



Borate cross-linked layer-by-layer assembly of green polyelectrolytes on polyamide 66 fabrics for flame-retardant treatment

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ABSTRACT

Borate cross-linked thin coatings made from green polyelectrolytes, chitosan (CS) and phytic acid (PA), were deposited on polyamide 66 (PA66) fabrics via layer-by-layer (LbL) assembly to develop a durable flame retardant method. The surface and morphological characterization showed that CS and PA were successfully deposited onto the PA66 fabrics and cross-linked by borate. The presence of the coating slightly changed the limiting oxygen index (LOI) values, but suppressed flame spread and completely stopped melt-dripping of PA66 in UL 94 vertical burning test. The CS-PA coating also decreased the peak heat release rate of PA66 observed in cone calorimeter tests, and a maximum reduction of 31% was observed for PA66-10BL fabric sample. The addition of CS, PA and borate moieties lowered the initial decomposition temperature of PA66, but the char yield and char quality were improved. Especially, the char of the PA66 fabrics treated by borate exhibited better thermal resistance in thermogravimetric analysis (TGA) tests. More importantly, it was noticed that the stability of deposited CS-PA coating in sodium dodecyl sulfate (SDS) solution was enhanced significantly after cross-linking by borate, which would be favourable to durable flame-retardant treatment.

1. Introduction

Over the past few decades, considerable efforts have been devoted to developing new products from renewable resources owing to increasing concerns over environmental issues and depletion of petroleum resources [1]. Chitosan (CS) is a natural polysaccharide obtained from the shells of crustaceans [2]. Among its numerous applications in different fields, CS has found its use in flame retardant treatment of textiles and has become an effective intumescent additive, since it can act as a char-forming agent (carbon rich) and a blowing agent (releasing ammonia as it degrades) [3,4]. Phytic acid (PA) is the major storage form of phosphorus available in cereal grains, beans, and oil seeds [5]. Its structure consists of six phosphate groups with high phosphorus content (28 wt.%) which can deliver more active flame retardant atoms per molecule [6]. In the previous reports, CS has been combined with PA to form a fully renewable intumescent flame retardant system with a favourable phosphorus-nitrogen synergism between CS and PA [7,8]. However, these coatings are composed of water soluble compounds and might lose flame retardant performance after laundering cycles which is a great concern and rarely addressed recently. In our previous work, we used oxidized sodium alginate (OSA) as a cross-linker in LbL deposition with CS and PA to enhance the durability of such deposition and a slight improvement was observed in

SDS solution [9]. Also, other groups also reported UV-curable aliphatic acrylic polyurethane latex in LbL deposition to enhancing the stability of the deposited coatings in the flame retardant treatments of polypropylene films [10] and cotton fabrics [11].

As well, it was reported that boron-containing compound like calcium tetraborate was used a cross-linking agent and formed non-covalent or covalent bonds with polyvinyl alcohol and alginate chain [12]. Sodium tetraborate was also used to prepare transparent borate cross-linked chitosan/graphene oxide (CS/GO) nanocomposites through aqueous solution casting followed by low-temperature thermal treatment [13]. These composite films exhibited improved mechanical properties and it was found that the covalently assembled multilayers could potentially display enhanced stability compared with the layer-by-layer (LbL) ionic assembled films [14]. In addition, the co-addition of boron-containing compounds with phosphorus [15,16] and nitrogen [17] in the flame-retardant systems could further enhance the flame retardant efficiency. Very recently, Davis et al. prepared a flexible, highly fire resistant, and bioinspired coatings on flexible polyurethane foam using a boron fire retardant (boric acid or derivative) along with a polysaccharide binder (starch or agar), and a dirt char former (montmorillonite) through LbL deposition [18]. In another study, sodium polyborate along with polyhexamethylene guanidine phosphate was used to compose a nitrogen-phosphorus-boron intumescent flame

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retardant coating on cotton fabric via LbL technique and they were able to increase the LOI value up to 41% with 20 bilayers (BLs) deposition [19]. However, to the best of our knowledge, boron compounds have not simultaneously used as a flame retardant and a crosslinking agent in stabilizing the deposited layers in an LBL assembly process previously.

Polyamide 66 (PA66), also known as nylon66, is a thermoplastic textile material used in many fields including apparels and industrial textiles due to its excellent properties like good mechanical behavior, low cost, resistance to shrinkage and pleasant aesthetics. However, PA66 is highly flammable and also has dripping problem that limits its use in a wide range of applications [20,21]. In this work, a renewable intumescent nano-coating made from CS and PA was deposited onto the PA66 fabrics followed by sodium tetraborate mediated cross-linking between chitosan to reduce the flammability of PA66 fabrics. The main goal of this work was to develop an effective and durable flame retardant finishing on PA66 fabrics by only using green materials, explore the effect of expected synergism among P, N and B moieties and subsequently investigate the durability of deposited coatings.

2. Experimental

2.1. Materials

Sodium hydroxide and concentrated hydrochloric acid (HCl, 36.5–38%) were received from Changzheng Chemical Reagent Corp. Chitosan (viscosity 50–800 mPa s, degree of deacetylation: 80–95%), phytic acid (PA, 70 wt.% in H₂O) and sodium tetraborate decahydrate were purchased from Sinopharm Reagent Co., Ltd. (Shanghai, China). Deionized water with a resistance of 18.2 MΩ was used for all experiments. 100% PA66 woven fabrics with the density of 100 g/m² were obtained from Jiaying Weaving Industry Co. Ltd. (Yangzhou, China). The fabric swatches were previously scoured and subsequently air-dried at room temperature.

2.2. LbL deposition

Firstly, cationic polyelectrolyte solution was obtained by adjusting the pH of deionized water to 4 using acetic acid and then introducing 10 g/L chitosan. Anionic polyelectrolyte solution was obtained by adding 20 g/L phytic acid to deionized water. Both the solutions were under magnetic stirring (300 rpm) overnight at ambient atmosphere, and finally, their pH was kept at 4. Then, the substrates were immersed successively into solutions containing cationic (CS) and anionic (PA) species, which was called one bi-layer (BL). The immersion time in the CS and PA solutions of the first BL was 5 min each and subsequent immersion was 1 min each. Each immersion step was followed by rinsing the substrates with deionized water in order to remove weakly adsorbed species. The rinsing step time was set as 1 min. It was worth to mention that the samples were not blown dry between successive deposition steps. After the deposition of a desired number of BL, the samples were rinsed in water and dried at ambient temperature. Later, the above LbL deposited fabric samples were immersed in 1 wt.% and 5 wt.% borate solution for designated time followed by thermal treatment at 90 °C. The samples obtained were labeled as PA66-xBL-ByW, where x meant PA66 treated by x bilayers of CS and PA followed by cross-linked by y wt.% borate solution. Dry weight pickup (add on) is determined as follows:

$$\text{dry weight pick up} = \frac{W_1 - W}{W} \times 100\% \quad (1)$$

Where, W is the weight of the original PA66 fabric sample, while W₁ is the weight after the deposition of desired BLs of CS and PA. Moreover, the LBL assembly and the cross-linking mechanisms was proposed in Scheme 1 and their corresponding formulations and add on % were listed in Table 1.

2.3. Characterization

The FTIR spectra of the samples were recorded on Nicolet 6700 FT-IR spectrophotometer using thin KBr disk. The transmission mode was used and the wavenumber range was set from 4000 to 500 cm⁻¹.

The attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrum was obtained from a Thermo Nicolet Avatar 6700 FTIR equipped with an attenuated total reflectance device.

The morphologic information of the samples was observed by JSM-6700F scanning electron microscopy (JEOL, Japan). The samples were sputter-coated with a conductive gold layer before observation.

The XPS analysis was conducted on a PHI-TFA XPS spectrometer (Physical Electronics, Inc.). The analyzed area was 0.4 mm in diameter with a depth of approximately 3–5 nm.

Combustion property was investigated by a cone calorimeter (Fire Testing Technology, UK) on the basis of ISO 5660-1 standard. All the fabric samples (100 mm × 100 mm × 0.6 mm) were horizontally irradiated under a heat flux of 35 kW/m² and an air flow of 24 L/s.

Limiting oxygen index (LOI) tests were measured according to ASTM D2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 150 mm × 58 mm × 0.2 mm.

Vertical burning (UL-94) tests were performed according to ASTM D6413-08 using a vertical burning tester (CZF-3, Nanjing Jiangning Analytical Instrument Company, China). The samples (300 mm × 76 mm × 0.2 mm), held 19 mm over the Bunsen burner, were first exposed to the flame for a period of 12 s and then removed.

Thermogravimetric analysis (TGA) was carried out on a Q5000 IR thermogravimetric analyzer (TA Instruments, USA) using a heating rate of 20 °C/min under both air and nitrogen atmosphere.

Thermogravimetric analysis/infrared spectrometry (TGA-IR analysis) of the fabric sample was performed using the TGA Q5000 IR thermogravimetric analyzer that was interfaced to the Nicolet 6700 FT-IR spectrophotometer. The heating rate was set as 20 °C/min (nitrogen atmosphere, flow rate of 55 mL/min).

UV-vis spectra were recorded on a Hitachi U-3900H spectrophotometer (Japan).

Raman spectra of the char were obtained using a SPEX-1403 laser Raman spectrometer (SPEX Co., U.S.A.) from 500 to 2000 cm⁻¹.

Wash fastness test of treated samples was carried out according to AATCC test method 61(2A)-1996 in presence of non-ionic detergent in ambient conditions at 38 ± 3 °C where each cycle of washing process is equivalent to five home laundries. The flame retardant durability of the coated fabric samples was evaluated through UL-94 vertical burning test after 5 times washing.

3. Results and discussion

3.1. Surface characterization and film morphology

ATR-FTIR spectra of PA66-Control (a), PA66-CS-PA-5, 10 BL (b, c), and PA66-CS-PA-5, 10 BL-B5W (d, e) fabric samples are shown in Fig. 1. The characteristic peaks of CS were detected in a region around 1700–1500 cm⁻¹ corresponding to amino group [22,23]; while PA exhibited some characteristic absorptions at 1635 cm⁻¹ (stretching vibration of O–P–O) [24]. However, the characteristic peaks of the control PA66 like stretching vibration of C=O at around 1639 cm⁻¹ and –CONH– at 1540 cm⁻¹ [25] was still visible on treated fabric samples with reduced intensity. Moreover, the sodium tetraborate treated fabric samples showed a new peak at around 1415 cm⁻¹ assigning to B–O–C and B–O–P [17], indicating the cross-linking structure induced by borate moieties with the hydroxyls of chitosan and phytic acid.

The surface morphology of the control and coated PA66 fabrics was observed by SEM, as shown in Fig. 2. The conformal coating of individual PA66 fiber can be clearly observed for all coated samples; the

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