

NIST Technical Note 1674

**Fabrication, Characterization and
Flammability Testing of Carbon
Nanofiber Layer-By-Layer Coated
Polyurethane Foam**

Rick Davis
Yeon Seok Kim

September 2010

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Rick Davis
Yeon Seok Kim
*Fire Research Division
Engineering Laboratory*

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U.S. Department of Commerce
Gary Locke, Secretary

National Institute of Standards and Technology
Patrick D. Gallagher, Director

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National Institute of Standards and Technology Technical Note 1674
Natl. Inst. Stand. Technol. Tech. Note 1674, 31 pages (September 2010)
CODEN: NTNUE2

Abstract

This is the first reported use of Layer-by-Layer (LBL) assembly to fabricate thin film coatings on polyurethane foam, of incorporating carbon nanofibers (CNF) into LBL fabricated coatings, and of using LBL fabricated coatings to reduce the flammability of polyurethane foam. The (359 ± 36) nm thick four bilayer coating of polyethyleneimine/CNF (cationic layer) and poly(acrylic acid) (anionic layer) contained (50.9 ± 0.1) mass fraction % CNF. This CNF coating covered the entire internal and external surfaces of the porous foam. The distribution of the CNFs was non-uniform on the microscale with regions of large CNF aggregation to regions with individual CNFs and isolated regions that appeared to contain no CNFs. Even though the microscopic CNF distribution was non-uniform, the macroscopic CNF network armor that was generated from this LBL process significantly reduced the flammability of the foam; i.e., $55\% \pm 6\%$ reduction in total heat release and peak heat release rate. This reduction caused by the CNF coating is 50% better than previously reported by incorporating twice as much CNFs directly into the foam and 12% to 47% greater than other technologies currently used to reduce foam flammability.

Keywords

Layer-By-Layer assembly; thin films; carbon nanofibers; polyurethane foam; Cone Calorimetry; flammability; soft furnishings

Acknowledgements

Appreciation is extended to Dr. Alexander Morgan of the University of Dayton Research Institute for assisting with Cone Calorimetry and Prof. Jaime Grunlan from Texas A&M for his assistance with the Layer-by-Layer coatings.

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List of Acronyms

ANPR	Announced notice of proposed rulemaking
ASTM	American Society for Testing Materials
BF	Barrier fabric
BL	Bilayer
CNF	Carbon nanofibers
CNF/PUF	Carbon nanofiber coated standard polyurethane foam
CPSC	Consumer Product Safety Commission
DI	Deionized (water)
LBL	Layer-by-Layer assembly/coating
NIST	National Institute of Standards and Technology
PAA	Poly(acrylic acid)
PEI	Branched Polyethyleneimine
PHRR	Peak heat release rate
PUF	Standard polyurethane foam
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
THR	Total heat release

1. Introduction

The estimated annual total societal cost of fire to the United States economy is \$340 billion[1] with fires in structures, such as single and multi-family dwellings, and fixed mobile homes, accounting for an estimated \$90 billion of this total cost [2]. There are a reported 135,000 residential home fires annually, 5% of which are accounted for by soft furnishings (mattresses, bedclothes, upholstered furniture) as the first item ignited. However, first item ignited soft furnishings are annually estimated to account for a disproportionately high amount of fire losses (33% of the civilian fatalities, 18% of civilian injuries, and 11% of the property losses) [3,4]. Even though no amount of money can adequately represent personal injury and deaths, the estimated annual societal cost of fire associated with soft furnishings as the first item ignited is estimated at \$5 billion using the \$5 million per fatality and \$230,000 per injury used by Hall [1] in calculating the total societal cost of fire.

The Consumer Products Safety Commission is responsible for existing and proposed United States flammability regulations of soft furnishings [5,6,7], which are based on extensive research and review of the fire behavior of soft furnishings [8,9,10,11,12,13,14,15,16,17,18,19,20]. These regulations, as well as the introduction of Reduced Ignition Propensity cigarettes [21], are expected to significantly reduce the \$5 billion annual cost of soft furnishing fires. In order to comply with the 2007 open flame mattress regulation (CPSC 16 CFR 1633 [6]), manufacturers inserted fire blocking barrier fabrics around the soft polyurethane foam core. In house research (unpublished) suggests that upholstered furniture manufacturer's will likely also require fire blocking barrier fabrics in order to comply with the proposed open flame/smoldering ignition regulation for upholstered furniture (CPSC ANPR 16 CFR 1634 [7]). Similar to manufacturers of other fire safe products, the technical and engineering options to comply with national and/or international fire performance regulations are quickly diminishing because of mandated sustainability regulations, such as REACH[22] and EcoLabel [23], for consumer products.

Layer-by-Layer (LBL) assembly has been extensively studied for the past 30 y as a methodology to create multifunctional films generally less than 1 μm thick [24,25,26]. The thin film coatings were commonly fabricated by alternate deposition of a positively charged layer and negatively charge layer (called a bilayer, BL). By taking advantage of electrostatic, H-bonding [27], covalent bonds [28], and/or donor/acceptor interactions, these bilayers were continuously assembled on the surface of flat substrates. The LBL process is quite flexible and robust, which allows it to be tuned for specific coating characteristics and for coating a range of substrate types. For example, altering the concentration, pH, and/or temperature of the LBL solutions can result in a 1 nm rather than 100 nm thick BL [29,30].

LBL thin films have been used in an extensive breadth of applications, such as oxygen barriers [31] and sensors [32], and have useful properties, such as antimicrobial [33] and antireflection [34]. A more recent application, which is directly aligned with the research presented in this manuscript, was LBL clay coatings (sodium exchanged montmorillonite) of cotton fabric to improve the fire performance characteristics of this textile [26]. Clay has been extensively studied in LBL thin films [31,35,36] and, when used as an additive filler, has been shown to simultaneously improve the mechanical and fire performance attributes of polymers [37,38,39].

The uniqueness of Li's research is the concept of improving fire performance by using LBL assembly and creating LBL clay coatings on cotton fabric (clay/cotton) [26]. The results are exciting in that Li achieved complete and uniform high quality clay based coatings on cotton. In addition, the clay coatings resulted in a significant retention of fabric like char after conducting vertical burn tests and there was no or less ember afterglow when the flame was removed. These results suggest the coating may better prevent thermal and flame penetration from reaching and igniting the foam (PUF), and therefore, the clay/cotton may reduce fire spread in residential homes if used in soft furnishings.

Carbon nanofibers (CNFs) are cylindrical nanostructures constructed of stacked graphitic cones or cups. Compared to carbon nanotubes (CNT), CNFs can be at least an order of magnitude larger with a diameter and length in the range of 5 nm to 300 nm and 0.1 μm to 1000 μm , respectively. Due to the intrinsic electrical, thermal, and mechanical properties of CNFs, the thermal and electrical conductivity, tensile and compressive strength, ablation resistance, damping properties, and flammability of polymers [40] have been significantly altered with incorporation of CNF [41].

Zammarano recently reported a reduction in PUF flammability by the incorporation of CNFs directly into the polyurethane matrix [40]. At a 4 mass fraction % CNFs loading, the CNFs formed a network structure that reduced the peak heat release rate (PHRR) by 35% and prevented melt dripping, which in a real fire scenario, could result in an additional 30% reduction in PHRR. The approach of incorporating CNFs into the PUF has a few potential drawbacks. For example, commercialization may be difficult as the foam manufacturing process is extremely sensitive to small changes in recipe, especially the presence of solid particles, and the manufacturing conditions.

Another potential drawback is based on the mechanism by which nanoparticles are believed to reduce polymer flammability [42]. It has been proposed the reduction in flammability primarily results from the formation of a char at the surface that thermally protects the polymer and prevents volatilization of polymer degradation products. Since the nanoparticles are dispersed and distributed throughout the polymer matrix, it takes time for enough of the polymer to pyrolyze and nanoparticles to migrate to the surface that the protective char is formed.

The research presented in this manuscript is unique in that it is the first published report of fabricating carbon nanofiber (CNF) based thin films/coatings using LBL assembly, of fabricating LBL coatings on foam (polyurethane foam, PUF), and of altering the fire performance attributes of foam using LBL fabricated coatings. The large CNF dimensions are undesirable for typical applications of LBL coatings as the coating thickness is generally comparable to the CNF dimensions and it facilitates aggregation both in the LBL fabrication solutions and in the coatings. However, for reducing flammability, the larger dimensions may enable the formation of a CNF network armor that protects the foam. The LBL approach, we believe, is ideal for reducing the flammability of foam as it may more quickly form the char-like armor because the high concentration of nanoparticles are already at the surface rather than randomly mixed throughout the polymer. This approach may also be more commercially viable as it is a post-foam manufacturing process. Provided are the details of fabricating CNF coated polyurethane

foam (CNF/PUF) using LBL, the physical characteristics of the LBL CNF coatings on PUF, and the measured fire performance of PUF and CNF/PUF.

2. Experimental [43,44,45]

Unless otherwise indicated all measured values are reported with a 2σ standard uncertainty.

2.1. Materials

Unless otherwise indicated all materials were used as-received from the supplier. Branched polyethylenimine (PEI, branched, M_w of 25,000 g/mol) and poly(arylic acid) (PAA, M_w of 100,000 g/mol) was obtained from Sigma-Aldrich. PR-24-XT-PS carbon nanofibers (CNF, average diameter = 100 nm, length was 30 μ m to 100 μ m) were obtained from Pyrograf Products Incorporated.

The standard (untreated) polyurethane foam (PUF) [46] coated in this study was stored as-received from the supplier (cardboard box with no packaging material at $25\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$). On the day of coating, nine substrates (length/width/height of $(10.2\text{ cm} / 10.2\text{ cm} / 5.1\text{ cm}) \pm 0.1\text{ cm}$) were cut from a single as-received substrate (length/width/height of $(30.6\text{ cm} / 30.6\text{ cm} / 5.1\text{ cm}) \pm 0.1\text{ cm}$). These smaller substrates were rinsed and wringed out (discussed below in the coating process) to remove debris and other extractables ($0.6\text{ mass fraction \%} \pm 0.1\text{ mass fraction \%}$). After drying, the post-extraction mass of these substrates was $12.669\text{ g} \pm 0.316\text{ g}$.

2.1.1. Polyelectrolyte stock solutions of PEI (cationic) and PAA (anionic)

The polyelectrolyte ($0.1\text{ mass fraction \%} \pm 0.03\text{ mass fraction \%}$) and deionized (DI, $< 0.5\text{ }\mu\text{S}$) water solutions were prepared as follows. A 2 L glass container was charged with DI water (1300 mL) and PEI ($0.1\text{ mass fraction \%} \pm 0.03\text{ mass fraction \%}$, $1.3\text{ g} \pm 0.4\text{ g}$). This PEI cationic stock solution was slowly agitated for 6 h at room temperature before using. The preparation of the PAA anionic stock solution was similar to the PEI cationic solution, except PAA ($0.1\text{ mass fraction \%} \pm 0.03\text{ mass fraction \%}$, $1.3\text{ g} \pm 0.4\text{ g}$) was used instead of PEI. The pH value was 10 and 3 for the PEI and PAA solutions, respectively.

2.1.2. CNF/PEI cationic suspension

The CNF/PEI suspension in DI water was prepared by charging a plastic bottle (250 mL) with the PEI cationic stock solution ($150\text{ mL} \pm 1\text{ mL}$) then adding CNF powder ($0.050\text{ mass fraction \%} \pm 0.003\text{ mass fraction \%}$ relative to total PEI stock solution (600 mL), $0.30\text{ g} \pm 0.02\text{ g}$). The suspension was sonicated at 40 watts for 1 h with the temperature never exceeding $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$. The sonicated suspensions was diluted with more PEI stock solution (450 mL) and was manually agitated for $3\text{ min} \pm 1\text{ min}$. The CNF/PEI suspension was used immediately for coating the PUF.

2.2. CNF coating methodology

CNF/PUF fabrication took approximately 30 min per specimen (14 min for first bilayer and

15 min for the remaining 3 bilayers). In general, the fabrication process was alternately depositing cationic (CNF and PEI) and anionic (PAA) layers on the surface of the PUF and removing unbound material (polymer and CNF) by rinsing with DI water and wringing out the excess water several times (Figure 1 and Figure 2). The process of removing excess water using a convection oven and dessicator extended over a period of 3 d.

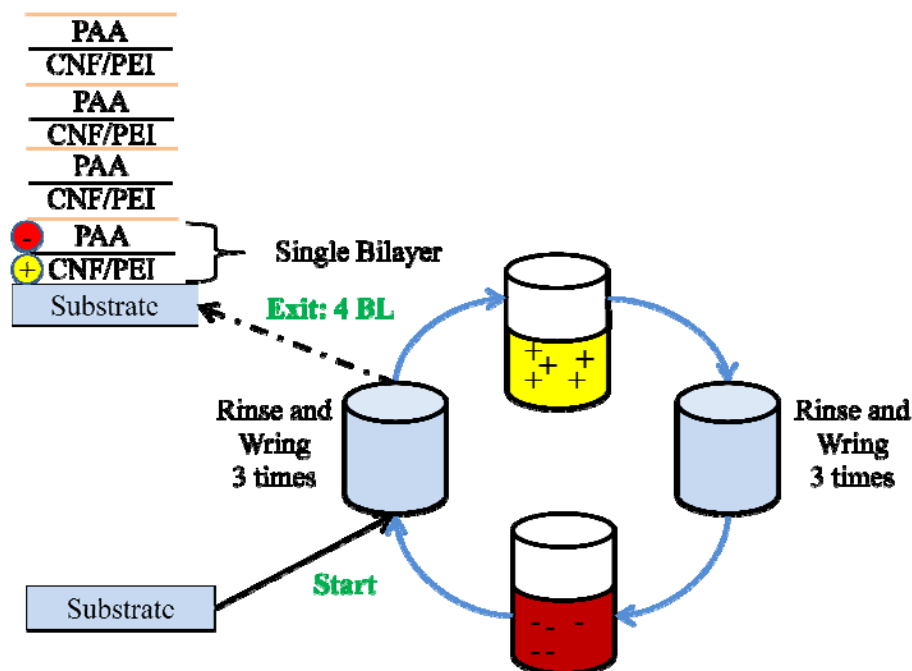


Figure 1. The CNF/polymer coating process was an alternating submersion in a cationic (CNF/PEI) and an anionic (PAA) solution with washing (rinse and wring) between each solution. After creating 4 bilayers (a CNF/PEI layer and a PAA layer), the specimen was dried in a convection oven for 12 h at $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ to remove excess water.

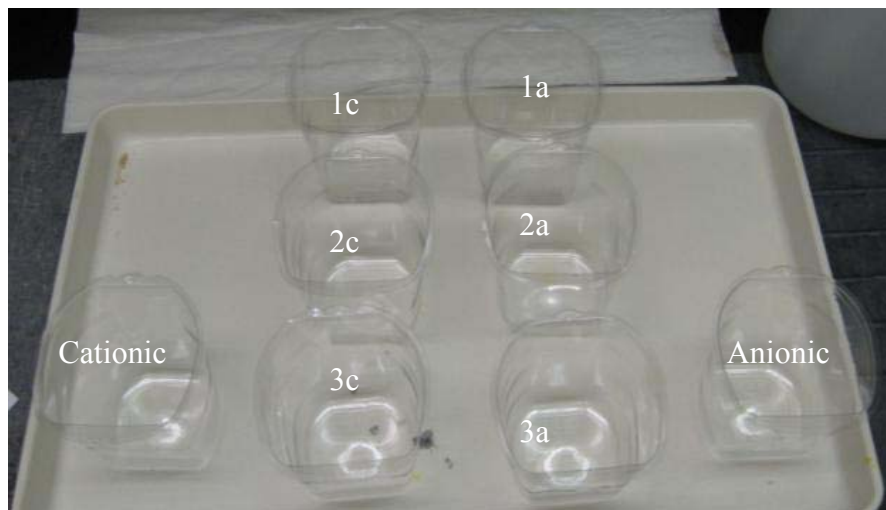


Figure 2. Experimental layout for fabricating CNF/PUF. The CNF/PEI layer was deposited on PUF by submersion, squeezing, and releasing in the cationic suspension and then unbound PEI and/or CNF were removed in containers 1c to 3c by also submersion, squeezing, and releasing of

the substrate. Using the same technique, the PAA layer was then deposited and the unbound PAA was removed by rinsing in containers 1a to 3a. This process creates a single BL and it was repeated three additional times to create four BL.

More specifically, a plastic container (2 L) was charged with the CNF/PEI cationic suspension ($600 \text{ mL} \pm 10 \text{ mL}$), a similar container was charged with the PAA anionic solution ($600 \text{ mL} \pm 10 \text{ mL}$), and six more containers were charged with deionized water ($600 \text{ mL} \pm 10 \text{ mL}$ each) (Figure 2). A PUF substrate was submersed into the CNF/PEI cationic suspension and after squeezing and releasing the substrate four times in the CNF/PEI suspensions, the substrate was soaked in the suspension for an additional 5 min. The substrate was removed and the excess solution was squeezed back into the cationic dipping container.

To remove unbound PEI and/or CNF, the substrate was thoroughly rinsed in three separate containers (Figure 2). Since most of the cationic materials were typically removed in the first rinsing container (Figure 2 #1c), the rinsing water in this container was replaced with fresh deionized water after each washing cycle. Excess water was removed by passing the substrate twice through a manually powered wringer.

The PAA anionic layer was then deposited and the unbound PAA was removed using the same procedure as described above, except the washing was performed using #1a, #2a, and #3a rinsing containers. This deposition of the CNF/PEI layer followed by the PAA layer created a single bilayer (CNF/PEI:PAA). The procedure for depositing the next three bilayers was similar to the first bilayer, except the substrate was only submersed in the coating solutions for 1 min rather than 5 min. After the four bilayers were deposited, the specimen was dried in a convection oven ($70 \text{ }^{\circ}\text{C} \pm 1 \text{ }^{\circ}\text{C}$, 12 h) and stored in a dessicator (at least 3 d) with anhydrous calcium sulfate before weighing and analyzing.

The physical characteristics of the CNF/PUF are provided in Table 1. The increase in substrate mass due to the coating (Mass fraction % coating) was measured using a laboratory microbalance. The amount of CNF on the PUF (Mass fraction % CNF on CNF/PUF) was measured by Thermal Gravimetric Analysis. The amount of CNF in the coating (Mass fraction % CNF in coating) was calculated from TGA and microbalance values. The coating thickness was measured using Scanning Electron Microscopy.

Table 1. Provided are the average physical characteristics of CNF/PUF. All values are reported with 2σ standard uncertainty.

Mass (g)	Mass fraction % coating	Mass fraction % CNF on CNF/PUF	Mass fraction % CNF in coating	Coating thickness (nm)
13.048 ± 0.363	3.18 ± 0.4	1.62 ± 0.03	50.9 ± 0.1	359 ± 36

2.3. CNF coating characterization

2.3.1. Scanning Electron Microscopy (SEM)

A Zeiss Ultra 60 FE-SEM (Carl Zeiss Inc., Thornwood, NY) was used to collect images of the CNF coatings, from which, the coating thickness was approximated, and the distribution of

nanoparticles and 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.

2.3.2. Thermal Gravimetric Analysis (TGA)

A Q-500 GA from TA instruments (New Castle, DE) was used to measure CNF concentration. The samples ($20 \text{ mg} \pm 3 \text{ mg}$) were placed on a ceramic pan ($250 \mu\text{L}$, TA Instruments) then loaded into the furnace by the autosampler. Under a nitrogen atmosphere, the temperature was stabilized at $90^\circ\text{C} \pm 1^\circ\text{C}$ (30 min) then ramped to $800^\circ\text{C} \pm 2^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$. The reported CNF content was based on the remaining mass fraction % at 600°C . All values are reported with 2σ standard uncertainty.

2.3.3 Cone Calorimetry (Cone)

FTT dual cone calorimeter (East Grinstead, United Kingdom), operating at $35 \text{ kW}/\text{m}^2$ with an exhaust flow of $24 \text{ L}/\text{s}$, was used to measure the fire performance of uncoated and CNF coated PUF. The experiments were conducted according to standard testing procedures (ASTM E1354-07). A $((10.2 \text{ cm} / 10.2 \text{ cm} / 5.1 \text{ cm}) \pm 0.1 \text{ cm})$ sample was placed in a pan constructed from aluminum foil. The pan was slightly larger than the test sample and the pan sides were flared away from the sample. This allowed the sides as well as the top of the sample to be exposed during testing.

Following the methodology developed by Zammarano [47], the Cone data was normalized to account for a change in surface area of the specimens during testing. When exposed to the external heat flux, the PUF melted and the MWCNT/PUF shrank slightly. However, by the end of the experiment, the MWCNT/PUF had an averaged 2 times larger surface area than the PUF melt pool. Therefore, the MWCNT/PUF data presented here was reduced by a factor of 2. All values are reported with 2σ standard uncertainty ($\pm 5\%$ in HRR and $\pm 2 \text{ s}$ in time).

3. Results and Discussion

3.1. CNF coating morphology

SEM was used to characterize the LBL fabricated CNF coatings on PUF. The SEM images of the as-received and washed PUF are provided in Figure 3 and Figure 4. The images of the CNF/PUF in Figure 5 are of a section near the center of a CNF/PUF specimen. These images are representative of the type of CNF coating observed on several CNF/PUF specimens. The bright white CNFs were those not or only partially covered with polymer. The images of the cross section of the coating are provided in Figure 6 and Figure 7.

Other than dust and debris on the surface of the PUF, the as-received PUF surface appeared to be smooth and featureless even at high magnification (Figure 3). Prior to depositing the first layer, the PUF was washed with DI water, which completely removed all of the debris (Figure 3h and Figure 4). The wavy edges of the PUF walls are most likely a result of the manufacturing process. During manufacturing, the PUF was initially closed cell with a very thin membrane connecting the walls. When the membrane was “popped” there was a slight relaxation of the

strained edges of the walls and the membrane material snapped back onto the walls and created the wavy appearance observed in Figure 3h and Figure 4.

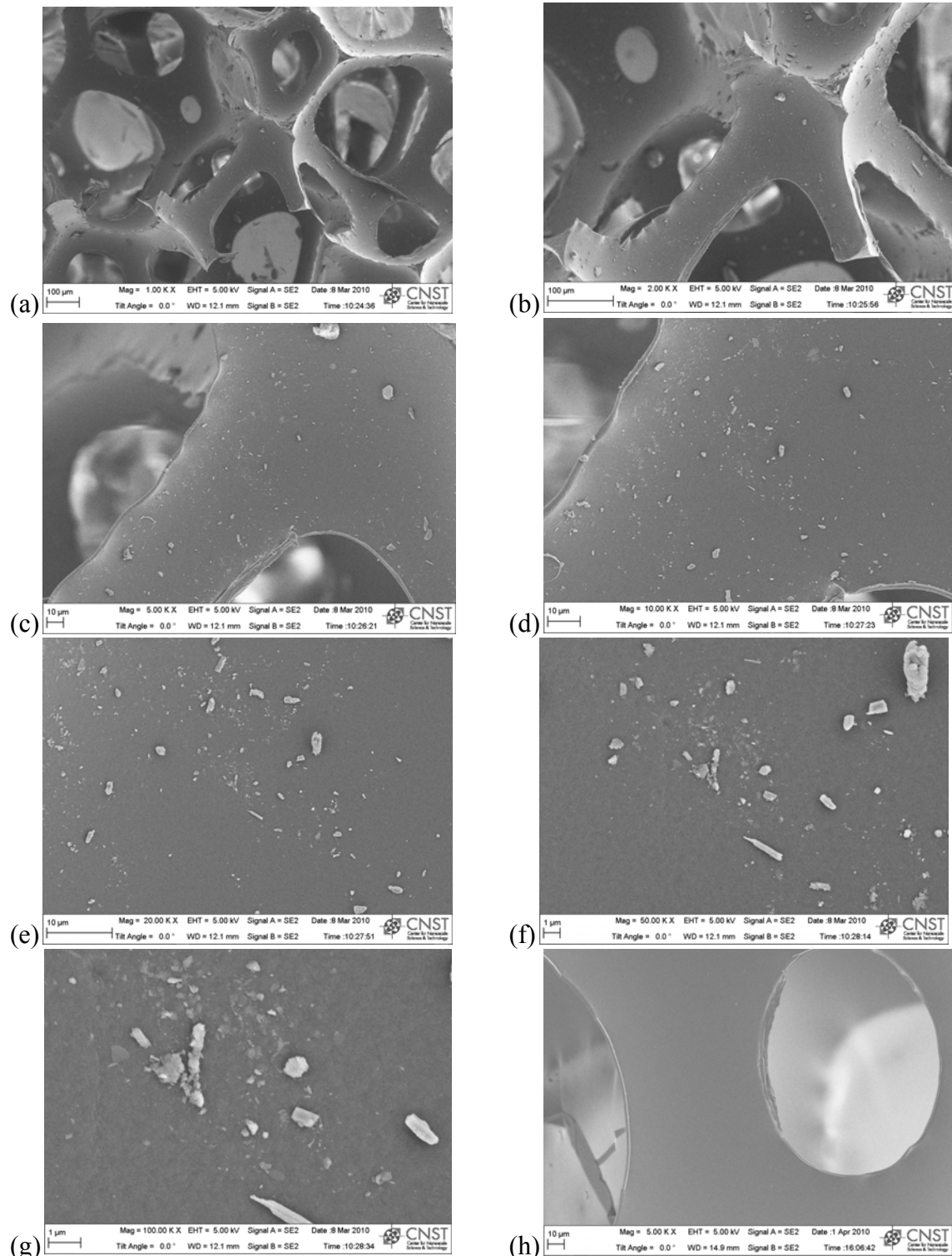


Figure 3. SEM images of as-received PUF at (a) 1x, (b) 2x, (c) 5x, (d) 10x, (e) 20x, (f) 50x and (g) 100x and washed PUF at (h) 5x. The PUF surface contained a significant amount of debris

(dust, etc.) that was removed upon washing (h). The wall surface was smooth and featureless. The edges of some struts are wavy due to recoiling of material from breaking the membrane and/or shrinkage due to solvent loss during the PUF manufacturing.

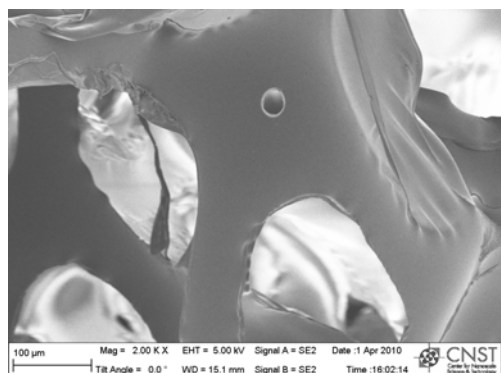


Figure 4. SEM image of a washed PUF showing that the thin film of polymer forming the cell membrane can collapse on to the cell walls when the PUF sets during manufacturing. A membrane is still intact on the right side of the image.

The images in Figure 5 indicate that the CNFs were well distributed along the walls of the PUF. At low magnification (Figure 5a), the wall surfaces appeared to be sparsely populated with approximately 10 µm by 10 µm sized aggregates of CNFs with the area between the aggregates populated with a network of CNF whiskers and regions that appeared to be free of CNFs. However, at higher magnifications (Figure 5c to Figure 5g), it became apparent that a portion of these regions actually did contain CNFs and these CNFs were not visible at lower magnifications because they were embedded in the polymer coating.

Along the surface there were also “islands” of CNFs that have the appearance of dewetting from the surface (Figure 5d to Figure 5g). The larger islands (approximately 10 µm) appeared to contain more single CNFs, rather than the bundles observed in the larger aggregates. The smaller islands (less than a few microns) either contained no CNFs or what appeared to be short individual CNFs (less than 1 µm).

SEM images of a fractured CNF/PUF were taken with the fracture surface in the plane of the image, which provided cross section views of the PUF and the coating (Figure 6). The CNF coating was $359 \text{ nm} \pm 36 \text{ nm}$ based on 10 measurements of 5 different CNF/PUF specimens. The surface morphology at the low magnification (Figure 6a) was consistent with those described in Figure 5 (large aggregates, CNF network, and areas without CNF). Based on all the images taken of fractured CNF/PUFs, the CNF coating appeared to cover the entire surface; however, the coating thickness was not uniform.

The thicker islands, one of which is shown in Figure 6d, was $374 \text{ nm} \pm 100 \text{ nm}$ (as defined by the insert) and constructed of at least twenty CNF fibers randomly oriented in the plane of the coating. Similar to other thicker islands, it contained a fairly uniform coating of polymer over very closely packed CNFs. The tight grouping of the CNF suggests the islands were probably deposited as loosely interacting group of CNFs and not as isolated and independent CNFs. The thickness ($34 \text{ nm} \pm 2 \text{ nm}$) of the coating on top is similar to regions between the islands where

little to CNFs were detected (Figure 6a and 6d, oval insert), which suggests this island was likely formed during the first BL deposition.

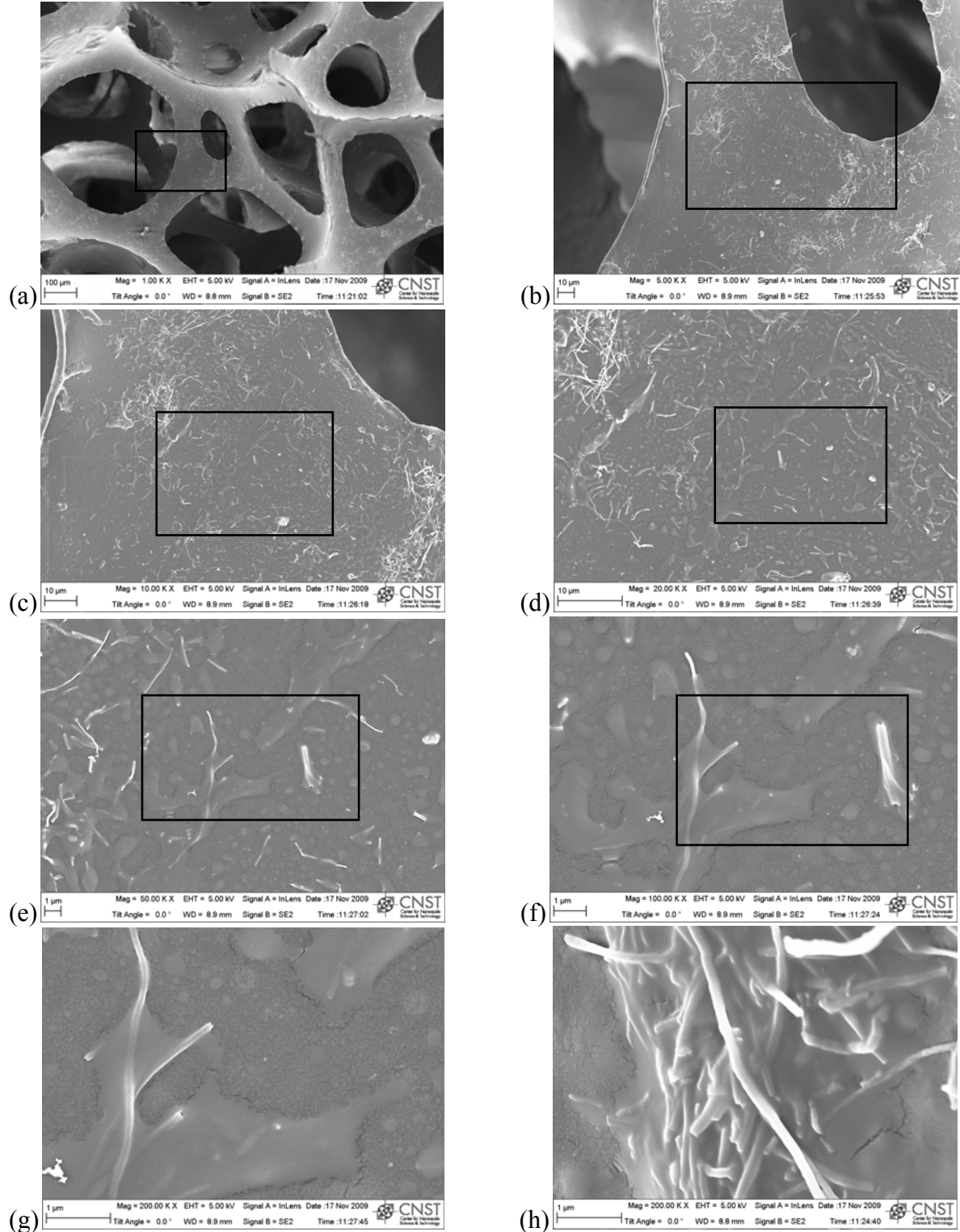


Figure 5. SEM images of the inside section of a CNF coated PUF at (a) 1x, (b) 5x, (c) 10x, and (d) 20x, of a thicker island at (e) 50x (f) 100x, and (g) 200x, and of an aggregate at (h) 200x. The box inserts represent the area in the next higher magnification image. The appearance of these thicker island and aggregate morphologies in these images are representative of these morphologies observed in other CNF coated PUFs.

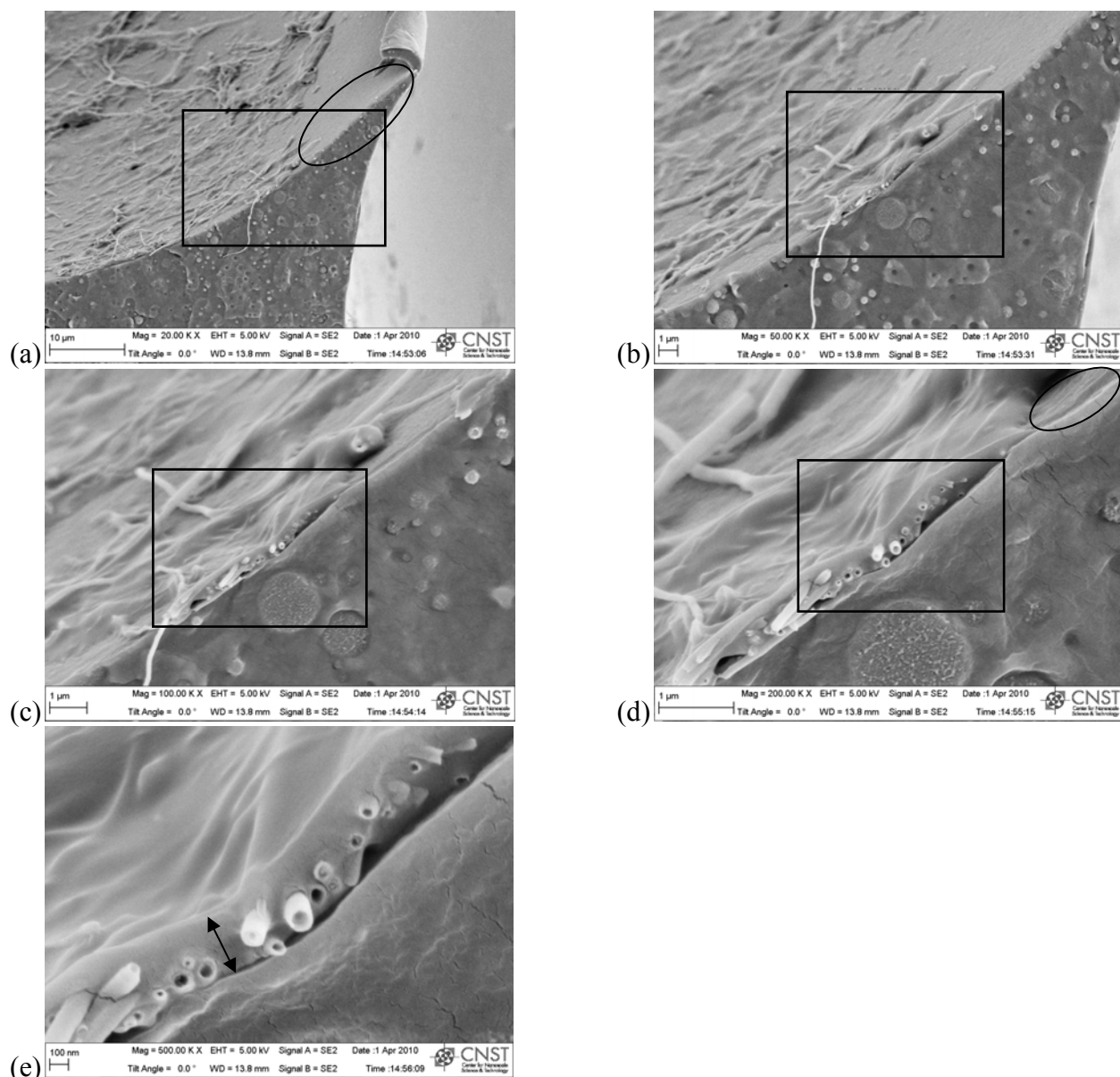


Figure 6. SEM images of a fractured edge of CNF coated PUF at (a) 20x, (b) 50x, (c) 100x, (d) 200x, and (e) 500x. The CNF coating was $359 \text{ nm} \pm 36 \text{ nm}$ based on 10 measurements of five different CNF/PUF specimens. The box inserts represents the area in the next higher magnification image. The oval insert are of a region that appeared to have little or no CNF ($34 \text{ nm} \pm 2 \text{ nm}$). This thicker island (the subject of the higher magnifications) is $374 \text{ nm} \pm 100 \text{ nm}$ thick. The values are reported with 2σ standard uncertainty.

A delaminated section of the coating was heavily filled with CNFs welded together with polymer (Figure 7). Delamination may have resulted from the freeze fracture process or poor adhesion to the surface due to heavy CNF loading. Delamination appears to be a rare occurrence as it was never observed in any other images.

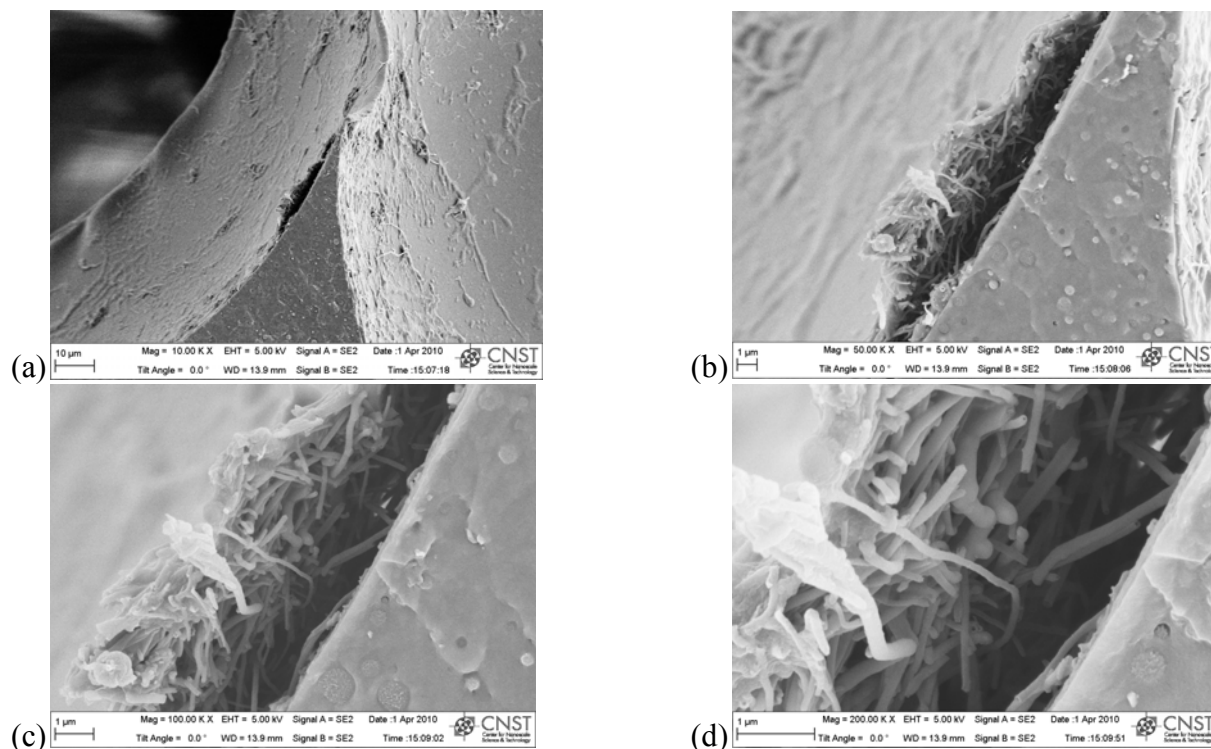


Figure 7. SEM images of a delaminated CNF coating on PUF at (a) 10x, (b) 50x, (c) 100x, and (d) 200x. The heavily concentrated CNF below the surface was welded together with polymer. The root cause of delimitation was uncertain as it could be a result of the fracture process or poor adhesion due to the high CNF and low polymer at the PUF/coating interface.

3.2. CNF/PUF fire performance

Cone Calorimetry (Cone) is a routine bench scale fire test that simulates a developing fire scenario on a small specimen and is used to measure the forced burning fire performance of polymers. The parameters reported from the test, such as time to ignition of the combustion gases, the time to peak and the peak maximum heat release rate (PHRR), and the total heat release (THR), are directly related to the potential fire threat of the burning polymer and, therefore, the values of these parameters are the bases of the performance metrics for several existing or proposed national fire regulations.

Cone heat release rate measurements are referenced to sample surface area (kW/m^2). The raw data collected in this study was adjusted as the surface area of the PUF and CNF/PUF changed during the test. More specifically, the PUF melted to form a pool fire (flaming drips began at $27 \text{ s} \pm 2 \text{ s}$, all PUF was a pool fire at $40 \text{ s} \pm 2 \text{ s}$) with an exposed surface dimensions of $10.2 \text{ cm} \pm 0.1 \text{ cm}$ by $10.2 \text{ cm} \pm 0.1 \text{ cm}$. However, the CNF/PUF only shrank (no melting) during the test because of the CNF network created by the LBL coating. The averaged surface area of the CNF/PUF at the end of experiments was two times larger than the average PUF pool fire surface area. In other words, the same fuel load was spread over a two times larger area in the CNF/PUF. The result was all exposed surfaces (top and sides) of the CNF/PUF were contributing to the HRR, whereas, only the top surface of the PUF pool fire contributed to HRR. The Cone data presented here has been processed to account for the larger surface area of CNF/PUF samples (Figure 8 and Table 2).

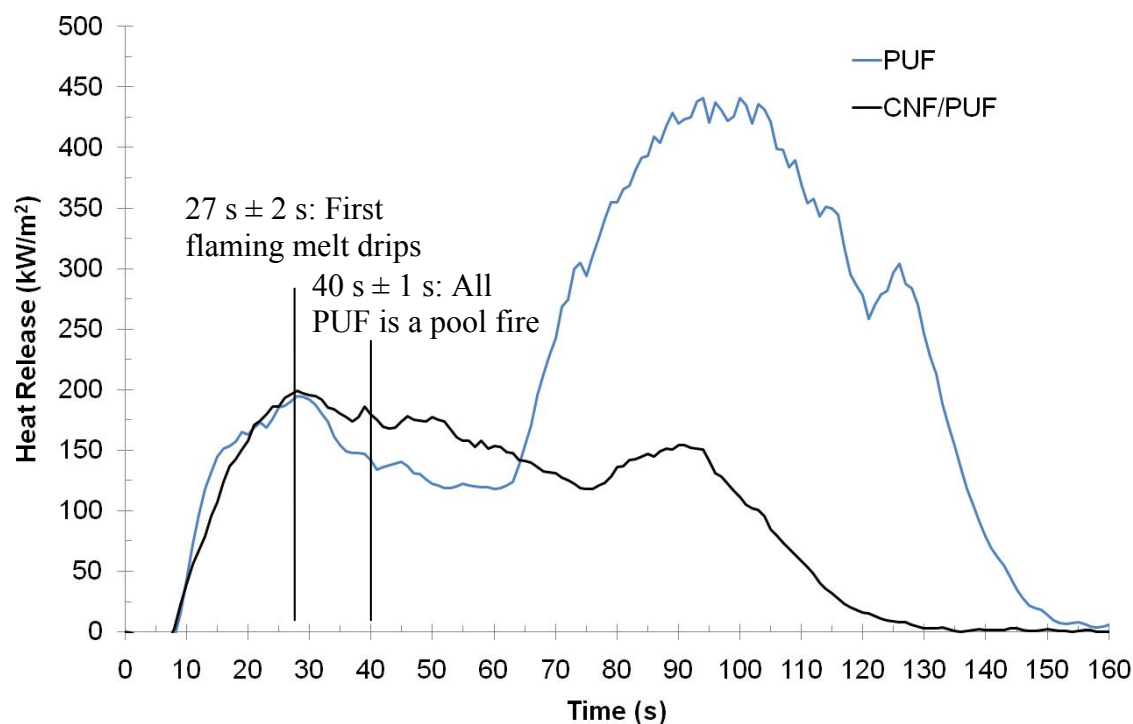


Figure 8. HRR curves from Cone experiments of the washed PUF and the CNF/PUF. The CNF coating resulted in a $55\% \pm 6\%$ reduction in Total Heat Release Rate (THR) and peak Heat Release Rate (PHRR). The time to PHRR occurred 75 s earlier for the CNF/PUF because the coating had sufficiently reduced the HRR of the second peak that the first peak (not the second peak) was the peak maximum for the CNF /PUF. Even though the first was the peak maximum for the CNF/PUF, the PHRR value was still $29\% \pm 3\%$ lower than the first peak of the uncoated PUF. The 2σ standard uncertainty is $\pm 5\%$ in HRR and ± 2 s in time.

Table 2. Cone Calorimetry data of the PUF and CNF/PUF samples. The CNF coating resulted in a $55\% \pm 6\%$ reduction in Total Heat Release Rate (THR) and peak Heat Release Rate (PHRR) and a $29\% \pm 3\%$ reduction in HRR of the first peak. All values are reported with 2σ standard uncertainty.

	Peak 1		Peak 2		THR (MJ/m ²)	Residue Mass Fraction %	Burn time (s)
	HRR (kJ/m ²)	Time (s)	HRR (kJ/m ²)	Time (s)			
PUF	195 ± 12	28 ± 2	435 ± 26	103 ± 3	33 ± 2	2.2 ± 0.1	158 ± 2
CNF/PUF	199 ± 12	28 ± 2	152 ± 9	93 ± 2	15 ± 1	11.0 ± 0.4	128 ± 2

The Cone heat release curves and data (Figure 8 and Table 2) indicate the CNF coating significantly improved the fire performance of the PUF substrate. The $359 \text{ nm} \pm 36 \text{ nm}$ CNF coating that resulted in a $1.62 \text{ mass fraction \%} \pm 0.03 \text{ mass fraction \%}$ CNF loading on the PUF caused a decrease of

- $55\% \pm 6\%$ in the PHRR ($435 \text{ kW/m}^2 \pm 26 \text{ kW/m}^2$ to $199 \text{ W/m}^2 \pm 12 \text{ kW/m}^2$),
- $55\% \pm 6\%$ in the THR ($33 \text{ MJ/m}^2 \pm 2 \text{ MJ/m}^2$ to $15 \text{ MJ/m}^2 \pm 1 \text{ MJ/m}^2$),
- $19\% \pm 1\%$ in total burn time ($158 \text{ s} \pm 2 \text{ s}$ to $128 \text{ s} \pm 2 \text{ s}$),

as compared to PUF.

The only other reported reduction of PUF using CNFs measured a 35% reduction in PHRR by incorporating 4 mass fraction % CNF into the PUF (CNFs were added to the foam recipe).[40] In comparison, the LBL fabricated CNF coated PUF specimen had a 20% greater reduction in PHRR using 57 mass fraction % less CNFs. In other words, incorporating CNF as a coating rather than into the polyurethane will have a significantly greater reduction in the PUF flammability. This information may be of particular interest to foam manufacturers, as it is assumed the post-manufacturing coating of CNFs and using less CNFs will be easier and more cost effective to implement than incorporating CNFs into the foam recipe.

The post-Cone residual mass (char yield) was four times higher for the CNF/PUF specimens ($8.8 \text{ mass fraction \%} \pm 0.2 \text{ mass fraction \%}$ as compared to $2.2 \text{ mass fraction \%} \pm 0.1 \text{ mass fraction \%}$ for the CNF/PUF and PUF, respectively). Adjusting for CNF content and PUF char yield and assuming a negligible impact of the coating polymers (PEI and PAA) on char yield, the CNF coating resulted in $5.0 \text{ mass fraction \%} \pm 0.2 \text{ mass fraction \%}$ increase in non-pyrolyzed polymer (char yield). The improved fire performance measured in the Cone is partially attributed to this increased char yield; however, the primary driver was shape retention and hence the 3 times larger burning surface area of the CNF/PUF.

As indicated previously, the PUF melts to form a pool fire, whereas, the CNF/PUF retains most of its original dimensions. In a real fire scenario and full scale tests, the formation of a pool fire, which is created by PUF, but not CNF/PUF, approximately increases the fire threat (as calculated from HRR, THR, and burn time) of the burning product by 35% [48]. This impact is not captured in Cone data because there is no product (soft furnishing, etc.) for the pool fire to pose an additional flux upon. Therefore, the Cone data is a conservative measure of the improved fire performance created by the CNF coating; however, the actually benefit in regulations, standards, and real fires from using a CNF/PUF rather than PUF, could be 35% greater than reported here.

3.2.1. Comparison to other flame retarding technologies

Najafi-Mohajeri measured the impact of 17 flame retardant additive packages (five non-halogen, four halogen, and seven halogen-phosphorous) on the Cone measured flammability of a standard PUF [49]. These additive packages are commercially available and reported to be commonly used by the PUF industry. The five non-halogens reduced the PUF PHRR and THR by an average of 15% and 14%, respectively. The best performing non-halogen additive was a silicon additive with amine functionality (Dow Corning® I-9641), which reduced PHR and THR by 40% and 6%, respectively, at a 3.3 mass fraction % loading. The four halogens reduced the PUF

PHRR and THR by an average of 31% and 16%, respectively. The best performing halogen additive package was a pentabromodiphenyl oxide additive blend (Great Lakes DE-60F), which reduced PHRR and THR by 37% and 31%, respectively, at a 20 mass fraction % loading. The seven halogen-phosphorous reduced the PUF PHRR and THR by an average of 14% and 7%, respectively. The best performing halogen-phosphorous additive package was a 28 mass fraction % halogenated phosphate ester (Great Lakes Firemaster® HP-36, 44.5% halogen and 5.5% phosphorous) and 7 mass fraction % antimony oxide (Laurel Industries), which reduced PHRR and THR by 43% and 7%, respectively.

Price measured the flammability impact of incorporating melamine based flame retardants into PUF [50]. The exact composition of the PUF and these flame retardant PUFs are unknown as they were purchased from a supplier. The melamine and melamine chlorate phosphate blend reduced the PHRR by 10% and 15%, respectively. As an alternative to the flame retardants, the authors also measured the impact of using fire blocking barrier fabrics to reduce the PUF flammability. Of the six specimens tested, the best performing combination was wrapping the standard PUF with zirconium hexafluoride flame retardant treated wool (FR-wool), which gave a 29% reduction in PHRR. This FR-wool also gave the greatest reduction in PHRR of the flame retardant foams (32%). However, this reduction was quite similar to what was reported for wrapping the standard PUF with this FR-wool, which suggests the fire performance benefits gained by using these flame retardants are partially mitigated by the FR-wool.

The CNF coatings developed in this project delivered a 12% to 47% greater reduction in PHRR and/or THR using less than 2 mass fraction % CNF as compared the 3 mass fraction % to 35 mass fraction % of the other FR additives reported by Najafi-Mohajeri [49] and Price [50]. More specifically, the reduction in PHRR and THR for the CNF/PUF was 18% and 24% greater, respectively, than measured for the best performing halogen flame retardant filled PUF and 12% and 47% greater, respectively, than measured for the best performing halogen-phosphorous flame retardant filled PUF. Compared to melamine chlorate phosphate filled PUF and FR-wool wrapped PUF, the reduction in PHRR for the CNF/PUF was 40% and 26% greater, respectively.

4. Conclusion

This is the first published report of fabricating a LBL coating on foam, fabricating a LBL coating containing CNFs, and using LBL to modify the fire performance of foam. The LBL process and conditions generated excellent thin film coatings that completely covered all internal and external surfaces of the porous foam. The CNF coating was consistently non-uniform with regions of high CNF aggregation to isolated regions that appeared void or contained only a few CNFs. The highly aggregated CNF regions contained CNFs that were only partially embedded in the polymer coating, whereas, regions of smaller aggregation (island) generally contained CNFs almost completely embedded in the polymer coating. Even though the CNF distribution was non-uniform and CNFs were not completely embedded in the polymer coating, the CNF coating significantly reduced the flammability of foam by significantly reducing the heat release rate, total heat release, and total burn time of the foam. In comparison to previously reported reduction of PUF flammability by incorporating CNFs into the PUF during foaming process, these CNF coatings had a significantly greater reduction in PUF flammability using significantly lower CNF concentrations. The CNF coating also prevented the formation of a melt pool of

burning foam, which in a real fire scenario or full scale tests, may further reduce the resulting fire threat of burning soft furnishings in residential homes. Compared to other technologies reported to be commercially used to reduce the flammability of PUF, the CNF coating approach resulted in a significantly less flammable PUF at a lower additive loading level.

5. Future Research

This research has laid the foundation for using LBL to fabricate coatings on foam and barrier fabrics using a range of nanoparticles and other performance enhancing additives. We are currently fabricating and analyzing multiwall carbon nanotubes coatings, clay coatings, cellulosic fiber coatings, and mixed additive coatings on both foam and barrier fabrics. In addition, we are measuring the release of nanoparticles during aging and measuring the change in fire performance due to aging.

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