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Two-Step Polyelectrolyte Complex Coating for Flame Retardant Flax

Danixa Rodriguez-Melendez, Dallin L. Smith, Sarah G. Fisher, Rodolphe Sonnier, Henri Vahabi,* and Jaime C. Grunlan*

Flax fabric textile is of great interest as bio-fiber reinforcement in composites, which has gained popularity due to the high demand for sustainable materials. Despite its sustainability, flax is inherently flammable. This study demonstrates a two-step polyelectrolyte complex (PEC) coating that renders flax fabric self-extinguishing. The PEC coating consists of polyethylenimine (PEI) and sodium hexametaphosphate (PSP), cured with a citric acid buffer. Sonication employed during the curing process improves the infiltration of the coating into the flax fibers and maintains the fabric's hand. When comparing non-sonicated and sonicated flax samples, the latter achieves self-extinguishing behavior and passes the vertical flame test. Pyrolysis-combustion flow calorimetry reveals that this PEI/PSP coating (with sonication) reduces the peak heat release rate and total heat release by 40% and 67%, respectively. The intumescent mechanism is predominantly observed in the condensed phase, as suggested by differential scanning calorimetry and X-ray photoelectron spectroscopy. The results demonstrate that the two-step PEC treatment with sonication effectively reduces the flammability of flax fabric, making it a promising option for the development of functional fibers, particularly for bio-composite reinforcement.

composites has gained popularity in recent years.^[2,3] Its exceptional strength-to-weight ratio, low density, and biodegradability make it an environmentally friendly substitute for synthetic fibers. This is because flax possesses a cellulosic polymer structure similar to cotton, but with increased crystallinity, imparting greater strength and stiffness.^[4,5] Unfortunately, much like cotton and other materials derived from cellulose, flax exhibits a high susceptibility to combustion. In order to mitigate its inherent flammability, it is crucial to develop an effective flame-retardant (FR) treatment that can impede or prevent the spread of flames upon exposure to an ignition source.

As an alternative to halogenated compounds and other hazardous flame retardants, several environmentally benign FR treatments have been developed.^[6,7] In recent years, the deposition of FR coatings via layer-by-layer (LbL) assembly has gained great interest due to ambient processing, environmental friendliness, and

versatility. This water-based coating technique consists of alternately exposing a substrate to oppositely charged polyelectrolytes, which typically interact through electrostatic attractions.^[8] Intumescent coatings deposited via LbL assembly have been known to impart FR behavior to flax fabric through the promotion of char formation.^[9–12] An effective intumescent system is comprised of an acid source, a blowing agent, and a carbon source, which reacts upon heating to form an insulating and protective char layer

1. Introduction

Flax is one of the most widely used bio-fibers. It has gained significant recognition and adoption in fashion, home textiles, and various technical applications due to its aesthetic appeal, functional properties, and sustainability.^[1] With the increasing demand for sustainable materials, the use of flax fibers as reinforcement in


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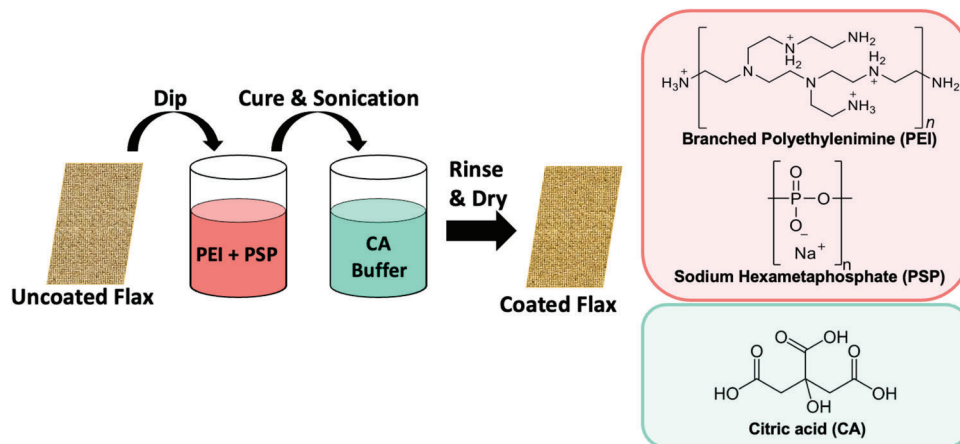


Figure 1. Schematic of the PEC coating deposition and components for coating flax fabric.

on the substrate's surface.^[6] Despite the numerous advantages of LbL assembly, the number of processing steps required to deposit an intumescent FR coating remains industrially impractical.

An approach to overcome the number of processing steps involved in the LbL method has been the adoption of water-soluble polyelectrolyte complex (PEC) coatings. A PEC is an insoluble precipitate produced by the ionic crosslinks formed when polycations and polyanions are mixed in solution.^[13] This two-step strategy consists of creating a stable solution of two weak polyelectrolytes by adjusting the pH so that one of the species is highly charged and then exposing it to a buffer solution to charge the uncharged polyelectrolyte and induce complexation.^[14] These coatings have been gaining interest due to their ambient and simple processing, with minimal weight added. In an effort to improve the flame performance of flax fabric and reduce the required deposition steps, an intumescent PEC strategy has been adopted here.

Previously, intumescent PEC coatings have been deposited on cellulosic materials (e.g., cotton fabric and wood) using two environmentally benign polyelectrolytes: polyethylenimine (PEI) and sodium hexametaphosphate (PSP). In this intumescent system, PSP acts as an acid source, while PEI serves as a blowing agent and the cellulosic substrate as a carbon source or char former.^[14–16] In addition, incorporating sonication in the coating process has demonstrated improvements in the fabric's hand, as well as its FR and mechanical properties, particularly when employed during the rinse step in LbL deposition to eliminate loosely attached substances.^[17,18] This improves uniformity and coating infiltration into the fabric by dispersing aggregates in fabric processing.^[19,20]

In the present study, a two-step PEC coating with sonication, using environmentally benign polyelectrolytes, is employed to reduce the flammability of flax fabric. This intumescent PEC is comprised of PEI and PSP. The treatment is cured with a citric acid buffer at pH 3. Sonication is applied during the buffer curing step to improve the coating infiltration into the flax fibers and therefore the FR behavior. Non-sonicated and sonicated coated flax samples, adding 14.9 and 17.0 wt%, respectively, exhibit self-extinguishing behavior, but only the sonicated fabric passes the vertical flame test. Pyrolysis-combustion flow calorimetry reveals that the sonicated PEI/PSP coating reduces the peak heat release

rate and the total heat release by 40 and 67%, respectively. These findings demonstrate that the two-step PEC treatment can reduce the flammability of flax fabric, extending its utility for sustainable textiles and composite reinforcement.

2. Experimental Section

2.1. Materials

Branched PEI ($M_w = 25\,000\text{ g mol}^{-1}$), PSP (crystalline, 200 mesh, 96%), sodium hydroxide (NaOH, ACS reagent, 97%), and citric acid monohydrate (CA, reagent grade, 98%) were purchased from Sigma Aldrich (Milwaukee, WI). Hydrochloric acid (HCl, 5.0 M) was purchased from VWR Chemicals (Batavia, IL). Flax fabric (200 g m^{-2} , 81 wt% cellulose, 13 wt% hemicellulose, and 2.7 wt% lignin) was provided by Hexcel (Stamford, CT). Cotton fabric (98 g m^{-2}) was supplied by Testfabrics Inc. (West Pittston, PA). A 10 wt% PEI solution was prepared and adjusted to pH 9 by adding 5 M HCl dropwise. A 20 wt% PSP solution was prepared and allowed to remain at its natural pH. The PEC solution was prepared by mixing equal amounts of 10 wt% PEI and 20 wt% PSP solutions. This mixture results in a stable and transparent PEC solution with 5 wt% PEI and 10 wt% PSP. 100 mM CA solution was prepared and adjusted to pH 3 by adding 5 M NaOH dropwise. All solutions were prepared with 18 M Ω deionized (DI) water.

2.2. PEC Deposition

Prior to deposition, flax and cotton fabrics (12 in \times 3.5 in) were rinsed with DI water in a sonication bath (5510 Branson Ultrasonic Cleaner, Branson Ultrasonics, Brookfield, CT) and dried in a 70 °C oven for 30 min. Subsequently, the substrates were then immersed into the PEC solution for 1 min. This was followed by wringing the fabrics to remove excess PEC solution. Fabric samples were then cured by immersion into the CA buffer solution while sonicating for 1 min and wrung out. Next, the samples were rinsed by dragging them in DI water back and forth three times and wrung out. Coated fabrics were dried at 70 °C for 2 h before testing. The overall coating process and components used are shown in **Figure 1**.

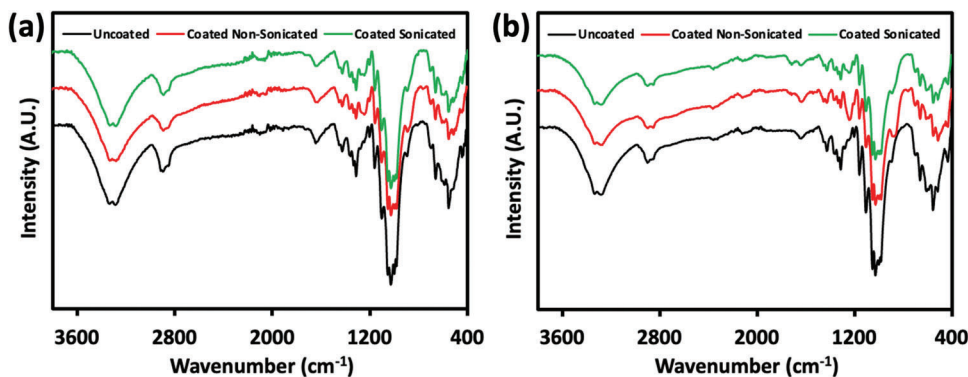


Figure 2. FTIR spectra of uncoated (black), coated non-sonicated (red), and coated sonicated (green) a) flax and b) cotton fabric.

2.3. Characterization

Vertical flame testing (VFT) was used to evaluate the flame retardancy of flax and cotton fabric samples (12×3.5 in.), in compliance with ASTM D6413-15. Pyrolysis-combustion flow calorimetry (PCFC, from Fire Testing Technology (FTT), UK) was conducted to measure the flammability of samples. Samples (2–4 mg), tested in duplicate, were pyrolyzed under nitrogen flow at a heating rate of $1 \text{ }^\circ\text{C s}^{-1}$ up to $750 \text{ }^\circ\text{C}$. The gases released were combusted in an excess of oxygen (O_2/N_2 20/80) at $900 \text{ }^\circ\text{C}$. Thermogravimetric analysis (TGA) was performed with a Q50 thermogravimetric analyzer (TA Instruments, New Castle, DE) under air and nitrogen atmospheres. Samples (6–10 mg) were held at $100 \text{ }^\circ\text{C}$ for 20 min to remove residual water and then heated at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ to $705 \text{ }^\circ\text{C}$. Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC Q20 (New Castle, DE) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from 0 to $400 \text{ }^\circ\text{C}$ under nitrogen. The surface morphologies of the uncoated and coated fabric samples were observed by sputter coating the samples with 5 nm of gold prior to imaging using a field emission scanning electron microscope (SEM) (TESCAN, Brno, Czechia). Fourier transform infrared (FTIR) spectroscopy was used to characterize preburn and postburn fabrics using an attenuated total reflectance (ATR) fixture (Frontier PerkinElmer, Inc., Shelton, CT). X-ray photoelectron spectroscopy (XPS) was performed using an Omicron XPS/UPS (Denver, CO), with a DAR 400 Mg/Al X-ray source and a 0.8 eV energy resolution detector. The mechanical properties of the fabric samples were measured with an Instron 6800 Universal Testing Machine (Instron, Norwood, MA) using a 500 N load cell. The samples (12×2 cm) were tested according to ASTM D5034, with a tensile speed of 5 mm min^{-1} .

3. Results and Discussion

3.1. Confirming Coating Deposition

The surface of uncoated and coated flax and cotton samples was characterized using ATR-FTIR spectroscopy (Figure 2). Untreated fabric contains a broad band at 3310 cm^{-1} that corresponds to the hydroxyl groups of cellulose. Furthermore, absorptions at 2895 , 1644 , and 1028 cm^{-1} indicate C–H stretching, O–H bending, and C–O–C asymmetrical stretching, respectively.^[21] The intensity of these bands is decreased in the

PEI/PSP-treated flax fabric spectrum, while new bands are observed at 1575 , 1220 , and 948 cm^{-1} corresponding to N–H bending, P=O stretching, and P–C–O bending vibrations, respectively. It is expected that the spectra of flax and cotton would exhibit substantial similarities, given their nearly identical composition, with cellulose as the primary component. The differing factor between them lies in their respective morphologies. Additionally, elemental analysis with XPS further confirms the deposition of the PEI/PSP coating onto the flax fabric, as shown in Figure S1b, Supporting Information. XPS phosphorus and nitrogen peaks were detected on the surface of the coated sample. These findings confirm that the coating components were interacting with the fabric, indicating successful deposition onto the substrate.

3.2. Surface Morphology

Scanning electron microscopy was used to analyze the morphology of flax and cotton fabrics before and after PEC deposition, with and without sonication (Figure 3). High-magnification SEM images of the fibers before and after coating are shown in Figure S2, Supporting Information. Flax fibers have a cylindrical shape longer and narrower than cotton fibers. When comparing the surface of the uncoated and coated fibers, the latter exhibit a smoother surface, indicating the presence of the PEC coating. Furthermore, there is a noticeable contrast between the non-sonicated and the sonicated coated fabrics. In the non-sonicated coated fabric (14.9 wt% for flax and 10.5 wt% for cotton), the weave structure remains discernible, but it is evident that the coating has bridged most of the fibers. Conversely, in the sonicated samples (17.0 wt% for flax and 14.0 wt% for cotton), individual fibers are highly visible due to minimal bridging.

3.3. Mechanical Properties

The effect of the PEC coating on the mechanical properties (i.e., hand) of flax and cotton fabric was investigated via tensile testing. Table 1 shows the elongation and stiffness of uncoated, coated non-sonicated, and coated sonicated fabric. Stress–strain curves for flax and cotton fabric are displayed in Figure S3, Supporting Information. Flax fibers seem to be more rigid and stronger than

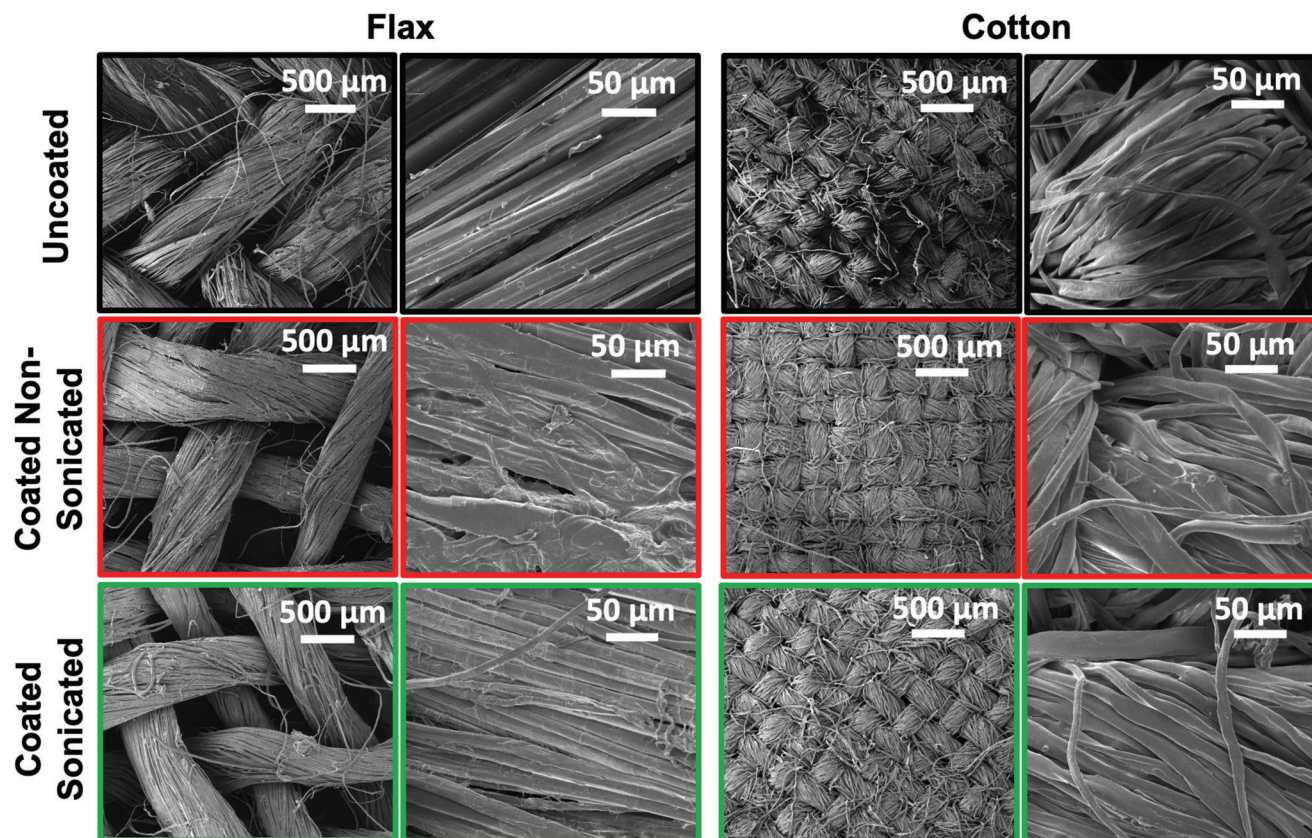


Figure 3. SEM images of uncoated (black), non-sonicated (red), and sonicated (green) coated flax and cotton fabric.

cotton fibers, resulting in lower elongation and higher stiffness. This confirms what is observed in the SEM images where cotton exhibits twisted and flexible fibers, whereas flax fibers are more aligned and compact. In addition, the application of the PEC coating with and without sonication does not result in significant improvements or harm to the fabric texture or feel (hand). The mechanical properties of coated fabric remain within 10% of those for uncoated fabric.

3.4. Flame Retardancy

To evaluate the flame behavior of uncoated and coated fabric (with and without sonication), vertical flame testing was performed. Uncoated and coated samples were exposed to a direct flame for 12 s. Figure 4 shows images of flax and cotton before and after VFT. Upon exposure to the flame, uncoated fab-

ric (Figure 4a,f) burns entirely, leaving little residue behind. Fabric coated with PEI/PSP self-extinguishes immediately after ignition. Interestingly, coated cotton with and without sonication passes VFT with char lengths around 4 in and $\approx 97\%$ residue. In contrast, non-sonicated flax does not pass VFT, yielding a char length of 7.5 in and 88% residue. With sonication, coated flax achieves the best performance, passing the VFT with 98% residue and a char length of 4.8 in. Table S2, Supporting Information provides a summary of additional data regarding the VFT results. It should be noted that for flax fabric, sonicated samples have a higher weight gain than the non-sonicated ones, suggesting greater coating diffusion into the flax fibers. SEM images of the char residues for each PEI/PSP-treated fabric (Figure 4,d,e,i,j) show the cellulosic fibers preserve their morphology after ignition, especially the sonicated samples. The presence of visible bubbles on the surface of the fibers is evident, which is indicative of the micro-intumescence phenomenon.^[18]

Table 1. Mechanical behavior of coated flax and cotton.

Sample	Elongation [%]		Stiffness [N mm ⁻¹]	
	Cotton	Flax	Cotton	Flax
Uncoated	10.4 ± 0.8	5.0 ± 0.4	13.0 ± 0.5	85.9 ± 0.2
Coated non-sonicated	9.8 ± 0.3	3.4 ± 0.5	13.9 ± 0.3	87.2 ± 0.6
Coated sonicated	10.1 ± 0.2	4.0 ± 0.8	13.7 ± 0.7	86.7 ± 0.5

3.5. Flammability Analysis

Pyrolysis-combustion flow calorimetry was carried out to evaluate the flammability of the uncoated and PEC-treated fabric.^[22] According to Huggett's relation, 1 kg of oxygen consumed corresponds to 1 MJ of energy released,^[23] so the heat release rate can be calculated from oxygen consumption. PCFC provides the heat release rate (HRR), the total heat release (THR), the peak

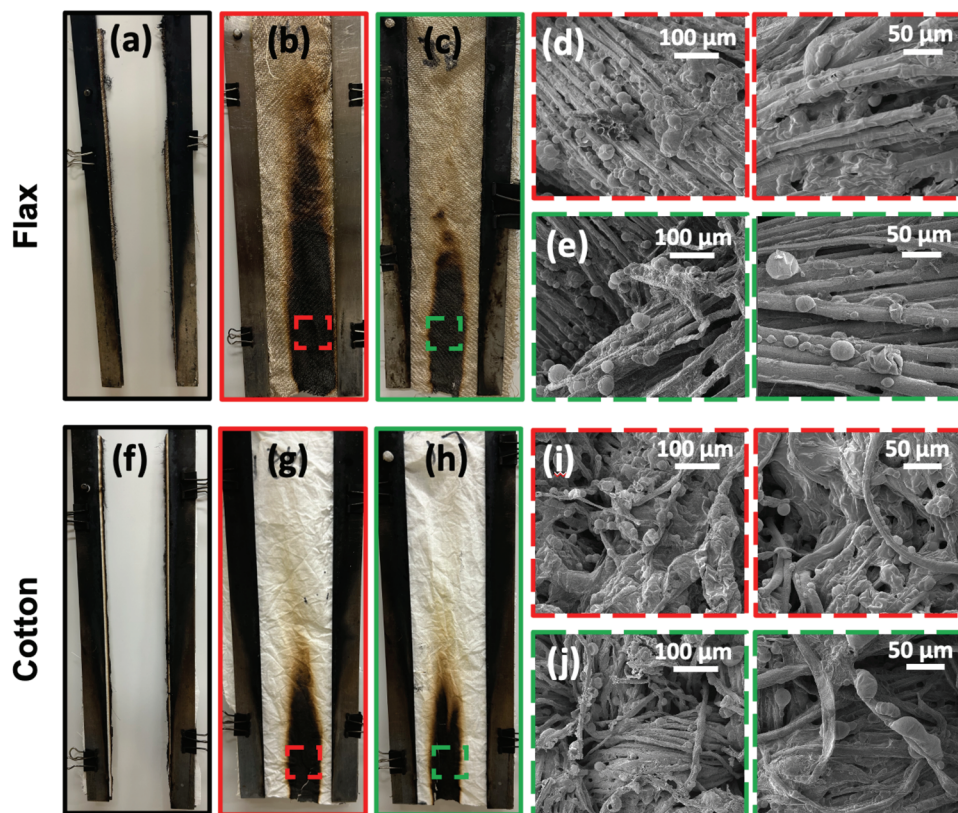


Figure 4. Camera images after vertical flame testing of a, f) uncoated, b, g) coated non-sonicated, and c, h) coated sonicated flax (top) and cotton (bottom) fabrics. SEM images of d, i) coated non-sonicated and e, j) coated sonicated flax (top) and cotton (bottom) fabrics, after vertical flame testing.

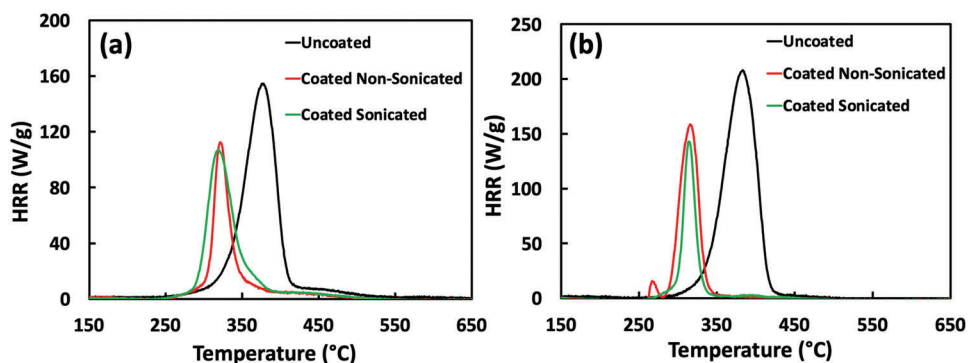


Figure 5. Representative graph of heat release rate as a function of temperature for uncoated, coated non-sonicated, and coated sonicated a) flax and b) cotton fabric.

of heat release rate (pkHRR), and the char yield. **Figure 5** and **Table 2** reveal that both PEI/PSP-treated flax samples provide fire protection by reducing the pkHRR by 36% (non-sonicated) and 39% (sonicated) and THR by 44% (both), while increasing the char residue by 50% (non-sonicated) and 67% (sonicated). When compared to neat flax, cotton results in higher pkHRR, THR, and maximum temperature, while yielding less residue. On the other hand, coated cotton exhibits a greater reduction in THR and maximum temperature, and leaves more residue than coated flax samples. In terms of sonication, there is not a significant difference in the flammability performance of cotton or flax. The fact

Table 2. PCFC results for flax and cotton.

Substrate	Sample	pkHRR [W g ⁻¹]	Max. temp. [°C]	THR [KJ g ⁻¹]	Residue [%]
Flax	Uncoated	155 ± 1	377 ± 1	9.0 ± 0.1	12 ± 2
	Coated non-sonicated	94 ± 15	323 ± 5	5.0 ± 0.2	20 ± 2
	Coated sonicated	99 ± 2	327 ± 1	5.0 ± 0.1	18 ± 4
Cotton	Uncoated	205 ± 4	382 ± 1	11.0 ± 0.1	5 ± 1
	Coated non-sonicated	151 ± 9	313 ± 1	3.0 ± 0.4	31 ± 4
	Coated sonicated	160 ± 2	316 ± 0	4.0 ± 0.1	26 ± 1

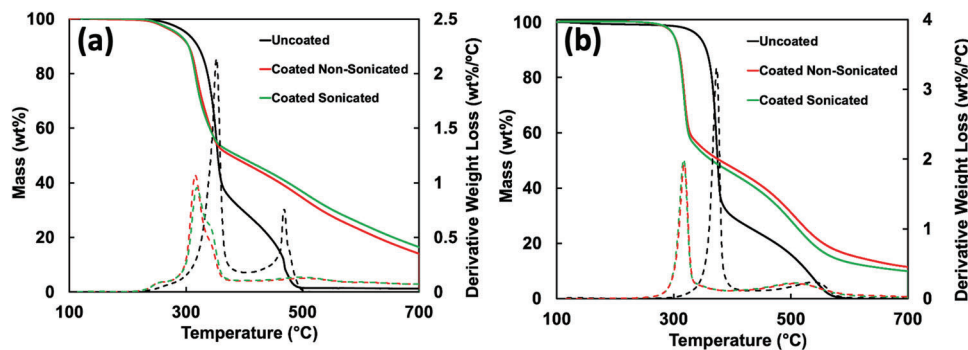


Figure 6. Thermogravimetric analysis of mass loss as a function of temperature for uncoated, coated non-sonicated, and non-sonicated a) flax and b) cotton fabric under air atmosphere.

that the reduction in the pkHRR and THR of this FR coating is not as large as seen in other intumescent systems indicates the fire protective mechanism could be primarily condensed phase (large amount of char residue), with only a very small amount of gas released.^[18]

3.6. Thermal Stability

Thermogravimetric analysis was used to observe the thermal degradation of both uncoated and coated flax and cotton samples in the presence of air and nitrogen atmospheres. **Figure 6** displays the TGA curves, illustrating three distinct stages of mass loss for both uncoated and coated samples under air. The initial stage of mass loss, occurring at 100 °C, corresponds to moisture evaporation. The second stage (290–360 °C for flax and 310–410 °C for cotton) involves dehydration and decomposition reactions of cellulose, hemicellulose, and lignin chains (only for flax), resulting in the production of nonflammable gases, aliphatic char, and levoglucosan.^[24] The third stage, around 450 °C (flax) and 480 °C (cotton), is attributed to the generation of CO and CO₂ as a result of the oxidation of the char.^[25,26] The presence of the coating lowers the degradation temperature of flax fabric from 300 to 265 °C, and from 330 to 280 °C for cotton fabric. This earlier onset of decomposition ($T_{\text{onset}} = 265$ and 280 °C) is attributed to the activation of intumescence, which forms a char layer that suppresses oxidation and slows mass loss.^[18] Despite seeming counterintuitive for a thermally protective coating, it is ideal for the FR mechanism to begin before the underlying substrate starts to degrade, thereby maximizing protection.^[17]

While the uncoated fabric burns completely, the coated fabric yields a residual char of $\approx 15\%$ (at 700 °C). This degradation event is also apparent in the derivative curves, indicating a roughly 50% (flax) and 40% (cotton) reduction in the rate of mass loss compared to uncoated fabric. It should be noted that coated flax, having a higher reduction in the rate of mass loss than coated cotton, suggests that crystalline cellulose degrades more slowly than amorphous cellulose. Figure S4, Supporting Information presents the TGA curves for uncoated and coated flax and cotton samples in a nitrogen atmosphere, revealing a single degradation step attributed to the depolymerization of cellulose into volatile gases and aromatic char.^[18] Under pyrolysis conditions, the coated flax samples leave behind a greater residual char (40%)

once the temperature reaches 700 °C. In either atmosphere, no significant change is observed in degradation between the coated non-sonicated and sonicated samples. Likewise, the degradation pathway and events of flax and cotton fabric are very similar, meaning the cellulose morphology (crystalline or amorphous) does not alter the thermal behavior.

DSC was carried out to study the role of the condensed phase action of the PEI/PSP-coated sonicated fabric during pyrolysis (**Figure 7**). The DSC curve of both uncoated textiles shows an endothermic peak at 367 °C and at 369 °C indicating the heat absorption associated with the thermal decomposition of amorphous and crystalline cellulose, respectively.^[27] Neat cotton is more endothermic (-194.7 J g^{-1}) compared to flax (-40.8 J g^{-1}), suggesting that amorphous cellulose has a higher heat absorption than crystalline cellulose (Table S3, Supporting Information). Cellulose generates 1-glucose during thermal decomposition, which subsequently breaks down into carbon monoxide and other smaller molecules (e.g., pyroglucosan and levoglucosan), absorbing a significant amount of heat.^[28] Conversely, deposition of the PEC coating leads to an exothermic event around 310–315 °C (51.8 J g^{-1}) for flax and 290–303 °C (31.1 J g^{-1}) for cotton. The early appearance of these exothermic peaks is due to the release of phosphoric acid by the decomposition of the PEI/PSP coating, which catalyzes the dehydration of cellulose. This reaction produces a more stable and conjugated system (i.e., char), without forming volatile products, and releases a significant amount of heat.^[29]

Further insight into the condensed phase action and char composition was investigated using elemental analysis with XPS. Table S1, Supporting Information shows the corresponding XPS-derived atom percentages and atomic ratios for pre-burn uncoated and pre-burn and post-burn coated flax fabric. After subjecting the coated sample to the flame, an increase in the C/O ratio and a decrease in the P/N, C/N, and C/P ratios is observed. This suggests that the decomposition of cellulose releases water, carbon monoxide, and carbon dioxide, while PEI degrades into nitrogen-containing molecules that participate in char formation (i.e., heteroaromatic compounds).^[30,31] Likewise, the presence of phosphorus in the aromatic char indicates PSP could be phosphorylating and crosslinking cellulose.^[32] Overall, the effectiveness of this intumescent coating relies on the decomposition of the phosphate groups in PSP, which then catalyze the dehydration reaction of cellulose toward the formation of an aromatic

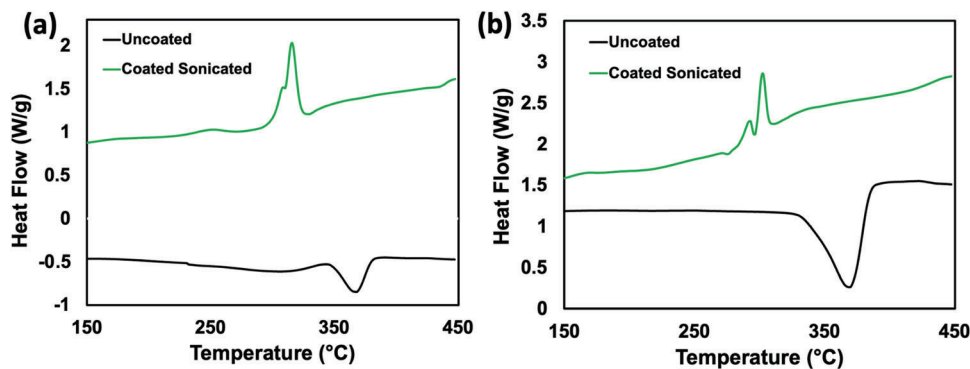


Figure 7. Differential thermogram for uncoated and coated a) flax and b) cotton fabric.

char.^[18] The char is then expanded by gases produced (e.g., N_2 , H_2O , and CO_2) in the decomposition of the blowing agent, (i.e., PEI). This char layer eventually solidifies through crosslinking and condensation reactions, which slows the heat flow from the fire to the fabric.^[6,33]

4. Conclusions

An intumescent PEC coating composed of two environmentally-benign polyelectrolytes (PEI and PSP) was deposited on flax fabric to reduce its flammability using a simple two-step deposition process. Incorporating sonication into the curing step removes the excess coating and prevents fiber bridging, while improving the FR performance of flax fabric and maintaining hand. Sonicated substrates achieved self-extinguishing behavior and passed vertical flame testing, yielding 98% residue. When comparing crystalline and amorphous cellulose morphologies, there is no significant difference in thermal behavior or performance. DSC and XPS analysis suggest the PEI/PSP mechanism is mainly condensed phase. The performance of this simple two-step PEC treatment provides an opportunity of producing sustainable and FR flax with relatively minimal processing time and under ambient conditions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

flame-retardant, flax fabric, natural fiber, polyelectrolyte complex, sonication

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