Polymeric Coacervate Coating for Flame Retardant Paper

Bethany Palen

Texas A&M University

Matthew G Rabaey

Texas A&M University

Danixa Rodriguez-Melendez

Texas A&M University

Ethan T Iverson

Texas A&M University

Jaime Grunlan (✉ jgrunlan@tamu.edu)

Texas A&M University College Station <https://orcid.org/0000-0001-5241-9741>

Research Article

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Abstract

Cellulosic paper (from wood fibers) is a highly flammable material that is used in corrugated cardboard, packaging, printing, and construction. While there is significant work focused on depositing a flame retardant coating onto the individual wood pulp fibers, there are very few studies that apply flame retardant coatings to already-cast paper. In an effort to improve the flame retardant properties of paper, a polymer-dense coacervate composed of polyethylenimine (PEI) and poly(sodium phosphate) (PSP) was deposited in a single step and subsequently crosslinked with glutaraldehyde. In a vertical flame test, the crosslinked PEI/PSP coacervate-coated paper achieves self-extinguishing behavior, and an average char length of 3.4 in, with only a 35% weight gain. Additionally, the crosslinked coating retains its flame retardant properties after water immersion and conditioning tests. This coacervate system is the first polymeric coating to be successfully deposited onto commercially available cellulosic paper for the purpose of flame retardancy.

Introduction

Contractor's paper is typically constructed from wood pulp fibers due to its biodegradability, recyclability, and low cost (Ek et al. 2009). This type of cellulosic paper is currently used in a wide variety of applications including corrugated cardboard, packaging, construction, and printing. Like other cellulosic materials, paper fabricated from these fibers is highly flammable (Lewin and Basch 1978). This flammability has resulted in the loss of precious historical documents (Lawrence 2018). Furthermore, this paper is typically used in roofing and other home improvement projects, which can lead to the propagation of house fires. Cotton exhibits similar flammability, so researchers have mimicked different strategies used to flame retard cotton in an attempt to flame retard cellulosic paper.

Previous efforts in flame retarding paper have deposited flame retardant materials on individual wood pulp fibrils and subsequently cast those coated fibers into a paper using a variety of deposition methods, one of which is layer-by-layer (LbL) assembly (Zhang et al. 2020; Wang et al. 2017; Köklükaya et al. 2015; Pan et al. 2018). LbL deposition is a widely studied coating method in which cationic and anionic polyelectrolytes and/or nanoparticles are alternately deposited onto a given substrate and are held together via electrostatic interactions. Coatings deposited using this technology have been shown to yield excellent properties for gas barrier (Priolo et al. 2015; Chaitoglou et al. 2021; Zhan et al. 2021), heat shielding (Long et al. 2021; Nakamura et al. 2018), and flame retardancy (Lazar et al. 2020; Holder et al. 2017; Zilke et al. 2020; Chen et al. 2020) on a wide range of substrates, including cotton and other cellulosic materials. While this methodology does yield effective flame retardant behavior, LbL processing can be quite time consuming due to the large number of processing steps.

Polyelectrolyte complexes (PEC) are an alternative to LbL assembly, in which oppositely charged polyelectrolytes can be deposited simultaneously in a single step. The mixing of cationic and anionic polymers can either result in an insoluble complex, a coacervate (i.e., elastic liquid), or a soluble solution. This entropically driven complexation is governed by both intrinsic (polymer-polymer) and extrinsic

(polymer-counter ion) interactions, which can be manipulated through adjustments in pH and salt concentration (Wang et al. 2014). When the electrostatic interactions between the polyelectrolytes are limited by the presence of counter ions, a mixture of two distinct phases emerge: a polymer-dense coacervate phase and a polymer-poor solution phase (Sing and Perry 2020). The PEC coacervate has liquid-like properties and is viscous, which is amenable to traditional coating techniques. While coacervate coatings have proven effective in improving gas barrier and flame retardant properties (Chiang et al. 2021; Demirbağ and Aksoy 2016), these films absorb a significant amount of moisture, which can be mediated by the incorporation of clay nanoplatelets or addition of a crosslinking agent (Yang et al. 2012; Vartiainen and Harlin 2011; Tsurko et al. 2017).

In the present work, a coacervate consisting of polyethylenimine (PEI) and poly(sodium phosphate) (PSP) was deposited onto contractor's paper in one step and subsequently crosslinked with glutaraldehyde (GA) to reduce moisture sensitivity. The crosslinked coating self-extinguishes in vertical flame testing, with a resulting char length of 3.4 in. This PEI/PSP film is also able to withstand prolonged water exposure and bending/conditioning with minimal weight loss and unaltered flame performance. It is believed that this is the first coacervate coating to be deposited onto cellulosic paper for the purpose of flame retardancy. While the system reported in this work is on cellulosic paper prepared from wood fibers, the PEI/PSP coating can likely be deposited onto a variety of paper substrates to yield similar self-extinguishing behavior.

Experimental

Chemicals

Polyethylenimine (PEI, MW $\sim 25,000 \text{ g mol}^{-1}$), poly(sodium phosphate) (PSP, crystalline, 96%), glutaraldehyde (GA, 50 wt% in solution), and hydrochloric acid (37 wt% in solution) were purchased from Sigma Aldrich (Milwaukee, WI). Contractor's paper (TRIMACO Easy Mask, 254 μm thick) was purchased from Home Depot (College Station, TX).

Preparation of PEI/PSP coacervate

A 15 wt% solution of polyethylenimine and a 45 wt% solution of poly(sodium phosphate) were prepared with 18 M Ω deionized water and adjusted to a pH of 4 using 5 M HCl. The two solutions were then combined in equal volumes and vigorously shaken. The resulting mixture was annealed in an oven for 2 hours at 70 °C and was slowly cooled to room temperature. The supernatant was then discarded, leaving behind the polymer-rich coacervate.

Fabrication of films

The PEI/PSP coacervate solution was deposited onto both sides of the contractor's paper using the 50 μm clearance of a multiple clearance square applicator (GARDCO, Pompano Beach, FL). The paper was subsequently placed in a 70 °C oven until dried. The complete coating process is depicted in Fig. 1. For

crosslinked samples, the coated paper was taken from the oven, submerged in a 0.5 wt% glutaraldehyde solution for 30 minutes, and hung in a 70 °C oven to dry.

Characterization

Fourier transform infrared (FTIR) spectroscopy was performed on coated paper samples with an α platinum attenuated total reflectance (ATR) FTIR spectrometer (24 scans with a resolution of 2 cm^{-1}), equipped with a diamond ATR module (Bruker, Billerica, MA). Prior to scanning electron microscope (SEM) imaging (FESEM, Model JSM-7500, JEOL; Tokyo, Japan), samples were sputter coated using 5 nm of platinum/palladium alloy. Samples were masked to a 5 cm^2 area for gas barrier testing. Oxygen transmission rate (OTR) was measured with room air (20.9% O_2) exposure by MOCON Inc. (Minneapolis, MN) using an OPTech-O2 Model P instrument. The testing temperature was 23 °C and the test gas humidity was 39% RH. Vertical flame testing (VFT) was performed on 13x5 in samples in accordance with ASTM D6413 using a model VC-2 vertical flame cabinet (Govmark, Farmingdale, NY).

Microcombustion calorimetry (MCC) experiments were conducted at the University of Dayton Research Institute using method A of ASTM D7309. Samples were heated at a rate of 1 °C/sec under nitrogen from 150 °C to 650 °C. Differential Scanning Calorimetry (DSC) was performed using a DSC Q20 (TA Instruments, New Castle, DE) at a heating rate of 10 °C/min. All samples were dried at 70 °C prior to testing.

Conditioning

Crosslinked samples were subjected to conditioning and wash testing to evaluate the durability of the coating. For conditioning, the paper was crumpled into a ball and unfolded back to its original flat shape. For wash durability testing, the crosslinked paper was soaked in DI water for 30 minutes and hung in a 70 °C oven to dry. The samples were then burned to determine if the coating integrity was maintained after conditioning/washing.

Results And Discussion

Confirmation of crosslinking

FTIR was performed on PEI/PSP-coated papers to confirm crosslinking. Glutaraldehyde crosslinks the amine groups in the film, sourced from PEI, by forming a Schiff base (Yang et al. 2011), which is evidenced by the disappearance of the primary amine peak. Fig. 2 shows that the primary amine stretch (N-H) (3500 cm^{-1}) is present in the PEI/PSP film, but after crosslinking this peak is no longer detected. There is also a broad hydroxyl stretch ranging from $3500\text{-}3200\text{ cm}^{-1}$ in the PEI/PSP film that is not present in the crosslinked film. This stretch can be attributed to significant water uptake of the film, which results in a noticeable tackiness of the PEI/PSP coating. After GA treatment, the coating is no longer tacky, resulting in the disappearance of the hydroxyl peak for the crosslinked film. Along with the reduction in tackiness, crosslinking can be observed through an obvious color change following exposure

to GA, which can be seen in Fig. 3. In Fig. 3a, the original color of the paper is brown, which is maintained after application of the PEI/PSP film, as shown in Fig. 3b. Following GA crosslinking, the coating changes from colorless to opaque (Fig. 3c), which suggests a chemical change has taken place.

Surface morphology

SEM images reveal that uncoated cellulosic paper is extremely porous, as shown in Fig. 3d. Following the application of the PEI/PSP coacervate, the pores of the paper are filled, yielding the smooth, conformal surface shown in Fig. 3e. The deposition of the coacervate onto the cellulosic paper results in a 64% weight gain, which is likely due to the high surface area of the paper and particulates of polymeric material on the surface of the coating, as shown in Fig. 3e. After glutaraldehyde crosslinking, the PEI/PSP particulates have been washed away, leaving a uniformly crosslinked film, while simultaneously reducing the weight gain to 35%. Fig. 3f also reveals a rougher surface texture compared to the non-crosslinked film, with small craters appearing throughout the film.

Gas barrier properties

Based on the smooth surface due to pore-filling, and previous coacervate studies (Chiang et al. 2021; Haile et al. 2017; Li et al. 2021), it was hypothesized that the PEI/PSP coating on cellulosic paper could have excellent gas barrier properties. The oxygen transmission rate (OTR) was measured for uncoated, coated, and crosslinked paper and it was found that the deposition of the PEI/PSP coacervate, which sufficiently clogs the pores in the substrate, yields a 90% reduction in the OTR compared to the uncoated paper. After crosslinking, the film only results in a 30% reduction in OTR. This worsened barrier for the crosslinked film is likely due to a combination of surface morphology and weight gain (i.e., thickness and coverage). As previously discussed, SEM images of the crosslinked film show microscopic craters throughout the film, which act as weak points for oxygen and other molecules to more easily penetrate the film. Additionally, the weight gain of the crosslinked film is half that of the PEI/PSP coated film, which suggests poorer surface coverage. With its relatively smooth texture, the uncrosslinked PEI/PSP coacervate film has an optimal surface morphology suitable for significant reduction in OTR.

Flame retardant behavior

Vertical flame testing was used to evaluate the flame retardant behavior of the uncoated, coated, and crosslinked paper by subjecting each sample to a methane flame for 12 s. As shown in Fig. 4a, the uncoated paper is completely consumed by the flame, leaving virtually no residue in the exposed area. With the addition of the PEI/PSP coacervate coating, the flame still travels up the entirety of the sample, shown in Fig. 4b, but the resulting charred area has a much higher residue compared to the uncoated paper. While all of the necessary flame retardant components are present in the PEI/PSP coacervate coating, the high amount of polymeric material, which is flammable, could be hindering the flame retardant performance. After crosslinking the PEI/PSP coated sample with GA, the paper achieves self-extinguishing behavior with nearly half the weight gain of the coacervate coated sample. As shown in Fig. 4c and Table 1, the ignition of the crosslinked paper results in an average char length of only 3.4 in.

While the char of the PEI/PSP coated film, as shown in Fig. 4d, is completely black. The charred area of the crosslinked sample appears to have several different colored sections surrounding the blackened char. These colorful areas are likely due to a variance in the coating’s heat exposure. The black char of the crosslinked paper appears to be very layered compared to the coated residue without crosslinking, as shown in Fig. 4e. SEM images of the secondary discolored area (Fig. 4f) reveal that the coating that was exposed to the tip of the flame is still intact, with intumescent bubbling beginning to appear in an attempt to extinguish the flame. As a result of the self-extinguishing behavior, the area directly above the char had minimal exposure to the flame, which results in only a slight discoloration of the paper substrate.

Table 1

Vertical flame test results for uncoated, coated, and crosslinked paper.

Sample	Weight Gain (%)	Afterburn (s)	Char Length (in)
Uncoated	-	57.0 ± 3.6	Entire sample
PEI/PSP	63.9 ± 3.8	25.8 ± 15.6	Entire sample
PEI/PSP crosslinked	35.3 ± 3.6	0 ± 0	3.4 ± 0.5

Microcombustion calorimetry measures the oxygen consumption rate of a given material exposed to a heat source and can be used to assess flame retardant efficacy (Lyon et al. 2013). Fig. 5 shows MCC results for uncoated, coated, and crosslinked paper. The uncoated cellulosic paper exhibits one distinct peak, with an average peak heat release rate (pkHRR) of 152 W/g, as shown in Table 2. The coacervate-coated paper and the crosslinked paper also display one distinct peak with a significant decrease in the pkHRR compared to the uncoated substrate. The similarity between the PEI/PSP and PEI/PSP crosslinked HRR, despite vastly different behaviors in the vertical flame test, is likely due to the crosslinked intumescent system primarily working in the condensed phase rather than the gas phase. As previously stated, MCC measures the oxygen consumption of the system, which can limit the detection of other flame retardant mechanisms (Leistner et al. 2015; Lyon and Walters 2004). As shown in Fig. 4, charring is a crucial component of the self-extinguishing crosslinked system.

Table 2

MCC and DSC data for coated, crosslinked, and uncoated paper.

Sample	MCC		DSC
	pkHRR (W g ⁻¹)	THR (kJ g ⁻¹)	Energy Balance (J g ⁻¹)
Uncoated	152 ± 3	8.5 ± 0.1	+0.21
PEI/PSP	73 ± 4	6.1 ± 0.2	-0.65
PEI/PSP crosslinked	85 ± 8	6.9 ± 0.1	-12.85

Differential scanning calorimetry (-20 °C-500 °C) was performed to determine the role of the condensed phase energetic effects of the coated and crosslinked paper samples during pyrolysis. DSC reveals that

the crosslinked film exhibits stronger endothermic behavior than the PEI/PSP coated paper. As shown in Table 2, the thermal degradation of uncoated paper appears as an exothermic peak (0.21 J/g). When the PEI/PSP coacervate was applied to the substrate, the coated paper degrades slightly endothermically (-0.65 J/g), resulting in an overall cooling effect during pyrolysis. After crosslinking the PEI/PSP film, additional endothermic reactions occur upon heating, which may be attributed to initiation of combustion (-12.85 J/g) (Gliko-Kabir, et al. 1999). This significant cooling effect reaffirms that the crosslinked coating acts in the condensed phase through system cooling and charring to self-extinguish the flame.

Conditioning of the paper

The PEI/PSP crosslinked film is able to withstand various conditioning tests, including water soaking and manual conditioning (i.e., paper crumpling). Following a 30-minute water soak, the integrity of the PEI/PSP crosslinked film is maintained, which can be confirmed by the minimal weight loss after water exposure (-3.4 wt%) and unaltered flame performance (average char length of 3.8 in.), as shown in Table 3 and Fig. 6a. To further investigate the durability of the crosslinked coating, the paper was manually conditioned by crumpling the paper into a ball to mimic the possible manipulation that the coating may be subjected to in practical applications. After the paper was conditioned, the coating did have some small cracks, but as shown in Fig. 6b and Table 3, the crosslinked film maintained the ~35% weight gain and was still able to self-extinguish with a char length of 3.8 in. The same conditioning tests were performed on uncrosslinked paper. The uncrosslinked paper had a 15% weight loss after water soaking and an unaltered weight following crumpling. Both types of conditioned samples burned the length of the paper in a vertical flame test.

Table 3
Vertical flame test results for crosslinked coating on paper after conditioning tests.

Sample	Conditioning	Weight Loss (%)	Afterburn (s)	Char Length (in)
PEI/PSP crosslinked	Water soak	3.40 ± 0.66	0 ± 0	3.8 ± 0.4
PEI/PSP crosslinked	Crumple	0.23 ± 0.21	0 ± 0	3.8 ± 0.6

Conclusions

A polymer-rich coacervate consisting of polyethylenimine and poly(sodium phosphate) was deposited onto cellulosic paper made from wood fibers and subsequently crosslinked with glutaraldehyde. Prior to crosslinking, the PEI/PSP coacervate film displays good gas barrier properties, yielding a 90% reduction in OTR. The crosslinked coating exhibits self-extinguishing behavior in vertical flame testing, with a 35% weight gain and an average char length of 3.4 in. Additionally, the crosslinked coating was able to withstand conditioning tests (i.e., water soaking and manual crumpling) with unaltered weight gain and flame protection. This unique water-based flame retardant coating is the first coacervate deposited onto commercially available paper for the purpose of flame retardancy. It is likely that the gas barrier could be improved, while maintaining flame retardant performance, through modification of crosslinker chemistry and/or concentration.

Declarations

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Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Author contributions

All authors contributed to the study conception and data collection. All authors read and approved the final manuscript.

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Author Information

*Corresponding Author: jgrunlan@tamu.edu

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Figures

Figure 1

Preparation (a) and application (b) of the PEI/PSP coacervate.

Figure 2

FTIR spectra of PEI/PSP coated (red) and crosslinked (blue) paper.

Figure 3

Photographs (top) and SEM images (bottom) of uncoated (a,d), coated (b,e), and crosslinked (c,f) paper, respectively.

Figure 4

Pre- (left) and post-burn (right) images of uncoated (a), coated (b), and crosslinked (c) paper. Post-burn SEM images of PEI/PSP coated char (d), and PEI/PSP crosslinked char exposed to the flame tip (e), and the discolored area above the tip (f). Colored boxes in the photographs show where SEM images were taken.

Figure 5

Representative heat release rate as a function of temperature in the microcombustion calorimeter for uncoated, coated, and crosslinked paper.

Water Soak

Crumple

Figure 6

Pre- (left) and post-burn (right) images for PEI/PSP crosslinked coating on paper after water soak (a) and crumpling (b).