Flame retardant polyester fabric from nitrogen-rich low molecular weight additives within intumescent nanocoating

Igor Jordanov a,**, Eva Magovac b, Abbas Fahami c, Simone Lazar d, Thomas Kolibaba d, Ryan J. Smith d, Sandra Bischof b, Jaime C. Grunlan c, d, e,*

a Department of Textile Engineering, Faculty of Technology and Metallurgy, St. Cyril and Methodius University, Ruder Boskovic 16, 1000, Skopje, Macedonia
b Department of Textile Chemistry and Ecology, Faculty of Textile Technology, University of Zagreb, Prilaz baruna Filovipca 28a, Zagreb, Croatia
c Department of Mechanical Engineering, Texas A&M University, 3123 TAMU, College Station, TX, 77843, United States
d Department of Chemistry, Texas A&M University, 3123 TAMU, College Station, TX, 77843, United States
e Department of Materials Science and Engineering, Texas A&M University, 3123 TAMU, College Station, TX, 77843, United States

ARTICLE INFO

Article history:
Received 16 July 2019
Received in revised form 2 October 2019
Accepted 12 October 2019
Available online 14 October 2019

Keywords:
Flame retardancy
Ignition
Chitosan
Ammonium polyphosphate
Layer-by-layer
Assembly

ABSTRACT

An intumescent nanocoating composed of chitosan (CH) and ammonium polyphosphate (APP), with and without low-molecular weight nitrogen and nitrogen/sulphur based derivatives, was deposited on polyester fabric using the layer-by-layer-technique. Guanidine sulfamate (GSM), urea and thiourea were added to the aqueous chitosan deposition solution in an effort to improve flame retardancy. Exceptional self-extinguishing behavior is observed with a 10 bilayer (BL) CH:GSM/APP coated fabric. This water-based coating added 19.6 wt% to the polyester and reduced peak heat release rate by 61.7%, relative to uncoated fabric. Furthermore, the polyester is not fully ignitable because of earlier decomposition of GSM that helps to generate a thicker sponge-like char that acts as a physical barrier. This unique addition of low-molecular weight molecules in traditional intumescent polyelectrolyte pairs is a new opportunity for imparting flame retardancy to highly flammable synthetic fibers used in clothing and home furnishing.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

Polyester is a widely used synthetic textile fiber that is compatible with cotton in wearable fabric blends due to its high mechanical stability, durability and chemical, abrasion, shrinkage and wrinkle resistance [1]. Despite these numerous advantages, polyester is highly flammable and can spread fire through molten drops produced during burning [2]. Flame retardant (FR) polyester fibers can be obtained by incorporating co-monomers in the process of chain polymerization [3], mechanical incorporation of FR additives into the filament during extrusion [4], and through surface modification by coating [5]. Halogens and halogen-based derivatives are the most efficient flame retardants [6], but their toxicity has caused them to be banned or restricted in many places.

As a result, significant development of FR using phosphorous, nitrogen, silica, sulphur and their mixtures has occurred [7–12].

Flame retardant coatings can be applied to fibers by traditional finishing processes, resulting in a thick coating [13], or by nanocoating deposition. Layer-by-layer (LBL) assembly has emerged as an effective FR nanocoating technique in recent years [9,14]. This is a simple, highly tailorable, water-based technique, performed by alternate exposure of a substrate to oppositely-charged polyelectrolyte solutions or suspensions, giving rise to a multilayer thin film. The variety of different ingredients that can be used for this technique (polyelectrolytes, inorganic nanoparticles, organic nanomaterials, and renewable macromolecules) makes it possible to design an unlimited combination of assemblies [15,16]. LBL-coated wool [17–19] and cotton [20,21], polyester [22,23], polyamide [24,25] and fiber blends [26,27] have been shown to be flame retardant. Several studies using LBL nanocoatings to improve the flame retardancy of polyester fabric have been conducted. Oppositely charged silica particles were applied to PET as a first attempt to improve FR. This coating eliminated melt dripping and reduced time to ignition and peak heat release rate (pkHRR) [28]. Zirconium phosphate was paired with polydiallyldimethylammonium chloride (PDDA)-functionalized polyhedral oligomeric silsesquioxane
2. Materials and methods

2.1. Substrate and chemicals

Polyester 720H knitted fabric, with a weight of 206 g/m², was used as the substrate (Testfabrics, Inc., Pittston, PA). Chitosan (CH) was purchased from G.T.C. Bio Corporation (Qingdao, China), with Mw ~ 60,000 g/mol. Exolit AP422 ammonium polyphosphate (APP) was supplied by Clariant Corp. (Charlotte, NC). Hydrochloric acid (HCl) and then adjusted to pH 3 using 0.1 M NaOH. 1 wt% APP solution was prepared according to a previously reported procedure and used for coating immediately upon preparation [35]. 1 wt% APP, 11.1 wt% 1 M NaOH, 11.1 wt% 1 M HCl, and 76.8 wt% DI water were prepared by first mixing APP in water until a homogenous suspension was obtained. NaOH was then added and the solution was mixed until completely dissolved (a noticeable increase in viscosity occurs). Finally, HCl was added to reduce viscosity. The control flame retardant recipe consists of a positively charged aqueous solution of 1 wt% CH at pH 3 and a negatively charged solution of 1 wt% APP at pH 4.2. From this recipe, three combination solutions were prepared by dissolving 13 wt% each of GSP, U and THU in the chitosan solution [(1% CH - 13% GSM)/1% APP] and [(1% CH - 13% THU)/1% APP]. 13 wt% was chosen because the maximum solubility of THU at room temperature is 142 g/L. pH is indicated by the subscript on a given solution.

2.2. Layer-by-layer (LBL) deposition

LBL deposition was carried out by hand dipping, as shown schematically in Fig. 1. The polyester fabric was first immersed into the CH solution for 5 min, followed by rinsing in DI water for 1 min. The same dipping and rinsing procedure was carried out with the APP solution. This cycle creates one bilayer. The solution dips were reduced to 1 min for additional layers and the cycle was repeated until the desired number of bilayers was deposited. Each solution and the rinse water were renewed after every five bilayers. Once the desired numbers of BL were deposited, the fabric was rinsed with DI water and dried for 2 h at 70 °C.

2.3. Characterization

Vertical flame testing (VFT) was performed on three 76 × 300 mm samples, according to ASTM D 6413, by applying a propane flame for 12 s at the bottom of the fabric. The combustion behavior was tested with micro cone calorimeter (MCC) according to ASTM D 7309, using MCC-2 instrument (Govmark, Farmingdale, NY). A 5 mg sample (three samples per each recipe) was evaluated from 25 to 650 °C at a heating rate of 1 °C/s in a nitrogen gas stream of 80 ml/min. Limiting oxygen index (LOI) was measured in a Dynisco LOI chamber (Heilbronn, Germany), according to ISO 4589:1996, using fabric strips (14 cm × 5.2 cm). The presented results are average values of three measurements. Thermal stability of control and coated polyester (± 15 mg) were also evaluated by thermogravimetric analysis (TGA) using a Q-50 thermogravimetric analyzer (TA Instruments; New Castle, DE) under a controlled heating ramp of 10 °C min⁻¹, from ambient temperature to an isothermal hold at 100 °C for 30 min and then ramping up to 850 °C. A sample purge flow of 60 mLs⁻¹ air and a balance purge flow of 40 mLs⁻¹ nitrogen were used for testing in an air atmosphere. A sample purge flow of 40 mLs⁻¹ nitrogen and a balance purge flow of 60 mLs⁻¹ nitrogen were used for testing in a nitrogen atmosphere. Scanning electron microscope (SEM) images were collected using a LYRA3 TESCAN scanning electron microscope (Brno, Czech Republic) at a beam voltage of 5 kV. Prior to imaging, a 5 nm Pt/Pd coating was applied to the surface of the fabric to minimize charging.

3. Results and discussion

Polyester fabric coated with 10, 25 and 30 BL of CH/APP is shown in Fig. 2, following vertical flame testing. By increasing the number of bilayers from 10 to 25, weight gain nearly doubles (from 16.1 to 31.8%), and burning rate decreases (from 7.8 to 5.9 mm/s), but the samples are not self-extinguishing. Samples with 10 and 25 BL create significant char after VFT, indicating the intumescent character of the CH/APP pair. With 30 BL of CH/APP, the polyester has 38.8% weight gain and exhibits self-extinguishing behavior. Fig. 2(c) shows this fabric after vertical flame testing. It has residual weight of 98.8% and LOI of 26%, as summarized in Table 1. Limiting oxygen index is a widely used parameter for measuring the flammability of textiles. Generally, fabrics with a LOI greater than 25 vol% are said to be flame retardant [36,37]. Without the multilayer coating, the LOI of the polyester fabric is 20–21% [36,38]. In an effort to achieve better flame retardant behavior with fewer bilayers deposited, low molecular weight nitrogen and nitrogen/sulphur-based derivatives were added to the CH/APP intumescent system (solubilized in the CH solution). Guanidine sulphamate, urea and thiourea were each added as 13 wt% into the chitosan solution for deposition. Fabric coated with 10BL of CH:GSP/APP has a weight gain of 19.6%, as shown in Table 1. The VFT results summarized in Table 1 show that only the CH:GSP/APP system exhibits good flame retardancy, achieving self-extinguishing behavior with only 10 BL and nearly half the weight gain required for CH/APP to achieve the same behavior. Polyester coated with 10 BL CH:GSP/APP has a LOI of 26%, it is not ignitable and does not burn under exposure to flame in a vertical configuration. Although the other two systems, containing urea and thiourea, did not achieve this behavior, they have lower burning rate and higher LOI than polyester fabric coated with 10 BL CH/APP.

Weight percent and derivative weight loss (measured in air) as a function of temperature are shown in Fig. 3 and the data are summarized in Table 2. The uncoated fabric exhibits two degradation steps: the first starts around 430 °C and the second starts...
The first step is due to degradation of PET chains into smaller fragments by an initial scission of the chain end. The second weight loss is related to thermo-oxidative degradation of the small fragments into volatile products, leading to a final residue of 0.6% \[23,39\]. The presence of the nanocoating reduces the decomposition temperature of polyester. The \( T_{\text{onset,10\%}} \) decreases as the number of deposited CH/APP bilayers increase. Fabric with 10 BL is 8% and with 30 BL it is almost 30% lower than the \( T_{\text{onset,10\%}} \) of uncoated polyester. The initial temperature of decomposition (\( T_{\text{max,1}} \)) is around 220–230 °C, which corresponds to the starting temperature of decomposition of APP \[40\]. The CH/APP pair represents a traditional intumescent-like system. Chitosan is a polysaccharide that acts as the carbon source, while its amino groups serve as a blowing agent. APP is an acid source that generates \textit{in situ} phosphoric acid at high temperature that dehydrates chitosan, generating water vapor and promoting char formation. The residue at \( T_{\text{max,1}} \) decreases, while the residue at \( T_{\text{max,4}} \) and at 600 °C increases as number of deposited bilayers increase. The greater weight of APP with added bilayers degrades more at \( T_{\text{max,4}} \), so less residue is left on the polyester fiber surface. Additionally, this greater amount of APP and CH produce more residue at \( T_{\text{max,4}} \) and at 600 °C because more acid is produced that acts on the CH by forming more char at elevated temperatures, as shown in Table 2.

The thermo-oxidative behavior of CH/APP enriched with low-molecular weight additives are also summarized in Table 2. Polyester coated with 10 CH:GSM/APP BL shows an additional \( T_{\text{max,2}} \) at 385 °C (Fig. 3(b)), which likely corresponds to the decomposition of GSM. Similar data were obtained for polyamide filament extruded with 5% GSM \[41\]. Polyester fabric is self-extinguishing when coated with 30 BL CH/APP and 10 BL CH:GSM/APP, but the latter has 34% lower residue at \( T_{\text{max,4}} \) and about 40% lower residue at 600 °C. The extinguishing behavior of 10 BL CH:GSM/APP coated fabric is believed to be the result of decomposition of GSM that acts as a blowing agent to create gases that will create thicker char under exposure to flame.

Thermal degradation of the samples under pyrolysis conditions in a nitrogen atmosphere are shown in Fig. 4 and the data are summarized in Table 3. These results are similar to TGA in an air atmosphere (Table 2). The uncoated fabric tested in nitrogen exhibits two degradation steps, CH/APP samples exhibit three, and CH:GSM/APP exhibits four, degradation steps. The shoulder at 385 °C of the CH:GSM/APP derivative weight loss curve measured around 560 °C. The first step is due to degradation of PET chains into smaller fragments by an initial scission of the chain end. The second weight loss is related to thermo-oxidative degradation of the small fragments into volatile products, leading to a final residue of 0.6% \[23,39\]. The presence of the nanocoating reduces the decomposition temperature of polyester. The \( T_{\text{onset,10\%}} \) decreases as the number of deposited CH/APP bilayers increase. Fabric with 10 BL is 8% and with 30 BL it is almost 30% lower than the \( T_{\text{onset,10\%}} \) of uncoated polyester. The initial temperature of decomposition (\( T_{\text{max,1}} \)) is around 220–230 °C, which corresponds to the starting temperature of decomposition of APP \[40\]. The CH/APP pair represents a traditional intumescent-like system. Chitosan is a polysaccharide that acts as the carbon source, while its amino groups serve as a blowing agent. APP is an acid source that generates \textit{in situ} phosphoric acid at high temperature that dehydrates chitosan, generating water vapor and promoting char formation. The residue at \( T_{\text{max,1}} \) decreases, while the residue at \( T_{\text{max,4}} \) and at 600 °C increases as number of deposited bilayers increase. The greater weight of APP with added bilayers degrades more at \( T_{\text{max,4}} \), so less residue is left on the polyester fiber surface. Additionally, this greater amount of APP and CH produce more residue at \( T_{\text{max,4}} \) and at 600 °C because more acid is produced that acts on the CH by forming more char at elevated temperatures, as shown in Table 2.

The thermo-oxidative behavior of CH/APP enriched with low-molecular weight additives are also summarized in Table 2. Polyester coated with 10 CH:GSM/APP BL shows an additional \( T_{\text{max,2}} \) at 385 °C (Fig. 3(b)), which likely corresponds to the decomposition of GSM. Similar data were obtained for polyamide filament extruded with 5% GSM \[41\]. Polyester fabric is self-extinguishing when coated with 30 BL CH/APP and 10 BL CH:GSM/APP, but the latter has 34% lower residue at \( T_{\text{max,4}} \) and about 40% lower residue at 600 °C. The extinguishing behavior of 10 BL CH:GSM/APP coated fabric is believed to be the result of decomposition of GSM that acts as a blowing agent to create gases that will create thicker char under exposure to flame.

Thermal degradation of the samples under pyrolysis conditions in a nitrogen atmosphere are shown in Fig. 4 and the data are summarized in Table 3. These results are similar to TGA in an air atmosphere (Table 2). The uncoated fabric tested in nitrogen exhibits two degradation steps, CH/APP samples exhibit three, and CH:GSM/APP exhibits four, degradation steps. The shoulder at 385 °C of the CH:GSM/APP derivative weight loss curve measured around 560 °C. The first step is due to degradation of PET chains into smaller fragments by an initial scission of the chain end. The second weight loss is related to thermo-oxidative degradation of the small fragments into volatile products, leading to a final residue of 0.6% \[23,39\]. The presence of the nanocoating reduces the decomposition temperature of polyester. The \( T_{\text{onset,10\%}} \) decreases as the number of deposited CH/APP bilayers increase. Fabric with 10 BL is 8% and with 30 BL it is almost 30% lower than the \( T_{\text{onset,10\%}} \) of uncoated polyester. The initial temperature of decomposition (\( T_{\text{max,1}} \)) is around 220–230 °C, which corresponds to the starting temperature of decomposition of APP \[40\]. The CH/APP pair represents a traditional intumescent-like system. Chitosan is a polysaccharide that acts as the carbon source, while its amino groups serve as a blowing agent. APP is an acid source that generates \textit{in situ} phosphoric acid at high temperature that dehydrates chitosan, generating water vapor and promoting char formation. The residue at \( T_{\text{max,1}} \) decreases, while the residue at \( T_{\text{max,4}} \) and at 600 °C increases as number of deposited bilayers increase. The greater weight of APP with added bilayers degrades more at \( T_{\text{max,4}} \), so less residue is left on the polyester fiber surface. Additionally, this greater amount of APP and CH produce more residue at \( T_{\text{max,4}} \) and at 600 °C because more acid is produced that acts on the CH by forming more char at elevated temperatures, as shown in Table 2.

The thermo-oxidative behavior of CH/APP enriched with low-molecular weight additives are also summarized in Table 2. Polyester coated with 10 CH:GSM/APP BL shows an additional \( T_{\text{max,2}} \) at 385 °C (Fig. 3(b)), which likely corresponds to the decomposition of GSM. Similar data were obtained for polyamide filament extruded with 5% GSM \[41\]. Polyester fabric is self-extinguishing when coated with 30 BL CH/APP and 10 BL CH:GSM/APP, but the latter has 34% lower residue at \( T_{\text{max,4}} \) and about 40% lower residue at 600 °C. The extinguishing behavior of 10 BL CH:GSM/APP coated fabric is believed to be the result of decomposition of GSM that acts as a blowing agent to create gases that will create thicker char under exposure to flame.
in nitrogen (Fig. 4(b)) corresponds to the temperature of GSM decomposition in air (Fig. 3(b)) and confirms decomposition of GSM. Final residual weight measured in nitrogen is more intense than that measured in air. Uncoated polyester has 17.4% residual weight and it rises as a number of deposited CH/APP bilayers increases (Table 3). CH:GSM/APP has the lowest final residual weight compared with 10 and 30 BL CH/APP on polyester.

The thermal behavior of coated and uncoated polyester was further probed with micro-cone calorimetry, with the results summarized in Fig. 5 and Table 4. Uncoated polyester fabric degrades at 450 °C and exhibits a peak heat release rate of 482 W/g, while CH/APP coated fabric degrades earlier and produces less heat. Fabric coated with 10, 25 and 30 CH/APP BL yields pkHRR of 240, 206 and 187 W/g, respectively. $T_{pkHRR}$ of these samples decrease with increasing bilayers and are similar to the $T_{max3}$ (Table 2) when weight loss is greater than 50%. Polyester coated with 10 CH:GSM/APP BL has the lowest $T_{pkHRR}$ and produces the lowest pkHRR of 184 W/g. This fabric has 4% lower $T_{pkHRR}$ and about 62% lower pkHRR than uncoated fabric. This CH:GSM/APP-coated fabric has similar $T_{pkHRR}$ and pkHRR to 30 CH/APP BL coated fabric, which has much higher weight gain (38.8%) and triple the bilayers. Fig. 5 compares MCC data for 30 BL CH/APP and 10 BL CH:GSM/APP

![Fig. 3. Weight loss (a) and derivative weight loss (b) as a function of temperature for uncoated and LbL-coated polyester obtained in an air atmosphere.](image)

![Fig. 4. Weight loss (a) and derivative weight loss (b) as a function of temperature for uncoated and LbL-coated polyester obtained in a nitrogen atmosphere.](image)

**Table 2**

<table>
<thead>
<tr>
<th>Recipe</th>
<th>BL</th>
<th>$T_{insert101}$ [°C]</th>
<th>$T_{max1}$ [°C]</th>
<th>$T_{max2}$ [°C]</th>
<th>$T_{max3}$ [°C]</th>
<th>$T_{max4}$ [°C]</th>
<th>Residue at $T_{max1}$ [%]</th>
<th>Residue at $T_{max2}$ [%]</th>
<th>Residue at $T_{max3}$ [%]</th>
<th>Residue at $T_{max4}$ [%]</th>
<th>Residue at 600 [°C] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Polyester</td>
<td>396</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>429</td>
<td>560</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>53.6</td>
<td>5.4</td>
</tr>
<tr>
<td>1% CH$<em>3$/1% APP$</em>{x2}$</td>
<td>10</td>
<td>363</td>
<td>225</td>
<td>–</td>
<td>422</td>
<td>533</td>
<td>96.1</td>
<td>–</td>
<td>–</td>
<td>48.3</td>
<td>16.5</td>
</tr>
<tr>
<td>25</td>
<td>330</td>
<td>227</td>
<td>–</td>
<td>426</td>
<td>535</td>
<td>94.7</td>
<td>92.7</td>
<td>–</td>
<td>47.1</td>
<td>22.2</td>
<td>17.3</td>
</tr>
<tr>
<td>30</td>
<td>278</td>
<td>232</td>
<td>–</td>
<td>427</td>
<td>535</td>
<td>92.7</td>
<td>92.7</td>
<td>47.1</td>
<td>22.2</td>
<td>17.3</td>
<td></td>
</tr>
<tr>
<td>(1% CH-13% GSM)$<em>{y}$/1% APP$</em>{x2}$</td>
<td>10</td>
<td>345</td>
<td>225</td>
<td>385</td>
<td>421</td>
<td>532</td>
<td>97.1</td>
<td>67.8</td>
<td>37.2</td>
<td>14.6</td>
<td>10.4</td>
</tr>
<tr>
<td>(1% CH-13% U)$<em>{y}$/1% APP$</em>{x2}$</td>
<td>10</td>
<td>355</td>
<td>230</td>
<td>–</td>
<td>420</td>
<td>529</td>
<td>95.0</td>
<td>–</td>
<td>44.9</td>
<td>15.4</td>
<td>9.4</td>
</tr>
<tr>
<td>(1% CH-13% THU)$<em>{y}$/1% APP$</em>{x2}$</td>
<td>10</td>
<td>360</td>
<td>232</td>
<td>–</td>
<td>420</td>
<td>527</td>
<td>96.0</td>
<td>–</td>
<td>45.0</td>
<td>16.2</td>
<td>9.4</td>
</tr>
</tbody>
</table>
deposited on the polyester fabric. These systems exhibit similar pkHRR, but the GSM-containing coating has an additional shoulder around 385 °C that correspond to the $T_{\text{max}2}$ from the TGA data, shown in Tables 2 and 3. These data suggest that degradation of the GSM at a lower temperature creates gas that is responsible for creating a thicker sponge-like char that improves flame retardancy of the CH:GSM/APP coated polyester. The heat release rate data from MCC (Fig. 5) and TGA in nitrogen (Fig. 4(b)) match well because micro-cone testing is based on a controlled pyrolysis in an inert nitrogen atmosphere. The gases produced are mixed with excess oxygen and combusted. The heat of the combustion is measured as heat release rate by oxygen consumption calorimetry.

Fig. 6 shows SEM images of uncoated and coated polyester fabric. 10 and 30 BL CH/APP-coated samples are shown in Fig. 6 (b) and (c), respectively. More coating is clearly evident with more bilayers, with 10 BL having more coating into the yarn (between the fibers) and between the loop structure of the knitted fabric and negligible amount between the stitch columns. The 30 BL coating covers the whole knitted structure, making a continuous film on the fabric surface. The fabric coated with 10 BL of CH:GSM/APP (Fig. 6(d)), shows conformal coverage into the yarns and into the loop structure, without coating between the knits columns. Fig. 7 shows SEM images of the fabric samples following vertical flame testing. Polyester coated with 10 and 30 BL CH/APP have the same chemical composition and therefore their char looks similar, although greater char is generated with more coating. With more bilayers deposited a more continuous char is formed with smaller holes. Comparing 10 BL CH/APP (Fig. 7(b)) with 10 BL CH:GSM/APP (Fig. 7(c)) shows a contrast in char structure. The GSM-containing sample appears to have denser char than 10 BL CH/APP. Small holes in the GSM-containing char are likely due to gas formation and release during burning. This char has a sponge-like structure (Fig. 7(d)).

As mentioned above, the intumescence process is a combination of charring and foaming at the surface of the substrate during exposure to flame. The formed char layer acts as a physical barrier to slow heat and mass transfer between the gas and condensed phases. The formation of an effective char occurs with gas formation and expansion at the surface. Adding low-molecular nitrogen and nitrogen/sulphur based derivatives into the CH layer provides blowing agents that further expand the char structure on polyester. The sponge-like structure of CH:GSM/APP char illustrates this effect (Fig. 7(c) and (d)). The GSM shows better performance than U and THU. It decomposes earlier (Figs. 3(b) and Fig. 4(b)), creating more gas that serves as a blowing agent, making thicker char with a sponge-like structure that acts as a physical barrier that slows heat and mass transfer between the gas and condensed phases.

### 4. Conclusions

Layer-by-layer deposition of the traditional intumescent CH/APP system, with and without low-molecular weight nitrogen and nitrogen/sulphur based derivatives is shown to render polyester fabric self-extinguishing. A 30 BL CH/APP coating adds 38.8 wt% to the polyester fabric, resulting in a 61.1% reduction in pkHRR (and it is not ignitable in vertical flame testing). With only 10 BL of CH:GSM/APP the weight of polyester fabric increases 19.6% and pkHRR is reduced 61.7% relative to uncoated polyester. This 10 BL coating is also non-ignitable in VFT, with only one third of the coated layers and half the weight gain of CH/APP. Improved flame

### Table 3
Thermogravimetric data of uncoated and LbL-coated polyester obtained in a nitrogen.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>BL</th>
<th>$T_{\text{onset}}$ [°C]</th>
<th>$T_{\text{max}1}$ [°C]</th>
<th>$T_{\text{max}2}$ [°C]</th>
<th>$T_{\text{max}3}$ [°C]</th>
<th>$T_{\text{max}4}$ [°C]</th>
<th>Residue at 600 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Polyester</td>
<td>409</td>
<td>–</td>
<td>–</td>
<td>425</td>
<td>595</td>
<td>–</td>
<td>51.2</td>
</tr>
<tr>
<td>1% CH/1% APP$_{4.2}$</td>
<td>10</td>
<td>395</td>
<td>230</td>
<td>438</td>
<td>599</td>
<td>97.6</td>
<td>52.8</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>364</td>
<td>232</td>
<td>436</td>
<td>585</td>
<td>95.8</td>
<td>52.6</td>
</tr>
<tr>
<td>(1% CH-13% GSM)$<em>3$/1% APP$</em>{4.2}$</td>
<td>10</td>
<td>354</td>
<td>232</td>
<td>430</td>
<td>584</td>
<td>96.9</td>
<td>45.5</td>
</tr>
</tbody>
</table>

### Table 4
MCC data for uncoated and LbL-coated polyester fabrics.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Number of bilayers</th>
<th>$T_{\text{onset}}$ [°C]</th>
<th>$\Delta T_{\text{flame}}$ ($%$)</th>
<th>pkHRR (W/g)</th>
<th>$\Delta \text{pkHRR} ($%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Polyester</td>
<td>10</td>
<td>430.1</td>
<td>–2.2</td>
<td>481.8</td>
<td>–50.2</td>
</tr>
<tr>
<td>1% CH/1% APP$_{4.2}$</td>
<td>10</td>
<td>440.2</td>
<td>–2.2</td>
<td>239.7</td>
<td>–50.2</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>435.4</td>
<td>–3.3</td>
<td>205.6</td>
<td>–57.3</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>434.5</td>
<td>–3.5</td>
<td>187.3</td>
<td>–61.1</td>
</tr>
<tr>
<td>(1% CH-13% GSM)$<em>3$/1% APP$</em>{4.2}$</td>
<td>10</td>
<td>432.1</td>
<td>–4.0</td>
<td>184.2</td>
<td>–61.7</td>
</tr>
<tr>
<td>(1% CH-13% U)$<em>3$/1% APP$</em>{4.2}$</td>
<td>10</td>
<td>439.8</td>
<td>–2.3</td>
<td>258.9</td>
<td>–46.3</td>
</tr>
<tr>
<td>(1% CH-13% THU)$<em>3$/1% APP$</em>{4.2}$</td>
<td>10</td>
<td>439.3</td>
<td>–2.4</td>
<td>245.4</td>
<td>–45.1</td>
</tr>
</tbody>
</table>
retardancy with GSM addition is believed to be due to its earlier decomposition at a lower temperature (around 385 °C), making thicker char with a sponge-like structure that acts as a physical barrier that slows heat and mass transfer between the gas and condensed phases. Adding low-molecular weight derivatives to traditional intumescent polyelectrolyte pairs is an effective approach for imparting flame retardancy to synthetic textiles, while also reducing weight gain and processing steps.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Acknowledgments

The authors acknowledge to the Fulbright Visiting Scholar Program at the US Department of State for supporting Professor Igor Jordanov stay/research at Texas A&M University (Grant number E0581973).

References

[10] Z. Han, A. Fina, G. Camino, Organosilicon compounds as polymer fire retardants, in: Polymer Green Flame Retardants Edited by Papaspyrides CD, M University (Grant number 750).