

Enhancement of Flame Retardancy of Cotton Fabrics by Calcium Hypophosphite-Chitosan Solution Compound Silica Sol

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Abstract. To enhance the thermal stability and flame retardancy of cotton fabrics, a hybrid sol was prepared by using silica (SiO₂) sol, calcium hypophosphite (CaHP) and chitosan (CS), then finished on the surface of cotton fabrics through dipping-baking (drying) method. The results show that the CaHP-CS and SiO₂ are successfully attached to the cotton fabric surface. Remarkably, the limiting oxygen index (LOI) value of the CaHP-CS-SiO₂@COT was 31.30 % (the highest of all samples). In the cone calorimetry test (CCT), the study revealed that the CaHP-CS-SiO₂@COT has the lowest peak heat release rate (PHPP), fire growth rate (FGR) and CO₂/CO. Its flame retardancy is mainly enhanced by the SiO₂ (provides a gel coating with dimensional structure to block the transmission of oxygen and heat, CaHP (promotes cotton cellulose to dehydrate and form aromatic chars) and CS (dilute gaseous products and cool down heated areas).

Keywords: Cotton fabric, gel coating, aromatic chars, flame retardancy

1. Introduction

As a natural fiber textile raw material, cotton fiber is widely used in manufacture textile clothing, decorative fabric home furnishing and other fields because of its outstanding comfort, hygroscopic properties, biodegradability and good mechanical strength [1]. However, cotton fabrics are flammable with a relatively low LOI (only 18 %). Therefore, it is extremely urgent to improve the flame retardancy levels of cotton fabrics [2].

In the past few decades, halogen flame retardants have been known for their efficient flame retardancy, most of them scavenge the active free radicals in the gas phase, but most halogen flame retardants release toxic gases during combustion[3], such as dioxins and benzofurans [4], therefore, halogen flame retardants are banned in more and more countries, especially in European countries [5]. Phosphorus flame retardants have received increasing attention due to their low toxicity and low dosage, they can provide excellent flame retardancy onto cotton fabrics [6]. However, the most common reactive phosphorus flame retardants are Proban and Pyrovatex CP, they have high volatility [7]. In addition, they can react with cellulose to form covalent bonds to improve durability, but they contain N-CH₂-OH group in the process of use, which will release formaldehyde carcinogenic substances, then pollute the environment and damage human health [8]. Nitrogen flame retardants produce a small amount of smoke, but their flame retardant efficiency is low. They need to be combined with other flame retardants to produce a synergistic flame retardant effect, such as phosphorus-nitrogen flame retardants, the same is true for boron-based flame retardants [9]. Therefore, more and more researchers have begun to study flame retardants that are synergistic and eco-friendly with multiple elements. However, the SiO₂ is easy to crack during the drying process, in response to the national green development strategy, the CS used is a hydroxyl-rich biomass polysaccharide, which has excellent adsorption [10]. CaHP not only has high phosphorus content, but also cheap, which can reduce certain economic costs [11].

In this paper, the CS solution has a certain viscosity and good adsorption performance. CaHP-CS solution is obtained by dissolving CaHP in CS solution, and SiO₂ sol is prepared by dehydration and polycondensation of hydrolytic condensation of ethyl orthosilicate (TEOS) in an acidic environment, the CaHP-CS solution and SiO₂ sol were successively finished on the surface of

cotton fabric by dipping-drying method. scanning electron microscope (SEM) were used to test the surface micromorphology of the treated cotton fabrics. And LOI, CC and SEM to characterize the flammability level, reaction characteristics to fire and surface morphology of char residues on the treated cotton fabrics. To explore the flame retardant properties of cotton fabrics after CaHP-CS solution compounded with SiO₂ sol and the synergistic mechanism of each component.

2. Experimental

2.1 Material

The cotton fabrics were obtained from the market with an area density of 111 g/m² each. Hydrochloric acid (HCl, AR, 37.0 %) was provided by Shanghai Pilot Chemical Co., Ltd (Shanghai, China). Anhydrous ethanol (C₂H₅OH, AR, ≥ 99.6 %) was supplied by Wuxi Yasheng Chemical Co., Ltd (Jiangsu, China). Tetraethylorthosilicate (TEOS, AR, ≥35.0 %) and CS (IR, 80.0-95.0 %) were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water (DI, IR, ≥ 99.9 %) was purchased from Nanjing Wanqing Chemical Glassware Instrument Co., Ltd (Jiangsu, China). CaHP and acetic acid (CH₃COOH, AR≥99.5 %) were gained by Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China) and Shanghai Shenbo Chemical Co., Ltd (Shanghai, China), respectively.

2.2 Sample preparation

The original cotton fabric was soaked in CaHP-CS solution for 30 min and then immersed in SiO₂ sol for 10 min. The cotton fabrics were taken out and dried and placed in a drying oven at 80 °C and 120 °C for 30 min and curing for 10 min, respectively.

2.3 Testing and Characterization

Surface microscopic morphologies and element mapping of original and treated cotton fabrics before and after combustion were observed by scanning electron microscopy (SEM, SU8010, Hitachi Co., Ltd., Tokyo, Japan) along with an energy dispersive spectroscopy (EDX, max20 EDX mapping module, Oxford Instrument Technology Co., Ltd., Shanghai, China), respectively. The limiting oxygen index (LOI) test of the original and treated samples was carried out by operating a JF-3 oxygen index meter (ZY6155A, Zonsky Instrument Co., Ltd., Dongguan, China.) with samples of 150 × 58 mm². The cone calorimetry test (CCT, Fire Testing Technology Ltd, UK)) was used to assess the combustion performance and fire safety of original and treated cotton fabrics. Based on ISO 5660 standard, the square specimen size was 100 mm×100 mm×3.2 mm and with a heat flux of 35 kW/ m². Each sample was tested three times.

3. Results and discussion

3.1 Surface morphology and elemental composition of original and treated cotton fabrics before combustion

The SEM images, element mapping images and EDX spectra of original and treated cotton fabrics before combustion are shown in Fig. 1 and Table 1.

For original cotton fabrics, the fibers are interwoven independently, with a longitudinal fiber structure without obvious cracks or sticking points. From the Table 1, the original cotton fabrics only contain 55.53 % C and 44.47 % O elements, while SiO₂@COT contains 46.51% C, 45.14% O and 8.36% Si, also has 8.36 % Si elements. Indicating that silica sol is successfully arranged on the cotton fabrics surface. Besides, when treated with silica sol, it forms a smooth and obvious coating, which is because the hydrogen bond formed by the dehydration between the abundant hydroxyl groups and the silica sol makes the two closely bonded [12]. Apart from C and O, the CaHP@COT includes P (5.26 %), Ca (3.95 %), the CS@COT contains N (2.02 %). In addition, the texture and

direction of the single fiber are still very clear, but the appearance is slightly rougher than the original fabric. All of these show that the CaHP and CS have successfully deposited on the surface of cotton fabrics by physical adsorption and chemical combination. Different from the SiO₂@COT, the CaHP-SiO₂@COT are cross-linked, and the surface is covered with a uniform coating with a certain thickness and continuity. Compared with CS@COT, the morphological direction of CS-SiO₂@COT is no longer obvious. This is because that during the gelation process, the gel coat occurs contraction and cracking, resulting in cracks of varying sizes in the gel between the fiber bundles. The surface of CaHP-CS@COT is rough due to the formation of a coating after the drying of the CaHP-CS solution. On the contrary, the voids between the fiber bundles of CaHP-CS-SiO₂@COT were filled with silica sol, the cracking phenomenon was improved, and the spacing and orientation of the cotton fibers were almost indistinguishable, indicating that the SiO₂ sol coating coated with CaHP-CS solution has been successfully adsorbed on the fabric surface. For the original fabric sample, the C element content is 55.53 %, and the O element content is 44.47 %. After being treated with CaHP-CS solution and SiO₂ sol, a large amount of C, O, and Si elements were detected on the surface of the fabric, and the presence of Si indicated that the SiO₂ sol covered the surface of the cotton fabric. Since CS is rich in a large number of hydroxyl groups, the Si-OH content in the compound sol increases, which promotes the dehydration and condensation reactions between silica-based sols and sols and cotton fibers, resulting in the formation of Si-O-Si and Si-O-C bonds. All of these prove that the CaHP-CS solution and SiO₂ sol have been successfully adhered onto the cotton fabric surface and the surface of original and treated cotton fabrics is within the acceptable range, with little change.

Fig. 1 SEM images of original and treated cotton fabrics before combustion

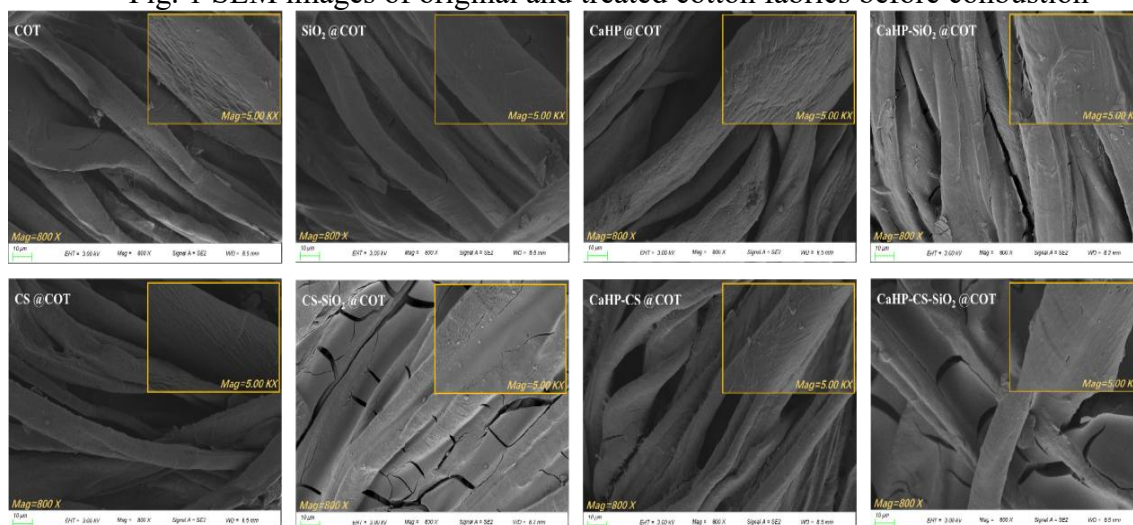


Table 1. EDX element content of original and series treated cotton fabric samples

Samples	C (%)	O (%)	Si (%)	P (%)	N (%)	Ca (%)
COT	55.53	44.47	-	-	-	-
SiO ₂ @COT	46.51	45.14	8.36	-	-	-
CaHP@COT	47.07	43.71	-	5.26	-	3.95
CaHP-SiO ₂ @COT	41.51	45.55	8.42	2.32	-	2.20
CS@COT	55.87	42.11	-	-	2.02	-

CS-SiO ₂ @COT	41.47	43.86	12.34	-	2.33	-
CaHP-CS@COT	48.21	43.57	-	3.73	1.05	3.44
CaHP-CS-SiO ₂ @COT	42.93	44.17	8.27	1.59	1.19	1.86

3.2 Flame-retardant properties of the cotton fabrics

3.2.1 CCT values

CCT was employed to analyze the combustion behaviors of original and treated cotton fabrics. The heat release rate (HRR) and total heat release (THR) curves are presented in Fig. 2 and Fig. 3. And the relevant parameters, such as TTI (time to ignition), pHRR (peak heat release rate), FGR (fire growth rate, THR and CO₂/CO are list in Table 2.

When the original cotton fabric was at 36.0 s, the pHRR reached 183.05 kW/m², the THR reached 7.45 MJ/m², the FGR was as high as 5.08 kW/(m²·s), and the CO₂/CO was 30.12 kg/kg. This shows that original cotton fabrics are extremely flammable, and the flame spreads very quickly, with a high fire hazard. For SiO₂@COT, the PHRR (104.22 kW/m²) was significantly reduced compared with original cotton fabrics. Meanwhile, the FGR (2.89 m²·s) decreased to 56.89 % of the corresponding value of the original cotton fabric, which indicated that the SiO₂ sol had an obvious effect on improving the fire safety of cotton fabrics. CS belongs to the rare basic polysaccharide in natural polymer, rich in carbon elements, active hydroxyl group and amino side bonds [13], when it is compounded with silica sol, the CS-SiO₂@COT corresponds to the TTI delay of 3.0 s, Compared with CS@COT, pHRR and THR decreased by 19.07 % and 7.95 %, respectively, which can verify the protective effect of SiO₂ sol in the previous LOI and VFT to a certain extent, indicating that there is a certain synergistic flame retardant effect between CS and SiO₂. The CO₂/CO of the fabrics treated with CaHP is significantly reduced, because the decomposition of CaHP to generate phosphoric acid and polyphosphoric acid can promote the carbonization of cotton fibers and form a stable char layer structure, block the transmission of flame heat and oxygen, and inhibit the escape of internal flammable volatiles, so that the carbonization of the treated cotton fabric is slowed down. Overall, the CaHP-CS-SiO₂@COT has the lowest pHRR (90.93 kW/m²), FGR (2.67 kW/(m²·s)), and CO₂/CO (2.54 kg/kg), indicating that the P/N synergy of CaHP and CS and the SiO₂ coating have a good flame retardant effect on cotton fabrics, which can prevent the rapid spread of flames in large-scale fires and greatly improve fire safety.

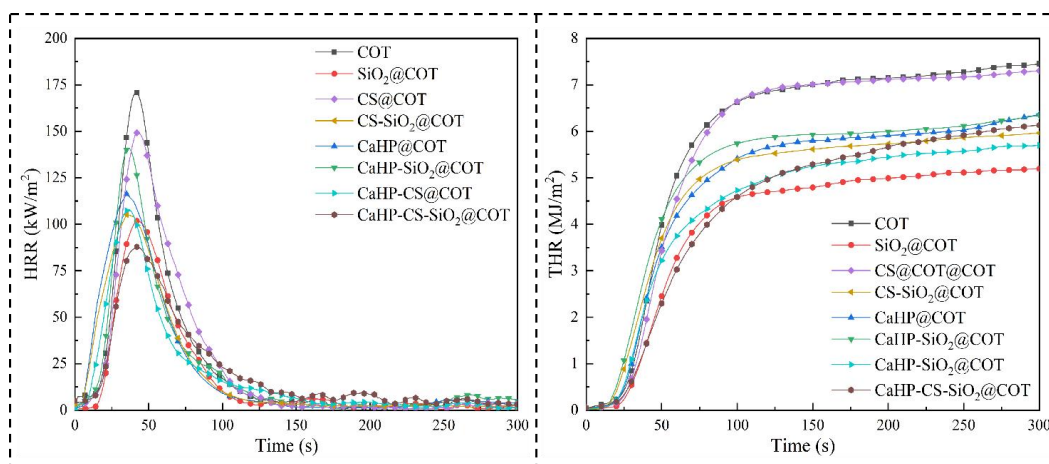


Fig. 2 The HRR and THR of original and treated cotton fabrics



Fig. 3 The residual char of original and treated cotton fabrics

Table 2. Cone calorimetry test data of original and treated cotton fabrics

Samples	TTI (s)	pHRR (kW/m ²)	tpHRR (s)	FGR(kW/ (m ² ·s))	THR (MJ/m ²)	CO ₂ /C O (kg/kg)
COT	7	183.05	36	5.08	7.45	30.12
SiO ₂ @COT	8	104.22	36	2.89	5.19	16.85
CS@COT	6	153.88	37	4.16	7.30	23.75
CS-SiO ₂ @COT	10	124.54	25	4.98	6.72	16.92
CaHP@COT	7	115.04	23	5.0	6.36	12.30
CaHP-SiO ₂ @COT	10	138.99	22	6.32	7.69	5.33
CaHP-CS@COT	5	111.88	24	4.66	5.70	5.16
CaHP-CS-SiO ₂ @COT	9	90.93	34	2.67	6.13	2.54

3.2.2 LOI values

The LOI values of the original and treated cotton fabrics are recorded as shown in Table 3. Compared with the original cotton fabric, the LOI of the treated cotton fabric was improved to varying degrees, and the LOI of the original fabric was only 18 %, indicating that it was easily ignited and spread rapidly when exposed to a fire source. For SiO₂@cotton, its LOI value (20.20 %) is increased by 12.22 % compared with the original fabric, but the flame retardant level is still flammable. The reason is that the SiO₂ sol is connected to the surface of the cotton fabric by physical adsorption and hydrogen bonding before being ignited, thereby acting as a physical barrier to prevent the transmission of oxygen and heat, but the coating is prone to cracking at high temperatures, therefore, it cannot effectively inhibit the spread of flames on the surface of cotton fabrics. The LOI of CS@COT was not significantly improved, which corresponds to its flame retardancy analysis in the above thermogravimetric analysis. However, the samples treated with CaHP all showed high flame-retardant properties. The LOI corresponding to CaHP@COT and CaHP-CS@COT was significantly improved, and the flame retardant grade reached ignitable. This is due to the thermal decomposition of CaHP to generate phosphoric acid and polyphosphoric acid, which accelerates the conversion of cellulose into carbon. It can be found that the LOI of CS-SiO₂@COT and CaHP-SiO₂@COT increased by 19.44 % and 51.67 % compared with the original fabrics, respectively. For CaHP-CS-SiO₂@COT, its LOI is as high as 31.30 %. The phosphoric acid and polyphosphoric acid generated by the thermal decomposition of CaHP catalyze the formation of carbon by cellulose and form P/N synergy with the amino group in CS and combine with the gel coating to form a P/N/Si flame retardant system, thus, an expanded char layer structure is formed on the surface of the cotton fiber, which insulates heat and prevents the escape

of combustible products [14], which verifies the excellent synergistic effect of the CaHP-CS composite system and silica sol, which can effectively improve the fire resistance of cotton fabrics.

Table 3. The LOI of original and series treated cotton fabric samples

Samples	LOI (%)	Δ LOI (%)	Δ m (g)	Δ LOI/ Δ m (%/g)	Level
COT	18.0	-	-	-	flammable
SiO ₂ @COT	20.20	2.20	2.54	0.87	flammable
CS@COT	19.10	1.10	2.32	0.47	flammable
CS-SiO ₂ @COT	21.50	3.50	2.30	1.52	flammable
CaHP@COT	22.40	4.40	2.03	2.17	ignitable
CaHP-SiO ₂ @COT	27.30	9.30	3.60	2.58	flame-retardant
CaHP-CS @COT	24.60	6.60	2.71	2.44	ignitable
CaHP-CS-SiO ₂ @COT	31.30	13.30	4.21	3.16	non-flammable

3.3 Surface morphology and elemental composition of original and treated cotton fabrics after combustion

Fig. 4 is the SEM image after combustion of original and treated cotton fabrics. The original cotton fabric shows a flocculent char residue in Fig. 4. The char residue morphology of the CS@COT was similar to the original fabric. For SiO₂@COT, the sol is gradually transformed into a gel coating, thus forming a flame-retardant protective layer on the surface of the cotton fabric, therefore, the wrapped fibers still maintain a relatively complete shape, but the silica sol has poor adhesion, and a few cracks can be observed in the picture. The phosphorus-containing components in CaHP react rapidly with oxygen to generate phosphoric acid and polyphosphoric acid, which can promote cellulose to form a stable carbon layer containing C-C, P-O-P and P-O-C structures. For CaHP-SiO₂@COT and CS-SiO₂@COT, a large number of pores are distributed on the surface of the char residue, and the pyrolysis products are released, so they cannot play a good isolation effect. The surface of CaHP-CS@COT has spherical particles of different sizes, and part of the surface is smooth, which is because CaHP decomposes at high temperature to generate phosphoric acid and polyphosphoric acid, which forms a P/N synergy with the amino group in CS, and the abundant active hydroxyl groups on the surface of CS combine with the hydroxyl groups on the surface of cotton fabric through chemical bonds to form an expanded carbon layer structure on the fiber surface, phosphoric acid Calcium and calcium pyrophosphate particles are formed on the surface of the carbon layer. The CaHP-CS-SiO₂@COT and CaHP-CS@COT show similar morphology, the bubble size is relatively uniform, the cracking phenomenon is obviously better than that of CaHP-SiO₂@COT and CS-SiO₂@COT, and a relatively complete dense char layer is formed on the surface of the sample, which can play a good role in heat insulation and flame retardant.

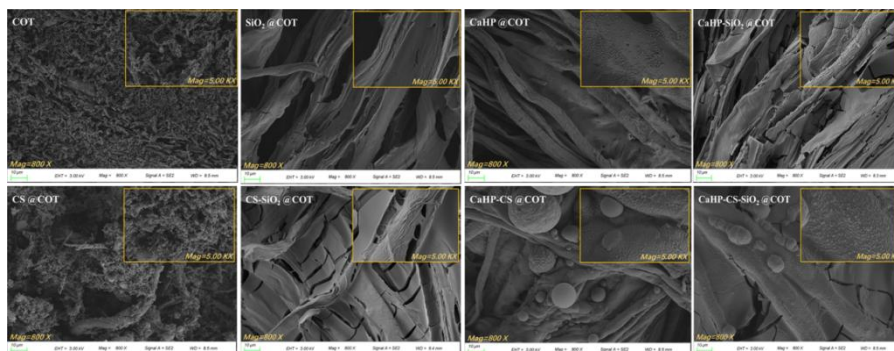


Fig. 4 SEM images of original and treated cotton fabrics after combustion

4. Summary

In this paper, a hybrid system of a CaHP-CS solution and a silica sol were successfully adhered to the surface of cotton fabrics through the dipping-baking (drying) method. Results show that the CaHP-CS-SiO₂@COT exhibits the highest LOI of 31.30 %, and the CaHP-CS-SiO₂@COT has the lowest pHRR (90.93 kW/m²), FGR (2.67 kW/(m²·s)), and CO₂/CO (2.54 kg/kg). All of these indicate that the flame retardant performance of the treated cotton fabrics are significantly improved. The PO radicals generated by CaHP during the decomposition process can react with the active OH and H radicals in the gas phase to interrupt the combustion reaction, while the phosphoric acid and polyphosphoric acid generated by the decomposition of CaHP can promote the dehydration of cellulose to form aromatic carbon and forms a P/N synergy with the amino group in CS. Thus, a thermally stable protective char layer is formed on the surface of the cotton fabric. Meanwhile, when heated, the CS will decompose and release NH₃ and H₂O to dilute and cool the heated area. In addition, due to the high thermal stability of the SiO₂ three-dimensional network structure, it can play a role as a physical barrier and effectively isolate external heat and oxygen transfer. Therefore, the flame retardant can be used as a new durable, halogen-free, formaldehyde-free, and environmentally friendly flame retardant system for cotton fabrics. This novel flame retardant system is also believed to provide a new strategy for developing durable and environmentally friendly flame retardant cellulose fibers.

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