

Innovative Approach to Flame Retardant Cotton Fabrics with Phosphorus Rich Casein via Layer-by-Layer Processing

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Abstract: Flame retardant behaviour was imparted using the layer-by layer assemblies of phosphorus rich casein milk protein with eco-friendly inorganic chemicals on cotton fabrics. The cotton twill fabrics were prepared using two solutions; a mixture of positively charged branched polyethylenimine (BPEI) with urea and diammonium phosphate (DAP), and negatively charged casein. Layer-by-layer assemblies for flame retardant properties were applied using the pad-dry-cure method, and each coating formula was rotated for 20 bi-layers. The effectiveness to resist flame spread on treated fabrics was evaluated using vertical (ASTM D6413-08) and 45° angle flammability test (ASTM D1230-01) methods. In most case, 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. Thermal properties were tested the extent of char produced by untreated and treated fabrics at 600°C by thermogravimetric analysis (TGA). Micro-scale combustion calorimeter (MCC) and Limiting oxygen indices (LOI, ASTM D2863-09) were also assessed. All untreated fabrics showed LOI values of about 21% oxygen in nitrogen. LOI values for the treated casein with BPEI/urea/DAP fabrics were greater than 29-34% between 5.80-9.59 add on wt%. Their structural characterizations were revealed by TGA/FT-IR and SEM methods. The treated fabrics exhibited improved thermal stability, as evidenced by increased ignition times and lower heat release rates. The results of this study show that flame retardant nanocoatings can be readily applied to textile fabrics using a continuous process that is ideal for commercial and industrial applications.

Keywords: Layer-by-Layer, Cotton, Flame Retardant, TGA/FTIR, Thermogravimetric Analysis

1. Introduction

Cotton fiber is broadly used to produce clothing, home furnishings, and various industrial products, such as medical supplies, industrial fiber, and canvases. While cotton is highly valued for its softness, breathability, and ability to absorb moisture, cotton is generally more combustible than most synthetic fibers [1, 2]. 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 [3-6]. 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, 8]. Unlike the halogen-containing compounds, which generate toxicity or may produce toxic gases, corrosive smoke, or harmful substances, the phosphorus-containing flame retardants are known to transform into phosphoric acid during combustion or thermal

degradation. This further causes the formation of non-volatile phosphoric acid that can react with the decomposing polymer by esterification and dehydration to promote the formation of char residue [9]. 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.

Casein is the major fraction milk protein obtained as a co-product during the production of skim milk. Casein is in a family of phosphoproteins in their micelle structure, which is beneficial due to the high concentrations of phosphorus and nitrogen, potential flame retardant additives in cotton cellulosic materials [10, 11]. In earlier research, phosphorus-nitrogen synergism containing urea-derivative compounds created better flame retardant properties. Diammonium phosphate (DAP) is often used as a flame retardant chemical to yield semi-durable finishes on cotton [6, 12]. It causes a drop in the temperature of combustion of the material, decreases the highest rates of weight loss, and gives higher char yields. In an effort to make flame retardant cotton fabrics, urea and DAP were used for phosphorus and nitrogen components because they are economic and environmentally friendly compounds. As a non-durable or semi-durable flame retardant, DAP is broadly used on infrequently washed or disposable products [7]. Literature states that DAP is the most effective within non-durable and durable flame retardants in delivering flame retardant properties to cellulosic materials and in yielding char [13].

One of the newest methods of textile surface modification is the layer-by-layer (LBL) method. Initially, this method was used for materials other than textiles. The usage of multilayered polymeric films offered the possibility of creating new types of materials with enhanced levels of reproducibility and controlled architectures. The most important principle of the LBL method consists in alternately depositing oppositely charged layers of polyelectrolytes, which ion-pair through electrostatic forces. The LBL process was created by G. Decher [14, 15] and others [16, 17], who based the approach 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. In recent years, researchers have used the LBL process to modify the surface of textile fabrics to impart or improve upon numerous surface properties, including mechanical integrity [18, 19], UV-protection [20], hydrophobicity/hydrophilicity [21, 22], dyeability [23], antimicrobial [24, 25], and flame retardancy [26-29].

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 cotton fabrics by the deposition of multilayer films containing BPEI, DAP, urea, and casein nanoparticles using a newly developed continuous LBL self-assisted process. The imparted flame retardancy of the cotton fabrics with the deposited casein nanolayers was tested using thermogravimetric analysis (TGA), limiting oxygen index (LOI, ASTM D2863-09) [30], 45° angle (clothing textiles test, ASTM D1230-01) [31], vertical flammability testing (ASTM D6413-11), and microscale combustion calorimeter (MCC) [32]. In order to understand their thermal degradation, the TGA/FTIR technique was used to study the control and treated cotton samples. 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. Materials

Commercial grade diammonium phosphate (DAP) and urea were obtained from Magnolia Chemical Co. (New Orleans, LA, USA). Casein powder (casein sodium salt from bovine milk, ~20 micro), sodium hydroxide, and branched polyethylenimine (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, mercerized twill (258 g/m², Style 423) cotton fabrics were obtained from Test Fabrics Inc. and used as received. This fabric was desized (starches removed), bleached, and free of all resins and finishes.

2.2. Layer-by-Layer Processing for Fabric Treatment

A modified laboratory pad-steam unit (Mathis, model PSA-HTF, Figure 1) was used to apply the 20 bilayer (BL) casein-BPEI-DAP-urea coatings to the twill cotton fabrics in a continuous layer-by-layer self-assisted 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 inches (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 10-20 wt% urea and diammonium phosphate (DAP). The second chamber was filled with 10 L of an aqueous solution of 1.5 wt% Casein (anionic) that was brought to pH~11 using sodium hydroxide (NaOH). The water was added to the casein and the solutions allowed sitting for 10 minutes to minimize clumping of the casein. The casein 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. Upon completion of the deposition process, the

rinsing chambers of the pad-steam unit were drained, and the fabric was cut for removal. The 20 BL 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 removed from the curing dryer, the fabric was

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

2.3. Thermal Gravimetric Analysis (TGA)

Untreated control and treated fabric samples with casein and urea/DAP were tested by thermogravimetric analysis (TGA) for thermal stability (TA Instrument, Q500). Under a continuous nitrogen atmosphere, samples (5-7mg) were analyzed at a heating rate of 10°C/min starting at room temperature and ending at 600°C.

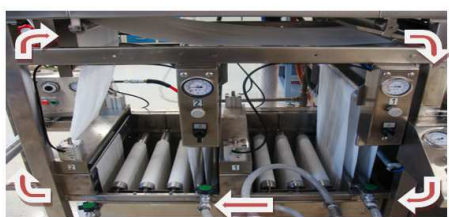


Figure 1. Picture of the Layer-by-Layer self-assisted process used to apply the 20 bilayers casein–BPEI–DAP–urea coatings. Arrows indicate the directional flow of the fabric as it is processed.

2.4. Micro-scale Combustion Calorimeter (MCC)

The MCC (Govmark, MCC-2) consisted of a sample mounting post, which contained a thermocouple in the post with its tip at the top directly below the sample holder to monitor temperature. A small fabric sample was inserted in a ceramic cup and placed on the sample holder. This assembly was then inserted into a furnace so that everything was inside the furnace. The heat release combustion (HRC) correlated directly to flow rates of the gases involved in the combustion process and to the oxygen concentrations. HRC used oxygen reduction as a determining factor.

2.5. Thermogravimetric Analysis/Fourier Transform Infrared (TGA/FTIR) Spectroscopy

The TGA–FTIR experiment was conducted by a TA Instruments Q500 thermogravimetric analyzer and a Bruker Tensor-27 spectrometer. In this experiment, 5–8 mg of each sample were heated between 20 and 550°C in the thermogravimetric analyzer at a rate of 10°C/min and under a nitrogen flow rate of 60 mL/min. The resulting volatile decomposition products then traveled through a transfer line to reach the gas cell of the FTIR spectrometer. Although the TGA experiment investigated the thermal degradation of the samples from 20 to 600°C, the FTIR experiment examined the gaseous products released during the main degradation ranging from 100 to 500°C. Both transfer line and gas cell were maintained at 200°C. When the evolved gases reached the gas cell, they were analyzed by a liquid-nitrogen cooled MCT detector, which was equipped with Zn Se windows. The gas components were then recorded as the absorption peaks in the 4000–600 cm⁻¹ region at

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):

a resolution of four wavenumbers. This data was obtained every 5 degree increment along the TGA heating profile, and there was a 30s delay between the timed measurements for the FTIR. When the experiment was completed, the data was analyzed using the Opus software, which measures the intensity of the absorption band (representing the functional groups) as a function of temperature. For analytical purposes, OriginLab 9 software was utilized to retain the three dimensional images of the FTIR spectra.

2.6. Flammability Tests and Limiting Oxygen Index (LOI)

Control twill and treated fabrics were subjected to the vertical flammability (The Govmark Organization, Inc.), 45° angle flammability (The Govmark Organization, Inc.) and LOI (Bynisco Polymer test) tests. In these tests, the specimen sizes were 30 x 9, 15 x 6 and 13 x 6 cm for vertical, 45° angle flammability, and LOI, respectively. In the 45° angle flame test, a strip of fabric was inserted in a frame and held in a special apparatus at an angle of 45°. A standardized flame was applied to the surface near the lower end for 10 seconds. The time required for the flame to travel the length of the fabric and break the trigger string was recorded, as well as the fabric's physical reaction at the ignition point. In the vertical flame test, a specimen was positioned vertically above a controlled flame and exposed for a 12 second 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 behavior of the sample was observed to compare 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.

2.7. Scanning Electronic Microscopy (SEM)

Unburned samples and samples from burned areas of the control and treated fabrics before and after vertical flammability test were examined using the Philips XL30 ESEM with magnifications between 792x-1500x and a setting of 12 kV. For analysis purpose, all samples were coated with gold.

3. Results and Discussion

3.1. Fabric Treatment

The multilayer continuous deposition process consisted of two steps, the immersion of the cotton fabrics in the 1.5 wt%

BPEI/urea/DAP solution, which passed through a roller, immediately followed by immersion of the fabrics in the 1.5 wt% Casein solution, which also passed through a roller. The two steps were continuously repeated for each formulation, without rinsing, for a total of 20 cycles using a roller speed of 2 m/min and a pad pressure of 3 bar (300 kPa). Formulation and percent add on values (wt%) following wet pickup, drying, curing, and reconditioning of 20 bilayer coated mercerized twill fabric samples are shown in Table 1. 20 bilayers (BL) casein–BPEI/urea/DAP coatings solutions

were prepared as following: 1.5% casein solution in deionized water and 1.5% BPEI, 10% urea and 10% DAP in deionized water (CM-10 sample); 1.5% casein solution in deionized water and 1.5% BPEI, 15% urea and 15% DAP in deionized water (CM-15 sample); 1.5% casein solution in deionized water and 1.5% BPEI, 20% urea and 20% DAP in deionized water (CM-20 sample). Formulations of casein with BPEI, urea, DAP treatment; CM-10, CM-15 and CM-20 showed 5.80, 7.22 and 9.59 add-ons (wt%) for twill cotton fabrics, respectively.

Table 1. Fabric treatment formulations and TGA data for untreated and treated twill cotton fabrics.

| Samples | Formulations (casein: BPEI: urea: DAP) | Average add-ons (wt%) | Onset of Degradation, °C | Char% at 600°C |
|---------|--|-----------------------|--------------------------|----------------|
| Control | N/A | 0 | 330.68 | 13.97 |
| CM-10 | (1.5%: 1.5%: 10%: 10%) | 5.80 | 275.24 | 31.11 |
| CM-15 | (1.5%: 1.5%: 15%: 15%) | 7.22 | 274.94 | 33.97 |
| CM-20 | (1.5%: 1.5%: 20%: 20%) | 9.59 | 276.60 | 35.77 |

3.2. Thermogravimetric Analysis (TGA)

Also shown in Table 1, are the TGA values for onset of degradation temperature (°C) and char yield (% at 600°C) for untreated and treated cotton fabrics. Figure 2 compiles TGA curves from room temperature to 600°C of the control and treated fabrics. In a nitrogen atmosphere, all the untreated and treated fabrics exhibited mostly mono mass-loss curves. With regard to the control, the TGA curve showed 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 continued losing more weight until it reaches 86% weight loss close to 600°C. During this process, cotton produced volatiles, including combustible and non-combustible species at around 350°C. At higher temperatures, the degradation generated a smouldering phenomenon leading to a slower mass loss [33]. According to

Figure 2, when twill fabrics were treated, they showed onsets of degradation between 274.94 and 276.60°C, and provided char yields between 31.11 and 35.77%. Decomposition temperatures of treated fabrics were lower than untreated control fabrics. This may be due to phosphonic acid derivatives accelerating fabric degradation. From the data in Table 1, it is evident that the char yields generated by higher add-ons (wt%) are greater than those produced by lower add-ons (wt%) due to the higher phosphorus and nitrogen contents. Chars protected against heat and flame propagation because they generated thermally stable cohesive phases having decomposition temperatures that exceeded the temperatures of the oxidizing zones of flames. Furthermore, chars were intumescent. They foamed and released gases that suppressed flammability. Therefore, it is very important to produce flame retardants that support intumescent and char formation [34, 35].

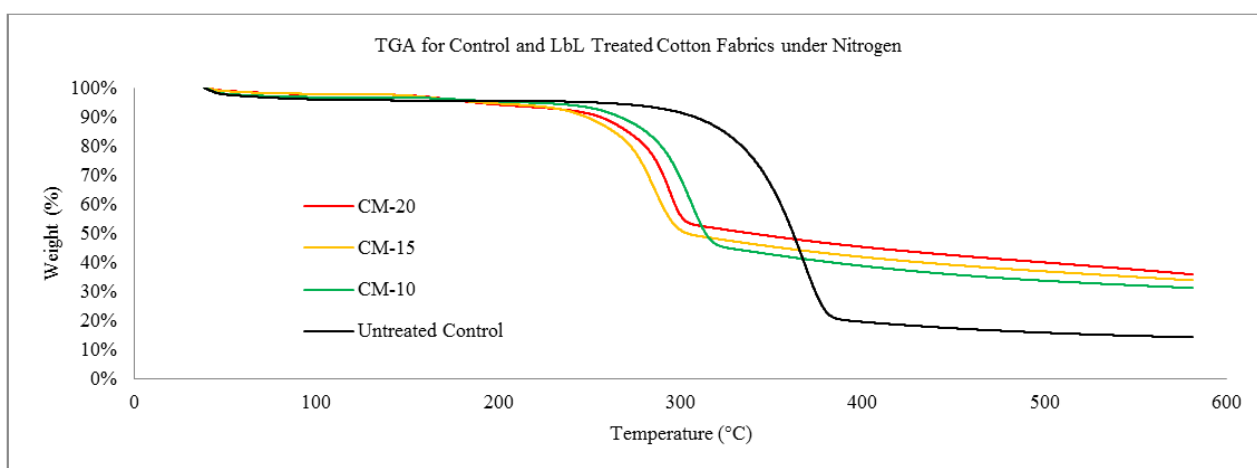


Figure 2. Degradation thermogram curves of the untreated control and treated twill cotton fabrics coated with 20 bilayers (CM-10, CM-15, and CM-20).

The onset of degradation of the treated fabrics initiated roughly around 270°C. Evidently, the flame retardants lowered 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 known that phosphorus additives reduce the onset

temperature for the second stage of treated cellulose by 50 - 150° [36, 37]. Again, phosphorus-nitrogen containing flame retardants obviously promoted char generation, and therefore, flame resistance in the treated fabrics.

3.3. Microscale Combustion Calorimeter (MCC)

HRR (heat release rate) versus temperature of the untreated control fabric and casein with BPEI/urea/DAP treated fabrics are shown in Figure 3. The flammability parameters, heat release combustion (HRC), total heat release (THR), and temperature of maximum of heat release combustion (T_{max}), were computed and are presented in Table 2. The thermal decomposition of the untreated control sample started around 300°C. The thermal decomposition as indicated by rising HRC strengthened as the temperature increased. Then, it attained a maximum point at 390.0°C and

ended around 420°C with an approximate value of 12.00 kJ/g in THR. When treated using the casein with BPEI/urea/DAP, cotton fabric showed a substantial reduction in THR, HRC and T_{max} values. In Table 2, as the concentrations of CM-10, CM-15 and CM-20 increased, the initial decomposition temperature, THR, and HRC values all continuously decreased. All treated fabrics had lower THR, HRC and T_{max} values than the untreated control. The protective layer then prevented the cotton fabrics from igniting, and reduced the normal thermal degradation of cotton fabrics and structural disintegration of the char to release volatiles and gases. Once the urea had burned, the main material started to burn and gave rise to the second peaks at around 250-320°C. These peaks on the same shoulder slightly decreased with increasing add-on values from 5.80 to 9.59 wt%.

Table 2. Microscale combustion calorimetry (MCC) data of control and treated fabrics (reported value is the average from three observations).

| Samples | Add-ons (wt%) | HRC (J/gK) | pHRR (J/gk) | THR (KJ/g) | T_{max} (°C) |
|---------|---------------|------------|-------------|------------|----------------|
| Control | 0 | 270.0 | 269.4 | 12.0 | 390.0 |
| CM-10 | 5.80 | 136.3 | 136.6 | 3.5 | 304.5 |
| CM-15 | 7.22 | 122.3 | 122.5 | 3.2 | 303.9 |
| CM-20 | 9.59 | 100.5 | 100.6 | 2.5 | 300.1 |

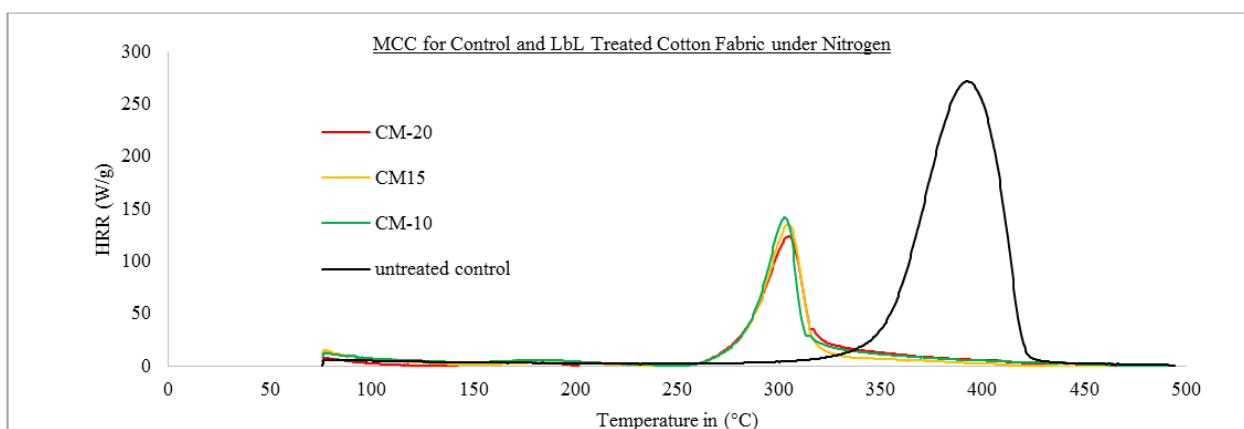


Figure 3. Microscale combustion calorimeter (MCC) graphs of heat release combustion curves for untreated control and treated samples of casein with BPEI/urea/DAP at various add-ons (wt%), CM-10, CM-15, and CM-20.

3.4. Pyrolysis Volatiles Analysis During Thermal Decomposition by TGA/FTIR

In order to further discover the thermal degradation mechanism of the casein with BPEI/urea/DAP treated cotton fabric, TGA-FTIR was used to study the pyrolysis volatiles during thermal decomposition. By coupling with TGA, FTIR can detect the real-time gaseous products released in the pyrolysis process. During the experiment, the FTIR data were plotted one on top of the other with a total of 70 scans to form a 3D spectrum in which the evolution of gas products were shown as a function of both wavenumber and temperature. TGA-FTIR spectra output from higher add-on CM-20 treated sample and the corresponding FTIR spectra under different temperatures are shown in Figure 4. As for these treated cotton fabrics,

no pyrolysis product was detected below 250°C. After that, most of absorption bands began to appear at 290°C. The gases released are mainly water vapor (~3900-3500 and 1770-1550 cm^{-1}), hydrocarbon OH and N-H for urea and DAP (~3400-3100 cm^{-1}), hydrocarbon CH (~3010-2750 cm^{-1}), CO_2 (~2360-2310 cm^{-1}), some hydrocarbon CO (~1850-1600 cm^{-1}), C=O (urea, ~1740 cm^{-1}), N-H (urea, ~1610 cm^{-1}), C-N (urea, ~1430 cm^{-1}), and a mix of P-O stretching (DAP, ~1250-800 cm^{-1}). They are the products of the reduction of the cellulose molecule, the appearance of free radicals, oxidation, dehydration, decarboxylation, decarbonylation and decomposition of cellulose to tarry pyrolyzate-containing levoglucosan, which vaporizes and then decomposes at a later time or higher temperature [38, 39].

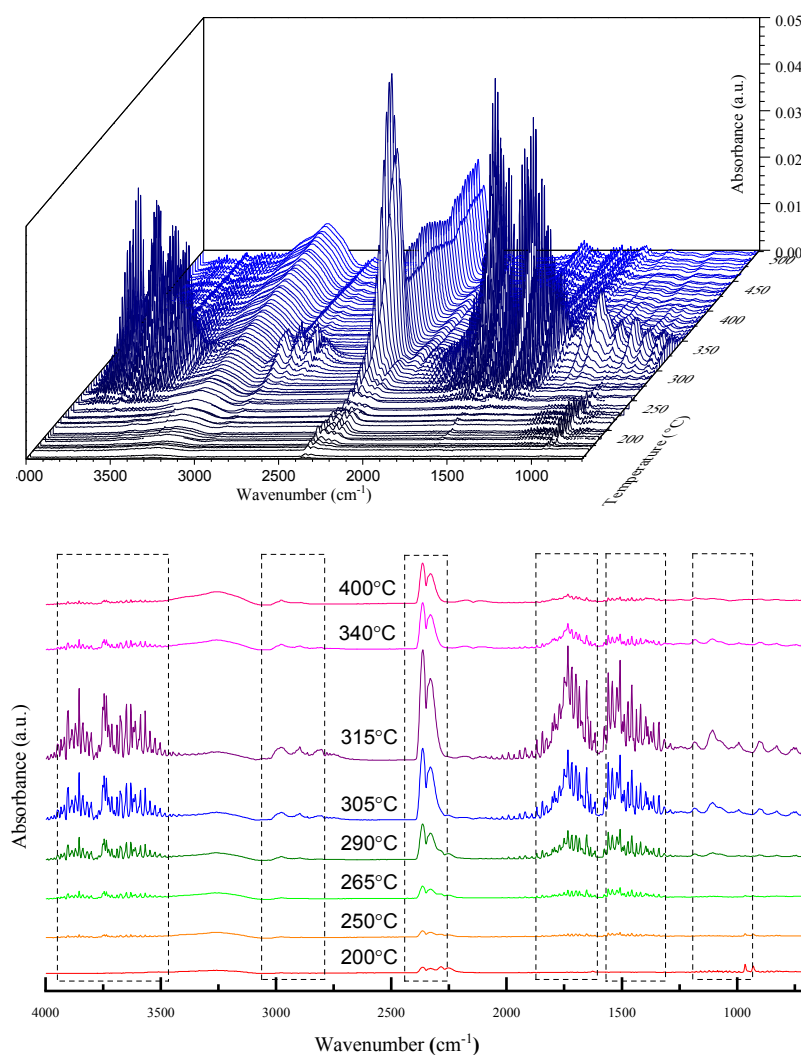


Figure 4. 3D TGA-FTIR (top) and the corresponding FTIR spectra (bottom) of volatiles released under different temperatures for CM-20 treated samples.

3.5. Flame Retardant Properties (LOI, Vertical and 45° Angle Flammability Tests)

Limiting oxygen index (LOI), vertical and 45° angle flammability tests are important in the evaluation of the flame retardant properties for treated cotton fabrics. The details of all three tests have been described elsewhere. 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 [34]. 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 3, the average LOI values for all samples are provided. LOI values of untreated fabrics give $21 \pm 1\%$ oxygen in nitrogen. LOI values for treated fabrics with

casein and BPEI/urea/DAP yield $34 \pm 1\%$, $32 \pm 1\%$, and $29 \pm 2\%$ when add-on values are 9.59 wt%, 7.22wt% and 5.80wt%. The values for LOI increased in Table 3 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. Figure 5 and Figure 6 show images and test data from 45° angle and vertical flame tests. Following a 12 second exposure to flame in the vertical flammability test, 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. During the vertical testing, there was no occurrence of afterglow burning upon the removal of the flame, as well as no melting or dripping during the burning of all samples. From Figure 6, it is obvious that all treated fabrics had shorter char length and after-flame and after-glow time when compared with the control. All of the treated sample types passed the vertical flame test regardless of add-on wt%. For all of these cases, the char lengths of treated fabrics were <50% of the original length of 30 cm, and the after-flame and after-glow times were between 0 and 2 s.

Flammability requirements for all clothing textiles, before sale or introduction into trade, are instituted in the 45° angle flammability test. The standard offers a consistent method to test textiles, and divides textile products used for clothing into three classes of flammability performance, thus limiting the use of flammable clothing in textiles. During the test procedure, a 16 mm (5/8 in) flame was positioned to touch the bottom of a specimen fixed at a 45° angle for 10 seconds. The fabric sample burned its full length or until the thread that stopped the timer was broken, a distance of 127 mm (5 in). Class 1 or 2 specimens meet the requirements of the

standard. Class 3, rapid and intense burning, does not meet the requirements of the standard. Figure 6 shows that untreated control fabric was completely burned and was totally consumed during the test. The test also showed the effectiveness of CM-10, CM-15 and CM-20 with 5.80-9.59 add ons (wt%). None of the treated CM-10, CM-15 and CM-20 samples ignited once exposed to the flame. Therefore, based on the classifications for textile products, all treated fabric samples are class 1, and are suitable for clothing due to slow burning or no combustibility.

Table 3. LOI (ASTM D2863-09) and 45° angle flammability (ASTM D-1230-01) of different add-ons (wt %) of treated fabrics. All reported values for 45° angle tests are data from two observations on the same fabric type.

| Samples | Add-ons (wt%) | Average LOI (vol%) (# of trials) | 45° angle flammability Classification |
|---------|---------------|----------------------------------|---|
| Control | 0 | 21 ± 1 (3) | Class 3 |
| CM-10 | 5.80 | 29 ± 2 (3) | Class 1 ^(a) , DNI ^(b) |
| CM-15 | 7.22 | 32 ± 1 (3) | Class 1, DNI |
| CM-20 | 9.59 | 34 ± 1 (3) | Class 1, DNI |

(a) Class 1: textiles are considered by the trade to be generally acceptable for apparel and are limited to the following:

1. A flat fiber surface with an average time of flame spread in the test of 3.5 s or more
2. A raised fiber surface with an average time of flame spread in the test of more than 7 s or that burn with a surface flash (time of flame spread less than 7 s), provided the intensity of the flame is insufficient to ignite, char or melt the base fabric

(b) DNI: did not ignite. Average time in seconds of flame spread for specimens of fabric which ignite as received. If specimen does not ignite, DNI is reported for the sample.

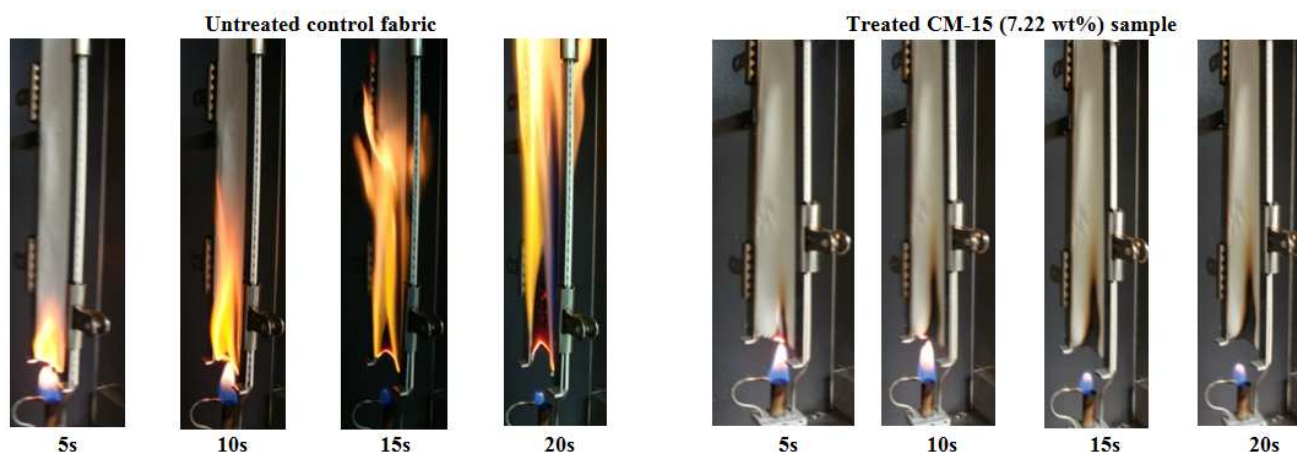


Figure 5. Picture of control untreated twill fabric (left) and treated twill fabric (7.22 wt% add-on, CM-15, right) during vertical flammability test by ASTM D-6413-11 method.

| Samples | Control | CM-10 | CM-15 | CM-20 |
|----------------------|---------------|-------|-------|-------|
| Add on (wt%) | 0 | 5.80 | 7.22 | 9.59 |
| 45° angle flame test | | | | |
| Vertical flame test | | | | |
| After-flame time (s) | 29.9 | 2 | 2 | 0 |
| After-glow time (s) | 98.0 | 0 | 0 | 0 |
| Char length (cm) | >30 (no char) | 15 | 12 | 4 |

Figure 6. Summaries of 45° angle (ASTM D-1230-01) and vertical (ASTM D-6413-11) flammability tests for different add-ons (wt%) of treated fabrics. All values for 45° angle and vertical tests are averages from two observations on the same fabric type.

3.6. Scanning Electron Microscope (SEM)

To investigate morphology and distribution of the 20 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 control (top) and 20 BL treated (bottom) cotton fabrics are shown in Figure 7. The fibers of the untreated fabrics were smooth and generally free of defects. Under the influence of flame and heat, the shape and the appearance of the control untreated fibers were completely destroyed. The LBL treated fibers, however, exhibited a noticeable change in surface morphology and developed particulate-like aggregates on the surface, indicating a successful deposition of multiple polyelectrolyte casein bilayers. The SEM images of the treated fabrics illustrate that the 20 LBL deposition process resulted in a

thick coating that fully covered the cotton fabric surfaces. The appearance of this layer may be due to the creation of gases formed during the 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 retards the degradation of underlying materials effectively; therefore, combustion cannot be self-sustained.

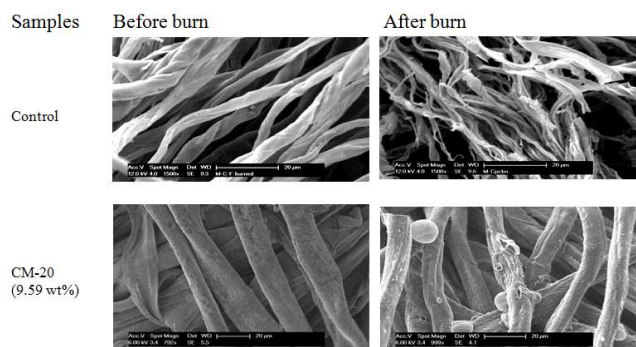


Figure 7. SEM Micrographs of untreated control (top) and highest add-on (CM-20) fabrics before burn (left) and after burn (right) at a magnification between 792x-1500x.

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 labor-intensive. In this work, a continuous LBL self-assisted deposition process was developed and used to apply flame-retardant nanocoatings to cotton fabrics. A total of 40 alternating layers (20 bilayers) of casein milk protein nanoparticles with BPEI/urea/DAP were applied to the 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 control fabrics. The 20 bilayers for treated cotton fabrics passed the vertical and 45° angle flame test when add-on values were 5.80, 7.22 and 9.59 wt% add-on. In all cases, the char lengths of treated fabrics were less than 50% of the original length of 30cm and the after-flame and after-glow times were between 0 and 2 seconds. TGA-FTIR techniques were performed to present volatile depolymerization by thermal degradation for the treated cotton fabric with casein, BPEI, urea and DAP. The results showed that most evolved gases are from flammable substances, which are products of the depolymerization of cotton cellulose. 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 substrates.

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