Biorenewable Polyelectrolyte Nanocoating for Flame-Retardant Cotton-Based Paper

Danixa Rodriguez-Melendez, Matthias Langhansl, Alexander Helmbrecht, Bethany Palen, Cordt Zollfrank,* and Jaime C. Grunlan*

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ABSTRACT: Cotton-based raw paper, made of 100% cellulose, is used to make humidity-sensing, cottonid for bio-architecture applications. Despite its renewability and excellent mechanical properties, it is inherently flammable. In an effort to reduce its flammability, thin films of fully renewable and environmentally benign polyelectrolytes, chitosan (CH) and phytic acid (PA), were deposited on raw paper via layer-by-layer (LbL) assembly. Only four bilayers (BL) of the CH/PA coating are required to achieve self-extinguishing behavior, with a 69% reduction in peak heat release rate measured by microscale combustion calorimetry. These results demonstrate that this renewable intumescent LbL-assembled film provides an effective flame-retardant treatment for these environmentally friendly, climate-adaptive construction materials and could potentially be used to protect many cellulosic materials.
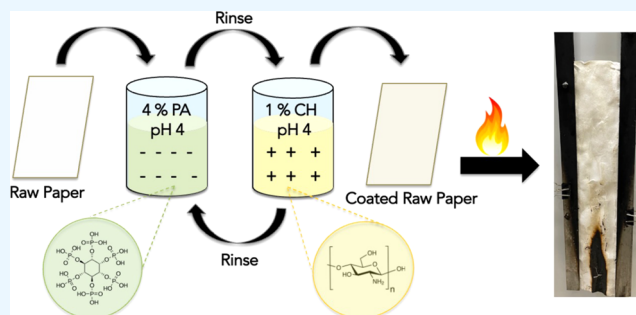
1. INTRODUCTION

In bio-architecture, renewable and environmentally responsive materials are utilized for the development of smart building skins, which play an important role in the reduction of global energy consumption. These stimuli-responsive materials can directly use primary energy (e.g., solar radiation, hydraulic energy, biomass, etc.) to produce motion by reacting to external stimuli such as temperature, relative humidity, or light.[1,2] Pure cellulosic materials are attractive candidates for this application, not only because cellulose is the most abundant biopolymer and a sustainable resource, but they also exhibit a pronounced swelling and shrinking behavior in response to relative humidity.[3] Cellulose-based cottonid is one such humidity-responsive actuating material.[4] Recent studies have demonstrated that the mechanical properties of this humidity-sensing material are comparable to wood and some technical plastics like polyamide or poly(vinyl chloride). Particularly, cotton-based raw paper has been used to manufacture cottonid, which is based on a parchmentizing process. This raw paper is made from cotton linters and is 100% cellulose.[5−8]

Unfortunately, much like wood and other cellulose-based materials, cottonid is highly flammable. As a potential construction component, it is crucial to develop an effective flame-retardant (FR) treatment for its raw material, cotton-based raw paper. Several environmentally benign FR treatments have been developed as an alternative to halogenated compounds and other toxic flame retardants.[9,10] In recent

years, the incorporation of flame-retardant coatings via layer-by-layer (LbL) assembly has gained great interest due to their 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.[11−13]

Intumescent coatings constructed via LbL assembly are known for imparting FR behavior on cellulosic material, including cotton fabric and wood.[14−20] An effective intumescent system contains an acid source, a blowing agent, and a carbon source, which react upon heating to form an insulating and protective char layer on the surface of the substrate.[9] Renewable and environmentally benign intumescent systems have previously been deposited on cotton fabric by coupling cationic chitosan (CH) and anionic phytic acid (PA).[14] Chitosan is an amino polysaccharide most commonly derived from chitin, which is the structural component in the shells of crustaceans. PA is the predominant form of phosphorus in cereal grains and oil seeds.[21,22] PA acts as the acid source, while the raw paper (cellulose) acts as a carbon source for char formation. CH serves as both a char-former and blowing agent.
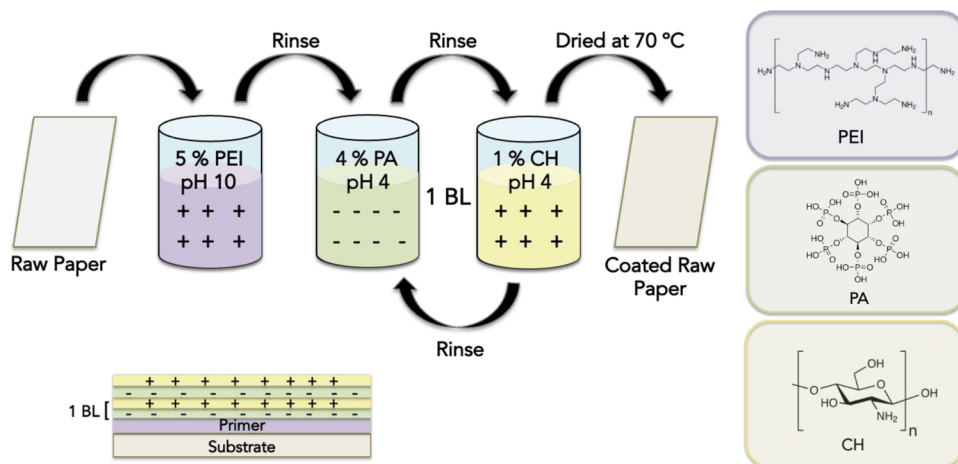
Figure 1. Schematic of layer-by-layer deposition and components for coating raw cellulose paper.
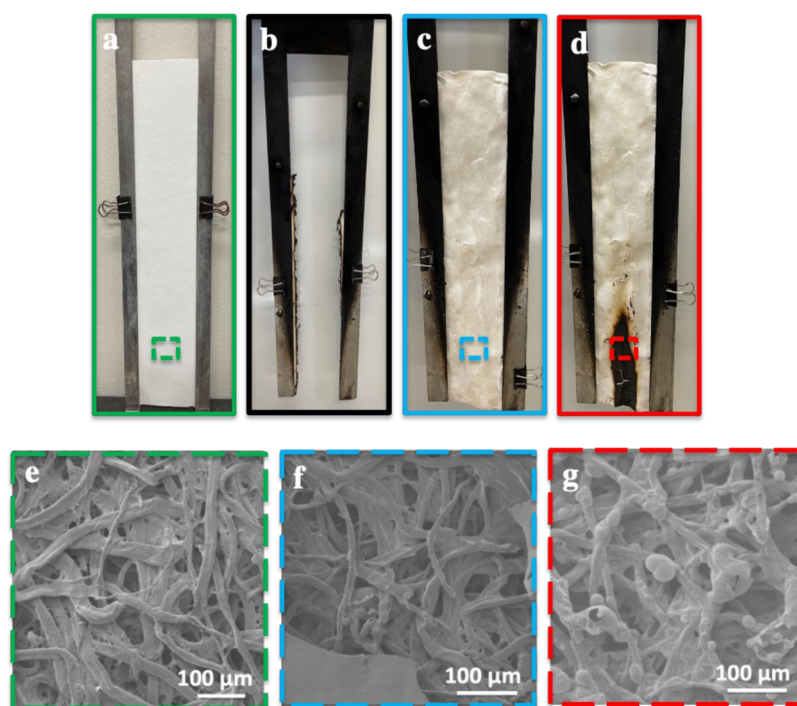

Figure 2. (Left) Pre- and post-vertical flame test samples: (a, b) uncoated and (c, d) 4 BL CH/PA coated raw paper. SEM images of (e) uncoated raw paper before VFT and coated raw paper (f) before and (g) after VFT.

Here, the first-ever self-extinguishing cotton-based raw paper using two biorenewable polyelectrolytes, chitosan and phytic acid, is reported. The four bilayer (BL) CH/PA coating on raw paper (adding 14.6 wt %) exhibits self-extinguishing behavior, and the peak heat release rate (pkHRR), as measured by microscale combustion calorimetry (MCC), is reduced by 69%. Fewer bilayers result in lower weight gain and do not self-extinguish, as shown in Table S1. The overall layer-by-layer process and components used for coating the raw paper are shown in Figure 1. This study defines the first proof of concept for the development of a renewable and effective flame-retardant treatment for this environmentally friendly, climate-adaptive construction material.

2. RESULTS AND DISCUSSION

2.1. Confirmation of Coating Deposition. After LbL assembly, uncoated and coated samples were characterized using ATR-FTIR spectroscopy (Figure S1). Untreated raw paper contains a broad band at 3332 cm^{-1} that corresponds to the hydroxyl groups of cellulose. The absence of the O−H band is observed in the CH/PA-treated raw paper spectrum, while new bands are observed at 1635, 1532, 1153, and 965 cm^{-1} corresponding to the C = O (amide) stretching, N−H bending, P=O stretching, and P−C−O bending vibrations, respectively. These findings confirm that the coating components were interacting with the raw paper, indicating successful deposition onto the substrate.

2.2. Flame-Retardant Behavior. Self-extinguishing behavior of the raw paper was evaluated by performing vertical flame testing (VFT), according to ASTM D6413. Coated and
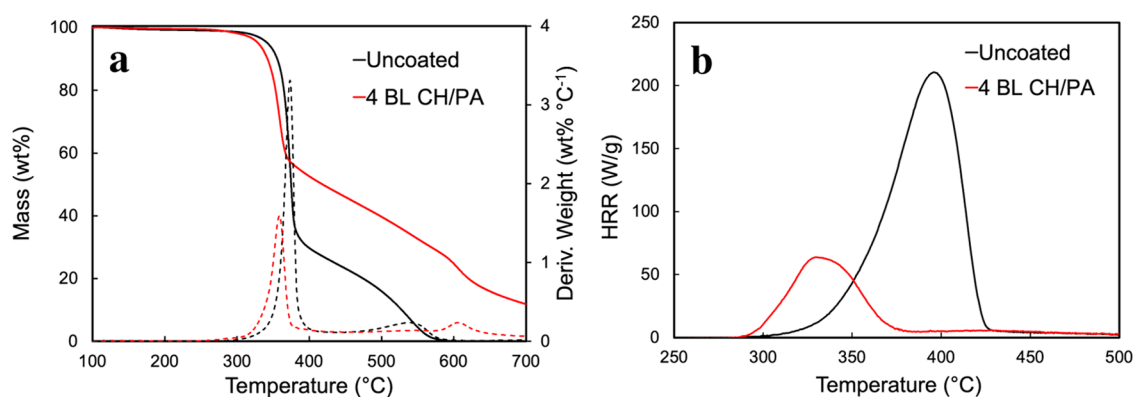
Figure 3. (a) Thermogravimetric analysis of mass loss (solid lines) and derivative mass loss (dashed lines) as a function of temperature for uncoated and coated raw paper under air atmosphere. (b) Representative graph of heat release rate (HRR) as a function of temperature from microcombustion calorimetry testing.

uncoated raw paper samples (12 × 3.5 in.) were exposed to a direct flame for 12 s. Figure 2a−d shows images of the uncoated and coated raw paper samples before and after VFT. Upon exposure to the flame, uncoated raw paper (Figure 2b) burned completely, leaving little residue behind. In contrast, paper coated with 4 BL CH/PA (Figure 2d) self-extinguished immediately after ignition, resulting in a 95% residue and a char length of 4.5 in. More data about VFT results are summarized in Table S1.

2.3. Surface Morphology. Scanning electron microscopy (SEM) was used to analyze the raw paper's morphology before and after VFT. When comparing the surface of the cellulose fibers in the uncoated (Figure 2e) and coated raw paper (Figure 2f), the latter exhibits a smoother surface, confirming the presence of the coating. High-magnification SEM images of the fibers before and after coating are shown in Figure S2. The image of the char residue for CH/PA-treated samples (Figure 2g) shows that the cellulosic fibers preserve their morphology after burning. Bubble formation on the top of the fibers is clearly visible, which is indicative of the micro-intumescence phenomenon.[16]

2.4. Conditioning of the Cotton-Based Paper. The durability of the CH/PA coating was investigated by manually conditioning (i.e., folding and crumpling) the coated samples. Figure S3a,b shows the coated raw paper being folded and crumpled, imitating possible manipulation when used in practical applications. Although a small fraction of the coating was lost after conditioning (3.3 wt %), the coated samples were still able to self-extinguish, with a char length of 6 in. when subjected to VFT (see Figure S3). It should also be noted that coated raw paper initially exhibits much greater stiffness than the uncoated sample, but its flexibility is restored when conditioned.

2.5. Thermal Characterization. The thermal degradation and decomposition process of uncoated and coated raw paper was monitored by thermogravimetric analysis (TGA) under air and nitrogen atmospheres. Figure 3a shows TGA curves of uncoated and coated samples under air, with three stages of mass loss. The first mass loss starts at 100 °C, corresponding to evaporation of moisture. The second stage (300−380 °C) involves dehydration and decomposition reactions of cellulose, which produce nonflammable gases, aliphatic char, and levoglucosane. The third step, around 490 °C, is attributed to the conversion of aliphatic char into aromatics, producing CO and CO_2 due to simultaneous carbonization.[19,23] The

coating decreases the degradation temperature of the raw paper from 343 to 329 °C. This earlier onset of decomposition (T_{onset} = 329 °C) is due to the activation of the instumescent ingredients, which form a char layer that suppresses combustion and protects the underlying material from the flame.[16] Although seemingly counterintuitive for a thermally protective coating, it is ideal for the FR mechanism to begin before the underlying substrate begins to degrade to maximize protection.[15] While the raw paper burns completely in the absence of the coating, the coated raw paper yields a char residue of ∼15%. This degradation event can also be seen in the derivative curves in Figure 3a, showing an ∼50% reduction in mass loss rate relative to uncoated raw paper. Figure S4 shows TGA curves of uncoated and coated raw paper under nitrogen atmosphere, with a single degradation step that is attributed to the depolymerization of cellulose into volatile gases and aliphatic char.[16] Under pyrolysis conditions, the coated raw paper leaves behind a greater char residue (30%) when the temperature reaches 700 °C. This CH/PA coating in either atmosphere delays the maximum decomposition of the raw paper.

Further analysis of flame-retardant properties was carried out using microcombustion calorimetry (MCC). MCC can measure several fire reaction parameters such as mass loss, heat release rate (HRR), peak heat release rate (pkHRR), and total heat release (THR), and can quantitatively explain the combustion phenomena of materials in a well-defined fire scenario.[24] Figure 3b and Table 1 reveal that the 4 BL CH/PA

Table 1. Microcombustion Calorimetry Results for Uncoated and Coated Raw Paper

sample	pkHRR (W/g)	max. temp. (°C)	THR (kJ/g)	char yield (%)
uncoated	212 ± 5	395 ± 2	10.4 ± 0.1	9.17 ± 0.03
4 BL CH/PA	65 ± 2	328 ± 3	3.1 ± 0.3	36.0 ± 0.4

intumescent coating provides fire protection by reducing the pkHRR by 69% and THR by 70%, while increasing the char residue by 75% (see Figure S5 for char residue images). These results correlate with the data obtained from TGA by demonstrating that the intumescent coating decreases the onset decomposition temperature of the raw paper. The effectiveness of this renewable intumescent coating relies on the decomposition of the phosphate groups in PA, which then catalyze the dehydration reaction of cellulose toward the

formation of an aromatic char.[16] The char is then expanded by gases produced (e.g., N_2, H_2O, and CO_2) in the decomposition of the blowing agent. Chitosan acts as both a carbon source and a blowing agent, so there is a continuous release of foaming gases over the entire char-forming area. This char layer eventually solidifies through crosslinking and condensation reactions, which slows the heat flow from the fire to the raw paper.[9,14]

3. CONCLUSIONS

In summary, an intumescent nanocoating composed of two biorenewable polyelectrolytes (CH and PA) was deposited on cotton-based raw paper using LbL assembly to reduce its flammability. Only four bilayers of CH/PA were needed to achieve self-extinguishing behavior during vertical flame testing, yielding a 95% residue. MCC revealed that the coating reduces both the peak heat release rate and the total heat release by 69 and 70%, respectively, compared to the uncoated raw paper. The performance of this bio-based coating provides an excellent opportunity to extend its application to a new generation of cellulose-based materials for building/architectural applications.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Materials. High-bulk-density chitosan (CH, 95% deacetylation) was purchased from Greentech Biochemicals (Qingdao, China). Branched polyethylenimine (PEI, 25,000 g/mol), phytic acid (PA, 50 wt % in water), hydrochloric acid (HCl, 37%), and sodium hydroxide (NaOH, 97%) were purchased from MilliporeSigma (Burlington, MA). Cotton-based raw paper (210 × 297 × 0.9 mm), made of 100% cotton linters without any additives, was purchased from Hahnemühle FineArt GmbH (Dassel, Germany). A BD-20C Corona Treater (Electro-Technic Products, Inc., Chicago, IL) was used to impart negative charge to both sides of the raw paper. A 5 wt % PEI solution was adjusted to pH 10 by adding 5 M HCl dropwise. A 4 wt % PA solution was adjusted to pH 4 by adding 5 M NaOH dropwise. A 1 wt % CH solution was adjusted to pH 2 by adding 5 M HCl dropwise. This solution was stirred for 15 min to completely dissolve the precipitated CH, and then it was adjusted to pH 4 using 5 M NaOH prior to deposition. All solutions were prepared with 18 MΩ deionized water.

4.2. Layer-by-Layer Deposition. Prior to deposition, a pretreatment is needed to improve adhesion between the substrate and coating. Corona treatment was used to impart a negative charge to both sides of the raw paper samples (12 × 3.5 in.). Subsequently, the substrates were immersed in a 5.0 wt % PEI solution (pH 10) for 5 min, followed by a rising step with DI water for 1 min. Following pretreatment, the substrate was immersed in the 4.0 wt % PA solution (adjusted to pH 4) for 5 min and rinsed with DI water for 1 min to remove excess solution. Raw paper samples were then immersed in the 1.0 wt % CH solution (adjusted to pH 4) for 1 min, followed by a DI water rinsing step for 1 min, to complete one bilayer. Successive bilayers were immersed in aqueous solutions of 1.0 wt % CH and 4.0 wt % PA, with 1 min deposition times, until the desired number of bilayers was achieved. Raw paper samples were dried at 70 °C for 2 h before testing.

4.3. Characterization. Vertical flame testing (VFT) was used to evaluate the flame retardancy of the raw paper samples (12 × 3.5 in.), in compliance with ASTM D6413-15. Micro

combustion calorimetry (MCC) was conducted at the University of Dayton Research Institute using Method A of ASTM D7309-21a (pyrolysis under nitrogen). Samples were tested at a 1 °C/s heating rate under nitrogen from 180 to 650 °C and run in triplicate to afford heat release data. 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 °C for 20 min to burn off residual water and then heated at a rate of 10 °C/min to 705 °C. The surface morphologies of the uncoated and coated raw paper samples were observed by sputter coating the samples with 5 nm of platinum/palladium alloy prior to imaging using a field emission scanning electron microscope (SEM) (model JSM-7500, JEOL; Tokyo, Japan). Fourier transform infrared (FTIR) spectroscopy was used to characterize preburn and postburn composites using an attenuated total reflectance (ATR) fixture (Frontier PerkinElmer, Inc., Shelton, CT).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04194.

> ATR-FTIR spectra of uncoated and coated raw paper; weight gain of the coated samples, char lengths, and % residues after VFT; images of conditioned coated samples; TGA under nitrogen; char images following MCC (PDF)
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> Vertical flame testing of uncoated cotton-based paper (MOV)
>
> Vertical flame testing of coated cotton-based paper (MOV)

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

CH, chitosan; PA, phytic acid; PEI, polyethylenimine; LbL, layer-by-layer; FR, flame-retardant; VFT, vertical flame testing; MCC, microscale combustion calorimetry; HRR, heat release rate; pkHRR, peak heat release rate; THR, total heat release; TGA, thermogravimetric analysis; SEM, scanning electron microscopy; ATR-FTIR, attenuated total reflectance-Fourier transform infrared spectroscopy

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