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Adsorption and flame retardant properties of potassium diphenyl sulfonate on nylon 6 fabric

Wen Zhang, Ren-Cheng Tang*

National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, 199 Renai Road, Suzhou 215123, China

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ABSTRACT

Flame retardant (FR) functionalization is widely recognized as one of the most difficult problems in the chemical processing of nylon 6 and 6.6 textiles. In the present work, potassium diphenyl sulfonate (KSS) originally used as an effective additive of FR polycarbonate was employed to improve the FR ability of nylon 6 fabric for the first time. A dipping adsorption process similar to acid dyeing was applied, and the adsorption and FR properties of KSS on nylon fabric were studied. The adsorption quantity of KSS depended greatly on the pH of its solution. The adsorption isotherm of KSS on nylon at pH 2 fitted a dual adsorption mechanism consisting of Langmuir and Nernst type models. The adsorption kinetic process of KSS followed the pseudo-second-order kinetic model. The limiting oxygen index and vertical burning tests demonstrated that a low dosage of KSS could impart good FR performance to nylon fabric. However, such FR nylon fabric suffered from poor washing resistance due to the good water solubility of KSS. The syntan originally designed for improving the wash color fastness of acid dyes on nylon could be employed to greatly enhance the washing durability of the FR nylon fabric.

1. Introduction

Polyamide fiber is one of the most important textile fibers, and possesses good resistance to abrasion and wear, good resilience, low coefficient of friction, and high impact strength [1]. In textile industry, the most widely used polyamide fibers are nylon 6 and nylon 6.6. Although nylon fabrics have the attractive properties mentioned above, their uses as flame retardant (FR) textiles are under restrictions because of their inadequate FR ability and severe flammable dripping as well as lack of commercially available, high-efficient FR agents [2–4]. The FR functionalization is widely recognized as one of the most difficult problems in the chemical processing of nylon 6 and 6.6 textiles [5]. In recent years, the improvement in the flame retardancy of nylon textiles has gained great attentions because of their excellent end-use properties in both military and civilian areas [3].

According to the previous reports [1,6,7], there are three technical approaches to make FR nylon fibers: the use of phosphorus-containing monomers in the fiber-forming polymers, the addition of FR additives to nylon polymers during fiber spinning, and the post-treatment of nylon fibers and fabrics using FR agents. As the two former approaches have the shortcomings of polymer degradation and changes in fiber properties, the post-treatment or finishing is often proposed. *N*-methylol dimethylphosphonopropionamide (Pyrovatex CP), hydroxy-functional organophosphorus oligomer (HFPO), and sulfur-containing FR agent (SFR) synthesized from polyphosphoric acid, epoxy chloropropane and thiourea, have been used to enhance the flame retardancy of nylon fabrics [1,4,5]. The combined application of Pyrovatex CP and formaldehyde increased the limiting oxygen index (LOI) from 23.6% for the original nylon fabric to 31.4% for the treated fabric [6]. The application of HFPO along with dimethyloldihydroxyethyleneurea (DMDHEU) obviously reduced the peak heat release rate (PHRR) and heat release capacity (HRC) of nylon fabric [5]. The SFR treatment led to the increase in the LOI of nylon fabric from 21.2% to 29.4%, and after 10 laundrying cycles, the LOI and char length of the treated fabric were 26.8% and 7.7 cm, respectively, revealing the good washing durability of FR effect [4]. Recently, some intumescent FR systems have also been found to be efficient in improving the flame retardancy of nylon fabric [3,8]. For example, ditrimethylolpropane di-*N*-hydroxyethyl phosphoramide was able to greatly decrease the char length of nylon fabric in the vertical burning test [8]. The mixture of ammonium polyphosphate, melamine and pentaerythritol with a mass proportion of 3:1:1 imparted good flame retardancy and dripping resistance to nylon 6,6 fabric with a LOI value of 27.9% [3]. In addition, the grafting with vinyl monomers (acrylamide and vinyl phosphonic acid) [9–11] as well as the photografting modification with maleic anhydride followed by a post reaction with triethanolamine [12] has been employed to render flame resistance to nylon fabric. The nylon textiles grafted with these monomers showed high levels of FR

* Corresponding author.
E-mail address: tangrencheng@suda.edu.cn (R.-C. Tang).

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performance with good dripping resistance and passed a vertical burning test for protective clothing, and the nylon fabrics grafted with acrylamide and maleic anhydride had the LOI values of 24.0% and 25.7% after 10 cycles of washing [10,12], respectively.

Among the FR treatment methods mentioned above, the application of Pyrovatex CP and HFPO involves the release of formaldehyde during processing and use, and the application of the intumescent FR system and the grafting with vinyl monomers cause a great increase in the weight of nylon fabric. Furthermore, most of the aforementioned approaches involve the formation of macromolecules or polymers on the surface of nylon fiber. Both the increase of fabric weight and the formation network structure can negatively affect the contact comfort and handle of nylon textiles. Except the grafting with vinyl monomers where a dipping technique is employed and processing conditions should be severely controlled, other FR agents are usually applied by using a pad-dry-cure technique. Additionally, all the aforementioned approaches can not be simultaneously carried out together with dyeing. Therefore, more FR agents and related treatment methods deserve to be explored.

Potassium diphenyl sulfonate (KSS) as an effective additive of sulfur-based and halogen-free FR for polycarbonates has been widely applied [13]. A small addition of KSS caused a significant increase in the LOI of polycarbonates [14–16]. As shown in Fig. 1, KSS contains one sulfonate group, and its chemical structure is similar to those of acid dyes, indicating that KSS can be bound to nylon fiber by virtue of the electrostatic interaction between its anionic sulfonate group and the positively charged amino group in nylon. This prompts us to apply KSS as a FR agent for the improvement of the flame resistance of nylon fabric. In the present work, a dipping process that is similar to the acid dyeing was employed to treat nylon fabric with KSS. The main application conditions of KSS such as pH, temperature and KSS concentration were determined, and the adsorption mechanism of KSS on nylon fiber was discussed according to the equilibrium adsorption isotherm. The combustion and thermal properties of the treated nylon fabric were evaluated via the LOI, vertical burning test, thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses. The surface morphology of the melting drops from the vertical burning test was observed by using scanning electron microscopy (SEM). Finally, the FR mechanism of the KSS treated nylon fabric was suggested.

2. Experimental

2.1. Materials

The woven nylon 6 fabric was purchased from Wujiang Zhiyuan Textile Co. Ltd., China. The specifications of this fabric are as follows: warp count 55.6 dtex/48F, and weft count, 50.0 dtex/34F; warp density, 75 threads/cm, and weft density 50 threads/cm; weight per unit area, 59 g/m^2. Potassium diphenyl sulfonate (KSS) was obtained from Nanjing Chemlin Chemical Industry Co. Ltd., China. Sulphuric acid of analytical reagent grade was purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. A commercial fixing agent (Erional RN) for improving the color fastness of acid dyes on nylon was generously supplied by Huntsman International, USA, and used to treat the FR nylon fabric for enhanced washing durability. A commercial detergent was purchased from Shanghai Zhengzhang Laundering and Dyeing Co. Ltd., China.

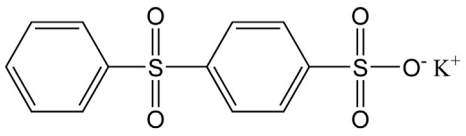

Fig. 1. Chemical structure of KSS.

2.2. FR treatment

The FR treatment of nylon fabric was carried out using a dipping approach. In brief, the fabric was soaked in KSS solution for a desired time using a liquor ratio (ratio of liquor volume to fabric weight) of 40:1. The pH of KSS solution was adjusted with dilute sulphuric acid and detected by a PHS-3C pH meter (Shanghai REX Instrument Factory, China). All the treatments were performed in the open conical flask placed in the XW-ZDR low-noise oscillated dyeing machine (Jiangsu Jingjiang Xingwang Dyeing and Finishing Machinery Factory, China). After each treatment, the fabric was removed, washed in distilled water, and allowed to dry in the air.

The influence of four factors including pH, temperature, time, and KSS concentration on the adsorption of KSS on polyamide fabric was investigated. In order to study the effect of pH on the uptake of KSS, nylon fabrics were immersed with 1% owf (on the weight of fabric) KSS in the pH range of 2 to 6 at 25 °C, the temperature was raised to 70 °C at a heating rate of 2 °C/min, and the treatment continued for 60 min. In order to study the effect of temperature on the uptake of KSS, nylon fabrics were immersed with 1% owf KSS at pH 2 and 25 °C, and the temperature was raised to 50, 60, 70, 80 and 90 °C at a heating rate of 2 °C/min with a holding time of 60 min. In the experiment of the time dependence of KSS adsorption, nylon fabrics were treated with 1% owf KSS at pH 2 and 70 °C for different times (0–60 min). In order to discuss the mechanism of the adsorption of KSS on nylon together with the building-up property of KSS, the equilibrium adsorption of KSS and the quantity of KSS adsorption at different KSS concentrations were determined. In this experiment, a series of KSS solutions of various concentrations (1–20% owf) were used, and the treatment was carried out at a constant temperature of 70 °C and at pH 2 for 60 min.

2.3. Fixation treatment of KSS

In order to improve the washing durability of KSS on nylon, a fixing agent (Erional RN) originally used for improving the washing color fastness of acid dyes on nylon was employed to treat the nylon fabric modified with 10% owf KSS. Briefly, the nylon fabric was treated in 15% owf Erional RN solution at pH 3, the temperature was raised to 70 °C from 25 °C at a heating rate of 2 °C/min, and at 70 °C the treatment continued for 30 min.

2.4. Measurements

2.4.1. KSS concentration

At the end of each treatment, the concentration of KSS remained in the treatment solution was determined by reference to the extinction coefficient of a calibration plot of KSS at the maximum adsorption wavelength of 237 nm. The absorbance of the treatment solution was measured using the Shimadzu UV-1800 UV–vis spectrophotometer (Shimadzu Co. Ltd., Japan). The exhaustion percentage of KSS was determined using Eq. (1), where m_0 and m_1 are the quantities of KSS in solution before and after treatment, respectively. The quantity of KSS on nylon was calculated by taking into account the initial and final concentrations of KSS in solution as well as the weight of nylon fabric.

$$\text{Exhaustion}\ (\%) = 100 \times (m_0 - m_1)/m_0 \quad (1)$$

2.4.2. Flammability

The limiting oxygen index (LOI) of nylon fabric was determined according to the ASTM Standard Method D2863 using the FTT0080 (Fire Testing Technology Ltd., UK) oxygen index apparatus. The vertical burning test was carried out on the YG815B automatic vertical flammability cabinet (Ningbo Textile Instrument Factory, China) according to the ASTM Standard Method D6413.