Polymer 56 (2015) 284–292

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Layered double hydroxide-based fire resistant coatings for flexible polyurethane foam

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ARTICLE INFO

Article history:
Received 15 September 2014
Received in revised form
30 October 2014
Accepted 5 November 2014
Available online 15 November 2014

Keywords:
Layer-by-Layer
Layered double hydroxide
Polyurethane foam

ABSTRACT

Montmorillonite clay (MMT) is frequently used to create fire resistance in Layer-by-Layer (LbL) applied coatings. This manuscript reports that switching the MMT with layered double hydroxides (LDH) produced a more effective fire resistant coating on flexible foam. Most of the formulations required at most two trilayers (TL) to produce ignition resistant and very low heat release rate polyurethane foam. The best coating (greatest flammability reduction with the least amount of coating) delivered a 41% reduction in peak heat release rate. This was a 2TL, 10% mass coating produced using a coating solution with a high LDH content. This manuscript discusses the impact of the LDH-based coating formulations and number of monolayers on the LbL coating growth rate, composition, and fire resistance.

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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.

Over the past 20 years, LbL assembly has been used to create multifunctional films [2–4] for a variety of applications, such as sensing [5,6], antimicrobial surfaces [7], battery electrodes [8,9], water repellents [10,11], oxygen barriers [12,13], fire resistance [14–17] and drug delivery and biomedical applications [18–20]. As the name suggests (Layer-by-Layer), the films were assembled/fabricated by depositing one layer (a monolayer) at a time. The LbL films can be constructed of several hundred monolayers and are generally less than one micrometer thick [21]. The monolayers can be a polymer, additive, nanoparticle or a mixture of multiple materials.

A majority of these thin multilayer LbL films were constructed from a two monolayer repeat unit (AB) that was held together by electrostatics. More recently, trilayer (ABC, TL) [14,22] and quadlayer (ABCD, QL) [23] constructions were reported, which produced properties not easily achieved by the conventional BL construction. Others forces used to hold the films together have been covalent [24,25] or hydrogen bonds [26,27]. In addition to changing the materials and the construction, the film properties (e.g., transparency and permeability) have been controlled by changing the conditions of the depositing solutions, such as pH [28,29], temperature [30,31], and ionic strength [32] and molecular weight [32,33] of the coating materials.

In 2009, Grunlan (Texas A&M) et al. first published using Layer-by-Layer (LbL) assembled coatings to produce a low flammability fabric [34]. Since then, researchers have developed LbL FR coatings for textiles [34–36], plastic plaques [37–39], and polyurethane foam (PUF) [40,41]. The coatings were constructed of synthetic and bio-based polymer binders (e.g., polyacrylic acid and DNA) [42], and have contained a wide range of fire retardants and protective residue formers (e.g., montmorillonite clay [16,33,34], silica [43–45], α-zirconium phosphate [46], and carbon nanotubes and nanofibers [48,49]). Montmorillonite clay (MMT) continues to be the most frequently used nanoparticle to enhance the fire resistance of these coatings.

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http://dx.doi.org/10.1016/j.polymer.2014.11.023
0032-3861/Published by Elsevier Ltd.

Similar to MMT, layered double hydroxides [50,51] (LDH) have been shown to promote/enhance the formation of an inorganic-reinforced carbonaceous residue that thermally protects the underlying polymer. The formation of this residue slows down/stops the combustion process. For example, adding a 5 mass % Zn–Al LDH in polyethylene caused a 50% reduction in peak heat release rate [52]. At elevated temperatures, LDH has been shown to release water (by loss of interlayer water and by decomposition of the OH group of the sheet surface) and go through endothermic decomposition. In some studies, LDH was more effective than MMT presumably because of these additional fire retarding pathways [53,54]. However, MMT continues to be more widely used as a fire retardant than LDH. LDH's limited commercial success as a fire retardant may be because it was more difficult to disperse and distribute in polymers, which limits its effectiveness as a fire retardant. In LbL coatings, dispersion and distribution are less important as long as the coatings completely encapsulate the substrate. Therefore, the assumption of this research is that replacing the MMT with LDH will result in a more effective fire resistant coating because LDH has additional pathways by which to reduce the flammability of the substrate.

The research presented in this manuscript was inspired by our previous study of MMT TL LbL coatings on polyurethane foam [14]. We reported finding an ideal combination of coating attributes that provided rapid coating growth with an excellent balance of flammability, mechanical, and physical attributes. In this manuscript, we replaced the MMT with LDH and investigated the impact of the coating formulation and number of layers on the coating quality, growth rate, and fire resistance on polyurethane foam. We further characterized (e.g., SEM, FTIR) the post fire test samples to better understand the fire retarding mechanism and how this could be used to further advance LbL fire resistance coatings.

2. Experimental description [55,56]

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

2.1. Chemicals and substrates

Branched polyethylenimine (BPEI, Mw 25,000 g/mol) and poly(acrylic acid) (PAA, Mw 100,000 g/mol, 35% in H_2O) were purchased from Sigma–Aldrich (Milwaukee, WI). Layered doubled hydroxide, (LDH, Perkalite LD-20SL, 20% aluminum magnesium layered double hydroxide slurry in water, OH^-as interlayer anions), was supplied by AkzoNobel Polymer Chemicals (Chicago, IL). Polymer solutions and LDH suspensions were both prepared at a low (L) and high (H) concentration. Polymer low and high solutions were 0.1% and 0.5%, respectively. LDH low and high suspensions were 0.2% and 1%, respectively. All depositing and washing solutions are water-based and were prepared using water purified from a Nanopure II system (18.2 MΩ cm, pH of 5.8, Sybron/Barnstead).

Standard (untreated) polyurethane foam (PUF, 29.1 kg/m^3 density) was purchased from FXI Inc. (Media, PA) and was stored in a conditioning room (25% relative humidity, 23°C ± 2 °C, no sunlight). The PUF was stored in these conditions until cut for coating, ((10.2 × 10.2 × 5.1) ± 0.1) cm and ((22.9 × 15.2 × 7.6) ± 0.1) cm, for cone and open flame testing, respectively. After cutting, the PUF was dried in a desiccator for two days, then the mass of the PUF was measured. The 100% cotton and 78% polyethylene/22% polyester cover fabrics used in open flame tests were purchased from Jo-Ann fabrics store.

2.2. Coating process

The LbL coatings were constructed of 1, 2, 3 or 5 TL [14]. A TL consisted of three monolayers: PAA, LDH, and BPEI. A monolayer was applied by 1) submersing a piece of PUF in one of the aqueous depositing solutions (PAA, LDH, or BPEI), 2) repeatedly squeezing and releasing the PUF while submersed, 3) soaking the PUF in the solution, 4) removing the PUF, and 5) squeezing the excess solution back into the deposition container. The soak time (step #3) was 5 min for each monolayer in the first TL and 1 min for all subsequent TLs. Next, the PUF was rinsed with DI water using the same squeeze and release process as described for depositing the monolayers then the next monolayer was applied. After coating, the coated PUF was placed in a 70°C ± 3 °C convection oven overnight, stored in a desiccator for one day, and then the mass was measured. The difference between the mass measured prior to and after coating was used to calculate the % mass increased caused by the coating.

To investigate the impact of coating composition on coating growth and flammability, we used four different coating formulations that were based on the concentration of the polymer and LDH in the depositing solution. The coating formulations were polymer/LDH at low/low (LL), low/high (LH), high/low (HL), and high/high (HH), concentrations.

2.3. Coating and residue characterization

Coating mass was measured using a QCM200 quartz crystal microbalance Digital Controller and a QCM25 crystal oscillator (Standard Research System Inc., Sunnyvale, CA). The coatings were applied to a 5 MHz Cr/Au crystal. Prior to coating (using the procedure described in Section 2.2 (coating process)), the crystal was prepared by depositing a BPEI monolayer using a 0.1% BPEI solution.

Fourier Transform Infrared Spectroscopic (FTIR) spectra of coated PUF (before and after burning) and neat LDH powder (prepared by drying the slurry under the oven) were measured with a TENSOR 27 spectrometer (Bruker Optics Inc., Billerica, MA) operating in attenuated total reflectance (ATR) mode. The samples were scanned 64 times with a resolution of 4 cm^{-1} over the wavenumbers ranging from 4000 cm^{-1} to 600 cm^{-1}.

A Zeiss Ultra 60 Field Emission-Scanning Electron Microscope (FE-SEM, Carl Zeiss Inc., Thornwood, NY) was used to characterize the surface of the coatings on PUF. The SEM was operated at 5 kV accelerating voltage. All SEM samples were sputter coated with an 8 nm Au/Pd coating (60%/40% by mass) prior to imaging.

2.4. Thermal, combustion, and fire testing

A TG 449 F1 Jupiter® Thermogravimetric analyzer (TGA, Netzsch, Burlington, MA) was used to qualify the amount of inorganics in the coatings. A 10 mg specimen was isothermed at 90 °C for 30 min, then the temperature was increased at 100 °C/min to 850 °C under a nitrogen atmosphere. The residual mass at the end of the test is LDH (without crystal water, 60.6% of its original mass) and PUF residue (0.9%). LDH % on the PUF is calculated by subtracting the residual mass of PUF from the residual mass of coated PUF and dividing the resultant by 60.6%. LDH % in the coating is calculated by dividing the LDH % on PUF with the coating mass % calculated in section 2.2.

A dual Cone Calorimeter (35 kW/m^2 with an exhaust flow of 24 L/s), operated according to ASTM E1354-07, was used to measure the flammability characteristics of the PUF samples ((10.2 × 10.2 × 5.1 ± 0.1) cm). A sample was placed in a pan constructed from a heavy gauge aluminum foil (Reynolds® Heavy Gauge Aluminum Foil) with only the top of the sample exposed to

the cone heater. Exposure to the 35 kW/m [2] 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 stopped when there were no visible flames. The standard uncertainty was ±10% in heat release rate (HRR) and ±2 s in time.

A modified Mydrin test was used for bench scale open flame testing of a composite [57,58]. The composite consisted of PUF wrapped with of a commercial cotton or polyester residential furniture fabric (approximately (38.1 × 30.4 ± 0.1) cm). All sides of the PUF were covered with the fabric, expect for the backside (opposite of the flame impingement side). The ignition source was a 40 mm butane flame that was applied to the face of the composite for 20 s and then removed. Only the control and control and HH5-coated PUF samples were tested ((22.9 × 15.2 × 7.6 ± 0.1) cm). Three replicates were recorded and the after burn residue was photographed by a digital camera.

3. Results and discussion

In a previous publication, we reported that the coating growth and fire resistance imparted to flexible PUF was strongly dependent on the number of TLs in the coating, and the concentration of the polymer and MMT [14]. The best flammability reduction was achieved with 3 TL PAA-BPEI-MMT coating produced with a high MMT content depositing solution; the polymer content had no impact. Under these conditions, there was no reason to exceed 3 TL because it only added more mass without providing any significantly decrease in PUF flammability. The research described in this manuscript used the same approach as the MMT study (vary the concentration of the depositing solutions and measure the impact on coating growth and flammability), except the MMT was replaced with LDH. In thermoplastics where MMT and LDH were incorporated by solution or melted mixing, the LDH generally produced a lower flammability material. Our expectation was in these LbL coatings, the LDH could produce a lower flammability PUF than previously reported for using MMT.

The PAA-LDH-BPEI TL coatings were fabricated on PUF by sequential submersing in aqueous depositing solutions (Fig. 1). The coatings were constructed of 1, 2, 3 and 5 TL. The depositing solutions were low or high polymer concentration and low or high LDH concentration. This resulted in four coating formulations (LL, LH, HL, and HH) (Table 1) and four coating architectures (1, 2, 3, and 5 TL).

The pH value during the coating process was critical to the development of these coatings. The pH was 3.2 for the PAA depositing solution. At this pH, the PAA (pKa 6.5) charge was partially negative and PAA had a structure that was more globular

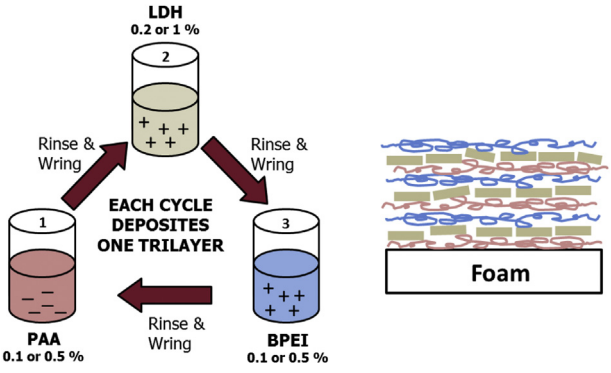

Fig. 1. Schematic of the LDH-based LbL procedure and coating on the foam.

Table 1
Mass % of the coating components in the depositing solutions.

ID (Polymer-LDH)	Formulation		
	PAA (%)	LDH (%)	BPEI (%)
LL	0.1	0.2	0.1
LH	0.1	1.0	0.1
HL	0.5	0.2	0.5
HH	0.5	1.0	0.5

than linear [59]. The sample was rinsed with DI water (pH of 5.8) and was then submersed in the LDH depositing solution, which had a pH of 11. At this higher pH, the PAA became more linear due to an increased charge density [59], which should have promoted adhesion of the positive charged LDH. After rinsing with DI water, the sample was submersed in the BPEI depositing solution, which had a pH of 10.3. The pKa of the primary, secondary, and tertiary amines of BPEI were 4.5, 6.7 and 11.6, respectively [60]. Therefore, at a pH of 10.3, none of the amine groups were protonated. This suggested that the interaction between LDH and BPEI was likely H-bonding (similar to reports with MMT) [14]. BPEI adhesion could also have been promoted by interaction with the PAA layer under the LDH layer. Researchers have reported that the polymer chains of linear PAA (fully negatively-charged) and BPEI monolayers will penetrate into each other by extending through the gaps of MMT platelets (interdiffusion) [61]. This interdiffusion was used to explain why fast coating growth and high MMT retention was achieved even though the PAA and BPEI monolayers were separated by a MMT monolayer. We assume this same phenomenon has occurred for these LDH-based coatings.

The coating growth and composition trends were similar for all four formulations (Table 2). The coating mass and LDH % in the coating increased as the number of TL increased. On average, the % mass coating was 3.5%, 8.5%, 10.7%, 18.5%, for the 1, 2, 3, and 5 TL, respectively. The coating mass tended to be higher for the high polymer depositing solutions. The difference in the actual mass % tended to be greater with a higher number of TL. On average, the LDH on the PUF was 2.4%, 7.4%, 8.6%, 9.9%, for the 1, 2, 3, and 5 TL, respectively. The LDH % on the foam tended to be higher when using the higher LDH depositing solutions. There was no relationship between the LDH % in the coating and the number of TL or the concentration of the depositing solution. What was important was with just 2 TL (all formulations), the amount of the coating and the amount of LDH in the coating was above the threshold defined as critical for reducing PUF flammability (5%–10% coating and above 30% inorganic sheets in the coating) [14].

Table 2
Coating mass %, and LDH % on PUF and in the coating. The uncertainty is ±5% of the measured value.

ID	Number of TL	Coating mass %	LDH % on PUF	LDH % in the coating
LL	1	3.5	0.5	15
	2	6.8	6.1	90
	3	8.3	7.1	85
	5	15	7.9	54
LH	1	3.1	2.3	75
	2	11	8.9	82
	3	14	11	79
	5	15	13	88
HL	1	4.4	2.9	66
	2	6.3	5.3	84
	3	7.4	6.1	83
	5	25	8.6	34
HH	1	4.0	3.8	96
	2	9.7	9.1	94
	3	13	10	77
	5	19	10	54

The coatings were characterized using ATR-FTIR and SEM. Several hundred SEM images were collected. In all the SEM images, the coatings completely encased the PUF (Fig. 2) and appeared to be uniform, fracture free, and have an occasional large aggregate of LDH/polymer. There were no regions of unexposed PUF. The surface roughness was created by the high LDH concentration in the coatings and because LDH was the last layer deposited. The FTIR spectra of all coated foams (except LH1, peaks were overlapped by the peak of PUF) showed strong peaks for LDH at 3435 cm^{-1} (O–H stretchings [62,63]), 1362 cm^{-1} (carbonate stretching from Mg Al-carbonate [63–65]), and 781 cm^{-1} and 680 cm^{-1} (lattice vibration of M–O and O-M-O [62,64]) Fig. 3.

3.1. Flammability testing

The Cone Calorimeter (cone) is a commonly used instrument to measure bulk flammability characteristics of materials [66,67]. 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 as well as 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 (PHHR), 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 HHR curves for the LDH-coated PUF are provided in Figs. 4 and 5.

The PUF used for this study exhibited typical foam combustion behavior in the cone (Figs. 4 and 5). The PUF was completely consumed very quickly (<150 s) and released a total heat (THR) of 41 MJ/m^2. The average amount of heat released (aHRR) was 199 kW/m^2. The heat release rate (HRR) curve consisted of two peaks associated with the combustion of polyurethane decomposition products; polyisocyanate (337 $kW/m^2 \pm 34$ kW/m^2) and polyol (451 $kW/m^2 \pm 45$ kW/m^2). The pHRR value for PUF was the polyol peak (451 $kW/m^2 \pm 45$ kW/m^2).

Other than a few exceptions (to be discussed below), these LDH-based coatings significantly decreased all flammability attributes of PUF (Figs. 4 and 5). The flammability reduction was in the range of

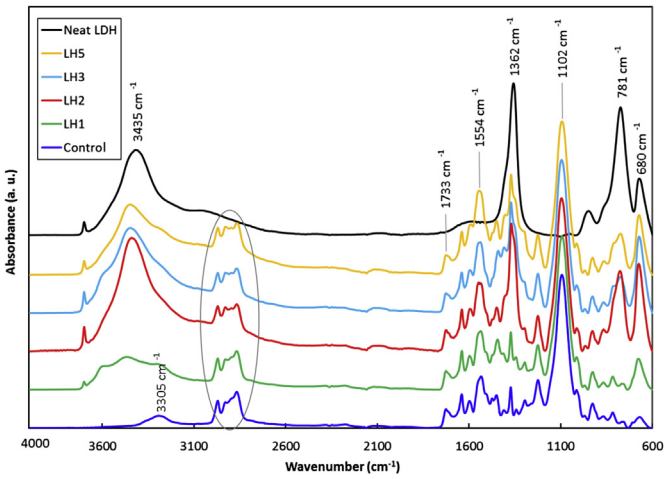

Fig. 3. FTIR spectra of neat LDH, PUF (control) and LH coated PUF.

20%–40% for pHRR, 50%–80% for aHRR, and 5%–30% for THR. In general, only 2 TL was needed to achieve a significant reduction in PUF flammability. Above 2 TL, there was little to no further flammability reduction. The HRR curves contained a single and very sharp HRR peak after which there was a sustained low HRR plateau until the test was stopped (no visible flames). These characteristics suggested the coatings formed an effective and durable protective residue.

The least fire resistant coatings were the 1 TL LL, LH, and HL formulations. These coatings exhibited the classical standard PUF two peak HRR curves. For LL1, the pHRR and THR actually increased (20% and 2%, respectively) indicating that the coatings effectively added fuel and did not form a protective residue during combustion. For LH1 and HL1, the suppression of the 2nd HRR peak, 20% decrease in pHRR, and 50% decrease in aHRR suggested a protective residue formed, but it was likely porous, thin, and/or not durable. Since coating mass was similar for LL1, LH1, HL1 (~4%), we believe the LL1 was much less effective because the LDH content was too low to enable the formation of an effective residue. The LDH content was 0.5% for LL1 and ~2.5% for LH1 and HL1.

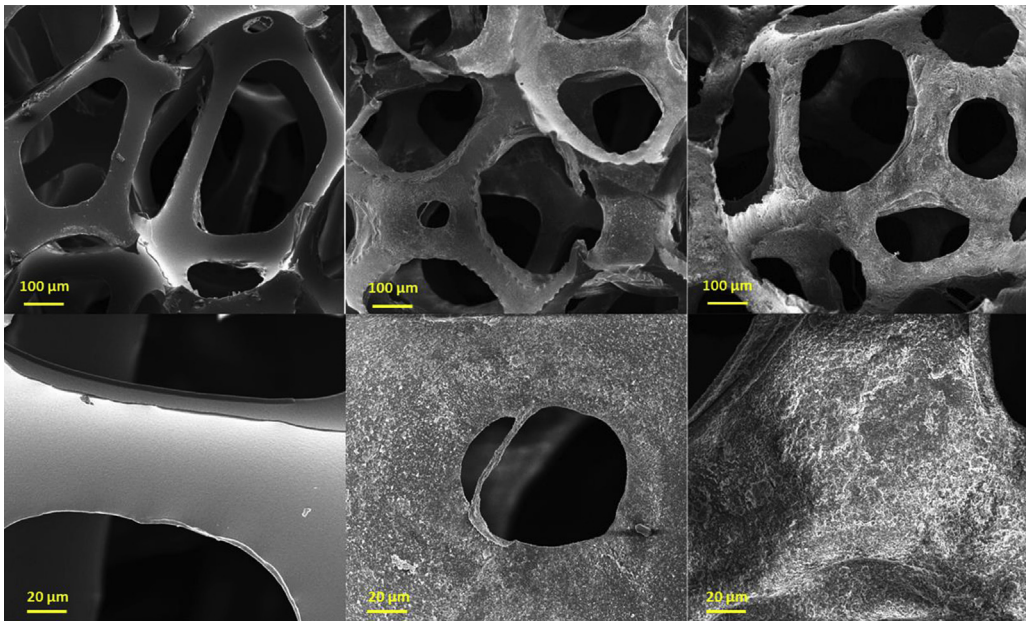

Fig. 2. SEM images of (left) PUF, (middle) LH1 PUF, and (right) LH2 PUF at (top) 100× magnification and (bottom) 500× magnification.

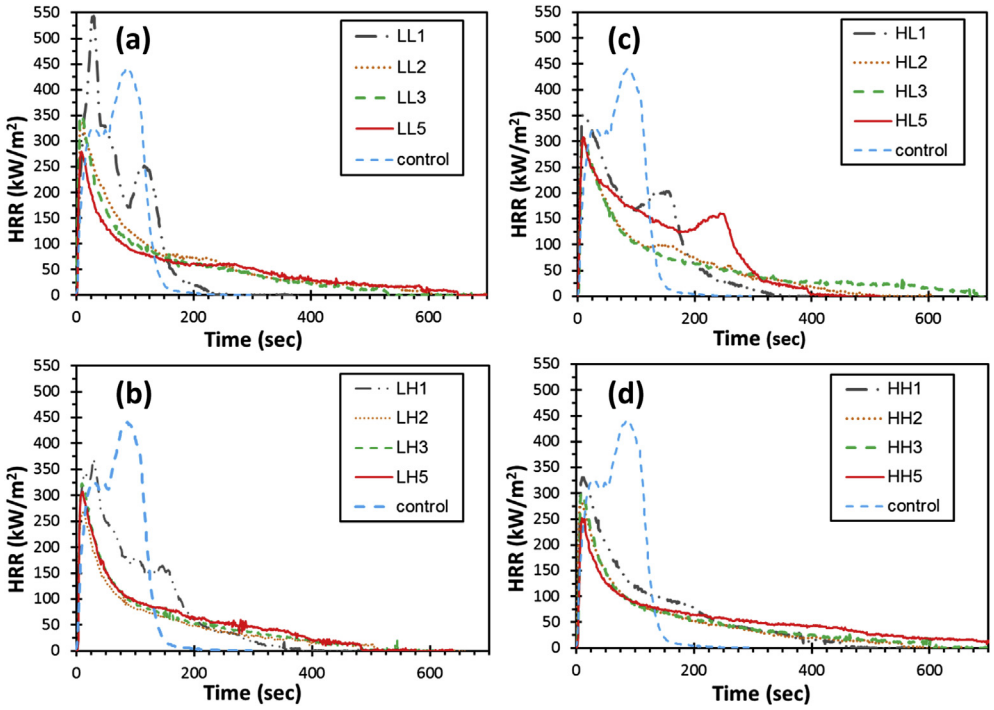

Fig. 4. Heat release rate of 1, 2, 3 and 5 TLs of (a) LL, (b) LH, (c) HL, and (d) HH of LDH-coated foams. The standard uncertainty was ±10% in heat release rate (HRR) and ±2 s in time.

HH1 performed much better, not because of the reduced pHRR (27%), but because of the overall quality of the residue. Unlike the other 1 TL formulations, the residue formed quickly and produced a plateau-like HRR for the remainder of the fire test. This resulted in a 68% reduction in aHRR and 10% reduction in THR. We believe this coating was at the borderline of what constitutes as an effective FR coating with this formulation (4% mass coating and 3.8% LDH). The largest difference between the HL1 coating and the best performing coatings (2 TL or greater for all formulations) was primarily the significant reduction in pHRR and the value of the plateau.

The best flammability reduction coatings were LH2 and HH2. Within the uncertainty of the cone measurements, the pHRR, aHRR, and THR values were similar (250 kW/m^2, 42 kW/m^2, and 31 MJ/m^2, respectively). Both also had similar coatings masses (about 10%). Since both formulations were comparable we could have chosen either to investigate further. We selected LH2 because it required less material to produce the coating solutions.

3.2. Residue characterization

During cone testing, the PUF collapsed almost immediately to form a liquid pool fire. When the test was over, the PUF was completely consumed. During cone testing of previous LbL fire retardant coatings, the coatings formed a protective layer that reduced the extent of the PUF collapse [14,41]. When the test was over, there was a black structure remaining in the pan. The black structure was a deformed square and was at least 50% thinner then the pre-test coated PUF. Characterization of the black structure revealed all of the polyurethane was completely consumed during combustion leaving behind only carbon and MMT. This indicated that the black structure was a carbonaceous residue reinforced by the MMT. The MMT coatings, while effective at slowing down combustion, but still were not sufficient to stop complete combustion of the polyurethane.

Unlike the MMT coatings, the LDH-based coating stopped combustion before all the polyurethane was consumed. There was no dimensional change between the pre- and post-test LH2 sample (Fig. 6). The top third of the post-test sample was structurally comparable to the previously reported MMT samples (black and a brittle powder), except the top surface contained a fine white powder (Fig. 7a and b). The middle third was black with a hint of yellow. The surface and structure morphology was similar to the unburned foam, except for a signs of surface cracks (Fig. 7c and d). The bottom third was yellow-orange, sticky, and structurally similar to the pre-test foam. The surface was completely covered with coalesced-like bubbles (Fig. 7e and f). According to the FTIR (Fig. 6), there were characteristic peaks of polyurethane (1102 cm^{-1}, 2877 cm^{-1} to 2977 cm^{-1}), and LDH (675 cm^{-1}, 850 cm^{-1}, and 3200 cm^{-1} to 3500 cm^{-1}) in all three sections. The intensity of polyurethane peaks relative to LDH peaks was higher near the bottom than at top of the sample, which suggested more polyurethane was burnt off nearer the top (closer to the external cone heater). The white powder on the surface was inorganic oxides from the decomposition of LDH. There was no evidence of decomposed LDH below the foam top surface.

Based on these findings we believe the LDH coatings produced a LDH-reinforced carbonaceous protective residue in the top 2/3 of the foam sample. The residue provided sufficient protection that the temperature in the bottom 1/3 was too low to support the formation of a protective residue and pyrolysis of polyurethane. In fact, other than a yellow discoloration, the post-test sample near the bottom of the PUF was completely indistinguishable from the pre-test sample.

3.3. Mock-up open flame testing

A real product (e.g., upholstered furniture) is constructed of various materials, geometries, shapes, and sizes, which all greatly influence the burning behavior (e.g., flame and fire spread, and HRR) of the real product. To fully understand burning behavior requires conducting full-scale fire tests (e.g., burn a whole chair), but these experiments are expensive and time consuming. A

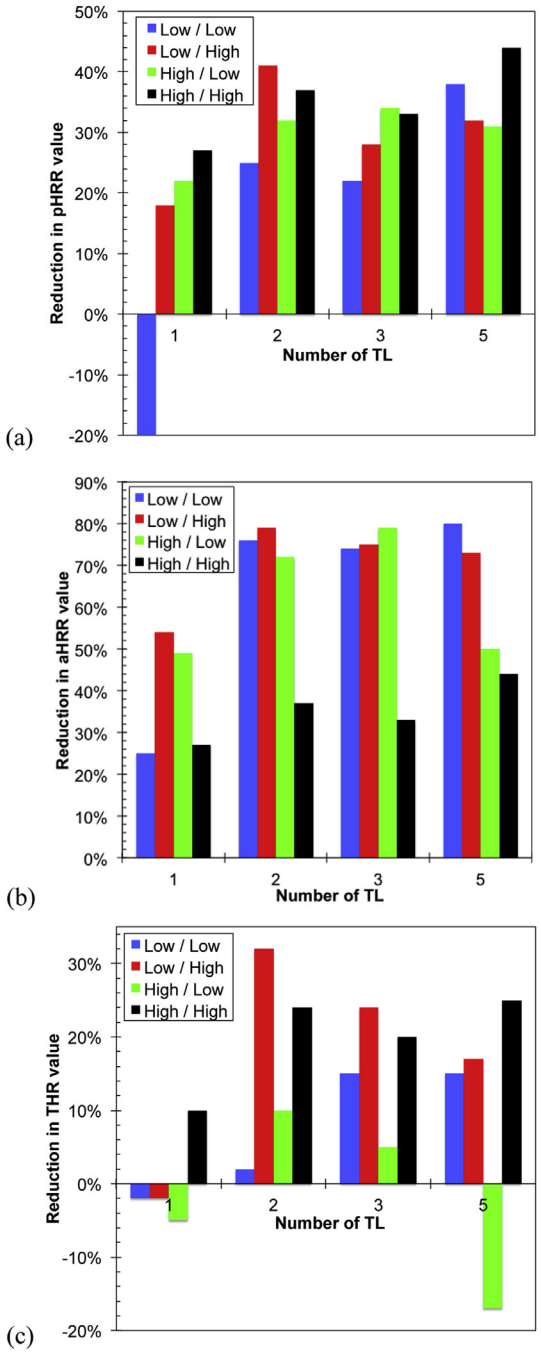

Fig. 5. Reduction of cone (a) pHRR, (b) aHRR, and (c) THR values caused by the LDH-based FR coatings. A negative value indicates an increase in a flammability parameter. The values for the PUF control were 451 kW/m^2 (pHRR), 199 kW/m^2 (aHRR), and 41 MJ/m^2 (THR). The uncertainty is ±2% of the reported reduction values and ±10% of the pHRR, aHRR, and THR values.

compromise is to conduct bench-scale fire tests using a "mock-up". A mock-up is a test specimen constructed to represent the real product. Since the mock-up is less complex and smaller, the fire tests are less expensive and quicker.

The mock-up fire test conducted in this study was a modified Mydrin test [58]. The test was conducted to qualitatively evaluate the fire resistant impact of the LDH-based foam when used in a construction that mimics what may be seen in furniture. The foam samples (PUF and HH5-coated) were (22.9 × 15.2 × 7.6 ± 0.1) cm, which was significantly thicker than used in the cone. We were concerned that the coating may not penetrate to the center of the thicker foam; therefore, we chose a higher mass gain formulation for this test (i.e., the HH5 rather than LH2 or HH2). The foam mock-ups were tested in three configurations: unwrapped (just the foam), wrapped with a thermoplastic fabric, and wrapped with a cotton fabric. The testing process was to apply a 20 s butane flame directly to the surface of the mock-up. The flame was then removed and the burning behavior was recorded (e.g., time to self extinguish). After the test was completed (no visible flames), pictures of each layer were taken (Fig. 8) and the burnt area was recorded.

The PUF unwrapped (U) and wrapped in the thermoplastic fabrics (TP) were significantly more flammable than the cotton fabric (C) wrapped. For U PUF and TP PUF, within 30 s after removing the open flame igniter, the flames rapidly spread across the surface and flaming polymer melt drips rapidly formed. By 60 s, the entire mock-up was engulfed in flames and the flames extended at least 40 cm above the top of mock-up. By 90 s, the mock-up was completed consumed. For C PUF, flame spread was slower and the flame size was smaller, but eventually the mock-up was completed consumed (170 s). All the PUF mock-ups fell off the test rig to form a pile of flaming fabric and foam decomposition products.

Using the LDH-coated PUF had a significant impact on the flammability of the mock-up. For a given construction, there was very little difference in the ignitability and flame spread using the HH5 foam and PUF. The drastic drop in flammability observed was attributed to the HH5 forming a protective residue that caused the size of the flames to decrease and then to extinguish. Unlike PUF mock-ups, all of the HH5 mock-ups stayed on the rig and did not form any pool fires. The coatings caused the mock-ups to self extinguish leaving behind 31%, 66%, and 71% mass for U, TP, and C HH5 mock-ups, respectively. The smaller flames, no pool fire, and high post-test residue suggested in a real fire that furniture containing the LDH-based coated foam would produce a much slower developing and severe fire.

3.4. Comparison with other LbL coatings

It is often difficult to compare flammability results reported from different publications. Slight differences in the test sample chemistry, size, and conditioning, the test conditions and configuration, and how the data is analyzed can have a large impact on the reported values. With that said, we wanted to gauge how this technology compared to others that were recently reported. To the best of our knowledge, those listed in Table 3 are the most recent and best reported LbL FR coatings applied to PUF. To minimize dependence on the foam type, the % reduction of the cone flammability parameters are reported rather than the actual values. The data is sorted by numbers of monolayers needed to produce the coating (e.g., 1TL is 3 monolayers, whereas 1 quadlayer (QL) is 4 monolayers).

The six coatings fell into three pHRR reduction categories; about 30%, 40%, and 50% reduction (Table 3). They have all had an approximate mid-70% reduction in aHRR, except for the CHI/PVS [68] (24%) and the PAA/CHI/PPA/CHI (not reported) [23]. From a purely flammability reduction impact, the best coatings were CHI/DNA + MMT [69], CHI/PVS, and PAA/CHI/PPA/CHI. These coatings required 20 monolayers to produce an approximate 50% reduction in pHRR. The CHI/PVS may be the best option from this group since it was the lightest coating (5.5% coating mass). The next group had a slightly lower impact on pHRR reduction. The PAA + MMT/BPEI [17] and PAA/LDH/BPEI (from this study) caused an approximate 40% reduction in pHRR. Of these two, the PAA/LDH/BPEI was clearly the better option; it was 3 times lighter and required ½ the number of layers. The worst performing coating was PAA/BPEI/MMT, which only had a 33% reduction in pHRR.

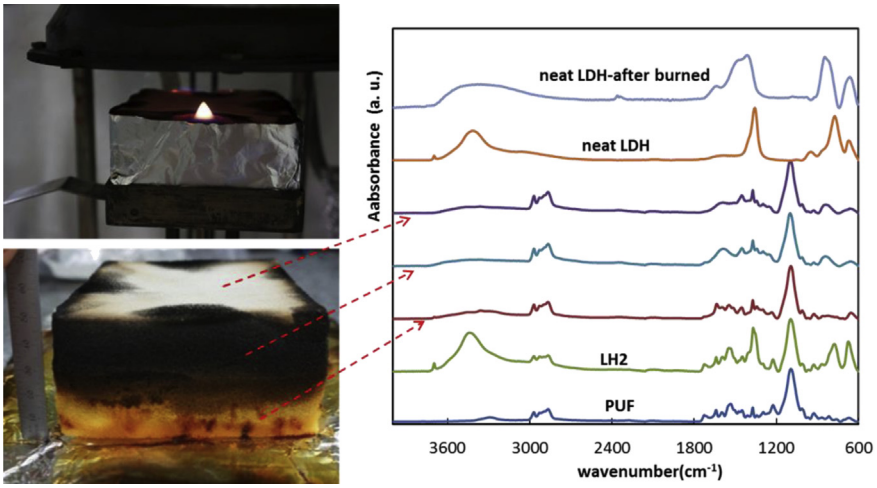

Fig. 6. The images of LH2 coated foam during and after cone testing, and the FTIR spectra of the after-burn coated foam.

The purpose of the study presented in this manuscript was to determine if a more effective fire resistant coating could be produced by using LDH rather than MMT. The results in Table 3 suggested LDH were the better option. The primary reason may be that LDH reduced flammability by additional pathways not accessible by MMT.

The two MMT-based coatings in Table 3 provided the basis for this LDH research. The coatings are constructed of the same materials (PAA, MMT, and BPEI), but are assembled differently (i.e., mixed BL and a TL). This difference impacts the coating growth and pHRR reduction. For the same number of monolayers (~10), the PAA + MMT/BPEI BL produced a coating that was 6 times heavier and had a 10% greater pHRR reduction than the PAA/BPEI/MMT TL coating. Extrapolating the data in the publication, we believe the PAA/BPEI/MMT could produce a similar pHRR reduction (~40%) by adding only 3 to 5 more monolayers, which would only increase the coating mass to ~10%. Therefore, the basis for determining which is a better coating will depend on what one determines to be more important: the less number of monolayers, but a higher coatings mass (PAA + MMT/BPEI) or lower coating mass, but a higher number of monolayers (PAA/BPEI/MMT). The best option may be to replace the MMT with LDH.

LDH produced a more effective fire resistant coating than MMT. Using LDH rather than MMT, required ½ the number of monolayers to produce an approximate 40% pHRR reduction. This is the same pHRR reduction as the PAA + MMT/BPEI, but with only 1/3 the coating mass. This is a 10% greater pHRR reduction than the PAA/BPEI/MMT, but with a 2 times heavier coating. However, a 10% mass increase is still low for a typical fire retardant loading and therefore, not considered to be a drawback for LDH.

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. LDH and MMT disrupt pyrolysis (condensed phase) by forming a protective residue layer between the polymer sample and the flame. This residue is a barrier that thermally protects the underlying polymer and hinders the transport of combustible products to the flame. If the residue has the right attributes (e.g., sufficiently think, dense, and durable), combustion will stop and the sample will not reignite. Factors that can influence these residue attributes include nanoparticle shape, size, surface chemistry, dispersion and distribution, and the chemistry of the rest of the sample. In these coatings, these attributes are sufficiently similar that the improvement in fire retardancy must be due to LDH's ability to reduce flammability through

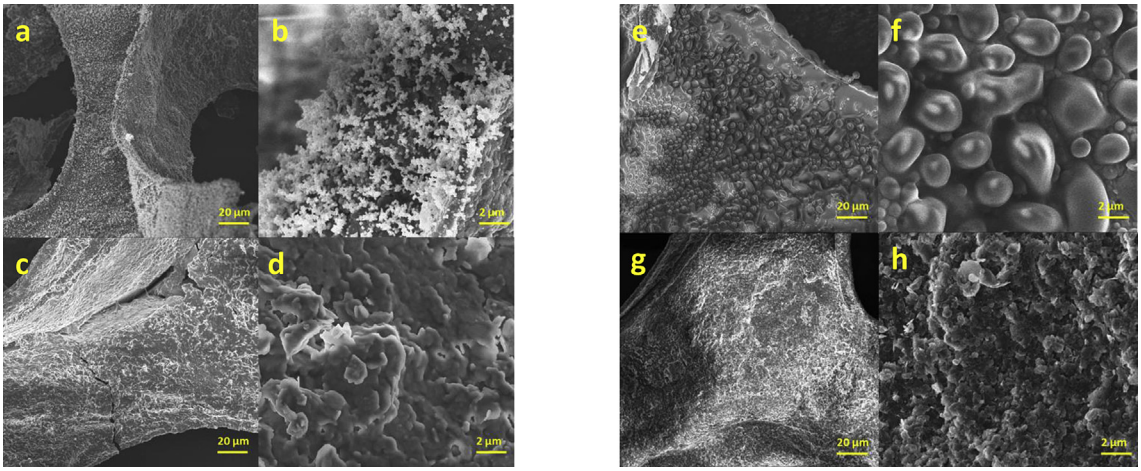

Fig. 7. The SEM images of three regions of LH2 foam after cone testing: top white (a, b), middle black (c, d), and bottom yellow (e, f) are compared with LH2 foam before cone testing (g, h). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

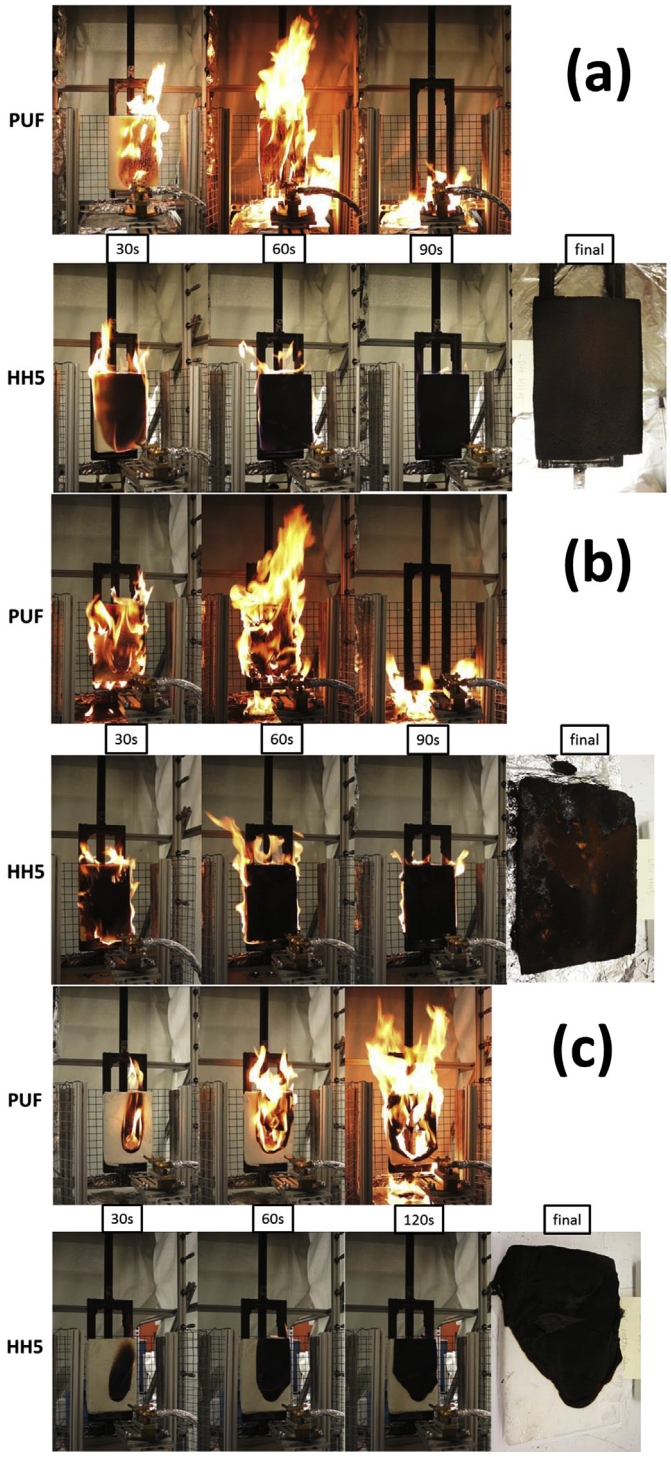

Fig. 8. Photos taken during the open flame testing of PUF and HH5-coated foam (a) without fabric (U), (b) wrapped with a thermoplastic fabric (TP), and (c) wrapped with a cotton fabric (C).

additional pathways not available by MMT. In addition to forming a protective residue, LDH releases water, which acts in the gas-phase to dilute of the fuel [51]. LDH also goes through an endothermic decomposition of the metal hydroxide layers, which causes the temperature in the polymer to decrease and slows down pyrolysis.

Taking all this information into consideration, our recommendation is to use (1) LDH rather than MMT because LDH delivers a greater reduction in flammability with a lower coating mass and uses less fabrication steps, (2) the CHI/(DNA + MMT) or CHI/PVS coatings for maximum flammability reduction is important, and (3) the LDH-based LH2 coating from this study for the best flammability reduction with the least amount of coating mass and fabrication.

Table 3
Comparison of published cone data from LbL coatings on PUF. The uncertainty is ±2% of the reported values for LH2. CHI-chitosan, PVS-poly(vinyl sulfonic acid), PPA-poly(phosphoric acid). *This study.*

Recipes	# of Monolayers	Coating Mass %	pHRR %	aHRR %
PAA/LDH/BPEI (LH2)*	5	10	41%	79%
0.1% PAA/0.1% BPEI/1% MMT [14]	9	4.8	33%	78%
0.5% (PAA + MMT) pH2/0.5% BPEI [17]	10	31	42%	71%
0.5% CHI/1% (DNA + MMT) [69]	20	16	51%	81%
0.5% CHI/2% PVS [68]	20	5.5	52%	24%
PAA/CHI/PPA/CHI [23]	20	48	55%	–

4. Conclusions

In a previous publication we conducted an extensive study on the impact of the concentration of the polymer and montmorillonite clay (MMT) depositing solutions, and the number of layers in the coating on the coating growth rate and fire resistance. The study reported in this manuscript was similar, except the MMT was replaced with another layered nanoparticle that has been shown to deliver better fire resistance than MMT. The nanoparticle was a layered double hydroxide (LDH). The only difference between these studies was switching the MMT with LDH. This switch resulted in a greater reduction with less layers and lower mass than the previously reported MMT coating.

Most of the LDH-based coatings significantly decreased important flammability attributes of the polyurethane foam (e.g., pHRR – peak heat release rate). In general, the flammability reduction was achieved with only 2 trilayers (TL). Above 2 TL, there was little to no further flammability reduction. The flammability reduction was in the range of 20%–40% for pHRR, and 50%–80% for aHRR (average heat release rate). These reductions were comparable to previously reported by MMT-based coatings on foam, but because LDH released water and went through an endothermic reaction these LDH-based coatings were significantly more effective. For example, a 40% pHRR reduction was achieved using a LDH coating that was at least 60% lighter and 50% faster to fabricate than the best MMT-based coating.

The best LDH formulation was LH2. It produced the greatest flammability reduction with the least number of coating layers and mass (41% (pHRR) and 79% (aHRR) reduction with a 10% coating mass). The fire resistance of the LDH-based coatings was also demonstrated on bench-scale fire tests using sample mock-ups constructed of foam and real furniture covering fabrics. The LDH coating on foam caused the fire to extinguish leaving behind as much as 71% of the original test specimen. In comparison, the standard foam was completely consumed and produced a large pool fire. These mock-up tests suggested furniture containing the LDH-based coated foam would produce a much less severe fire in a home.

Supporting information

A graph of the QCM mass growth trend of LL, LH, and HL systems can be found in http://pubs.acs.org.

Author contributions

Yu-Chin Li and Rick Davis contributed equally to this work.

Notes

The authors declare no competing financial interest.

Acknowledgments

The authors would like to thank Dr. Shonali Nazare for assisting with the open-flame testing.

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