



Multi-walled carbon nanotube layer-by-layer coatings with a trilayer structure to reduce foam flammability

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ABSTRACT

In order to improve the stability and growth speed of coating, a trilayer (TL) methodology was adapted and resulting film shows high thickness compared to the dimensions of the carbon nanotube. First, the multi-walled carbon nanotubes were functionalized via simple direct amination to be stabilized in the water with positive surface charge. Amine functionalized carbon nanotubes were deposited on polyurethane foam using layer-by-layer assembly with a TL approach. Additional polyethyleneimine layer promote the interaction between carbon nanotube and polymer layers resulting in uniform, durable and thick coating. The 440 ± 47 nm thick 4 TL coatings of polyacrylic acid, polyethyleneimine functionalized multi-walled carbon nanotubes, and polyethyleneimine completely covers the entire internal and external surfaces of the foam. Microscopic images confirm strong polymer/nanotube interaction due to additional polyethyleneimine layer and well dispersed carbon nanotube network on the polyurethane foam surface. The carbon nanotube network created by the layer-by-layer process significantly reduces the flammability of foam (e.g., $35 \pm 3\%$) reduction in peak heat release rate and prevents pool fire by creating protective layer.

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1. Introduction

Layer-by-layer (LbL) assembly has been studied for last two decades as a thin film fabrication technique [1–3]. LbL coatings/thin films are commonly fabricated through alternate deposition of a positively charged layer and negatively charged layer (one pair of positive and negative layers are called a bilayer, BL) [4]. Their characteristics and functional purpose (e.g., oxygen barriers [5] and sensors [6]) are controlled by the fabrication parameters (e.g., pH of solution, solution concentration, and temperature) and the materials that form the coatings (e.g., polymer type) [7–11]. Recently LbL coatings were shown to significantly reduce the flammability of cotton fabrics, polymeric films, and polyurethane foams (PUF) [11–18]. During combustion, the polymer/nanoparticle coatings form a protective residue, which inhibit flame spread and fire growth. Studies have shown polymer only LbL coatings can reduce the flammability of cotton fabrics [16–18]; however, it appears nanoparticles in the assembled coatings can greatly reduce the flammability of PUF. A carbon nanofiber (CNF) and a montmorillonite clay based LbL coatings in previous studies reduced the PUF peak maximum heat release rate (PHRR) PUF by 40% [19,20]. The CNF-based coating naturally grew exponentially due to the inter-diffusion of polyethylenimine (PEI) and poly(acrylic acid) (PAA). The clay-based coating, unlike the CNF-based, has a slow and a linear growth [10], which is not practical for commercialization of this FR technology. However, the growth rate was significantly accelerated by using a using

a trilayer (TL) approach; the clay-based coating thickness was up to $1 \mu\text{m}$ after 8 TL of deposition [20]. The conventional clay-based LbL coatings utilize electrostatic attraction between the clay platelet and polyelectrolyte, which is a very poor interaction. The TL approach combines the electrostatic attraction and hydrogen bonding by depositing an additional polyelectrolyte layer after clay layer, which helps retain clay in the coating and enables interdiffusion between the two polymer layers.

Since the discovery of carbon nanotubes (CNT) in early 1990, the characteristics of carbon nanotubes (e.g., such as small size and high aspect ratio [21,22], high modulus [23], and high thermal conductivity [24]) have been attractive to enhancing the performance of polymeric materials. Compared to CNFs, which have similar composition and much larger geometry, CNTs have superior physical properties along with at least an order of magnitude higher surface area. Recently, CNTs were deposited via LbL assembly and the resulting films showed excellent property improvement for various applications [25–27]. However, these CNT-based coatings would not be practical as a fire retardant (FR) because the coatings were too thin (less than 100 nm even after 10 BL).

Compared to the previous reports of CNF [19] and clay-based [20] LbL coatings, the MWCNT-based coating have significant challenges stemming from the MWCNT size and surface chemistry that make it difficult to disperse and maintain dispersed in aqueous solutions. Researchers have reported improving MWCNT dispersion, distribution, and stability using non-covalent stabilizing agents (e.g., surfactants [28–30], water-soluble polymers [31–33], and inorganic nanoparticles [34,35]) and have chemically modified the CNTs. Covalent functionalizing is generally

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preferred to enhance CNT solubility, but the fabrication process is complicated and involves strong acid treatment. Liao et al. reported a one step MWCNT functionalization method via direct amination without strong acid treatment [36]. The functionalized MWCNT showed excellent dispersion and stability in water without any dispersion agent.

Reported here is a multi-walled carbon nanotube (MWCNT) LbL coating with exceptional coating thickness and high MWCNT concentration that was fabricated via the TL approach. Discussed are direct amination of MWCNT to promote the stability and deposition of MWCNT, advantage of TL methodology, and characterization of the coatings including microstructure and fire performance.

2. Experimental details [37,38]

2.1. Materials

All measured values are reported with a 2 σ uncertainty, unless otherwise indicated. All materials were used as-received from the supplier unless otherwise indicated. Branched polyethylenimine (PEI, branched, $M_w = 25,000$ g/mol) and poly(acrylic acid) (PAA, $M_w = 100,000$ g/mol) were obtained from Sigma-Aldrich (Milwaukee, WI). The polymer solutions (0.10 ± 0.03 mass %) were prepared by charging a 2 L glass bottle with deionized (DI) water and either PAA or PEI, then tumbling the solution for 6 h at room temperature using a compact roller system manufactured by Wheaton (Millville, NJ). The pH was not adjusted as the natural pH of the solutions (3 and 10 for PAA and PEI, respectively) are close to the reported pH value for a fast coating growth [39]. Baytubes C150HP multi-walled carbon nanotubes (MWCNT, average diameter was 14 nm, length was 1 μm to 10 μm) were obtained from Bayer MaterialScience AG (Pittsburgh, PA). The standard (untreated) polyurethane foam received from Future Foam Inc. (Fullerton, CA) was stored as received from the supplier. Nine substrates (length/width/height of $(10.2/10.2/5.1) \pm 0.1$ cm) were cut from a single substrate ($(30.6/30.6/5.1) \pm 0.1$ cm). Prior to coating fabrication, the PUF was stored in a desiccator for 3 days to remove moisture.

2.2. MWCNT amination and LbL methodology

The MWCNTs were first functionalized with PEI to facilitate dispersion and distribution in DI water and to improve retention of the MWCNTs in the coating. Amination of MWCNTs was prepared according to the procedure by Liao et al. [36]. A plastic vial (500 mL) was charged with $200 \text{ g} \pm 1 \text{ g}$ of N, N-dimethylformamide (DMF), $10 \text{ g} \pm 0.1 \text{ g}$ of PEI, and $2.0 \text{ g} \pm 0.1 \text{ g}$ of MWCNTs. The suspension was sonicated at 40 W for 1 h then agitated with a stir bar for 2 days at $50 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$. The functionalized MWCNTs (MWCNT-PEI) were isolated from the suspension by filtering through a 0.20 μm nylon membrane and washing four times with alternating methanol and water washes to remove excess PEI and DMF. The MWCNT-PEIs were dried in a desiccator with anhydrous calcium sulfate for a minimum of 3 days prior to use. The MWCNT-PEI in DI water suspension (for coating fabrication) was prepared by charging a plastic bottle (250 mL) with $150 \text{ mL} \pm 1 \text{ mL}$ DI water and $0.60 \text{ g} \pm 0.02 \text{ g}$ of MWCNT-PEI and sonicating at 40 W for 1 h. The suspension was diluted with DI water (450 mL) then used immediately in the coating process.

The LbL coatings were constructed by depositing a PAA monolayer, a MWCNT-PEI monolayer, and a PEI monolayer to form a single trilayer (Fig. 1). The coatings consisted of this TL being repeated four times (4TL). For the first TL, the substrate was held in each of the depositing solutions for 5 min. The substrate was held in each of depositing solutions for only 1 min, for each subsequent TL. After each monolayer the specimen was rinsed with water three times to remove unbound material then the excess water was removed by running it through a Dyan-Jet hand wringer (Dyan-Jet Products, Overland Park, KS). After creating the four TLs, the specimens were dried in a convection oven for 12 h at

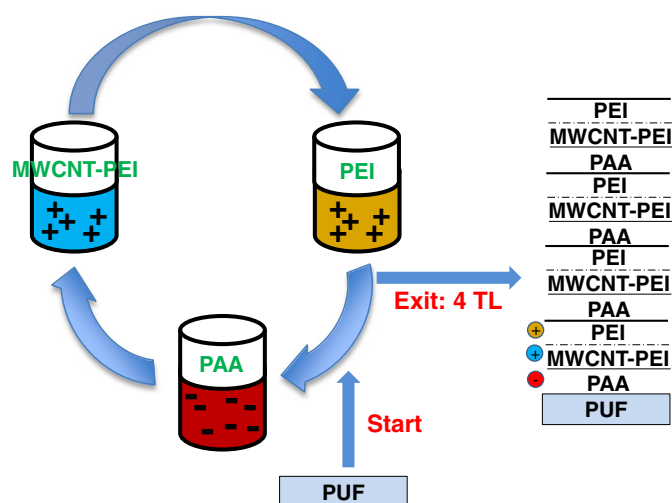


Fig. 1. The MWCNT/polymer coating process was an alternating submersion in an anionic (PAA) solution, cationic (MWCNT-PEI) and another cationic (PEI only) solution with washing (rinse and wring) between each solution. Fabrication step for BL systems is identical without the additional PEI deposition after MWCNT-PEI layer. The repeating unit for BL system is PAA/MWCNT-PEI.

$70 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ then stored in a desiccator for 3 days to remove water. A MWCNT coating fabricated using a conventional BL LbL approach was prepared as a reference material. The BL coating fabrication process is identical to the TL system, except there was no PEI monolayer between MWCNT-PEI monolayer and PAA monolayer.

2.3. Coating characterization

The change in mass (as measured by a laboratory microbalance) of the specimen after stored in a desiccator (before coating and after coating) is the mass of the LbL coating. The MWCNT mass concentration in the coating was the measured residual mass at $800 \text{ }^\circ\text{C}$ from a Thermal Gravimetric Analysis (TGA) operated at $10 \text{ }^\circ\text{C}/\text{min}$ heating rate to $800 \text{ }^\circ\text{C}$ in nitrogen atmosphere. A Zeiss Ultra 60 Field Emission-Scanning Electron Microscope (FE-SEM, Carl Zeiss Inc., Thornwood, NY) at 5 kV was used to image of the MWCNT coatings, from which, the coating thickness was approximated, and the distribution of nanoparticles and overall coating quality of the LbL coating was qualitatively evaluated. All SEM samples were sputter coated with 4 nm of Au/Pd ((60/40) mass fraction %) prior to SEM imaging. A dual Cone Calorimeter (Cone, Fire Testing Technology, East Grinstead, UK), operating at $35 \text{ kW}/\text{m}^2$ with an exhaust flow of 24 L/s, was used to measure the fire performance of uncoated and MWCNT coated PUF. The experiments were conducted according to ASTM standard testing procedure E1474-10. A $(10.2/10.2/5.1) \pm 0.1$ cm sample was placed in a snug fitted pan constructed from heavy grade aluminum foil. The 2 σ standard uncertainty of the Cone values is $\pm 5\%$ in heat release rate (HRR) and ± 2 s in time.

3. Results and discussion

3.1. MWCNT coating characteristics

After several attempts at fabricating a MWCNT-based BL coating on PUF, it was apparent the as-received MWCNTs would not yield a fire blocking coating on PUF. In the aqueous depositing solution, the MWCNTs immediately precipitated once agitation ceased. Attempts to coat using this MWCNT solution resulted in a substrate with an inhomogeneous light gray color, which indicated a coating with a low concentration of poorly distributed MWCNTs. During rinsing, the water solutions turned a light gray color (due to the MWCNTs) and the substrate returned to its starting off-white color, indicating the MWCNTs

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