
Anti-Flammable Properties of Cotton Fabrics Using Eco Friendly Inorganic Materials by Layering Self-Assisted Processing

Sechin Chang^{*}, Brian Condon, Elena Graves, Jade Smith

United States Department of Agriculture, Agricultural Research Service - Southern Regional Research Center, New Orleans, USA

Email address:

sechin.chang@ars.usda.gov (S. Chang), brian.condon@ars.usda.gov (B. Condon), elena.graves@ars.usda.gov (E. Graves),

jade.smith@ars.usda.gov (J. Smith)

^{*}Corresponding author

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Abstract: A flame retardant surface has been prepared by the layer-by layer assemblies of branched polyethylenimine (BPEI), kaolin, urea, and diammonium phosphate (DAP) on cotton fabrics. Four different kinds of cotton fabrics (print cloth, mercerized print cloth, mercerized twill, and fleece) were prepared using solutions of BPEI, urea, DAP, and kaolin. Layer-by-layer assemblies for flame retardant properties were applied by the pad-dry-cure method and each coating formula was rotated for 10, 20, 30, or 40 bilayers. To assess the effectiveness to resist flame propagation on treated fabrics of different constructions the vertical flammability test (ASTM D 6413-11) was used. In most cases char lengths of fabrics that passed the vertical flammability tests were less than 50% of the original length and after-flame and after-glow times were less than one second. Thermogravimetric analysis (TGA) and limiting oxygen indices (LOI, ASTM D 2863-09) were also used to test for flame retardancy. All untreated fabrics showed LOI values of about 19-21% oxygen in nitrogen. LOI values for the four types of treated fabrics were greater than 35% when add-on wt% values were between 11.1 – 18.6 wt %. In addition, structural characterizations of treated fabrics were studied by SEM methods.

Keywords: Cotton Fabric, Flame Retardant, Layering, Flammability Test

1. Introduction

Cotton fiber is widely used to produce apparel, home furnishings, and various industrial products, such as medical supplies, industrial thread, and tarpaulins. Although cotton is prized for its softness, breathability, and ability to absorb moisture, cotton is generally more combustible than most synthetic fibers [1]. To meet fire safety regulations and expand the use of cotton in textile applications that require flame resistance, a significant number of flame-retardant treatments for textiles were developed in the second half of the last century. The majority of these flame-retardant treatments can be classified into four distinct groups: inorganic, halogenated organic, organophosphorus, and nitrogen based [2-6]. Earlier works on phosphorus-nitrogen systems showed that such combinations produced greater

flame resistance in cotton textiles at a lower level of phosphorus than when phosphorus was used alone [7-9]. Unlike the halogen-containing compounds, which generate toxicity or may produce toxic gases, corrosive smoke, or harmful substances [10], the phosphorous-containing flame retardants are known to transform into phosphoric acid during combustion or thermal degradation. This further causes the formation of non-volatile polyphosphoric acid that can react with the decomposing polymer by esterification and dehydration to promote the formation of char residue [11, 12]. The char residue can act as a barrier to protect the underlying polymer from attack by oxygen and radiant heat, achieving the purpose of extinguishing the fire.

Recently, the layer-by-layer (LBL) assembly of nanocoatings onto fabrics has attracted a lot of attention as a simple and cost effective method of imparting specific

chemical finishes to natural and synthetic fabrics. The LBL process was modernized by G. Decher [13-17] and is based on the alternating deposition of charged anionic and cationic polyelectrolytes to create nanometer thin multilayer coatings on the surface of a material via electrostatic interactions. A wide variety of functional molecules can be incorporated within the coatings, including nanoparticles, dyes, and proteins, to modify the physical and chemical properties of the material surface. Although the LBL process is dependent on such parameters as the chemistry of the polyelectrolyte, temperature, and pH, the process is not limited by the size, shape, and topography of the material surface, which makes the technique well-suited for tailoring the surface properties of nonplanar textile fabrics [18-26]. J. Grunlan and co-workers have extensively studied the LBL deposition of clay and nanoparticles with branched polyethylenimine (BPEI) on cotton fabric to produce flame-retardant multilayer coatings of an environmentally friendly, all-polymer nanocoating capable of extinguishing flame on cotton fabrics [27-29].

The nanocoating of textile materials to impart flame retardancy is a relatively new field, and although the use of LBL technology to modify the surfaces of textile fabrics and fibers has been widely studied in recent years, the overall process is still not well understood. Previous LBL flame retardant research has primarily focused on the development and characterization of simple clay/polyelectrolyte thin films with no additional small molecule flame retardants added to the formulation. In addition, current laboratory-based LBL techniques that use multiple immersion/rinse cycles to develop multilayer coatings can be labor-intensive and time-consuming, which often limits the use of the coating technique in commercial applications. In the present study, an attempt was made to improve the flame retardancy of four cotton fabrics; print cloth, mercerized print cloth, twill, and fleece cotton fabrics by the deposition of multilayer films containing BPEI, DAP, urea, and kaolin nanoparticles using a newly developed continuous LBL self assisted process. The imparted flame retardancy of the cotton fabrics with the deposited clay nanolayers was tested using thermogravimetric analysis (TGA), limiting oxygen index (LOI, ASTM D 2863-09), and vertical flammability testing (ASTM D 6413-11). Scanning electron microscopy (SEM) measurements were performed to verify the presence of the deposited nanolayers and study the morphology of the various nanocoatings.

2. Experimental

2.1. Material

Commercial grade diammonium phosphate (DAP) and urea were obtained from Magnolia Chemical Co. (New

Orleans, LA, USA). Kaolin powder, sodium hydroxide, and BPEI with a molecular weight of 1200 were purchased from Aldrich and used as received. The reagents were used without further drying or purifying. In the testing experiments, print cloth (102 g/m²), mercerized print cloth (110 g/m²), mercerized twill (258 g/m²), and fleece (241 g/m²) cotton fabrics were obtained from Test Fabrics Inc. and used as received. This fabric was desized (starches removed) and bleached and was free of all resins and finishes.

2.2. Layer-by-Layer Self-Assisted Processing and Fabric Treatment

A modified laboratory pad-steam unit (Mathis, model PSA-HTF, Figure 1) was used to apply the 10-40 BL kaolin-BPEI-DAP-urea coatings to the print cloth, mercerized print cloth, twill and fleece cotton fabrics in a continuous layer-by-layer process. The steam range of the pad-steam unit was bypassed, and the fabrics were directly loaded onto the rinsing section of the unit, which consisted of two separate rinsing chambers. The fabrics were cut to a width of 16 in. (405 mm) for processing and hand fed through the individual rollers of the rinsing chambers before the ends were sewn together to create a continuous piece of fabric. The first rinsing chamber was filled with 10 L of an aqueous-based 1.5 wt % BPEI solution (cationic) containing 20 wt % urea and diammonium phosphate (DAP). The second chamber was filled with 10 L of an aqueous solution of 1.5% Kaolin (anionic) that was brought to a pH of 11 using NaOH. The kaolin nanoparticles were dispersed in deionized water using a shear mixer (Silverson, model L5MA) set to 3000 rpm, and a stable colloidal solution was obtained after 3 h of mixing. The detailed contents of each treatment are outlined in Figure 2. The multilayer continuous deposition process consisted of two steps, the immersion of the cotton fabrics in the 1.5 wt % BPEI solution, which pass through a roller, immediately followed by immersion of the fabrics in the 1.5% Kaolin solution which also pass through a roller. The two steps were continuously repeated for each formulation, without rinsing, for a total of 10-40 cycles using a roller speed of 2 m/min and a pad pressure of 3 bar (300 kPa). Upon completion of the deposition process, the rinsing chambers of the pad-steam unit were drained and the fabric was cut for removal. The 10-40 LBL coated cotton fabrics were dried at 110 °C and cured at 140 °C via a continuous dryer (Mathis, model KTF-S) set to a speed of 2 m/min. Once taken out of the curing oven, the fabric was immediately placed in a desiccator to cool to room temperature, and its weight was obtained after cooling. All samples were weighed before and after the treatment and the values were fitted to the equation (1) to obtain add-on percents (or add-on levels)

$$\text{Add-on (\%)} = [(\text{weight}_{\text{after drying}} - \text{weight}_{\text{before treatment}}) / \text{weight}_{\text{before treatment}}] \times 100 \quad (1)$$

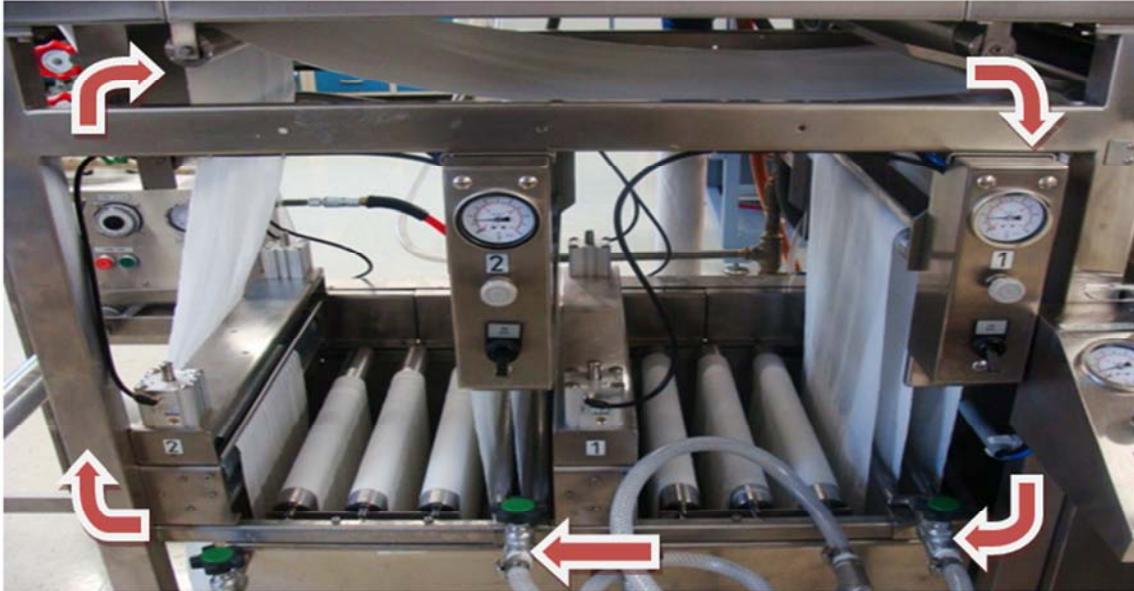


Figure 1. Picture of the Layer-by-Layer self-assisted deposition process used to apply the 10-40 bilayers kaolin–BPEI–DAP–urea coatings. Arrows indicate the directional flow of the fabric as it is processed.

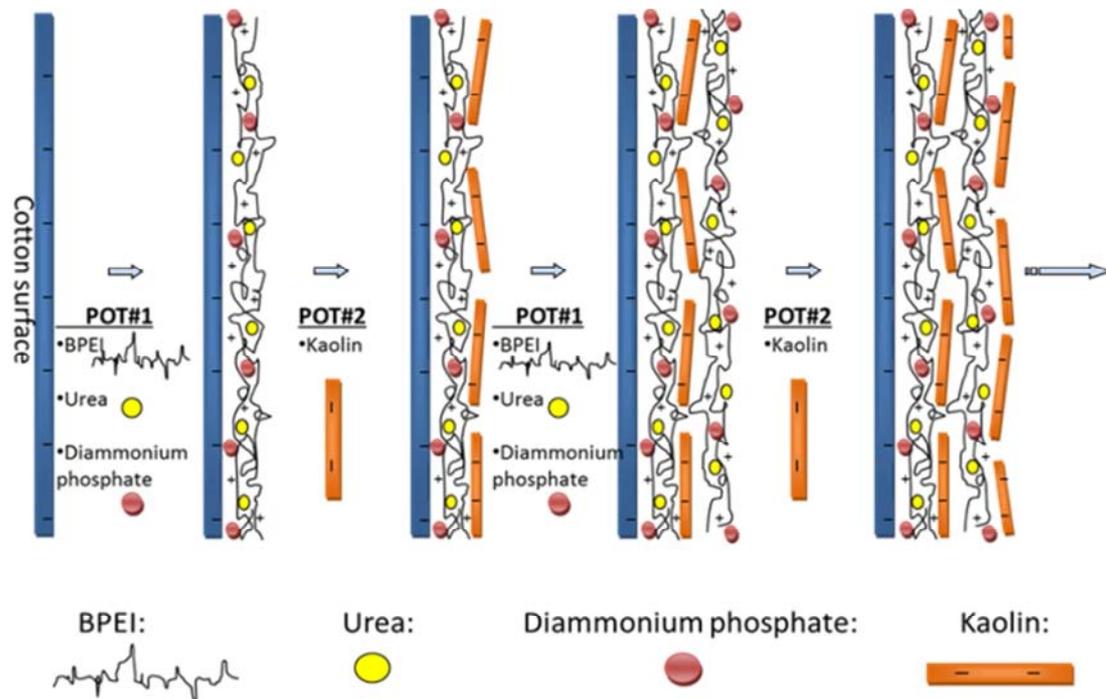


Figure 2. Schematic diagram of the layer-by-layer application on the surface of cotton fabrics.

2.3. Thermal Gravimetric Analysis (TGA), Vertical Flame Test and Limiting Oxygen Index (LOI)

TGA was measured using a TGA Q 500 thermal gravimetric analyzer (TA Instruments). A sample of 5–6 mg was heated from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen at a flow rate of 60 mL/min. Three runs were performed to obtain average thermal decomposition parameters. Control twill and all treated fabrics were subjected to the vertical flammability (The Govmark Organization, Inc.) and LOI (Bynisco Polymer

tests. In these tests, the specimen sizes were 30 x 9 and 13 x 6 cm for vertical flammability and LOI, respectively. In the vertical flame test, a specimen was positioned vertically above a controlled flame and exposed for a specified time, and an afterglow time was measured. Char length was measured under a specified force and any evidence of melting or dripping was noted. In the LOI test, a small sample of fabric was supported vertically in a mixture of oxygen and nitrogen flowing upwards through a transparent chimney. When the upper end of the sample was ignited, the subsequent burning behaviour of the sample was observed to

record the period for which burning continued or the length of sample burned. Minimum concentration of oxygen was determined by testing a series of samples in different oxygen concentrations.

2.4. Scanning Electron Microscopy (SEM)

SEM was used to observe the microstructure and the surface morphology of the coated and uncoated cotton samples. The instrument was a Phillips XL 30 ESEM with the acceleration voltage set at 12 kV and a beam current of 0.5 nA. The samples were coated with a gold–palladium alloy to provide a 200 Å gold–palladium layer of thickness using a vacuum sputter coater. Both the burned and unburned cotton samples were examined at magnifications ranging from 798× to 1500×.

3. Results and Discussion

3.1. Fabric Treatment

Table 1 shows percent add on values following wet pickup, drying, curing, and reconditioning of 10-40 bilayer coated print cloth, mercerized print cloth, mercerized twill and fleece fabric samples. Following application, the treated fabrics appeared as white as the original fabrics. Bilayers of 10, 20, 30 and 40 showed 14.8, 15.8, 17.8, and 18.6 wt % add-ons for print cloth, 11.2, 11.1, 15.4, and 14.6 wt % add-ons for mercerized print cloth, 15.7, 13.4, 17.6, and 13.7 wt % add-ons for twill, and 11.1, 13.5, 12.0, and 13.5 wt % add-ons for fleece cotton fabrics, respectively. There was not any significant evidence for increased add-on by number of increased layer-by layer procedures. The majority of add-ons appear to be the result of adding DAP and urea to the BPEI solution. In fact, when the fabrics were treated with an aqueous solution of 20 wt % DAP and urea, the percent add-ons ranged from 15.5 to 17.3% depending on the fabric by 40

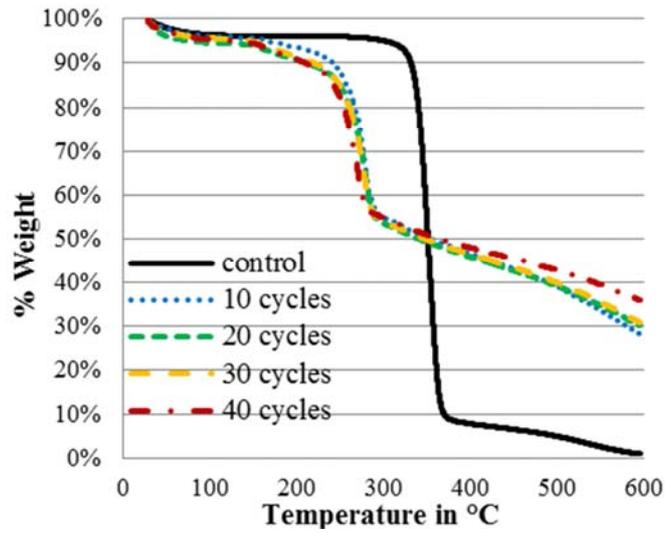
bilayers processing. At this stage no attempt was made to test the durability of the flame-resistant formulations with multiple laundering tests.

3.2. Thermogravimetric Analysis (TGA)

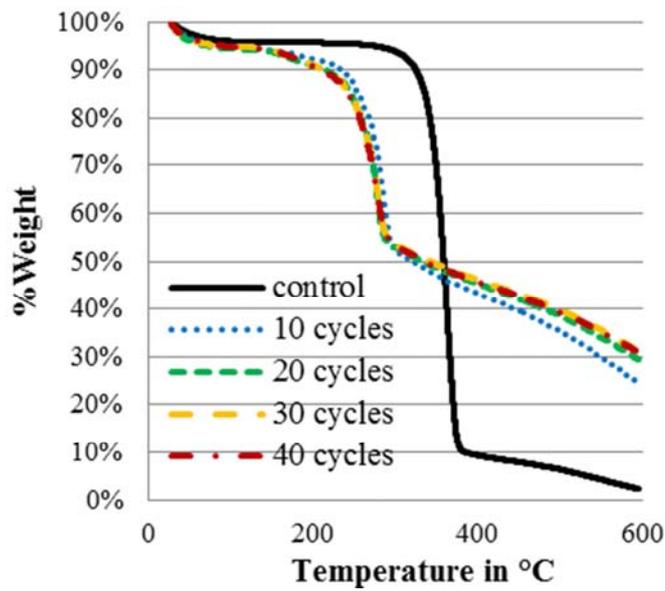
Table 1 shows the TGA values for onset of degradation temperature (°C) and char yield (% at 600 °C) for untreated and treated cotton fabrics. Figure 3 compiles TGA curves from 25-600°C of the control and treated fabrics. In a nitrogen atmosphere, all the untreated and treated fabrics exhibit mostly mono mass-loss curves. With regard to the control, the TGA curve shows the loss of mass starting around 330-340°C, then displays a turning point at 360°C, which is where the rate of its mass loss reaches its maximum. It then continues losing more weight until it reaches 85 % weight loss close to 600°C. During this process, cotton produces volatiles including combustible and non-combustible species at around 350°C. At higher temperatures, the degradation generates a smouldering phenomenon, leading to a slower mass loss [30]. All untreated cotton fabrics showed char residues between 1.0 and 2.3% of original weight at 600 °C. According to Figure 3a, when the print cloth was treated, it showed onsets of degradation between 250 and 262 °C and provided char yields between 27.7 and 35.8%. Mercerized print cloth (Figure 3b) degraded between 243 and 265 °C and showed char yields between 24.8 and 31.2%. Treated twill fabric (Figure 3c) degraded between 263 and 269 °C and provided char residues between 22.8 and 24.7% of original weight. Treated fleece fabrics (Figure 3d) showed onsets of degradation between 244 and 256°C and char residues between 31.5 and 35.0%. Decomposition temperatures of treated fabrics were lower than those of untreated fabrics. This may be due to the phosphonic acid derivatives accelerating fabric degradation.

Table 1. Fabric treatment and TGA data for untreated and treated print cloth, mercerized print cloth, twill, and fleece cotton fabrics.

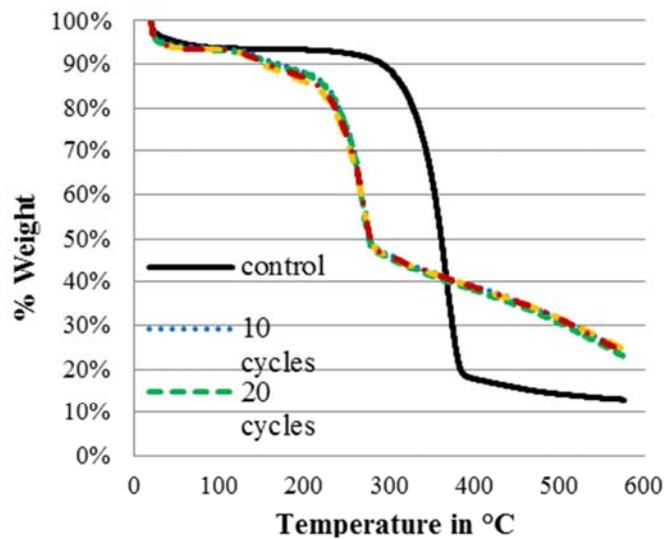
Fabric	Number of bilayer	Add on (wt %)	Onset of degradation °C	TGA char% at 600°C
Print cloth	0	0	337.3	1.0
	10	14.8	261.5	27.6
	20	15.8	143.4/ 261.2	29.9
	30	17.8	143.3/ 257.9	31.1
	40	18.6	143.5/250.5	35.8
Mercerized print cloth	0	0	342.4	2.3
	10	11.2	162.8/265.2	24.8
	20	11.1	144.3/260.2	29.3
	30	15.4	142.7/258.2	31.2
	40	14.6	247.2	30.5
Twill	0	0	334.7	2.3
	10	15.7	144.5/267.9	24.1
	20	13.4	145.2/269.0	22.8
	30	17.6	142.6/263.0	24.7
	40	13.7	142.7/265.8	23.7
Fleece	0	0	340.7	1.4
	10	11.1	140.7/244.1	32.1
	20	13.5	143.2/255.8	31.5
	30	12.0	143.5/250.4	34.2
	40	13.5	141.4/249.3	35.0



(a) Print cloth



(b) Mercerized print cloth



(c) Twill

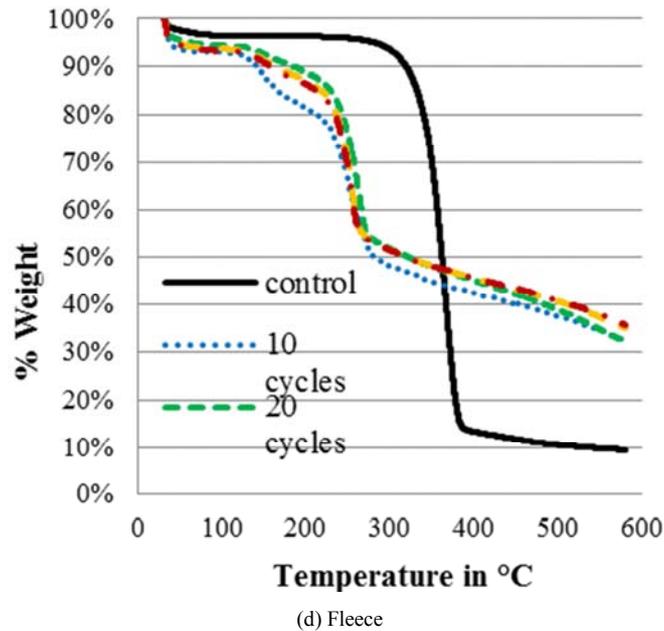


Figure 3. Degradation thermogram curves of the untreated and treated cotton (a) print cloth, (b) mercerized print cloth, (c) twill, and (d) fleece fabrics coated with 10-40 bilayers.

From the data in Table 1, it is evident that the char yields generated by high add-ons (wt %) are 10–20% greater than those produced by low add-ons (wt%) due to the higher phosphorus and nitrogen contents. Chars protect against heat and flame propagation because they generate thermally stable cohesive phases having decomposition temperatures that exceed the temperatures of the oxidizing zones of flames. Furthermore, chars are intumescent; they foam and release gases that suppress flammability. Therefore, it is very important to design flame retardants that support intumescent and char formation. [31-33]

The onset of degradation of the treated fabrics initiates roughly at 240-270 °C. Evidently, the flame retardants lower the heat resistance of the bulk material when compared to the control. Thermal degradation curves of treated fabrics normally comprise of at least two stages: the first is the degradation of the flame retardants, the chemicals, and the second is the degradation of main materials, the fabrics. Depending on concentration of the flame retardants on the fabrics, the first stage may or may not be obvious. It is well known that phosphorus additives reduce the onset temperature for the second stage of treated cellulose by 50 - 150 °C [34] - [36]. Again, phosphorus flame retardants obviously promote char generation, and therefore, flame resistance in the treated fabrics.

3.3. Limiting Oxygen Index (LOI) and Vertical Flammability

Limiting oxygen index (LOI) values indicate the minimum amount of oxygen needed to sustain a candle-like flame

when a sample is burned in an atmosphere of oxygen and nitrogen. Textiles are considered to be flammable when LOI values are below 21% oxygen in nitrogen and are considered to be flame-retardant when LOI values fall in the range of 26-28%. At these LOI values, flame retarded test fabric samples are expected to pass open flame tests in either the horizontal or vertical direction [31-32]. Passing an open flame test means that the ignited test sample self-extinguished following a very short after-flame time, the sample did not glow after the flame extinguished by itself, and showed a char length that did not equal the length of the test sample.

In Table 2, the average LOI values for all samples are provided. LOI values of untreated fabrics are shown between 19 ± 5 and 21 ± 5 % oxygen in nitrogen. LOI data for treated fabrics are shown between 32 ± 5 and 48 ± 5 %. Print cloth treated with kaolin, BPEI, DAP and urea provided LOI values of $36 \pm 5 \sim 48 \pm 5$ when add-on values were 14.8 ~ 18.6 wt %. For treated mercerized print cloth, LOI values are very similar to those of treated print cloth, $35 \pm 5 \sim 46 \pm 5$ %, when add-on values were 11.1 ~ 15.4 wt %. Treated twill fabric has high LOI values of $42 \pm 5 \sim 47 \pm 5$ % when add-on values were 13.4 ~ 17.6 wt%. Additionally, LOI values for treated fleece are $32 \pm 5 \sim 35 \pm 5$ when add-on values are 11.1 ~ 13.5 wt %. For each type of fabric construction, the values for LOI increase in Table 2 before reaching a limiting value with respect to add-on, which strengthens the case for concentration of formulations that afford both higher phosphorus and nitrogen content and crosslinking of polymer for improved flame resistance.

Table 2. Vertical flammability (ASTM D-6413-11) and LOI (ASTM D 2863-09) of different add-ons (wt %) of treated fabrics. All reported values for vertical and LOI tests are data from five observations on the same fabric type.

Fabric	No.Cycles	%AO	Vertical flame test*			LOI (%)
			Afterflame (sec)	Afterglow (sec)	Char (in)	
Print cloth	0	0				19±5
	10	14.8	0.7	0	2.4	36±5
	20	15.8	0	0	2.9	42±5
	30	17.8	0	0	1.9	47±5
	40	18.6	0	0	2.3	48±5
Mercerized print cloth	0	0				19±5
	10	11.2	0	0	2.6	35±5
	20	11.1	0	0	2.4	37±5
	30	15.4	0	0	2.0	46±5
	40	14.6	0	0	2.0	45±5
Twill	0	0				21±5
	10	15.7	0	6	2.4	43±5
	20	13.4	0	1	1.8	42±5
	30	17.6	0	0	1.8	43±5
	40	13.7	0	0	1.3	47±5
Fleece	0	0				20±5
	10	11.1	0	0	1.5	32±5
	20	13.5	0	0	2.0	34±5
	30	12.0	0	0	1.8	33±5
	40	13.5	0	0	1.5	35±5



Figure 4. Picture of control untreated twill fabric (left) and treated twill fabric (15.7 wt% add-on, right) during vertical flammability test by ASTM D-6413-11 method.



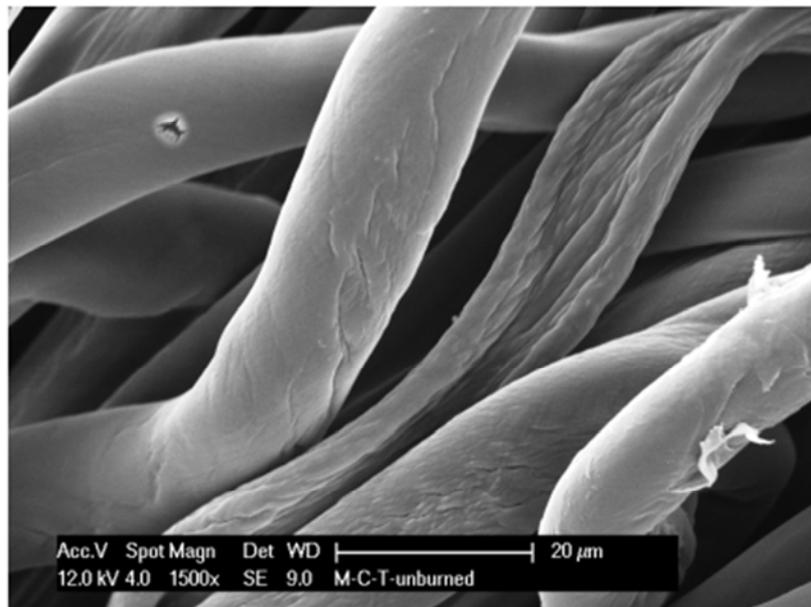
Figure 5. Picture of treated twill fabric (15.7 % add-on, left) and untreated control twill fabric (0 % add-on, right) after vertical flammability test by ASTM D-6413-11 method.

Convinced that formulations with our new monomers will afford flame resistance to fabrics of different constructions, we tested the treated print cloth, mercerized print cloth, twill and fleece fabrics by the vertical flame test (ASTM D 6413-11) and observed satisfying results. Figure 4 and Figure 5 show images from vertical flame tests, and Table 2 shows vertical flame test data results. Following a 12 s exposure to flame, most of the treated fabric samples showed no observable after-flame or after-glow times and char lengths were less than half the sample length. All of the treated sample types passed the vertical flame test regardless of cycle number and with % add-on of 11.1-18.6 wt %. In these cases, the char lengths of treated fabrics that passed the vertical flame test were <50% of the original length of 30 cm and the after-flame and after-glow times were between 0 and 6 s. Furthermore, for the first time, fleece fabric was shown to pass the more rigorous vertical flame test with all add-on values and no dripping of polyester was observed.

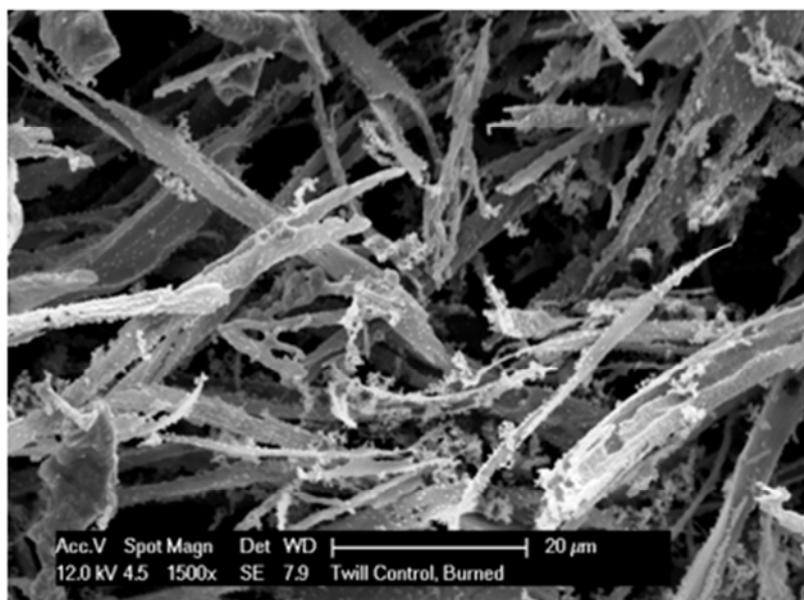
3.4. Scanning Electron Microscope (SEM)

To investigate morphology and distribution of the 10 BL coating, the cotton fabrics used in this study were imaged before and after LBL treatment via electron microscopy. The SEM images of the untreated (top row) and 10 BL treated (bottom row) cotton fabrics are shown in Figure 6. As seen in Figure 6, the fibers of the untreated fabrics are smooth and generally free of defects. Under the influence of flame and heat, the shape and the appearance of the control untreated fibers are completely destroyed. The LBL treated fibers, however, exhibit a noticeable change in surface morphology and develop particulate-like aggregates on the surface, indicating a successful deposition of multiple

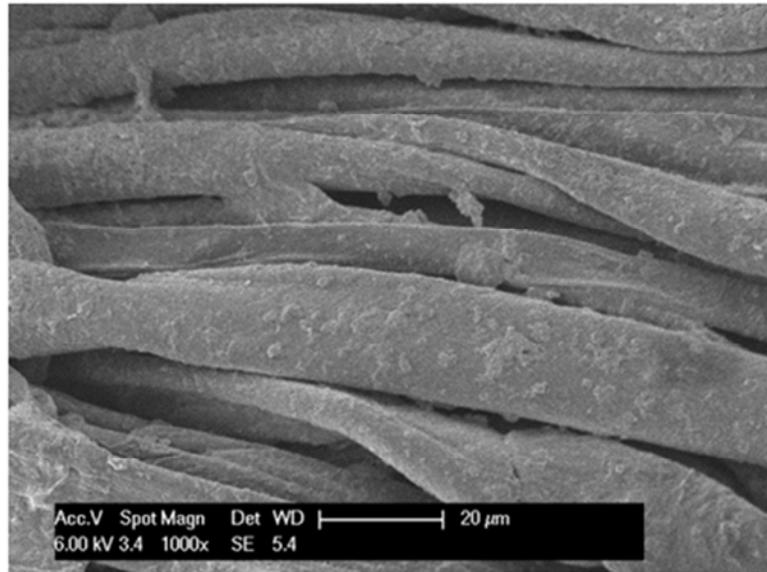
polyelectrolyte–kaolin bilayers. The SEM images of the treated fabrics illustrate that the 10 LBL deposition process results in a thick coating that fully covers the cotton fabric surfaces. Furthermore, treated 10 BL coatings wrapping around each fiber as a layer are observed. The appearance of this layer may be explained as being primarily due to the formation of gases formed by a burning mechanism of the chemical components of flame retardants during the thermal decomposition. This result indicates that the structure of the chars on the surface of each fiber provides the resistance of heat transfer and retard the degradation of underlying materials effectively; therefore combustion cannot be self-sustained.



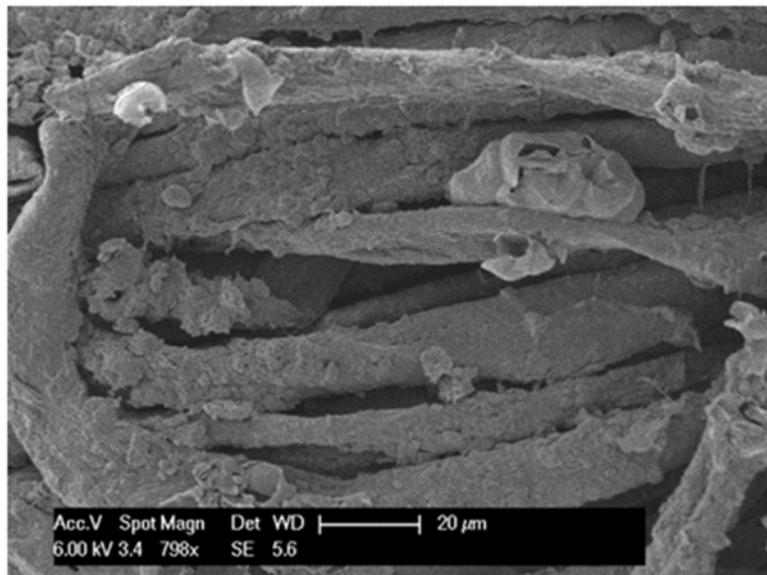
(a) Untreated control before b.



(b) Untreated control after burn.



(c) Treated 10 bilayers 15.7 wt % twill fabric before burn.



(d) Treated 10 bilayers 15.7 wt % twill fabric after burn

Figure 6. SEM micrographs of different regions: untreated control twill fabric sample (before and after burn, first row, a and b) and treated 10 bilayers, 15.7 wt% twill fabric samples (before and after burn, second row, c and d).

4. Conclusions

Layer-by-layer self-assembly has been successfully used to apply a wide variety of functional nanocoatings to textiles, but the deposition process is often time-consuming and labour-intensive. In this work, a continuous LBL self-assisted deposition process was developed and used to apply flame-retardant nanocoatings to four different cotton fabrics. A total of 20-80 alternating layers (10-40 bilayers) of kaolin nanoparticles and BPEI with urea and DAP were applied to the four different fabrics from aqueous solution using a modified pad-steam unit. SEM imaging of the treated fabrics revealed that the continuous LBL deposition process

produced even coatings that completely covered fabrics. The flame-retardant properties of the coated fabrics were characterized using a variety of flammability test methods, and found to be significantly greater than the uncoated fabrics. The 10-40 bilayers for print cloth, mercerized print cloth, twill, and fleece fabrics passed the vertical flame test when add-on values were 11.1-18.6 wt %. In all cases, the char lengths of treated fabrics were less than 20% of the original length of 30cm and the after-flame and after-glow times were between 0 and 6 seconds. These initial results lay the groundwork for scale-up and future development of commercial grade systems capable of continuously applying functional nanocoatings to a wide variety of surfaces and substrates.

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