

DNA-based nanocomposite biocoatings for fire-retarding polyurethane foam

Yu-Chin Li PhD

Guest Researcher, Flammability Reduction Group, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA

You-Hao Yang PhD

Guest Researcher, Flammability Reduction Group, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA

Yeon S. Kim PhD

Guest Researcher, Flammability Reduction Group, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA

John Shields BS

Physical Scientist, Flammability Reduction Group, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA

Rick D. Davis PhD*

Group Leader, Flammability Reduction Group, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA

Layer-by-layer (LbL)-assembled multilayer thin films of deoxyribonucleic acid (DNA), chitosan (CHI) and montmorillonite (MMT) were studied in an effort to produce fully renewable, bio-based, fire-retardant coatings for flexible polyurethane foam. The polyurethane foam (PUF) biocoatings constructed of ten bilayers (BLs) of CHI/DNA+MMT (16.2 % mass), ten trilayers of CHI/MMT/DNA (8.1 % mass) and five quadlayers of CHI/DNA/CHI/MMT (4.9 % mass) all resulted in a significant reduction in critical flammability metrics, peak heat release rate (pHRR) and average HRR (aHRR). The mix BL, CHI/DNA+MMT, is the best formulation as it resulted in the greatest flammability reduction (51% pHRR and 81% aHRR) with the fastest biocoating growth and the least amount of preparation and waste. This DNA- and MMT-based biocoating is the greatest flammability reduction of PUF reported to date using the LbL process. Constructed of bio-based and non-toxic materials combined with the fast-growing BL approach, which has minimal waste, this is presumably the most environmental and bio-friendly fire-retardant LbL coating on flexible polyurethane foam reported. This article contains supporting information that will be made available online once the issue is published. In the meantime, if you wish to get a copy of the supplementary file please contact the Managing Editor, Sohini Banerjee, at sohini.banerjee@icepublishing.com

1. Introduction

In response to an increased global concern toward the potential environmental, health and safety (EHS) issues associated with fire retardants (FR), FR and consumer product manufacturers are searching for EHS compliant alternatives that maintain flammability performance and are cost-attractive.

A recent technology showing great promise as an EHS-friendly FR is layer-by-layer (LbL) assembled thin films/coatings. These LbL coatings are constructed of various inorganic nanoparticles and cost-effective commercial polymers, and have been applied to several different substrates (e.g. fabrics,^{1–5} plastic films^{6–8} and polyurethane foams (PUFs)).^{9–14} Montmorillonite clay (MMT), which when organically modified and melt blended with a polymer can enhance the fire resistance of that polymer,^{15–17} has also been used to improve the fire performance of the LbL coating when the MMT is paired with branched polyethylenimine (BPEI),¹ poly(allylamine) (PAH)^{6,7} and chitosan (CHI).¹² Quite frequently,

this FR technology is applied to textiles, for example 20 bilayer (BL) BPEI/MMT coatings with less than 4 % mass gain on cotton fabric acted as a protective sheath preserving a significant amount of the residue, as well as the shape of the fibers and the weave structure of the fabric on exposure to an open flame. From this study, a high concentration (1 % mass) deposition solution of MMT gave the highest clay loading in the film and best reduction in critical flammability attributes (e.g. 15% in the total heat release (THR) and 20% in heat release capacity).¹ More recently, this technology has been applied to polymer films, for example, 18-μm-thick 60 BL PAH/MMT coatings on polylactide (PLA) showed reduction on PLA flammability. By impregnating the coating with poly(sodium phosphate) (PSP; by soaking the coated PLA in a PSP solution) significantly decreased the peak heat release rate (pHRR; 37%) and increased the time-to-ignition (TTI; 111% increased), as compared to the uncoated PLA.⁶ The same coating (20 BL) applied to polyamide-6 (PA6) caused a 60% reduction in the pHRR, as compared to the uncoated PA6.⁷ These flammability improvements

*Corresponding author e-mail address: rick.davis@nist.gov

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

were explained by the coatings forming an expanded continuous char layer during the combustion, which acts as a protective layer that limits heat and mass transfer and in some cases, extinguishing.

Recently, bio-based materials have been used in LbL coatings. CHI, an aminopolysaccharide derived from deacetylation of chitin that was extracted from shells of lobsters and shrimps, was paired with MMT and applied as a flame-retardant coating on PUF. A 4 % mass, 10 BL CHI/MMT coating on a 1-inch-thick polyester-based PUF, caused a 50% reduction in the pHRR.¹² Since CHI is a natural source of amines, it was then paired with phosphorus-containing materials (phytic acid (PA) and ammonium polyphosphate (APP)) in order to enhance the formation of the protective intumescent char layer.¹⁸ A 30 BL CHI/PA coating (16 % mass gain) on cotton fabric reduced the pHRR and THR by 60 and 76%, respectively and was able to extinguish the flames under vertical flame testing.¹⁹ Performing even better, a 20 BL of CHI/APP (mass gain not reported) on a polyester-cotton blend also suppressed the after glow phenomenon and left a significant residue after the vertical flame testing.²⁰ CHI was also paired with poly(vinyl sulfonic acid sodium salt) (PVS) to reduce the flammability of PUF.²¹ The 10 BL CHI/PVS coating (with 5.5 % mass gain) on a 2.5-cm-thick foam reduced ignition and prevented flame propagation when exposed to a direct torch-like flame. In a cone calorimeter, the coating caused a 52% reduction in pHRR relative to an uncoated control PUF. On the basis of these studies, CHI appears to be a good natural positively charged polymer for use in LbL-assembled FR coatings.

A trilayer (TL) LbL strategy^{11,14} on PUF caused rapid coating growth and a significant reduction in PUF flammability without deteriorating the mechanical and physical properties.¹⁴ Inspired by the benefits reported for the TL strategy and the CHI-based coating, we sought to combine these to create a CHI-based TL FR coating on PUF. The bio-based negatively charged polyelectrolyte selected to pair with CHI and MMT was deoxyribonucleic acid (DNA). DNA is considered an intrinsic intumescent system that contains carbon backbones made with alternating sugars (deoxyribose, as the carbon source) and phosphate groups (as the acid source), and four different nitrogen-rich nucleobases (guanine, adenine, thymine and cytosine, as the blowing agents) that are attached to the sugars.²² DNA from herring sperm was recently used as a novel flame-retardant system on cotton fabric. The 19 % mass coating on the fabric rendered the fabric ignition resistant when exposed to an irradiative heat flux of 35 kW/m².^{22,23} More recently, the same research group paired DNA with CHI as a LbL coating on cotton fabric. In a horizontal flammability test, the 20 BL coating (14 % mass gain) prevented flame propagation and eventually caused the flames to self-extinguish. In a cone calorimeter, a 40% reduction in pHRR was reported.²⁴

In this study, three different natural ingredients, DNA, CHI and MMT are combined to create four different LbL coating formulations

intended to reduce the flammability of PUF. Two BL systems were prepared to compare the barrier/FR effect of clay (CHI/DNA and CHI/DNA+MMT). A TL and quadlayer (QL) systems (CHI/MMT/DNA and CHI/DNA/CHI/MMT) were prepared in an attempt to further improve the processing strategy, efficacy and flammability performance. To the best of our knowledge, this is the first time that DNA is incorporated into LbL assemblies with two other natural materials with the purpose of reducing PUF flammability.

2. Experimental

Unless indicated, all materials were used as-received, and all per cent values are mass fraction per cent (% mass).

2.1 Chemicals and substrates

Poly(acrylic acid) (PAA, Mw ~100 000 g/mol, 35 % mass in water), CHI (low molecular weight (Mw ~50 000 to 190 000 g/mol based on viscosity, 75–85% deacetylated) and DNA (double stranded, partially degraded from herring sperm, Mw ~10 000–30 000 g/mol) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Sodium MMT clay (trade name Cloisite Na⁺) was obtained from Southern Clay Products Inc. (Gonzales, TX, USA). 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). A 0.1 % mass PAA solution (pH 3.2) was prepared and used as the primer layer solution for coating the foam. A 0.5 % mass CHI solution (pH 6) was prepared by dissolving CHI in aqueous hydrochloric acid (pH 2), then adding 1 M sodium hydroxide until a pH of 6 was measured. A 1 % mass DNA solution (pH 5) was prepared by dispersing DNA in deionized (DI) water then adding 1 M sodium hydroxide until a pH of 5 was measured. A 1 % mass DNA and 1 % mass MMT solution (pH 5) was prepared by first creating a 1 % mass DNA solution (as-described above) then adding MMT powder. The pH of the solution was adjusted to 5 by adding 1 M hydrochloric acid. The solution was then lightly agitated overnight using a tumbler/roller. A 1 % MMT suspension (pH 10) prepared by adding MMT powder to DI water, mixed using a magnetic stirrer at high speed for an hour, and then tumbling/rolling (usually overnight) until deposition. Non-flame retarded reticulated PUF (32–39 pores/cm, 22.4 kg/m³ density) was purchased from UFP Technologies (Grand Rapids, MI, USA), then stored as-received in a conditioning room (25% relative humidity, 23±2°C, no sunlight). The PUF was stored in these conditions until cut for coating ((10.2×10.2×5.1) ± 0.1 cm³). After cutting, the PUF was dried in a desiccator for 2 d. The mass of the dry PUF was measured and was used to calculate the mass gained caused by the coating. The PUF was coated within 30 min after the mass was measured.

2.2 LbL deposition

A schematic of the LbL process is shown in Figure 1. There were three coating strategies: 10 BL CHI/DNA and 10 BL CHI/DNA+MMT, 10 TL CHI/MMT/DNA and 5 QL CHI/DNA/CHI/

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

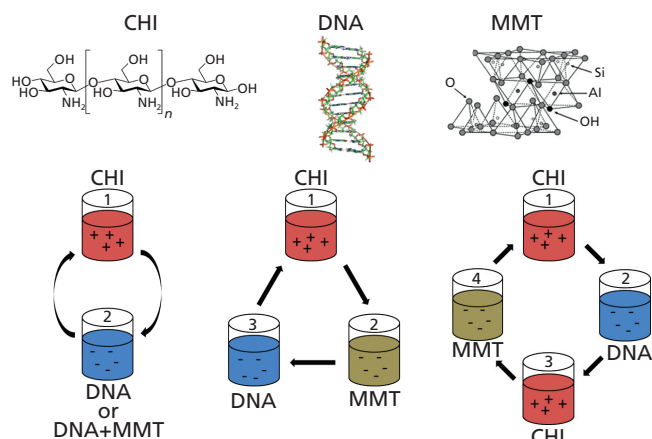


Figure 1. Schematic diagram of the LbL deposition process for producing BL, TL and QL coatings on PUF. BL, bilayer; LbL, layer-by-layer; PUF, polyurethane foam; QL, quadlayer; TL, trilayer

MMT. The first step in all the biocoatings was to prepare the PUF surface and the first layer (CHI) by soaking in three different solutions. This involved soaking the PUF in a solution, squeezing out the excess solution, soaking in water for washing (except the soak in 0.1 N nitric acid), and then squeezing out the excess water. The order of the solutions for preparing the PUF was as follows: (a) Soak in aqueous 0.1 N nitric acid for 5 min, which increased the positive charge density of the foam surface. (b) Soak in 0.1 % mass PAA solution for 5 min, served as the primer layer, which further facilitated adhesion of the subsequent layers. (c) Soak in the CHI solution, as the first layer of all the coating systems. Now the BL, TL and QL biocoatings were deposited. The coating layers were deposited similar to what was described for preparing the PUF (i.e. soak in a solution, squeeze, soak in water, squeeze), except this soaking process was repeated until the desired number of layers was deposited and the soak time was reduced to only 1 min. After the coating was applied, the substrate was placed in a $70 \pm 3^\circ\text{C}$ convection oven overnight, stored in a desiccator for 1 d, and then the mass was measured. The difference between the mass measured prior to and after coating was used to calculate the % mass increase caused by the coating.

2.3 LbL coating characterization

The mass of each monolayer of the biocoatings was measured using a QCM200 quartz crystal microbalance Digital Controller and a QCM25 crystal oscillator (Standard Research System Inc., Sunnyvale, CA, USA). A 5 MHz chromium/gold crystal was soaked in the CHI solution as the first layer of all four systems, then the biocoatings were deposited following the same sequence as described for the PUF. After each monolayer was deposited, the crystal was rinsed with DI water and dried with air. The crystal was placed on the balance and allowed to reach equilibrium prior to taking a measurement (approximately 5 min). The mass change was calculated using the Sauerbrey equation

$$1. \quad \Delta f = C_f \times \Delta m$$

where Δf represents the frequency change, C_f represents the sensitivity factor for the crystal and Δm represents the change in mass per unit area (in gram/square centimeter). Fourier transform infrared spectroscopic (FTIR) spectra of the substrates (before and after flammability testing) were measured with a TENSOR 27 spectrometer (Bruker Optics Inc, Billerica, MA, USA) operating in attenuated total reflectance mode. The samples were scanned 64 times with a resolution of 4 cm^{-1} over the wavenumbers ranging from 4000 to 600 cm^{-1} . Surface images of the biocoatings on PUF were obtained using a Zeiss Ultra 60 field emission-scanning electron microscope (FE-SEM, Carl Zeiss Inc., Thornwood, NY, USA) under 5-kV accelerating voltage. All SEM samples were sputter coated with 6 nm of gold/palladium (60/40% by mass) prior to imaging.

2.4 Thermal and combustion testing

Mass of the postflammability test residues were measured with a TG 449 F1 Jupiter Thermogravimetric analyzer (TGA, Netzsch, Burlington, MA, USA). A 10-mg specimen was maintained at 90°C for 30 min; then, the temperature was increased by $20^\circ\text{C}/\text{min}$ to 850°C (in a nitrogen atmosphere). Flammability was measured using a dual cone calorimeter ($35\text{ kW}/\text{m}^2$ external heat flux with an exhaust flow of 24 l/s) following the standard protocol defined in ASTM E1354-07. The substrate was placed in a pan constructed from aluminum foil with only the top of the specimen exposed to the cone heater. The standard uncertainty is $\pm 5\%$ in heat release rate (HRR) and $\pm 2\text{ s}$ in time.

3. Results and discussion

Prior to applying the biocoatings onto the PUF substrate, the formulations were optimized and the mass growth was monitored using quartz crystal microbalance (QCM). Using QCM, mass growth of each monolayer and for the entire coating assembly was measured for the four DNA-based formulations deposited on a quartz crystal (CHI/DNA, CHI/DNA+MMT, CHI/MMT/DNA and CHI/DNA/CHI/MMT). The CHI/DNA showed a two-stage growth (each stage linear, transition occurred at the eighth layer) (Figure 2), which is aligned with a previous report for the same coating on a silicon wafer that was monitored by FTIR.²⁴ The three other formulations in this report showed either a similar two-stage (CHI/DNA+MMT) or a linear growth (CHI/MMT/DNA and CHI/DNA/CHI/MMT), but because the growths were slower, the pure polymer BL system resulted in the highest QCM mass gain for the same number of monolayers (mass gain: CHI/DNA > CHI/DNA+MMT > CHI/MMT/DNA ~ CHI/DNA/CHI/MMT).

The role of MMT was to improve the FR effect of the polymer formulation.^{1,6,7,12,14,25} MMT added to the DNA solution resulted in what visually appeared to be a well-dispersed and stable suspension,

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

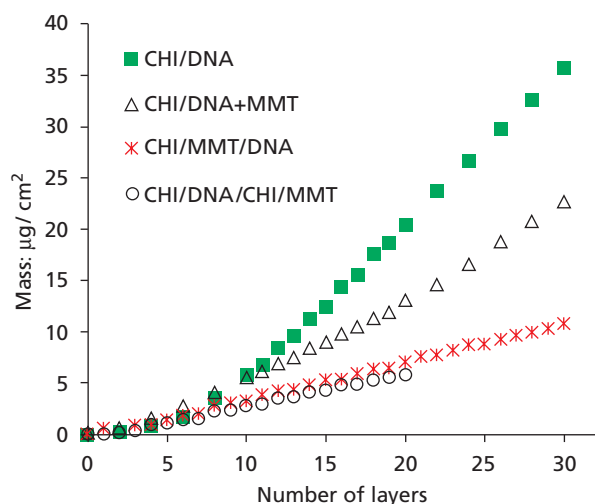


Figure 2. Step growth mass measurement of four different DNA-based layer-by-layer coatings on quartz crystals. DNA, deoxyribonucleic acid

which is necessary for producing a coating with the right attributes to be an effective FR, for example, good MMT dispersion. The QCM growth with MMT was slower than the pure polymer system, which suggests the MMT may be restricting the interdiffusion on CHI and DNA into each other's monolayers. This phenomenon has been previously reported for other polymer systems.¹¹

Since researchers reported an acceleration in coating growth by switching from a BL to a TL strategy,^{11,14} we prepared TL and QL biocoatings (CHI/MMT/DNA and CHI/DNA/CHI/MMT) in an attempt to increase MMT content and coating growth; both factors critical to an effective FR coating.^{14,26} A FR coating produced by the TL approach was first introduced as PEI/MMT/PAA.¹¹ PAA and MMT are both negatively charged, but because the electrostatic repulsion was overcome by the H-bonding,²⁵ the researchers were able to produce a very effective and rapid growing FR coating.¹⁴ It was thought the same principal would apply here (CHI/MMT/DNA) with hydroxyls and acid groups of DNA H-bonding with the oxides and hydroxides on MMT. The QL approach of CHI/DNA/CHI/MMT, was constructed by two different BL systems, CHI/DNA and CHI/MMT, which were studied and applied on cotton fabric²⁴ and polyester-based PUF.¹² Up to eight monolayers, all the coating approaches evaluated in this study showed very similar QCM coating growth. Above eight monolayers, the approaches diverged with the QL and TL continuing to grow at a similar linear rate, and the two BL approaches showing a faster linear growth rate. There were reports indicating that CHI is a relatively hydrophobic and rigid polymer, when pairing with MMT into a BL system, the thickness and mass growth are not as efficient as the PEI/MMT BL system.^{1,12} In addition, similar TL and QL systems used as gas-barrier biocoatings (CHI/MMT/CR (carrageenan, a

negatively charged polysaccharide) and CHI/CR/CHI/MMT)²⁷ both showed significantly slower growth rates when compared to the TL and QL coatings constructed of PEI, PAA and MMT.^{11,26} The linear growth behavior was caused by the relatively strong association of the H-bonding between CR and MMT reducing the diffusion of CR between the coating monolayers.²⁷ Likewise, the same explanation can be used in the DNA-containing TL and QL films. Therefore, the TL and QL approaches did not increase coating growth as much as we expected.

PUF was coated with four different formulations: 10 BL CHI/DNA+MMT, 10 TL CHI/MMT/DNA, 10 BL CHI/DNA, 5 QL CHI/DNA/CHI/MMT. Each coated PUF and uncoated PUF (control) was characterized by TGA, SEM, FTIR, inductively coupled plasma mass spectrometry and tested using cone calorimetry.

The hierarchy mass gained caused by the biocoatings is as follows: CHI/DNA+MMT (16.2%) > CHI/MMT/DNA (8.1%) > CHI/DNA (6.4%) > CHI/DNA/CHI/MMT (4.9%). Normalizing based on the number of monolayers, the coating mass hierarchy at 20 monolayers is CHI/DNA+MMT > CHI/DNA > CHI/MMT/DNA > CHI/DNA/CHI/MMT. This order is different from the mass order measured with QCM. For example, the 10 BL CHI/DNA+MMT and 10 TL of CHI/MMT/DNA coatings were fabricated using the same concentration of each ingredient (1% DNA and 1% MMT and 0.5% CHI). Both have a similar QCM mass growth (mass at 20th monolayer for CHI/DNA+MMT and 30th monolayers of CHI/MMT/DNA); however, the coating mass gain on foam was two times higher with the 10 BL approach than the 10 TL. The faster growth on PUF may be due to the difference in geometry and chemistry of the substrates (flat 2D QCM substrate against macroporous 3D PUF), the completeness of the initial monolayer to coat the substrate, and the extent to which this impacts the deposition of the subsequent monolayers. From this specific case, we learned that QCM is a method best used to evaluate whether a coating can form and what conditions are right for growing the coating, rather than as a measure of the absolute values of thickness and/or mass expected on the PUF.

The topical morphology of these four DNA-base coated PUFs and the control PUF was imaged by SEM (Figure 3). The control PUF has a smooth surface with few features (Figure 3(a)). The polymer-only coated PUF (Figure 3(b)) has a very similar surface except for the presence of a few cracks, presumably due to the mechanical stress from handling. Incorporation of MMT causes the surface to be very rough with an appearance resembling that of reptilian scales. These scale-like features are MMT aggregates, which can be clearly observed on the three clay-based coated PUFs (Figure 3(c)–3(e)). The amount of clay aggregates is related to the amount of the coating on the PUF, therefore, the CHI/DNA+MMT-coated PUF showed the most MMT on the surface, and under the high magnification, MMT platelets can be clearly seen (Figure 3(f)). The presence of MMT on the surface of the three coated PUFs was

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

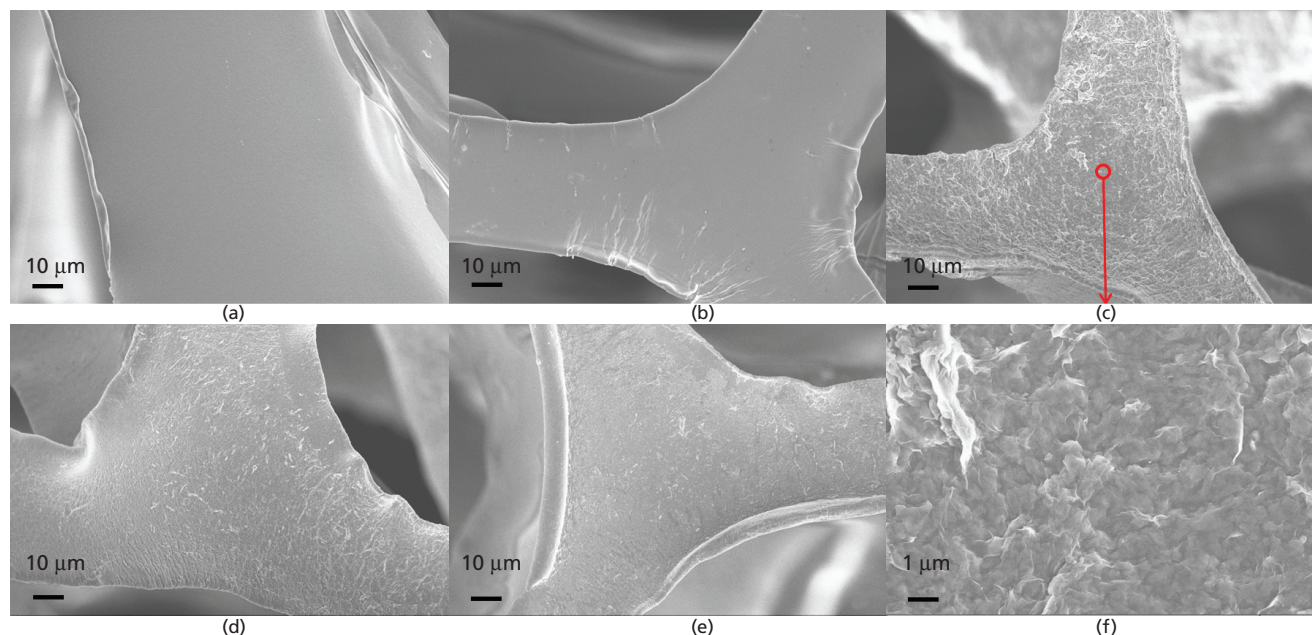


Figure 3. SEM images of (a) control and coated foams of (b) CHI/DNA, (c) CHI/DNA+MMT, (d) CHI/MMT/DNA and (e) CHI/DNA/CHI/MMT at 2000 \times . (f) is (c) under 20 000 \times magnification. CHI, chitosan;

DNA, deoxyribonucleic acid; MMT, montmorillonite; SEM, scanning electron microscopy

verified by FTIR (information can be viewed in Supplementary Data for this measurement).

Thermal stability of uncoated and coated PUFs was assessed with a thermogravimetric analyzer under nitrogen atmosphere (Figure 4). The control (uncoated) PUF showed a two-step degradation. The first stage is the degradation of urethane linkages (between 200 and 250°C) and the volatilization of toluene diisocyanate (TDI).²⁸ The residue is polyol based, which degrades (250–300°C) to produce volatiles containing hydroxyl, carboxyl, carbonyl and ether groups.²⁹ The relative higher mass loss for the second peak indicates the PUF contains more polyol than TDI. In general, the TGA curves of the coated PUF are quite similar to the control indicating the coating had very little impact on the thermal stability. However, there was a difference in the residues at 850°C. The order of the residual masses is as follows: CHI/DNA+MMT (10.6%) > CHI/DNA (6.0%) > CHI/MMT/DNA (4.4%) ~ CHI/DNA/CHI/MMT (4.3%). If the residual mass % is normalized by the coating mass %, then the order of the thermal stability is as follows: CHI/DNA (94%) > CHI/DNA/CHI/MMT (88%) > CHI/DNA+MMT (65%) > CHI/MMT/DNA (54%). Without MMT in the coating, CHI/DNA PUF has the highest residue-to-coating rate, indicating that MMT is not the only residue left at the end of the TGA testing. The thermally more stable CHI/DNA residue suggests that there should be some reactions happened between nitrogen (from CHI and DNA) and phosphorus (from DNA).³⁰

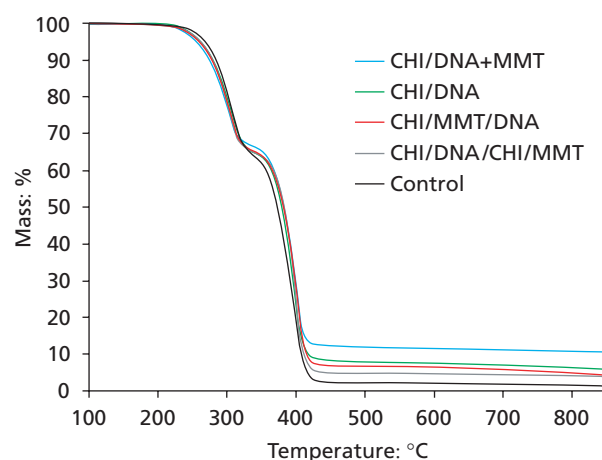


Figure 4. TGA of PUF uncoated (control) and for the four DNA-based coated PUFs. The residual masses are 10.6% for CHI/DNA+MMT PUF, 6% for CHI/MMT/DNA PUF, 4.4% for CHI/DNA PUF, 4.3% for CHI/DNA/CHI/MMT PUF and 1.6% for PUF. CHI, chitosan; DNA, deoxyribonucleic acid; MMT, montmorillonite; PUF, polyurethane foam; TGA, thermogravimetric analyzer

Cone calorimeter is one of the most frequently used tools to measure the flammability of materials. The specimen is exposed to an external heat flux, which forces the specimen to thermally degrade. A spark igniter placed over the specimen ignites the pyrolysis products, initiating combustions. The amount of oxygen

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

combusted is measured and used to calculate the heat generated. Most common parameters of interest are time to ignite the pyrolysis product (TTI), the maximum amount (peak) of heat released during the test (pHRR), the time it takes to get to pHRR after ignition (t-pHRR), the total amount of heat released during the test (THR) and the average amount of heat released during the test (aHRR).

Cone calorimeter flammability tests of the PUF specimens were conducted according to standard protocols (ASTM E-1354) with an external heat flux (35 kW/m^2). Cone HRR curves and relevant test data are provided in Figure 5 and Table 1. The control PUF HRR curve consists of two peaks associated with the combustion of polyisocyanate (pHRR at $371 \text{ kW/m}^2 \pm 17 \text{ kW/m}^2$, smaller peak) and polyol (pHRR at $488 \text{ kW/m}^2 \pm 25 \text{ kW/m}^2$ larger peak). The aHRR is measured as $286 \pm 13 \text{ kW/m}^2$. The PUF is completely consumed (test over) at 118 s. The goal for the biocoatings is to reduce the pHRR and aHRR values, and ultimately, to reduce the fire threat (flammability).

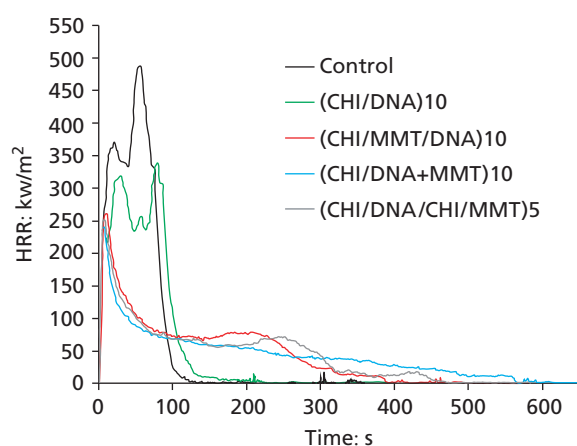


Figure 5. Heat release rate curves of uncoated and DNA-based coated foams. DNA, deoxyribonucleic acid

The HRR curve for the polymer-only (CHI/DNA) PUF is quite similar to the uncoated PUF (e.g. two well-defined HRR peaks). However, the coating does cause a marginal reduction in the flammability, that is, 15 and 31% reduction in the aHRR and pHRR, respectively. Regardless of the layering architecture (BL, TL or QL), incorporation of MMT into the coating causes a significant reduction in flammability. All these MMT-containing DNA-based coating have similar first HRR peaks ($250 \pm 10 \text{ kW/m}^2$), which is the pHRR for these HRR curves. These biocoatings result in a $48 \pm 2\%$ reduction in pHRR, as compared to the control. After the first peak, the HRR drops from approximately $250 \pm 10 \text{ kW/m}^2$ to $77 \pm 4 \text{ kW/m}^2$, due to these MMT biocoatings probably forming a protective residue that limits the transport and release of combustion reactants (fuel), and thermally protects the remaining PUF. This rapid and sustained drop in HRR resulted in a $77 \pm 4\%$ reduction in the aHRR, as compared to the control. Only the CHI/MMT/DNA and CHI/DNA/CHI/MMT biocoatings had a second peak, but compared to the control, this peak was significantly smaller, later, and not considered to be a fire concern. The CHI/DNA+MMT is the only coating that did not have a second peak, possibly related to the amount of MMT loading on each foam sample (measured by inductively coupled plasma optical emission spectroscopy, detail description and calculation are in the Supplementary Data): 3.6% MMT on CHI/DNA+MMT PUF, 1.5% MMT on CHI/MMT/DNA PUF, and 1.1% MMT on CHI/DNA/CHI/MMT PUF. The higher MMT loading (3.6%) along with the absence of the second peak suggests that CHI/DNA+MMT produces a more stable and stronger protective residue. Because of the low MMT loading ($<1.5\%$), the protective residues of CHI/MMT/DNA and CHI/DNA/CHI/MMT have weaker structural integrity and, therefore, form cracks that cause a small increase in the release of combustion products.^{17,31}

Even though the level of fire protection provided by CHI/DNA+MMT (10 BL) is only slightly better than the CHI/MMT/DNA (10 TL) and CHI/DNA/CHI/MMT (5 QL) biocoatings, we consider it the best FR option because it is likely to be

	Coating mass: %	pHRR: kW/m^2	t-pHRR: s	aHRR: kW/m^2	THR: MJ/m^2	Mass loss: %
Control	—	488 ± 25	57	286 ± 13	30.3	100
(CHI/DNA)10	6.4	339 ± 16	80	204 ± 9	26.6	91
(CHI/DNA+MMT)10	16.2	239 ± 8	8	53 ± 3	26.5	82
(CHI/MMT/DNA)10	8.1	260 ± 12	11	77 ± 4	25.4	84
(CHI/DNA/CHI/MMT)5	4.9	251 ± 11	7	69 ± 4	25.5	89

The uncertainty for all values in Table 1 is $\pm 5\%$

aHRR, average heat release rate; DNA, deoxyribonucleic acid; pHRR, peak heat release rate; THR, total amount of heat released during the test; t-pHRR, time taken to get to pHRR after ignition

Table 1. Cone calorimetry data of uncoated and DNA-based coated foams

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

easier, faster and less expensive to fabricate since it uses less depositing solutions, requires less water washes and less number of coating layers.

The postfire residues of the coated PUF were imaged using SEM. The uncoated PUF collapses into a pool and is completely consumed during the test. In contrast, all the coated PUFs retained their prefire cellular structure. This was especially noticeable for CHI/DNA+MMT PUF, presumably because it had the highest coating mass (Figure 6(a)). Under high magnification, the difference in surface morphology can be distinguished. The MMT-containing biocoatings have a surface that appears rough and ‘bubbly’. This is the remnant of the intumescence-like protective layer that formed during the fire test. The surface of CHI/DNA+MMT residues was rough and contained well-defined and large bubble-like formations (Figure 6(b)). The CHI/MMT/DNA and CHI/DNA/CHI/MMT residues were comparatively smoother with more ripple-like features (Figure 6(c)), as compared to CHI/DNA+MMT. These differences are attributed to the extent the coating swells to form the protective residue, which is related to the amount of coating deposited in the PUF. At high magnification, the MMT platelets were more easily viewed, as shown in Figure 6(d). The residue of the CHI/DNA PUF was very different from the other coated PUFs (Figure 6(e) and 6(f)). The cell-like structure still existed, but the residue was more consistent with a powder and was not structurally sound. These observations indicate the MMT is critical to promoting the formation and enhancing the strength of the protective residue.

Combining all the data discussed above, polymer-only (CHI/DNA) coating, even if it has a relatively fast growth rate on a substrate and shows better thermal stability at 850°C under inert atmosphere, when under the cone calorimetry, the coated foam does not perform as well as the other three coated foams that contain MMT. The TL strategy for CHI/MMT/DNA was developed in an attempt to obtain a faster growth rate and better flammability performance, but the growth rate was slower than the CHI/DNA+MMT, which was comprised of the same materials and the same unit dipping cycles, and showed the least pHRR reduction among three MMT-containing recipes. The CHI/DNA+MMT recipe has the highest mass gain (16.2%) on foam, and less dipping process compared to TL coating, and it has the best performance in cone testing. As for the CHI/DNA/CHI/MMT, under the same number of dipping cycles, it deposits the least amount of coating on foam (4.9%), but the flammability performance was comparable to the CHI/DNA+MMT recipe. Regardless, both recipes are attractive candidates for biosustainable flame-retardant coatings on foam as both have the same amount of dipping cycles and processing time, with similar flame-retardant performance, but different coating masses. Depending on the end-use needs in terms of mass restriction on a substrate, both recipes are candidates for biosustainable FR coatings.

4. Conclusions

Four different DNA-based biocoatings were successfully fabricated on PUF. On QCM, CHI/DNA had a linear two-step growth, while CHI/DNA+MMT, CHI/MMT/DNA and CHI/

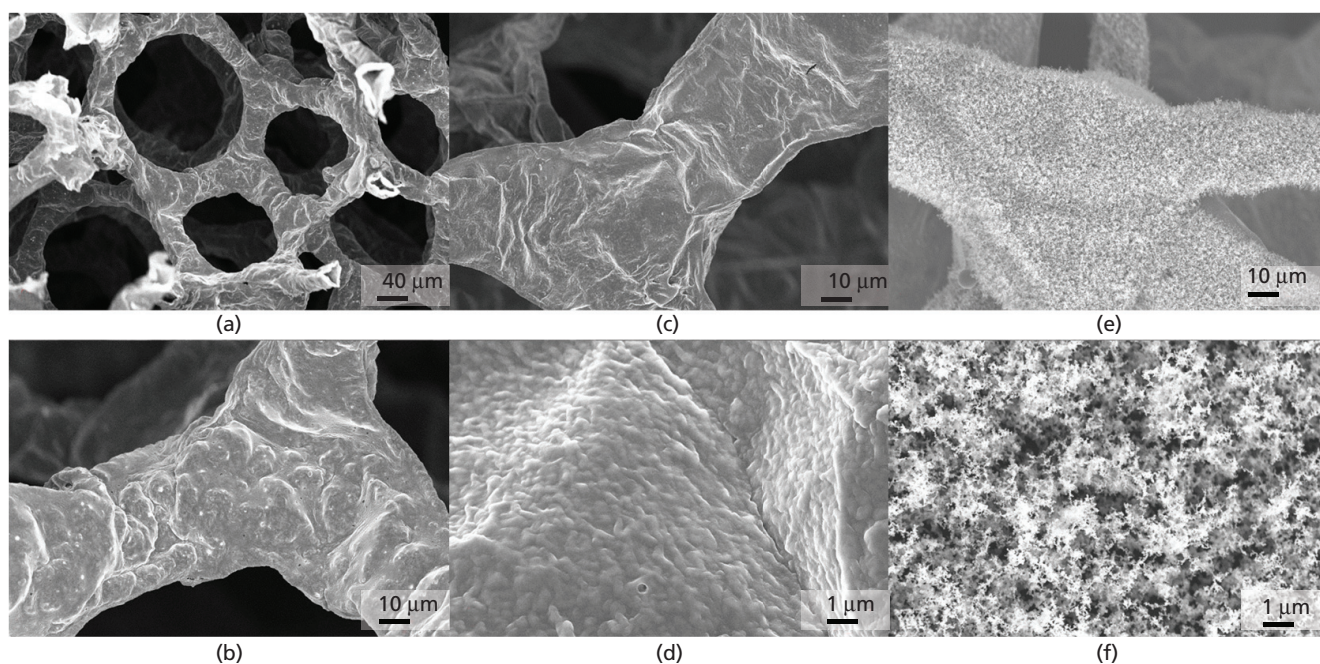


Figure 6. SEM images of postfire test PUF residues: (a, b) CHI/DNA+MMT; (c, d) CHI/DNA/CHI/MMT; (e, f) CHI/DNA. CHI, chitosan;

DNA, deoxyribonucleic acid; MMT, montmorillonite; PUF, polyurethane foam; SEM, scanning electron microscopy

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

DNA/CHI/MMT had a relatively linear and slower growth. On PUF, the coating trends were similar to that observed by QCM, but the coating rates and % mass were much higher on PUF than on the quartz crystal. On PUF, the pure polymer biocoating, CHI/DNA, had relatively better thermal stability under inert atmosphere, and slightly reduced the flammability of PUF, as compared to the uncoated PUF. Incorporation of MMT into the biocoating was critical for fire retardancy. All of the MMT-containing DNA-based biocoatings delivered exceptional fire retardancy of PUF ($48 \pm 2\%$ and $77 \pm 4\%$ reduction in pHRR and aHRR, respectively). The mixed BL (CHI/DNA+MMT) on PUF yielded the greatest reduction in this study and reported by any LbL process (51 and 81% reduction in pHRR and aHRR, respectively).^{9,14} Our previous research has shown these types of FR coatings are sufficiently durable that there is no change in flammability after simulated wear and tear; therefore, durability was not investigated in this study.¹⁴ We are currently planning for full-scale fire tests to determine the performance of furniture containing PUF coated with this DNA-based coating.

Acknowledgements

The authors would like to thank Dr Savelas Rabb for assisting the ICP-OES experiment for the clay mass measurement.

REFERENCES

- Li, Y.-C.; Schulz, J.; Mannen, S.; Delhom, C.; Condon, B.; Chang, S.; Zammarano, M.; Grunlan, J. C. Flame retardant behavior of polyelectrolyte-clay thin film assemblies on cotton fabric. *ACS Nano* **2010**, *4*, 3325–3337.
- Li, Y.-C.; Schulz, J.; Grunlan, J. C. Polyelectrolyte/nanosilicate thin-film assemblies: influence of pH on growth, mechanical behavior, and flammability. *ACS Applied Materials & Interfaces* **2009**, *1*, 2338–2347.
- Carosio, F.; Laufer, G.; Alongi, J.; Camino, G.; Grunlan, J. C. Layer-by-layer assembly of silica-based flame retardant thin film on pet fabric. *Polymer Degradation and Stability* **2011**, *96*, 745–750.
- Alongi, J.; Carosio, F.; Malucelli, G. Influence of ammonium polyphosphate/poly(acrylic acid)-based layer by layer architectures on the char formation in cotton, polyester and their blends. *Polymer Degradation and Stability* **2012**, *97*, 1644–1653.
- Li, Y.-C.; Mannen, S.; Schulz, J.; Grunlan, J. C. Growth and fire protection behavior of poss-based multilayer thin films. *Journal of Materials Chemistry* **2011**, *21*, 3060–3069.
- Laachachi, A.; Ball, V.; Apaydin, K.; Toniazio, V.; Ruch, D. Diffusion of polyphosphates into (poly(allylamine)-montmorillonite) multilayer films: flame retardant-intumescent films with improved oxygen barrier. *Langmuir* **2011**, *27*, 13879–13887.
- Apaydin, K.; Laachachi, A.; Ball, V.; Jimenez, M.; Bourbigot, S.; Toniazio, V.; Ruch, D. Polyallylamine–montmorillonite as super flame retardant coating assemblies by layer-by-layer deposition on polyamide. *Polymer Degradation and Stability* **2013**, *98*, 627–634.
- Carosio, F.; Di Blasio, A.; Alongi, J.; Malucelli, G. Layer by layer nanoarchitectures for the surface protection of polycarbonate. *European Polymer Journal* **2013**, *49*, 397–404.
- Kim, Y. S.; Li, Y.-C.; Pitts, W. M.; Werrel, M.; Davis, R. D. Rapid growing clay coatings to reduce the fire threat of furniture. *ACS Applied Materials & Interfaces* **2014**, *6*, 2146–2152.
- Kim, Y. S.; Davis, R.; Cain, A. A.; Grunlan, J. C. Development of layer-by-layer assembled carbon nanofiber-filled coatings to reduce polyurethane foam flammability. *Polymer* **2011**, *52*, 2847–2855.
- Kim, Y. S.; Harris, R.; Davis, R. Innovative approach to rapid growth of highly clay-filled coatings on porous polyurethane foam. *ACS Macro Letters* **2012**, *1*, 820–824.
- Laufer, G.; Kirkland, C.; Cain, A. A.; Grunlan, J. C. Clay–chitosan nanobrick walls: Completely renewable gas barrier and flame-retardant nanocoatings. *ACS Applied Materials & Interfaces* **2012**, *4*, 1643–1649.
- Kim, Y. S.; Davis, R. Multi-walled carbon nanotube layer-by-layer coatings with a trilayer structure to reduce foam flammability. *Thin Solid Films* **2014**, *550*, 184–189.
- Li, Y.-C.; Kim, Y. S.; Shields, J.; Davis, R. Controlling polyurethane foam flammability and mechanical behaviour by tailoring the composition of clay-based multilayer nanocoatings. *Journal of Materials Chemistry A* **2013**, *1*, 12987–12997.
- Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Harris, R.; Manias, E.; Giannelis, E. P.; Wuthenow, M.; Hilton, D.; Phillips, S. H. Flammability properties of polymer-layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites. *Chemistry of Materials* **2000**, *12*, 1866–1873.
- Gilman, J. W.; Harris, R. H.; Shields, J. R.; Kashiwagi, T.; Morgan, A. B. A study of the flammability reduction mechanism of polystyrene-layered silicate nanocomposite: layered silicate reinforced carbonaceous char. *Polymers for Advanced Technologies* **2006**, *17*, 263–271.
- Kashiwagi, T.; Harris, R. H.; Zhang, X.; Briber, R. M.; Cipriano, B. H.; Raghavan, S. R.; Awad, W. H.; Shields, J. R. Flame retardant mechanism of polyamide 6-clay nanocomposites. *Polymer* **2004**, *45*, 881–891.
- Li, Y.-C.; Mannen, S.; Morgan, A. B.; Chang, S.; Yang, Y.-H.; Condon, B.; Grunlan, J. C. Intumescent all-polymer multilayer nanocoating capable of extinguishing flame on fabric. *Advanced Materials* **2011**, *23*, 3926–3931.
- Laufer, G.; Kirkland, C.; Morgan, A. B.; Grunlan, J. C. Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame-retardant cotton. *Biomacromolecules* **2012**, *13*, 2843–2848.
- Carosio, F.; Alongi, J.; Malucelli, G. Layer by layer ammonium polyphosphate-based coatings for flame

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

- retardancy of polyester–cotton blends. *Carbohydrate Polymers* **2012**, 88, 1460–1469.
21. Laufer, G.; Kirkland, C.; Morgan, A. B.; Grunlan, J. C. Exceptionally flame retardant sulfur-based multilayer nanocoating for polyurethane prepared from aqueous polyelectrolyte solutions. *ACS Macro Letters* **2013**, 361–365.
 22. Alongi, J.; Carletto, R. A.; Di Blasio, A.; Carosio, F.; Bosco, F.; Malucelli, G. DNA: a novel, green, natural flame retardant and suppressant for cotton. *Journal of Materials Chemistry A* **2013**, 1, 4779–4785.
 23. Alongi, J.; Carletto, R. A.; Di Blasio, A.; Cuttica, F.; Carosio, F.; Bosco, F.; Malucelli, G. Intrinsic intumescent-like flame retardant properties of DNA-treated cotton fabrics. *Carbohydrate Polymers* **2013**, 96, 296–304.
 24. Carosio, F.; Di Blasio, A.; Alongi, J.; Malucelli, G. Green DNA-based flame retardant coatings assembled through layer by layer. *Polymer* **2013**, 54, 5148–5153.
 25. Huang, G.; Liang, H.; Wang, X.; Gao, J. Poly(acrylic acid)/clay thin films assembled by layer-by-layer deposition for improving the flame retardancy properties of cotton. *Industrial & Engineering Chemistry Research* **2012**, 51, 12299–12309.
 26. Podsiadlo, P.; Michel, M.; Lee, J.; Verploegen, E.; Kam, N. W. S.; Ball, V.; Lee, J.; Qi, Y.; Hart, A. J.; Hammond, P. T.; Kotov, N. A. Exponential growth of lbl films with incorporated inorganic sheets. *Nano Letters* **2008**, 8, 1762–1770.
 27. Laufer, G.; Kirkland, C.; Cain, A. A.; Grunlan, J. C. Oxygen barrier of multilayer thin films comprised of polysaccharides and clay. *Carbohydrate Polymers* **2013**, 95, 299–302.
 28. Allan, D.; Daly, J.; Liggat, J. J. Thermal volatilisation analysis of tdi-based flexible polyurethane foam. *Polymer Degradation and Stability* **2013**, 98, 535–541.
 29. Grassie, N.; Perdomo Mendoza, G. A. Thermal degradation of polyether-urethanes: Part 1 — thermal degradation of poly(ethylene glycols) used in the preparation of polyurethanes. *Polymer Degradation and Stability* **1984**, 9, 155–165.
 30. Gaan, S.; Sun, G.; Hutches, K.; Engelhard, M. H. Effect of nitrogen additives on flame retardant action of tributyl phosphate: phosphorus–nitrogen synergism. *Polymer Degradation and Stability* **2008**, 93, 99–108.
 31. Kashiwagi, T.; Du, F. M.; Douglas, J. F.; Winey, K. I.; Harris, R. H.; Shields, J. R. Nanoparticle networks reduce the flammability of polymer nanocomposites. *Nature Materials* **2005**, 4, 928–933.

WHAT DO YOU THINK?

To discuss this paper, please email up to 500 words to the managing editor at gmat@icepublishing.com

Your contribution will be forwarded to the author(s) for a reply and, if considered appropriate by the editor-in-chief, will be published as a discussion in a future issue of the journal.

ICE Science journals rely entirely on contributions sent in by professionals, academics and students coming from the field of materials science and engineering. Articles should be within 5000–7000 words long (short communications and opinion articles should be within 2000 words long), with adequate illustrations and references. To access our author guidelines and how to submit your paper, please refer to the journal website at www.icevirtuallibrary.com/gmat