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Construction of intumescent flame retardant and antimicrobial coating on cotton fabric via layer-by-layer assembly technology

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ABSTRACT

In this work, polyhexamethylene guanidine phosphate-ammonium polyphosphate (PHMGP–APP) assembly coating was designed on cotton fabric to achieve enhanced flame retardant and antimicrobial treatment by layer-by-layer (LBL) technology. Attenuated total reflection infrared spectroscopy results indicate that PHMGP-APP coating grows linearly during the assembly process. In vertical flammability test, the assembly coated fabric shows efficient flame retardant properties, such as a reduced burning time, no afterglow, and enhanced residue with intact textile structure. The residue after burning was analyzed by scanning electron microscopy, infrared spectroscopy and X-ray photoelectron spectroscopy and their results suggest that the coating performs perfect flame retardant effect on cotton owing to the synergistic effect of PHMGP with APP by facilitating the formation of char. Antimicrobial tests confirm that the coating has effective antimicrobial action on *Escherichia coli* and *Staphylococcus aureus*.

1. Introduction

Textile fabrics, especially cotton textiles, have been widely used in the daily life. However, the textiles suffer from their highly flammable nature, which greatly restricts their applications. Thus, it is necessary to improve the flame retardant performance of the textile fabrics. To date, several strategies, such as nanoparticle adsorption [1–4], graft polymerization [5,6], plasma [7] and sol–gel treatment [8,9], have been developed to enhance the flame retardancy of fabrics. Recently, layer-by-layer (LBL) assembly technique has been identified as one of the most promising methods capable of rendering given substrate flame retardant properties [10,11]. This method is an environmentally friendly and industrialized technique since water is chosen as the solvent for most of the self-assembly material and the ambient conditions are room temperature and atmospheric pressure [12]. In addition, compared to the mentioned methods, LBL assembly approach can easily fabricate high performance and versatility multilayer coating on cotton fabric by adjustably alternating the deposition of positively and negatively charged functional polyelectrolytes or nanoparticles. The first LBL flame retardant coating applied on fabric was demonstrated by the assembly of hybrid organic–inorganic structure composed of branched polyethylenimine and laponite clay [13]. The "brick-wall" structure nanocoating, capable of protecting the substrate during combustion, can significantly improve the heat stability and impart the flame retardant properties of cotton. After this research, a variety of flame retardant nanocoatings have been constructed on the fabric surface via LBL assembling of polyelectrolyte or nanoparticle [10, 14–17]. Among the reported coatings, the polymer-based intumescent coatings present better flame retardant performance, due to the powerful alliance of an acid source, a blowing agent and a carbon source within the coating. The intumescent flame retardant coating can transform into an intumescent protective char layer, which can effectively shield the underlying substrate from heat and oxygen. Grunlan [15] first created a polymer-based intumescent coating on cotton fabric by LBL assembly of poly(sodium phosphate) (PSP) and poly(allylamine) (PAAm), and 20 BL nanocoating could completely inhibit ignition of the cotton. Afterwards, several polyelectrolytes were employed in the current intumescent system, such as renewable chitosan (CH) and phytic acid [17], cationic polyethylenimine and anionic APP [18], and green CH and deoxyribonucleic acid (DNA) [19]. Our previous work has reported an intumescent CH–APP assembly coating which shows an excellent flame retardant efficiency on cotton by significantly reducing the burning time and effectively controlling the propagation of fire [20].

Meanwhile, in order to further broaden the application field of cotton fabric, in addition to flame retardance, great effort has also been devoted to endowing cotton with some other functionality by varying the compositions in coating, such as antistatic property [21], super hydrophobic [22–25], UV resistance [26–28] and so on. Especially, antimicrobial action is gradually concerned due to the need of health and safety [29,30]. It is well known that cotton is greatly susceptible to microbes, due to its porous hydrophilic structure that easily absorbs

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moisture, air, and nutrients, providing a good growing environment for microbes [31]. Microbes thrived on textile fabrics can trigger the degradation of cotton fiber and also cause severe skin diseases [32,33]. Hence, increasing tendency in fabricating multifunctional cotton fabric with flame retardant and antimicrobial properties has been recently recognized. However, it is notable that there are currently no reports on simultaneously endowing cotton fabric with flame retardant and antimicrobial properties.

Here, PHMGP can be considered as one of the potential materials to achieve multifunctional fabric. On one hand, due to the presence of abundant phosphorus and nitrogen elements, PHMGP can be considered as a potential candidate of blowing agent and acid source for building intumescent coating [34], as shown in Fig. 1a [17]. On the other hand, the guanidyl groups in guanidine-based polymer render them positively charged, allowing them to be coupled with other negatively charged materials to produce LBL assembly coating. Furthermore, guanidine-based polymer can endow cotton with antimicrobial property by electrostatic linking with the anionic carboxylate groups on cotton [35]. As a type of odorless, colorless, water-soluble polymer, guanidine-based materials with a concentration of less than 1% are basically harmless to human beings [36,37]. In addition, polymeric guanidine families, has been widely commercially used as antisepsis agent in wound care [36], food production [38], and aquatic agriculture [39–41]. Recently, they have been considered as a disinfector in household and healthcare industry [37,42]. Thus, it is possible to achieve multifunctional modification of cotton with flame retardant and antimicrobial property by introducing PHMGP via LBL assembly technique.

In this work, PHMGP was coupled with APP, an efficient intumescent flame retardant, to prepare intumescent flame retardant and antimicrobial multifunctional LBL assembly nanocoatings on cotton fabrics. The coating growth was monitored by attenuated total reflection Fourier transform infrared (ATR-FTIR) Spectroscopy. Thermal stability and fire resistance of the samples were investigated by thermo gravimetric analysis (TGA) and vertical and horizontal flammability tests (VFT and HFT), respectively. The antimicrobial performances on *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were evaluated by agar disk diffusion method.

2. Experimental

2.1. Materials

PHMGP (polymerization degree >60) was purchased from Shanghai Scunder Industry Co., Ltd. APP (polymerization degree >1000) was obtained from Shandong Shian Chemical Co., Ltd. NaOH was provided by Sinopharm Chemical Reagent Co., Ltd. Cotton fabric with a density of 230 g/m^2 was purchased from an online fabric store. All reagents were used as received, without further purification.

2.2. LBL assembly process

Cationic deposition solution was prepared by dissolving 0.1 wt.% PHMGP in deionized water. Anion deposition solutions were prepared by adding 0.1 wt.% APP to deionized water. Then the pH value was adjusted to 11 by adding 1 M sodium hydroxide solution, and finally this solution was magnetically stirred for 24 h until APP was completely dissolved. Prior to deposition, cotton fabric was immersed in deionized water for 24 h and then dried at 60 °C.

All coated cotton fabrics were prepared using the same procedure, as shown in Fig. 1a. Cotton fabrics were first immersed into the APP solution for 5 min, washed with deionized water, and dried with air. Then these fabrics were immersed into the PHMGP solution for 5 min, washed with deionized water, and dried with air. Subsequently, fabrics were alternately dipped into the anionic and cationic deposition solutions. Each dipping was followed by rinsing with deionized water for 30 s and drying with air at 60 °C, and the dipping times were changed to only 1 min. Finally, these coated fabrics were dried in air at 60 °C for 2 h after the desired number of bilayers (5, 10 and 20 BL) on fabrics was achieved. In addition, to explore the flame retardant and antimicrobial mechanisms, fabrics were correspondingly deposited with pure PHMGP or APP with coating weight equal to that of 10 BL coated fabric, and termed as 10 P or 10 A, respectively.

2.3. Measurement and characterization

The coating growth of the LBL assembly on cotton fabrics and infrared spectra of the char residues after VFT were recorded with a Nicolet 8700 Fourier transform infrared spectrometer (32 scans and 0.1 cm^{-1} resolution, Thermo Scientific Corporation, USA), equipped with a Ge crystal.

TGA was performed on a Pyris 1 TGA thermo-analyzer (PerkinElmer, USA) from 50 °C to 600 °C at a heating rate of 10 °C/min under air atmosphere (air flux: 40 mL/min).

VFT and HFT were conducted with an AG5100A horizontal vertical flame tester (Zhuhai Angui Testing Instrument Corporation, Limited). The fabrics for VFT and HFT were tailored into 120 × 37 and 330 × 50 mm^2, and exposed to the flame (40 and 19 ± 2 mm) for 12 and 15 s.

Limiting oxygen index (LOI) tests were carried out by using a JF-3 oxygen index apparatus (Jiangning Nanjing Analytical Instrument Corporation, Limited) according to ASTM D2863 standard.

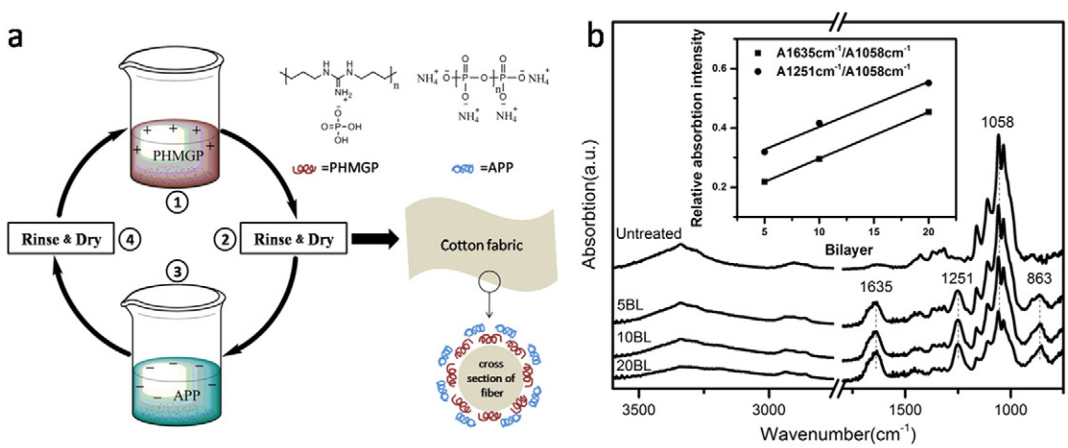

Fig. 1. a. Schematic of LBL PHMGP–APP assembly coating on cotton fabric; b. ATR-FTIR spectra of the untreated and coated cotton fabrics (5 BL, 10 BL and 20 BL). The inset shows the relative absorbance intensities of NH_2^+/C–O–C and P=O/C–O–C. The square, circle and lines represent the experiment data and fitting results of A1635 cm^{-1}/A1058 cm^{-1} and A1251 cm^{-1}/A1058 cm^{-1}, respectively.