

One-Pot, Bioinspired Coatings To Reduce the Flammability of Flexible Polyurethane Foams

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S Supporting Information

ABSTRACT: In this manuscript, natural materials were combined into a single “pot” to produce flexible, highly fire resistant, and bioinspired coatings on flexible polyurethane foam (PUF). In one step, PUF was coated with a fire protective layer constructed of a polysaccharide binder (starch or agar), a boron fire retardant (boric acid or derivative), and a dirt char former (montmorillonite clay). Nearly all coatings produced a 63% reduction in a critical flammability value, the peak heat release rate (PHRR). One formulation produced a 75% reduction in PHRR. This technology was validated in full-scale furniture fire tests, where a 75% reduction in PHRR was measured. At these PHRR values, this technology could reduce the fire threat of furniture from significant fire damage in and beyond the room of fire origin to being contained to the burning furniture. This flammability reduction was caused by three mechanisms—the gas-phase and condensed-phase processes of the boron fire retardant and the condensed-phase process of the clay. We describe the one-pot coating process and the impact of the coating composition on flammability.

KEYWORDS: fire retardant, boron, polyurethane foam, biopolymers, one pot



1. INTRODUCTION

In the United States, there are more than 366 000 residential fires each year. Annually, these fires cause more than 2500 civilian fatalities and 13 000 civilian injuries.¹ Though one of the lowest in frequency, fires involving residential furniture and mattresses are responsible for the largest fraction of these fatalities and injuries. To significantly reduce the fire severity of soft furnishings, it is critical to eliminate the flexible polyurethane foam from participating in the fire. However, existing fire retardant technologies are not viable options due to their ineffectiveness and their banning because of potential environment and health concerns. One approach showing significant promise as a “greener” fire retardant for flexible polyurethane foam and textiles is fire resistant coatings fabricated by layer-by-layer (LbL) assembly.

Layer-by-layer (LbL) deposition^{2–4} is a technique for fabricating multifunctional thin coatings/films. These coatings are generally formed by repeatedly depositing alternating layers of oppositely charged materials. The multilayer assembly of the coating is enabled by attractive forces (e.g., electrostatic,⁵ van der Waals,^{6,7} and H bonding^{8,9}) and self-regulated by electrostatic repulsion within the individual layers. LbL coatings/films can be applied in many different ways (e.g., dip coating^{10,11} and spray coating^{12,13}) and have a wide variety of properties and applications (e.g., as a conducting film,^{14–16} antireflection film,^{17,18} and oxygen barrier^{19,20} for biomedical and sensor applications).

In 2009, Grunlan et al. (Texas A&M University) first used LbL deposition to produce a fire retardant coating on fabric.²¹

Since then Grunlan et al. have continued to be a pioneer in this area by advancing this technology through the research at Texas A&M University, National Institute of Standards and Technology (NIST), and Polytechnic of Turin. Over the last several years, these three research groups have been the epicenter of LbL fabricated fire retardant coatings^{22–28} developing FR coatings applied to flexible foam and fabrics, constructed of synthetic and biobased polymer binders (e.g., poly(acrylic acid) and chitosan), and have contained a range of fire retardants (e.g., sodium polyphosphate and phytic acid) and protective residue formers/enhancers (e.g., montmorillonite clay and layered double hydroxides). These variations and extensions of the original concept have resulted in more rapidly fabricated and highly fire resistant coatings (e.g., a single-step process for fabricating a fire retardant coating on fabric²⁹).

Starch, agar, and boron are natural materials. Starch is a carbohydrate typically consisting of amylose and amylopectin. Starch is one of the most common carbohydrates in human diets and found in green plants, potatoes, wheat, and corn. Agar is a gelatinous material obtained from algae. Agar is composed of a linear polysaccharide, agarose, and a mixture of smaller molecules called agaropectin. Boric acid and its salts (e.g., sodium polyborate) are found in saltwater, fruits, vegetables, grains, and nuts.

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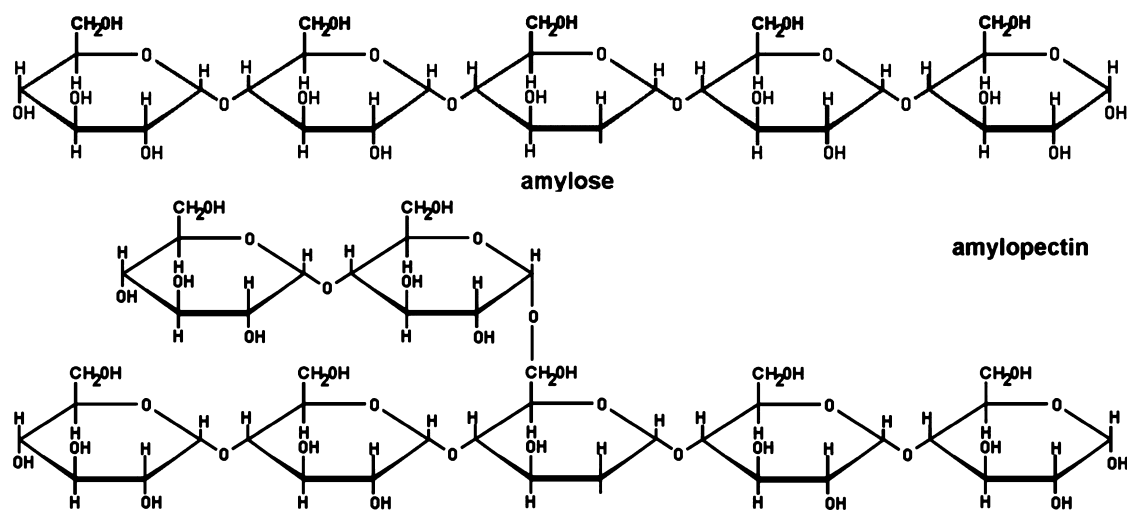


Figure 1. Potato starch binder is 20% amylose and 80% amylopectin.

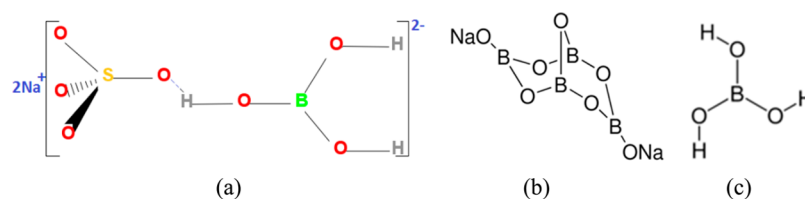


Figure 2. Boron-based fire retardants. (a) Sodium polyborate (Boron-10), (b) sodium tetraborate decahydrate (Borax), and (c) boric acid.

In 2011, Tsuyumoto et al. reported using starch and sodium polyborate (SPB) to form a fire resistant coating on poly(ethylene terephthalate) and polypropylene nonwoven fabrics^{30,31} and rigid polyurethane foam.³² Flammability was investigated by measuring the time for flame penetration through the sample and the temperature at the backside of the sample. The researchers reported these starch–SPB–based coatings were able to take these substrates from a few second flame penetration time to no flame penetration in 12 min. In general, this type of flammability reduction required a coating that added more than 50% to the mass of the substrate and contained 12–40% SPB. In 2012, Glenn et al. reported using starch and sodium boronite (a layered silicate) to form fire resistant gel coatings for protecting structures against wildland fires.³³ The coatings were applied to exterior cement board lap siding. The fire protective performance was evaluated by measuring the temperature and heat flux through the coatings on the siding exposed to a 42 kW/m² infrared heater. These coatings increased the time to reach 200 °C on the siding surface (a critical fire metric) by as much as 30 min.

This manuscript describes a one-pot process and the chemical formulations to produce flexible, bioinspired, and highly fire resistant coatings for flexible polyurethane foam (PUF). The coatings were constructed of two different polysaccharide binders (agar and starch), three different boron fire retardants (sodium polyborate, sodium tetraborate decahydrate, and boric acid), and a protective residue former/enhancer (MMT). The impact of the formulations on flammability was determined by measuring ignition propensity and heat released during the combustion of small-scale PUF-coated samples. Full-scale chair fire tests were conducted to better understand the actual impact of this FR technology under realistic fire conditions.

2. EXPERIMENTAL SECTION

Unless otherwise indicated, all materials were used as received, all % values are mass fraction %, and all data is reported with a 2 σ uncertainty.

2.1. Materials. Potato starch (Bob's Red Mill) and agar (Agar Flakes) were obtained from a local grocery store. Sodium polyborate was obtained from InCide Technologies (SPB, Boron-10). Sodium tetraborate decahydrate was obtained from Sigma-Aldrich (STB, Borax). Boric acid was obtained from the NIST storeroom (BA, Mallinckrodt Baker Product). Sodium montmorillonite clay was obtained from Southern Clay Products Inc. (MMT, Sodium Cloisite). Standard (untreated) polyurethane foam (PUF) was obtained from Future Foam Inc. (Fullerton, CA) and stored in a climate-controlled room with no direct sunlight exposure. The chemical structures are provided in Figures 1 and 2.

2.2. Coating Process and Characterization. The coating solutions were prepared by first making the boron FR solution, then adding MMT, and last adding the polysaccharide. When the formulation did not require one of these components then that step was skipped. For example, if there was no boron FR then the preparation was to make the MMT solution and then add polysaccharide. All depositing and washing solutions were water based and prepared using water purified from a Nanopure II system (18.2 M Ω -cm, Sybron/Barnstead).

This procedure was used to create 100 mL of a 3% starch, 23% SPB, and 2% MMT solution for coating foam samples for flammability screening (5 cm \times 5 cm \times 5 cm PUF). For coating foam samples for Cone tests (10 cm \times 10 cm \times 5 cm PUF), the total solution was increased to 600 mL. For coating foam samples for full-scale tests (47.0 cm \times 47 cm \times 10.2 and 47 cm \times 37 cm \times 10.2 cm), the total solution was increased to 10 L per piece. SPB (23%) aqueous solutions were prepared by adding SPB (30 g) to DI water (100 mL). The solution was heated (60 °C) and stirred until the SPB fully dissolved and the reaction to form SPB was complete (30 min). If MMT was used in the recipe, MMT powder (2 mass % of the current total mixture) was added to the SPB solution. The SPB–MMT solution was stirred for a couple hours. If starch was used in the receipt, the starch

powder (3 mass % of the current total mixture) was added to the SPB–MMT solution. Then, the solution was heated (90 °C) and stirred until the solution formed a gel. Coating began once the solution cooled to ~50 °C. The foam was squeezed and released several times in the solution and then left to soak. After 2 min of soaking, the excess material was squeezed out of the sample and the sample was dried overnight at 70 °C in an air convection oven.

If BA or STB was used, the SPB was replaced with the other boron FR and the same preparation steps were followed. If agar was used, the starch was replaced with agar and the solution was heated (100 °C) until boiling. The remaining coatings steps were the same.

A Zeiss Ultra 60 Field Emission-Scanning Electron Microscope (FE-SEM, Carl Zeiss Inc., Thornwood, NY) was used to acquire surface images of the coatings on the PUF under a 5 kV accelerating voltage. All SEM samples were sputter coated with 8 nm of Au/Pd (60%/40% by mass) prior to imaging. The elementary compositions of the coating were analyzed using energy-dispersive X-ray spectroscopy (XEDS) equipped with FE-SEM under 15 kV accelerating voltage. The same samples were used for both SEM and XEDS analysis.

2.3. Flammability Testing. Flammability testing spanned from screening to full-scale fire tests. The first step was to use ignition resistance to identify promising formulations. These promising formulations were reproduced and their combustion behavior under an external heat source was measured using a Cone calorimeter (Cone). The best candidates from the Cone were reproduced at a larger scale to measure their impact on real furniture.

Flammability screening was conducted by placing the foam sample on a wire mesh suspended 16 cm off the bottom of a chemical fume hood. The ignition process was to apply a hand-held torch (~1430 °C) to the bottom right corner of the sample for 5 s. The torch was applied again for another 5 s if the sample did not ignite or if it self-extinguished. This ignition process was repeated no more than three times. The test was complete when there were no visible flames. The worst fire behavior was used to qualitatively rank the formulations. The type of behavior used for ranking included the following: number of applications of the torch before ignition, time until flames extinguished, and extent of flame propagation across the foam surface.

Cone calorimetry was conducted according to a standard testing procedure (ASTM E-1354-07). The dual Cone was operated with an incident target flux of 35 kW/m² and an exhaust flow of 24 L/s. The sample (10 cm × 10 cm × 5 cm) was placed in a pan constructed from heavy-gauge aluminum foil (Reynolds Heavy Gauge Aluminum Foil). The sides and bottom of the sample were covered by aluminum foil so that only the top surface of the sample was exposed to the Cone heater. Exposure to the 35 kW/m² external heater caused pyrolysis of the sample. Once sufficient fuel (pyrolysis products) was released, ignition occurred, which was activated by a spark igniter. The test was over when there were no visible flames. The standard measurement uncertainty was ±10% of the reported reduction values and ±2 s in time.

The chairs used for full-scale fire tests were constructed with four cushions (two small ones for the arms and two large ones for the seat and back cushions) in accordance with California Technical Bulletin 133.³⁴ All cushions were upholstered with 78% polyethylene/22% polyester or 100% cotton “common stock” cover fabrics purchased from JoAnn Fabrics. The cushions were assembled on a steel frame representing a chair. The mockup was ignited using a wand constructed from 0.95 cm diameter stainless steel tubing to apply a 3.50 cm long flame, generated by igniting propane gas, at the center of the cavity between the seat and the back cushions for 20 s. Heat flux gauges, a One (1) Megawatt (MW) Fire Product Collector (FPC), and a weighing device were used to obtain measurements of the test assembly during the experiments. The experiments were conducted in the Medium Burn Room (MBR) of the Bureau of Alcohol, Tobacco, Firearms and Explosives Fire Research Laboratory (ATF FRL) located in Beltsville, MD.

3. RESULTS AND DISCUSSION

In a single processing step, polysaccharide-based fire resistant coatings were applied to polyurethane foam. Boron FRs and/or a clay char former/enhancer were added to enhance the fire resistance of the coating and by extension the PUF. The coatings were characterized to determine coating quality and the presence of MMT and boron. All coatings were evaluated for ignition resistance and forced combustion behavior (Cone calorimeter). One formulation was evaluated in full-scale furniture fire tests.

3.1. Starch-Based Coatings: Fabrication and Flammability Screening. Fourteen FR-coated PUF formulations were produced by soaking PUF in a single aqueous solution containing starch (0%, 1.5%, or 3%), SPB (0%, 5.8%, 11.5%, or 23%), and/or MMT (0% or 2%). The coating composition is provided in the colored boxes, and the coating mass % is provided in the white boxes of Figure 3.

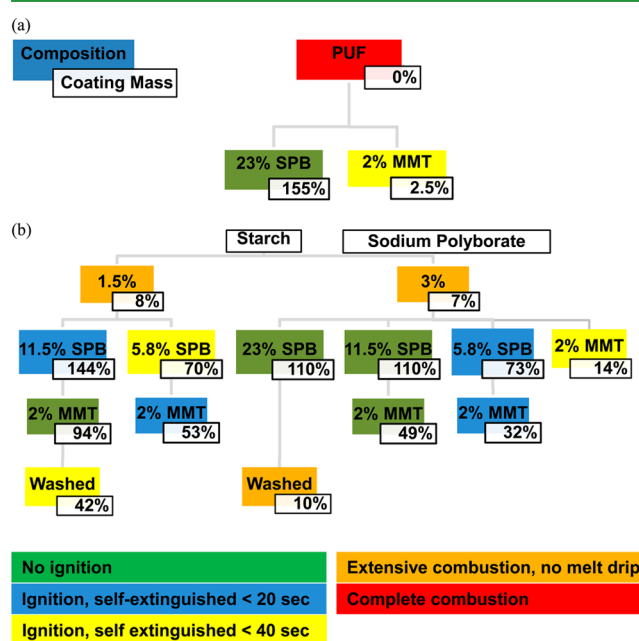


Figure 3. Coating composition, coating mass %, and open flame fire screening for foam (a) MMT or SPB coatings and (b) starch-based coatings with or without SPB and MMT. Box color represents the open flame screening results. Text in the colored box is the coating composition. Value in the white box is the mass coating %. Color scheme also applies to Figures 7 and 8.

Ignition resistance tests were used as a quick/qualitative screen of flammability. As previously reported, this approach was best used to coarsely identify promising coating formulations for further investigation (e.g., Cone calorimeter).^{35–37} In these reports, samples that did not ignite or self-extinguished within 40 s performed better in Cone calorimeter flammability tests. In the research presented in this manuscript, these observations were used as the basis for identifying promising coatings. The results from the flammability screening tests (e.g., no ignition and self-extinguished within 20 s) are indicated by the color of the boxes in Figure 3.

All FR formulations improved the PUF flammability performance in the flammability screening tests. PUF ignited quickly, formed flaming melt drips, and was completely consumed within 60 s. Soaking the PUF in the starch-only solutions, formed a light starch coating (approximately 7%) that

was sufficient to prevent melt dripping, but was unable to stop complete combustion. SPB-only and MMT-only coatings on PUF produced better flammability screening results than the starch-only coatings (no ignition for SPB and self-extinguishing < 40 s for MMT), but these coatings easily released when the sample was submerged in water. Therefore, starch was added to the coating formulation to keep the boron FR and MMT in the coating.

Starch and SPB coatings significantly improved the flammability screening results but added a lot of mass to the substrate. The starch–SPB coatings caused a 70–144% increase in the PUF mass. The coating mass increased with increasing SPB concentration in the depositing solution and was higher at the lower starch solution concentration. Presumably, the coating mass was primarily SPB, which alone (no starch) resulted in a 155% mass coating (23% SPB depositing solution). These samples did not ignite as long as the depositing solution was at least 3% starch and 11.5% SPB. At lower SPB or starch concentrations, the samples ignited but quickly self-extinguished. The trend appeared to be that ignition resistance or faster self-extinguishing can be achieved with increased SPB or starch in the coating solution.

Adding MMT to the starch–SPB coatings further improved the foam flammability performance. For the 1.5% starch formulations, adding MMT improved ignition resistance. For example, the 11.5% SPB went from self-extinguishing in <20 s to ignition resistant because of the MMT. Adding MMT also helped recover the drop in performance that was observed by reducing the SPB concentration from 11.5% to 5.8%. Adding MMT also reduced the coating mass for an effective coating. This indicated that the coating was a more effective fire retardant technology with the incorporation of MMT and then without. However, SPB was critical to the overall flammability as the MMT added to the 3% starch formulation (no SPB) performed no better than the lowest SPB formulation. Incorporating MMT did have one drawback. The coated foams tended to be stiffer and take a longer time to recover after compression (Supporting Information).

3.2. Starch-Based Coatings: Flammability Testing. The Cone calorimeter (Cone) is a commonly used instrument to measure bulk flammability characteristics of materials. The sample is exposed to an external heat flux, which forces the material to undergo pyrolysis. Once sufficient fuel (pyrolysis products) is produced, ignition will occur and the sample will undergo combustion and continue to pyrolyze. The most common parameters reported from the test are time to ignition (TTI), maximum amount (peak) of heat released during the test (PHRR), time after ignition to reach the PHRR (t-PHRR), total amount of heat released during the test (THR), and average amount of heat released during the test (AHRR). Cone data and HRR curves for the starch-based coatings are provided in Figure 4 and Table 1.

While the Cone is an excellent tool to measure the potential of this fire resistant technology, ultimately the measure of its impact requires full-scale fire tests. The end-use product (e.g., furniture) for this technology is a composite construction (e.g., foam wrapped with fabric and batting) where each component interacts with each other. This interaction can strongly alter the fire behavior. Other factors that influence the fire behavior are the size, shape, and geometry of the product. None of these factors are present in the Cone tests. Therefore, the Cone data was used to quantitatively access the fire resistance of the coatings, whereas full-scale data was used to quantitatively

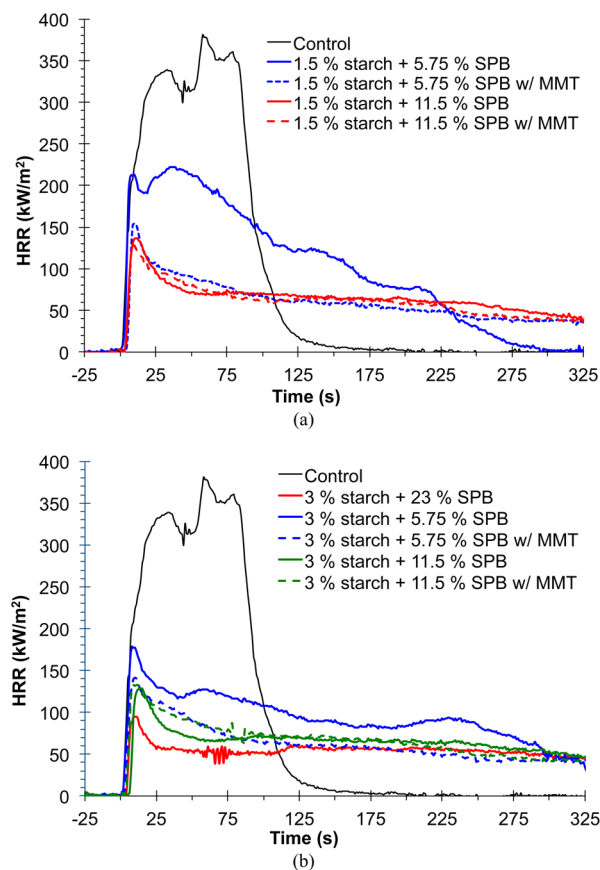


Figure 4. Cone calorimeter heat release rate curves for (a) 1.5% and (b) 3.0% starch-based FR coatings on foam. Uncertainty is $\pm 10\%$ of the reported reduction values. External heat flux was 35 kW/m^2 .

Table 1. Cone Flammability Reduction Caused by Starch-Based FR Coatings^a

ID	Cone calorimeter		
	% PHRR reduction	% AHRR reduction	$H_{c,eff}$ reduction
3.0S-23SPB	75	81	25
1.5S-5.8SPB	42	55	6
1.5S-5.8SPB-MMT	60	71	17
3.0S-5.8SPB	53	65	10
3.0S-5.8SPB-MMT	63	73	14
<i>1.5S-11.5SPB</i>	64	73	23
1.5S-11.5SPB-MMT	66	73	15
3.0S-11.5SPB	66	73	23
3.0S-11.5SPB-MMT	66	73	14
PUF (control)	387 kW/m^2	155 kW/m^2	25.4 MJ/kg

^aReduction values are relative to the actual PUF Cone PHRR, AHRR, $H_{c,eff}$ values, which are provided at the bottom of this table. Formulation in italics was scaled up for full-scale fire tests. Uncertainty is $\pm 10\%$ of the reported reduction values. Within the uncertainty of the measurement, the THR was similar for all the formulations (30 MJ/m^2).

access the decrease in flammability of furniture built using the fire resistant coated PUF. Full-scale furniture calorimeter data is provided in Figure 5 and Table 2. Time-captured images of the full-scale tests are provided in Figure 6.

All of the starch-based coatings reduced the Cone flammability (PHRR and AHRR) of PUF but had no impact on the THR value ($30 \pm 3 \text{ MJ/m}^2$). This indicates the coated

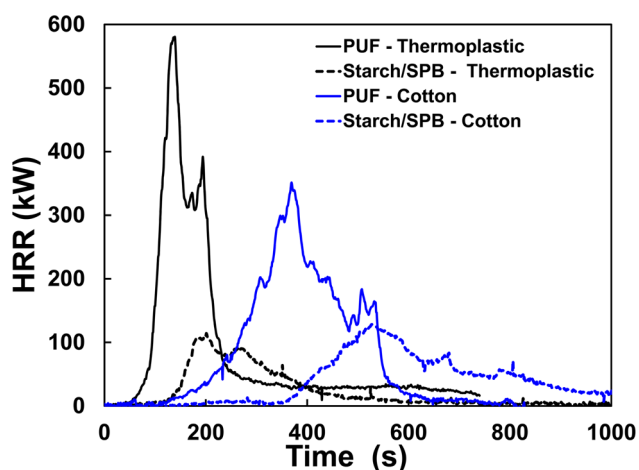


Figure 5. Full-scale fire heat release curves of thermoplastic cover fabric furniture and cotton cover fabric furniture with PUF and 1.5% starch and 11.5% SPB foam. Uncertainty is $\pm 10\%$ of the measured values. External heat flux was 35 kW/m^2 .

Table 2. Full-Scale Furniture Flammability Data for PUF and Starch-Based Coated Foam with a Thermoplastic Cover Fabric and a Cotton Cover Fabric^a

	full-scale furniture			
	PHRR (kW/m^2)	tPHRR (s)	AHRR (kW/m^2)	THR (MJ/m^2)
	thermoplastic fabric			
PUF	580	132	63	121
1.5% starch–11.5% SPB	113	199	21	50
% Delta	–75	+50	–61	–71
	cotton			
PUF	350	369	64.6	107
1.5% starch–11.5% SPB	129	530	35	48
% Delta	–63	+43	–46	–55

^aThe percent change in the flammability caused by the coatings is provided as “% Delta”. Uncertainty is $\pm 10\%$ of the reported values.

PUF was completely consumed during combustion but created a much smaller sized fire than the standard PUF. The best performing formulation was the 3% starch with 23% SPB, which produced a 75% and 81% reduction in the PHRR and AHRR values. The next best formulation was a group of six

formulations. These six formulations gave similar Cone results: an average of 63% reduction in PHRR and 72% reduction in AHRR. These formulations include all those that contained 11.5% SPB and those that contained 5.8% SPB with MMT. For the 5.8% formulations without MMT, the 3% starch performed better than the 1.5% starch (approximately 10% better reduction in PHRR and AHRR), but neither performed as well as the six just discussed. However, the 5.8% formulation improved and became one of these six by incorporation of the MMT. Also, the flammability was no longer dependent on the % starch in the formulation. Adding MMT had no impact for the higher SPB concentration.

The Cone data indicated that SPB itself was sufficient to obtain high fire resistance but only with a high concentration formulation (e.g., 23%). At lower SPB formulations, a slightly lower flammability was achieved ($\sim 10\%$ lower PHRR and AHRR). MMT was needed if the SPB was below a critical threshold (e.g., 5.8%). We decided to conduct full-scale testing on the 1.5% starch–11.5% SPB formulation because we were only slightly compromising flammability in exchange for less raw materials and an easier formulation to coat (higher concentration formulations are more viscous).

Full-scale tests indicated the starch–SPB coating might be a better fire retardant technology than suggested by the Cone tests. The back, seat, and arms were all constructed of foam wrapped with a cover fabric. Using a thermoplastic cover fabric and standard PUF, the chair ignited easily and flames rapidly spread across the surface (Figure 6). Within 90 s after ignition, the entire chair was completely engulfed in flames. At 132 s, a PHRR value of 580 kW/m^2 was measured. Less than 2 min later, the test ends with the chair being completely consumed releasing a total heat (THR) of 121 MJ/m^2 . The chair was much less flammable by replacing the thermoplastic with a cotton covering fabric. The PHRR was significantly lowered and delayed (350 kW/m^2 at 369 s). The chair was still completely consumed but released a lower amount of total heat (107 MJ/m^2). This THR difference was due to the thermoplastic releasing more heat than the cotton fabric.

Replacing PUF with the 1.5% starch–11.5% SPB-coated foam slowed flame spread, reduced flammability, and caused the furniture to self-extinguish. For the thermoplastic covering fabric chair, at 90 s the PUF chair was completely engulfed in flames whereas the flames still had not spread across the seat of the starch–SPB foam chair (Figure 6). The 71% reduction in THR was due to the starch–SPB foam slowing down pyrolysis to the point that the fuel was insufficient to sustain combustion

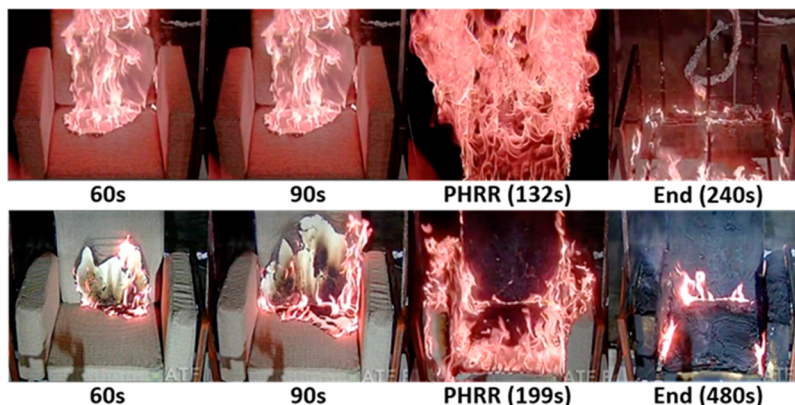


Figure 6. Images from full-scale furniture fire tests with a thermoplastic cover fabric and (top) PUF and (bottom) 1.5% starch and 11.5% SPB foam.

(Table 2). Since the thermoplastic cover fabric was completely consumed in both tests, this 71% reduction was directly related to the amount of foam remaining after the test (recall with PUF that the chair was completely consumed). The slower flame spread and lower amount of chair consumed was the reason why this starch–SPB foam resulted in a 75% and 61% reduction in PHRR and AHRR reduction, respectively (Table 2). For the cotton covering fabric chair, the starch–SPB foam had a similar flammability reduction as observed for the thermoplastic (Table 2). Normally, the type of covering fabric significantly influences the flammability of a piece of furniture. This was not that case for the starch–SPB-coated foam chairs, as the actual test values (except for tPHRR) were independent of the type of covering fabric. From a manufacturer point of view, this may be exciting as it offers the flexibility of changing the covering fabric without needing to make any other design changes to maintain a high level of fire safety.

The most exciting outcome from this study may be the actual PHRR values for the starch–SPB foam chairs. There are no validated approaches to accurately predict the severity of a real fire based on bench and full-scale fire tests of residential furniture. However, Ohlemiller et al. conducted such a study for residential beds of different fire sizes.³⁸ Their calculations were based primarily on the PHRR values from the burning of actual beds. Using the data from Ohlemiller's study and the PHRR values from our full-scale fire furniture fire tests, we approximated the decrease in the severity of a real fire caused by using the starch–SPB foam in furniture.

Ohlemiller et al. estimated for burning beds with PHRR values in the range of 400–700 kW/m² that the flames would cause a piece of furniture to immediately ignite a piece of furniture if it was located within 35 cm (1.1 ft) of the bed. Also, the intense heat generated from the burning bed would cause a piece of furniture to immediately ignite if located anywhere in the bedroom (4.6 m × 4.6 m (15 ft × 15 ft)), if there was any other ignition source present (e.g., match or burning paper). Their calculations showed that the ignition of this piece of furniture would be sufficient to cause rapid fire spread outside the bedroom. Therefore, to drastically increase life and property safety it was recommended not to put furniture in the bedroom or to use a bed with a lower PHRR. For example, the researchers calculated a piece of furniture would only ignite during the burning of a 150 kW/m² (PHRR) bed if the furniture was in intimate contact with the bed (direct flame impingement) or within a meter of the bed (another ignition source needed).

On the basis of the results from the Ohlemiller et al. study and the PHRR values from our full-scale furniture fire tests, we approximated the fire environment created by a piece of furniture burning that contains standard flexible foam and the starch–SPB foam. The PHRR values for the standard foam furniture tests (580 and 350 kW/m²) were similar to the first burning bed scenario discussed above. The PHRR values for the starch–SPB foam furniture tests (113 and 129 kW/m²) were similar to the last burning bed scenario discussed above. This suggested that in a 4.6 m × 4.6 m living/family room containing furniture with standard foam there was a high probability that multiple pieces of furniture would be involved in a fire. However, using the starch–SPB foam the fire would likely not extend beyond the burning furniture. This reduction in fire spread caused by replacing the standard foam with a starch–SPB foam should translate into a fire scenario where an occupant in the living room is at severe risk of death and the

fire rapidly spreads, putting occupants outside the room in danger (phenomenon called flashover) to a scenario where there is a significantly lower risk of injury and the slow growing fire is confined to the burning furniture.

3.3. Different Boron Sources and Type of Polysaccharide. The starch-based FR coatings had a few drawbacks we hoped could be mitigated by using a different type of boron and/or polysaccharide. The starch-based coatings tended to be flaky, added a large amount of mass, and produced stiffer foam when using MMT (Supporting Information). There was also a concern that the starch may be susceptible to deterioration in the presence of water. Starch and SPB also required elevating processing temperatures, which may be considered a drawback to using the technology.

In general, replacing the starch with agar and replacing SPB with sodium tetraborate (STB) or boric acid (BA) provided no performance or processing benefits (Figures 7–9). However,

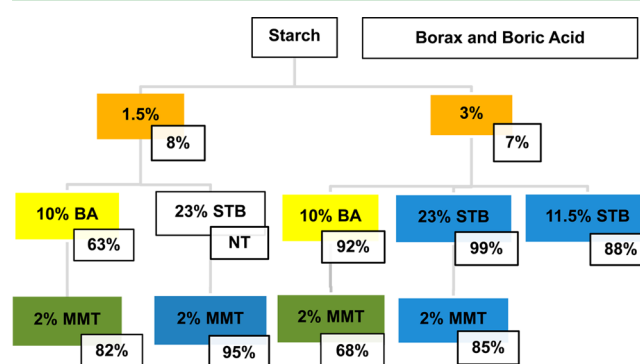


Figure 7. Impact of switching boron FR from SPB to STB and BA on coating mass and open flame fire screening.

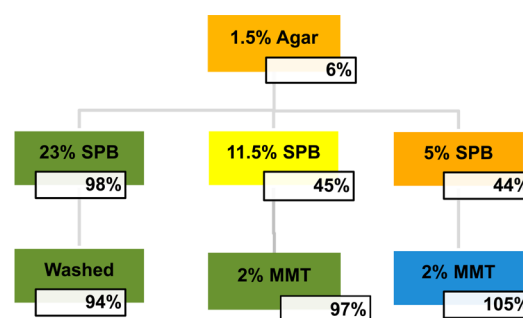


Figure 8. Impact of switching polysaccharide binder from starch to agar on coating mass and open flame fire screening.

there were exceptions such as adding MMT to the starch–BA coatings and to the agar–23% SPB coating produced ignition resistant foams. Due to limited solubility, the maximum BA content was restricted to 10%, which may be the reason BA without MMT did not produce ignition resistant foams.

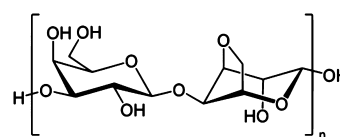


Figure 9. Agar binder is 70% agarose (shown here) and a 30% heterogeneous mixture of smaller molecules (e.g., galactose and substituted galactose).

Compared to the SPB coatings, the starch-based coatings with only STB or BA produced lower mass coatings. These coatings did not extinguish the flames, but unlike the SPB, they were not ignition resistant. This is likely due to a difference in boron crystal structure and not the amount of the FR coating because adding MMT to the formulation gave a similar coating mass to the SPB–MMT formulations but still did not produce an ignition resistant coating, except for the 10% BA with either starch formulation. Perhaps SPB and BA performed better because they are the acid forms of STB. Other studies have shown the acid form can be a better FR (e.g., phosphoric acid rather than phosphonate).

The 1.5% agar-based coatings with only SPB produced lower mass coatings, but when MMT was added to the formulations the coating mass was comparable to what was measured for the starch-based coatings. For the same SPB formulation, the starch performed better than agar in the flammability screening tests. None of these starch- or agar-based formulations with only a boron FR resulted in ignition resistant foam, but with starch the FR was able to self-extinguish faster than observed for agar. The fire resistant deficiencies that resulted from switching to agar were overcome by adding MMT. Both the 1.5% starch and 1.5% agar with 11.5% SPB- and MMT-coated foams were both ignition resistant.

Water durability was investigated for three of the best performing FR coatings: 1.5% starch–11.5% SPB–2% MMT, 1.5% agar–11.5% SPB–2% MMT, and 3% starch–23% SPB. The process for accessing water durability was similar to the process for fabricating the coatings. While submerged in DI water, the sample was aggressively squeezed and released (18–20 times) and then the sample remained soaking in the water for 5 min. The sample was removed and excess water squeezed out, and then the sample was dried in a convection oven overnight. The sample was removed from the oven and allowed to cool in a desiccator for a couple hours. The sample mass and flammability (ignition screening) was measured. Any change in mass and flammability after conducting this process was related to the coatings' water durability.

The agar sample had less than a 0.5% mass loss and was still ignition resistant. As expected, the starch-based coatings released in the water (Figure 8). The starch–SPB formulation dropped significantly from 110% to a 10% mass coating (Figure 1). This caused a drop in flammability from being ignition resistant to being completely consumed during combustion. The starch–SPB–MMT formulation was more resilient only dropping from 94% to 42% coating mass. Even though the formulation was no longer ignition resistant it did extinguish within 40 s and the inner core of the foam was still intact. The high coating retention we believe was attributed to both MMT and agar; therefore, future research will likely place a stronger emphasis on using these materials.

More than 60 SEM images and XEDS spectrum were taken of the formulations. SEM images and XEDS spectrum of a starch–SPB–MMT coating are provided in Figure 10. SEM images and XEDS spectrum of an agar–SPB–MMT, starch–STB–MMT, and starch–SPB coatings are provided as Supporting Information (Figures S2, S3, and S4).

All coatings completely encased the foam (Figures 10 and S2, S3, and S4, Supporting Information). There were no features in the SEM images that distinguished one coating from another. All coatings near the outside edge of the foam appeared rough with frequent, large, and flaky aggregates. Near the center of the foam, the coatings appeared significantly smoother with fewer

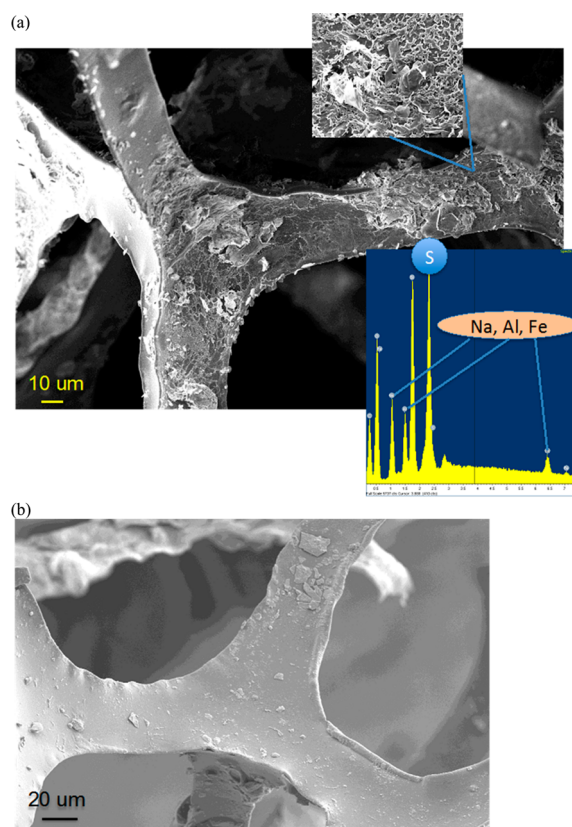


Figure 10. SEM image of 1.5% starch–11.5% SPB–2% MMT coating at the (a) edge and (b) center of the foam. Coating was thicker and has larger flakes and aggregates near the edge. XEDS insert in (a) shows the presence of S and Na, Al, and Fe in the coatings, which indicate the presence of SPB and MMT. Other peaks are associated with the coating and/or foam.

and smaller aggregates. Most of these near the center aggregates appeared to be embedded in the coatings, whereas these aggregates appeared more as flakes near the edge. Mass of foam samples (1 cm × 1 cm × 1 cm) taken from the edge was on average 20% heavier than from the center. This indicated that the coatings were thicker on the edge, which may explain the rougher and flaky features. We believe the coatings were thicker on the edge because the high viscosity of the depositing solution and the thickness of the coatings significantly slowed down transport into the center of the foam.

XEDS was used to determine the presence of MMT and SPB in the coatings. Detecting sodium (Na), magnesium (Mg), iron (Fe), aluminum (Al), and/or silicon (Si) indicated the presence of MMT. Detecting sulfur (S) indicated the presence of SPB. Since boron (B) cannot be resolved from carbon (C), boron could not be detected in any of the coatings. Therefore, there was no unique element that could be used to detect the presence of STB and boric acid.

XEDS analysis of a starch–SPB–MMT-coated PUF showed the coating contained SPB (S) and MMT (Na, Al, Fe). These elements were detected in all formulations containing SPB and MMT, which indicated these compounds were in the coatings. S was not detected in any of the BA and STB coatings (Figure S3, Supporting Information), which was further support that S was associated with SPB. Na, Al, and Fe was not detected in any of the coatings not containing MMT (Figure S4, Supporting Information).

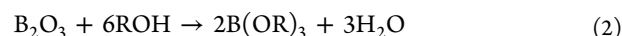
3.4. Fire Retardant Mechanism. Fire retardants reduce the flammability of polymeric materials by physical or chemical processes in the condensed phase or by chemical processes in the gas phase. Understanding where the fire retardant is impacting the combustion process helps understand the retarding mechanism and what types of materials can be used to further enhance the effectiveness of the fire retardant. This can be determined by considering the specific heat of combustion, $H_{c,eff}$. The $H_{c,eff}$ is the energy released as heat per unit area of a material when that material undergoes complete combustion. The value is calculated from the HRR and mass loss rate (MLR) values obtained from the Cone calorimeter test

$$H_{c,eff}(\text{MJ/kg}) = \text{HRR}(\text{kW/m}^2)/\text{MLR}(\text{kg/m}^2) \quad (1)$$

The $H_{c,eff}$ for the starch-based coatings suggests that all starch-based coatings reduced the flammability of PUF by a combination of condensed-phase and gas-phase processes (Table 1). If the $H_{c,eff}$ for these formulations was the same as that for PUF then the flammability reduction would be due to processes in the condensed phase only. For example, incorporating MMT into a polymer does not change the $H_{c,eff}$ because MMT only causes the formation of a protective layer (condensed phase).³⁹ For these formulations, the calculated $H_{c,eff}$ was 6–25% lower, indicating there was a partial gas-phase retardancy effect associated with the coatings.

The $H_{c,eff}$ reduction increased with increasing SPB concentration but plateaued at 11.5% SPB loading (Table 1). At low SPB loadings (5.8% SPB), the $H_{c,eff}$ reduction was greater with a higher starch loading. Adding MMT to these formulations caused a greater reduction in the $H_{c,eff}$. However, above the plateau value (11.5% SPB), adding MMT caused the $H_{c,eff}$ to increase. This suggested that there were formulation-dependent competing processes—in the condensed phase caused by the char-forming MMT and in the condensed and the gas phase caused by the boron fire retardant.

We believe the combination of starch and SPB resulted in fire retardancy by both condensed- and gas-phase processes. During combustion/pyrolysis, SPB formed boron–oxygen bonds with starch, which inhibited starch thermal oxidation and promoted the formation of a protective residue. Boron also reacted with the decomposition products of PUF, diol or isocyanate, to form a highly cross-linked borate-ester-based intumescent residue layer. Both of these reactions not only formed a protective residue (condensed process) but also formed water and/or carbon dioxide that diluted the fuel in the flame (gas phase). For example



where R is typically CH_2 .

At a lower SPB loadings, incorporation of MMT caused a greater reduction in the $H_{c,eff}$. This suggested incorporating MMT actually increased the effectiveness of the gas-phase process caused by the SPB. A possible explanation is MMT enabled the formation of a more effective char layer, which slowed down the release of fuel, but still allowed the release of water and/or carbon dioxide. Since there was less fuel, a lower amount of water and carbon dioxide was needed from the boron reactions to slow down the combustion process in the gas phase. At higher SPB loadings, the MMT caused a decrease

in the $H_{c,eff}$ reduction. This suggested that the protective layer restricted the release of the SPB.

3.5. Comparison with LbL Fire Resistant Coatings on PUF. To the best of our knowledge, Table 3 lists the most

Table 3. Comparison of Cone Data for These Bioinspired Starch-Based Coatings (bold) to the Previously Reported LbL Coatings on PUF^a

recipes	no. of monolayers	coating mass %	% reduction in Cone data	
			PHRR	AHRR
3.0% starch–23% SPB	1	155	75	81
3.0% starch–5.8% SPB–2% MMT	1	94	66	73
0.1% PAA–1.0% LDH–0.1% BPEI (LH2) ³⁷	5	10	41	79
0.1% PAA–0.1% BPEI–1% MMT ³⁵	9	4.8	33	78
0.5% (PAA + MMT) pH 2–0.5% PEI ⁴⁰	10	31	42	71
0.5% CHI–1% (DNA + MMT) ³⁶	20	16	51	81
0.5% CHI–2% PVS ⁴²	20	5.5	52	24
PAA–CHI–PPA–CHI ⁴¹	20	48	55	

^aUncertainty is $\pm 10\%$ of the reported values for starch-based formulations.

recent and best reported fire resistant coatings applied to PUF.^{36,37,40–42} These coatings were produced using LbL assembly and constructed from synthetic and natural polymer binders (poly(acrylic acid) (PAA), branched poly(ethylene imine) (BPEI), chitosan (CHI), poly(vinyl sulfonic acid) (PVS), deoxyribonucleic acid (DNA)) and char formers (layered double hydroxides (LDH), MMT). The LbL coatings ranged from 5 monolayers to 20 monolayers and resulted in a mass increase of 5–48% and a PHRR reduction of 33–55%.

All six of the LbL coatings were very effective at reducing the flammability of PUF. The best formulation may be the 0.1% PAA–1.0% LDH–0.1% BPEI because it produced the best balance between the speed of fabrication and the reduction of flammability.³⁷ This 5 monolayer coating only added 10% mass to the substrate and produced a 41% reduction in PHRR. Three other coatings produced a greater reduction in PHRR (~50%) but had other drawbacks (e.g., required significantly more monolayers or had a much lower AHRR). Each additional monolayer is one more depositing and washing step; therefore, these 20 monolayer coatings required 30 more steps in the fabrication process than the PAA–LDH–BPEI coating. A lower reduction of AHRR suggests the protective residue was less effective and durable.

The bioinspired coatings reported in this manuscript are a superior fire resistant technology for PUF. In a one-pot process, nearly all coatings produced ~63% reduction in PHRR and one coating (3% starch–23% SPB) produced as high as a 75% reduction in PHRR. This was approximately 20–30% greater PHRR reduction than previously reported for the best LbL coatings (Table 2). Additionally, because this was a one-pot process, the fabrication steps were reduced to only 1 step rather than the 10–30 steps used in the LbL coatings. A potential drawback was the higher coating mass for the these one-pot coatings (as high as 10 times), but because these coatings were still quite flexible we believe the additional mass gain will not limit the application of this technology.

3.5. Future Work. Commercialization of a new technology or using an existing technology in a new application may require extensive testing and characterization to ensure the technology complies with environmental, health, and safety requirements. Often this requires understanding how the technology deteriorates the routes of exposure and the toxicity of the deterioration products and the probability of the deterioration and exposure. Regulatory agencies (e.g., Environmental Protection Agency (EPA) and Consumer Product Safety Commission (CPSC) in the United States) could use this information as a basis for restricting or banning the use of a technology from certain applications. Any restriction/ban is typically limited to the scope of what is defined in these studies because the deterioration mechanisms, exposure, and toxicity may be strongly dependent on the end-use product. For example, from the early 1900s through the 1970s asbestos was ideal for a wide range of general and construction applications (e.g., flooring, textiles, and insulation). The EPA and CPSC have since banned asbestos because research has shown that it causes a very aggressive form of cancer (mesothelioma). However, asbestos is still used today in few products (e.g., roofing materials and corrugated sheeting) provided that the manufacturers and products comply with very strict regulations.

Boric and the salt derivatives are a component of our fire resistant coating we introduced in this manuscript. Boron is commonly found in the environment (e.g., fruits and nuts) and used in a variety of commercial products (e.g., cotton fabrics, contact lens, nutritional supplements, and drywall).⁴³ The EPA considers boric acid to be moderately acutely toxic due to acute effects including oral and dermal toxicity and eye and skin irritation. The EPA has classified boric acid as a "Group E" carcinogen, indicating that it shows "evidence of non-carcinogenicity" for humans.⁴⁴ The EPA and CPSC have not restricted the use of boric acid or salt derivatives, but they do indicate these materials should be handled and used with care.

Though there is evidence that some boron compounds can be hazardous, the risk of exposure at levels to cause an adverse affect can be quite low, which is the reason why these compounds are still used in a variety of commercial products. Additional research may be needed to determine if the boron compounds in these coatings poses any environmental, health, and safety risk. This should include determining (and quantifying) if boron compounds are released under conditions relevant to residential furniture, what is the nature of the released materials, and the probability of exposure to the released boron. This release and exposure information combined with previous toxicity data may provide the basis for a risk assessment of this coating technology for residential furniture. The risk assessment and toxicity are outside the scope of this manuscript and best conducted in collaboration with regulation agencies and its partners.

Additional research may be needed to improve the wash durability of these coatings. There was a significant decrease in coating mass when the starch-based coated foam was washed in water (e.g., 110% coating mass decreased to 10% for 3% starch–23% SPB). Switching from starch to agar appears to have improved the water wash durability of the coating as there was negligible mass loss after washing (98% coating mass decreased to 94% for 1.5% agar–23% SPB). Other approaches could include postprocess cross-linking or application of a hydrophobic layer.

4. CONCLUSIONS

Polysaccharide-based coatings applied in a one-step process significantly reduced the flammability of flexible polyurethane foam. The fire resistant coatings were constructed of a polymer binder (starch or agar), a boron fire retardant (SPB, STB, or BA), and/or a char former (MMT). The flammability (ignition resistance and HRR) was dependent on the coating composition. The best performing formulation was 3% starch–23% SPB, which produced a 75% reduction in the PHRR (as compared to PUF). Most of the starch-based formulations produced excellent but slightly lower reductions than this 3% starch–23% SPB (~63% reduction in PHRR). The effectiveness of this coating technology was validated in full-scale fire tests. Full-scale fire tests of furniture containing a 1.5% starch–11.5% SPB coating produced a 75% lower PHRR than when a standard flexible foam was used. The actual PHRR values were approximately 120 kW/m² for the starch–SPB foam chairs as compared to the 580 and 350 kW/m² for the standard PUF chairs. Estimates suggested that the furniture PHRR reduction caused by the starch–SPB coating could reduce the fire threat from potential death and rapid fire spread to low risk of injury and the fire being contained near the burning furniture.

Only the starch formulations with 23% SPB or 11.5% SPM–2% MMT were ignition resistant when tested without an external heat source. In all cases, adding MMT to the formulation caused a further reduction in flammability. In general, replacing the starch with agar and replacing SPB with STB or BA led to a reduction in the ignition resistance. However, there are exceptions such as adding MMT to a starch–BA coating, and the agar–23% SPB coating produced ignition resistant foams.

■ ASSOCIATED CONTENT

📄 Supporting Information

Tables and figures describing the DMA results of the coated foams; SEM images with XEDS spectrum of agar–SPB–MMT and starch–STB–MMT coatings. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Ahrens, M. National Fire Protection Report: Home Structure Fires; 2013, Available online at <http://www.nfpa.org/~media/Files/Research/NFPAREports/Occupancies/oshomes.pdf>.
- (2) Decher, G., *Polyelectrolyte Multilayers, An Overview. In Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials*, Decher, G., Schlenoff, J. B., Eds.; Wiley-VCH: Weinheim, Germany, 2003; Chapter 1.

- (3) Hammond, P. Form and Function in Multilayer Assembly: New Applications at the Nanoscale. *Adv. Mater.* **2004**, *16*, 1271–1293.
- (4) Laschewsky, A.; Bertrand, P.; Jonas, A.; Legras, R. Ultrathin Polymer Coatings by Complexation of Polyelectrolytes at Interfaces: Suitable Materials, Structure and Properties. *Macromol. Rapid Commun.* **2000**, *21*, 319–348.
- (5) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. Assembly of Multicomponent Protein Films by Means of Electrostatic Layer-by-Layer Adsorption. *J. Am. Chem. Soc.* **1995**, *117* (22), 6117–6123.
- (6) Sano, M.; Sato, M. Van der Waals Layer-by-Layer Construction of a Carbon Nanotube 2D Network. *Langmuir* **2005**, *21*, 11490–11494.
- (7) Podsiadlo, P.; Kaushik, A. K.; Shim, B. S.; Agarwal, A.; Tang, Z. Y.; Waas, A. M.; Arruda, E. M.; Kotov, N. A. Can Nature's Design be Improved Upon? High Strength, Transparent Nacre-Like Nanocomposites with Double Network of Sacrificial Cross Links. *J. Phys. Chem. B* **2008**, *112*, 14359–14363.
- (8) Zhang, H. Y.; Wang, Z. Q.; Zhang, Y. Q.; Zhang, X. Hydrogen-Bonding-Directed Layer-by-Layer Assembly of Poly(4-vinylpyridine) and Poly(4-vinylphenol): Effect of Solvent Composition on Multilayer Buildup. *Langmuir* **2004**, *20*, 9366–9370.
- (9) Bai, S. L.; Wang, Z. Q.; Zhang, X.; Wang, B. Hydrogen-Bonding-Directed Layer-by-Layer Films: Effect of Electrostatic Interaction on the Microporous Morphology Variation. *Langmuir* **2004**, *20*, 11828–11832.
- (10) Jang, W.-S.; Grunlan, J. C. Robotic Dipping System for Layer-by-Layer Assembly of Multifunctional Thin Films. *Rev. Sci. Instrum.* **2005**, *76*, 1–4.
- (11) Gamboa, D.; Priolo, M. A.; Ham, A.; Grunlan, J. C. Note: Influence of Rinsing and Drying Routines on Growth of Multilayer Thin Films using Automated Deposition System. *Rev. Sci. Instrum.* **2010**, *81*, 1–3.
- (12) Porcel, C. H.; Izquierdo, A.; Ball, V.; Decher, G.; Voegel, J. C.; Schaaf, P. Ultrathin Coatings and Poly(glutamic acid)/polyallylamine Films Deposited by Continuous and Simultaneous Spraying. *Langmuir* **2005**, *21*, 800–802.
- (13) Krogman, K. C.; Lowery, J. L.; Zacharia, N. S.; Rutledge, G. C.; Hammond, P. T. Spraying Asymmetry into Functional Membranes Layer-by-Layer. *Nat. Mater.* **2009**, *8*, 512–518.
- (14) Walton, M. D.; Kim, Y. S.; Jan, C. J.; McConnel, E. P.; Everett, W. N.; Grunlan, J. C. Deposition and Patterning of Conductive Carbon Black Thin Films. *Synth. Met.* **2007**, *157*, 632–639.
- (15) Everett, W. N.; Jan, C. J.; Sue, H. J.; Grunlan, J. C. Micropatterning and Impedance Characterization of an Electrically Percolating Layer-by-Layer Assembly. *Electroanalysis* **2007**, *19*, 964–972.
- (16) DeLongchamp, D. M.; Hammond, P. T. Highly Ion Conductive Poly(ethylene oxide)-based Solid Polymer Electrolytes from Hydrogen Bonding Layer-by-Layer Assembly. *Langmuir* **2004**, *20*, 5403–5411.
- (17) Hiller, J.; Mendelsohn, J. D.; Rubner, M. F. Reversibly Erasable Nanoporous Anti-Reflection Coatings from Polyelectrolyte Multilayers. *Nat. Mater.* **2002**, *1*, 59–63.
- (18) Wu, Z. Z.; Nolte, A. J.; Walish, J.; Zhai, L.; Rubner, M.; Cohen, R. Layer-by-Layer Assembled Nanoparticles on Flexible Substrates: Toward Deformable Anti-Reflection Coatings. *230th ACS National Meeting*, Washington, DC, Aug 2005; American Chemical Society: Washington, DC, 2005; pp U3688–U3688.
- (19) Priolo, M. A.; Gamboa, D.; Holder, K. M.; Grunlan, J. C. Super Gas Barrier of Transparent Polymer-Clay Multi layer Ultrathin Films. *Nano Lett.* **2010**, *10*, 4970–4974.
- (20) Yang, Y. H.; Haile, M.; Park, Y. T.; Malek, F. A.; Grunlan, J. C. Super Gas Barrier of All-Polymer Multilayer Thin Films. *Macromolecules* **2011**, *44*, 1450–1459.
- (21) Li, Y.-C.; Schulz, J.; Grunlan, J. C. Polyelectrolyte/Nanosilicate Thin-Film Assemblies: Influence of pH on Growth, Mechanical Behavior, and Flammability. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2338–2347.
- (22) Laufer, G.; Kirkland, C.; Morgan, A. B.; Grunlan, J. C. Intumescent Multilayer Nanocoating, Made with Renewable Poly-electrolytes, for Flame-Retardant Cotton. *Biomacromolecules* **2012**, *13*, 2843–2848.
- (23) Li, Y.-C.; Mannen, S.; Morgan, A. B.; Chang, S.; Yang, Y.-H.; Condon, B.; Grunlan, J. C. Intumescent All-Polymer Multilayer Nanocoating Capable of Extinguishing Flame on Fabric. *Adv. Mater.* **2011**, *23*, 3926–3931.
- (24) Carosio, F.; Laufer, G.; Alongi, J.; Camino, G.; Grunlan, J. C. Layer-by-Layer Assembly of Silica-based Flame Retardant Thin Film on PET Fabric. *Polym. Degrad. Stab.* **2011**, *96*, 745–750.
- (25) Carosio, F.; Alongi, J.; Malucelli, G. Layer by Layer Ammonium Polyphosphate-based Coatings for Flame Retardancy of Polyester-Cotton Blends. *Carbohydr. Polym.* **2012**, *88*, 1460–1469.
- (26) Carosio, F.; Di Blasio, A.; Alongi, J.; Malucelli, G. Green DNA-based Flame Retardant Coatings Assembled Through Layer by Layer. *Polymer* **2013**, *54*, 5148–5153.
- (27) Kim, Y. S.; Davis, R.; Cain, A. A.; Grunlan, J. C. Development of Layer-by-Layer Assembled Carbon Nanofiber-filled Coatings to Reduce Polyurethane Foam Flammability. *Polymer* **2011**, *52*, 2847–2855.
- (28) Alongi, J.; Carosio, F.; Malucelli, G. Current Emerging Techniques to Impart Flame Retardancy to Fabrics: An Overview. *Polym. Degrad. Stab.* **2014**, *106*, 138–149.
- (29) Cain, A. A.; Murray, S.; Holder, K. M.; Nolen, C. R.; Grunlan, J. C. Intumescent Nanocoating Extinguishes Flame on Fabric Using Aqueous Polyelectrolyte Complex Deposited in Single Step. *Macromol. Mater. Eng.* **2014**, *299*, 1180–1187.
- (30) Tsuyumoto, I.; Miura, Y.; Hori, Y. Fire-Resistant Nonwovens of EVOH and PET Treated with Amorphous Sodium Polyborate. *J. Mater. Sci.* **2010**, *45*, 2504–2509.
- (31) Tsuyumoto, I.; Miura, Y.; Nirei, M.; Ikurumi, S.; Kumagai, T. Highly Flame Retardant Coating Consisting of Starch and Amorphous Sodium Polyborate. *J. Mater. Sci.* **2011**, *46*, 5371–5377.
- (32) Tsuyumoto, I.; Onoda, Y.; Hashizume, F.; Kinpara, E. Flame-Retardant Rigid polyurethane Foams Prepared with Amorphous Aodium Polyborate. *J. Appl. Polym. Sci.* **2011**, *122*, 1707–1711.
- (33) Glenn, G. M.; Bingol, G.; Chiou, B.-S.; Klamczynski, A. P.; Pan, Z. Sodium Bentonite-based Coatings Containing Starch for Protecting Structures in Wildfire Emergency Situations. *Fire Saf. J.* **2012**, *51*, 85–92.
- (34) CBHFTI, California TB 133 Flammability Test Procedure for Seating Furniture for Use in Public Occupancies, 1991; available online at <http://www.bhfti.ca.gov/industry/tb133.pdf>.
- (35) Li, Y.-C.; Kim, Y. S.; Shields, J.; Davis, R. Controlling Polyurethane Foam Flammability and Mechanical Behaviour by Tailoring the Composition of Clay-based Multilayer Nanocoatings. *J. Mater. Chem. A* **2013**, *1*, 12987–12997.
- (36) Li, Y.-C.; Yang, Y.-H.; Kim, Y. S.; Shields, J. R.; Davis, R. D. DNA-based Nanocomposite Bio-Coatings for Fire Retarding Polyurethane Foam. *Green Mater.* **2014**, *2*, 144–152.
- (37) Li, Y.-C.; Yang, Y.-H.; Shields, J. R.; Davis, R. D. Layered Double Hydroxide-based Fire Resistant Coatings for Flexible Polyurethane Foam. *Polymer* **2015**, *1*, 284–292.
- (38) Ohlemiller, T. J.; Gann, R. G. Estimating Reduced Fire Risk Resulting From An Improved Mattress Flammability Standard. *NIST Technical Note 1446*; NIST: Gaithersburg, MD, 2002.
- (39) Kashiwagi, T.; Harris, R. H.; Zhang, X.; Briber, R. M.; Cipriano, B. H.; Raghavan, S. R.; Awad, W. H.; Shields, J. R. Flame Retardant Mechanism of Polyamide 6-clay Nanocomposites. *Polymer* **2004**, *45*, 881–891.
- (40) Kim, Y. S.; Li, Y.-C.; Pitts, W. M.; Werrel, M.; Davis, R. D. Rapid Growing Clay Coatings to Reduce the Fire Threat of Furniture. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2146–2153.
- (41) Carosio, F.; Di Blasio, A.; Cuttica, F.; Alongi, J.; Malucelli, G. Self-Assembled Hybrid Nanoarchitectures Deposited on Poly(urethane) Foams Capable of Chemically Adapting to Extreme Heat. *RSC Adv.* **2014**, *1*, 16674–16680.
- (42) Laufer, G.; Kirkland, C.; Morgan, A. B.; Grunlan, J. C. Exceptionally Flame Retardant Sulfur-Based Multilayer Nanocoating

for Polyurethane Prepared from Aqueous Polyelectrolyte Solutions.

ACS Macro Lett. **2013**, *2*, 361–365.

(43) <http://www.borax.com>, <http://www.natbat.com/docs/TestProven.pdf> (accessed Feb 2, 2015).

(44) <http://www.epa.gov/oppt/newchemicals/pubs/npchemicalcategories.pdf> (accessed Feb 2, 2015).