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Intumescent flame retardant coatings on cotton fabric of chitosan and ammonium polyphosphate via layer-by-layer assembly

Fei Fang [a], Xian Zhang [b,*], Yuedong Meng [a], Zhen Gu [b], Chao Bao [b], Xin Ding [b], Shiyuan Li [b], Xiaoxuan Chen [b], Xingyou Tian [b,**]

[a] Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[b] Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

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ABSTRACT

Intumescent flame retardant coating, composed of cationic chitosan and anion ammonium polyphosphate, has been constructed on cotton fabric by layer-by-layer assembly technique. The result of Fourier transform infrared spectroscopy confirmed that the assembly coating was successfully deposited on fabric and the coating quantity increased linearly with the growth of bilayer number. Evaluation of thermal and flammability properties showed increased residual chars at 700 °C in air during thermogravimetric analysis and decreased peak heat release rates and total heat releases in microscale combustibility test for the coated fabrics, as compared with the uncoated. Significantly, in vertical flame test the residues of the coated fabrics perfectly remained the textile structure and fiber shape with respectable strength, indicating that the intumescent coating show an excellent flame retardant efficiency on cotton. These results demonstrated a completely intumescent coating for cotton via layer-by-layer assembly technique which provides an effective alternative to phosphorus-based coating.

1. Introduction

As a kind of the most popular natural fabrics, cotton shows extensive applications in clothing, house furnishing, and many industrial goods, because of its personal warmth, excellent breathability and comfortableness [1]. But the high flammability of cotton for its low ignition temperature and oxygen index, which can potentially result in dangerous fire disaster, drives people to focus on imparting outstanding flame-retardant properties to cotton. Up to now, various methods, such as plasma [2–5], UV-curable [6,7], and sol–gel treatment [8–11] have been developed to construct flame-retardant coating on fabric. However, those strategies which always involve multistep chemical or physical processes under complicated conditions have led to more difficulties in their industrial applications [12–16].

Recently, layer-by-layer (LBL) assembly technique, as one of the most promising methods capable of enhancing flame retardancy, attracts people's wide attention both in academic research and future industrial application [17–21]. This method is a sample, environmental friendly and water-based technique to manufacture thin multilayer films, assembled by alternating the deposition of positively and negatively charged polyelectrolytes or nanoparticles, on complex substrates such as textile fabric [22]. Various flame retardant coatings were applied to textiles by LBL assembly, such as hybrid organic–inorganic system [17,23–25], all-inorganic system [26,27] and all-polymer intumescent system [16,18,19,28,29]. Among above systems, the phosphorus-based intumescent system has been identified as the most hopeful alternative flame retardant for fabrics, owing to its high efficiency and environmental protection [30]. Li et al. in 2011 applied intumescent coating assembly of poly(sodium phosphate) (PSP) and poly(allylamine) (PAAm) on fabric which completely avoided the ignition of cotton in a vertical flame test [18]. Afterwards, more phosphorus-based intumescent systems were introduced into LBL assembly coating, such as chitosan and phytic acid, poly(acrylic acid) and ammonium polyphosphate, polyethylenimine and ammonium polyphosphate, chitosan and DNA, and polyallylamine and polyphosphate. Among above ammonium polyphosphate (APP)-based coating was quite popular [13,25]. APP (as mainly an acid source) would cooperate with fabric (carbon source) to form an intumescent flame retardant system at the cost of consuming fabric substrate during burning. However, the flame retardant efficiency depending on the mutual matching between the APP-based coating and fabric substrate could become poor in the case of improper proportion or different substrates. So, an additional carbon source is necessary to construct an integrated intumescent flame retardant coating with APP in order to get the efficiency and applicability improved [31].

Remarkably, chitosan (CH), which is widely applied in biological medicine [32,33], is an environmental-friendly and carbon-rich polymer and can serve as a carbon source in an intumescent system. Meanwhile, it would become positively charged in an acid solution that is proper to be paired with negatively charged polyelectrolyte by LBL

* Corresponding author. Tel.: +86 55165592752; fax: +86 55165591434.
** Corresponding author. Tel.: +86 55165591418; fax: +86 55165591434.
E-mail addresses: xzhang@issp.ac.cn (X. Zhang), xytian@issp.ac.cn (X. Tian).

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Table 1
The add-on and P content deposited on cotton fabrics.

Sample	Add-on (wt.%)	P (wt.%)
Uncoated	–	–
5 BL	6.5	0.21
10 BL	11.7	0.63
20 BL	14.3	0.96

Table 2
TGA and DTG data of the uncoated and coated cotton fabrics.

Sample	$T_{-5\%}$ (°C)	T_{max1} (°C)	Residue at T_{max1} (wt.%)	T_{max2} (°C)	Residue at 700 °C (wt.%)
Uncoated	298	362	52.2	477	3.9
5 BL	307	348	59.1	559	4.2
10 BL	271	318	69.3	527	7.2
20 BL	269	320	72.1	568	10.9

assembly [34,35]. Moreover, chitosan contains nitrogen element in its molecular structure and can be coupled with APP to provide an entirely intumescent flame retardant system during burning. However, as far as we know, there is few report about CH–APP intumescent coating on cotton fabric [36,37].

In the present work, we deposited CH and APP assembly films on cotton fabric in an effort to create a completely intumescent flame retardant coating, in which chitosan acts as carbon donor and blowing agent, whereas APP mainly plays a role as an acid donor. The attenuated total reflection Fourier transform infrared spectra (ATR-FTIR) has been used to monitor the coating growth on cotton. Thermogravimetry, vertical flame test and microscale combustibility test have been exploited for evaluating the thermal properties and observing the combustion behavior of the coated fabrics.

2. Experimental

2.1. Materials

Chitosan (CH, viscosity: 50–800 mPa·s) was obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Ammonium polyphosphate (APP, n > 1000, Mn > 208,000) was purchased from Shandong Shian Chemical Co., Ltd. (China). Hydrochloric acid (HCl) was acquired from Shanghai Suyi Chemical Reagent Co., Ltd. (China). Sodium hydroxide (NaOH, ≥96.0%) was received from Sinopharm Chemical Reagent Co., Ltd. (China). All the above reagents were used as received, without any further modification. Cotton fabric (230 g/m^2) was purchased from an online fabric store.

2.2. LBL deposition

The 0.1 wt.% CH solution was prepared using deionized water, followed by adjusting the pH value to 4 by adding 1 M HCl, then was magnetically stirred for 24 h until the CH was completely dissolved. For the preparation of APP solution, 0.1 wt.% APP was added to deionized water. This was followed by adjusting the pH value to 11 using 1 M NaOH solution and stirring for 24 h.

Before LBL assembly, cotton was soaked in deionized water for 24 h, followed by drying at 60 °C for 2 h. After that cotton fabric was first dipped into the CH solution for 5 min, followed by rinsing with deionized water for 1 min and drying in air; then dipped into the APP solution for 5 min, followed by rinsing with deionized water for 1 min and drying in air. One bilayer (BL) of CH and APP was obtained in the complete assembly cycle process, and then these fabrics were alternately immersed into CH and APP solutions until the desired number of bilayers on fabric was obtained. But subsequent dipping time was only 1 min, followed by washing with deionized water for 30 s and then drying in air at 60 °C for 2 h until the desired number of bilayer on fabrics was achieved. At last, the add-on deposited on cotton fibers was obtained through the measurement of the weight before and after LBL assembly treatment, and the results are listed in Table 1.

2.3. Measurements and characterization

The P element contents on the coated fabrics were analyzed with an inductive coupling plasma atomic emission spectrometer (ICP-AES, Optima 7300 DV, Perkin-Elmer Corporation, USA). The coated fabrics (0.1 g) were treated with 8.0 mL concentrated HNO_3 (65%) until completely dissolved. Then the clear solutions were transferred to a 100 mL volumetric flask and diluted with deionized water. The accuracy was 1 mg/mL. The attenuated total reflection Fourier transform infrared spectra (ATR-FTIR) of cotton fabrics were recorded by a Nicolet 8700 spectrometer (32 scans and 4 cm^{-1} resolution, Thermo Nicolet Corporation, USA). Thermogravimetric analysis was conducted on a Pyris 1 TGA (PerkinElmer, USA). The sample was heated up from 50 to 700 °C at a rate of 10 °C/min^{-1} under air atmosphere. The experimental error was ±1 °C for temperature and ±0.1% for residual mass. The vertical flame test was performed according to GB/T 5455-1997, using a AG5100A Horizontal vertical flame tester (Zhuhai Angui Testing Instrument Co., Ltd). The fabrics (120 * 37 mm^2) were exposed to the flame (height: 40 mm ± 2 mm, gas: methane) for 12 s. Surface morphologies of the uncoated and coated cotton fabrics as well as residue chars were observed by a Sirion 200 field emission scanning electron microscope (FEI Corporation, USA). Prior to observation, all the samples were gold-sputtered to increase their conductivity. The microscale combustibility test was carried out on an MCC-2 microscale combustion calorimeter (Govmark Organization, Inc., Farmingdale, NY). All the specimens were firstly kept at 100 °C for 5 min, followed by heating up to 650 °C at a rate of 1 °C/s, and the oxygen/nitrogen flow rate was set at 20/80 mL/mL. The repeatability of the heat release rate is ±5%.

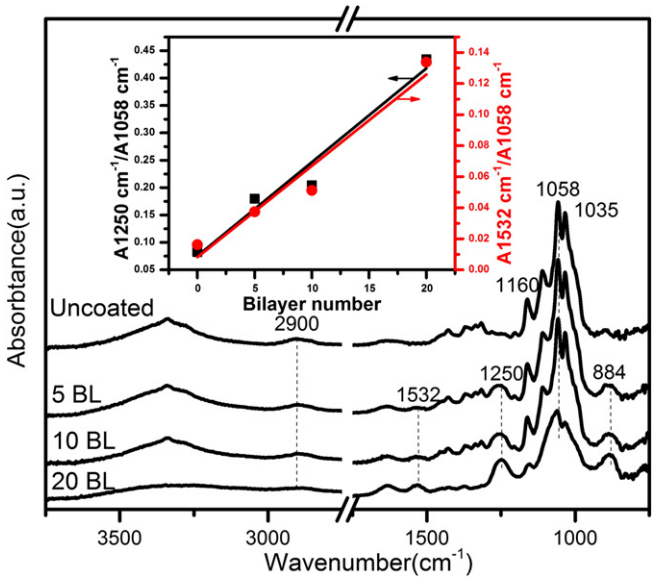

Fig. 1. The ATR-FTIR spectrum of the uncoated and coated cotton fabrics. The inset shows the relative absorbance intensities of P–O–P/C–O–C and P═O/C–O–C, the black squares and red solid circles represent the experimental data of A1250 cm^{-1}/A1058 cm^{-1} and A1532 cm^{-1}/A1058 cm^{-1}, respectively; the black line and red line represent the fitting results of A1250 cm^{-1}/A1058 cm^{-1} and A1532 cm^{-1}/A1058 cm^{-1}, respectively.