Fabrication of a Thermoregulating Cotton Fabric with Enhanced Flame Retardancy via Layer-by-layer Assembly

Yunbo Chen1,2, Xiangyu Zhu1,2, Luying Chen1,2, Bijia Wang1,2, Zhiping Mao1,2,3, Xiaofeng Sui1,2,*, and Hong Xu1,2,*

1Key Lab of Science and Technology of Eco-Textile, Ministry of Education, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China
2Innovation Center for Textile Science and Technology of DHU, Donghua University, Shanghai 201620, China
3National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 201620, China

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Abstract: The lack of thermoregulating functionality and high flammability for cotton fabrics greatly restricts their application in high-performance fields. Herein, we report a versatile layer-by-layer (LBL) assembly strategy for introducing a multilayered film consisting of phase change microcapsules and ammonium polyphosphate to cotton fabric, endowing cotton with thermoregulation and flame retardant properties. The coated fabrics were characterized based on scanning electron microscopy (SEM), water-vapor transmission rate (WVT), thermogravimetry (TG), differential scanning calorimetry (DSC), limiting oxygen index (LOI) and infrared thermal imaging. A fabric deposited with 20 bilayers (MCPM/APP-20) shows an appropriate WVT (50.57 g/m2·h) and improved flame retardancy with an LOI of 24.5% and residual carbon of 34.53%. It also shows a melting enthalpy of 30.09 J/g, which results in a temperature difference of 6.4 °C compared with pristine cotton. The functional properties endowed by the LBL assembly are found to be reasonably durable, with the melting enthalpy and residual carbon of MPCM/APP-20 reduced to 17.69 J/g and 19.64%, respectively, after 30 laundering cycles. This study provides a convenient way to develop multifunctional cotton fabrics that can be good candidates for high-performance textiles.

Keywords: Cotton fabrics, Phase change microcapsules, Flame retardancy, Thermoregulation, Layer-by-layer assembly

Introduction

Cotton is the most important natural substrate for the textile and clothing industry because of its excellent wearability, biodegradability and renewability [1]. Nevertheless, apparel made from plain cotton fabrics cannot provide adequate protection to wearers in specific scenarios, such as fire hazards or extreme weather conditions [2]. To solve these issues, researchers have recently been working to impart thermoregulating functionality to cotton fabrics by introducing phase change materials (PCMs) in the form of microcapsules (MPCMs) [3-5]. PCMs are thermal energy storage materials that can absorb and release thermal energy during a phase transition and are widely used in textile and thermal management [6,7].

MPCMs can be conveniently introduced to cotton fabrics using conventional finishing methods [5,8-10]. Alay et al. [11] constructed a cotton-based thermal regulating fabric, which showed a temperature difference of up to 3.1 °C compared to pristine cotton fabric by incorporating MPCMs via the pad-dry-cure method. Saraç et al. [12] developed stretch denim-based and cotton-based thermal regulating fabrics via a knife-coating technique. MPCMs have also been introduced to fabrics by coating [13], printing [14], grafting [15], exhaustion [16,17] and spinning [18-20].

However, the durability of the thermoregulating function imparted by these methods is generally poor. Moreover, these fabrics are susceptible to fire hazard due to the intrinsic flammability of paraffin wax which is commonly applied as the phase change core. Using flame-retardant MPCMs is a good approach to overcome this deficiency [21]. Demirbağ et al. [22] imparted flame retardancy to MPCMs by introducing clay nanoparticles (Clay-NPs) into a gelatin/sodium alginate shell and observed an improvement in the flame retardancy of finished cotton fabrics (burning time increased from 19.24 s to 34.48 s). Nevertheless, the preparation of flame-retardant MPCMs is complex, and the durable property is also unsatisfactory.

Recently, the layer-by-layer (LBL) assembly technique as a facile, versatile and cost-effective strategy has supplied a viable solution. This technique was used to fabricate thin multilayer films by alternating the deposition of different polyelectrolytes or nanoparticles [23,24]. Using the LBL technique, various functional films can be manufactured on textiles, such as flame retardant [25], anti-ultraviolet [26,27], hydrophobic [28,29], antibacterial [30,31], and thermoregulation [32]. However, very few researchers have been committed to preparing a multifunctional film on cotton fabric to improve its thermoregulating and flame retardancy via the LBL assembly technique.

Ammonium polyphosphate (APP) is a phosphorus-based intumescent flame retardant (IFR), and chitosan (CH) can serve as a carbon source in intumescent systems. They have
been recently found to be capable of forming flame retardant films via the LBL technique. Therefore, in this paper, we introduced CH, MPCMs and APP onto cotton fabrics via the LBL assembly technique to improve their thermoregulating performances and flame retardant properties. The treated fabrics were examined for water-vapor transmission rate, thermoregulating performance, flame retardant property, thermal stability and durability. The results show that highly durable thermoregulating and flame-retardant cotton fabrics can be obtained by this facile and cost-effective strategy.

**Experimental**

**Materials**

Woven cotton fabric (100 %, plain weave, 120 g/m²) was supplied by Luthai Textile Co., Ltd., China. n-Octadecane, acetic acid, hydrochloric acid (HCl) and ethanediamine were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ammonium polyphosphate (APP), isophorone diisocyanate (IPDI) and sodium hydroxide (NaOH) were provided by Adamas Co., Ltd. Chitosan (CH, high viscosity, >400 mPa·s) was supplied by Macklin Biochemical Co., Ltd., Shanghai. Glycidyltrimethylammonium chloride (CHTAC) was purchased from Energy Chemical Co., Ltd. Regenerated nanochitin solution was lab made. All chemicals were used as received.

**Preparation of the MPCM**

Phase change microcapsules were prepared by interfacial polymerization using a procedure modified from our previous report [33]. IPDI (2.00 g) and n-octadecane (6.00 g) as the oil phase were mixed into a 100 ml beaker at 60 °C. An aqueous suspension of regenerated nanochitin (RCh, 48.0 g, 0.20 wt%) was added as the aqueous phase. A stable Pickering emulsion was achieved by subjecting the mixed sample to homogenization for 3 min at 9000 rpm and 60 °C. An aqueous suspension of regenerated nanochitin (RCh, 48.0 g, 0.20 wt%) was added as the aqueous phase. A stable Pickering emulsion was achieved by subjecting the mixed sample to homogenization for 3 min at 9000 rpm and 60 °C. Then, the stirring speed was lowered to 100 rpm, and the mixture was cooled to ambient temperature. Finally, microcapsules were collected through filtration and dried for 24 hours at ambient temperature. Blank polyurea (blank PU, microcapsules without PCM) was prepared using the same procedure as for the blank sample.

**Cationization of Cotton Fabric**

Cotton fabric (5.00 g) was impregnated in a mixed solution of 18.8 g/l CHTAC and 9.00 g/l NaOH at a liquor ratio of 1:30. The mixture was stirred for 1 h at 70 °C. Subsequently, the fabric was washed using deionized water and dried in an oven at 60 °C to yield positively charged cotton fabric.

**Preparation of the APP Solution and CH/MPCM Suspension**

APP (1.50 g) was dissolved in deionized water (33.5 g). The mixture was stirred until transparent, after which 2 M NaOH (7.50 ml) was added. Then, the pH was adjusted to a value of 10 with 2 M HCl to obtain a 3.0 wt% APP solution. The zeta potential of the APP solution was measured, and the results showed that a maximum negative potential of -30.8 mV was recorded at pH=10 (Figure S1, Supporting information).

Chitosan (1.00 g), acetic acid (1.00 g) and MPCMs (2.00 g) in deionized water (96.0 g) were combined and stirred for 2 h to obtain the 2.0 wt% CH/MPCM suspension, which was used as the polycationic solution for the LBL process.

**Thermoregulating and Flame-retardant Treatment of Cotton Fabric**

A schematic representation of the thermoregulating and flame-retardant coating on cotton fabrics is illustrated in Figure 1. In detail, the positively charged cotton fabrics were successively impregnated in 3.0 wt% APP solution and 2.00 wt%) was added. More ethanediamine was added as a more concentrated solution (21.6 g, 10.0 wt%) over the course of 4 hours. Then, the stirring speed was lowered to 100 rpm, and the mixture was cooled to ambient temperature. Blank polyurea (blank PU, microcapsules without PCM) was prepared using the same procedure as for the blank sample.

![Figure 1. Schematic illustration of thermoregulating and flame retardant cotton fabric prepared using layer-by-layer assembly.](image-url)
2.0 wt% CH/MPCM suspension for 10 min each. The samples were dried at 60 °C after each immersion. By repeating this process in a cyclic manner, multilayered fabrics (MPCM/APP-n) were obtained, where n represents the cycle number. A flame retardant cotton (APP-20) was prepared as the blank sample by assembling CH and APP on cotton fabric for 20 cycles. The zeta potential of the CH/MPCM solutions after various numbers of layer-by-layer coatings was measured and is plotted in Figure S2. The zeta potential of the solution shows a continuous decrease with increasing number of layer-by-layer samples due to the neutralization of positive and negative charges but remains positive after 20 cycles, illustrating that CH/MPCM solutions can be used for up to 20 cycles of the self-assembly process.

Characterization

The Pickering emulsions were observed using an ECLIPSE E100 O.M (Nikon, Japan).

The particle size distributions and average diameter of the microcapsules were analyzed by a laser particle size analyzer (S3500, Microtrac, America) at ambient temperature. Prior to observation, the microcapsules were dispersed in deionized water by ultrasonication for 10 minutes.

The morphology of the MPCMs and cotton fabrics was characterized by scanning electron microscopy (SEM, TM3030, Hitachi, Japan) with an acceleration voltage of 15 kV. Before the test, all the samples were sputter coated with gold.

A Malvern Zetasizer (Nano-ZS, UK) was used to determine the zeta potential of the samples. The samples to be tested were prediluted a thousand times, and the measurements were repeated three times.

The limiting oxygen index (LOI) of the fabrics was determined using an oxygen index testing instrument (5801A, Suzhou Vouch Testing Technology Co., Ltd., China) according to the ASTM D2863 standard; Test temperature: 10-30 °C; relative humidity: 30-80 %.

Specifically, the samples were fixed on a water-vapor transmission cup and placed in a constant temperature and humidity chamber for 1 h with a humidity of 90 % at 40 °C. This operation was repeated three times. The water-vapor transmission rates (WVT) for the samples were determined according to ISO standard 139: 2005. The water-vapor transmission rates (WVT) for the samples were determined according to ISO standard 139: 2005. Specifically, the samples were fixed on a water-vapor transmission cup and placed in a constant temperature and humidity chamber for 1 h with a humidity of 90 % at 40 °C. The weight changes before and after the test were recorded. The WVT was calculated using the following equation (1):

\[ WVT = \frac{m_1 - m_2}{S \times T} \]  

where \( m_1 \) and \( m_2 \) are the weights of the samples before and after the test, respectively, \( S \) is the area of the water-vapor transmission cup, and \( T \) is the test time.

Thermogravimetry tests were performed using a TG-209F1 thermal analyzer (Netzsch, Germany) to observe the thermal decomposition behavior of MPCMs and cotton fabrics. All samples were heated from 30 °C to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

Differential scanning calorimetry (DSC 4000, Netzsch, Germany) was used to record the heat storage/releasing capacities of the MPCMs and treated fabrics. Measurements were performed by varying the temperature in the range from 0 °C to 70 °C with a heating rate of 10 °C/min. The melting enthalpy (\( \Delta H_m \)) and crystallization enthalpy (\( \Delta H_c \)) were defined by the integral areas under the DSC curves in the melting (15 °C to 45 °C) and crystallization (0 °C to 30 °C) temperature regions, respectively.

The encapsulation efficiency (\( E_{\text{enc}} \)) of the MPCMs was calculated from the DSC results using the following equation (2) [34]:

\[ E_{\text{enc}} = \frac{\Delta H_{m,\text{core}}}{\Delta H_{m,\text{PCM}}} \times 100\% \]  

where \( \Delta H_{m,\text{core}} \) and \( \Delta H_{m,\text{PCM}} \) are the melting enthalpies of pure n-octadecane and the MPCM, respectively.

The thermo-regulating performance analysis of MPCM/APP-20 and pristine cotton was performed using an infrared thermal camera (Fluke TiX450, USA). The samples were set on a heating plate (≈45 °C), and an infrared thermal camera was used to capture changes in the temperature of the samples during the heating process.

To test the wash-fastness of the treated fabrics, the samples (1.00 g) were soaked in a solution of standard soap (2.00 g/l) at a liquor ratio of 1:50 and washed for 30 min at 45 °C in an SBW-12 laundry machine. This operation was repeated 30 times, and the sample was coded as Wash-30.

Results and Discussion

Characterization of the MPCMs

Due to the superior emulsifying ability of RCh, Pickering emulsions stabilized by RCh were successfully developed. Figure 2a shows photographs of the RCh suspension and Pickering emulsion of n-octadecane in water stabilized by 0.20 wt% RCh. It was confirmed that RCh is homogeneous without aggregation and stratification. The Pickering emulsion shows obvious stratification, and the lower layer is clear, indicating that the Pickering emulsion was successfully prepared. The optical microscopy (OM) image of this Pickering emulsion shows that the sphere shape of the emulsion droplets is almost perfect (Figure 2b). The morphology of the corresponding MPCMs generated from the emulsion is shown in Figures 2c-2d. It can be observed from the images that the microcapsules are well separated, and no agglomeration is noticeable. The diameter of the spherical MPCMs corresponds well with that of the droplets,
ranging in size from 5 μm to 30 μm, according to the particle size distribution curves obtained for the MPCMs (Figure 2e). The surfaces of the microcapsules appear to be wrinkled with protrusions and indentations likely caused by the volumetric shrinkage of n-octadecane during the liquid to solid transition [35].

The thermal stability of n-octadecane, MPCMs and pure PU was evaluated by TG (Figure 2f and Table S1, Supporting information). The results show that pure n-octadecane exhibits a typical one-step weight loss curve spanning from 133.6 °C to 235.3 °C, with a $T_{\text{max}}$ (temperature at which the maximum weight loss rate occurs) of 230.9 °C due to evaporation and leaving behind almost no residue [36,37]. An obvious enhancement of thermal stability is achieved for the MPCMs, as indicated by the upshift of the main $T_{\text{max}}$ by approximately 45.00 °C compared with pure n-octadecane, because the mass loss due to evaporation is effectively delayed by the PU shell encapsulation, with a $T_{\text{onset}}$ of 240.5 °C. The initial mass loss of MPCM before 193.9 °C is due to free n-octadecane from incomplete encapsulation, while the second $T_{\text{max}}$ at 275.5 °C is due to the decomposition of the PU shells [38].

Melting enthalpy ($\Delta H_m$) and crystallization enthalpy ($\Delta H_c$) are two important indices representing the thermal storage/release capability of MPCMs. Figure 2g displays the DSC curves obtained for the MPCMs compared with that of pure n-octadecane. From Figure 2g, the melting and crystallization temperatures of MPCM are slightly lower than those of pure n-octadecane. This is because the motion of the n-octadecane molecules is limited by the confined internal spaces of the microcapsules, resulting in crystallization defects [39]. Based on the $\Delta H_m$ of pure n-octadecane (246.8 J/g) and MPCMs (191.1 J/g), the encapsulation rate of the microcapsules was calculated to be 77.4 % according to equation (1).

**Preparation of the Multilayered Film**

The surface morphologies and cross-sections of the pristine cotton and treated cotton fabrics are shown in Figure 3. First, it can be observed that the typical micromorphy of the pristine cotton is smooth and clean. The cross section shows the presence of spaces between the cellulose fibers, and each fiber is clearly visible. After 5 cycles of repeated LBL treatment (MPCM/APP-5), the cellulose fibers are clearly covered as discrete films of layered MPCM/APP but remain distinguishable, and the space between the fibers is also decreased with film coverage. When the number of bilayers is increased to 10 (MPCM/APP-10) and 15 (MPCM/APP-15), the films covering the surface of the cellulose fibers are clearly observed to become continuous, thicker and more evenly distributed. For MPCM/APP-20, the fibrous morphology of the fabric surface becomes completely undistinguishable, and the gaps between the fibers are completely filled due to coverage of the multilayered film. Meanwhile, the change in the fabric surface zeta potential with added layers is presented in Figure S3, which shows that the surface charge of the treated fabric is decreased with the addition of CH/MPCM-APP layers but remains positive after deposition of 20 layers of CH/MPCM-APP.

In addition, Figure S4 shows the weight gain and volume density of the treated cotton fabrics. As the number of cycles
increases, the weight gain percent and volume density of the cotton fabric gradually increase. When the number of layers is 20, the weight gain rate is 45%, and the volume density is increased from 119.75 g/m$^2$ to 170.25 g/m$^2$. Moreover, the thickness of the fabric was determined using a Vernier caliper. It was found that with an increasing number of LBL cycles from 0 to 20, the fabric thickness is increased from 0.21 mm (pristine cotton) to 0.44 mm (Figure S5, Supporting information). These results confirm that APP, CH and MPCMs are successfully deposited on the surface of the cotton fabrics.

To characterize the breathability of the treated fabrics, the water-vapor transmission rate (WVT) of the samples was determined and compared to that of the untreated cotton fabric (67.55 g/m$^2$·h). Despite being visually observed to be “fully” coated by the LBL film, MPCM/APP-20 has a WVT of 50.57 g/m$^2$·h, which is only 25.14% lower than that of the untreated cotton, showing that it remains reasonably breathable.

These results show that the multilayered film is evenly distributed on the fabric surface. This is because the oppositely charged solution/suspension (APP solution and CH/MPCM suspension) forms a very low (poly)electrolyte concentration zone (the so-called depletion zone) proximate to the cotton surface, through which the charged particles slowly diffuse to form a uniform film on the fabric surface. As the number of coated layers is increased, the fabric becomes less permeable to water vapor (reducing WVT) so that its wearability is compromised to a certain extent.

The changes in chemical composition during the preparation process were studied by FT-IR. As shown in Figure 4a, the FTIR spectrum of pure n-eicosane shows the stretching vibration of alkyl -CH bonds from methylene groups at 2916 cm$^{-1}$ and 2847 cm$^{-1}$. For the CH spectrum, the absorption observed at 1030 cm$^{-1}$ is attributed to chitosan C-O-C glycosidic linkages [40]. MPCMs show a broad peak at approximately 3330 cm$^{-1}$ corresponding to stretching vibrations of -NHs and -OHs. The stretching vibrations of -NH and -C=O at 1556 cm$^{-1}$ and 1637 cm$^{-1}$ show that the PU shell is successfully formed by the isocyanate-amidogen reaction [41,42]. These peaks also appear in the spectrum obtained for treated cotton fabrics, which also show additional peaks at 1069 cm$^{-1}$ and 1240 cm$^{-1}$ due to the presence of P-O
and P=O moieties [43,44] compared with pristine cotton. These results suggest that the LBL treatment yields a physical composite of CH, APP, MPCM and cotton.

The XRD results (Figure 4b) demonstrate that the characteristic cellulose I diffraction peaks at 2θ=14.8°, 16.5° and 22.5°, corresponding to the (110), (110) and (200) crystallographic planes, respectively, are retained in the diffractograms measured for all MPCM/APP-20 sample fabrics, indicating that the LBL treatment does not change the crystal structure of cotton. This is not surprising because CH/MPCM and APP are physically assembled onto the fabric by electrostatic interactions.

**Thermal Stability**

Figure 5a shows the TG curves of the pristine and treated cotton fabrics heated to 700 °C. The corresponding thermal degradation data are listed in Table 1. The pristine cotton exhibits a one-step weight loss curve due to the depolymerization of glycosyl units and leaves behind a residue of approximately 6.49%. In contrast, all treated fabrics display a two-stage weight loss pattern. The first weight loss occurs at approximately 150 °C, which is significantly lower than the T_{onset} of pristine cotton (261.2 °C) and can be attributed to the evaporation of n-octadecane, as observed in the TG curve for the MPCMs. The resulting polyphosphoric acid promotes the carbonization of cotton cellulose to form an intumescent char layer [29] that prevents further decomposition of cellulose and MPCMs [23,45]. As a result, although the T_{max2} values for MPCM/APP-5, MPCM/APP-10, MPCM/APP-15 and MPCM/APP-20 are all lower than that of the pristine cotton, their yields for char are significantly higher. It is well known that the flame retardancy of materials is reflected by their yield of char in pyrolysis [46]. Therefore, APP treatment is effective in enhancing the flame retardancy of cotton fabrics by promoting charring to suppress thermal oxidation degradation [47].

**Thermal Storage Capacity and Thermoregulating Performance**

The MPCMs possess a high phase change enthalpy measured to be 191.1 J/g, which is expected to endow the
cotton fabrics with an active thermoregulating function. The heat storage capacities of the treated fabrics were measured by DSC, and the results are presented in Figure 5b and Table 2. As expected, all the treated fabrics exhibit a single endothermic peak and a single exothermic peak resembling that obtained for the MPCMs. The overlapping T_onset for MPCMs and the treated fabrics at approximately 27 °C illustrates that the phase transition properties of the MPCMs are unaffected by CH and APP in the LBL film. According to thermodynamic data, the latent heat of the treated fabrics is gradually increased from 12.95 J/g to 30.09 J/g with an increasing number of deposited layers from 5 to 20. The melting and crystallization temperatures of all treated fabrics are approximately 30 °C and 22 °C, respectively. Thus, it can be considered that the layer-by-layer coating process has little effect on the melting and crystallization performance of the microcapsules.

Garments produced using MPCM-containing textiles can afford superior protection to the wearer in extreme environmental conditions because they are endowed, due to the MPCMs, with the ability to store and release energy in a certain temperature range. Herein, the temperature-regulating performance of MPCM/APP-20 was evaluated and compared to that of pristine cotton using a hot plate set at approximately 45 °C. An infrared thermal camera was used to capture changes in temperature of these samples. As shown in Figure 5c, a significant temperature difference between MPCM/APP-20 and pristine cotton is observed during the heating process. Pristine cotton is quickly heated to 40.9 °C within 10 s, by which time the surface of MPCM/APP-20 was measured to be at a temperature of 34.5 °C, which is 6.4 °C lower than that of pristine cotton. At 40 s, the surface temperature of MPCM/APP-20 is still 3.8 °C lower than that of the pristine cotton. These results confirm that an efficient thermoregulating ability can be imparted to cotton fabrics by using the LBL strategy.

| Sample          | Melting | Crystallization |
|-----------------|---------|-----------------|
|                 | T_onset (°C) | ΔH_m (J/g) | T_c (°C) | ΔH_c (J/g) |
| n-octadecane    | 27.09   | 246.8±0.5      | 19.11    | 245.7±0.6  |
| MPCM            | 27.22   | 191.1±0.6      | 25.19    | 190.5±0.4  |
| MPCM/APP-5      | 27.43   | 12.95±0.8      | 22.53    | 11.78±0.8  |
| MPCM/APP-10     | 27.81   | 19.88±1.2      | 22.16    | 19.51±1.5  |
| MPCM/APP-15     | 27.39   | 24.36±1.4      | 22.31    | 24.13±1.4  |
| MPCM/APP-20     | 27.65   | 30.09±1.9      | 21.67    | 29.37±2.2  |
| Wash-30         | 27.64   | 17.69±1.8      | 19.42    | 16.33±1.6  |

T_onset: the temperature at which the initial weight loss takes place, ΔH_m: melting enthalpy, T_c: peak temperature during cooling, ΔH_c: crystallization enthalpy.

Flame Retardancy of the Treated Fabric

LOI was used to evaluate the fire resistance of treated fabrics, and the results are shown in Figure 6. The LOI of the cotton fabrics is increased from 17.9 % to over 24 % after 15 cycles of LBL treatment, suggesting that the incorporated APP is effective in improving the flame retardancy of the fabrics. However, a further increase in the number of deposited layers from 15 to 20 did not lead to an appreciable improvement in LOI. Considering that the handle and wearability of the treated fabrics will inevitably deteriorate as more layers of MPCMs and APP are incorporated, MPCM/APP-20 offers the optimum balance of function and comfort.

The treated fabrics were burned, and their surface morphology was analyzed by SEM (Figure 7). Surprisingly,
not only did the fibers in the burnt fabrics remain distinguishable, but some of the MPCMs also remained intact, indicating that the presence of APP also protects the microcapsules from being destroyed by burning.

**Durability Test**

The washfastness of MPCM/APP-20 was evaluated by repeatedly washing the sample using an SBW-12 laundry machine. Figure 8a shows the SEM image of MPCM/APP-

![Figure 8](image_url)  
**Figure 8.** Durability of MPCM/APP-20; (a) SEM image of MPCM/APP-20 after being washed 30 times, (b) TG curves, (c) DSC curves, and (d) FT-IR spectra for MPCM/APP-20 after being washed 30 times.

![Diagram](image_url)  
**Figure 9.** Synergistic flame retardance mechanism of the LBL films.
20 after being washed 30 times. The film and MPCMs covering the surface of the fabric are still present, while some of the underlying fibers are also revealed, indicating that MPCM and APP are partially lost after repeated laundering. The results from the TG analysis (Figure 8b) shows that the TG curve of the washed sample is very similar to that of the unwashed sample, but with a markedly reduced amount of residue char (decreased by 42%). The results indicate that although washing has no significant impact on the thermal stability of the treated fabric, the flame retardancy is moderately impaired.

The DSC curves and data obtained for MPCM/APP-20 after being washed are presented in Figure 8c. The melting and crystallization enthalpies of the washed samples were calculated to be 24.89 J/g and 25.39 J/g, respectively, representing a 43.1 % drop compared with the prewash values. From Figure 8d, after being washed, the characteristic peaks of APP, CH and PCM in the infrared spectrum of MPCM/APP-20 do not show a change, which indicates that both the thermoregulating property and flame retardancy are moderately durable against repeated washing. These results are due to the attachment of APP to cotton fabric through electrostatic attraction, with MCPM and CH bonded to cotton fibers by APP via electrostatic attraction or hydrogen bond interaction.

**Flame Retardant Mechanism**

The well-accepted mechanism of the flame-retarding effect of APP and CH is illustrated in Figure 9 [48-50]. Upon heating, APP will absorb heat and decompose to release ammonia, and the remaining polyphosphates will react with -OH in chitosan to form a nonstable phosphate ester. In the next step, the dehydration of the phosphate ester occurs, and a carbon foam is built up on the surface of the cotton. This expanded carbonized layer acts as an insulating barrier, which reduces heat transfer between the flame and undecomposed polymers and limits the diffusion of combustible gaseous products from the decomposed polymers toward the flame and oxygen from the opposite direction. Due to the flammable nature of paraffin in the MPCM, the LOI of MPCM/APP-20 was measured to be 24.5 %, which is slightly lower than that of APP-20 (34.2 %).

**Conclusion**

In this paper, MPCMs as thermoregulating materials and APP as a flame retardant were used to fabricate thermoregulating and flame retardant cotton fabric via layer-by-layer assembly technology. The morphology of the treated fabrics was examined by SEM, illustrating that MPCMs and APP are successfully deposited onto the fabrics. A fabric with 20 deposited multilayers (MPCM/APP-20) shows a superlative performance. It displays a WVT of 50.57 g/m²·h, latent heat of 30.09 J/g and reasonable thermoregulating performance. The LOI of MPCM/APP-20 can reach 24.4 %, which is mainly attributed to APP and CH combining to form an intumescent flame retardant composite. After washing for 30 cycles, MPCM/APP-20 is able to maintain 56.9 % of its original enthalpy and still shows moderate flame retardancy, demonstrating that LBL technology is a facile and eco-friendly strategy for imparting durable thermoregulating ability and flame retardancy to cotton fabrics.

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**Conflict of Interest**

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

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