Clay-Filled Polyelectrolyte Complex Nanocoating for Flame-Retardant Polyurethane Foam

Bethany Palen, Thomas J. Kolibaba, Jacob T. Brehm, Ruiqing Shen, Yufeng Quan, Qingsheng Wang, and Jaime C. Grunlan*

ABSTRACT: Polyurethane foam (PUF) is a highly flammable material typically used for cushioning in furniture and automobiles. A polyelectrolyte complex coating containing polyethylenimine, ammonium polyphosphate, and halloysite clay was applied to PUF using a two-step deposition process in an attempt to reduce its flammability. Electron microscopy confirms that this conformal thin film preserves the porous morphology of the foam and adds 20% to the foam’s weight. Directly exposing coated foam to a butane torch flame yields a 73% residue after burning while keeping the internal structure of the foam intact. Cone calorimetry reveals a 52.5% reduction in the peak heat release rate (pkHRR) of the clay-based coating compared to that of the uncoated foam. This significant reduction in pkHRR and preservation of the porous structure of the foam highlights the utility of this easy-to-deposit, environmentally benign treatment to reduce the foam’s flammability.

1. INTRODUCTION

Polyurethane foam (PUF) is an extremely flammable material commonly found in household furniture such as mattresses, couches, and chairs. From 2013 to 2017, home fires first ignited by upholstered furniture were the leading cause of home fire deaths and accounted for $243 million in property damage. While burning, PUF releases a great deal of smoke and melt drips, which can cause further spread of the flame. Finding a way to increase the flame-retardant (FR) behavior of PUF is crucial to minimize the destruction caused by household fires. The addition of halogenated compounds to PUF has been explored due to their ability to reduce the flammability of various textiles, but recent studies have shown these compounds to have severe toxicity issues, necessitating the development of alternative nonhalogenated FR coatings and additives.

Layer-by-layer (LbL) assembly is a popular coating technique in which cationic and anionic polymers or nanoparticles are alternately deposited onto a substrate and typically held together via electrostatic interaction. Coatings deposited by this method have had tremendous success in increasing the fire protection of foam by using a variety of polyelectrolytes in conjunction with nanomaterials such as carbon nanotubes, graphene oxide, and vermiculite clay. These materials not only reduce the flammability of the material but can also reduce the smoke production the occurs during the burning process, even after condition. Additionally, coated foams have been shown to maintain effective FR behavior following compression testing that restores flexibility (in cases where the coating adds stiffness). While LbL deposition is a relatively simple process, it can require an impractical number of processing steps to achieve effective FR behavior, which limits its commercial potential.

Polyelectrolyte complex coatings (PECs), composed of oppositely charged polymers, can be deposited in just two steps. First, the complex is made water-soluble by manipulating pH, concentration, and ionic strength and deposited on a substrate. Subsequent “curing” with a buffer solution yields excellent flame-retardant properties when appropriate FR materials are applied to various textiles. In this study, a first-ever clay-filled polyelectrolyte complex consisting of polyethylenimine (PEI), ammonium polyphosphate (APP), and halloysite clay (HNT) is deposited onto PUF with this two-step process. The coating reduces the peak heat release rate (HRR) of the foam by 52.5% while only increasing the foam’s weight by 20%. Additionally, the structure of the foam is preserved and melt dripping is eliminated when the coated sample is exposed to a direct flame. This coating is a simple, easy-to-deposit, environmentally benign treatment to reduce the foam’s flammability.
Figure 1. Schematic of the polyelectrolyte complex coating procedure.

Figure 2. SEM images of (a) uncoated polyurethane foam and foam coated with (b) PEI/APP and (c, d) PEI/APP/HNT. Panel (d) shows a magnified portion of (c), as indicated by the orange border.

Figure 3. Postburn images of (a) PEI/APP and (b) PEI/APP/HNT-coated PUF. Cross-sectional SEM images of (c) PEI/APP and (d, e) PEI/APP/HNT-coated PUF after burning (magnified locations (d, e) are indicated in (b)). Photographs are courtesy of Bethany Palen. Copyright 2020.
effective, and environmentally benign approach toward achieving fire resistance of polyurethane foam.

2. RESULTS AND DISCUSSION

2.1. Surface Morphology. A schematic of the process to deposit the flame-retardant coating is shown in Figure 1. The buffer-cured PEC was deposited onto the foam in just two steps, in contrast to the numerous steps required for layer-by-layer assembly. This greatly reduces the processing time and steps necessary to deposit an effective flame-retardant coating. Scanning electron microscope (SEM) images show that the porous structure of the foam is maintained after coating, as shown in Figure 2. It is also apparent that the once smooth surface of the uncoated foam (Figure 2a) is textured following the application of the nanocomposite (Figure 2b). The surface of the PEI/APP/HNT film (Figure 2c,d) appears significantly rougher than that of the PEI/APP control coating, which can be attributed to the presence of the tubular clay. Much like the layer-by-layer approach, this buffer-curing process generates a conformal nanocoating on the polyurethane foam.

2.2. Flame-Retardant Behavior. A direct flame test was used to evaluate the performance of the PEC coating. Coated and uncoated foam had similar after-flame times of about 50 s, but there are some notable differences in their performance. The initial 10 s flame burns directly through the uncoated foam and it continues to burn after the flame is removed, exhibiting a significant amount of smoke release and melt dripping. This melt dripping is very problematic, as it contributes to the spread of the fire via secondary ignition. As shown in Figure 3a, the PEI/APP coating was not able to retain its original structure and only yielded a 35% residue. In contrast, a cross-sectional image in Figure 3b of the coated foam residue shows that the formation of the char layer (red) protects a substantial portion of the inner foam (blue). SEM images confirm the disappearance of the porous PUF structure after burning (Figure 3c). In contrast, the PEI/APP/HNT coating exhibits no melt dripping and the porous structure of the foam is not compromised (Figure 3d,e). While the uncoated foam has virtually no residue after flame testing, the clay-coated foam has a residue of 73%.

Standard cone calorimetry measurements (ASTM E-1354-12) confirm the effectiveness of this PEI/APP/HNT nanocomposite coating. The oxygen consumption during combustion is used to measure the heat release rate (HRR) of a given material, which provides insight into how it will behave in a fire. As shown in Figure 4, the uncoated PUF has two distinct degradation steps with peaks of ~225 and ~375 kW m⁻². The first degradation step is the hard-segment degradation of the polyurethane foam into alcohols, amines, isocyanates, and olefins. The second degradation step is linked to polyol degradation. The hard-segment degradation is responsible for a large amount of the smoke production that occurs during fires, while the undesired melt dripping can be attributed to the polyol degradation. The PEI/APP coating without clay has a nearly identical degradation pattern to the uncoated PUF, with a slightly elevated peak HRR. Without clay, the polymers in the complex degrade alongside the foam, which modestly increases the HRR. The PEI/APP/HNT-coated foam shows a significant reduction in the peak HRR (52.5%) compared to the uncoated foam, with only a 20% weight gain (Table 1). It is noteworthy that this clay-containing coating delays the second degradation step by nearly 1 min and dramatically reduces the HRR. Delaying the second degradation step means slowing down the spread of the fire and allowing more time for escape or rescue. The coated foam’s char formation during the first decomposition step protects it against further degradation, while the uncoated and PEI/APP-coated foams completely decompose.

3. CONCLUSIONS

A water-soluble clay-based polyelectrolyte complex coating, composed of polyethylenimine, ammonium polyphosphate, and halloysite clay, was deposited onto PUF using a two-step process. The resulting nanocomposite coating is conformal and significantly reduces the flammability of PUF, with only a 20% weight gain. After undergoing a direct flame test, SEM images reveal that the porous morphology of the foam remains intact while yielding a 73% residue. Cone calorimetry demonstrates that the peak HRR is reduced by more than 52% compared to the uncoated foam. This simple halogen-free coating process makes the industrial-scale fire protection of polyurethane foam much more feasible and safe for the environment.

4. EXPERIMENTAL SECTION

4.1. Materials. Branched polyethylenimine, halloysite nanotube clay, poly(acrylic acid) (PAA), citric acid, nitric acid, and sodium hydroxide pellets were purchased from Sigma-Aldrich (Milwaukee, WI). Ammonium polyphosphate was supplied by Century Multitech, Inc. (Flushing, NY). Flexible polyurethane foam (0.028 g cm⁻³) was supplied by Century Multitech, Inc. (Flushing, NY). 2 M HNO₃ was used to adjust the 1% PAA solution to pH 2, while the citric acid buffer was adjusted to a pH of 3 using 5 M NaOH.

4.2. Preparation and Deposition of Polyelectrolyte Complex. A solution of 4 wt % polyethylenimine in water and a solution of 8 wt % ammonium polyphosphate in water, with and without 10 wt % halloysite, were each placed on mechanical rollers to allow the polymer to fully dissolve. Subsequently, HNT-containing solutions were submerged in an ice bath and tip-sonicated at 15 W for 30 min (Model VCX750; Sonics & Materials, Inc., Newtown, CT). The two solutions were then combined to form the water-soluble polyelectrolyte complex solution. A 10.2 × 10.2 × 2.5 cm³ piece of PUF was primed with a 1% poly(acrylic acid) solution by submerging the entirety of the sample into the solution for 5 min. The substrate was then similarly dipped into the polyelectrolyte complex solution for 1 min and dried for 1 h at 70 °C. The foam was immersed in a 100 mM citric acid buffer for 5 min, followed by a 5 min distilled water rinse and once
Table 1. Cone Calorimeter Data for Coated and Uncoated Foam

| coating          | weight gain (%) | pkHRR (kw m⁻²) | THR (MJ m⁻²) | TSR (m² m⁻²) |
|------------------|-----------------|----------------|--------------|--------------|
| uncoated         |                 | 377 ± 11       | 19.1 ± 0.3   | 110 ± 60     |
| PEI/APP          | 5.6 ± 1.5       | 394 ± 41       | 19.2 ± 1.0   | 400 ± 80     |
| PEI/APP/HNT      | 20.0 ± 2.9      | 179 ± 3        | 18.5 ± 1.7   | 330 ± 210    |

again dried for 16 h at 70 °C. Immediately following immersion into each solution, the substrate was squeezed three times to ensure complete liquid uptake. After the completion of each dipping step, the substrate was wrung out using mechanical rollers (Figure 1).

4.3. Characterization. A direct flame test was performed on the neat PUF and coated samples (5 × 5 × 2.5 cm³) by exposing the foam to a handheld butane torch flame (1400 °C) (Bernzomatic ST2200, Worthington Industries, Columbus, OH) for 10 s. The inner blue flame was adjusted to a length of ~2 cm, and the torch was held so that the entirety of the sample was ~5 cm. Cone calorimetry followed ASTM E-1354-12. Samples (10.2 × 10.2 × 2.5 cm³) were placed in aluminum foil and subjected to a heat flux of 35 kW m⁻². Samples were sputter-coated using 5 nm of platinum/palladium alloy prior to scanning electron microscope (SEM) imaging (FESEM, Model JSM-7500, JEOL; Tokyo, Japan).

■ AUTHOR INFORMATION

Corresponding Author
Jaime C. Grunlan – Department of Chemistry, Department of Materials Science and Engineering, and Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United States; orcid.org/0000-0001-5241-9741; Email: jgrunlan@tamu.edu

Authors
Bethany Palen – Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States
Thomas J. Kolibaba – Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States
Jacob T. Brehm – Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United States
Ruiqing Shen – Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843, United States
Yufeng Quan – Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843, United States
Qingsheng Wang – Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05354

Author Contributions
†T.J.K. is the co-first author.

Notes
The authors declare no competing financial interest.

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