# Self-extinguishable Non-toxic Layer-by-Layer Coating on Flexible Polyurethane Foam

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INTRODUCTION

Layer-by-layer (LbL) assembly is a popular method to fabricate multifunctional films that are typically less than one micrometer thick[1-3] A variety of LbL-assembled functional thin films are evaluated for properties that include antimicrobial,[4, 5] sensing,[6-8] anti-reflection,[9] electrochromic,[10-12] oxygen barrier[13] and biomedical applications.[14] Films are created by alternately exposing a substrate to positively- and negatively-charged molecules or particles, as shown in Figure 1(a). Steps 1 – 4 are continuously repeated until the desired number of "bilayers" (or cationic-anionic pairs) is achieved. Recently, flame retardant properties were successfully imparted *via* LbL assembly on cotton fabric with sodium montmorillonite clay,[15] and intumescent coating.[16] In this study, two coating systems were applied on polyurethane foam (PUF), branched polyethylenimine-montmorillonite/poly (acrylic acid) (BPEI/MMT/PAA) trilayer (TL) system (Fig. 1(b)), and poly (allylamine)/poly (sodium phosphate) (PAAm-PSP) bilayer (BL) system. PAA in TL system can seal the MMT layer and achieve a more uniform negatively-charged surface coverage.[17] Two coating systems were also combined and applied onto PUF (Fig 1(c) and (d)), in order to prevent the melt-dripping problem of PUF once it was ignited, and to delay the burning process resulted from the intumescent phenomenon. This LbL process is environmentally friendly, carried out under ambient conditions and uses only water-based solutions.
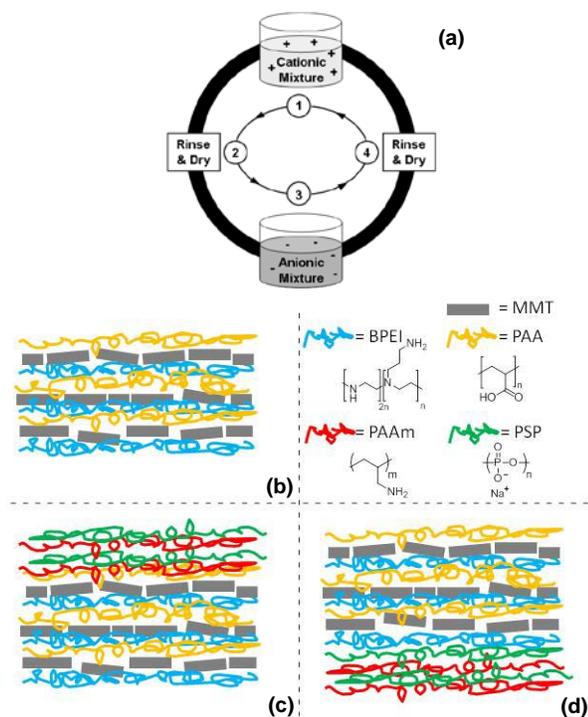
Figure 1. Schematic of the layer-by-layer self-assembly procedure for creating flame retardant thin films (a). Steps 1 – 4 are repeated to create three different multilayer coatings on the substrate (b), (c) and (d).

Unless others indicated all values are reported with 2σ uncertainty.

Materials. Polyelectrolyte deposition solutions were prepared by dissolving 0.1 mass fraction % of BPEI (Molecular Mass = 25,000 g/mol) and PAA (Molecular Mass = 100,000 g/mol) (Aldrich, Milwaukee, WI), 1 mass fraction % of PSP (Aldrich) and PAAm (Molecular Mass = 15,000 g/mol, Polysciences, Warrington, PA) into deionized (< 0.5 μS) water respectively. MMT (trade name Closite Na$^+$, Southern Clay Product, Inc., Gonzales, TX), was exfoliated by adding it to deionized water (0.2 mass fraction %) and slowly rolling for 24 h, to produce the anionic deposition mixtures. 1M HCl and 1M NaOH (Aldrich) were used for adjusting the pH of the deposition solutions. The standard (untreated) PUF coated in this study was stored as-received from the supplier.

Film Deposition and Characterization. The substrate was dipped alternately into BPEI (cationic), MMT and PAA (anionic) aqueous mixtures, with each cycle corresponding to one TL. The first dip into each mixture was for 5 min, beginning with the cationic solution. Subsequent dips were for 1 minute each. Every dip was followed by rinsing with deionized water and wringing the water out 3 times. The same procedure was also applied to PAAm/PSP system, except it creates a BL each coating cycle. After achieving the desired number of layers, the coated foams were dried in the 70 °C oven overnight. A Zeiss Ultra 60 Field Emission-Scanning electron microscope (FE-SEM, Carl Zeiss Inc., Thornwood, NY) was used to collect images of the nanocoating, from which was approximated the distribution of clay and one overall quality of the LbL coating was inspected. All SEM samples were sputter-coated with 4 nm of Au/Pd (60 mass fraction %/40 mass fraction %) prior to SEM imaging. A Q-500 Thermal Gravimetric Analyzer (TA Instruments, New Castle, DE) was used to measure the concentration of clay on the substrates. Each sample (20 mg ± 3 mg) was run under a nitrogen atmosphere, from 90 °C (30 min. stabilization) to 800°C, at a heating rate of 10 °C/minute. The remaining mass fraction is the reported clay content.

Open Flame Testing. (5.1cm / 5.1 cm / 5.1 cm) ± 0.1 cm of a uncoated and coated foams were pierced in the center by a long needle horizontally and were held in the air. Foams were ignited by a lighter in the right bottom corner for 3 seconds, and the burning process was video-recorded and the images captured. The videos were then analyzed.

PRELIMINARY RESULTS AND DISCUSSION

The increase in substrate mass due to the coating was measured using a laboratory microbalance. The amount of clay in the coating was calculated from TGA and microbalance values. 8 TL of MMT coating on PUF increases the mass of the substrate by 3.2 mass fraction % ± 0.6 mass fraction %. In this coating, 66 mass fraction % ± 13 mass fraction % is MMT, which is 2.1 mass fraction % ± 0.2 mass fraction % on PUF. This loading level on the substrate is similar to what is used to improve the fire performance of polymers. In contrast to those conventional nanocomposites, clay in LbL coating is concentrated on the surface rather than randomly distributed throughout the polymer matrix.

The images in Figure 2(a) indicated the entire PUF surface was coated with a non-uninform distribution of clay. The surface was covered with regions of high MMT aggregation that can be as large as 100 µm by 100 µm. Fracture surface images (Fig. 2(c)) indicated that these regions can be several microns thick. The coating was 1000 nm ± 450 nm. The large uncertainty in the thickness stems from a large variation in the degree of clay aggregation. The smooth and featureless regions between these large aggregates are actually completely filled with clay (fig. 2(b)). The coating thickness in these regions is closer to what was expected from this process (500 nm ± 120 nm). A cross section of a thickness average region of the coating (1000 nm) indicates the coating is highly filled with MMT sheets stacked upon each other similar to a deck of cards (Fig. 2(d)).
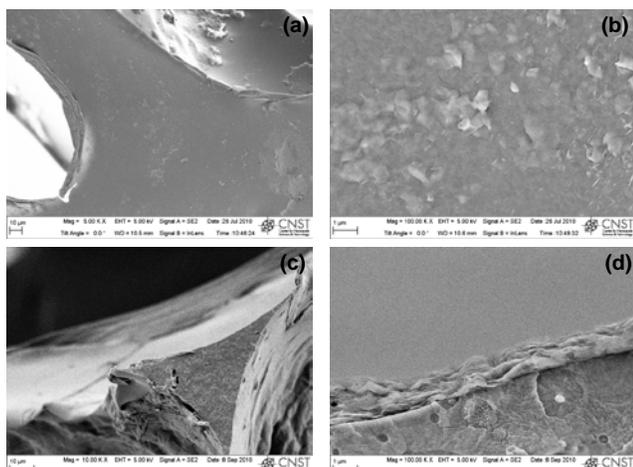

Figure 2. SEM images of the inside section of 8 TL MMT coated PUF at (a) 5,000x, (b) 100,000x, and a fractured edge at (c) 10,000x and (d) 100,000x.

Uncoated and coated foams were ignited to observe melt-dripping and flame spread rate qualitatively. Once on fire, the uncoated foam burned and collapsed to form a pool fire, and no solid char was left at the end of burning. On the other hand, there was no melt-dripping for 5 TL MMT-coated foam, but the flame crossed the surface slightly faster than the uncoated foam, and the flame was more vigorous. But the shape of the coated foam was retained with a certain degree of shrinkage at the end of the burning. 20 BL PSP-coated foam had the slowest flame spread among the samples, and the flame was much less vigorous compared to the 5TL coated sample. After a while, when the interior of the foam exposed more and more, the flame started growing and the whole piece was burned completely with melt-dripping. In order to prevent the melt-dripping and slow down the burning process, two combined coatings on the foam (5 TL of clay plus 20 BL of PSP, or in reversed order) were prepared. The flame spread of these two foams was faster than the PSP-coated foam but slower than the MMT-coated foam qualitatively and there was no dripping. At the end of the burning, foam coated with clay on the top had more residue than the other foam. Lower residue may be a result of a low on MMT (released during coating) (Fig. 3).

CONCLUSIONS AND FUTURE WORK
MMT TL and PSP BL coatings were successfully applied on PUF. MMT-coated foam retained the foam shape at the end of the direct flame testing, but the flame spread was faster. PSP-coated foam reduced the flame spread and scale, but the foam was melt-dripping. The combined coatings improved the melt-dripping of PSP-coated foam, and still had some residues left at the end of the burning. Even though this was not a regular fire performance test, it gave us the initial idea of how these coatings behave during a real fire scenario. More studies are currently under investigation.
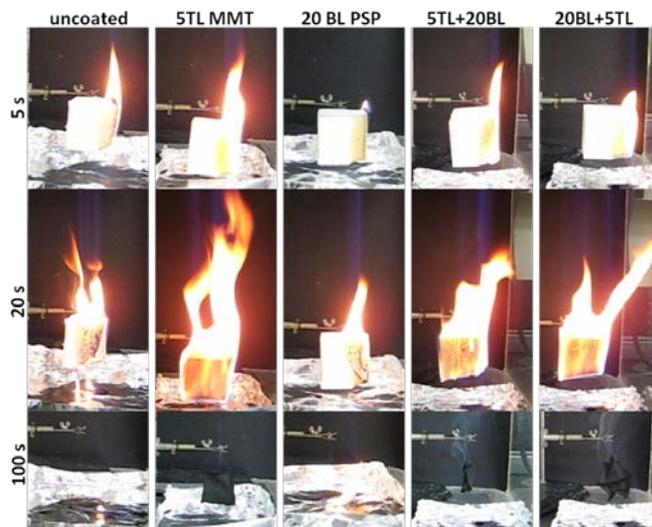
Figure 3. Uncoated and 4 different coated foam samples were video-recorded for the open flame testing, and the images were captured at 5, 20 and 100 s.

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