabric after 1000 rub cycles started to lose its fibers, while flax fabric/PA/PEI/PA was still in very good condition until the 30,000 rub cycles. This outcome not merely confirm surface friction resistance improvement by surface modification of fabrics, which itself is important besides flammability improvement, but also brings about some beneficial features such as washability and indirectly hydrophobicity enhancement [32].

3.5. Thermogravimetric Analysis (TGA)

Thermal decomposition of flax fabrics was investigated using thermogravimetric analysis (TGA). Figures 7a and 5b demonstrated the TGA and derivative thermo-

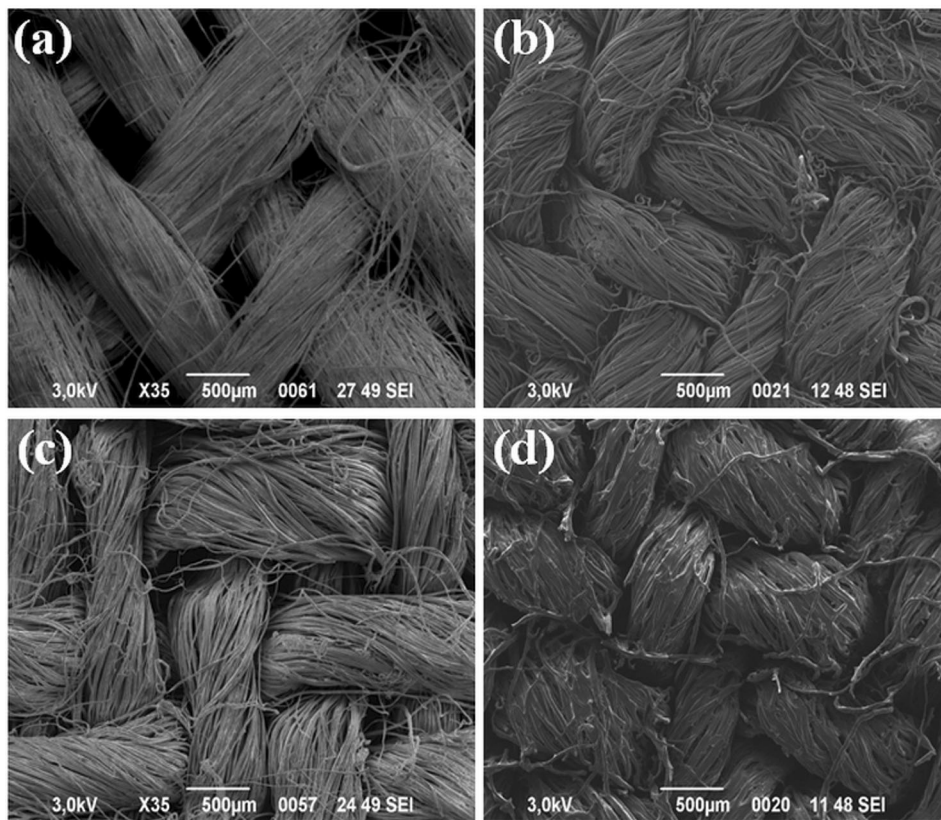


Figure 3. SEM images of flax fabric (a), flax fabric/PA (b), flax fabric/PA/PEI (c) and flax fabric/PA/PEI/PA (d) samples.

gravimetric (DTG) curves, respectively. Some important parameters (including T_5 , T_{10} and T_{max} , temperatures corresponding to 5%, 10% and maximum weight loss, as well as residue at 800°C) obtained from TGA and DTG were also summarized in Table 1. All samples showed two main apparent steps of degradation. The first stage was occurred between 50°C and 120°C for all samples. This step corresponds to the release of absorbed water on flax fabrics. The second stage was occurred at 230°C for untreated flax fabric. The treatment led to decrease the thermal stability of fabric up to 380°C. After that, flax fabric/PA/PEI/PA sample showed a higher thermal stability compared with other samples. At 380°C, the remaining mass for flax fabric/PA/PEI/PA sample was 60% which then decreased slowly and reached 41% at 800°C. It clearly shows that the chemical modification with phosphorus agent was efficient to stabilize and significantly increase the char residue. It was also concluded that the first layer of treatment with phytic acid is not solely highly efficient, since the char residue for this sample (Flax fabric/PA) was 28.7%. The high charring obtained for flax fabric/PA/PEI/PA sample is a promising result for flammability behavior. The formation of char plays a key role

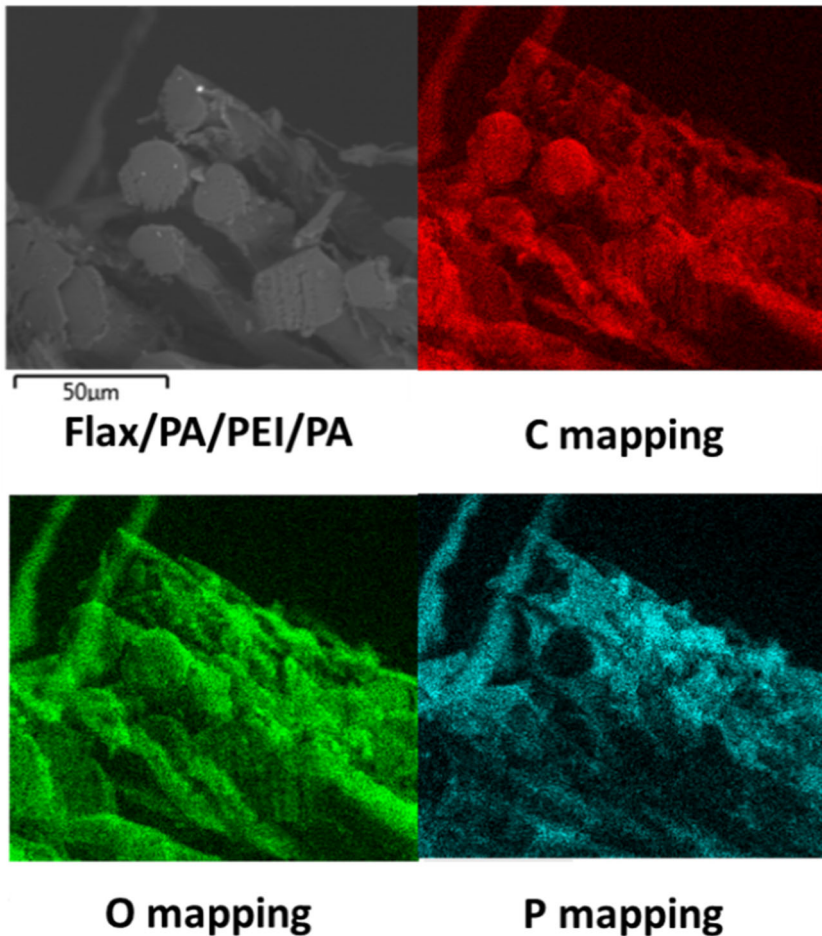


Figure 4. SEM observations of flax fabrics modified with PA/PEI/PA and elemental mappings.

in flame retardancy of materials [33] in the condensed phase by limiting the release of combustible gases due to transformation of combustible material to non-combustible char. Moreover, the char may act as barrier effect and limit the transfer of heat flux to material.

3.6. Pyrolysis Combustion Flow Calorimetry (PCFC)

Flammability at microscale was assessed using pyrolysis-combustion flow calorimetry (PCFC). Untreated flax fabric releases 11 kJ/g (THR) in one main step and its pHRR was 215 W/g at 363°C, Fig. 8. The char yield was 12% and the heat of complete combustion (calculated as the ratio between THR and mass

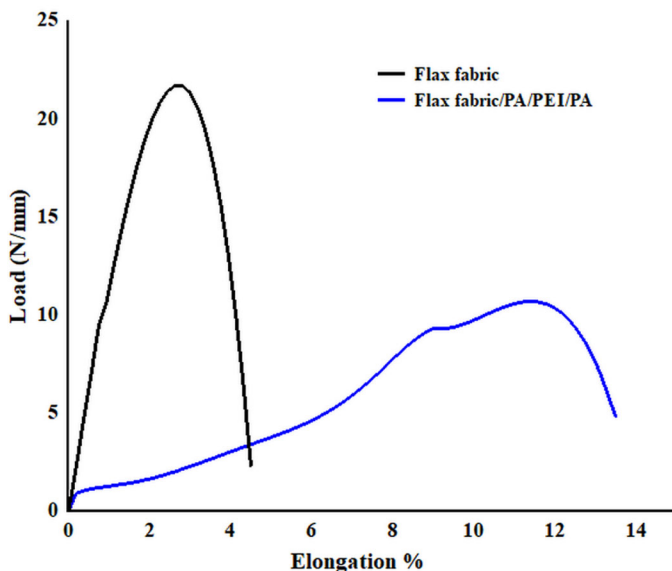


Figure 5. Tensile test for treated (flax fabric/PA/PEI/PA) and non-treated fabrics.

loss fraction) is 12.1 kJ/g for untreated flax fabric. All these values are in good agreement with those previously reported [33]. After chemical modification with phytic acid, the pHRR strongly decreased (60 W/g) as well as the THR (5.7 kJ/g). Concomitantly, the thermal stability is affected as demonstrated by the temperature at pHRR at 307°C. Moreover, a shoulder on the curve at low temperature proves that the decomposition started earlier (220°C). The char yield was reached 28 wt.%. The heat of combustion also decreased to 7.9 kJ/g. Most of the properties were close to those for unmodified fabric, such that pHRR and THR reached 172 W/g (at 352°C) and 10.8 kJ/g, respectively. The char yield is 15 wt.% and the heat of combustion increases to 12.6 kJ/g. Finally, after the last step, the high amount of phosphorus (3.4 wt.%) ensures a high flame retardancy. The pHRR was less than 50 W/g and THR is 3.2 kJ/g. The peak is observed at 298°C, but without any shoulder at low temperature. The char yield reaches 33 wt.% and the heat of combustion is 4.5 kJ/g. Based on previous works [34–37], such performances should ensure high flame retardancy at higher scale. All obtained results are summarized in Table 2.

In another work, the flax fabric used in the current study has already been treated using different procedures especially through radiografting of phosphonate-based molecules by pre-irradiation or mutual irradiation [33–36]. The same qualitative tendencies (namely a decrease in pHRR, THR and also in thermal stability) versus phosphorus content were recorded. Figure 9 shows that the pHRR of the flax fabric modified by the layer-by-layer procedure are quantitatively in agree-








Cycles	Flax	Flax/PA/PEI/PA
1000		
5000		
20 000		
30 000	Rupture	

Figure 6. Abrasion test results for treated (flax fabric/PA/PEI/PA) and non-treated fabrics.

ment with these previous results. This is also true for other flammability properties. In other words, whichever the phosphorylation procedure, the flammability at microscale depends mainly on the phosphorus content. A possible exception con-

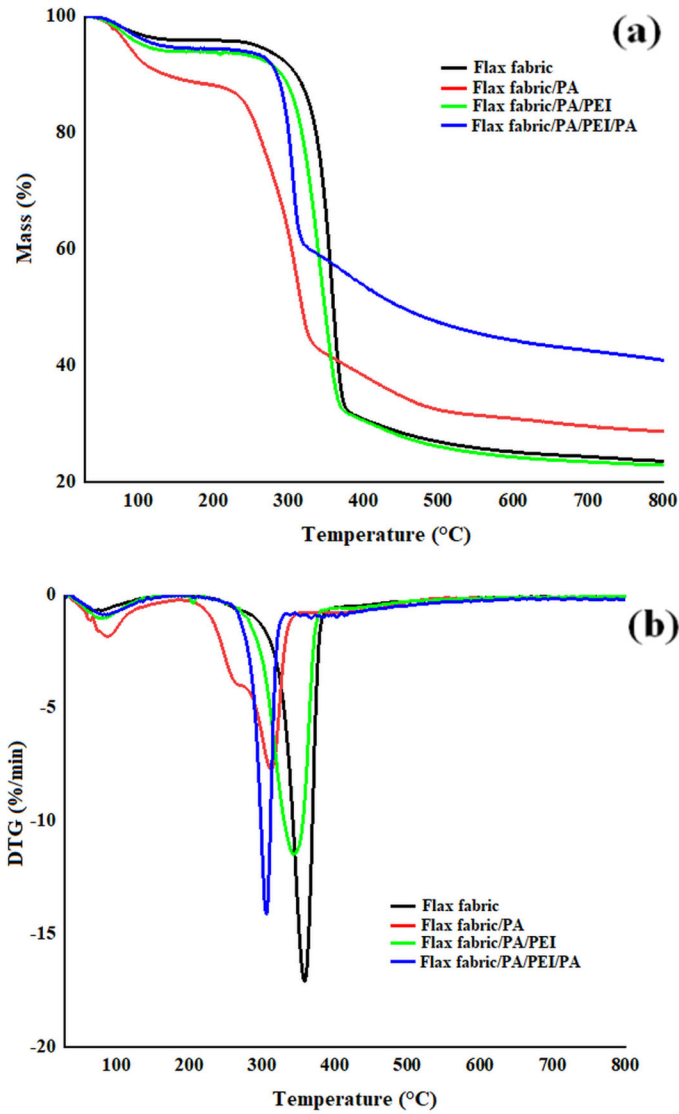


Figure 7. TGA thermograms of flax fabric and treated flax fabrics (a) and corresponding DTG curves (b), under nitrogen 10°C/min.

cerns the thermal stability. The decrease in temperature at pHRR may be more limited for the flax fabric modified with the present layer-by-layer procedure (Fig. 10).

Table 1
Quantitative Analysis of TGA Results (T_5 , T_{10} and T_{max} : Temperatures at Which 5%, 10% and Maximum Weight Loss Take Place, Respectively)

Sample code	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	Residue at 800°C (%)
Flax fabric	259	311	359	23.6
Flax fabric/PA	87	138	314	28.7
Flax fabric/PA/PEI	108	293	349	22.9
Flax fabric/PA/PEI/PA	129	286	307	41.0

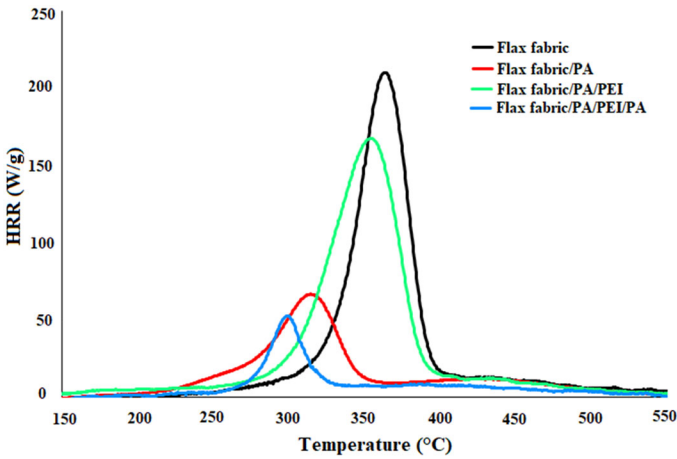


Figure 8. HRR curves versus pyrolysis temperature obtained using PCFC.

Table 2
Summary Results Obtained in PCFC Tests for the Treated and Untreated Flax Fabrics

Sample code	pHRR (W/g)	T_{pHRR} (°C)	THR (kJ/g)	Char yield (%)	Variation in pHRR (%)
Flax fabric	215	363	11	12	–
Flax fabric/PA	60	307	5.7	28	72
Flax fabric/PA/PEI	172	352	10.8	15	20
Flax fabric/PA/PEI/PA	50	298	3.2	33	76

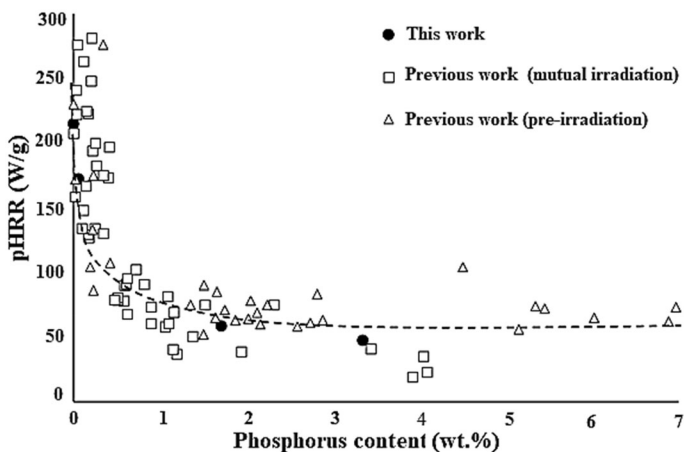


Figure 9. Peak of HRR in PCFC versus phosphorus content data from mutual irradiation are published in [35-37], data from pre-irradiation are published in [34] (The dashed line is for eye-guideline and underlines general trend in data spread).

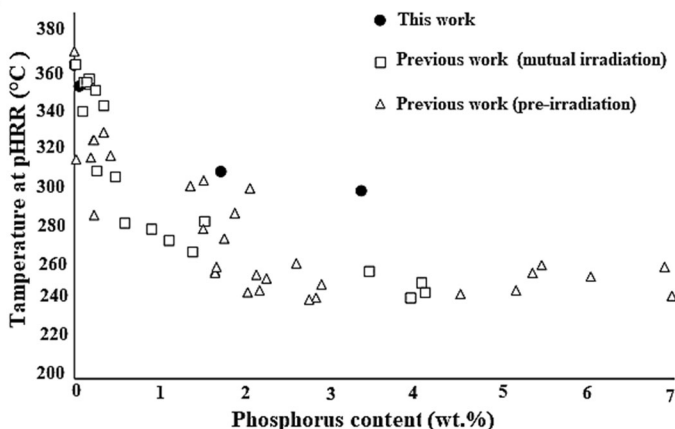


Figure 10. Temperature at peak of HRR in PCFC versus phosphorus content data from mutual irradiation are published in [35-37], data from pre-irradiation are published in [34].

3.7. Vertical Burning Test

A vertical burning test was used to analyze the combustion behavior of samples. Figure 11 displays the digital photos of vertical burning tests applied on flax fabric (a) and flax fabric/PA/PEI/PA (b) samples at different time of burning. Untreated flax fabric was totally burnt after 25 s without remaining residue. In opposite, the treated flax fabric was burnt slowly with high quantity of residue at

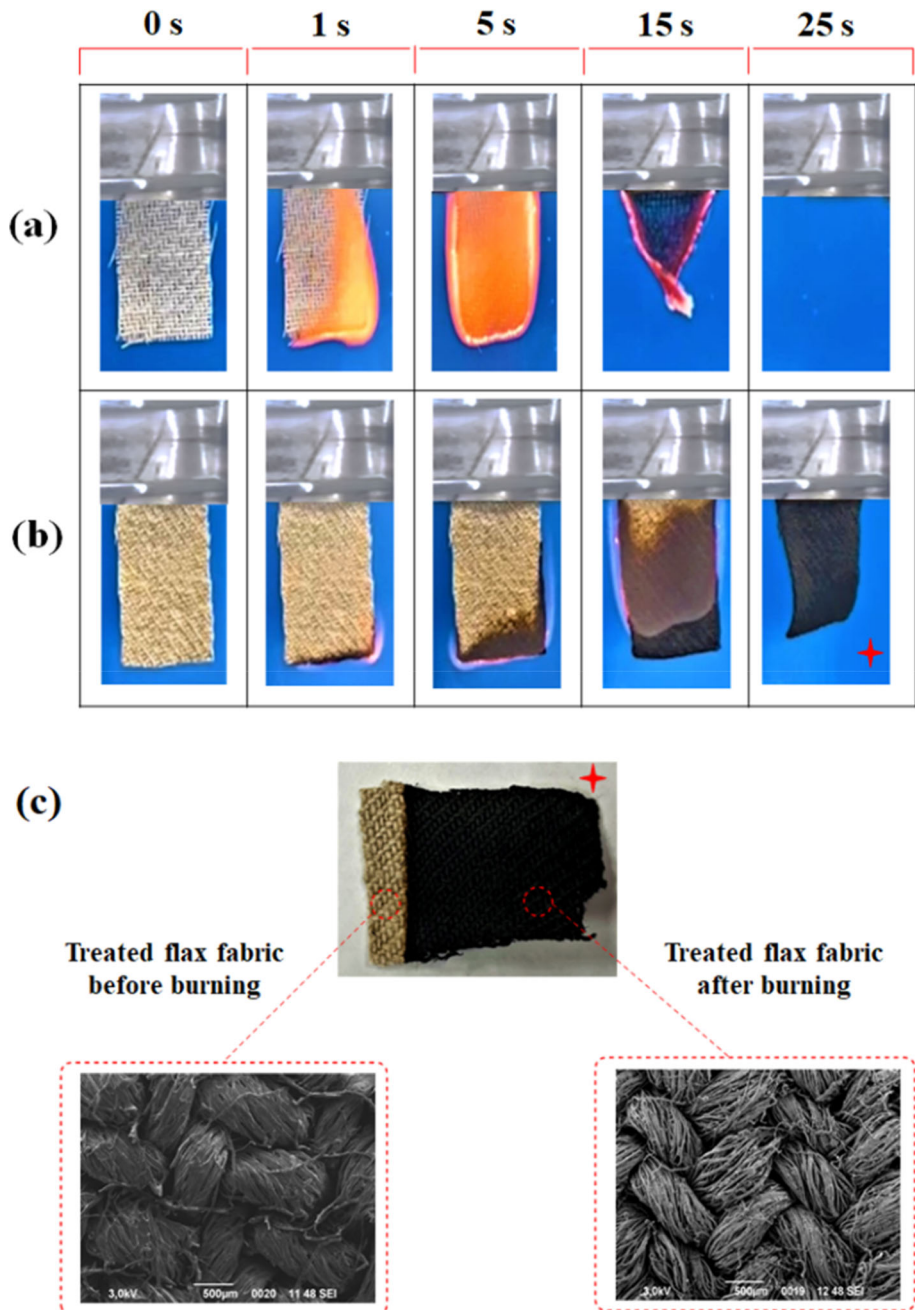


Figure 11. Digital photos of vertical burning tests applied on flax fabric (a) and flax fabric/PA/PEI/PA (b) samples. SEM images obtained before and after burning of flax fabric/PA/PEI/PA sample (c).

the end of test. For untreated flax fabric the flame was spread very fast along the sample, while the height and intensity of flame was less important for flax fabric/PA/PEI/PA. The SEM images after burning of flax fabric/PA/PEI/PA, Fig. 11c, showed that the fibers were not damaged and the integrity of fabric was preserved, demonstrating the efficiency of flame retardant action during burning. Ignition of any polymer substrate is a cyclic process that needs sufficient combustion by flame. Under heat flux, the untreated flax fabric decomposes and releases CO₂, water, flammable gases, and smoke. These flammable gases release then heat by reacting with oxygen. Herein, the mechanism of action of flame retardancy can be explained by the presence of phytic acid and its action in the condensed phase by promoting charring and also its reaction with nitrogen presented in PEI which stabilizes more the condensed phase. During combustion, these phosphates decompose and produce phosphoric acid. The resulting phosphoric acid reacts with hydroxyl groups of cellulose presented in flax fabric and initiates the dehydration reaction. The creation of radicals promotes the crosslinking reaction and then the cyclic carbonaceous structures formed will help the stabilization of condensed phase and improve the flame retardancy behaviour. The action of phosphorus and nitrogen in gas phase to scavenge the H° and OH° radicals which are responsible of flame propagation can be also considered, Fig. 12. However, there is no evidence of this mode of action and further investigation is required.

4. Conclusions

The production of sustainable and flame-retardant textile material is a challenging field of research. The present work has shown that it is possible to achieve this product using a layer-by-layer coating arrangement aided by a biobased phosphorous compound (phytic acid) to treat natural flax fabrics. Three layers were coated on flax fabric using phytic acid, PEI, and again phytic acid successively. Several techniques were applied to characterize the treated fabrics including FTIR, TGA, SEM, EDX, ICP, PCFC, tensile, abrasion and flame tests. The TGA showed that a high charring (around 40%) material is obtained after the flax fabric are treated, resulting in a promising low flammability monitored by PCFC test. The peak of heat release rate (pHRR) significantly dropped from 215 W/g for the untreated to 50 W/g for Flax fabric/PA/PEI/PA sample (~ - 77%), in the same order the total heat release (THR) decreased from 11 to 3.2 kJ/g (~ - 70%). The burning test demonstrated that the char residue obtained at the end of combustion was cohesive and efficient in improvement of flame retardancy. Moreover, the tensile test revealed a better elongation character of treated fabric compared with untreated sample. The abrasion test clearly showed the effectiveness of chemical treatment in increasing the abrasion resistance up to 30,000 rub cycles without rupture.

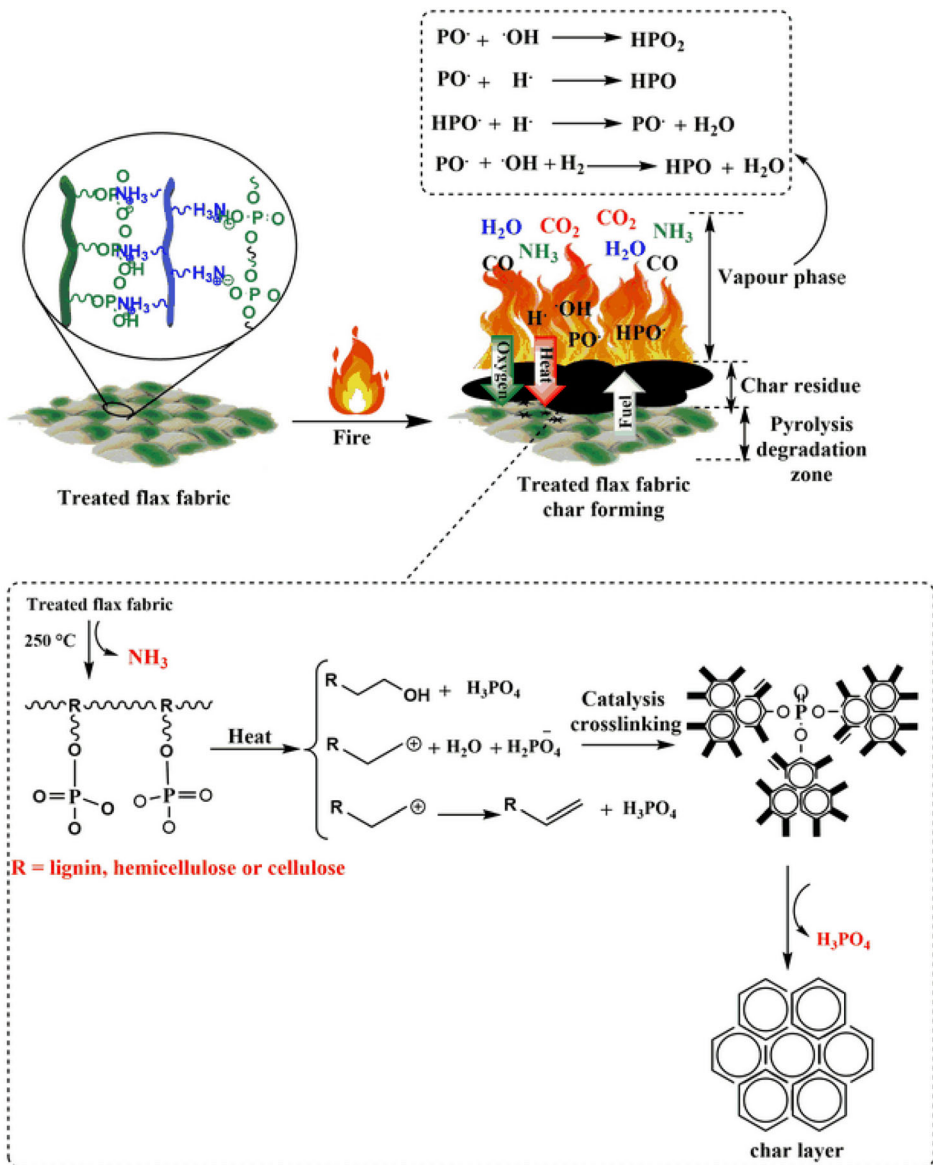


Figure 12. Possible mechanism of flame retardancy action in flax fabric/PA/PEI/PA sample.

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Declarations

Conflict of interest The authors of this manuscript certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers’ bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

Ethical Approval Hereby, we consciously assure that for the present manuscript the following is fulfilled: (1) This material is the authors’ own original work, which has not been previously published elsewhere. (2) The paper is not currently being considered for publication elsewhere. (3) The paper reflects the authors’ own research and analysis in a truthful and complete manner. (4) The paper properly credits the meaningful contributions of co-authors and co-researchers. (5) The results are appropriately placed in the context of prior and existing research. (6) All sources used are properly disclosed. 7) All authors have been personally and actively involved in substantial work leading to the paper, and will take public responsibility for its content.

Informed Consent This research work does not involve human or animals.

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