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Full Length Article

Silk flame retardant finish by ternary silica sol containing boron and nitrogen

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ABSTRACT

A ternary flame retardant sol system containing Si, B and N was prepared via sol gel method using tetraethoxysilane (TEOS) as a precursor, boric acid (H_3BO_3) and urea ($CO(NH_2)_2$) as flame retardant additives and then applied to silk fabric flame retardant finish. The FT-IR and SEM results showed that the nitrogen-boron-silica ternary sol was successfully prepared and entrapped onto the surface of silk fibers. The limiting oxygen index (LOI) test indicated that the silk fabric treated with 24% boric acid and 6% urea (relative to the TEOS) doped ternary silica sol system performed excellent flame retardancy with the LOI value of 34.6%. Furthermore, in order to endow silk fabric with durable flame retardancy, the silk fabric was pretreated with 1,2,3,4-butanetetracarboxylic acid (BTCA) before the ternary sol system treatment. The BTCA pretreat ment applied to silk could effectively promote the washing durability of the ternary sol, and the LOI value of the treated sample after 10 times washing could still maintain at 30.8% compared with that of 31.0% before washing. Thermo gravimetric (TG), micro calorimeter combustion (MCC) and smoke density test results demonstrated that the thermal stability, heat release and smoke suppression of the nitrogen-boron-silica ternary system decreased somewhat compared with the boron-silica binary flame retardant system.

1. Introduction

With the development of science and technology as well as the improvement of people's living standard, the textile species become more and more diverse from the medical application, decoration to the common apparels. However, most of the textiles composed of C, H, O are of flammability and ignitibility [1]. Accordingly, the wide usage of textile in all kinds of fields has brought more and more seriously potential fire hazards accidents. It is reported that there is about 165000 death in the fire accidents every year. And there has been beyond 20% of all the fires caused by the textile ignition and spread, which caused 50% death in all of the accidents [2]. Consequently, there has practical significance to improve the textile flame retardance for the protection of people's life and property.

Silk, as a kind of excellent natural fiber for decoration and garments, cannot be ignited easily for the composition of N and S and its good hygroscopicity. The limiting oxygen index (LOI) of silk fiber is 23.0%, which is higher than that of the cellulose fibers. However, silk fiber still belongs to the category of flammable textile [3]. Silk can be ignited and continue to burn when there is source of flame, and it will cause serious human physical burns once on fire for its intimate contact with skin. The combustion of silk also creates mass of poisonous matter including CO, CO_2, H_2S, CH_4, HCN etc., which will threaten people's life [4]. Therefore, treatment for silk fabric by flame retardant not only has a contribution to extension the silk applications and its additional value but also has practical importance for the protection of people's life and property.

Sol gel method, as an emerging flexible surface modification technique, can create excellent hybrid material with high degree of molecular homogeneity and potentially extraordinary physical and chemical properties [5,6]. Sol can easily be modified in the sol stage by physical doping or chemical hybrid with any other functional material [7]. In current years this method has already been used in super hydrophobic [8,9], antibacterial [10,11], anti-UV [12] and antistatic applications [13,14]. Whereas recently the sol gel method has been introduced into the flame retardant finishing of textiles. S.A. Chapple et al. [15] has once doped the urea and ammonium dihydrogen phosphate in the silica sol system for the flame retardance of cotton in 2006, and the strength, handle and the flame retardance of the treated samples was evaluated. After that,

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J. Alongi group [16–18] in 2012 began to systematically study the sol gel method application on the cotton flame retardancy. So far, this method has been widely used for investigation the synergism between silica and phosphorus in textile flame retardancy [19].

In the present work, a ternary nitrogen and boron doped silica sol system was prepared derived from the sol gel method. In this ternary system, the urea was used as the N source. As we all know, the nitrogen containing urea can release mass of nonflammable gases such as N_2, and NH_3 at high temperature of silk combustion process, which effectively dilute the flammable gases like CH_4 and CO creating in the combustion and prevent the flammable micromolecules continuing burning [20]. The decomposition of the urea at high temperature can also take away a large amount of heat to decrease the system energy of the combusting silk fabric improving the flame retardancy of original binary sol coating. For the improvement of the coating washing durability, the 1,2,3,4-butanetetracarboxylic acid (BTCA) was used to enhance the linkage between the ternary nitrogen-boron-silica sol coating and fabric substrate [21,22]. The chemical modification of silica sol by boric acid is shown in Scheme 1. And the crosslinking mechanism of silk fabric with boron-silica binary sol by BTCA is shown in Scheme 2. BTCA, acted as a primer for the ternary sol coating, has good affinity both with silk and the coating, endowing the coating with endurance the fierce washing process. The thermal stability, micro combustion property and the smoke suppression of the treated samples was also investigated.

2. Experimental

2.1 Material and reagents Silk crepe satin (weight: 60.28(g/m^2); yarn count: 98(s); density: 54(ends/inch)) was supplied by Suzhou Kasen Silk Garments Co., Ltd. Standard soap flakes for textiles testing were provided by Shanghai Textile Industry Institute of Technical Supervision. Tetraethoxysilane (TEOS), boric acid (H_3BO_3), urea ($CO(NH_2)_2$), 1,2,3,4-butanetetracarboxylic acid (BTCA) and sodium hypophosphite monohydrate (SHP; $NaH_2PO_2{\cdot}H_2O$) were purchased from Sinopharm Chemical Regent Co., Ltd. Ethanol (EtOH) and hydrochloric acid (HCl) were purchased from Chinasun Specialty Products Co., Ltd. All the reagents were analytically pure and used without any further purification.

2.1. Flame retardant sol system preparation

The procedure of the boron-silica binary sol via sol-gel method was as follows: 1.48 g H_3BO_3 was weighed and added into a three neck flask (250 mL) contained 22.36 mL TEOS and 7.80 mL EtOH, which was equipped with a magnetic stirrer and reflux device. The mixture was stirred to absolutely dissolve H_3BO_3 at 70 °C for 1.5 h. Subsequently, 2.40 mL deionized water (pH = 2.5) was added dropwise into the flask while stirring, and the dropping process was maintained for 3.5 h. After that, the whole solution was heated up to 80 °C and stirred for another 1 h to obtain the final boron doped silica sol. The molar ratio was: n[TEOS]: n[H_2O]: n[EtOH]: n[H_3BO_3] = 1:1.33:1.33:0.24.

The preparation procedure of the nitrogen-boron-silica ternary sol via sol-gel method was as follows: 1.48 g H_3BO_3 was weighed and added into a three neck flask (250 mL) contained 22.36 mL TEOS and 7.80 mL EtOH, which was equipped with a magnetic stirrer and reflux device. The mixture was stirred to absolutely dissolve H_3BO_3 at 70 °C for 1.5 h. Then, 2.40 mL $CO(NH_2)_2$ solution (pH = 2.5) was added dropwise into the flask while stirring, and the dropping process was maintained for 3.5 h. After that, the whole solution was heated up to 80 °C and stirred for another 1 h to obtain the final urea and boron doped silica sol. The molar ratio was n[TEOS]: n[H_2O]: n[EtOH]: n[H_3BO_3]: n[$CO(NH_2)_2$] = 1:1.33:1.33:0.24:0.06.

2.2. Silk fabric pretreatment by BTCA solution

The silk fabric samples (240mm × 120 mm) were immersed into a series BTCA solution with different concentration for 5 min and underwent two-dip-two-pad for 80% pickup, then dried at 100 °C for 4 min for use.

2.3. Silk fabric treatment by the prepared sol

The pretreated samples were impregnated with the prepared sol for 5 min and underwent two-dip-two-pad for 80% pickup, then the sample was dried at 100 °C for 4 min and cured at 170 °C for 1.5 min. All samples were balanced at a standard atmosphere (25 ± 2 °C; 65% humidity) for 48 h before testing.

2.4. Washing procedure

The washing procedure was carried out referring to AATCC Test Method 61-2006 in the SWB-12A color fastness test machine without using stainless steel balls [23].

2.5. Characterization and measurements

Fourier transform infrared (FT-IR) spectra were recorded from 400–4000 cm^{-1} with 4 cm^{-1} resolution and 36 times scan by a Nicolet 5700 FT-IR spectrometer using KBr pellets.

Morphology of the samples was observed by a Hitachi TM3030 Desktop Scanning Electron Microscope (SEM) at an acceleration voltage of 3 kV under vacuum condition. The samples were mounted on a conductive adhesive tape and coated with gold before testing.

The flammability of the samples was determined by limiting oxygen index (LOI) according to ASTM D2863on a FTT 0002 oxygen index instrument (FTT, UK). The LOI index refers to the minimum concentration of oxygen in a mixture of oxygen and nitrogen which will just support flaming combustion over a length of 40 mm at 23 ± 2 °C. And the result was the average of five measurements.

The combustion performance of samples was measured by a FTT 0001 Micro Calorimeter Combustion (MCC) instrument(FTT, UK) equipped with a 40 μL alumina pan. The samples (~5 mg) were first heated from room temperature to 750 °C in an 80 cm^3/min nitrogen stream flowing at a linear heating rate of 1 °C. Then the gaseous pyrolysate mixture was mixed with a 20 cm^3/min oxygen stream flow and combustion in a furnace at 900 °C for 10 s.

Thermal stability property of the samples was performed with SDT 2960 TA instrument Thermogravimetric Analyzer. The sample, approximately 10 mg in weight, was introduced into an open alumina sample pan and was heated from ambient temperature to 600 °C at a heating rate of 10 °C/min. All runs were conducted in nitrogen atmosphere at a flow rate of 80 cm^3/min.

Smoke suppression of the samples was carried out with FTT 0064NBS smoke density test chamber (FTT, UK) according to the ISO 5659-2 testing standard in terms of flameless combustion mode at 560 °C for 600s, with the maximum radiant heat of 50 kW/m^2 and two sample layers of 80 × 80 mm^2.

3. Results and discussion

3.1. FT-IR analysis of the prepared sols

It can be seen from Fig. 1 that the 456 cm^{-1}, 800 cm^{-1} and 1070 cm^{-1} [24] absorptions in spectrum a (boron-silica binary system) and b (nitrogen-boron-silica ternary system) were attributed to the Si-O-Si deformation, rocking vibration and the Si-O asymmetric stretching vibration. There also existed the Si-O-B bending and stretching vibration at 675 cm^{-1} and 950 cm^{-1} [25] in both

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