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Enhanced Flame Retardancy of Cotton Fabrics with a Novel Intumescent Flame-Retardant Finishing System

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Abstract: Imidazole spirocyclic phosphoramidate (ISPA) has been synthesized through one-step reaction between spiralphosphodicholor (SPDPC) and imidazole. The optimal flame-retardant finishing for cotton fabrics process was designed by orthogonal experiment L_{25} (5^4) and the finished cotton fabrics with different formulas of aqueous solution containing ISPA, phosphoric acid, and cyanuric acid were prepared. The limiting oxygen index (LOI) to characterize the minimum amount of oxygen needed to sustain a candle like flame revealed that this novel intumescent SPDPC flame system exhibited an excellent flame retardant efficiency on the cotton fabric finished with the optimal formula possessing a high LOI value of 36.6 %. The cotton fabric was investigated by vertical flame test revealing a combustion characteristic of the lowest damaged length (64 mm) without continuing burning and no smoldering. The flame-retardant cotton fabric showed an acceptable decreased tensile strength by 13.3 % and enhanced excellent thermal stability compared with pure cotton fabric. Cone calorimeter test revealed a reduced heat release rate by 57 % and a decreased total heat rate by 60 % for the flame-retardant cotton fabric compared with pure cotton fabric. Scanning electron microscopy (SEM) indicated a solid and tough residue for the burned flame-retardant cotton fabric as compared with the very loose and brittle residue of the burned pure cotton fabric.

Keywords: Cotton fabric, Intumescent flame retardant, Flame retarding finishing, Orthogonal experiment, Fire properties

Introduction

Textiles are utilized extensively throughout clothing, firefighter uniform, student uniform, fabric furniture, institutional upholstery, military garments, professional racer's garments, mattresses, and bedding with an aim to make our lives more comfortable [1-3]. Cotton fabric is an important textile widely used to produce apparel, home furnishings, and various industrial products due to its characteristics of softness, breathability, and capability to absorb moisture [4-6]. Cotton fabrics have also been used in both military and civilian areas due to their comfortable, natural, renewable, and environmentally friendly properties [7,8]. However, a vital drawback of cotton fabric, i.e., flammability, limits its use. It ignites easily and is frequently implicated in fire. Cotton cellulose undergoes degradation on ignition, forming highly combustible volatile compounds mainly levoglucosan with the propagation of fire causing injuries and fatalities in fire accidents [9-11]. Low thermal stability, easy ignition, and rapid combustion of cotton fabric represent their weaknesses and limitations in the production of high performance and fire-protective textile products so that flame resistance is of importance for cotton textiles to meet various mandatory flammability standards [12,13]. For example, regulations adopted by the U.S. require all mattresses to meet the requirements set forth in the U.S. standard for flammability of mattresses. This regulation requires mattresses to be cigarette resistant and all fabrics used for clothing purposes must meet an open flame ignition standard. There are many approaches such as grafting flame retardant groups in polymer materials to improve flame resistance of the materials or adding fire retardant into polymer materials directly to retard inflaming in a material. Mechanical incorporation of flame retardant additives into cotton fabric is mostly low cost and fast blending technique to reduce the flammability of fabric [14].

There are many researches of flame retardant on cotton and the research of intumescent flame retardant on cotton is one of them [14,15-17]. Intumescent flame retardants (IFR) have attracted increasing attention in the flame retardation of materials because they produce low smoke and toxicity without producing corrosive gases [18]. The IFR system is usually composed of three components: an acid source, a carbonization agent, and a blowing agent [19,20]. The spiralphosphodicholor (SPDPC) has attracted great interests due to its unique functions to act as one of the most important reaction intermediates for introducing more functional groups and to improve the thermal stability of polymers [21]. SPDPC should be cooperated with other nitrogenous compounds to form IFR and a lot of researchers paid their attentions to synthesize IFR with a combined

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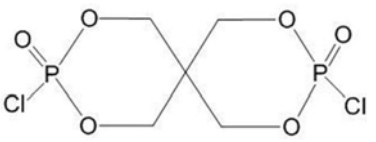


Scheme 1. Structure of SPDPC.

SPDPC and nitrogenous compounds in flame retarding of polypropylene [22], acrylonitrile-butadiene-styrene copolymer [23], polyethylene [24], ethylene vinyl acetate copolymer [25], polyurethane foam [26], epoxy resin [27], and polycarbonate [28]. However, there is no report about effective IFR with a combined SPDPC and nitrogenous compounds in flame retarding of cotton fabrics.

In this work, imidazole spirocyclic phosphoramidate (ISPA), a novel intumescent flame retardant containing a combined SPDPC and nitrogenous compounds is synthesized through one-step reaction of imidazole with SPDPC, which is a kind of effective and environment-friendly halogen-free IFR containing phosphorus-nitrogen elements flame retardant [29,30]. The molecular structure of SPDPC is shown in Scheme 1. The flame retardant finishing of cotton fabric is prepared through the finishing process with ISPA as intumescent flame retardant system, phosphoric acid as catalyst system, and cyanuric acid as cross-linking agent system. The optimum condition of finishing process is determined by the orthogonal experimental [31]. The flame retardancy of the samples was characterized by the limiting oxygen index (LOI) and vertical flammability testing. The oxidative thermal degradation was studied by thermogravimetry (TGA). The burning behavior was carried out by cone calorimeter. The mechanical properties were analyzed by unidirectional tensile testing. The evolution of surface morphologies of pure cotton fabric and fabric finished with optimal combination before and after cone calorimeter test were studied by a field emission scanning electron microscope (SEM).

Experimental

Materials

100 % cotton fabric with a fabric density of 261 g/m^2 was supplied by Jiulong Cloth Industry Co., Ltd. (Suzhou, China). Phosphoryl chloride, pentaerythritol, and imidazole were purchased from Guangfu Fine Chemical Research Institution. Dichloromethane, acetone, and triethylamine were purchased from Tianjin regent chemical company, China. Cyanuric acid was purchased from Qianruida Chemical Co., Ltd. (Puyang, China). Phosphoric acid was purchased from Shuangshuang Chemical Co., Ltd. (Laiyang, China).

The SPDPC was synthesized by pentaerythritol and phosphorus oxychloride in the laboratory containing two highly active functional groups in both ends, which was white powder and the melting point (M.P) was 234-236 °C [32,33]. The details of the preparation of SPDPC are in the literature [34]. Acetonitrile (CH_3CN, 1480 m*l*), pentaerythritol (PER, 80 g), and phosphorus oxychloride (136 m*l*) were slowly added into a 2 *l* glass flask, stirring for 1 h at 82 °C till the system turned to colorless solution under nitrogen atmosphere. $AlCl_3$ (0.5 g) powder was added as catalyst into system 1 h later since the system became colorless. And another 0.5 g catalyst was added to the system per half an hour for another six times then the reaction was refluxed for 1.5 h. The molecular structure of SPDPC is shown in Scheme 1.

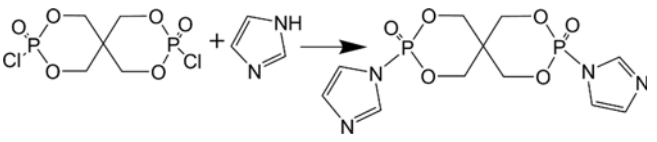
Synthesis of ISPA

The synthesis of ISPA is briefly described as follows. 1.64 g imidazole and 50 m*l* dichloromethane were added into a three-necked round-bottomed flask provided with a mechanical stirrer reflux condensing tube and temperature control system, then the mixture was stirred at room temperature till the mixture became clear from turbid. Then 3 g SPDPC and 2.8 m*l* triethylamine were added into the mixture, and the temperature was increased to 40 °C and maintained at that temperature for 6 h with stirring. The mixture was filtered and washed several times with acetone. The samples and methanol were added into a conical flask with an economical allihn condenser to reflux for 2 h, and then the liquid phase was filtered immediately. Colorless transparent acicular solid came out when the temperature was cooled down, and then filtered. Finally, the samples were dried in a vacuum oven overnight at 70 °C. The ISPA is white powder and M.P is 178-180 °C. Analysis calculated for $C_{10}H_{14}O_6N_4P_2$ is C (34.48 %), H (4.02 %), N (16.09 %), and P (17.81 %). Values found through elemental analysis are C (34.42 %), H (3.99 %), N (16.05 %), and P (17.76 %), indicating that the calculated element content correspond with the found one and the target product is obtained. The reaction process is represented in Scheme 2.

Flame Retardant Finishing of Cotton Fabric

Optimization of Finishing Process

In the present study, an orthogonal array experimental design was used for selecting the optimum condition of experimental factors on the limiting oxygen index (LOI) of cotton fabrics and twenty-five groups of experiment plans with five levels and four factors, L_{25} (5^4) were adopted where the following four variables were analyzed: the



Scheme 2. Reaction process of ISPA.

Table 1. Factors and levels of the orthogonal design

Level	Factor			
	ISPA loading (wt%) A	Catalyst content (wt%) B	Cross-linking agent loading (wt%) C	Cure temperature (^{o}C) D
1	10	0	0	140
2	15	0.5	0.5	150
3	20	1.0	1.0	160
4	25	1.5	1.5	170
5	30	2.0	2.0	180

loading of ISPA wt% (factor A), the content of catalyst wt% (factor B), the loading of cross-linking wt% (factor C), and cure temperature ^{o}C (factor D).

Flame-Retardant Finishing Process

First the cotton fabric (10 g) was boiled in boiling water (500 m*l*) for 30 min to remove the impurity from the cotton fabric and put them at room temperature till the moisture volatilize out completely. Then pure cotton fabrics were immersed in 300 m*l* aqueous solution containing some formulas shown in Table 1, where ISPA was used as intumescent flame retardant system, phosphoric acid as catalyst system, and cyanuric acid as cross-linking agent system with stirring for 30 min at room temperature. Afterward they were padded in a laboratory padding frame with an approximately 100 % wet pick-up, dried at 80 ^{o}C in an oven for 5 min and cured at a series of temperature that were also shown in Table 1 for 3 min [35].

Characterization

The LOI values of some samples were carried out on a JF-3 oxygen index instrument (Jiangning, China) according to ASTM D2863-09 standard method with sheet dimensions of 130×60 mm, and a mixture of oxygen and nitrogen is passed up through a cylinder containing the fabric specimen supported vertically [36]. The minimum fraction of oxygen in a mixture of oxygen and nitrogen in which one specimen was just sustained burning was determined and reported as the LOI value. Vertical flame test was performed on strips of cotton fabric (300×76 mm) according to ASTM D-6413-08 on a CZF-3 vertical flame test instrument (Jiangning, China), five pieces of the longitudinal (vertical) cotton fabrics and five pieces of latitudinal (horizontal) cotton fabrics were chosen for vertical flame test, respectively. The ignition time for the test is 12 s and the height of fire was approximately 40±2 mm [37,38].

Tensile properties of the cotton fabric before and after flame retardant treatment were carried out on a RGT-20 with microcomputer control electronic universal testing machine (Shenzhen, China) according to ISO 13934-1:1994. The gauge length of the tensile-testing machine was set to 200 mm for fabrics with elongation at maximum force up to 75 % or to 100 mm for fabrics having an elongation at maximum force of more than 75 % and the gauge speed was 100 mm/min [39].

The thermal stabilities of the treated samples were evaluated by thermogravimetric analysis (TGA), using a Perkin Elmer Pyris1 TG analyzer including 3-5 mg samples from 50 to 800 ^{o}C with a heating rate of 10 ^{o}C/min, and the atmosphere is continuous N_2 flow of 50 m*l*/min [40].

Thermal combustion behaviors of the cotton fabrics before and after flame retardant treated were examined using an oxygen consumption calorimeter (cone calorimeter, Fire Testing Technology, East Grinstead, UK) at an incident heat flux of 35 kW/m^2 according to ISO 5660 [41,42]. The specimens were wrapped in an aluminium foil and were fixed by a non-combustible mineral fiber mat. All samples (100×100 mm) were measured in the horizontal position using the retainer frame. The device consisted of a radiant electric heater in a trunk-conic shape, an exhaust gas system with oxygen monitoring and instrument to measure the gas flux, an electric spark for ignition, and a load cell to measure the weight loss.

The surface morphology of the cotton fabric before and after burning was studied using a FEI Quanta 200 scanning electron microscope. The fabric pieces (10×10 mm) were cut and fixed to conductive adhesive tape. All the samples were sputter-coated with a gold layer before test for better imaging.

Results and Discussion

Orthogonal Experiment for Determining LOI

Table 2 shows the result and analysis of the orthogonal experiment L_{25} (5^4). According to the L_{25} (5^4) matrix, 25 experiments were carried out. This table also illustrates the range of the LOI on various factors and levels. LOI values indicate the minimum amount of oxygen needed to sustain a candle like flame when the sample was burned in an atmosphere of oxygen and nitrogen.

It can be clearly seen from the results of orthogonal experiment that the higher the ISPA loading is, the higher the LOI value is not always. The maximum loading of ISPA is 30 % (level 5) and the minimum loading of ISPA is 10 % (level 1). In terms of level 5, there are five different values of LOI. The highest value of LOI of these five different values is for the cotton fabric treated with trial 21 and the other four values are lower than for trial 21. Even some of LOI values in level 1 are higher than that of other four values in level 5, indicating that the loading of ISPA synergistically plays an important role on flame retardancy of the cotton fabric with other factors. The best level for each factor is level 5 of ISPA loading, level 4 of catalyst content, level 5 of cross-linking agent loading, and level 4 of cure temperature, respectively, that is, the optimal combination is $A_5B_4C_5D_4$ from Table 2. The LOI value of the cotton fabric finished with the optimal

Table 2. Result and analysis of the orthogonal experiment of L_{25} (5^4)

Trial number	Factor A	Factor B	Factor C	Factor D	LOI (%)
Pure cotton fabric					18.7
1	1	1	1	1	24.9
2	1	2	2	2	27.8
3	1	3	3	3	29.8
4	1	4	4	4	30.1
5	1	5	5	5	29.5
6	2	1	2	3	26.2
7	2	2	3	4	26.6
8	2	3	4	5	26.8
9	2	4	5	1	28.7
10	2	5	1	2	28.2
11	3	1	3	5	26.9
12	3	2	4	1	26.6
13	3	3	5	2	27.4
14	3	4	1	3	27.7
15	3	5	2	4	27.1
16	4	1	4	2	26.6
17	4	2	5	3	28.2
18	4	3	1	4	27.4
19	4	4	2	5	26.9
20	4	5	3	1	27.7
21	5	1	5	4	34.2
22	5	2	1	5	27.3
23	5	3	2	1	27.1
24	5	4	3	2	34.0
25	5	5	4	3	27.7
K1	141.99	138.72	135.39	132.93	
K2	136.47	136.42	134.93	143.93	
K3	135.67	138.46	144.91	139.45	
K4	136.67	145.28	137.83	145.35	
K5	150.19	140.14	145.96	137.36	
k1	28.40	27.74	27.08	26.59	
k2	27.29	27.28	26.99	28.79	
k3	27.13	27.69	28.98	27.89	
k4	27.33	29.06	27.57	29.07	
k5	30.04	28.03	29.19	27.47	
Range (R)	2.91	1.78	2.20	2.48	
Best level	A_5	B_4	C_5	D_4	
Optimal combination	$A_5B_4C_5D_4$				

combination (using the level 5 of ISPA loading, level 4 of catalyst content, level 5 of cross-linking agent loading, and level 4 of cure temperature) is 36.6 % from Table 3. Compared with pure cotton fabric, the LOI with treatment of an optimal combination is increased by 95.7 %. Any materials with a LOI of less than 21 % will burn easily in air, and in the range of 21 to 27.9 % the materials are known as slow burning [43]. There are eight trials which the LOI values are over 28 % among all orthogonal experiments and they are trial (3rd, 4th, 5th, 9th, 10th, 17th, 21st, and 24th). For further research, these eight groups were used and the sample finished with the optimal combination of cotton fabric was used for vertical burning test and tensile test.

Vertical Flame Test

Vertical flame test results in Table 3 show that the cotton fabric finished with an optimal combination demonstrates the highest LOI compared with pure cotton fabric and trial 3rd, 4th, 5th, 9th, 10th, 17th, 21st, and 24th samples. The pure cotton fabric is damaged completely (300 mm), after ignition the cotton fabric with a continued burning along with black smoke. The ignition and smolder process continued for 33.6 and 103.0 s, respectively. Peoples often died from the smoke in the real fire rather than from burning. For samples of trial 3rd, 4th, 5th, 9th, 10th, 17th, 21st, 24th, and cotton fabric finished with an optimal combination, no additional combustion and smoke were observed after the fire was removed from the samples. Figure 1 shows the images of cotton fabric after vertical flame test. The damaged lengths of 17th, 24th, and cotton fabric finished with optimal combination are between 64-68 mm, the cotton fabric finished with optimal combination sample has the lowest damaged length (64 mm), 3th has the longest damaged length (104 mm). The 21th has a higher value of LOI (34.2 %) than that of other samples except the sample finished with an optimal combination treatment, though it has a high damaged length (85 mm), indicating that LOI is not necessary to be related with the vertical flame test.

Tensile Property

Breaking strength and breaking elongation data of trial 3rd, 4th, 5th, 9th, 10th, 17th, 21st, 24th, and cotton fabric finished with optimal combination are listed in Table 3.

The pure cotton fabric has the highest breaking strength and the breaking elongation (386.6 N and 87.5 %). The breaking strength of finished cotton fabric decreases a little from 338.3 to 308.1 N. The breaking elongation also declines after the finishing treatment. There is no apparent connection between the amount of ISPA and the value of tensile test and there is also no relationship between the value of LOI and the value of tensile test. After finishing treatment, however, the value of tensile test decreases. This is due to the introduction of ISPA and cross-link agent, which could make the cotton fabric hard and brittle. The hard and brittle

Table 3. Vertical flame test and tensile strength of the chosen flame-retardant cotton fabric

No.	No. in OE	LOI (%)	Vertical burning test				Tensile performance			
			T_c (s)	T_S (s)	DL (mm)	ΔDL (%)	BS (N)	ΔBS (%)	BE (%)	ΔBE (%)
1	Pure cotton	18.7	33.6	103	300	100	386.8±1.4	0	87.5	0
2	3	29.8	0	0	104	34.7	338.3±2.0	12.5	78.5	10.3
3	4	30.1	0	0	79	26.3	314.8±1.8	18.6	67.7	22.6
4	5	29.5	0	0	81	27	309.1±2.3	20.1	71.3	18.5
5	9	28.7	0	0	72	24	338.5±2.3	12.5	64.3	26.6
6	10	28.2	0	0	74	24.7	338.7±1.9	12.4	65	25.8
7	17	28.2	0	0	67	22.3	344.0±1.6	11	61.5	29.7
8	21	34.2	0	0	85	28.3	308.1±1.3	20.3	66.4	24.1
9	24	34.0	0	0	68	22.7	312.5±1.7	19.2	58.7	33
10	Optimal	36.6	0	0	64	21.3	335.4±1.3	13.3	64.1	26.7

OE: orthogonal experiment, T_c: time of continue burning, T_S: smouldering time, ΔL: damaged length, ΔDL: the percentage of the total damage length, BS: breaking strength, ΔBS: breaking strength declined percentage, BE: breaking elongation, ΔBE: breaking elongation decreased percentage.

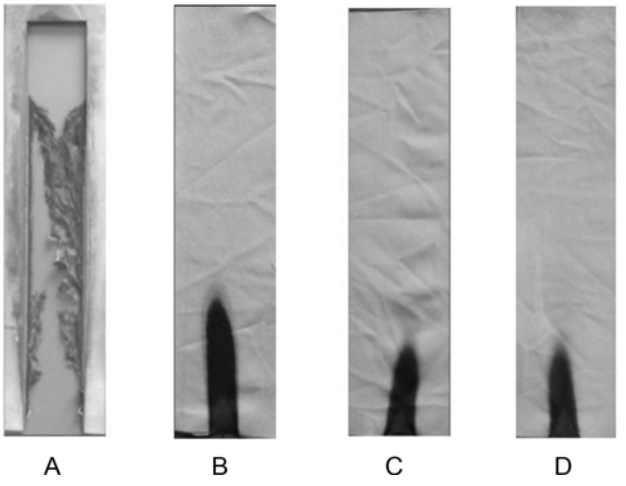


Figure 1. The damaged length after vertical flame test of (A) pure cotton fabric, (B) the 3th treatment, (C) the 24th treatment, and (D) the cotton fabric finished with an optimal combination treatment.

cotton fabric makes the tensile strength decrease but there is no significant decrease of the finished cotton fabric. The cotton fabric finished with an optimal combination treatment has the highest LOI value (36.6 %) and its breaking strength is decreased a little (335.4 N) compared with pure cotton fabric (386.8 N). It is just decreased by 13.3 % compared with pure cotton fabric. The cotton fabric finished with optimal combination has the highest value of LOI, the lowest damaged length and an acceptable decrease of tensile strength. So the optimal combination treatment was chosen to do TGA and cone calorimeter test.

Thermal Stability

The pyrolysis properties of pure cotton fabric and the

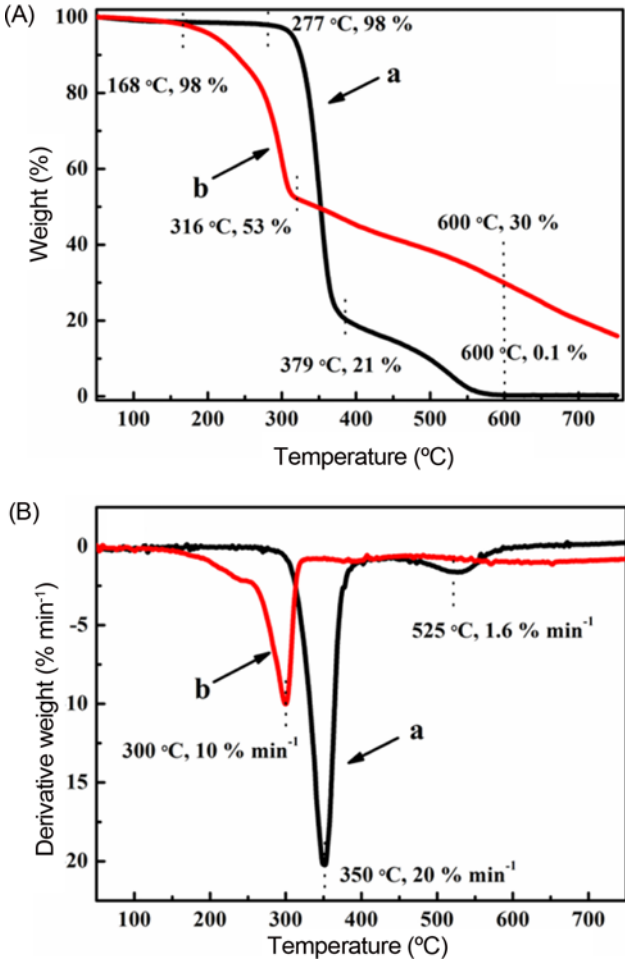


Figure 2. (A) TGA and (B) DTG curves of cotton fabric with and without finished treatment, (a) pure cotton fabric and (b) cotton fabric treated with optimal combination.

cotton fabric finished with optimal treatment in orthogonal experiments were investigated by TG/DTG (Figure 2). The pyrolysis process is a complex reaction containing various reactions, including endothermic bond rupture, volatilization, and exothermic bond formation [44]. Figure 2 shows that there are two main thermal degradation steps for pure cotton fabric, where the temperature range is below 300 °C, there is nearly no thermal degradation and only a very slightly weight loss (below 3.0 %) due to the physical properties that is the amorphous region of polymer damages occurred during this temperature [45]. The first main thermal degradation is in the temperature range of 300 to 380 °C. In this stage, the weight loss is very fast and significant due to the decomposition of cellulose [46]. The first maximum decomposition temperature of pure cotton fabric is at 350 °C with a maximum decomposition rate of 20 %/min. During this step, the aliphatic char was yielded delay the decomposition of cellulose so there is a slow decomposition in the second main thermal degradation step and the second maximum decomposition temperature of pure cotton fabric is at 525 °C with a maximum decomposition rate of only 1.6 %/min. There is scarcely any char left after 600 °C due to the degradation of the cellulose. The cotton fabric can be observed completely different in the TGA and DTG curves after finished. There is only one main degradation step of cotton fabric after finished. In case of finished cotton fabric, the temperature of degradation begins at a relatively lower temperature of 168 °C compared with that of pure cotton fabric (300 °C). After 168 °C, the fabric is degraded rapidly and reaches a maximum degradation rate of 10 %/min at 300 °C. Large amounts of char were formed after 316 °C and even though at 600 °C, it also left vast chars of 30 %. All of these could be ascribed to the addition of IFR system. The IFR has a barrier effect of intumescent carbonaceous char created by the combined actions of three components of IFR [47]. During the heating, the IFR is decomposed at a lower temperature (168 °C) before that of cotton fabric (300 °C) and the IFR forms the char quickly which can prevent the degradation of cotton so that the flame properties of cotton fabric were increased.

Cone Calorimeter

Figure 3 shows the curves of heat release rate (HRR) and total heat release (THR) of the cotton fabrics before and after flame retardant finishing. It is shown completely different curves between pure cotton fabric and finished fabric. The

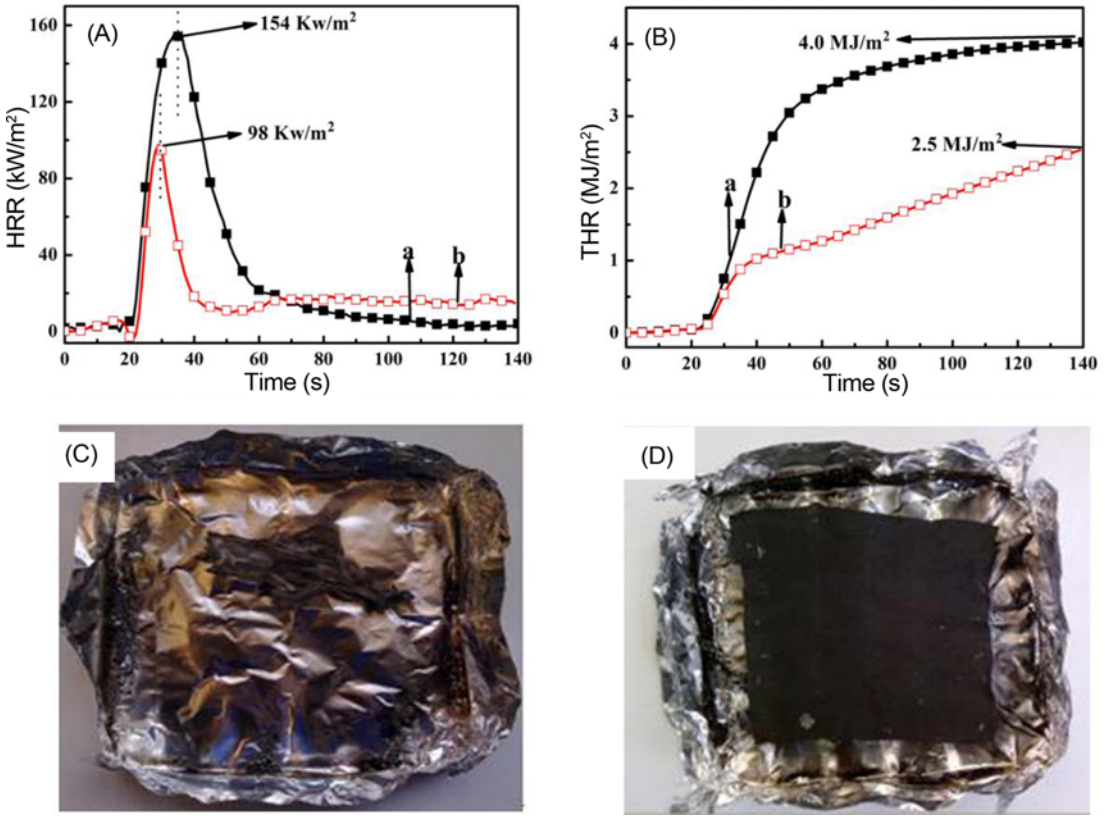


Figure 3. (A) Heat release rate curves, (B) total heat release curves of (a) pure cotton fabric and (b) cotton fabric finished with optimal combination, (C), (D) digital photos of the residues after cone calorimeter test for pure cotton fabric and the cotton fabric finished with optimal combination, respectively.

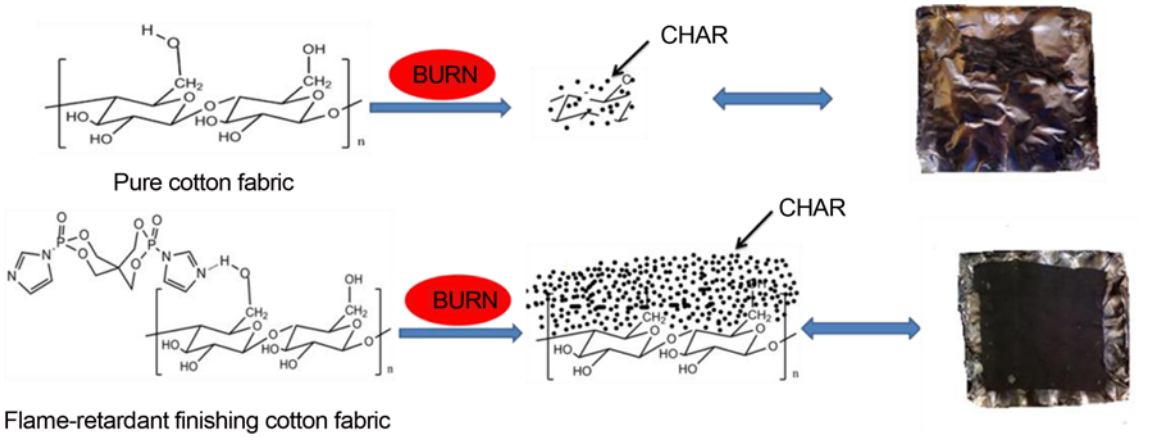


Figure 4. Schematic of the char formation.

pure cotton fabric has faster HRR than finished fabric (Figure 3(A)). Peak of heat release rate (PHRR) of pure cotton fabric is 154 kW/m^2, which is 57 % higher than that of finished fabric (98 kW/m^2). THR of pure cotton fabric (4.0 MJ/m^2 in 140 s) is also higher than that of finished fabric (2.5 MJ/m^2 in 140 s) with 60 % higher than that of finished fabric. PHRR and THR are believed by many fire scientists to be the major determinant of the onset of flashover for cotton fabric furniture in the real fire situation [48]. For our finished cotton fabric, it has an excellent flame property including very low PHRR and THR. It is due to the flame retardant decomposed to release nitrogen-containing gas which was diffused to the surface of cotton fabric and diluted the combustible gas at the same time, the phosphoric acid was formed coated on the surface of the fabric to promote cellulose fiber dehydration and carbonization. The carbonizing layer plays an important role in the isolation of heat radiation and oxygen transfer. Pure cotton fabric has no carbon layer during combustion, heat and oxygen could spread into the inner of cotton rapidly and promote the decomposition of cellulose, furthermore the decomposition of cellulose promotes the combustion [49].

The digital photos of residues of pure cotton fabric and the treated one after cone calorimeter test were shown completely different (Figure 3(C) and (D)). Pure cotton was observed to be almost burned out and the finished cotton formed coherent and dense char and maintained its original shape with little shrinking. The mechanism of the char formation is shown in Figure 4.

Evolution of Surface Morphology

SEM has been performed to assess the morphology of the cotton fabric before and after flame retardant finishing. Surface morphologies of pure cotton fabric and fabric finished with optimal combination before and after cone calorimeter test are shown in Figure 5(A) to (H). There is distinct difference between the pure cotton fabric and finished one. The surface of pure cotton fabric is smoother than that of finished one before cone calorimeter test indicating that the finished cotton fabric is coated by flame retardant system successfully. The pure cotton fabric left tiny residue after cone calorimeter test, however the finished fabric was carbonized and maintained its original shape after cone calorimeter (Figure 5(H)). The residue of pure cotton fabric looks loose and gossamer, however, the finished fabric has no change compared with pure cotton fabric. It can also be observed (Figure 5(G)) that the residue is thin and smooth for the finished cotton fabric, but the residue looks solid and full of many blocks on it. This is due to the fact that the finished cotton formed the char during burning. The carbon layer acts as a physical barrier, which can prevent heat to transfer into the surface of cotton fabric. It can also prevent the release of combustible gases and the contact of oxygen with the combustible gas at the same preventing the spread of fire [50,51].

Conclusion

A novel intumescent flame retardant, ISPA has been synthesized using SPDPC and imidazole. The flame retardant finishing of cotton fabric was prepared with finishing liquid formula containing ISPA, phosphoric acid, and cyanuric acid. The optimal formula was chosen through the orthogonal experiment L_{25} (5^4). LOI test demonstrated the cotton fabric finished with the optimal formula has a highest value of 36.6 % and vertical flame test shows that the cotton fabric finished with optimal formula has the lowest damaged length (64 mm) with no continuing burning and no smoldering. The cotton fabric finished with optimal formula has an acceptable tensile of 335.5 N, which is just decreased by 13.3 %. The finished cotton fabric with optimal formula with an excellent flame retardant left vast chars of 30 % even at 600 ^{o}C. Cone calorimeter indicates that the cotton fabric finished with optimal formula has good combustible properties.

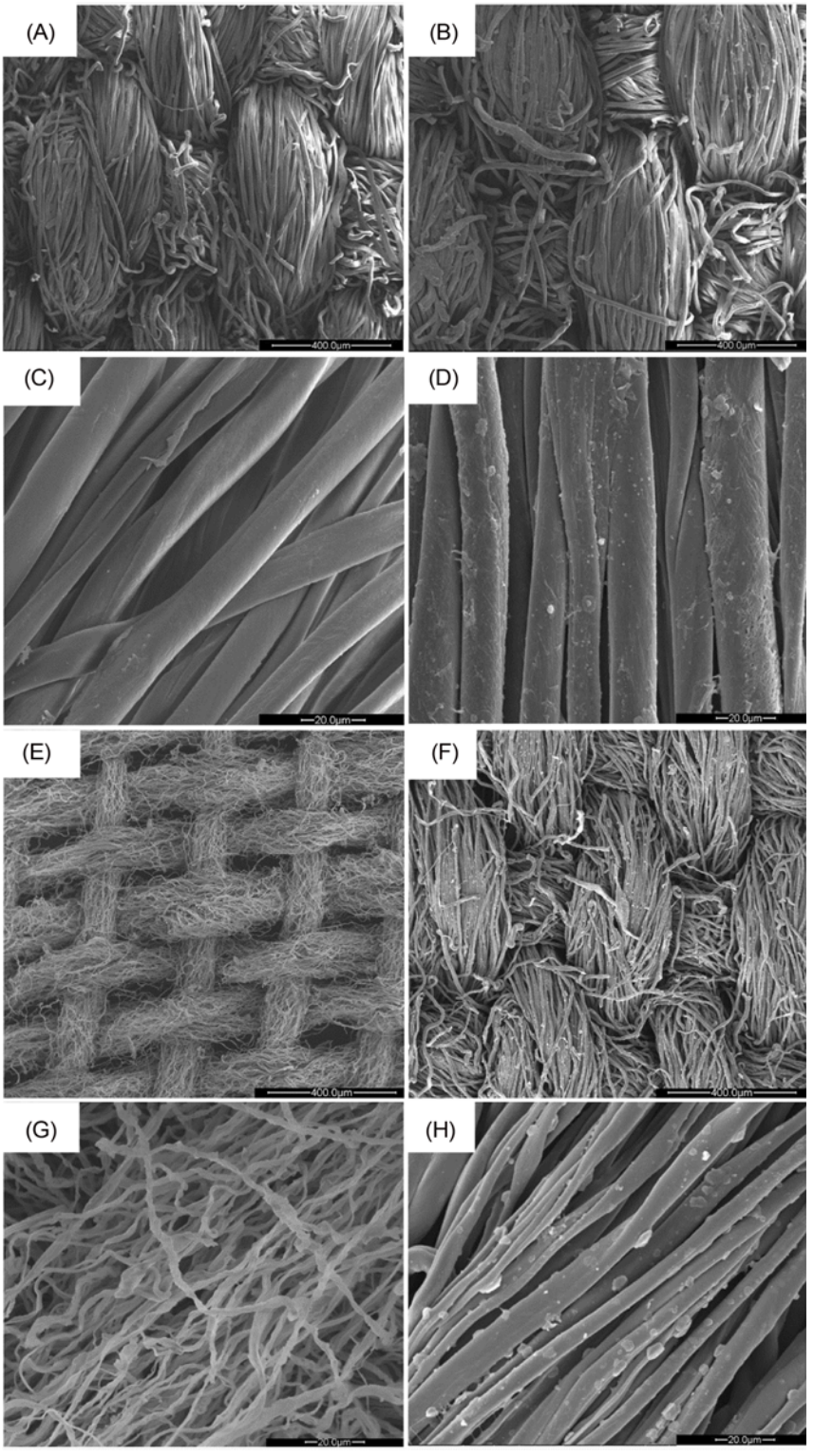


Figure 5. SEM microstructures of cotton fabric; (A) The pure cotton fabric×100, (B) the finished cotton fabric with optimal combination×100, (C) the pure cotton fabric×1000, (D) the finished cotton fabric with optimal combination×1000, (E) the residue of the pure cotton fabric after cone calorimeter×100, (F) the residue of finished cotton fabric with optimal combination after cone calorimeter×100, (G) the residue of the pure cotton fabric after cone calorimeter×1000, and (H) the residue of finished cotton fabric with optimal combination after cone calorimeter×1000.

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References

1. K. Fletcher, "Sustainable Fashion and Textiles: Design Journeys", Routledge, 2013.
2. M. Ghoranneviss and S. Shahidi, *J. Fusion Energy*, **33**, 119 (2014).
3. X. Zhou, Z. Zhang, X. Xu, X. Men, and X. Zhu, *Appl. Surf. Sci.*, **276**, 571 (2013).
4. S. Chang, R. P. Slopek, B. Condon, and J. C. Grunlan, *Ind. Egn. Chem. Res.*, **53**, 3805 (2014).
5. A. L. Mohamed, M. A. El-Sheikh, and A. I. Waly, *Carbohydr. Polym.*, **102**, 727 (2014).
6. P. Wakelyn, P. Adair, and R. Barker, *Fire Mater.*, **29**, 15 (2005).
7. S. Shahidi and M. Ghoranneviss, *J. Fusion Energy*, **33**, 88 (2014).
8. G. Rosace, R. Canton, and C. Colleoni, *Appl. Surf. Sci.*, **256**, 2509 (2010).
9. N. Balakrishnan and K. Mayilsamy, *J. Renew. Sustain. Energy*, **5**, 053121 (2013).
10. A. Abou-Okeil, S. El-Sawy, and F. Abdel-Mohdy, *Carbohydr. Polym.*, **92**, 2293 (2013).
11. J. Alongi, M. Ciobanu, and G. Malucelli, *Carbohydr. Polym.*, **85**, 599 (2011).
12. J. Vasiljević, S. Hadžić, I. Jerman, L. Černe, B. Tomšič, J. Medved, M. Godec, B. Orel, and B. Simončič, *Polym. Degrad. Stabil.*, **98**, 2602 (2013).
13. S. Chang, B. Condon, E. Graves, M. Uchimiya, C. Fortier, M. Easson, and P. Wakelyn, *Fiber. Polym.*, **12**, 334 (2011).
14. S. Liang, N. M. Neisius, and S. Gaan, *Prog. Org. Coat.*, **76**, 1642 (2013).
15. F. Lessan, M. Montazer, and M. Moghadam, *Thermochim. Acta*, **520**, 48 (2011).
16. C. Q. Yang and Q. He, *J. Anal. Appl. Pyrolysis*, **91**, 125 (2011).
17. H. A. Cheema, A. El-Shafei, and P. J. Hauser, *Carbohydr. Polym.*, **92**, 885 (2013).
18. H.-Q. Peng, Q. Zhou, D.-Y. Wang, L. Chen, and Y.-Z. Wang, *J. Ind. Eng. Chem.*, **14**, 589 (2008).
19. P. Lv, Z. Wang, K. Hu, and W. Fan, *Polym. Degrad. Stabil.*, **90**, 523 (2005).
20. G. Huang, Z. Fei, X. Chen, F. Qiu, X. Wang, and J. Gao, *Appl. Surf. Sci.*, **258**, 10115 (2012).
21. D. Jiang, L. Liu, J. Long, Y. Huang, Z. Wu, X. Yan, and Z. Guo, *Compos. Sci. Technol.*, **100**, 158 (2014).
22. B. Li, Z. Zhan, H. Zhang, and C. Sun, *J. Vinyl Addit. Technol.*, **20**, 10 (2014).
23. H. Ma, L. Tong, Z. Xu, Z. Fang, Y. Jin, and F. Lu, *Polym. Degrad. Stabil.*, **92**, 720 (2007).
24. G. Huang, Y. Li, L. Han, J. Gao, and X. Wang, *Appl. Clay Sci.*, **51**, 360 (2011).
25. G. Huang, S. Chen, S. Tang, and J. Gao, *Mater. Chem. Phys.*, **135**, 938 (2012).
26. D. Wu, P. Zhao, M. Zhang, and Y. Liu, *High. Perform. Polym.*, **25**, 868 (2013).
27. X. Wang, L. Song, W. Xing, H. Lu, and Y. Hu, *Mater. Chem. Phys.*, **125**, 536 (2011).
28. L. Li, P. Wei, J. Li, J. Jow, and K. Su, *J. Fire Sci.*, **28**, 523 (2010).
29. H. Ma and Z. Fang, *Thermochim. Acta*, **543**, 130 (2012).
30. X. Hu, Y. Guo, L. Chen, X. Wang, L. Li, and Y. Wang, *Polym. Degrad. Stabil.*, **97**, 1772 (2012).
31. T. Wang, X. Diao, and P. Ding, *Appl. Surf. Sci.*, **257**, 3748 (2011).
32. Q. Zhang, H. Xing, C. Sun, H. Xiang, D. Jiang, and L. Qin, *J. Appl. Polym. Sci.*, **115**, 2170 (2010).
33. H. Xiang, C. Sun, D. Jiang, Q. Zhang, C. Dong, and L. Liu, *J. Vinyl Addit. Technol.*, **16**, 161 (2010).
34. L. Bin, S. Caiying, and Z. Xiucheng, *C.N. Patent*, 02133071 (2004).
35. S. S. Abkenar, R. M. A. Malek, and F. Mazaheri, *Cellulose*, **20**, 3079 (2013).
36. T. M. D. Nguyen, S. Chang, B. Condon, M. Uchimiya, and C. Fortier, *Polym. Adv. Technol.*, **23**, 1555 (2012).
37. Standard Test Method for Flame Resistance of Textiles (vertical flame test), American Society for Standards and Testing, ASTM D-6413-08, 2008.
38. H. Gu, *Mater. Des.*, **30**, 4324 (2009).
39. F. Si, K. Yan, and X. Zhang, *Carbohydr. Polym.*, **103**, 581 (2014).
40. F. Carosio, A. Di Blasio, F. Cuttica, J. Alongi, and G. Malucelli, *Ind. Egn. Chem. Res.*, **53**, 3917 (2014).
41. M. Zanetti, T. Kashiwagi, L. Falqui, and G. Camino, *Chem. Mater.*, **14**, 881 (2002).
42. L. Wang, M. Sánchez-Soto, and M. L. Maspoch, *Mater. Des.*, **52**, 609 (2013).
43. A. R. Horrocks and S. C. Anand, "Handbook of Technical Textiles", Elsevier, 2000.
44. Q. He, T. Yuan, X. Yan, D. Ding, Q. Wang, Z. Luo, T. D. Shen, S. Wei, D. Cao, and Z. Guo, *Macromol. Chem. Phys.*, **44**, 655 (2014).
45. P. Zhu, S. Sui, B. Wang, K. Sun, and G. Sun, *J. Anal. Appl. Pyrolysis*, **71**, 645 (2004).
46. S. Nam, B. D. Condon, M. B. Foston, and S. Chang, *Cellulose*, **21**, 791 (2014).
47. B. Li and M. Xu, *Polym. Degrad. Stabil.*, **91**, 1380 (2006).
48. Ö. Ceylan, J. Alongi, L. Van Landuyt, A. Frache, and K. De Clerck, *Fire Mater.*, **37**, 482 (2013).
49. F. Y. Hshieh and H. D. Beeson, *Fire Mater.*, **19**, 233 (1995).
50. W. Liu, L. Chen, and Y.-Z. Wang, *Polym. Degrad. Stabil.*, **97**, 2487 (2012).
51. M. Spontón, J. Ronda, M. Galià, and V. Cádiz, *Polym. Degrad. Stabil.*, **94**, 102 (2009).