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Research Article

Synergistically Enhanced Flame Retardancy of A Cotton Fabric Finished by A Silica Sol and A Calcium Hypophosphite-Chitosan Solution

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Abstract

This work aims to improve flame retardant performance of a cotton fabric (COT) by combining a silica (SiO_2) sol with calcium hypophosphite (CaHP) and chitosan (CS) agents. A mixed solution of the latter two and the SiO_2 sol were successively arranged on the cotton fabric surface by a dipping-baking (drying) method. Surface microscopic morphologies of original and treated cotton fabrics were characterized by scanning electron microscopy (SEM) technique. Thermal stabilities and flame retardancy levels of cotton fabrics were evaluated by thermogravimetric (TG), limiting oxygen index (LOI) and vertical flammability (VF) experiments. The results show that CaHP-CS and SiO_2 are successfully sorted to the cotton fabric surface. The char residue rate at 700.0 °C of the treated cotton fabric increases 76.4 times by that of original cotton fabric in a TG experiment. It shows a LOI value of 31.3 % (non-flammable grade). It can self-extinguish with a char length of only 7.00 cm (0.23 times by that of original cotton fabric) in a VF experiment. Each component plays both individual and synergistic roles of char formation, heat/oxygen/gaseous product isolation, gaseous product dilution and heat removal in flame retarding the cotton fabric.

Keywords: Cotton Fabric; Flame Retardant; Silica Sol; Synergistic Effect; Sol-gel

Introduction

Cotton fabrics are favored by the world due to their excellent comfort, hygroscopicity, biodegradability and good dyeing properties [1]. However, cotton fabrics are usually flammable in nature reflected by a LOI value of only 18.0 %. Once ignited, smoldering or/and flaming combustion processes are induced. The flames tend to spread rapidly, a fire without control may occur and cause personnel injuries/deaths and property losses. Therefore, improving the flame retardant properties of cotton fabrics has always been an important research topic [2]. Phosphorus-based flame retardants have been widely used due to their advantages of low toxicity, low dosage, little harm to the environment and less effect on material processing [3]. Among them, calcium phosphate not only contains high phosphorus content, but also processes low cost [4]. Nitrogen-based flame retardants have excellent characteristics such as low smoke, low toxicity and low corrosion. When heated and decomposed, they will produce NH_3 and other non-combustible gases. When combustion occurs, they can play the role of heat absorption, cooling and dilution [5]. Among them, chitosan can be used as both a foaming agent by releasing NH_3 and a biomass polysaccharide. It contains many hydrogen bonds in its molecule and promotes dehydration and char formation processes [6]. SiO_2 sol can be used as a non-flammable surface modifier to cover cotton fiber surfaces in the form of a gel coating. Heat, oxygen and gaseous substances can thus be prevented from transferring effectively in a pyrolysis or combustion process [7]. In this sense, it is curious and natural to combine them together and explore whether they have synergistic flame retardant effects on a cotton fabric [8]. In this work, CaHP and CS were made into a mixed solution, then it and a SiO_2 sol were applied to the cotton fabric surface successively via a dipping-baking method. For original and treated cotton fabrics,

their surface micro-morphologies were determined by SEM. Their thermal stability and flame retardancy levels were investigated by TG, LOI and VF experiments. The flame retardant mechanisms of the cotton fabric finished by a CaHP-CS solution and a SiO_2 sol-gel system were discussed.

Materials and Methodology

Materials: Cotton fabrics (111 g/m^2) were purchased from Nanjing Caimei Textile Co., Ltd. (China). Tetraethylorthosilicate (AR, ≥35.0 %) and chitosan (IR, 80.0-95.0 %) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Calcium hypophosphite was provided by Shanghai Aladdin Reagent Co., Ltd. (China). Ethanol (AR, ≥99.6 %) was acquired from Wuxi Yasheng Chemical Co., Ltd. (China). All the reagents were used as received.

Cotton fabric treatment

After washing and drying with deionized water, a cotton fabric was soaked in a CaHP-CS mixed solution and a SiO_2 sol for 30 min and 10 min successively. The cotton fabric was taken out, dried and placed in an oven (PHG-9036A, provided by Shanghai Jinghong Experimental Equipment Co., Ltd., China) to dry at 80 °C for 30 min and cure at 120 °C for 10 min, respectively.

Testing and characterizations

Original and treated cotton fabrics were cut into pieces and sprayed with gold. Surface microscopic morphologies of their bulks and char residues after VF experiments were recorded by a ZEISS Gemini 300 scanning electron microscopy (SEM, Carl Zeiss Co., Ltd., Germany) at 800 magnification and at an accelerating voltage of 10 kV. Their thermal stabilities were investigated under N_2 atmosphere by a TGA/DSC3+ (Mettler-Toledo, USA) apparatus. About 10.0 mg of samples were tested from 30.0 to 700.0 °C at a flowing rate of 50 mL/min and a heating rate of 10 °C/min. Based on GB/T 5454-1997 standard, their LOI values were obtained by operating a JF-3 oxygen index meter (Jiangsu Zhuoheng Measurement & Control Technology Co., Ltd., China) with samples of 150×58 mm^2. Based on GB/T5455-2014 standard, their VF values were obtained by operating a CZF-5 vertical flammability tester (Jiangsu Zhuoheng Measurement & Control Technology Co., Ltd., China) with samples of 300×89 mm^2.

Results and Discussion

Surface morphologies of cotton fabrics

The SEM images of original and the treated cotton fabrics before and after a VF experiment are shown in Figure 1. It can be seen that original cotton fabric is interwoven independently without obvious cracks or adhesion points. The surface of treated cotton fabric is generally rough and covered by a CaHP-CS/SiO_2 gel coating (converted from a sol after baking) with noticeable cracks. After a VF experiment, the fiber surfaces of treated cotton fabric are covered with an obvious and thick char layer induced mainly by degradation and condensation processes of CaHP substance and the SiO_2 gel. Fine bubbles are observed in the char layer since CS substance and the SiO_2 sol-gel system can release NH_3 and H_2O molecules in their degradation and dehydration processes at high temperatures. There are also some cracks in the char layer induced mainly by multiple physical actions like capillary forces, Van der Waals' forces, surface tensions, diffusivity of the CaHP-CS/SiO_2 composite gel in dehydration and decomposition processes at high temperatures [9].

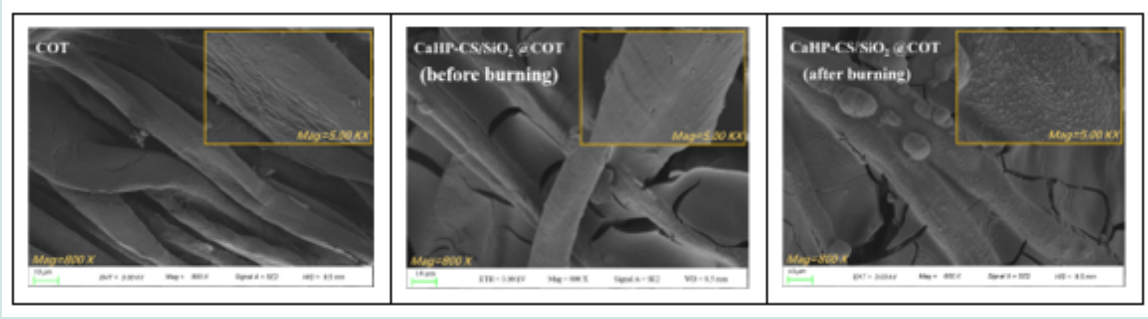

Figure 1: SEM images of original and treated cotton fabrics.

Thermal stabilities of cotton fabrics

Pyrolysis data of original and treated cotton fabrics, i.e., onset decomposition temperature (T_{onset}, defined as the temperature with 10 wt% mass loss), endset decomposition temperature (T_{endset}, defined as the temperature with 95 wt% mass loss), the temperature of maximum mass loss rate (T_{max}), the mass loss rate at Tmax (R_{max}) and char residue rate at 700.0 °C, are summarized in Table 1. According to the Table 1, for original cotton fabric, its R_{max} is up to 4.61 %/°C, while the char residue rate is only 0.55 %, indicating that original cotton fabric has a low thermal stability. It is easy to be pyrolyzed and burns relatively sufficient once ignited. The sample CaHP-CS/SiO_2 @COT exhibits a very high char residue rate of 42.03 % that is 76.4 times that of original cotton fabric. Its R_{max} (1.52 %/°C) is lower by 67.03 % than that of original cotton fabric. The entire pyrolysis stage becomes wider than that of original cotton fabric. All these facts fully reflect that thermal stability of the treated cotton fabric is dramatically enhanced. The flame retardant

components of CaHP, CS and SiO_2 gel should interact well with each other and play comprehensively excellent synergistic effects. These can also approve the microscopic surface morphologies of cotton fabrics before and after VF experiments as mentioned above.

Flame retardant properties of cotton fabrics

The flame retardant properties of original and treated cotton fabrics are reflected by LOI and VF results as shown in Table 2. WGR is weight gain rate, T1 represents after-flame time, T2 is after-glow time and R is damaged length. It can be seen that the LOI value of the treated cotton fabric increases by 73.9 % as compared with original cotton fabric. In addition, according to the VF experimental data, for original cotton fabric, it burns rapidly (a T1 value of 7.5 s) accompanying with a smoldering process (a T2 value of 15.0 s) after ignition, which is consistent with the char residue rate (0.55 %) of original cotton fabric (Table 1). For CaHP-CS/SiO_2@COT, its T1 and T2 values are 1.2 s and 0 s respectively (Table 2). Therefore, it reaches the B1 rating (char length ≤ 15.0 cm, after-flame time ≤ 5.0 s, after-glow time ≤ 5.0 s) in a VF test [10]. This shows that the SiO_2 gel coating is effectively deposited on the surface of the cotton fabric through hydrogen bonding and physical adsorption. Such a coating can act as a physical barrier to prevent oxygen transmission, heat exchange and oxidative decomposition processes [11]. Moreover, the decomposition process of CaHP generates phosphoric acid and polyphosphoric acid to catalyze cotton fibers into chars. As mentioned above, the decomposition process of CS releases NH_3 and H_2O molecules to dilute gaseous products and cool down heated areas. When they are combined together, a coordinated action of P-N-Si system is induced to behave like an intumescent flame retardant effect. All of these further indicate that each component plays both individual and synergistic roles in flame retarding the cotton fabric.

Table 1: TG data of original and treated cotton fabrics under N_2 atmosphere.

Sample	T_{onset} (°C)	T_{endset} (°C)	T_{max} (°C)	R_{max} (%/°C)	Char Residue Rate (%)
COT	336.97	356.93	344	4.61	0.55
CaHP-CS/SiO2@COT	306.17	338.5	316.67	1.52	42.03

Table 2: LOI and VF experimental data of original and treated cotton fabrics.

Sample	WGR (%)	LOI (%)	Flammability level	T1 (s)	T2 (s)	R (cm)
COT	0	18	inflammable	7.5	15	30
CaHP-CS/SiO_2@COT	38.5	31.3	non-flammable	1.2	0	7

Conclusion

This work focuses on the flame retardant performances of a cotton fabric finished by a hybrid system of a CaHP-CS solution and a silica sol. Results show that CaHP-CS/SiO_2 @COT has a non-flammable level. In detail, it has a high char residue rate of 42.03 % (76.4 times that of original cotton fabric) in a TG experiment, a high LOI value of 31.3 %, and a B1 rating in a VF experiment. Phosphoric acid and polyphosphate acid decomposed by CaHP can promote cotton cellulose to dehydrate and form aromatic chars. NH_3 and H_2O molecules decomposed by CS can dilute gaseous products and cool down heated areas. The silica sol can convert to a gel coating with dimensional stability and provide a structural support effect. When such actions are combined, a thick char layer can be produced as a physical barrier; heat exchanges, oxygen and gaseous product transfers can be hindered and isolated; heated areas can be cooled down; gaseous products can be diluted. Therefore, each component can act both individually and synergistically to enhance flame retardancy level of the cotton fabric. In a word, such an attempt is positive to develop a new halogen-free, formaldehyde-free, environmentally friendly flame retardant system for a cotton fabric.

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Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could probably influence this work.

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