



# Ammonium polyphosphate-based nanocoating for melamine foam towards high flame retardancy and anti-shrinkage in fire



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## ABSTRACT

In order to realize a more effective and environmentally friendly flame-retardant treatment for melamine foam, which is expected to be used as highly flame-retardant cellular polymeric materials for building and construction, a novel intumescent flame-retardant nanocoating, comprised of positively charged chitosan (CH) and negatively charged ammonium polyphosphate (APP), is deposited on high open-cell ratio melamine foam using layer-by-layer assembly. SEM images indicate that the bilayer CH-APP nanocoating is deposited on the surface of melamine foam successfully. The LOI value of foam coated with two-bilayer CH-APP is 47.0%, while that of pure melamine foam is 34.5%. Cone calorimetry shows the foam coated with two bilayers of CH-APP to possess excellent self-extinguishing property, and remarkably prevents the foam from shrinking, as a result of the expanded carbonized layer. The peak heat release rate and the total heat release of foam coated with two bilayers of CH-APP are decreased by 87% and 77%, respectively, with only 1.6 wt% of phosphorus incorporation. This CH-APP nanocoating deposited on melamine foam is unique because it needs only two bilayers to be applied, is composed of water-borne, environmentally-benign components, and can prevent ignition and shrinkage of melamine foam.

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## 1. Introduction

The increasing use of highly flammable foam materials, such as the polyurethane (PU) and polystyrene (PS) foams, poses a growing risk to civilization, and is resulting in the promulgation of new codes for fire protection design of buildings, and development of new flame-retardant materials. Melamine foam (MF) has found the increasing uses for acoustical and thermal insulation in buildings, vehicle, railroad, ships and aircraft construction. Stricter requirements have been placed on the fire performance of foams in the construction sector, for example in public spaces and highrise buildings in China. Current commercial MF products do not achieve fire-resistant class A of Chinese standard GB 8624, which is currently among the most stringent standards for the fire safety of building insulation materials in the world. MF is flammable and shrinks significantly when exposed to high temperatures.

Development of a suitable method to improve the combustion characteristics of MF is therefore urgently needed.

Layer-by-layer assembly (LbL) [1–3] is a simple and effective nanocoating technology in which flame-retardant (FR) coatings are deposited on a substrate by alternating adsorption of oppositely charged polyelectrolytes, used to improve the flame-retardant performance of cotton [4–9], ramie [10], polyester [11,12], and polyester–cotton blends fabrics [13], and flexible polyurethane foam [14–20]. Polyelectrolytes typically used are polyethyleneimine (PEI), chitosan (CH), ammonium polyphosphate (APP), and polyacrylamide and functionalized nanoparticles of multiwall carbon nanotube (MWNT-NH<sub>2</sub>), montmorillonite (MMT) [21], POSS, and silica. Each pairwise adsorption of positive and negative electrolytes constitutes a bilayer (BL), and the thickness of a single bilayer is typically 1–100 nm, capable of significantly tailoring on the nanoscale level [22–24].

Carosio et al. [20] developed the LbL nanoarchitectures deposited on polyurethane foams capable of chemically adapting to extreme heat, and the LbL-treated PU foam achieved the self-extinguishment within few seconds after ignition by a methane flame. What is more, this research group [25] has developed a

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series of nanoarchitectures through layer-by-layer assembly on cotton [6,8,9], polyester [11,12], and polyester–cotton blends fabrics [13], polycarbonate [26], and flexible polyurethane foam [20].

Grunlan et al. [4] developed an intumescent polymeric multi-layer nanocoating capable of extinguishing flame on fabrics. The layers were constructed of poly(sodiumphosphate) (PSP) and poly(allylamine) (PAAm). The mass of substrates coated with five of such bilayers increased only by 1.7%, and the peak heat release rate and total heat release of coated fabrics showed 43% and 51% reductions compared to the control fabric, respectively. Clay–Chitosan flame retardant nanocoatings have been deposited on polyurethane foam to improve the flame retardancy by Grunlan and his co-workers. Davis and co-workers have also studied the effect of LbL assemblies on open cell polyurethane foams [16,18]. Laachachi et al. developed flame retardant coating assemblies by layer-by-layer on polyamide and polyamide fabrics [27,28].

APP, the most widely used phosphorus-containing intumescent flame retardant, has been used to create the intumescent flame-retardant coatings via LbL assembly on polyester–cotton blends [13] and ramie fabrics [10]. The construction of CH-APP coating was first used by Carosio et al. [13] to improve the thermal stability and flame retardancy of polyester–cotton blends. Nevertheless, considering that the decomposition products of melamine that function as blowing agents in the typical intumescent system, more efficient than polyester–cotton blend, we combined melamine foam (comprised of melamine formaldehyde resin) and the CH-APP coating via layer-by-layer assembly and obtained CH-APP coated melamine foam. To our best knowledge, this intumescent-like system is more suitable for melamine foam, and the CH-APP coated melamine foam will probably show high flame retardancy in fire.

The fire protection of polymeric materials by intumescent flame-retardant coatings typically results from a condensed-phase mechanism [29,30]. The concept of intumescence mostly relies upon the formation of an expanded carbonized layer on the surface of the polymers during thermal degradation or combustion. This layer acts as an insulating barrier, reducing heat transfer between the heat source and the polymer surface, as well as limiting fuel transfer from the polymer towards the flame and diffusion of oxygen into the material [31–33]. Intumescent flame retardant systems are commonly composed of an acid source, a carbonization agent and a blowing agent. Coincidentally, APP and melamine are typical components of intumescent halogen-free flame retardants, and the reaction mechanism and kinetic study of the reaction between APP and melamine have been reported [34–36]. Traditional APP-based intumescent flame retardant systems are generally not durable, because APP exhibits poor compatibility with polymeric materials; APP-based coatings produced via layer-by-layer assembly have been shown to be more resistant to water [10,13].

To develop a highly flame-retardant flexible cellular polymeric material, we designed an APP-based nanocoating via LbL assemblies for melamine foams (comprised of melamine formaldehyde resin). To our best knowledge, this is the first paper for preparing highly flame-retardant flexible melamine foams via LbL assembly of CH and APP. Melamine foam is the substrate and acts as blowing agent in an intumescent system, CH acts as the carbon source in the system and is positively charged in aqueous solution; APP acts as acid source in the system and is negatively charged in aqueous solution. It is important to note that APP we used is of low degree of polymerization and is easy to hydrolyze. The chitosan also acts as a binder to keep all the components in place. The LbL deposition, film growth and structure, thermal properties, flame-retardant and anti-shrinking performances of the nanocoated melamine foam are reported herein.

## 2. Experimental

### 2.1. Materials

Melamine foam, with a density of  $8 \text{ kg m}^{-3}$  and without flame-retardant additives, was purchased from Sichuan Chemical Company Limited. Melamine foam is sold with the dimension of  $2500 \times 700 \times 200 \text{ mm}^3$ , and it is flexible foam and open cell. Chitosan (CH, MW 150 kDa, 85%–95% deacetylated) was purchased from Jinan Haidebei Marine Bioengineering Co. Ltd. Ammonium polyphosphate was purchased from ShifangTaifeng New Flame Retardant Co. Ltd (Sichuan, China). Deionized water and acetic acid were all manufactured by Chengdu Chemical Industries Co. (Chengdu, China). All materials were used as received without further purification.

### 2.2. Layer-by-layer deposition

Cationic deposition solutions were prepared by adjusting the pH of deionized water ( $17.8 \text{ M}\Omega$ ) to 4 with acetic acid and then dissolving 0.2 wt% chitosan. This aqueous solution was magnetically stirred for 12 h until the chitosan was completely dissolved. Anionic solutions were prepared by adding ammonium polyphosphate into deionized water. The concentration was 1.0 wt%, and the resulting solutions were used without adjusting pH value. Fig. 1 shows the schematic representation of preparing process of CH-APP layer-by-layer (LbL) assemblies. The assembly of CH and APP is based on electrostatic interaction as driving force, which is shown in Fig. 1, and it is easy for CH adsorbing on the surface of melamine foam as the first layer due to hydrogen bonding force. The substrate was dipped into the polyelectrolyte solutions, alternating between the CH and APP, with each cycle corresponding to one bilayer. The substrate was first immersed into the CH solution for 10 min and washed with deionized water twice each for 2 min and then dried. Melamine foam was dried at room temperature, and quartz slides were dried under nitrogen. After drying, the substrates were immersed into the APP solution for 10 min and washed with deionized water twice each for 2 min and then dried. This procedure describes a complete assembly cycle for one bilayer. The process was repeated until the required number of bilayers was built for each system. After achieving the desired number of bilayers, the coated foams were dried under vacuum at  $50^\circ \text{C}$  for 12 h. In order to characterize the CH-APP nanocoating, 5, 10, 15, and 20 BL CH-APP coatings were prepared on quartz slides. As two bilayers CH-APP coated melamine foam show significant results, only two bilayers of CH-APP coating was deposited on melamine foam.

### 2.3. Measurements and characterization

UV–vis spectra were measured by a Varian Cary 50 spectrophotometer. Surface structures of CH-APP coating were imaged with a SPA 400 atomic force microscope (AFM) (SPA 400, SII). Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet 6700 spectrometer with the ATR of Spectra-Tech Foundation Endurance using 32 scans in the frequency region of  $4000\text{--}400 \text{ cm}^{-1}$  at a  $4 \text{ cm}^{-1}$  resolution. Phosphorus content determination was determined using oxygen flask combustion-inductively coupled plasma atomic emission spectroscopy (ICP-AES) method. The testing sample was prepared as follows: about 20 mg coated foams were burned completely in a 1-L flask full of oxygen. KOH solution (concentration,  $0.001 \text{ mol L}^{-1}$ ) was used to absorb the gas when the phosphorus compound was oxidized by 0.1 wt%  $\text{KMnO}_4$ . By measuring the phosphorus contents of the foams, the content of APP deposited on the surface of the foam can be determined. Because the density of melamine foam is  $8 \text{ kg m}^{-3}$

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