

Rapid Growing Clay Coatings to Reduce the Fire Threat of Furniture

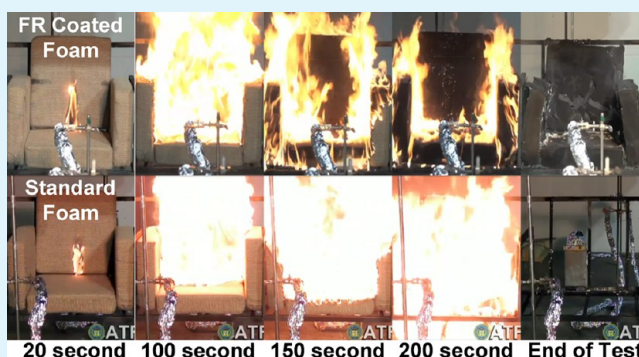
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S Supporting Information

ABSTRACT: Layer-by-layer (LbL) assembly coatings reduce the flammability of textiles and polyurethane foam but require extensive repetitive processing steps to produce the desired coating thickness and nanoparticle fire retardant content that translates into a fire retardant coating. Reported here is a new hybrid bi-layer (BL) approach to fabricate fire retardant coatings on polyurethane foam. Utilizing hydrogen bonding and electrostatic attraction along with the pH adjustment, a fast growing coating with significant fire retardant clay content was achieved. This hybrid BL coating exhibits significant fire performance improvement in both bench scale and real scale tests. Cone calorimetry bench scale tests show a 42% and 71% reduction in peak and average heat release rates, respectively.

Real scale furniture mockups constructed using the hybrid LbL coating reduced the peak and average heat release rates by 53% and 63%, respectively. This is the first time that the fire safety in a real scale test has been reported for any LbL technology. This hybrid LbL coating is the fastest approach to develop an effective fire retardant coating for polyurethane foam.

KEYWORDS: layer-by-layer assembly, polyurethane foam, sodium montmorillonite, flame retardant, real scale mockup



1. INTRODUCTION

In recent years, layer-by-layer (LbL) assembly has been the focus of significant research interest and studied for various applications including oxygen barrier,^{1,2} drug delivery,^{3–5} electrochemical film,^{6,7} and sensing application.^{8,9} These multilayered structures are constructed by repeated alternating absorption of oppositely charged polyelectrolytes and/or nanoparticles onto a substrate. Recently, researchers have investigated using LbL to fabricate fire retardant (FR) coatings on textiles,^{10–13} plastic plaques,^{14,15} and flexible polyurethane foam (PUF).^{16–18} Various nanoparticles have been used to enhance the fire performance of LbL coatings including carbon nanotube,¹⁹ carbon nanofiber,¹⁷ polyhedral oligomeric silsesquioxanes (POSS),²⁰ silica,²¹ and α -zirconium phosphate.¹³ Clay, more specifically sodium montmorillonite, is one of the most effective and common nano-FR additives used for LbL coatings.^{10,18,22} For FR application, it is desirable for the clay coating to grow exponentially with minimum number of layers. This has been achieved using rather complicated, multi-step quad-²³ or tri-layer (TL) methods.¹⁸ Here, we report a very effective FR coating fabricated using a novel and simple bi-layer (BL) method that yields fast growth and high clay content. This paper also includes the first time evaluation of this technology in a full scale fire test.

Over the past decade in the U.S., there was approximately 17 300 mattress and upholstered furniture fires per year, which annually accounted for approximately 871 civilian deaths, 2230

civilian injuries, and \$824 million in property losses.^{24,25} Traditionally, the FR chemicals used in these soft furnishings (e.g., halogenated) are ineffective in reducing the flammability of PUF, except at high loadings. In addition to ineffectiveness, many of these conventional FRs may have human health and environment concerns.^{26,27} LbL coatings are constructed of environmentally friendlier materials and have been shown to reduce foam flammability by creating a fire protective armor on the PUF surface. One of the keys to being commercially viable is to be able to generate an effective FR coating in the least number of steps.^{17,18,28,29}

A tri-layer approach has been shown to enable fast growth of polymer and nanoparticle coatings.^{18,28,29} For a clay-based coating, the underlying mechanism of the TL method is the combination of electrostatic attraction between polyethyleneimine (PEI) and polyacrylic acid (PAA) and hydrogen bonding between the montmorillonite clay (MMT) and PAA. Compared to a BL approach, a drawback of the TL is a 50% increase in fabrication steps due to the additional monolayer deposition, but this is offset by the fact that there was no other approach that was faster growing and with a >30 mass % content of the FR clay. This TL coating yielded the significant reduction of PUF flammability. Our goal was to achieve similar

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coating characteristics with the same or better impact on flammability as we measured for the TL with a fewer number of layers. We chose to take a hybrid BL approach where the MMT was mixed into a polyelectrolyte solution prior to the deposition process. This hybrid BL eliminates a monolayer per deposition cycle since the MMT is deposited along with polyelectrolyte. Additionally, the hybrid BL coating growth can be controlled by adjusting the pH, which cannot be done easily for the TL coating. This provides the hybrid BL approach with another level of tailorability and flexibility not possible with the TL. The resultant hybrid BL coating was comparable to what we reported for the TL, but because we eliminated a step in the deposition cycle, the coating was achieved faster than that with the TL approach. Similar to the original BL approach, the polymer and MMT components are held together by a combination of electrostatic attraction and hydrogen bonding. Provided are the details of fabrication and characterization of the hybrid BL coating on PUF and fire performance of coating foam in both the bench and full scale tests.

2. EXPERIMENTAL SECTION

2.1. Materials. Unless indicated, all materials were used as received. Polyethyleneimine (branched, $M_w = 25\,000$ g/mol) and poly (acrylic acid) ($M_w = 100\,000$ g/mol) were purchased from Sigma-Aldrich (Milwaukee, WI). 1 M HCl (Sigma-Aldrich) was used to control the pH of the PAA/MMT mixture. Sodium montmorillonite (Cloisite Na+) was obtained from Southern Clay Products Inc. (Gonzales, TX). Polyurethane foam was manufactured by FXI Inc. (Media, PA). Polyurethane foams used in this study were manufactured without any additives to eliminate the unknown effect of these additives. Prior to the coating, the foam was stored in desiccator for two days, and the foam mass was measured immediately before coating. (Note: Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose. The policy of NIST is to use metric units of measurement in all its publications and to provide statements of uncertainty for all original measurements. In this document, however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements.)

2.2. LbL Deposition and Characterization. $10.2 \times 10.2 \times 5.1$ cm³ foams were used for the cone calorimeter test, and two $47.0 \times 47.0 \times 10.2$ cm³ and two $47.0 \times 36.8 \times 10.2$ cm³ foams were used to assemble the real scale mockup furniture test. 0.5 mass % PEI and PAA solutions were prepared with deionized water and used as deposition solutions. 0.5 mass % MMT was added to one side or both solutions depending on the coating recipe. For the real scale test, 0.1 mass % PAA with 0.2 mass % MMT solution and 0.1 mass % PEI solution were used as anionic and cationic solution, respectively. All solutions were rolled overnight to reach and maintain a well-dispersed solution. Prior to coating, foams were pre-soaked in 0.1 M nitric acid solution for 5 min to protonate the PUF surface to increase the positive charge of surface. After acid treatment, the LbL coatings were fabricated by alternatively submerging PUF into a PAA and PEI solution. The dipping time is 5 min for the first BL and 1 min for each subsequent BL. PUF was washed 3 times with DI water and hand-squeezed after each deposition. The coated foams were dried at 70 °C overnight to remove excess water.

2.3. Coating Characterization. Mass change due to coating was measured by laboratory microbalance, and the mass of clay was measured using a TG 449 F1 Jupiter thermogravimetric analyzer (TGA, Netzsch, Burlington, MA) with 20 °C/min heating rate up to 850 °C under air. A Zeiss Ultra 60 Field Emission-Scanning Electron Microscope (FE-SEM, Carl Zeiss Inc., Thornwood, NY) at 5 kV

operating voltage was used to acquire surface and cross section images of the coatings on the PUF surface. All SEM samples were sputter coated with 5 nm of Au/PD (60 mass fraction %/40 mass fraction %) prior to SEM imaging.

2.4. Fire Performance Measurement. Cone calorimetry was conducted according to the standard testing procedure (ASTM E-1354-07) with a dual cone calorimeter, operating with an incident target flux of 35 kW/m² and an exhaust flow of 24 L/s. A cone size sample was placed in a pan constructed from heavy gauge aluminum foil. The sides and bottom of the sample were covered by the aluminum foil so only the top surface was exposed to the cone heater. The standard uncertainty is $\pm 5\%$ in HRR and ± 2 s in time. The real scale chair mockup was constructed with four cushions (two small ones for the arms and two large ones, as described in Materials section, for the seat and back cushions) accordance with California Technical Bulletin 133.³⁰ All cushions were upholstered with 78% polyethylene/22% polyester fabric. The cushions were assembled on the steel test stand. 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 a propane gas, to 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 Explosive Fire Research Laboratory (ATF FRL) located in Beltsville, MD.

3. RESULTS AND DISCUSSION

3.1. Coating Growth and Clay Content. Three different formulations were tested in this study: MMT in PAA, MMT in PEI, or MMT in both PEI and PAA solutions. Table 1

Table 1. Physical Characteristics of MMT-Based SBL Coatings on PUF^a

sample ID	formulation	coating mass %	clay mass % relative to PUF	clay mass % in coating
PMP2	(PAA+MMT pH = 2)/PEI	30.9	10.6	34.3
PMP	(PAA+MMT)/PEI	19.1	4.38	22.9
PPM	PAA/(PEI+MMT)	8.13	2.67	32.8
PMPM	(PAA+MMT)/(PEI+MMT)	7.44	2.18	29.3

^aThe uncertainty is $\pm 5\%$ of the measured value.

summarizes the sample characteristics. Mass changes in PUF due to coating were measured using analytical microbalance, and the MMT mass with respect to the PUF was measured using a thermogravimetric analyzer (TGA), which is shown in Figure 1. On the basis of these results, MMT concentration within the coating was calculated.

Formulations with MMT mixed into the PEI solution resulted in slow growing coatings with low MMT content. Only a 10 % mass gain was measured for SBL coatings with MMT in the PEI solution (PAA/(PEI+MMT), called PPM) and with MMT in both polymer solutions ((PAA+MMT)/(PEI+MMT), called PMPM). The MMT content (Figure 1 and Table 1) was low and similar for both formulations, which is comparable to what was previously reported for the low polymer and MMT formulation 5TL coating on PUF.²⁸ The reason for the low values is that PEI is an effective flocculating agent for MMT. Flocculation would cause the platelets to aggregate,³¹ thus hindering the MMT deposition and consuming the PEI molecules, both of which would lead to a low coating mass and MMT concentration in the coating. On

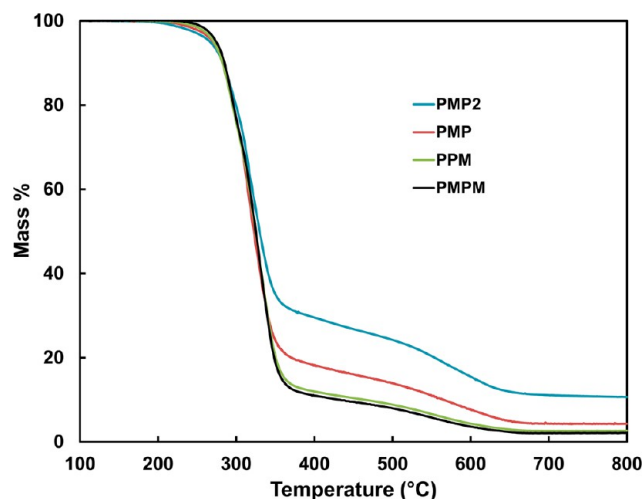


Figure 1. Mass loss as a function of temperature for MMT-based SBL coated foams. All systems show identical thermal behavior suggesting that they have the same chemical composition and there is no chemical reaction between coatings and substrate.

the basis of our past experiences, we knew these values were below a minimum threshold for significantly reducing the PUF flammability, which is 10 or more mass % of FR coatings.²⁸

Formulations with MMT only in the PAA solution had a significant increase in coating growth and MMT content (Figure 1 and Table 1). Compared to the PEI+MMT formulations, the coating mass and MMT content was approximately two times greater with the SBL (PAA+MMT)/PEI (PMP) formulation. Though PAA and MMT have the same weak electrostatic charge, presumably the hydrogen bonding between the MMT hydroxyl groups and PAA carbonyl

groups overcomes this repulsive force enabling these chemicals to form a stable depositing suspension with a high MMT retention in the coating.^{18,28,32} PEI molecules do not directly interact with MMT in one solution so they do not flocculate the MMT platelets, unlike PPM and PMPM systems; therefore, more of the PEI and PAA polyelectrolytes were able to inter-diffuse between the layers causing a higher coating mass.¹ Another advantage of the hybrid BL approach is the ability to control the deposition rate by adjusting pH of the dipping solution. When the pH value of the PAA+MMT solution was lowered from 3.6 (PMP) to 2 (PMP2), the coating growth and MMT content increased further. The PMP2 coating mass and MMT content (30.9 mass % and 10.6 mass %, respectively) was much higher than what was measured for PMP. Decreasing the pH of PAA+MMT solution not only enhances the hydrogen bonding between PAA and MMT³² but also promotes the polyelectrolyte inter-diffusion¹ and increases coating mass and MMT concentration. The two best fire retarding TL systems previously reported took seven TLs (21 monolayers) to achieve a similar coating mass and MMT content.²⁸ The SBL PMP2 coating achieved these same coating characteristics using 50% less layers than the 7TL coating, which translates into faster fabrication, using less material, and generating less water waste (factors critical for commercialization).

SEM images show the effect of pH on the SBL coating topography. At a pH of 3.6, all the PUF surfaces are covered with a fairly rough appearing LbL coating (Figure 2a). There are some aggregates of MMT near the surface, but they appear to be completely embedded in the polymeric coating layers (Figure 2b). Decreasing the pH of the solution to 2 significantly changes the coating characteristics. There are a few regions that appear similar to the pH 3.6 coating, but a majority of the coating is significantly rougher due to micrometer sized MMT

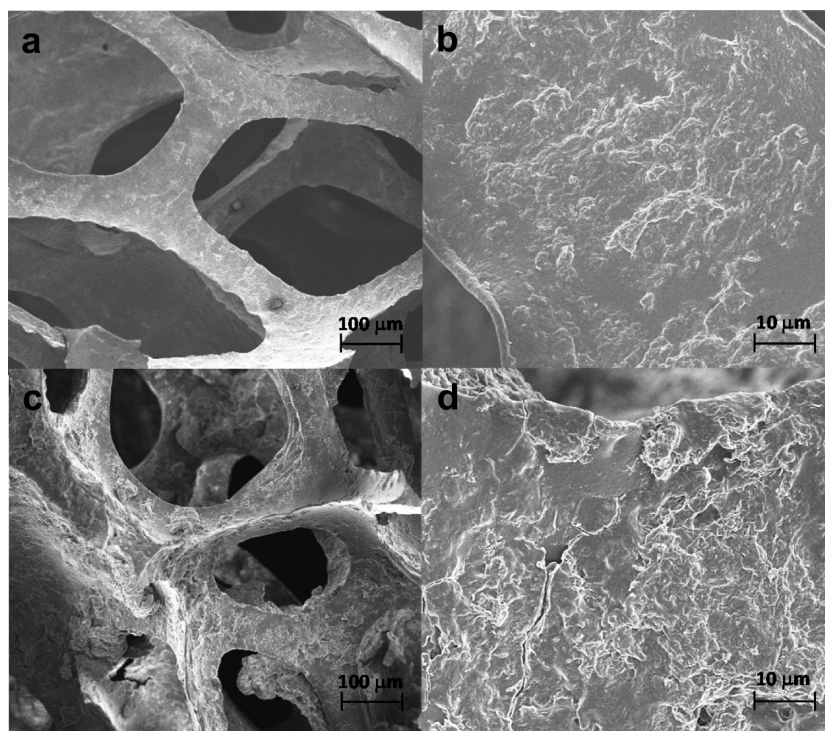


Figure 2. SEM image of PMP at 200 \times (a) and 2000 \times (b) and PMP2 at 200 \times (c) and 2000 \times (d). The surface of PMP is smooth, and all MMT is covered by polyelectrolyte. PMP2 has an excessive amount of MMT in the coating leading to a rough surface with tens of micrometers in size of MMT aggregate.

aggregates, and several surface fissures in regions where the coating is quite thick (Figure 2c,d). PMP2 shows a rougher surface than the PMP system due to relatively higher MMT concentration. These observations are aligned with the TGA values, which indicate the coating and MMT mass is approximately 10% higher with the lower pH.

3.2. Bench Scale Flammability Measurement. Impact of the coatings on the PUF flammability was accessed by a cone calorimeter using an ASTM E-1474 (Table 2 and Figure 3).

Table 2. Cone Calorimetry Result of MMT-Based SBL Coated PUF and Uncoated PUF^a

ID	PHHR (kW/m ²)	t _{PHHR} (s)	aHRR (kW/m ²)	burn time (s)	residual mass %
control	451	86	275	201	
PMP2	261	11	79.2	619	11.9
PMP	328	12	87.4	605	7.61
PPM	338	17	164	305	6.49

^aThe uncertainty is $\pm 5\%$ of the measured value.

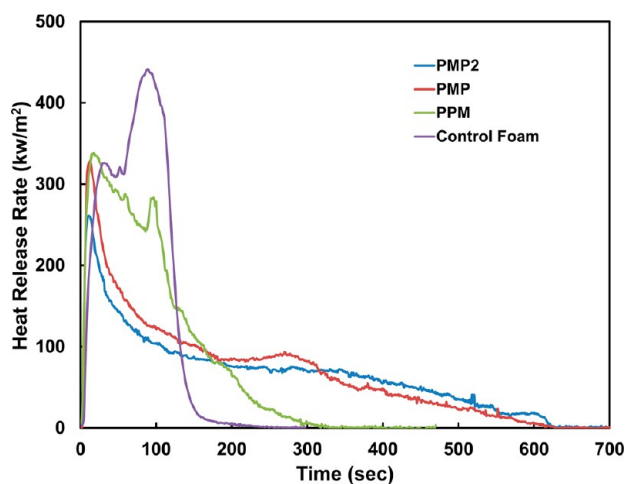


Figure 3. Cone calorimeter heat release rate as a function of time for MMT-based SBL coated and untreated PUF. All systems demonstrate the excellent flame retardancy. Coatings with higher coating mass and MMT loading exhibit superior fire performance.

The cone is a standard bench scale tool for measuring material flammability. Since the test is conducted in the presence of an external heat flux, the results are often used to predict full-scale flammability characteristics. Since PMP and PPM results were identical, only the PPM results are reported here.

The control (uncoated PUF) exhibited typical polyurethane foam burning behavior consisting of two peaks associated with combustion of the isocyanate (1st peak) and the polyol (2nd peak).³³ All three coatings (PPM, PMP, and PMP2) significantly reduced the two most frequent parameters reported from cone, which are the maximum amount of heat generated by the sample (peak heat release rate, PHHR), which represents the maximum fire threat in a real fire scenario, and the effectiveness/durability of the protective residue (average heat release rate, aHRR), which represents the average fire threat and is related to the probability to spread fire in a real fire scenario. The flammability reduction is directly aligned with the coating and MMT mass; the higher the mass, the greater is the reduction in PHHR and aHRR. MMT in the PEI solution (PPM) had the least impact among the three coatings causing a

25% and 40% reduction in the PHHR and aHRR, respectively. This is because the masses are below the critical values necessary to significantly impact PUF flammability.²⁸ MMT in the PAA solutions (PMP and PMP2) had a more dramatic flammability reduction (average of 35% and 70% for PHHR and aHRR, respectively). The lower pH value had no statistical impact on the aHRR but did produce the lowest PHHR value of this study (42% reduction). All the coated PUF curves exhibited classical intumescent fire protection characteristics with a very rapid HRR decrease of the first peak (indicating the formation of the protective residue). However, only the PAA + MMT curves exhibited sustained very low HRR after the first peak, which indicates the residues will provide long term and durable fire protection.

The reduction in PHRR and aHRR values caused by the PMP and PMP2 coatings is the best reported to date for this number of monolayers, 10. There are a few reports of similar reductions, of which, the 7TL system required the lowest number of coating layers (21). Compared to PMP and PMP2, this TL required two times more monolayers and the preparation of three depositing solutions.^{16,28,34} The key to the success of this BL system is PAA's ability to facilitate the formation of a stable and well-dispersed MMT depositing solution and high MMT retention in the coating. What this has also allowed is for PAA and PEI to diffuse across the monolayers with each layer deposited. LbL coatings constructed of PAA and PEI grow exponentially because of the diffusion of the polymer chains into each of the monolayers.¹ In the TL system, the MMT monolayers create a barrier that limits this polymer diffusion when the subsequent PAA layer is deposited. Since MMT is in the PAA monolayer, this barrier does not exist and PAA molecules have a better chance of diffusion into the existing layers. Therefore, these PMP and PMP2 BL systems grow much faster than the TL system. The result is the fast growth with the high MMT content, which is the reason for the greatest flammability reduction with the least number of monolayers.

3.3. Real Scale Mockup Test. Full-scale soft furnishings, such as residential upholstered furniture, are significantly more complex with the geometry, covering fabric, filling materials, threading, etc., playing a critical role in the real fire threat of this consumer product. While the cone is an excellent tool for screening the relative impact of the FR technology, ultimately the assessment in full-scale is necessary to understand its true potential.^{30,35,36}

This is the first ever report of a full-scale flammability assessment of the LbL technology. A 2.5 BL PMP coating on PUF (0.1 mass % PAA + 0.2 mass % clay)/(0.1 mass % PEI) was applied for full scale testing because we felt that it would have the best fire performance with the best fabrication conditions using a current manufacturing processes.²⁸ The large PUF cushions were not coated with the SBL PMP or PMP2 because the resultant specimen was too heavy and rigid to be suitable for soft furnishings. We also chose not to alter the solution pH because it may also increase the substrate mass and rigidity and may be cost prohibitive in a commercial manufacturing process. The pH of the PAA+MMT solution was measured as 3.8.

HRR values from a full-scale test show that the 2.5 BL coating reduced the PHRR from 580 to 274 kW (Figure 4) and the aHRR from 300 to 110 kW. These full-scale reductions (53% for PHRR and 63% for the aHRR) are not expected to be identical to what was measured in the cone calorimetry because

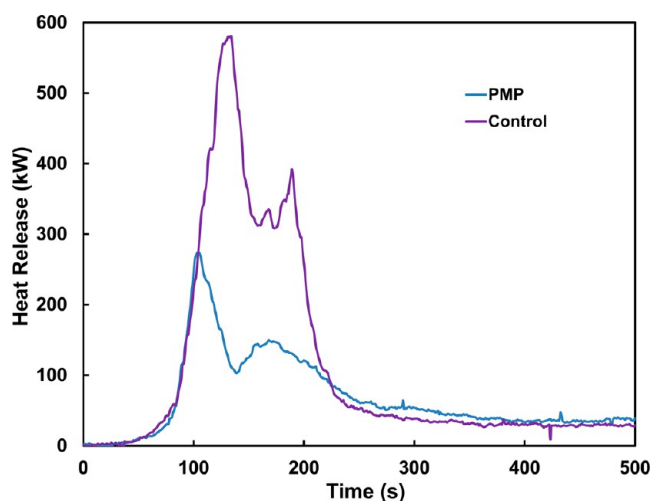


Figure 4. Heat release rate as a function of time for real scale testing of 2.5 BL PMP and untreated PUF encased in a covering fabric. Flammability reduction for coated specimen is significantly higher than the predicted value from the bench scale test since the bench scale test is not able to represent all the parameters in a real fire such as the RUF geometry, cover fabric, and pool fire.

the full-scale specimen included factors that increase flammability, such as a covering fabric and multiple PUF specimens in a chair configuration.

Images captured from videos taken during experiments clearly show the effectiveness of LbL coating (Figure 5). In the first 100 s after ignition, the flames spread slightly faster over the PMP mock-up; however, this is not a concern because the HRR values are the same as the control mock-up (Figure 4) and do not exceed what we believe to be critical HRR values for this product.³⁷ The residue layer forming on the surface of the PMP PUF is beginning to act as a fire barrier and protect the underlying foam that is not involved in pyrolysis or combustion. At 150 s, the control mock-up has reached its peak of HRR (600 kW), while the PMP protective layer has already taken effect and reduced the HRR to six times less than the control (100 kW). At 200 s for the PMP mock-up, the flames on the front and back of the top cushion have extinguished (there is still undisturbed foam within the black residue carcass), while the arms and crevices continue to burn.

The control mockup is now completely engulfed in the fire and has collapsed into a pool of flaming pyrolysis products on the floor.^{17,18,29} The HRR is still four times higher for the control. By the end of the test, the protective residue and PUF are still present in the PMP mock-up, whereas the mock-up was completely consumed when the control PUF was used.

Pictures of the PMP coated mockup residue give a better understanding of the role of the LbL coating against the open flame (Figure 6). Visually, the cushions had a few surface cracks and, in some cases, the edges were slightly warped; overall, the cushions maintained their original shape and integrity. The side and bottom cushions (Figure 6c,d) were broken by hand to observe the inside of the cushions. Unlike the small sample burning or bench scale test (cone calorimetry test), where a remarkable portion of coated PUF often remains intact and maintains the original color and texture of PUF, the flame reaches the inside of the sample and most of PUF is completely burnt. In bench scale tests, the bottom and the side of the sample are covered by aluminum foil so it protects the bottom part of the PUF from the flame as long as the LbL coating prevents the melting of PUF. In contrast, all surfaces of the real scale mockup are open to air and the flame can easily spread to the bottom and the side of the sample. The mass of the residue is measured as 13.63 ± 0.02 % of the initial mass, which corresponds to the LbL coating and char from PUF. The LbL coatings on PUF are a condensed-phase FR, which hinders the release of combustible gas generated from pyrolysis of PUF. Even though the flame magnitude and spread rate are low, the flame continues to spread until it completely covers all of the surface of the PUF. If LbL coatings could incorporate gas-phase active FR, there is a potential for a synergistic effect that could further reduce the substrate flammability.

4. CONCLUSION

MMT-based LbL coatings were successfully deposited on the complicated surface of PUF using a hybrid BL approach, which significantly increased the coating growth rate and MMT content. Coating mass growth rate and MMT mass content was ranked as follows: MMT in PAA at pH of 2 > MMT in PAA at pH of 3.6 \gg MMT in PEI \sim MMT in PEI and PAA. The impact of the coating to reduce PUF was directly aligned with the mass content (the higher the coating and MMT mass, the greater is the reduction). The best formulation, MMT in PAA

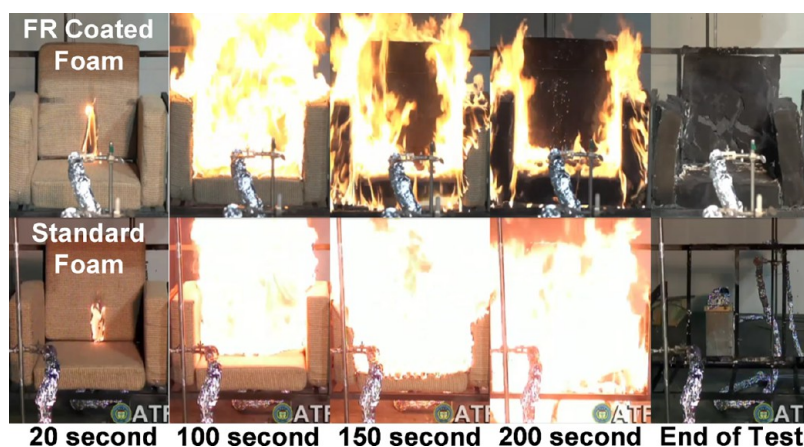


Figure 5. Images captured from the real scale fire test (captured from video records). The test is completed by approximately 250 s for the control PUF, which is completely consumed at the end of the test. The FR coated sample test lasts for 400 s, and it is still partially intact and maintains its shape.

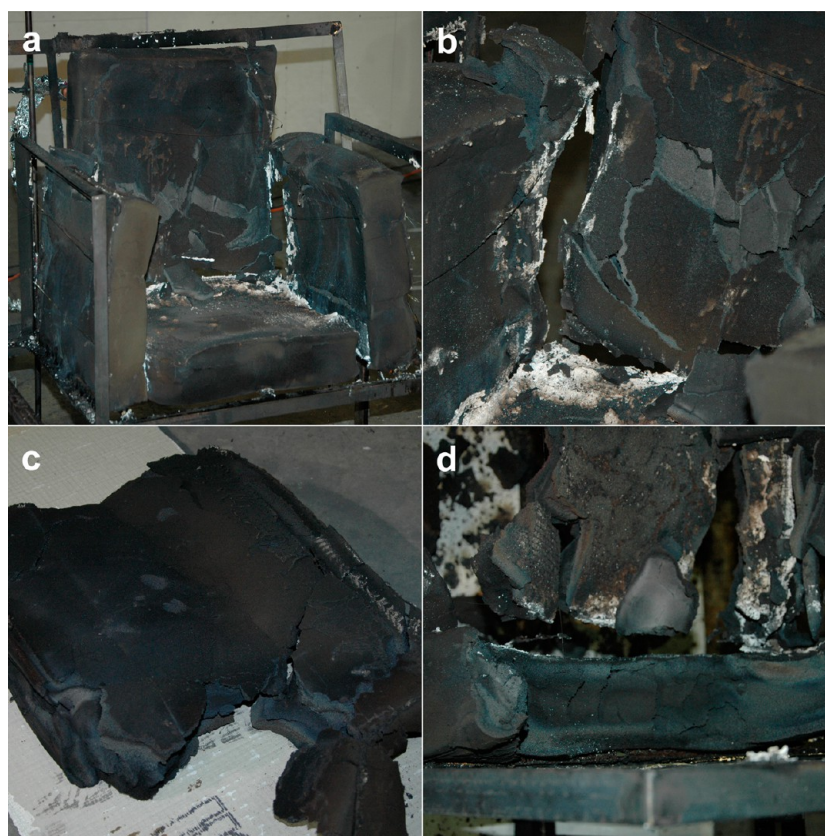


Figure 6. Overall (a), corner (b), side arm (c), and bottom cushion (d) pictures of LbL coated real scale mockup after the test. LbL coating maintains the original shape of the chair by creating flame retardant layers on the surface of PUF.

at pH of 2 (PMP2), resulted in a 42% and 71% reduction of PHRR and aHRR values, respectively, as compared to pure PUF. This was achieved using only 10 monolayers (SBL), which is two times fewer monolayers than the previous best performing LbL FR coating on PUF (7TL, 21 layers). In full-scale fire tests, the PMP coating outperformed what was predicted in cone by reducing the PHRR value by 53%. These results demonstrate the tremendous opportunities for LbL coatings to serve as an effective FR technology for PUF.

■ ASSOCIATED CONTENT

📄 Supporting Information

Figure S1: SEM images of untreated foam at 200× (a) and 2000× (b). This information 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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