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Flame retardation of cellulose-rich fabrics via a simplified layer-by-layer assembly

Jun-Chi Yang, Wang Liao*, Shi-Bi Deng, Zhi-Jie Cao, Yu-Zhong Wang*

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China

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ABSTRACT

Due to the high cellulose content of cotton (88.0–96.5%), the flame retardation of cotton fabrics can be achieved via an approach for the flame retardation of cellulose. In this work, a facile water-based flame retardant coating was deposited on cotton fabrics by a 'simplified' layer-by-layer (LbL) assembly. The novel coating solution was based on a mild reaction between ammonium polyphosphate (APP) and branched polyethyleneimine (BPEI), and the reaction mechanism was studied. TGA results showed that the char residues of coated fabrics were remarkably increased. The fabric with only 5wt% coating showed self-extinguishing in the horizontal flame test, and the peak heat release rate (pHRR) in cone calorimeter test decreased by 51%. Furthermore, this coating overcame a general drawback of flame-retardant LbL assembly which was easily washed away. Therefore, the simplified LbL method provides a fast, low-cost, eco-friendly and wash-durable flame-retardant finishing for the cellulose-rich cotton fabrics.

1. Introduction

Cotton is among the most important natural textile fibers because its broad planting area and huge output over the world. It is widely used in the productions closely related to daily life, such as apparel, home furnishings, etc. (Abou-Okeil, El-Sawy, & Abdel-Mohdy, 2013; Carosio, Laufer, Alongi, Camino, & Grunlan, 2011; Xie, Gao, & Zhang, 2013). However, cotton fabric catches fire easily and so brings high fire risk to life and property.

To impart cotton flame retardancy, effective halogen and phosphorus compounds were used, tetrakis (hydroxymethyl) phosphoniumchloride (THPC) (Horrocks, 2011), for instance. Although halogenated flame retardants are effective, they're found having noticeable disadvantages for their combustion products are toxic and corrosive. In addition, some combustion products can accumulate in food chain and seriously affect health of animals and human beings (Li, Wang et al., 2011; Li, Wang et al., 2010). Consequently, massive efforts have been made to develop halogen-free flame retardant (Chen & Wang, 2010). Flame retardants, containing phosphorus, nitrogen, boron, silicon and other nanoparticles, have been explored to improve the fire resistance of fabrics (Abd El-Hady, Farouk, & Sharaf, 2013; Doğan, Yılmaz, & Bayramlı, 2010; El-Shafei, ElShemy, & Abou-Okeil, 2015; Farag et al., 2013; Haile, Fincher, Fomete, & Grunlan, 2015; Martín, Ronda, & Cádiz, 2006).

Layer-by-layer (LbL) method has been fully developed as a convenient and versatile way to fabricate refined microstructures and multifunctional thin films to substrates (Alongi & Malucelli, 2015; Carosio, Alongi, & Malucelli, 2011; Kim, Davis, Cain, & Grunlan, 2011; Li, Wang et al., 2010; Li, Schulz et al., 2010). Recently, LbL has been used to assembly eco-friendly flame retardants on fabrics (Alongi, Carletto et al., 2013; Alongi, Carosio, Frache, & Malucelli, 2013; Carosio, Di Blasio, Alongi, & Malucelli, 2013; Yang, Cao, Wang, & Schiraldi, 2015). Through alternating deposition of oppositely charged polyelectrolytes, cotton fabrics, ramie fabrics and PET fabrics were coated in a control way (Carosio et al., 2011a; Carosio, Alongi, & Malucelli, 2012; Chang, Slopek, Condon, & Grunlan, 2014; Leistner, Abu-Odeh, Rohmer, & Grunlan, 2015; Li, Mannen et al., 2011; Pan et al., 2015; Zhang, Yan, Peng et al., 2013; Zhang, Yan, Wang, & Fang, 2013). Despite the enhanced flame retardancy, the washing fastness capacity of the add-on flame retardants via LbL assembly urgently requires improvement. Loss of add-on coatings inevitably diminish the fire resistance of the textiles (Horrocks, 2011). To the best of our knowledge, flame retardant LbL films with good washing fastness capacity are rarely reported (Cain, Murray, Holder, Nolen, & Grunlan, 2014; Chen, Li, Li, & Sun, 2015). Furthermore, during the assembly process of LbL method, the substrates should be alternatively dipped and washed in solutions or solvents, which is elaborate and time-consuming. Davis and his co-workers

* Corresponding authors.
E-mail addresses: liaowang@scu.edu.cn (W. Liao), yzwang@scu.edu.cn, polymers@126.com (Y.-Z. Wang).

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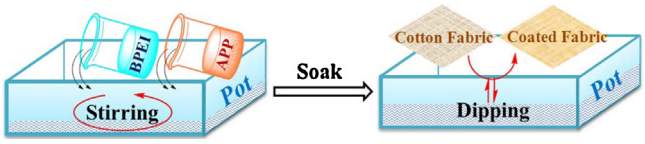

Fig. 1. Schematic representation of deposition on cotton fabrics with ammonium polyphosphate (APP) and branched polyethyleneimine (BPEI), and the fabrics can be dried at room temperature directly.

prepared a one-pot solution of potato starch, agar, sodium polyborate and/or sodium montmorillonite (Davis, Li, Gervasio, Luu, & Kim, 2015). After being coated with this solution, the fire safety of polyurethane foams was significantly improved with 63–75% reduction of the peak heat release rate (pHRR). This coating is fire resistant but the formula is somewhat complicated. And no incremental coating layers were tested. Cain et al. prepared a one-pot coating solution of poly(phosphate sodium salt) with branched polyethyleneimine (BPEI) (Cain et al., 2014). The fire behaviors of cotton fabrics with different soaking time in this solution were investigated. Improved fire safety could be achieved. However, this coating was not deposited 'layer' by 'layer' either, simplified assembly for the LbL are hence especially valuable.

Here, we prepared a halogen-free ammonium polyphosphate (APP) and BPEI aqueous solution in one-pot. The behavior of the mixture (APP and BPEI) was investigated and corresponding reaction mechanism was proposed. Cotton fabrics were coated by this single solution in a 'simplified' LbL way. The coating effectively enhances the flame retardancy of cotton fabrics and shows critical merit that withstanding washing. Thermal properties, flame-retardant performances of the coated cotton fabrics were also studied.

2. Experimental section

2.1. Materials

Cotton fabrics with a density of 120 g m^{-2} were purchased from Sichuan Cotton Printing and Dyeing (Sichuan, China). Ammonium polyphosphate was kindly supplied by ShifangTaifeng New Flame Retardant Co. Ltd. (Sichuan, China). Branched polyethyleneimine (BPEI, M_w = 20000) was purchased from Alfa Aesar. Laundry detergent (Ariel) was purchased from TRUST-MART (Sichuan, China). Deionized water was manufactured by Chengdu Chemical Industries Co. (Chengdu, China). All materials were used as received without further purification.

2.2. Simplified LbL deposition

Fig. 1 shows the schematic representation of deposition on cotton fabrics with ammonium polyphosphate (APP) and branched polyethyleneimine (BPEI), and it is realized simply through dipping as well as spraying. The APP and BPEI solutions were prepared with 17.8 MΩ deionized water and were magnetically stirred for 12 h until completely dissolved. The concentration of APP and BPEI aqueous solutions were 1.0wt% and 0.2wt% respectively, and the resulting solutions were used without adjusting pH value. By mixing the APP and BPEI solutions with the volume ratio of 1.2:1, the mixture was obtained. After that, the coating was deposited on cotton fabrics through dipping, and fabrics were dried at room temperature directly. Through the above deposition, about 0.8wt% coating was rapidly attached to fabrics. This process was repeated until the required weight of coating was deposited. It is worth pointing out that increasing the solution concentration and the drying temperature can certainly realize the deposition much faster, and this coating can be cured at room temperature or may cure with forced dry. As a consequence, we have obtained the film by pouring the mixture into polytetrafluoroethylenepetri dish and drying under vacuum overnight. Cotton fabrics and films were dried under vacuum at 50 °C for 12 h and stored in dryer prior to further testing.

2.3. Washing procedure for cotton fabrics

In order to characterize the flame retardant fastness to washing of fabrics, the coated fabrics were washed at 40 °C with mechanical stirring at 300 rpm in 0.5wt% detergent solutions for 3 and 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.

2.4. Measurements and characterization

The pH values of solutions and mixture were tested on the pH meter. The XRD patterns using Cu Kα radiation (λ = 1.542 Å) were performed with power DX-1000 diffractometer (Dandong Fangyuan, China) at the scanning rate of 0.02 per second in the 2θ range of 5–50°. Thermogravimetric analysis (TGA) was carried on a TG 209F1 (NETZSCH, Germany) thermogravimetric analyzer at a heating rate of 10 °C min^{-1} under nitrogen and air atmosphere. Flame resistance of fabrics in horizontal configuration was carried out applying a butane flame for 15 s on the short side of fabrics. The limiting oxygen index (LOI) value was tested on the Oxygen Index Flammability Gauge (HC-2C) according to ASTM D 2863-00 and the dimension of all samples was 140 × 52 × 0.3 mm^3. The flammability of the sample was measured with a cone calorimeter device (Fire Testing Technology) according to ISO 5660-1. The samples with a size of 100 × 100 × 0.3 mm^3 were exposed to a radiant cone at a heat flux of 35 kW m^{-2}. The morphologies of films and fabrics, along with the char residues collected after the cone calorimeter tests, were investigated using scanning electron microscopy (JEOL JSM 5900LV) with an energy-dispersive X-ray (EDX) analyzer.

3. Results and discussion

3.1. Simplified LbL coating

The novel coating solution was prepared by a reaction between APP and BPEI solutions. Fig. 2 shows the phenomenon of the reaction. In Fig. 2a, the bottles were filled with 0.2wt% BPEI solution (bottle No.1), 1.0wt% APP solution (bottle No.2), respectively. Once the two solutions were mixed, an opaque solution formed and finally converted into white precipitate in a month. The mixture of APP and BPEI solutions with a volume ratio of 1.2:1 is exhibited in Fig. 2a (bottle No.3).

To further investigate the reaction, wet pH test strips were placed above the bottle to monitor the chemical reaction (Fig. 2b). Comparing with the wet pH strips above the APP or BPEI solutions, the strip above the bottle of mixture turned into alkaline color (blue-green). Considering the reaction fundament, the alkaline gas was deduced as ammonia. Fig. 2c shows that large white precipitates are formed after a stationary time of one month. The precipitates finally formed a film at the bottom of the bottle.

Change of pH values was characterized by a pH meter for further investigation (Fig. 3a). Solutions were tested at 50 °C, which is beneficial to the pH stabilization and not too high that water vapors too fast. The pH values of 1.0wt% APP solution and 0.2wt% BPEI solution were 7.23 and 8.02, respectively. Once the solutions were mixed, the pH value increased to 8.48 immediately, which suggests the formation of larger quantities of ammonia. The alkaline gas gradually comes out from the solution by volatilizing, resulting in decrease of the pH value. After 50 min, the pH value stabilized at 7.66, indicating that the reaction reaches its equilibrium.