Applied Surface Science 428 (2018) 395–403

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Preparation of durable flame retardant PAN fabrics based on amidoximation and phosphorylation

Yue Zhang[b], Yuanlin Ren[a,b,*], Xiaohui Liu[c], Tongguo Huo[b], Yiwen Qin[b]

[a] Key Laboratory of Advanced Textile Composite, Ministry of Education, Tianjin Polytechnic University, Tianjin 300387, China
[b] School of Textiles, Tianjin Polytechnic University, Tianjin 300387, China
[c] School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China

ARTICLE INFO

Article history:
Received 1 August 2017
Received in revised form
14 September 2017
Accepted 19 September 2017

Keywords:
Polyacrylonitrile fabric
Hydroxylamine hydrochloride
Amidoximation
Phosphorylation
Flame retardancy

ABSTRACT

This paper aims to develop a method to impart polyacrylonitrile (PAN) fabric durable flame retadancy. PAN fabric was modified with hydroxylamine hydrochloride (HA) to prepare amidoxime PAN fabric (A-PAN) followed by phosphorylation with phosphoric acid (PA) to obtain flame retardant PAN fabric (P-A-PAN). Thermogravimetric (TG) analysis, differential scanning calorimetry (DSC), microscale combustion calorimetry (MCC) and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) were used to analyze the thermal degradation process and flame retardant mechanisms. The structure of the fabrics was characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS). The surface morphology of fabrics was observed by scanning electron microscope (SEM). Moreover, the flame retardancy of fabrics before and after washing was evaluated by Limiting oxygen index (LOI) and horizontal burning test. The results showed that the P-A-PAN possessed an excellent thermal stability with the highest LOI value of 34.1% and the highest char residue of 55.67% at 800 °C. Most importantly, the P-A-PAN possessed a wonderful flame retardant durability with a little decrease of LOI after 20 washing cycles. When they were ignited, the P-A-PAN fabrics before and after washing were both nonflammable due to the char residue formation of modified fabric.

1. Introduction

Polyacrylonitrile (PAN) fibers play an important role in the textile fields among the three important synthetic fibers (acrylics, polyester and polyamide) [1,2]. Compared with the other two fibers, PAN fiber has several excellent properties, such as light mass, good warmth retention, lasting compression elasticity, good performance of mildew resistance, and etc. However, PAN fiber belongs to an inflammable fiber with the limiting oxygen index (LOI) of only 17%. Thus PAN fabrics are also highly combustible, which brings enormous loss to people's lives and properties [3,4]. Therefore, the development of flame retardant PAN fibers or fabrics has become an urgent need to prevent fires and minimize losses caused by fire.

To date, more and more techniques are widely used for flame retardant modification of PAN or PAN fibers, mainly including finishing [5,6], blending [7,8], copolymerization [9–11] and chemical modification [12–14]. However, the blending modification has many defects, such as the excessive flame retardant addition and the poor compatibility with PAN, which can influence the process of spinning. Copolymerization modification can be used to improve flame retardancy of PAN fibers through the incorporation of halogen- or phosphorus-containing comonomers. Although the copolymerization of halogen-containing comonomer with acrylonitrile has been industrialized, it is not an environmentally-friendly method because the halogen-containing component in the copolymer can release toxic gas and heavy smoke during combustion. Alternatively, the chemical modification is a simple and easy route to prepare flame retardant PAN fiber or fabric that will not produce toxic gas and smoke.

In recent years, chemical modification of PAN has attracted great attention. Generally, PAN fibers are chemically treated with hydrazine hydrate, hydroxylamine or other amination reagent to impart flame retardant properties. Ren et al. [15] prepared the fire retardant PAN fiber through the reaction of hydrazine hydrate with PAN fiber. The appearance of new C=N bond indicated that hydrazine hydrate was really reacted with PAN fiber, and the flame retardant performance of PAN fiber increased greatly with the prolonged modification time. Similarly, Kang et al. [16] employed blending solution of sodium hydroxide and hydrazine hydrate to prepare PAN fibers with flame retardancy, good moisture absorption and mechanical properties. Moreover, Yan et al. [14] uti-

* Corresponding author at: Key Laboratory of Advanced Textile Composite, Ministry of Education, Tianjin Polytechnic University, Tianjin 300387, China.
E-mail address: yuanlinr@163.com (Y. Ren).

http://dx.doi.org/10.1016/j.apsusc.2017.09.155
0169-4332/

lized diethylenetriamine and zinc ions (Zn^{2+}) to modify PAN fiber and obtained better flame retardancy owing to numerous amino groups and the chelated mental ions. Feng et al. [17] prepared an amidoxime polyacrylonitrile (AOPAN) nanofibrous membrane through the reaction of electrospun polyacrylonitrile nanofibrous membrane and hydroxylamine hydrochloride (HA), then the modified membrane was used for Fe^{3+} adsorption. Likewise, Khalid et al. [18] applied amidoxime-modified PAN nanofibers to adsorb mental ions. Moreover, a phosphorylated polyacrylonitrile-based nanofiber mat was prepared and used for heavy metal ion removal [19].

PAN fiber modified with HA is mainly used for metal adsorption, however, the flame retardant study of PAN fiber or fabric modified with HA has rarely been reported to the best of our knowledge. Herein, we exploited a flame retardant PAN fabric by the amidoximation and phosphorylation. Firstly, PAN fabric was reacted with HA to form amidoxime groups functional PAN fabric (A-PAN). Then, A-PAN was reacted with phosphoric acid and urea to prepare fire retardant PAN fabric (P-A-PAN). Phosphorus is known as an efficient fire retardant element widely used for various materials. In this paper, amidoximation of PAN fabric followed by phosphorylation was performed to prepare flame retardant PAN fabric. The modified PAN fabric possessed durable flame retardant performance, remarkable thermal stability and char yield. The flame retardant mechanism and washing durability were investigated in detail.

2. Experimental section

2.1. Materials

Polyacrylonitrile (PAN) fiber with 95 wt% acrylonitrile and 5 wt% vinyl acetate was supplied by Jilin Chemical Fiber Co., Jilin, China. Scoured plain-woven PAN fabrics (400 g/m^2) were prepared by School of Textiles, Tianjin Polytechnic University, Tianjin, China. Hydroxylamine hydrochloride (HA, 98.5%) was obtained from Tianjin Kermal Chemical Reagent Co., Ltd., Tianjin, China. Phosphorus acid (PA, 85%) and urea (99%) were purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd., Tianjin, China. Sodium hydroxide (99.5%) was supplied by Tianjin Yingda Chemical Reagent Co., Ltd., Tianjin, China.

2.2. Amidoximation of PAN fabric

The amidoxime PAN fabric (A-PAN) was prepared via the reaction between nitrile group (—C≡N) of PAN and HA. 0.4 g HA was dissolved in 20 mL deionized water to prepare the HA aqueous solution (20 g/L), and the pH of the solution was adjusted to 6.5 with 0.5 mol/L NaOH solution. Next, the PAN fabric was impregnated in the prepared solution and was heated in water bath at 95 °C for 2 h. The treated PAN fabric was taken out, rinsed with deionized water several times to remove sodium salts and the remained HA, and dried in an oven at 60 °C for 12 h to constant weight.

2.3. Phosphorylation of A-PAN

Phosphorus acid (PA) was diluted to the concentration of 55 wt%. Subsequently, urea was added into the dilute PA at a bath ratio of 1:10, then, the mixture was heated and stirred at 95 °C for 1 h in a water bath. After that, A-PAN was impregnated into the above mixture, heated at 95 °C in a water bath for 2 h without stirring. The phosphorylated A-PAN (P-A-PAN) was taken out, washed with deionized water and dried in a vacuum oven at 60 °C for 10 h to constant weight. The schematic route is illustrated in Scheme 1.

The add-on value of P-A-PAN (A, wt%) was calculated by the following equation:

$$A = [(m_1 - m_0)/m_0] \times 100\%$$

Where, m_0 was the weight of original PAN fabric and m_1 was the weight of PAN fabric after phosphorylation.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) was recorded from 400 to 4000 cm^{-1} at room temperature. The resolution ratio of FTIR spectrometer (Nicolet iS50) was 4 cm^{-1}.

Thermogravimetric analysis (TGA) was carried out on a STA449F3 thermogravimetric analyzer (Netzsch, Germany). The samples were heated from room temperature to 800 °C at a heating rate of 10 °C min^{-1} in nitrogen atmosphere.

Differential scanning calorimeter (DSC) was performed on a DSC200F3 (Netzsch, Germany). A precise weighing sample (5 mg) was sealed in aluminum sample pans. The testing temperature was set from room temperature to 350 °C at a constant heating rate of 10 °C min^{-1} under a dry nitrogen atmosphere. DSC curves of all the samples were obtained from a single heating process.

Surface chemical composition of fabrics was evaluated by X-ray photoelectron spectroscopy (XPS) equipped with hemispherical electron energy analyzer using Al Kα. The energy of spectra was from 200 eV to 1400 eV.

The pyrolysis products and molecular structures of P-A-PAN fabric were measured by Pyrolysis –gas chromatography-mass spectrometry (Py-GC/MS). Py-GC/MS was conducted on a pyroprobe (EGA/PY 3030 D; Frontier, Japan) combined with the gas chromatography-mass spectrometry (6890 N; Agilent, America). The temperature of pyrolysis ranged from room temperature to 388 °C in nitrogen atmosphere at the rate of 10 °C min^{-1}. After pyrolysis, the volatile products were sent to the GC injector with the setting temperature of 280 °C.

The surface morphology of the fabrics was observed by scanning electron microscopy (S-4800, Hitachi, Japan). The samples were fixed on the conductive adhesive tape and sprayed with gold for 2 min (E1045, Hitachi ion sputter, Japan) before testing.

The flammability of the samples was measured by limiting oxygen index (LOI) according to GB 5454-85 on a HC-2 limited oxygen index instrument, and each sample was tested 5 times. Moreover, the combustion performance of different fabrics was assessed by horizontal spread test. The samples with the size of 5 mm × 15 mm were ignited several seconds in methane flame.

In order to verify the flame retardant durability of the fire retardant PAN fabric, the fabric with the size of 5 cm × 10 cm was washed according to AATCC Tets Method 61-2003 test No. 1A with 0.37 wt% detergent. One washing cycle lasting for 45 min equals to five commercial launderings.

The combustion performance of different fabrics was analyzed by microscale combustion calorimetry (MCC). The test was carried out using MCC instrument (Tianjin Textile Engineering Research Institute Co., Ltd., China) according to ASTM E 7309-13. The dried samples were placed in vacuum oven for 8 h at 75 °C before testing and heated from 100 °C to 750 °C at a heating rate of 1 °C/s in a 80 mL/min stream of nitrogen.

3. Results and discussion

3.1. XPS analysis

The chemical composition of control PAN, A-PAN, and P-A-PAN fabrics was analyzed by XPS. The spectra were illustrated in Fig. 1 and the corresponding data were given in Table 1. It is clearly that