A novel carbon nanohorn-based intumescent multilayer nanocoating on cotton fabrics: thermal degradation kinetics, flammability and flame-retardant mechanism

Jie Xu, Xiangrong Liu, Xuehui Yao, Manman Xue, Liqing Chen, Fanhui Guo, Yixin Zhang, Zhipeng Xie, Feng Liang and Jianjun Wu*

Creating eco-friendly flame retardants (FRs) that are highly effective for textiles while requiring minimal quantities is crucial for both human well-being and environmental conservation. Traditionally, halogen FRs have been the mainstay in this field. Yet, due to their harmful impacts on both human health and the environment, there is a growing demand to discontinue their use. Herein, in this work, a novel eco-friendly intumescent-based flame retardant for cotton fabrics, consisting of ammonium polyphosphate (APP), single-walled carbon nanohorns (SWCNHs), and melamine (MEL) was explored. The addition of SWCNHs demonstrated a clear synergistic effect with APP and MEL in enhancing the flame retardancy of cotton fabrics. After four spraying cycles, the treated cotton fabric ASM4 demonstrated outstanding flame retardancy and self-extinguishing properties. Additionally, its LOI value could reach 24.1 ± 0.1% and the damage length dropped to 4.6 ± 0.2% cm from 30.0 ± 0.1% cm for the pristine cotton fabric, while preserving its original morphology with partial carbonization. The pHRR and THR of ASM4 were dramatically decreased by 90% and 51%, respectively in the cone calorimeter test. Moreover, investigating the thermal degradation kinetics of treated cotton fabric and the physicochemical properties of the char residues revealed the crucial influence of SWCNHs on improving the flame resistance of cotton fabrics. The incorporation of SWCNHs improved both the thermal stability and the degree of graphitization of the char layer, which served as a protective barrier. This barrier efficiently blocked the release of volatile combustible substances while allowing for the emission of nonflammable gases. This work provides a theoretical basis for the feasible application of SWCNHs in intumescent FRs.

1. Introduction

Cotton fabric is renowned for its softness, comfort, moisture-absorption, breathability, biocompatibility, and hydrophilicity, catering to the requirements of everyday life. It finds extensive applications in clothing, household items, automobile interiors, and various other sectors, making it the most prevalent natural fiber textile currently in use. As indicated in the USDA report of January 2024, global cotton production reached 113.18 million (480-pound bales) with domestic consumption at 112.43 million (480-pound bales). The flammability of cotton fabrics poses significant risks to both human safety and property integrity. Recent data suggests that cotton fabric-related fires account for over one-third of global fire incidents. Consequently, enhancing the flame retardancy of cotton fabrics holds immense practical importance, aiming to mitigate the harmful effects of combustion, minimize casualties, and economic losses, while also broadening the potential applications of cotton textiles.

FRs are instrumental in fire resistance of textiles. Relevant data showed the global flame retardant market size was valued at US$ 2190 million in 2022 and is projected to reach US$ 3331 million by 2029, exhibiting a CAGR of 6.1% over the forecast period from 2023 to 2029. And the fire-resistant fabrics market is projected to grow from US$ 3.5 billion in 2023 to US$ 4.9 billion by 2028 at a CAGR of 6.6%. Numerous FRs have been created using formaldehyde and halogen-based compounds, known for their superb flame-retardant properties. However, during combustion, they release formaldehyde, hydrogen halide, and other corrosive toxic gases, posing risks to human health and causing environmental pollution. In light of these concerns, there has been a significant shift towards developing...
intumescent-based FRs, which are favored for their higher efficiency, reduced smoke production, lower toxicity, and environmental friendliness. Standard intumescent FRs consist of three key elements: an acid source, a carbonizing agent, and a blowing agent. Yet, traditional carbonization agents require high concentrations to form an effective char, which often adversely affects the fabric's properties. With advancements in nanotechnology, carbon nanomaterials have emerged as a novel alternative for enhancing the flame retardancy of polymeric materials. Notably, fullerenes, graphene, and carbon nanotubes have garnered significant interest for their ability to enhance flame retardancy efficiently with minimal addition, paving the way for the development of multifunctional flame retardant fabrics.

Given the constrained flame retardant capabilities of carbon nanomaterials, they are often employed as synergists alongside conventional FRs. Additionally, there is an ongoing challenge in devising cost-effective and low-toxicity preparation methods for the majority of carbon nanomaterials. These challenges hinder the widespread application of carbon nanomaterials. However, SWCNHs discovered incidentally during the production of SWCNTs, have recently received extensive attention across diverse areas, including adsorption, sensing, electromagnetic shielding, and drug delivery. In contrast to the production of CNTs, the synthesis of SWCNHs does not necessitate costly metal catalysts or rigorous process conditions. This aspect bodes well for future low-cost and large-scale industrial production. Despite our team has initially demonstrated the potential of SWCNHs in enhancing the flame resistance of cotton fabrics and the flame-retardant mechanism, remains uncertain.

Herein, in this work, a novel self-extinguishing intumescent-based FR for cotton fabric was prepared by combining APP, SWCNHs and MEL. Various properties like thermal stability and flame retardant performance were investigated. Additionally, the thermal degradation kinetics of cotton fabrics and flame retardant mechanism were also studied. To our best knowledge, it’s the first time to point out a novel perspective using thermal kinetic method to illustrate the role of SWCNHs in this intumescent-based flame retardant system.

2. Experimental section

2.1 Materials

Cotton fabrics with a density of 170 g m⁻² were sourced from Shaoxing Aobang Technology Co., located in Zhejiang, China. SWCNHs were prepared by utilizing the DC arc discharge technique under conditions of 70 kPa and 200 A in a nitrogen atmosphere. APP (n > 1000) and MEL were acquired from Aladdin Co., and sodium hydroxide was obtained from Macleans Co. All the chemicals used were of analytical grade.

2.2 Preparation of flame-retardant cotton fabric

Cotton fabrics treated with SWCNHs to be flame-retardant were developed using a spraying technique, offering a more commercially feasible and time-saving approach. Initially, the cotton fabrics underwent a mercerization process using 10 wt% NaOH solution, followed by multiple rinses with distilled water, and were then dried in an oven at 80 °C for 2 h prior to application. To prepare the coating solution, 1 g of APP was dissolved in 100 mL of deionized water and stirred until homogeneous. The pH value of the solution was then adjusted to 10 by adding NaOH solution. Next, 0.15 g of SWCNHs and 0.8 g of MEL were incorporated into the APP mixture, and the resulting solution was sonicated for 30 min to achieve a homogeneous APP/SWCNHs/MEL flame-retardant coating liquid.

4 mL of the APP/SWCNHs/MEL solution was evenly sprayed onto the cotton fabric, followed by drying at 80 °C for 20 min. This spraying and drying process was repeated on the opposite side of the fabric with an additional 4 mL of solution, constituting one cycle. This cycle was repeated one to four times each, yielding samples labeled ASM1, ASM2, ASM3, and ASM4, respectively. Comparable samples were also prepared, including pristine cotton fabric, cotton fabric solely coated with APP solution, and cotton fabric treated with APP/MEL solution. The weight loading of the treated cotton fabric was calculated using the method mentioned in our previous work.

2.3 Characterization

Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were applied to investigate the chemical structure of the samples and their residual char were analyzed using A field-emission scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) capabilities were used to analyze the surface morphology of the samples. The microstructural details of SWCNHs were observed using the transmission electron microscope (TEM). To assess the degree of graphitization in the combustion residue, a Raman spectroscopy device (Bruker Senterra II) equipped with a 532 nm laser and operating at a power of 5 mW was employed.

The thermal stability of the samples was evaluated using a thermogravimetric analyzer (TGA, Netzsch STA 449 F5 Jupiter, Germany) in a nitrogen atmosphere, employing a heating rate of 20 °C min⁻¹. FTIR-TG test was conducted under N₂ atmosphere, with a heating schedule ranging from 30 °C to 800 °C at a rate of 20 °C min⁻¹.

Vertical flame tests (VFT) were carried out according to the GB/T 5455-2014. Additionally, in accordance with the GB/T 5454 standard, the limiting oxygen index (LOI) values of specimens were measured using an oxygen index meter (model 5901A). A cone calorimeter (CC, 6810) was utilized to evaluate the combustion behavior of samples under an external heat flux of 35 kW m⁻².

3. Results and discussions

3.1 Characterization of uncoated and coated cotton fabric

The weight loadings of coated cotton fabrics with varying spray cycles were displayed in Fig. 1. As the number of spray cycles increased, the weight loadings of the coated fabrics also rose.
Specifically, at four spray cycles, the weight loadings for ASM4, APP4, and (APP/MEL)4 were 17.6%, 10.2%, and 15.4%, respectively. The weight loading of ASM4 was higher than that of APP4 and (APP/MEL)4, demonstrating the successful application of the APP/SWCNHs/MEL coating onto the surface of the cotton fabric. SEM and EDS analyses were employed to examine the microstructure and elemental composition of the samples. SEM images at various magnifications provided crucial details about all samples, as shown in Fig. 2. Fig. 2(a) depicted the smooth and near surface of pristine cotton fabric. As observed in Fig. 2(b), the fabric treated with APP exhibited a coarse surface, with nearby fibers adhering to each other, signifying the successful and uniform attachment of APP to the cotton fabric surface. Fig. 2(c) and (d) showed a compact and uniform coating, where fibers are completely interconnected, signifying the effective adherence of the flame-resistant coatings, either APP/MEL or APP/SWCNHs/MEL onto the surface of cotton fabrics. Furthermore, the elemental composition of four specimens was examined through EDS analysis, as depicted in Fig. 2(e). In contrast to the pristine cotton fabric, which only contained C and O, the modified samples APP4, (APP/MEL)4, and ASM4 were composed of C, O, P and N elements. Moreover, ASM4 exhibited a higher concentration of C and N compared to (APP/MEL)4. These findings subtly indicated that the APP/SWCNHs/MEL coating was effectively applied to the cotton fabric. The FTIR spectra of pristine cotton fabric, APP4, (APP/MEL)4 and ASM4 were recorded, as illustrated in Fig. 2(f). The observed peaks at 3456 cm\(^{-1}\) and 1622 cm\(^{-1}\) correspond to the stretching vibrations of O–H/N–H and C–H bonds, respectively. Additionally, the peaks at 1405 cm\(^{-1}\) were linked to the stretching vibrations of the C–C bonds and the bending vibrations of C–H bonds. The spectra for APP4, (APP/MEL)4, and ASM4 revealed new peaks at 1296 cm\(^{-1}\) and 867 cm\(^{-1}\), which were associated with the stretching vibrations of P=O and P–O–P, respectively. Notably, a distinct peak at 1160 cm\(^{-1}\) observed in (APP/MEL)4 and ASM4, which was absent in APP4, was identified as the stretching vibration of C–N. These spectroscopic analyses confirmed the successful incorporation of APP, SWCNHs, and MEL onto the surface of cotton fabric.

The XPS technique was utilized to examine the surface chemical composition of both untreated and treated cotton fabrics. As shown in Fig. 2(g), only the peaks corresponding to C 1s and O 1s were identified in pristine cotton fabric, while P 2p and N 1s appeared in APP4, (APP/MEL)4 and ASM4 besides C 1s and O 1s. The weak peak of N 1s noticed in APP4 could be attributed to the presence of residual NH\(_4^+\). Moreover, Fig. 2(h) and (i) illustrated high-resolution C 1s spectra of the pristine cotton fabric and ASM4, which were analyzed using XPSPEAK software. Compared with pristine cotton fabric, the C–C bond position in ASM4 experienced a slight shift, moving to 284.8 eV from the initial 284.6 eV. Furthermore, the intensity of C–C bonds depicted in Fig. 2(h) and (i) was found to be more pronounced than that of C–O bonds. Additionally, ASM4 revealed the emergence of new peaks at 283.4 eV for C–N and at 288.9 eV for C–O–C/C–O–P. As illustrated in Fig. 2(j), the N 1s spectrum for ASM4 displayed a division into three distinct peaks, corresponding to C≡N, C–N, and N–H, respectively, which confirmed that the presence of nitrogen covalently bonded within the structure. Moreover, as depicted in Fig. 2(k), the P 2p spectrum for ASM4 revealed two peaks at 133.9 and 134.6 eV, attributed to P–O–C and P=O, respectively. These findings further affirm the successful incorporation of APP, SWCNHs, and MEL into the cellulose fibers.

### 3.2 Thermal stability

#### 3.2.1 Thermal degradation of uncoated and coated cotton fabrics

The thermal stability of the pristine cotton fabric, APP4, (APP/MEL)4 and ASM4 was assessed using TGA, detailed in Fig. 3 and Table 1. According to Table 1, the temperature at which a mass loss of 5 wt% occurred is indicated by \(T_{5\%}\). Additionally, the highest rate of degradation and the temperature at which this peak degradation rate occurs are referred to as \(V_{\text{max}}\) and \(T_{\text{max}}\) respectively. Under \(N_2\) atmosphere, \(t\) the thermal degradation of all samples primarily occurred in a single stage. The pristine cotton fabric proved a \(T_{5\%}\) of 323 °C, \(T_{\text{max}}\) of 371 °C, \(V_{\text{max}}\) of −44.99%/°C respectively. By contrast, APP4, (APP/MEL)4 and ASM4 displayed lower \(T_{5\%}\), \(T_{\text{max}}\) and \(V_{\text{max}}\). Particularly, ASM4 exhibited excellent char forming ability and the residual mass reached to 40.9%. This enhances the protection of cotton fabrics by inhibiting the generation and spread of volatile substances and the transfer of heat or mass.

In the air atmosphere, the thermal decomposition process of the pristine cotton fabric, APP4, (APP/MEL)4 and ASM4 proceeded in two distinct stages. The primary thermal degradation of pristine cotton fabric took place during the initial stage, characterized by \(T_{5\%}\) at 319 °C, \(T_{\text{max}}\) at 352 °C and \(V_{\text{max}}\) at −75.1%/°C. This phase predominantly involves the depolymerization of cellulose, yielding volatile compounds, aliphatic carbon, and/or aromatic carbon. Furthermore, the residue mass reached approximately 6.7% at 700 °C. The secondary stage occurred within the temperature range of 400–600 °C, involving the additional decomposition of the produced aliphatic or aromatic carbon into carbon dioxide and/or CO\(_2\). Additionally, compared with the pristine cotton fabric, the thermal decomposition processes of APP4,
Fig. 2  Surface morphologies and structural characterization. SEM images and EDS elemental mapping analysis of pristine cotton fabric (a), APP4 (b), (APP/MEL)4 (c) and ASM4 (d). Mass percentages of each element from EDS analysis for the above samples (e); FTIR (f) and XPS (g) spectra of pristine cotton fabric, APP4, (APP/MEL)4 and ASM4. High-resolution XPS spectra of C 1s (h) of pristine cotton fabric, C 1s (i), N 1s (j) of ASM4 and P 2p (k) of ASM4.
(APP/MEL)4 and ASM4 displayed comparable trends and a lower thermal degradation rate. Furthermore, the residue masses of these samples at 700 °C surpassed 6.7% of the pristine cotton fabric. Compared with the pristine cotton fabric in both N2 and air atmosphere, the first-stage decomposition temperatures for APP4, (APP/MEL)4, and ASM4 were lower, while the char residues at 700 °C were higher. These observations suggest that the introduction of APP, SWCNHs, and MEL led to an earlier breakdown of cellulose and concurrently enhanced the production of char residue. Additionally, the further breakdown of cellulose at elevated temperatures was inhibited, a phenomenon attributed to the protective layer formed by the stable char. Importantly, the integration of SWCNHs with the APP/MEL coating significantly boosted the flame resistance of the cotton fabrics.

3.2.2 Thermal degradation kinetics of uncoated and coated cotton fabrics. In this work, the primary emphasis was placed on the kinetic analysis of the combustion process within the time interval from $T_i$ to $T_h$, encompassing the initial stage. Various techniques, including model-free approaches\textsuperscript{29,30} and model-fitting strategies, are available for identifying kinetic models. Within the realm of model-fitting techniques, the Coats–Redfern model, which relies solely on a single heating rate, can complement the shortcomings of model-free methods, where activation energy is the sole determinable parameter.\textsuperscript{31,32}

Therefore, the kinetic analysis of the thermal degradation of cotton fabrics before and after coating under different atmospheres was carried out using the Arrhenius law and the Coats–Redfern method:\textsuperscript{31,33}

The plots illustrating the determination of the activation energy ($E$) and the pre-exponential ($A$) for cotton fabrics based on seven reaction mechanisms at various atmospheres are depicted in Fig. 4. From Fig. 4, with the exception of the third-order kinetic equation (O3), the $g(x)$ function demonstrated a linear relationship between $\ln[g(x)/T^2]$ and $1/T$ for almost all cases. The data from these experiments were then aligned along a straight line. From this linear fit, the values of

![Fig. 3 TG and DTG curves of pristine cotton fabric, APP4, (APP/MEL)4 and ASM4 under N2 (a), (b) and air (c), (d).](image-url)
$E$ and $A$ were determined based on the slope and $y$-intercept of the line, respectively. Table 3 complied the values of $E$, $A$ and the most correlated kinetic models for both uncoated and coated cotton fabrics. This table indicates that the first-order kinetic equation (O1), which exhibited higher $R^2$ values in an air atmosphere, effectively described the combustion kinetics.
of the pristine cotton fabric. In contrast, the third-order kinetic equation (O3) showed the most significant correlation with APP4, (APP/MEL)4, and ASM4. Additionally, under the N₂ atmosphere, O₁ was found to be more fitting for capturing the combustion behavior of the pristine cotton fabric, along with (APP/MEL)4 and ASM4. Furthermore, O₃ was selected for accurately representing the thermal degradation kinetics of APP4, owing to its substantial R² value.

As illustrated in Table 2, the coated fabrics exhibited lower E and A values compared to the uncoated fabric in both air and N₂ atmospheres. The decrease in activation energies can probably be linked to the catalytic influence of the intumescent materials on cotton fabrics. This aligns with the noted rise in char yields, which is a result of cross-linking and dehydration reactions, ultimately improving the flame-retardant capabilities of the treated cotton fabrics. In tandem with the assessment of the E values associated with APP4, (APP/MEL)4, and ASM4, it was strikingly apparent that ASM4 boasted the greatest E value. This result robustly points to the enhancement of the char layer’s thermal stability through the inclusion of SWCNHs, safeguarding the char layer against supplementary harm when exposed to elevated thermal conditions.

### 3.3 Flame retardancy performance

#### 3.3.1 VFT and LOI tests. The vertical flammability test (VFT) and LOI were performed to evaluate the flame retardancy of the pristine cotton fabric, APP4, (APP/MEL)4 and ASM4. As shown in Fig. 5 and Table 3, the pristine cotton fabric indicated high flammability with LOI value of 17.9 ± 0.1%. The after flame time and the afterglow time of the pristine cotton fabric were 15 s and 22 s, respectively. Furthermore, minimal residue was observed post-burning. In comparison, both APP4 and (APP/MEL)4, as well as ASM4, significantly enhanced the flame-retardant properties of the fabric, achieving the UL94 V-0 rating and self-extinguishing capabilities. Additionally, the damage length decreased to 12.7 ± 0.2% cm for APP4, 8.5 ± 0.5% cm for (APP/MEL)4 and 4.6 ± 0.2% cm for ASM4 from 30.0 ± 0.1% cm for the pristine cotton fabric, maintaining their original morphology apart from partial carbonization. Evidently, the incorporation of SWCNHs had a beneficial impact on reducing fabric damage length during the burning process. Furthermore, the LOI values of APP4, (APP/MEL)4 and ASM4 increased to 21.8 ± 0.3%, 22.3 ± 0.2% and 24.1 ± 0.1%, respectively.

#### 3.3.2 Cone calorimeter test. Utilizing TG/DTG analysis, the combustion characteristics of the pristine cotton fabric, APP4, (APP/MEL)4 and ASM4 were assessed through a cone calorimeter. Fig. 6 and Table 4 illustrated that the pristine cotton fabric ignites quickly under a heat flux of 35 kW m⁻², with an ignition time (TTI) of 16 s. During the initial burning phase, the fabric absorbs substantial heat from its surroundings to break down and emit volatile combustibles. As the breakdown progresses, the continuous release of volatile substances accelerates the combustion process, leading to a flashover stage where a significant amount of heat is generated, thereby increasing the heat release rate (HRR) during this period. In Fig. 6(a), the HRR of the pristine cotton fabric reached its maximum at 284 kW m⁻². At the end of the combustion, the total heat release (THR) (Fig. 6(b)) of the pristine cotton fabric reached 8.1 MJ m⁻². By contrast, the HRR and THR profiles for APP4, (APP/MEL)4, and ASM4 showed a noticeable flattening effect. Meanwhile, it can be seen from Fig. 6(a) and (b) that the significant reduction in HRR and THR was influenced by the incorporation of SWCNHs, with no sharp peaks observed. Among these, ASM4 recorded the lowest peak of heat release rate (pHRR) (29 kW m⁻²) and THR (4.0 MJ m⁻²), indicating that SWCNHs act as an effective flame retardant synergist for cotton fabric, offering a marked improvement over the results seen with APP4 or (APP/MEL)4. Furthermore, the pHRR occurrence time for ASM4 was extended to 75 s, in contrast to the 26 s for the pristine cotton fabric, suggesting a reduction in fire propagation speed.

The plots of the average rate of heat emission (ARHE) over time were depicted in Fig. 6(c). This term, defined as the total heat emitted over time and its peak value (maximum average rate of heat emission, MARHE, as listed in Table 4), is widely used to evaluate the potential for fire growth in real scale conditions. A lower MARHE value signifies superior flame retardant effectiveness in fabrics. According to Table 4, the pristine cotton fabric emerged as the sample with the highest risk level. The ARHE slope and MARHE values of APP4, (APP/MEL)4 and ASM4 showed a marked decrease, indicating enhanced fire resistance in cotton fabrics. Specifically, ASM4 demonstrated an 88% reduction in MARHE, signifying the most significant improvement in flame retardancy among the tested fabrics. Thus, when considering the data gathered from HRR, THR and ARHE, ASM4 can be considered as the best performing material.

In particular, the Av-EHC value, indicating the burning rate of volatile compounds in the gas phase, notably decreased to 8.4 MJ kg⁻¹ for ASM4 compared to the pristine cotton fabric (26.2 MJ kg⁻¹). This reduction suggests the potential presence of a gas-phase flame retardant mechanism. As depicted in

<table>
<thead>
<tr>
<th>Samples</th>
<th>E (kJ mol⁻¹)</th>
<th>A (min⁻¹)</th>
<th>Mode</th>
<th>R²</th>
<th>E (kJ mol⁻¹)</th>
<th>A (min⁻¹)</th>
<th>Mode</th>
<th>R²</th>
</tr>
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<tr>
<td>Pristine cotton fabric</td>
<td>363.3</td>
<td>5.6 × 10⁻¹³</td>
<td>O₁</td>
<td>0.9994</td>
<td>222.3</td>
<td>1.7 × 10⁻¹⁹</td>
<td>O₁</td>
<td>0.9990</td>
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<tr>
<td>APP4</td>
<td>76.5</td>
<td>3.3 × 10⁸</td>
<td>O₃</td>
<td>0.9904</td>
<td>87.3</td>
<td>4.7 × 10⁹</td>
<td>O₃</td>
<td>0.9994</td>
</tr>
<tr>
<td>(APP/MEL)4</td>
<td>147.8</td>
<td>3.8 × 10¹⁴</td>
<td>O₃</td>
<td>0.9974</td>
<td>200.9</td>
<td>6.2 × 10⁻¹⁸</td>
<td>O₁</td>
<td>0.9990</td>
</tr>
<tr>
<td>ASM4</td>
<td>171.8</td>
<td>5.9 × 10⁻¹⁰</td>
<td>O₃</td>
<td>0.9962</td>
<td>208.9</td>
<td>3.0 × 10⁻¹⁹</td>
<td>O₁</td>
<td>0.9996</td>
</tr>
</tbody>
</table>

Notes: E is activation energy; R² is the correlation coefficient.
Fig. 6(d)–(f), the rise in TSP (total smoke production) and COP (CO production) values following the application of APP/SWCNHS/MEL coating is linked to the incomplete combustion of the material during a fire, leading to a decrease in the CO$_2$P (CO$_2$ production) value. This decrease is a result of the flame retardant coating creating a physical barrier that obstructions the flow of oxygen to the flame zone.

To enhance the evaluation of the fire safety performance of the fabric, the fire growth index (FGI) was calculated. Defined as the ratio of pHRR to the corresponding peak time ($t_{pHRR}$), FGI primarily measures how the size of the material influences its thermal response. A lower FGI suggests enhanced fire safety of the fabric. As indicated in Table 4, ASM4 registered the lowest FGI among other testing samples. Additionally, ASM4 was resistant to ignition and exhibited both a reduced pHRR and FGI compared to the control sample. This leads to the conclusion that ASM4 offers superior fire safety capabilities, significantly extending the time available for evacuation during a fire incident.

The flame retardant properties of various combination systems using carbon nanomaterials were evaluated, as shown in Table 5. Notably, SWCNHS exhibited a significant synergistic effect within the APP/MEL flame retardant system. With a lower SWCNHS dosage and fewer bilayers, ASM4 showed a 90% reduction in pHRR and a 51% reduction in THR in the cone calorimeter test. These results indicate that SWCNHS have considerable potential as an effective flame retardant synergist for fabrics.

### 3.4 Flame retardant mechanism

To explore the mechanism behind flame retardancy, the char residues from the pristine cotton fabric, APP4, (APP/MEL)4, and ASM4 following cone calorimeter test were analyzed using SEM, EDS, Raman, FTIR and XPS spectra. The study revealed the microstructural changes in the residues of the pristine cotton fabric, APP4, (APP/MEL)4, and ASM4, as depicted in Fig. 7(a) and (d). The findings showed that the pristine cotton fabric was completely consumed by fire, leaving behind only a small amount of fragile ash. In contrast, APP4 exhibited significant shrinkage after exposure to fire, and its original woven structure was compromised. The residues of (APP/MEL)4 and ASM4 both displayed well-preserved woven structures. Particularly, ASM4 exhibited a denser char layer on the cotton fabric surface compared to (APP/MEL)4. Additionally, the elemental mass ratios of the samples after combustion were illustrated in Fig. 7(e). In APP4, the C, N and P contents increased to 54%, 3% and 7%, respectively, while the O content decreased to 35% (Fig. 2(e)). Conversely, in (APP/MEL)4, the C content rose to 44% from 24%, while the O, N and P contents declined to 31 from 43%, 21% from 24% and 5% from 9%, respectively. Interestingly, the O and P contents in the char residues of the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Afterflame time (s)</th>
<th>Afterglow time (s)</th>
<th>Damage length (cm)</th>
<th>LOI (%)</th>
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</thead>
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<tr>
<td>Pristine cotton fabric</td>
<td>15 ± 2</td>
<td>22 ± 3</td>
<td>30</td>
<td>17.9 ± 0.1</td>
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<tr>
<td>APP4</td>
<td>5 ± 1</td>
<td>0</td>
<td>12.7 ± 0.2</td>
<td>21.8 ± 0.3</td>
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<tr>
<td>(APP/MEL)4</td>
<td>3 ± 1</td>
<td>0</td>
<td>8.5 ± 0.5</td>
<td>22.3 ± 0.2</td>
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<tr>
<td>ASM4</td>
<td>2 ± 1</td>
<td>0</td>
<td>4.6 ± 0.2</td>
<td>24.1 ± 0.1</td>
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</table>

**Table 3** The key data from VFT and LOI

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**Fig. 5** Digital photos during VFT for the pristine cotton fabric (a1, a2, a3), APP4 (b1, b2, b3), (APP/MEL)4 (c1, c2, c3) and ASM4 (d1, d2, d3).
ASM4 showed opposite trends. The N content reduced to 15% from 27%. Throughout the combustion process, the inclusion of the SWCNHs amplified the flame retardant efficiency of APP. This augmentation facilitated the dehydration and carbonization process, leading to the creation of the char layer and the emission of NH₃, H₂O, and CO₂. This indicates that the unique combination of SWCNHs and APP resulted in the development of a thicker film, thus forming a more efficient protective layer. Simultaneously, the sublimation of MEL was initiated, releasing NH₃ and aiding in the reduction of N element content.

Raman spectra for the char residues from the pristine cotton fabric, APP4, (APP/MEL)4 and ASM4 were displayed in

Table 4  The key data from CCT

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI (s)</th>
<th>pHRR (kW m⁻²)</th>
<th>tₚHRR (s)</th>
<th>THR (MJ m⁻²)</th>
<th>TSP (m²)</th>
<th>MARHE (kW m⁻²)</th>
<th>Av-EHC (MJ kg⁻¹)</th>
<th>FGI</th>
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<tr>
<td>Pristine cotton fabric</td>
<td>16</td>
<td>284</td>
<td>26</td>
<td>8.1</td>
<td>0.03</td>
<td>141.9</td>
<td>26.2</td>
<td>10.92</td>
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<tr>
<td>APP4</td>
<td>8</td>
<td>113</td>
<td>23</td>
<td>7.4</td>
<td>0.02</td>
<td>52.4</td>
<td>8.4</td>
<td>4.91</td>
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<tr>
<td>(APP/MEL)4</td>
<td>18</td>
<td>39</td>
<td>31</td>
<td>6.1</td>
<td>0.41</td>
<td>23.5</td>
<td>8.9</td>
<td>1.26</td>
</tr>
<tr>
<td>ASM4</td>
<td>6</td>
<td>29</td>
<td>75</td>
<td>4.0</td>
<td>0.42</td>
<td>17.2</td>
<td>8.4</td>
<td>0.39</td>
</tr>
</tbody>
</table>
Table 5  Comparison of flame retardant properties of different combination systems based on carbon nanomaterials

<table>
<thead>
<tr>
<th>Substrate</th>
<th>System</th>
<th>Number of bilayers</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton fabric</td>
<td>PHMGP/modified MWCNTs</td>
<td>20</td>
<td>MCC: pHRR-59%; THR-53%</td>
</tr>
<tr>
<td>Ramie fabric</td>
<td>Amino-MWCNTs/APP</td>
<td>20</td>
<td>MCC: pHRR-36%; THR-25%</td>
</tr>
<tr>
<td>Cotton fabric</td>
<td>FR-polyacrylamide/GO</td>
<td>20</td>
<td>CCT: pHRR-50%; THR-22%</td>
</tr>
<tr>
<td>Cotton fabric</td>
<td>Phosphorylated GO/PEI</td>
<td>10</td>
<td>CCT: pHRR-27%; THR-21%</td>
</tr>
<tr>
<td>Cotton fabric</td>
<td>CA/GO</td>
<td>10</td>
<td>CCT: pHRR-64%; THR-38%</td>
</tr>
<tr>
<td>Cotton fabric</td>
<td>GO/PDMAEMA/BN</td>
<td>3</td>
<td>CCT: pHRR-31%; THR-36%</td>
</tr>
<tr>
<td>Cotton fabric</td>
<td>APP/SWCNHs/MEL [this work]</td>
<td>4</td>
<td>CCT: pHRR-90%; THR-51%</td>
</tr>
</tbody>
</table>

Note: PHMGP refers to polyhexamethylene guanidine phosphate; MWCNTs refers to multi-walled carbon nanotubes; APP refers to ammonium polyphosphate; GO refers to graphene oxide; PEI refers to branched polyethylenimine; CA refers to casein; PDMAEMA refers to poly(dimethylaminoethyl methacrylate); BN refers to hexagonal boron nitride; MEL-SWCNHs refers to melamine-modified single-walled carbon nanohorns; MCC refers to microscale combustion calorimeter test; CCT refers to cone calorimeter test.

Fig. 7(f)–(i). Two significant peaks ranging from 1330–1370 cm$^{-1}$ and 1570–1590 cm$^{-1}$ were identified as the D-band and G-band, signifying disordered graphite structures and sp$^2$-bonded carbon atoms, respectively. The parameter $A_G/A_D$...
which represents the area ratio of G-band to D-band, is used to evaluate the degree of graphitization in the char residue. Notably, the \( A_G/A_D \) ratios for APP4, (APP/MEL)4 and ASM4 increased to 0.37, 0.42 and 0.51 from 0.15 of the pristine cotton fabric, respectively. According to the principle that the higher the degree of \( A_G/A_D \), it is obvious that the addition of SWCNHs increases the degree of graphitization of the residual char, which is beneficial to the formation of a denser and higher graphitized carbon layer. This observation aligns with the previously mentioned results obtained from SEM.

FTIR and high-resolution XPS spectrum were used to analyze the composition of the thermostable char in detail. Fig. 8(a) displayed the absorption peaks at 3132 and 1399 cm\(^{-1}\) of the char residues resulting from the combustion of the pristine cotton fabric and ASM4. These peaks are associated with the stretching vibration of C–H bonds and in-plane bending vibration of C–H bonds, respectively. Furthermore, the residual char from ASM4 displayed several distinctive absorption peaks at 1614, 1567 and 1251 cm\(^{-1}\), corresponding to stretching vibrations of N–H, N–O and C–N, respectively.\(^{44,45}\) Additionally, the FTIR spectrum of ASM4 revealed the presence of P=O and P–OH peaks at 1158 and 901 cm\(^{-1}\), respectively. Similarly, as depicted in Fig. 8(b), C and O elements were identified in both the pristine cotton fabric and ASM4, whereas P and N elements

![FTIR and XPS spectra](image-url)

**Fig. 8** FTIR (a) and XPS (b) spectra of the residual chars of pristine cotton fabric and ASM4. High-resolution XPS spectra of C 1s (c) of pristine cotton fabric, C 1s (d), N 1s (e) and P 2p (f) of ASM4.
Fig. 9  3D and 2D TG-FTIR spectra of pristine cotton fabric (a) and ASM4 (b); absorbance intensities of chosen volatiles vs. temperature in the thermal degradation of pristine cotton fabric and ASM4 (c).
were detected in the char residues of ASM4. In comparison to the pristine cotton fabric, the C 1s spectra of ASM4 revealed new peaks at approximately 286.7 eV and 288.8 eV, as shown in Fig. 8(c) and (d), which were attributed to C–O–P and O=C–O groups, respectively. The N 1s peaks of the residual char from ASM4 were categorized into C=–N, N–C and N–H, with corresponding binding energies around 398.7 eV, 399.7 eV and 401.5 eV. From Fig. 8(f), the P 2p spectrum of residual char of ASM4 were deconvoluted into P–O–C (133.6 eV) and P=O (134.6 eV). These findings suggest the existence of intricate crosslinking structures within the ASM4 char layers, interconnected by C–C, C=O/C–O, C–N/C–N, P=O, and C–O–P bonds.

To further elucidate the gas-phase flame retardancy mechanisms, this study examined the thermal degradation products of both unmodified cotton fabric and ASM4 through the FTIR-TG technique. As delineated in Fig. 9(a) and (b), the analysis revealed notable absorption peaks at the wavenumbers 3736 cm⁻¹, 2926 cm⁻¹, 2360 cm⁻¹, 2176 cm⁻¹, 1744 cm⁻¹ and 1064 cm⁻¹. These spectral features are indicative of the evolution of gaseous water or other hydroxyl (–OH) containing compounds, aliphatic hydrocarbons (C–H), carbon dioxide (CO₂), carbon monoxide (CO), carbonyl (C=O) groups, and ether linkages (C-O-C), respectively. 46,47 The thermal decomposition of cellulose results in the generation of these compounds, as evidenced by the analysis. Similarly, the investigation into ASM4 demonstrated analogous absorption peaks at equivalent positions (referenced in Fig. 9(b)). However, the TG-FTIR spectra of ASM4 disclosed additional absorption peaks at 1252 cm⁻¹, 3752 cm⁻¹ and 936 cm⁻¹, which are ascribed to the stretching vibration of P=O and the bending vibration of N–H, respectively. 48,49 The detection of the P=O stretching vibration signifies the emergence of phosphorus-containing compounds in the gas phase, which serve as free radical scavengers and play a pivotal role in flame retardation. Furthermore, the identification of the N–H bending vibration peak reveals the presence of nitrogenous entities, such as NH₃, in the gas phase. NH₃, being a non-combustible gas, contributes to fire suppression by diluting combustible materials and oxygen in the vicinity.

According to the Lambert–Beer law, the intensity of absorption peaks at specific wavenumbers directly correlates with the concentration of volatiles. 49 Therefore, to gain a deeper understanding of how the combination of APP, SWCNHs, and MEL affects the thermal degradation of cotton fabrics, selected decomposition products were used to plot a curve showing the relationship between absorption intensities and temperature, as illustrated in Fig. 9(c). The decomposition products of ASM4 reach their peak value earlier, indicating a more advanced decomposition process. This advancement can be attributed to the thermal breakdown of APP, which generates phosphoric acid or polyphosphoric acid, thereby accelerating the early decomposition of the coated cotton fabrics. The absorption peak intensities of H₂O and CO₂ for ASM4, aimed at diluting fuel and oxygen concentrations, are significantly higher compared to those of the pristine cotton fabric. Conversely, the absorption peak intensities of C–O–C, C=O and C₆H₅ for ASM4 decrease notably compared to those of the pristine cotton fabric, suggesting a significant reduction in the release of flammable gases. Additionally, the release of CO increases after coating, indicating a more challenging combustion process and incomplete burning of the cotton fabrics.

Based on the analysis of the gaseous and solid-phase products from the combustion of cotton fabric, the flame retardant mechanism for the APP/SWCNHs/MEL coating was proposed. During the initial phases of burning, APP functions as an acidic catalyst to expedite the carbonization process, concurrently yielding ammonia and water. Simultaneously, MEL, due to its abundance of amino groups, serves as a gaseous precursor, liberating substantial quantities of ammonia when subjected to combustion. The resultant ammonia dilutes the concentration of combustible gases, effectively lowering their flammability. 51 The primary role of SWCNHs in enhancing flame retardancy lies in its ability to improve charring effects and increase the stability of the char layer, thereby strengthening the protective efficacy of the physical barrier.

4. Conclusions

The innovative intumescent flame retardant, comprising of APP, SWCNHs, and MEL, was effectively applied onto cotton fabric using the spraying coating method. The addition of SWCNHs demonstrated a clear synergistic effect with APP and MEL, enhancing the flame retardant properties of the cotton fabric. Based on the TG analysis, LOI evaluation, cone calorimetry and the observation of the residue char, its flame retardant mechanism were confirmed to be the intumescent char-forming in the condensed phase. After undergoing four spraying cycles, the treated cotton fabric ASM4 demonstrated outstanding flame retardancy and self-extinguishing characteristics. Additionally, its LOI value reached 24.1 ± 0.1%, while the damage length reduced from 30.0 ± 0.1% cm to 4.6 ± 0.2% cm compared to the pristine cotton fabric. Despite partial carbonization, ASM4 maintained its original morphology. Notably, the pHRR and THR of ASM4 were significantly reduced by 90% and 51%, respectively. Meanwhile, from the perspective of thermal degradation kinetics, the high E value of ASM4 strongly reflected that the integration of SWCNHs enhanced the thermal stability of the char layer, effectively preventing additional damage to the char layer at elevated temperatures. The Raman analysis showed that the ratio of A₆/A₂ in the char residue of ASM4 rose to 0.51 from the initial 0.15 seen in pristine cotton fabric following the cone calorimeter test. This increase confirmed that incorporating SWCNHs enhanced the graphitization level of the char residue. Additionally, the TG-FTIR data indicated that the combined flame-retardant impact of APP, SWCNHs, and MEL aided in the development of a char layer. This layer acts to slow the spread of heat and oxygen. It serves as a protective shield, hindering the escape of flammable vapors and emitting non-combustible gases. This study demonstrates the viability of SWCNHs within intumescent flame retardant systems and offers fresh insights into the function of SWCNHs in enhancing flame retardancy mechanisms in cotton fabrics, employing a thermodynamic approach.
Data availability

Data are available on request to the authors.

Conflicts of interest

No conflict of interest exits in the submission of this paper and paper is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously and not under consideration for publication elsewhere, in whole or in part.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (no. 51974311 and 51704292), the Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX22_2597) and the Graduate Innovation Program of Nanjing University of Technology (2022WLX066).

References


44. D. Xu, S. Wang, Y. Wang, Y. Liu, C. Dong, Z. Jiang and P. Zhu, Preparation and Mechanism of Flame-Retardant


