

Influences of metal ions crosslinked alginate based coatings on thermal stability and fire resistance of cotton fabrics



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ABSTRACT

Bio-based and phosphorus-free coating was fabricated by layer-by-layer assembly method to obtain the flame retardant cotton fabric. For the first time, the modified cotton fabrics were prepared by utilizing positively charged polyethylenimine and negatively charged alginate together with subsequent crosslinking of barium, nickel and cobalt ions. Scanning electron microscopy and energy-dispersive X-ray demonstrated that the metal ions crosslinked coating was successfully constructed on the substrate. The thermal stability and flame retardancy were investigated by thermogravimetric analysis (TGA) and horizontal flame tests. TGA results showed that the degradation of the coated cotton fabrics were retarded at high temperature and the char residue of the cotton fabrics were improved after covered with the barium, nickel and cobalt ions crosslinked coatings. Furthermore, the fire resistance of cotton-Ba sample was enhanced significantly compared with the untreated sample, as evidenced by the obvious reduction (28%) of flame spread rate and complete char residue. Finally, the washing durability of coating on the fabric was enhanced after metal ions crosslinked with alginate based coating.

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1. Introduction

During past decades, renewable and biodegradable have attracted much attention and interest due to environment concerns and the realization of the gradual depletion of fossil resources. As a kind of biomass extracted from algae, alginate is composed of β -D-mannuronate (M) and α -L-guluronate (G) residues arranged in different M/G ratios and it is a polyelectrolyte that is considered to be biocompatible, non-toxic, non-immunogenic and biodegradable (Chen, Wang, Sánchez-Soto, & Schiraldi, 2012; Mi, Sung, & Shyu, 2002; Yang, Xie, & He, 2011). Meanwhile, alginate is known to form a hydrogel in the presence of divalent cations, such as calcium, which act as crosslinkers between the functional groups of alginate chains (Bu, Kjøniksen, Knudsen, & Nystrom, 2004). In recent years, various kinds of metal ions (Ni^{2+} , Co^{2+} , Mg^{2+} , Ba^{2+} , Cu^{2+}) were utilized to crosslink the alginate to prepare the flame retardant films and fibers (Liu et al., 2015, 2016; Liu, Zhao, Zhang, Guo, Cui, et al., 2015; Liu, Zhao, Zhang, Guo, Zhu et al., 2015; Zhang, Ji, Wang, Tan, & Xia, 2012). The effects of divalent metal ions on the flame retardant

properties, thermal stability of alginate fiber were investigated by Zhang et al. (2012). The Limiting oxygen index (LOI) value of alginate barium fiber could reach 45% and the heat release rate, total heat release and mass loss rate of the divalent metal alginate fibers were much lower than those of alginate acid fibers. Moreover, Wang et al.'s group investigated the flammability and thermal degradation behavior of nickel, copper, manganese and cobalt alginate films (Liu, Zhao, Zhang, Guo, Cui et al., 2015; Liu, Zhao, Zhang, Guo, Zhu et al., 2015). Cobalt alginate and nickel alginate films passed UL-94 V-0 rating and had much higher LOI values than those of manganese alginate, copper alginate and sodium alginate. These results provided useful information for designing bio-based materials with excellent fire-retardant properties.

Since Grunlan et al. first used a layer-by-layer (LbL) assembly method to produce a flame retardant coating on fabric in 2009 (Li, Schulz, & Grunlan, 2009), the LbL assembly technique has been an important method of flame retardant finishing to fabrics and polyurethane foams. The polyethylenimine (PEI) and Laponite clay were prepared using LbL assembly method by Grunlan et al. (Li et al., 2009). The LbL coating resulted in a significant improvement in the thermal stability of the cotton fabric and potential usage for flame retardant clothing and other materials. Then the phosphorus-containing polyelectrolytes were constructed on surfaces of the cotton fabrics via LbL assembly method (Laufer, Kirkland, Morgan, &

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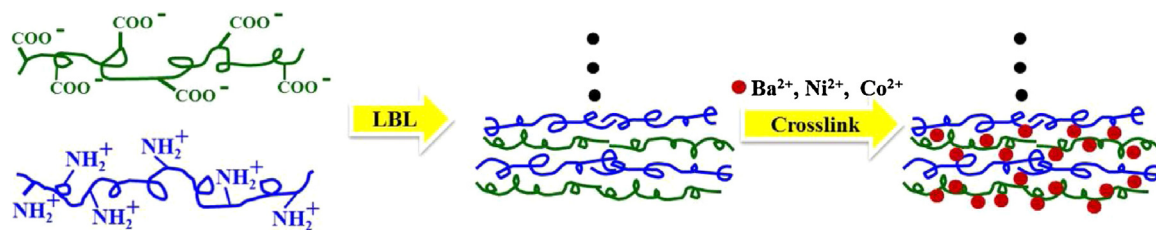


Fig. 1. Schematic of construction of PEI/alginate based coatings and crosslinking of coatings by metal ions on the cotton fabrics.

Grunlan, 2012; Zhang, Yan, Wang, & Fang, 2013). The flame could be self-extinguished on the modified fabrics during the vertical flame tests.

As a kind of natural fiber, cotton shows wide application in home textiles, because of its biodegradability, low price, low density, and good comfortableness. (El-Shafei, ElShemy, & Abou-Okeil, 2015; Shariatnia, Javeri, & Shekarriz, 2015) However, the highly flammable nature always limits its applications. (Pan et al., 2014) In the present work, the three kinds of excellent flame retardancy of metal ions crosslinked alginates were chosen ;1; to reduce the flammability of cotton fabric. As an anionic polyelectrolyte, alginate was combined with the PEI (cationic polyelectrolyte) to form a coating on the surface of cotton fabric via LbL assembly method. Then barium, nickel and cobalt ions were used to crosslink the alginate based coating. The objective of this work was to investigate the effect of barium, nickel and cobalt ions crosslinked alginate based coatings on thermal stability and flammability of cotton fabric.

2. Experimental section

2.1. Materials

Cotton fabric (120 g/m²) was bleached and obtained from Dongguan Lixingming Textile Co., Ltd. Alginate, barium chloride (BaCl₂), nickel acetate tetrahydrate (C₄H₆O₄Ni·4H₂O), and cobalt acetate tetrahydrate (C₄H₆O₄Co·4H₂O) were purchased from Sinopharm Chemical Reagent Co., Ltd. PEI (50 wt% aqueous solution, M_w ~ 70000) was kindly provided by Aladdin Chemistry Co., Ltd. Deionized water with a resistance of 18.2 MΩ was used for all experiments. PEI and alginate solutions of 0.5 wt% and 0.3 wt% were prepared by adding the PEI and alginate to deionized water and rolling for 12 h. Moreover, the pH values of PEI and alginate solutions were 9 and 7, respectively. Based on lots of previous works (Huang, Wu, Li, & Li, 2014; Li et al., 2010; Pan et al., 2015; Zhang et al., 2013), the PEI and alginate could as positive and negative polyelectrolytes respectively used in LbL process under these conditions.

2.2. Preparation of metal ions crosslinked alginate based coatings

Prior to the deposition, cotton fabrics were washed with deionized water then air-dried at room temperature overnight. Then the substrates were alternately dipped into PEI and alginate solutions for 2 min, each. Each time before soaking in the solutions, the fabrics were washed in water for 2 min to remove the unbound compounds that were left over at the previous step. One bilayer (BL) film was built up by a PEI single-layer and an alginate single-layer. The process of LbL assembly was presented in Fig. 1. When the bilayers reached to 10 bilayers, the samples were immersed in 5 mol/L BaCl₂, C₄H₆O₄Ni·4H₂O or C₄H₆O₄Co·4H₂O aqueous solutions for 2 h, respectively. Then the prepared fabric was washed using deionized water to remove the unreacted barium, nickel and cobalt ions. The obtained cotton fabrics were dried into a 70 °C con-

vection oven overnight and then stored in a desiccator for 24 h to eliminate the residual water.

2.3. Measurements

The content of the coating on the fabric (weight gain) was calculated according to the following equation: Weight gain = (W₁ - W)/W × 100%, where W and W₁ are the weight of the untreated and treated samples, respectively.

The microstructures of the samples were characterized using an FEI Sirion200 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) spectrometers. The specimens were previously coated with a conductive layer of gold.

The Thermogravimetric analysis (TGA) of the samples under nitrogen and air atmospheres were examined on a TGA-Q5000 apparatus (TA Instruments Inc., USA) from 50 to 700 °C at a heating rate of 20 °C/min.

The horizontal flame tests were carried out by using a methane flame for 3 s on the short side of the specimen (50 × 150 mm²). The total burning time and burning rate of the samples were evaluated.

In order to characterize the flame retardant durability of fabrics, the washing procedure for the cotton fabrics was referred to the previous work (Yang, Liao, Deng, Cao, & Wang, 2016). The coated fabrics were washed at 40 °C with mechanical stirring at 300 rpm in 0.5 wt% detergent solutions for 6 h, and then washed with deionized water to remove excess detergent, finally dried under vacuum at 50 °C for 12 h and stored in dryer prior to flammability testing.

3. Results and discussion

3.1. Characterization of metal ions crosslinked alginate based coatings

As shown in Table 1, the concentration of the dipping solution and weight gain of the coated cotton fabric are listed. It is seen that the weight gains of the fabrics with metal ions are increased obviously compared with that of cotton-blank. Among these three kinds of metal ions crosslinked coating modified fabrics, cotton-Co owns the maximum weight gain. SEM was used to observe the surface morphology of cotton fabric and Fig. 2 shows the SEM images of the untreated and coated cotton fabrics with different magnification. As presented in Fig. 2a–c, untreated cotton shows a smooth and clean surface with few defects. For all coated samples, the individual cotton fiber can be clearly observed in Fig. 2d, g, j, m. Compared with the untreated cotton fabric, the differences of the surface morphology are easily observable for the coated samples. Before the metal ions crosslinked the alginate/PEI coating, a thin and regular film is seen on the surface of cotton-blank. Rough surface can be observed in Fig. 2i, l, o for the three kinds of coated cotton fabrics owing to the presences of metal ions crosslinked alginate based coatings. However, the coatings crosslinked with Ba²⁺, Ni²⁺ and Co²⁺ present different morphologies. There exists some crystal-like on the surface of cotton-Ba sample and Ba²⁺ crosslinked coating is rougher than those of untreated cotton, cotton-Ni and cotton-Co. At high

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