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Exceptionally Flame Retardant Sulfur-Based Multilayer Nanocoating for Polyurethane Prepared from Aqueous Polyelectrolyte Solutions

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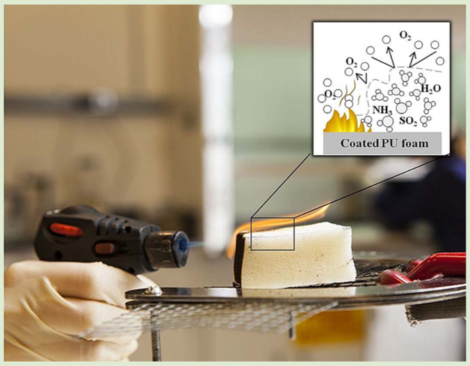
Supporting Information

ABSTRACT: Many current flame retardant (FR) strategies for polymers contain environmentally harmful compounds and/or negatively impact processing and mechanical properties. In an effort to overcome these issues, a effective flame retardant nanocoating comprised of positively charged chitosan (CH) and anionic poly(vinyl sulfonic acid sodium salt) (PVS) was deposited onto flexible polyurethane foam using layer-by-layer (LbL) assembly. This coating system completely stops foam melt dripping upon exposure to the direct flame from a butane torch. Furthermore, 10 CH-PVS bilayers (~30 nm thick) add only 5.5% to the foam's weight and completely stop flame propagating on the foam due to the fuel dilution effect from non flammable gases (e.g, water, sulfur oxides, and ammonia) released from the coating during degradation. Cone calorimetry reveals that this same coated foam has a 52% reduction in peak heat release rate relative to an uncoated control. This water-based, environmentally benign nanocoating provides an effective postprocess flame retardant treatment for a variety of complex substrates (foam, fabric, etc.).



The United States' National Fire Protection Association estimated that upholstery furniture and bedding were the items first ignited in an average of 17300 fires annually (from 2005 to 2009), which resulted in 871 civilian deaths and millions of dollars in property loss.[1,2] This is because the polyurethane foam in furniture and bedding is a highly flammable material, capable of setting a room to flashover (i.e., complete loss) in 5−10 min once ignited.[3,4] As a result, there are strict safety guidelines for home furnishings, such as mattresses and residential upholstered furniture (Consumer Product Safety Commission 16 CFR parts 1632−1634) in order to reduce the threat to human life and economic losses.[5] An additional concern is that some of the most common flame retardant (FR) chemistries (e.g., brominated small molecules compounds) for polyurethane foam are now known to be harmful to human health and the environment,[6,7] resulting in worldwide bans on the use of some of these compounds.[8−10] These concerns have resulted in numerous studies addressing the issue of foam flammability with new FR chemistries in an attempt to achieve both minimal environmental impact and reduced foam flammability.[11−13] Layer-by-layer assembly is a nanocoating technology that has been used to impart nonhalogenated flame resistance to highly flammable substrates like polyurethane foam,[14,15] nylon films,[16] cotton,[17−19] and PET fabric.[20,21]

Layer-by-layer (LbL) assembly is a deposition technique that has been used to grow thin films through consecutive adsorption of oppositely charged polyelectrolytes and nanoparticles onto a substrate.[22−24] This simple procedure is then repeated to deposit a given number of cationic and anionic pairs, known as bilayers (BL). With LbL assembly, nanocoatings are conformally deposited directly onto a surface as a thin layer, which eliminates the challenges associated with processing or adversely modifying mechanical behavior when incorporating FR into the substrate itself.[25,26] In addition to imparting FR, LbL thin films have been deposited to achieve high gas barrier,[27,28] antifouling,[29,30] antireflection,[31,32] self-healing,[33] and low sheet resistance[34,35] on various substrates.

Flame retardants that work in the condensed phase (working to slow fire by addressing the polymer "fuel") most commonly protect objects by forming a protective layer that may contain inorganic particles[36,37] or be an intumescent char.[38,39] LbL deposition provides the opportunity to place all FR at the surface of a substrate, exactly where it is needed, which is a unique advantage. In the present study, a novel flame retardant nanocoating is prepared by pairing chitosan (CH) with poly(vinyl sulfonic acid) sodium salt (PVS; see chemical structures in Figure 1). As this coating degrades, nonflammable gases are released (e.g., SO_2, H_2O, NH_3) that dilute the oxygen concentration at the foam surface, starve the flame, and may serve as a free-radical flame front scavenger. A similar protection mechanism is found with halogenated compounds, which primarily act in the gas phase,[40] and some mineral fillers, which release water and CO_2 endothermically during burning.[41]

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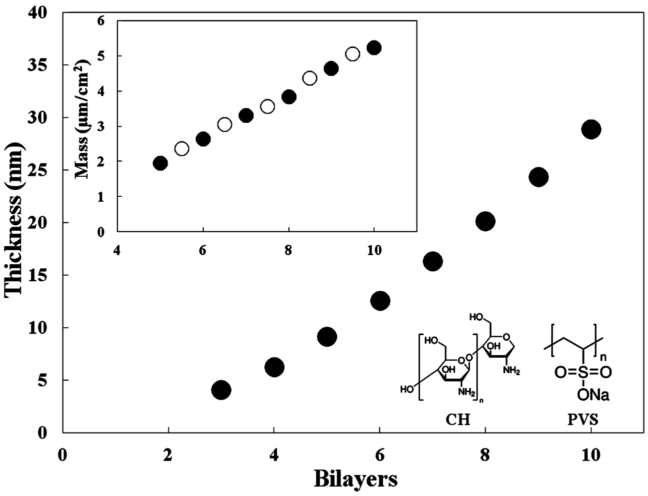

Figure 1. Thickness of CH-PVS assemblies as a function of bilayers deposited. The inset shows accumulated film mass as a function of deposited layers. Empty circles represent CH deposition.

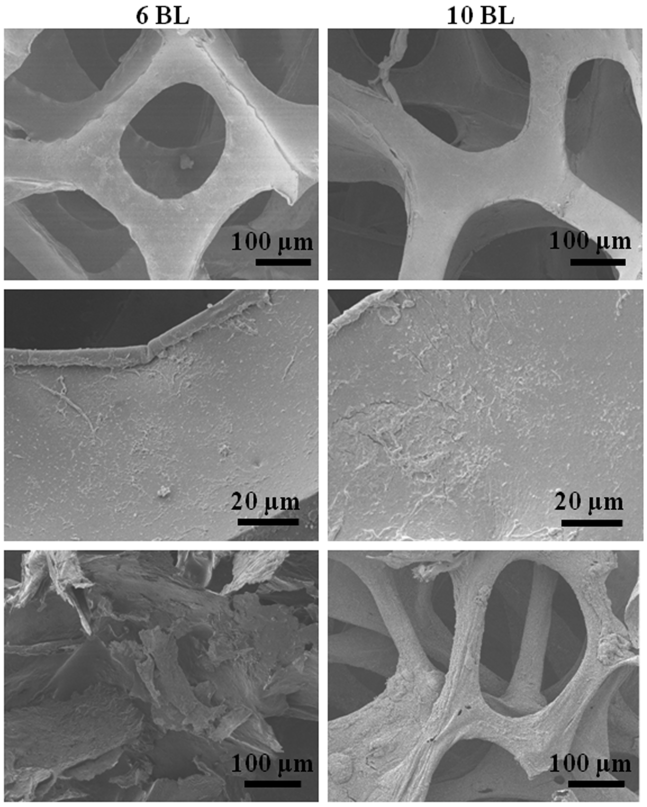

Figure 2. SEM images of coated foam before (top two rows) and after (bottom row) exposure to the flame from a butane torch. The image of coated foam before burning is representative of what is observed throughout the foam's entire thickness.

The present CH/PVS coating is the first of its kind to provide flame retardancy by addressing both heat release and foam dripping, the key fire risks of polyurethane foam, with the use of an environmentally benign, water-based technology.

CH/PVS bilayers were deposited on silicon wafers for thickness measurement, as shown in Figure 1. Chitosan exists in a globular conformation and deposits the thickest at pH 6,[14] which provides the most effective coating with the fewer layers. For consistency, the same pH was used for PVS. The weight growth trend (inset of Figure 1) confirms the linear growth trend and reveals the deposited film composition (60 wt % CH and 40 wt % PVS). This successfully grown CH-PVS recipe was next deposited onto flexible polyurethane (PU) foam in varying numbers of bilayers. The weight added to foam was determined by weighing before and after coating (reported as a percentage of the original mass in Table 1). Figure 2 shows the surfaces of foam coated with 6 and 10 BL of CH-PVS. All coated foams have uniform nanotexture throughout the foam thickness that confirms the conformal nature of LbL deposition (top row). At higher magnification, the nanocoating appears heavier at 10 bilayers, as expected (middle row).

Foam flammability was initially screened by holding the flame from a butane torch on the foam's surface for 10 s. The uncoated foam ignited immediately, formed a melt pool, and was completely consumed. No melt dripping was exhibited by either of the coated foam samples. With a 6 BL CH-PVS nanocoating that added 3.5% to the foam's weight, the flame self-extinguished after it traveled across the outermost surface. Foam coated with a 10 BL nanocoating actually stopped the flame from propagating soon after the torch was removed (see Figure 3a and video in Supporting Information). When examined under higher magnification, the char of burned foam coated with 6 BL consists mostly of damaged and collapsed struts. In contrast, the char of 10 BL coated foam looks more like a dehydrated foam structure, which is probably due to better shielding from the heavier coating (Figure 2, bottom row). It should be noted that this simple screening test is not satisfactory for truly quantifying flame retardancy and fire safe performance.

In an effort to better quantify FR behavior, and understand the influence of these CH-PVS nanocoatings on reducing the flammability of polyurethane foam, cone calorimetry (ASTM E1354, a scientific fire safety engineering testing) was performed on coated samples and an uncoated control. Figure 3 shows the heat-release rate (HRR) curves for control and coated foam samples. A typical curve with two different peaks is observed for the control foam (Figure 3b). The rapid rise to the first peak is associated with the initial "collapse" stage of foam combustion.[3] Subsequent formation of a quickly vaporizing melt pool leads to the second, larger peak heat release rate (pkHRR). The presence of the CH-PVS nanocoating significantly diminishes PU flammability. All coated foam exhibits a slight delay in time to ignition and lower HRR. The HRR curve's shape is changed as well, suggesting a change in PU decomposition mechanism. Coated foam shows no dripping during burning, but it still collapses/shrinks somewhat and changes the heat release curve.

Table 1. Cone Calorimeter Results for Coated and Uncoated Control Polyurethane Foam

sample		weight gain (%)	pkHRR (kW/m²)	avg HRR (kW/m²)	total HR (MJ/m²)	time to pkHRR (s)	FIGRA
control			780	266	17	39	19.9
CH/PVS	6 BL	3.5	465	234	17	54	8.7
	10 BL	5.5	370	201	15.1	49	7.3

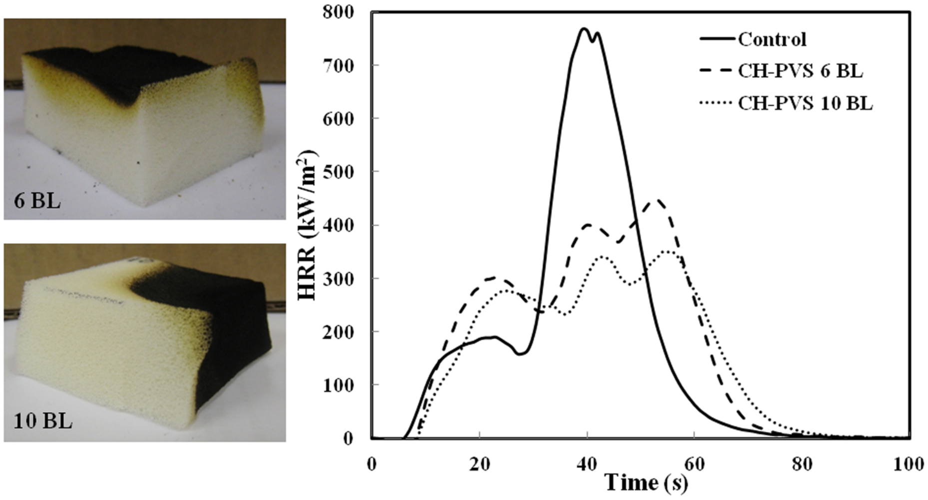

Figure 3. Images of CH-PVS coated foam after the torch burn testing (a) and heat release rate as a function of time, during cone calorimeter testing, for uncoated control and coated foams (b).

Through the use of thermal gravimetric analysis (TGA), which was performed on uncoated control foam and a 100 BL CH-PVS film, it was confirmed that foam and the nanocoating begin to degrade at similar temperatures (220−240 °C). It is likely that the degradation of the coating contributes to the additional heat being released during the first peak. It should be noted that the coating releases only nonflammable gases (water, ammonia, sulfur oxides). FTIR studies on thermal degradation of PVS by Jiang et al. confirmed the evolution of volatile products like water and sulfur dioxide.[42] These nonflammable gases dilute the oxygen supply to the flame and dilute the fuel vapors to reduce the fuel oxidation rates of the foam, which hinders gas-phase ignition and flaming.[43] For this reason, the time to pkHRR was delayed by 10−15 s and the pkHRR was decreased by 40−52% as compared to control PU foam (Figure 3b). The total heat release numbers from the cone calorimeter show that the LbL coatings provide an additional benefit. Total HR is reduced in the LbL foams when compared to the control foam, indicating that the LbL coatings are binding up some of the fuel in the form of char and inhibiting some of the combustion in the vapor phase (evidenced by less total oxygen consumed).

Elemental analysis of the residue left after cone testing showed no obvious S-peaks (mass concentration less than 0.5%), indicating that sulfur was vaporized into nonflammable gas. A study by Deng et al. compared concentration of S and P from FR compounds in the gas and condensed phases.[44] In contrast to phosphorus, which acts mainly in the condensed phase (confirmed by high concentration of P in the residue), sulfur mainly existed in the form of sulfur dioxide and sulfur trioxide in gas products and was not found in liquid products and solid residues. Some studies have demonstrated that sulfur species can also provide a degree of inhibition of $H^\bullet$ or $OH^\bullet$ radicals, which also contributes to lower HR values.[45−47] Between the two coated foams, the 10 BL coating produced the largest reduction (average ∼52%) in peak heat-release rate (pkHRR) and reduced the average heat-release rate (avg HRR) by almost 25%. Another fire safety engineering parameter, fire growth rate (FIGRA), represents the rate of fire growth for a material once exposed to heat. Higher FIGRA suggests faster flame spread and possible ignition of nearby objects. This value was reduced by as much as 63% with a 10 BL CH-PVS nanocoating. These cone calorimeter parameters are summarized in Table 1.

In conclusion, LbL assemblies of CH and PVS were successfully deposited on PU foam without altering its open pore structure. Flames self-extinguished in a simple open-flame test on foam coated with 10 BL of CH/PVS due to the release of nonflammable gases from the components of the coating during degradation. From cone calorimetry data, the peak heat release rate and total heat release show a 52 and 25% reduction, respectively, compared to the control foam, with only 5.5 wt % added. The heat release reductions are significant and likely would slow fire growth in real world fire scenarios, giving people more time to escape or to put out the foam, thus, preventing flashover events.[48] These all-polymer coatings provide a safe and effective alternative for protecting flammable materials without altering their processing and mechanical behavior. There is tremendous opportunity for further improvements through changing the ratio of CH and PVS in the coating and the use of nanoparticles that may act as a synergist and enhance the flame retardant behaviors observed here.

■ EXPERIMENTAL SECTION

Materials. Cationic deposition solutions were prepared by adjusting the pH of deionized water (18.2 MΩ, pH ∼ 5.5) to 2 with hydrochloric acid (HCl) and then adding 0.5 wt % chitosan (MW 50−190 kDa, 75−85% deacetylated) purchased from Aldrich (Milwaukee, WI). This aqueous solution was magnetically stirred for 24 h until the chitosan was completely dissolved. The solution pH was adjusted to 6 with 1 M NaOH just prior to deposition. Anionic solutions were prepared by adding 2.0 wt % of poly(vinylsulfonic acid, sodium salt) (Aldrich) to deionized water and rolling the solution for 24 h. Prior to deposition, the pH of PVS was also adjusted to 6 with 1 M HCl. Single-side-polished (1 0 0) silicon wafers (University Wafer, South Boston, MA) were used as the substrate for film thickness characterization. Polyether-based polyurethane (PU) foam type 1850 (Future Foams, High Point, NC), with a density of 28 kg/m^3 and without flame-retardant additives, was used for the flammability experiments.

Layer-by-Layer Deposition. Prior to deposition, the silicon wafers were rinsed with acetone and deionized water, and then dried with filtered air. Foam samples were dipped into a 1 wt % poly(acrylic acid) solution (pH 2, MW 100 kDa; Aldrich) for 30 s as a primer layer to improve adhesion. Substrates were then alternately dipped into the positive (i.e., CH) and negative (i.e., PVS) mixtures. Initial dips were 5 min each, while subsequent dips were for 1 min. Each dip was followed by rinsing with deionized water and, in the case of the silicon wafer, drying with air. Foams were squeezed by hand to expel liquid as an alternative to the traditional drying step. After the desired number of bilayers was deposited, foam samples were dried at 80 °C in an oven for 2 h before testing.

Characterization of Film Growth, Structure, and Properties. Film thickness was measured with an alpha-SE Ellipsometer (J.A. Woollam Co., Inc., Lincoln, NE). The weight per deposited layer was measured with a Maxtek Research Quartz Crystal Microbalance (RQCM) (Infinicon, East Syracuse, NY) with a frequency range of 3.8−6 MHz, in conjunction with 5 MHz quartz crystals. Surface images of coated foam samples were acquired with a field-emission scanning electron microscopy (FESEM; Model JSM-7500F, JEOL, Ltd., Tokyo, Japan). A platinum coating of 6 nm was deposited on all samples prior to SEM imaging, to prevent charging. Foam flammability was evaluated through exposure to direct flame from a butane microtorch (Model ST2200, Benzomatic, Huntersville, NC) for 10 s (the approximate blue flame temperature is 2400 °F). The thermal stability of uncoated foam and 100 BL CH-PVS coating was measured with a Q50 Thermogravimetric Analyzer (TA Instruments, New Castle, DE) under air from room temperature to 600 °C, at a heating rate of 20 °C/min. Cone calorimeter testing was performed at the University of Dayton Research Institute using an FTT Dual Cone Calorimeter at one heat flux (35 kW/m^2), with an exhaust flow of 24 L/s, using the standardized cone calorimeter procedure (ASTM E-1354−10). Testing was done in triplicate and samples were wrapped in aluminum foil only (no frame and grid). XPS analyses were carried out with a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer to obtain elemental content of char.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting videos. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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