

Environmental Friendly Flame Resistant Coatings for Soft Furnishing

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Abstract— Pending flammability regulations and scrutinizing of the environment and health consequences of fire retardants is creating opportunities for novel and “greener” technologies to reduce the flammability of residential furniture. This presentation will discuss bio-based fire resistant coatings applied to flexible polyurethane foam and fire blocking barrier fabrics. The waterborne coatings were fabricated using Layer-by-Layer assembly and an innovative one-step/one-pot process and were constructed from common natural materials. The coatings caused significant reductions in the flammability (e.g., heat release, ignition propensity, and flame spread) of these substrates. When used in full-scale fire tests, the coated foam caused as high as a 75% reduction in peak, total, and average heat release of furniture.

Index Terms—One-pot, flame retardant coating, soft furnishing, sodium polyborate, sodium montmorillonite

I. INTRODUCTION

In the United States, there are more than 366,000 residential fires each year. Annually, these fires cause more than 2,500 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.

In 2009, Grunlan et al. (Texas A&M University) first used LbL to produce a fire retardant coating on fabric [2]. Since then Grunlan et al. has continued to be a pioneer in this area by advancing this technology through the research at Texas A&M University, and collaborating with groups at the National Institute of Standards and Technology (NIST) and Polytechnic University of Torino. Over the last several years, these three research groups have been the epicenter of LbL fabricated fire retardant coatings [3-13]. These research groups have developed FR coatings applied to flexible foam and fabrics, constructed of synthetic and bio-based polymer binders (e.g., polyacrylic 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 fabric [14]).

In 2011, Tsuyumoto et al. reported using starch and sodium polyborate (SPB) to form a fire resistant coating on poly(ethylene terephthalate) and polypropylene non-woven fabrics,[15,16] and rigid polyurethane foam [17]. They reported that 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% to 40% SPB. In 2012, Glenn et al, reported using starch and sodium bentonite (a layered silicate) to form fire resistant gel coatings for protecting structures against wild land fires [18]. The coatings were applied to exterior cement board lap siding. These coatings increased the time to reach 200 °C on the siding surface (a critical fire metric) by as much as 30 min.

In this study, a one-pot process and the chemical formulations to produce a bio-inspired highly fire resistant coating for flexible polyurethane foam (PUF) are investigated. The coatings were constructed of the polysaccharide binder (starch), sodium polyborate, and a protective residue former/enhancer (MMT). Full-scale chair fire tests were conducted to better understand the actual impact of this FR technology under realistic fire conditions.

II. EXPERIMENTAL SECTION

Materials Potato starch (Bob’s Red Mill™) were obtained from a local grocery store. Sodium polyborate was obtained from InCide® Technologies (SPB, Boron #10). Sodium montmorillonite clay was obtained from Southern Clay Products Inc. (MMT, Sodium Cloisite™). Standard (untreated) polyurethane foam (PUF) was obtained from FXI Inc. (Media, PA) and was stored in a climate controlled room with no direct sunlight exposure.

Coating Process and Characterization The coating solutions were prepared by first making the boron FR solution, then adding MMT, and lastly adding the starch. All depositing and washing solutions were water based and were prepared using water purified from a Nanopure II system (18.2 MΩ•cm, Sybron/Barnstead).

SPB (23%) aqueous solutions were prepared by adding SPB to DI water. The solution was heated (60 °C) and stirred until the SPB fully dissolved and the reaction to form SPB was complete (30 min). 2 mass % MMT powder was added to the SPB solution. The SPB-MMT solution was stirred for a couple hours. Then, 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, 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.

A Zeiss Ultra 60 Field Emission-Scanning Electron Microscope (FE-SEM, Carl Zeiss Inc., Thornwood, NY) was used to acquire surface specimens 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.

Flammability Testing Cone calorimetry was conducted according to a standard testing procedure (ASTM E-1354-07) with a dual Cone Calorimeter. The Cone was operated with an incident target flux of 35 kW/m² and an exhaust flow of 24 L/s.

The chairs 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. [19] All cushions were upholstered with 78% polyethylene/22% polyester or 100% cotton cover 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 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.

III. RESULTS AND DISCUSSION

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. Cone data and HRR curves for the starch-based coatings are provided in Figure 1.

All of the starch-based coatings reduced the Cone flammability (PHRR and AHRR) of PUF, but had no impact on the THR value (30 ± 3 MJ/m²). This indicates the coated 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.

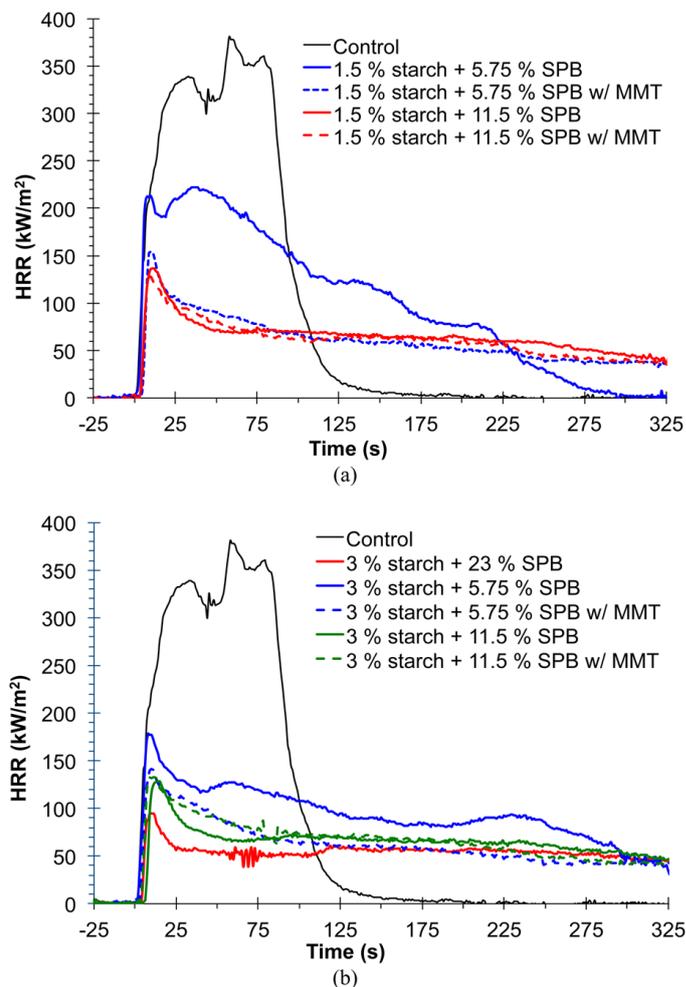


Figure 1. Cone calorimeter heat release rate curves for (a) 1.5% and (b) 3.0% starch-based FR coatings on foam. Uncertainty is ±10% of the reported reduction values. External heat flux was 35 kW/m².

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 (~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% SBP 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).

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 assess the fire resistance of the coatings, whereas, the full-scale data was used to quantitatively assess the decrease in flammability of furniture built using the fire resistant coated PUF. Full-scale furniture calorimeter data is provided in Figure 2. Time captured images of the full-scale tests are provided in Figure 3.

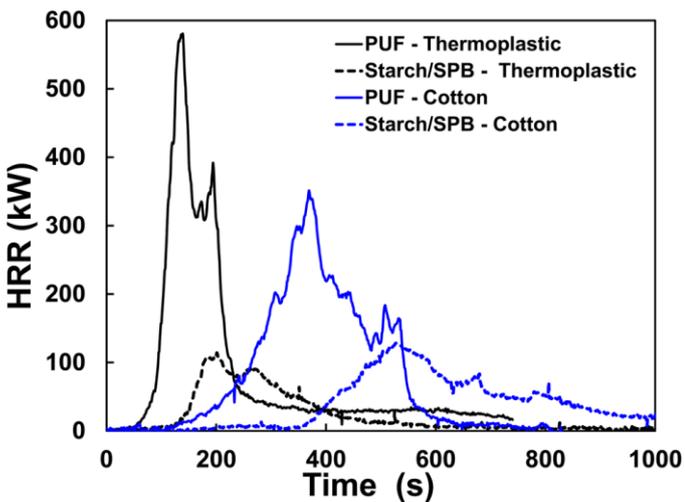


Figure 2. Full-scale fire heat release curves of thermoplastic cover fabric furniture and cotton cover fabric furniture with PUF and 1.5% starch and 11.5% SPB foam. Uncertainty is $\pm 10\%$ of the measured values. External heat flux was 35 kW/m^2 .

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. 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. 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. 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. For the cotton covering fabric chair, the starch-SPB foam had a similar flammability reduction as observed for the thermoplastic. 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.

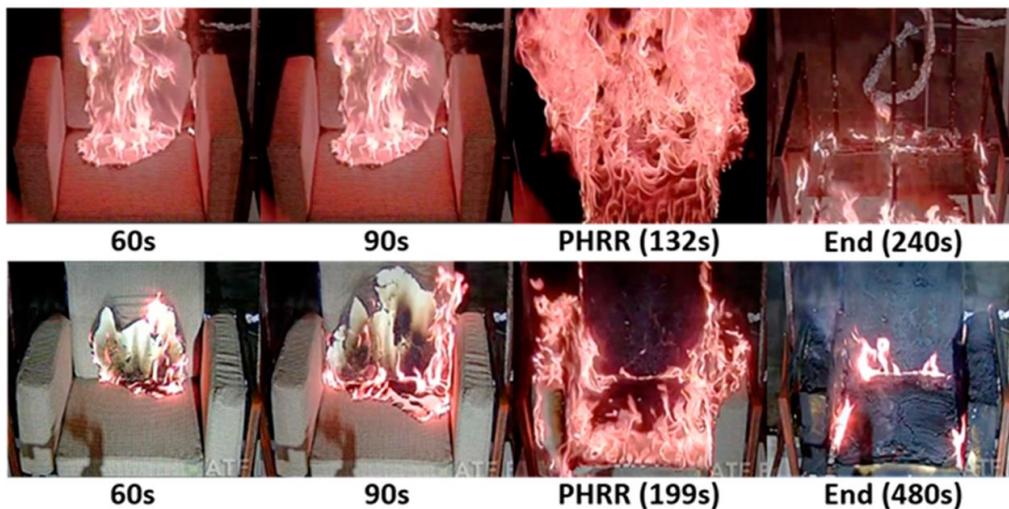


Figure 3. Images from full-scale furniture fire tests with a thermoplastic cover fabric and (top) PUF and (bottom) 1.5% starch and 11.5% SPB foam.

SEM images and XEDS spectrum of a starch-SPB-MMT coating are provided in Figure 4. All the coatings completely

encased the foam. There were no features in the SEM images that distinguished one coating from another. All the 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 and smaller aggregates. Most of these near the center aggregates appeared to be embedded in the coatings where as these aggregates appeared more as flakes near the edge. Mass of foam samples (1 cm by 1 cm by 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.

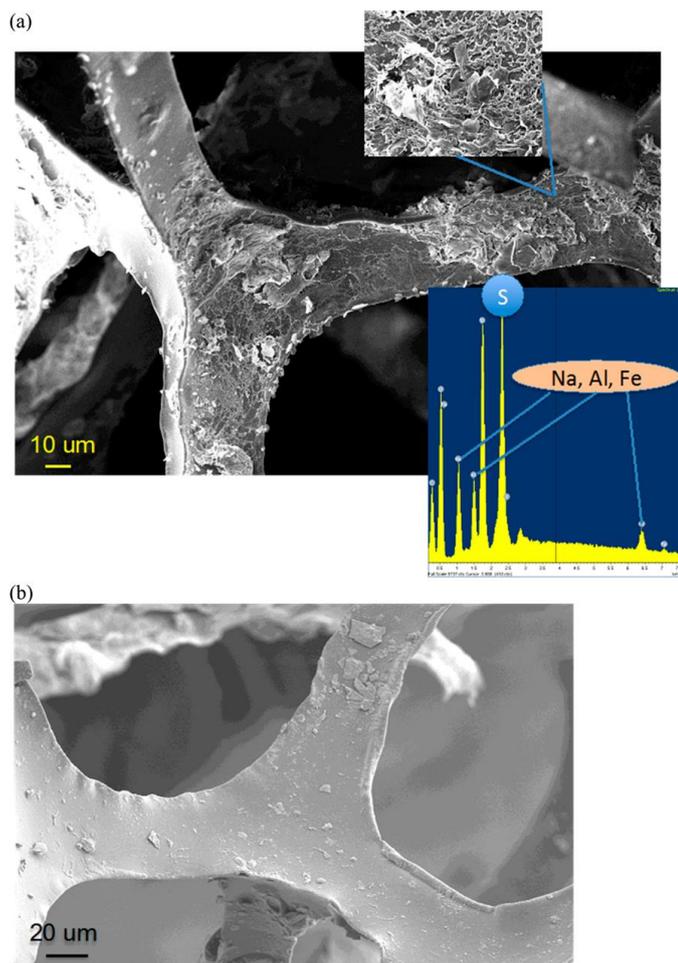


Figure 4. SEM image of 1.5% starch–11.5% SPB–2% MMT coating at the (a) edge and (b) center of the foam. Coating was thicker and has larger flakes and aggregates near the edge. XEDS insert in a shows the presence of S and Na, Al, and Fe in the coatings, which indicate the presence of SPB and MMT. Other peaks are associated with the coating and/or foam.

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.

IV. CONCLUSION

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 starch, sodium polyborate, and/or a MMT. The best performing formulation was a 3% starch-23% SPB, which produced a 75% reduction in the PHRR (as compared to PUF). 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 kW/m² 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. To the best of our knowledge, these coatings produced the largest flammability reduction of furniture reported for any fire retarding technology on/in flexible PUF.

Future work has already begun to investigate one-pot fire resistant coatings constructed from other binders, FR, and char forming compounds.

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