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Influence of nano-silica on flame resistance behavior of intumescent flame retardant cellulosic textiles: Remarkable synergistic effect?

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ABSTRACT

In recent years, nano-silica has emerged as a promising synergistic agent for improving the flame retardancy of intumescent flame retardant (IFR) polymer materials. However, few researches have been focused on the influence of the nano-silica on the flame retardant behavior of IFR cellulosic materials. In the paper, flame retardant mixtures of nano-silica and traditional IFR (NS-IFR) were applied on cotton fabric (CF) to investigate the synergistic effect of nano-silica on the thermal stability and fire resistance of IFR system. The results of the limited oxygen index (LOI) test and the vertical burning test (VBT) demonstrated that the flame retardancy of the treated cotton fabric was optimized when 4 wt% APP/PER/MEL was replaced by the 4% nano-silica. But it is impaired with increasing the concentration of nano-silica. Char residues, characteristic decomposition temperatures and heat release data from thermogravimetric (TG) and micro-scale combustion calorimeter (MCC) measurements revealed that appropriate addition of nano-silica into traditional IFR system can improve the fire protection properties of IFR-CF to a certain extent, but cause depress in thermal stability of IFR-CF. Therefore, for cellulosic textiles, it is not strongly recommended for use of nano-silica as synergistic agents in IFR system.

1. Introduction

Cellulosic textiles, such as cotton fabrics (CFs), have been widely used to produce apparel, home furnishings, and industrial products due to their advantages of vast quantities, pollution-free, excellent mechanical properties, and strong biodegradability [1,2]. One drawback of CF is its flammability with low limited oxygen (LOI = 18.4% only) and its application in firefighter's protective clothing, military and airline industry has been restricted [3,4,5]. Therefore, improvement of thermal stability of the CFs (or cotton-based material) becomes one of the important issues. Various flame retardants have been applied to modify the combustion characteristics of cotton-based fabrics and can be classified into four distinct groups: inorganic, halogenated organic, organ phosphorus, and nitrogen based [6,7]. Halogen based flame retardants have been shown be one of the most efficient ways of reducing the fire hazard, but they have such noticeable disadvantages as release of hydrogen halide toxic and corrosive gases during combustion [8,9]. Consequently, public interest concerning environmentally friendly, non-halogen-based flame retardants has been enhancing. Phosphorous and nitrogen, which are the main compounds of intumescent flame retardant (IFR) system, have been employed widely as a promising candidate for halogen-free flame retardant because of their environmentally friendly by-products, low toxicity and high effectiveness, due to the synergistic effect of P—N [10,11,12,13].

Generally, an IFR consists of a carbonization agent, a blowing agent, and an acid source. When the flame retarded textiles are heated, a protective charred layer is formed by the phosphorus on the surface the materials via dehydration of the carbonizing agent in the presence of an acid catalyst, which protects the underlying material from the external thermal radiation or flame. The charred layer acts as a physical barrier that insulates the heat and mass transfer between the gas and condensed phases, and also prevents direct contact with the flame and oxygen [14]. The most widely reported traditional IFR systems are ammonium polyphosphate (APP)/pentaerythritol (PER)/melamine (MEL) system, which are based on low molecular charring agent and have shown good inflame-retarding effect to CF or cellulosic fiber [15,16]. However, the APP/PER/MEL intumescent systems have some drawbacks, such as poor flame-retardant efficiency, low thermal stability, and the ease migration onto the matrix surface [17,18]. It has been indicated that the addition of a small amount of inorganic silicon in the intumescent retardant can not only reduce the amount of the intumescent flame retardant, but also improve the flame retardant properties of the matrix material. Mesoporous silica SBA-15 was synthesized from Pluronic P123 by Li et al. [19] and used as a synergistic agent on the flame retardancy of polypropylene (PP)/IFR system. The thermal stability of PP/IFR was improved in the presence of SBA-15. Zhang et al. [20] prepared acrylic nanocomposite and flame retardant coatings with different acrylic polymers and investigated the effect of molecular structure and molecular weight of acrylic resins and nanocomposite with nano-silica on the interaction and char formation of APP/DPER/MEL coating. Chen et al. [21] found that the flame retardant

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poly(butylene succinate) (PBS) exhibited both excellent flame retardance and antidripping properties when the APP, MEL and fumed silica coexisted at an appropriated proportion.

These previous works made it is believed that the introduction of nano-silica into the IFR polymer matrixes can form compact intumescent char layer during burning, and are more effective in reducing flammability and improving thermal stability of polymers. However, what will happen if nano-silica combined with IFR to form a flame retardation system for cellulosic textiles? To the best of our knowledge, the performance of tradition IFR system (APP/PER/MEL IFR) for cellulosic fiber fabric has not been reported in the presence of a synergistic agent, nano-silica. Here, we reported the effects of nano-silica on thermal stability, flame retardant property and flammability of flame resistant cotton fabric, which was based on an APP/PER/MEL system via LOI, VBT, TGA and MCC tests. Fourier transform infrared spectroscopy (FTIR) was also used to characterize the residues after heat treatment of the IFR and nano-silica/IFR (NS-IFR) cotton fabrics and to investigate the relevant mechanism.

2. Experimental procedures

2.1. Materials

Plain cotton fabric (115 g/m^2) were obtained from Zhuocheng Special Textile Co. Ltd., Xinxiang, China. Ammonium polyphosphate $(NH_4PO_3)_n$, with $n > 1000$, were supplied by Taixing Fine Chemical Co. Ltd., Jinan, China. Both melamine (MEL) (≥99.5%) and pentaerythritol (PER) (≥99%) were purchased from Tianjin Kemi'ou Chemical Reagent Co. Ltd. JL-G02FL-1 dispersing agent and JL-G02FX type end amine based polyol ester filler modifier were purchased from Jinlaiwang Plastic Technology Co. Ltd., Nanjing, China, and use as received. Yifu Industrial Co. Ltd., Shanghai, China supplied silicon dioxide. Potassium bromide was also purchased from Municipality Kemi'ou Chemical Reagent Co. Ltd., Tianjin, China.

2.2. Modification of nano-silica

In this work, the modified nano-sized silica were prepared by impregnating the nano-silica diluted in deionized water at a temperature of 130 °C, followed by added JL-G02FX type end amine based polyol ester filler modifier into the solution, stirring with high speed by WSJB-03 type magnetic stirred for 15 min. Then, the JL-G02FL-1 dispersing agent whose weight is equal to the JL-G02FX modifier was added to the solution with high speed stirring until the adsorbed water was completely removed. The slurry was dried in an oven at 90 °C for 180 min.

The prepared dry chips after the processing were ground in a bench top knife-mill (OMC), and sieved to average particle size of 100 nm.

2.3. Flame-retardant treatment of cotton fabric

Prior to flame-retardant treatment, the cotton fabric was desized with NaOH solution, and then dried. For the preparation of flame retardant finishing solution, a certain weight APP powder was added to deionized water at 85 °C, and the obtained solution was stirred with high speed by magnetic stirrer for 15 min. This was followed by addition of PER to the solution and stirring was continued for another 15 min, up to cooling down. After this, MEL and modified nano-silica were added to the cooling solution and stirred to uniformity. The cotton fabric was impregnated in the bath (bath ratio 1:40) to give an approximately 100% wet pickup regulated by two dips and two tips in the MU505 padder. After padding, fabric sample was pre-dried at 90 °C for 4 min, and then dried at 150 °C for 2 min. Finally, the treated fabric was washed in pure water, and dried naturally. All concentrations in this experiment were based on weight of bath solution (w/w, %). The pressure between the two rolls is 0.1 MPa.

The amount (wt%) of flame retardants and additives deposited on the cotton fabric can be determined by weighting each sample before (W_0) and after (W_1) the padding and thermal treatment using high resolution balance to (accuracy: $\pm 10^{-4}$ g). The amount of material charged (A) can be calculated according to the following formula

$$A = \frac{W_1 - W_0}{W_0} \times 100. \quad (1)$$

2.4. Measurements and characterization

The limiting oxygen index (LOI) was measured according to GB/T 2403-1993 by using LOI tester (COL, Motis Fire Technology Co Ltd., China) on sheets of 120 mm × 60 mm. The vertical flame test was performed according to GB/T 5455-1997, by using a vertical burning tester (LFY-601, Textile Science Institute, Shangdong, China). The samples (300 mm × 80 mm), held 19 mm over the Bunsen burner, were first exposed to the flame for a period of 12 s and then removed rapidly, after which the after-flame and after-glow times were measured. The thermal stability of treated fabrics was measured in a thermal gravimetric analyzer (TG209-F1, Netzsch, DE). Each sample was approximately 5–10 mg and was tested from 30 °C to 800 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere at a flow rate of 20 ml min^{-1}. Besides, the char residues processed by using a muffle furnace at the temperature of 800 °C were characterized by FTIR absorption spectra. The analysis was done by a spectrometer (Tensor37, Bruker, DE) in the frequency region of 4000 cm^{-1} to 400 cm^{-1} at a 4 cm^{-1} resolution and normalized to 1 mg cm^{-2}. The average number of scan was 32 scans. Simultaneously, the flammability of PI fiber was evaluated by MCC tests, which were conducted using a FTT0001 micro-scale combustion calorimeter produced by British. The sample, approximately 5 mg, was heated from 75 to 750 °C using a linear heating rate (1 °C/s) in a mixture stream of nitrogen flowing at 80 cm^3/min flow rate and oxygen flowing at 20 cm^3/min.

3. Results and discussion

3.1. Flame retardancy properties

The flame retardant behavior of treated cotton fabrics was assessed by VBT and LOI tests to describe a real fire scene. The LOI, after-flame time, after-glow time and damaged length in these tests are widely used to evaluate flame retardancy of textiles [22], which are summarized in Tables 1 and 2. Introduction of active group onto nano-silica by surface modification is to improve the surface dispersing properties. In order to investigate the amount of modified agent on the flame retardant properties of the treated fabrics, different ratios of modified agent to nano-silica were used (Table 1). The flame retardant properties changed with the increase of content of modifiers. When the percentage of modifier weight to nano-silica was 1.5%, the LOI had the maximum value. Therefore, the ratio (1.5:100) was used as the optimized percentage in the further experiments.

As we known, pure cotton fabric without any flame retardants and additives is high combustible as it has low LOI only 18.4%. Through the addition of APP, PER and MEL intumescent flame retardants (20 wt%),

Table 1
Effect of modified agent on flame retardant properties of flame retardant cotton fabrics.

Modifiers/ nano-silica	LOI%	After-flame time/s	After-glowtime/s	Damaged length/cm
0/100	27.5	9.05	0	17.1
1/100	28	6.79	0	14.8
1.5/100	28.4	6.33	0	13.7
2/100	28.1	6.71	0	15.1
2.5/100	28.3	8.95	0	14.7