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Durable flame retardant finish for silk fabric using boron hybrid silica sol

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ABSTRACT

A hybrid silica sol was prepared via sol gel method using tetraethoxysilane (TEOS) as a precursor and boric acid (H_3BO_3) as flame retardant additive and then applied to silk fabric. In order to endow silk fabric with durable flame retardancy, 1,2,3,4-butanetetracarboxylic acid (BTCA) was used as cross-linking agent for the sake of strong linkage formation between the hybrid silica sol and silk fabric. The FT-IR and XPS analysis demonstrated the Si-O-B formation in the sol system, as well as the linkage between the sol and silk after the treatment. The limiting oxygen index (LOI) and smoke density test indicated good flame retardancy and smoke suppression of the treated silk fabrics. The micro calorimeter combustion (MCC) test and thermo gravimetric (TG) analysis showed that the treated samples had less weight loss in the high temperature and lower heat release rate when burning. The washing durability evaluation results indicated that there was a distinct improvement for the silk samples treated with BTCA even after 30 times washing. In addition, the influence of the processing order of BTCA and silica sol treatment on the limiting oxygen index (LOI) of the finished silk fabric was also investigated. And the results demonstrated that the sample treated with BTCA first and then with the silica sol exhibited better LOI value (32.3%) than that of the sample by the conversed treatment order. Moreover the tensile property of treated samples was nearly unchanged, but the handle of sol treated samples obviously decreased.

1. Introduction

As we all know, it is the textiles, especially the interior decoration of curtains, carpets and beddings with feature of flammability and ignitibility that account for most of the fire hazards worldwide [1–3]. There has been an increasing consideration to improve the flame retardant property of textiles for the reduction of fire hazard over the past decades with the development of economy and the improvement of people's living standard. Silk, with its luster, comfortable and softness character, has been one of the most widely used textiles for clothing and decoration in daily life. However, silk will ignite 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. Nowadays, the safety laws and regulations regard to the textile flame retardant have become more and more strict and rigid. It is thus of practical importance to improve the flame retardant property of silk fabric in spite of its inherent less inflammability compared with other fibers [4,5].

In flame retardant textile field, the surface modification method using chemical flame retardant agents has become one of the most convenient and efficient ways for the endowment of fabric with flame retardancy, and the widely used traditional flame retardant agents are mainly halogen and phosphorus containing compounds [6,7]. However, it is noticeable that the halogen based compounds can generate toxic corrosive gases in the burning process [8]. And the phosphorus agents, such as the commonly used tetrakis hydroxymethyl phosphonium chloride (THPC) and *N*-methylol dimethyl phosphono propionamide (MDPA), have the formaldehyde release problem during curing and use of products [9]. Therefore it is urgent and necessary to develop eco-friendly, nontoxic and formaldehyde free flame retardants for the consideration of environment. Currently the emerging silicon, boron and nitrogen compounds have drawn much attention as flame retardants in the textile field for their green and eco-friendly characteristics [10].

It has been a long time before the sol gel method introduced into textile for functionalization by German scholar Textor [11]. As

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a simple and flexible surface modification technique, it can yield new coatings with a high degree of molecular homogeneity and potentially extraordinary physical and chemical properties [12,13]. Many functions such as super hydrophobicity [14,15], antibacterial property [16], UV-stability [17], abrasion-resistance [18] etc., has been achieved successfully on the fabric via this method in the past twenty years. Whereas it is very recently that the sol gel method was introduced into the flame retardant finishing of textiles. The Alongi J group [19] found that sol gel treatments are able to modify the thermal and combustion behavior of cellulose because of the shield effect of SiO_2 network as an insulator barrier at high temperature. Necla Y, Cireli A et al. [20,21] endowed the fabric with flame retardancy via sol gel process using the phosphorus compounds as flame retardant additives. And they found that the adding phosphorus compounds were able to help improve the flame retardant efficiency of silica sol due to the acid source derived from the phosphorus.

After the stage of simply doping flame retardants physically into silica sol during the sol gel process, at which the treated fabrics possessed poor washing durability, an increasing attention has focused on the use of an alkoxysilane precursor bearing a flame retardant atom such as phosphate, boron and nitrogen to form chemically hybrid silica sol via sol gel method. And Alongi J et al. [22] has successfully used diethyl phosphatoethyl triethoxysilane (DPTES) as a monomer to synthesis hybrid phosphorus-silicon organic-inorganic coatings for enhancing cotton flame retardancy. This strategy sounds promising to improve the washing durability of sol coating for the incorporation of hybrid element into the sol matrix via the chemical bonding. However, it is difficult to obtain these precursors carrying phosphorus, boron or nitrogen. It is reported that Yang ZY et al. [23] has synthesized a novel flame retardant precursor containing phosphorus and nitrogen using diphenylphosphinic chloride and (3-aminopropyl) trimethoxysilane as reactants for flame retardancy of cotton.

It is well known that the inorganic borax and borate are not washing durable for finishing, and the drawback of organic boron compounds as flame retardants are their poor hydrolytic stability owing to the electron deficiency of boron atom [24,25]. Consequently, effort has been done for the exploitation of boron composite flame retardants by introducing the boron and other element such as nitrogen or silicon into the same structure system to improve their washing durability. There has been reported that the authors Zhao X, et al. [26] synthesized a kind of flame retardant containing the boron and silicon or nitrogen element in one molecule and studied their applications in cotton flame retardant finishing.

In the present work, a boron hybrid silica sol was fabricated derived from the sol gel method. The precursor tetraethoxysilane (TEOS) reacted with boric acid (H_3BO_3) which played the role of flame retardant and catalyst via the cohydrolysis and condensation reaction at a relatively low temperature. Thus a homogeneous hybrid sol system was obtained, in which the trigonal BO_3 units would be incorporated into the siloxane network via Si-O-B bridges [27]. This is a simpler and more moderate routine for the incorporation of the flame retardant atom into the sol matrix and the improvement of boron hydrolytic stability via the Si-O-B combined. Thereafter this prepared boron hybrid sol was entrapped onto the silk fabric by simple pad-dry-cure process. The 1,2,3,4-butanetetracarboxylic acid (BTCA) was used to enhance the linkage between the hybrid sol coating and fabric substrate for the improvement of washing durability of the coating. The BTCA acted as a primer for the hybrid coating, having good affinity both with silk and the hybrid. Furthermore, BTCA may attribute to the improvement of flame retardancy for the treated fabrics due to the existence of sodium hypophosphite monohydrate (SHP) on the treated samples.

2. Experimental

2.1. Material and regents

Silk crepe satin (weight: 60.28(g/m^2); yarn count: 98(s); density: 54(ends/in.)) 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), 1,2,3,4-butanetetr carboxylic 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.

2.2. Preparation of boric acid doped silica sol and BTCA solution

The synthesis procedure of the boric acid doped silica sol via sol-gel method using tetraethoxysilane as precursor and boric acid as flame retardant additive was as follows: 2.04 g boric acid (H_3BO_3) was weighed and added into a three neck flask (250 mL) contained 22.36 mL tetraethoxysilane (TEOS) and 7.80 mL ethanol (EtOH) and equipped with a magnetic stirrer and reflux device. The mixture was stirred to absolutely dissolve boric acid (H_3BO_3) at 70 °C for 1.5 h. Subsequently, 2.40 mL deionized water with 2.50 of pH acidified by hydrochloric acid (HCl) 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 2 h to obtain the final boron doped silica sol. The molar ratio of the reactants was: n[TEOS]:n[H_2O]:n[EtOH]:n[H_3BO_3] = 3:4:4:1.

The BTCA solution was prepared by dissolving 3 g 1,2,3,4-butanetetracarboxylic acid (BTCA) and 2 g sodium hypophosphite monohydrate (SHP; $NaH_2PO_2{\cdot}H_2O$) into 45 g deionized water. The mass concentration of BTCA and SHP was 6% and 4%, respectively.

2.3. Fabric treatment

5 pieces of silk fabric samples (240 mm × 120 mm) numbered in sequence from 1 to 5 were used for the treatment. Sample 1 was a control silk fabric. Sample 2 was treated with BTCA solution under the condition of drying at 100 °C for 4 min and curing at 170 °C for 1.5 min. Sample 3 was treated with the prepared sol under the same condition of sample 2. For sample 4, the fabric was firstly impregnated with the obtained silica sol and dried at 100 °C for 4 min, the substrate was successively immersed into the BTCA solution and dried for another 4 min at 100 °C. The pre-treated sample was cured at 170 °C for 1.5 min in the end. The sample 5 was treated similarly to sample 4, just having a reversed processing order of silica sol and BTCA treatment. Scheme 1 depicted the treatment process of sample 2–5. All the treated samples underwent two-dip-two-pad through a padder for 80% pickup at a nip pressure of 2 kg/cm^2. And 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 of sample 1–5 was carried out referring to AATCC Test Method 61-2006 in the SWB-12A color fastness test machine without using stainless steel balls. In one washing cycle, the sample was immersed into a 200 mL and 40 °C of solution containing 0.37% of standard reference detergent and rotated in the machine at 40 r/min for 45 min, then rinsed with deionized water for 3 min for the next cycle. This one cycle (45 min) is approximately equivalent to 5 times soft washing [23,28], and the durability of the samples was evaluated through LOI test after 5, 10, 20 and 30 times