

# Durable Nanoparticle Coatings to Reduce Polyurethane Foam Flammability

Yeon Seok Kim and Rick D. Davis

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

## INTRODUCTION

Layer-by-layer (LbL) assembly has been extensively studied as a methodology to create multifunctional thin films that are generally less than 1 micron thick.<sup>1-3</sup> These thin films are commonly fabricated through alternate deposition of a positively charged layer and negatively charge layer (called a bilayer, BL). LbL thin films are used in an extensive breadth of applications, such as oxygen barriers<sup>4</sup> and sensors,<sup>5</sup> and have useful properties, such as antimicrobial<sup>6</sup> and antireflection.<sup>7</sup> More recently, fabrication of clay containing LBL thin films have been studied.<sup>4,8,9</sup> Li et al.<sup>10</sup> focused on using LbL clay coatings (sodium exchanged montmorillonite) on cotton fabric to improve the fire performance characteristics of this textile.

Reported here are the fabrication methodology and characterization of carbon nanofiber (CNF)-filled coatings deposited on the surface of polyurethane foam (PUF) using LbL assembly and the impact of the coatings to reduce PUF flammability. The large CNF dimensions are undesirable for typical applications of LbL coatings, as the coatings may be too thick as the CNF dimensions are comparable or larger than most LbL coating thicknesses. However, for reducing flammability, the larger dimensions may enable the formation of a CNF network armor that protects the foam. The thin coating approach is believed to be ideal for reducing the flammability of foam as it may more quickly form the char-like armor because the high concentration of CNFs are already at the surface (where the combustion is occurring) rather than randomly mixed throughout the polymer.

## EXPERIMENTAL<sup>i,ii</sup>

Unless indicated otherwise all values in the manuscript are reported with a  $2\sigma$  uncertainty.

**Materials.** Branched polyethylenimine (PEI, branched, mass average molecular mass = 25,000 g/mol) and poly (acrylic acid) (PAA, mass average molecular mass = 100,000 g/mol) were obtained from Sigma-Aldrich (Milwaukee, WI). PR-24-XT-PS carbon nanofibers (CNF, average diameter = 150 nm  $\pm$  100 nm, length was 65  $\mu$ m  $\pm$  30  $\mu$ m) were obtained from Pyrograf Products Inc., (Cedarville, Ohio). Two polyelectrolyte solutions were prepared by dissolving 0.1 mass fraction % PEI (cationic) and PAA (anionic) into deionized water and slowly rolling for 12 hour. CNF suspension was prepared by adding 0.05 mass fraction % CNF into 0.1 mass fraction % PEI solution and sonicating for one hour.

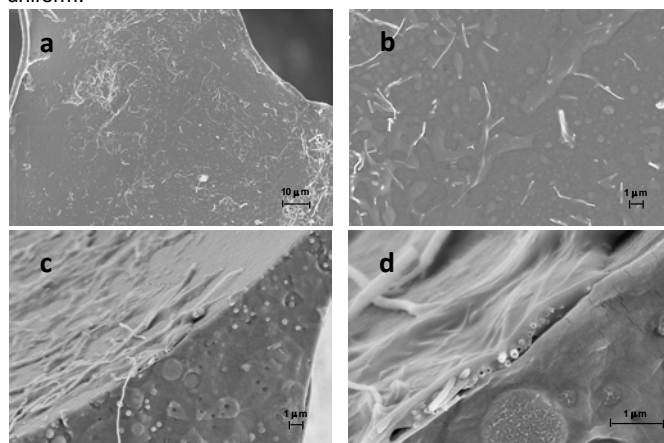
**LbL Deposition and Coating Characterization.** 4 BL of CNF coating was deposited using PAA solution and CNF/PEI mixture. PUF submerged into CNF/PEI suspension (cationic) and PAA solution (anionic) alternatively four times. Initial dipping was five minutes for both CNF/PEI and PAA followed by one minute dipping. PUF was rinsed with deionized water and dried by using hand wringer after each dipping. After the four bilayers were deposited, the specimen was dried in a convection oven at 70 °C for 12 hours and stored in a

dessicator (at least 3 days) with anhydrous calcium sulfate before weighing and analyzing. A more detailed description of a LbL coating process has been previously published.<sup>11</sup>

Mass change of substrate was measured by the laboratory microbalance, and Q500 Thermogravimetric analyzer (TA instrument, New Castle, DE) was used to measure the amount of CNF content with respected to the total mass of substrate and coating. A Zeiss Ultra 60 Field Emission-Scanning Electron Microscope (FE-SEM, Carl Zeiss Inc., Thornwood, NY) was used to acquire surface and cross section images of foam. A dual Cone Calorimeter (Fire Testing Technology, East Grinstead, United Kingdom), operating at 35 kW/m<sup>2</sup> with an exhaust flow of 24 L/s, was used to measure the fire performance of uncoated and CNF coated PUF. The experiments were conducted according to standard testing procedures (ASTM E-1354-07).

## RESULTS AND DISCUSSION

The images in Figure 1 indicate that the CNFs are well distributed along the walls of the PUF. At low magnification (Figure 1a), the wall surfaces appear to be sparsely populated, with approximately 10  $\mu$ m by 10  $\mu$ m sized aggregates of CNFs. The areas between the aggregates are populated with a network of CNF whiskers and regions that appear to be free of CNFs. At higher magnifications (Figure 1b), it becomes apparent that a portion of these regions actually do contain CNFs and these are not visible at lower magnifications because they are embedded in the polymer coating. SEM images of a fractured CNF/PUF were taken with the fracture surface in the plane of the image, which provides cross section views of the PUF and the coating (Figure 1c and 1d). The CNF coatings are 359 nm  $\pm$  36 nm (based on 10 measurements of five different CNF/PUF specimens). The surface morphology is consistent with that observed in Figure 1a and 1b (large aggregates, CNF network, and areas without CNF). Based on all the images taken of fractured CNF/PUFs, the CNF coating appears to cover the entire surface; although, the thickness is not completely uniform.



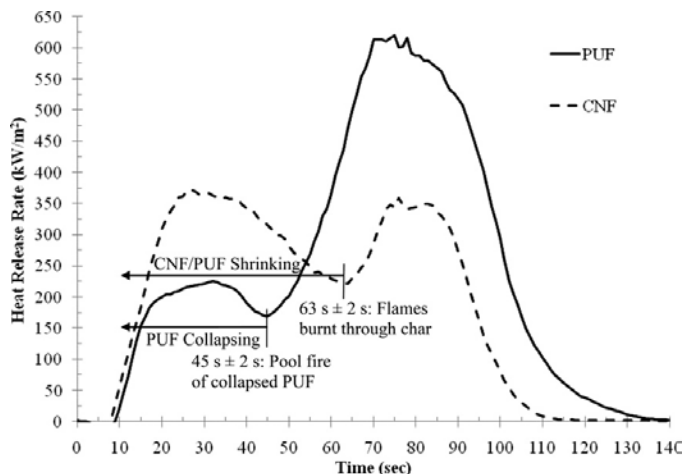
**Figure 1.** SEM images of the inside section of a CNF coated PUF at (a) 10,000x, and (b) at 50,000x, and a fractured edge of CNF coated PUF (c) at 50,000x and (d) at 200,000x.

TGA and a microbalance were used to determine the actual mass of CNFs and coating deposited onto the substrates. The 4 BL CNF coatings increase the mass of the substrate by (3.2  $\pm$  0.4) mass fraction %, of which, (51  $\pm$  1) mass fraction % are CNFs. The total CNF content relative to the substrate mass is (1.6  $\pm$  0.1) mass fraction %. Cone Calorimeter is an industry standard tool for measuring the flammability of a material. It is an open flame ignition test where the sample is exposed to a continuous heat source, thus it represents a forced burning fire scenario. The HRR data (from the Cone) indicates the CNF coatings significantly improved the fire resistance of foam (Figure 2). The HRR curves for CNF/PUF and PUF consist of two peaks. However, the attributes of the curves are quite different with both peaks of CNF/PUF being of similar HRR values

<sup>i</sup> Certain commercial equipment, instruments or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose.

<sup>ii</sup> The policy of NIST is to use metric units of measurement in all its publications, and to provide statements of uncertainty for all original measurements. In this document however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements.

( $371 \text{ kW/m}^2 \pm 10 \text{ kW/m}^2$  and  $348 \text{ kW/m}^2 \pm 10 \text{ kW/m}^2$ ) whereas in PUF the second peak is 2.8 times larger than the first peak ( $224 \text{ kW/m}^2 \pm 12 \text{ kW/m}^2$  and  $620 \text{ kW/m}^2 \pm 26 \text{ kW/m}^2$ ). The PHRR, which is often considered as one of the more critical values in accessing the flammability of a material, is  $40\% \pm 3\%$  lower for CNF/PUF than for PUF. The THR, which reflects the total size of the fire threat, and the total burning time of the foam was  $21\% \pm 3\%$  smaller for CNF/PUF. However, the time to PHRR, which is often considered a critical value in accessing the amount of time for escaping a fire, is  $66\% \pm 2\%$  earlier for CNF/PUF. In other words, the Cone data suggests the CNF coatings may result in smaller fires and reduced flame spread, but create an initially larger fire that reduces the time to escape. In a real scenario, the CNF/PUF would likely perform significantly better than the HRR data suggests, but before going into this discussion it is important to understand how the CNF coating altered the burning behavior of foam.



**Figure 2.** Heat Release Rate curves of the washed standard PUF and the CNF/PUF indicates the CNF coating significantly improved the fire performance of the PUF. All values reported with  $2\sigma$  uncertainty.

The attributes of the first HRR peak for both CNF/PUF and PUF are defined by pyrolysis of polyurethane decomposition gases (increase in HRR) and decrease in substrate surface area (decrease in HRR). During the first peak the CNF coating forms a protective char and enables the foam to maintain its shape (and surface area) that is qualitatively similar to an untested foam specimen. At  $63 \text{ s} \pm 2 \text{ s}$ , the flames penetrate this protective char, which causes the foam to shrink as the remaining polymer is pyrolyzed. At the end of the experiment, a brittle char remains that has a surface area  $90\% \pm 5\%$  smaller than the untested foam specimen. In contrast to CNF/PUF, during the first HRR peak PUF collapses to form a liquid-like pool of degraded polyurethane. The surface area of this pool (defined by the sample pan) is qualitatively two times smaller than CNF/PUF surface area, which is the reason the HRR maximum for the first peak is  $66\% \pm 2\%$  higher for CNF/PUF. The PUF pool rapidly pyrolyzes because there is no protective char and because the contents of the pool are volatile/combustible compounds (isocyanate and polyol based degradation products of polyurethane).

In a real fire scenario, the reduction in flammability due to replacing PUF with CNF/PUF will likely be greater than suggested by the Cone data for two main reasons. First, this CNF/PUF Cone data was not normalized, as suggested by Zammarano et al,<sup>12</sup> since the surface area for CNF/PUF was not quantitatively measured and changed significantly throughout the test. Based on the qualitative observations, the HRR for the first peak could be reduced by a factor of two while the second peak may only be slightly reduced. The result is the first peak for CNF/PUF would have a maximum HRR and time to peak similar to PUF and the second peak would then become the PHRR, which has a time to peak similar to PUF. Secondly, the Cone

data does not capture the real impact of the PUF pool fire since there is no product for the pool fire to pose an additional flux upon. Since a pool fire can approximately increase the fire threat (as calculated from HRR, THR, and burn time) of a burning product (e.g. upholstered furniture) by  $35\%$ <sup>13</sup> and the CNF coating prevents pool formation than it is assumed that in a real fire replacing PUF with CNF/PUF would decrease the HRR from a product by  $35\%$ .

## CONCLUSION

LbL assemblies made with CNFs are shown to improve the fire performance of polyurethane foam. The process described here generates thin film coatings that completely cover all internal and external surfaces of the porous polyurethane foam, and this coating significantly reduces the flammability of foam. This LbL coating significantly reduces the heat release rate, total heat release, and total burn time of the PUF with just four bilayers (e.g.,  $40\% \pm 3\%$  reduction in PHRR). The CNF coating also prevents the formation of a melt pool of burning foam, which in a real fire scenario, may further reduce the resulting fire threat of burning soft furnishings in residential homes. This research lays the foundation for using LbL to fabricate coatings on foam using a range of nanoparticles and other performance-enhancing additives. Multi-walled carbon nanotubes, clay, cellulosic fibers, and mixed additive coatings are currently being investigated. Additionally, the release of nanoparticles during aging and the change in fire performance due to aging are currently being measured. These nanoparticle filled LbL coatings are proven to be mechanically robust using two different aging experiments. These results will be discussed during presentation.

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