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Flame retardant study of formalized polyvinyl alcohol fiber coated with melamine formaldehyde resins and the synergistic effect of copper ions

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ABSTRACT

The formalized polyvinyl alcohol fibers (PVF fibers) were grafted with acrylic acids after being activated in dilute potassium permanganate solution, and then the grafted PVF fibers (PVF-g-AA fibers) were reacted with melamine formaldehyde (MF) oligomer solution to form flame-retardant coatings on their surface. The coated PVF fibers (PVF-g-AAMF fibers) were further treated with copper sulfate solution for absorbing copper ions to promote their flame retardant performance. The structure of the fibers was characterized by FTIR spectra and SEM photos. The flame-retardant performance of the fibers was evaluated by limiting oxygen index (LOI) and microcalorimeter tests (MCC tests). It is found that MF coatings effectively improved the flame resistance of PVF fibers, but the flame retardant efficiency was not satisfactory. Copper ions have an obvious synergistic effect on the flame resistance of the fibers. SEM photos of char residues, results of TGA and TG-IR revealed that the flame retardance of MF coatings is mainly due to gaseous phase.The effect of copper ions on the thermal decomposition of MF resins was analyzed with pyrolysis-gas chronograms-mass spectrometry (PyGC-MS), and it is found that copper ions catalyzed the thermal decomposition of MF resins, which synchronized the decomposition of MF resins and PVF fibers. Copper ions are also effective in improving the char residues of PVF-g-AAMF fibers. The flame resistance of the fibers was improved dramatically by the synergistic effect between the grafted MF resin and the copper ions.

1. Introduction

The formalized polyvinyl alcohol fibers (PVF fibers) have been widely used in many areas because of their excellent properties. However, PVF fibers are readily ignitable in the air, and their limiting oxygen index (LOI) is only about 19%. Although, there has been reported a lot of favorable flame retardants (FRs) that can be used to improve the flame resistance of polyvinyl alcohol (PVA) sheets and membranes [1–5]. Most of those FRs cannot be used for PVA fibers directly because of the rigorous preparation requirement of PVA fibers. As is well known, the as-spun PVA fibers have to be thermal stretched and heat set at about 220 °C to improve their crystallinity and orientation degree. Unfortunately, a lot of frequently-used FRs, such as many organo-siloxane FRs, will decompose at this temperature and thus PVA fibers will lose their flame retardancy after heat setting process [6]. Moreover, PVA fibers should be formalized to improve their resistance to hot water before being used in many cases. The formalization process should be catalyzed with the strong acidic environment, which would dramatically affect the structure of many effective FRs, such as melamine polyphosphate (MPP), melamine cyanurate (MCA), ammonium polyphosphate (APP) and most phosphate FRs. Therefore, adopting a post-treatment seems to be an attractive way to avoid these severe process conditions and obtain a flame retardant PVF fiber. Although the post-treatment methods are very convenient and effective, the flame-retardant durability should be taken into account as the flame retardants are easy to be washed away after long-time usage.

In this paper, permanent flame retardant coatings on the surface of PVF fibers were well designed. The PVF fibers were firstly grafted with acrylic acids, and then the carboxyl groups on the surface of the grafted PVF fibers were reacted with the melamine formaldehyde (MF) resin. As a result, the flame retardant coatings were

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finally formed on the surface of PVF fibers.

MF resin and its derivatives are always considered to be excellent flame retardant materials, and also have been widely used in many applications [7–9]. In our previous work, the MF resin and PVA composite fibers were prepared by wet spinning [10]. The obtained composite fibers were found to be self-extinguishing in the air when the content of MF resins is over 50%, i.e. The flame retardant efficiency of MF resins is not very high. So, it is interesting to investigate if the surface coating technic could make MF resin more efficient in flame retarding PVF fibers.

Moreover, the transition metal ions (such as Cu^{2+}, Ca^{2+} and Zn^{2+}) have been reported owning effective flame resistant effects to acrylic fibers, alginic acid fibers, viscose fibers, etc. [11–17] However, the synergistic effect of metal ions and MF resins has seldom been reported. Therefore, it is also worthwhile to study the synergistic effect of metal ions and MF resins.

In the present work, PVF fibers coated with MF resin were further treated in copper sulfate solution for absorbing copper ions to promote their flame retardant performance. The synergistic effect between copper ions and MF resin was studied in details.

2. Experimental

2.1. Materials

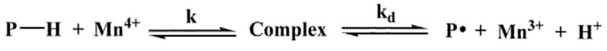
Potassium permanganate, concentrated sulfuric acid (≥98%), formaldehyde aqueous solution (≥37%), melamine, triethylamine, glacial acetic acid and copper sulfate pentahydrate (all from Ke Long Co., Ltd., Chengdu, China), were analytically pure and used as received. Acrylic acid (AA), also purchased from Ke Long Co., Ltd., was analytically pure and used after removing inhibitor. Formalized polyvinyl alcohol (PVF) fiber, a commercial product, whose acetylation degree was about 25%–30%, was kindly provided by Sichuan Vinylon Works, SINOPEC, Chongqing, China.

2.2. Preparation of acrylic acid grafted PVF fibers (PVF-g-AA fibers)

The acrylic acid grafted PVF (PVF-g-AA) fibers were prepared according to the method described in many reports [18,19], as is shown in Scheme 1. PVF fibers were firstly immersed into the 0.05 mol L^{-1} potassium permanganate solution at 40 °C for 10 min to generate free radicals on their surface. The solid-liquid ratio of the reaction system was 1:40. Then, the activated PVF fibers were washed with de-ionized water until the washing water became colorless. After squeezing out extra water, the activated PVF fibers were immersed into an aqueous acrylic acids solution (concentration: 20 wt%) at 50 °C for different times in a nitrogen atmosphere. Sulfuric acid was added into the system to initiate the grafting reaction, and the concentration of sulfuric acid in the reaction system was 0.08 mol L^{-1}. The solid-liquid ratio of the grafting reaction system was 1:80. PVF-g-AA fibers were finally obtained after washing and drying. The grafting degree was calculated according to the following formula:

$$G=(M_t-M_0)/M_0 \times 100\%$$

M_o and M_t are the weight of the fibers before and after grafting, respectively.



Scheme 1. The initiation reaction of dilute potassium permanganate solution.

2.3. Preparation of MF resin coating PVF fibers (PVF-g-AAMF fibers)

The prepolymer of MF resin was synthesized according to the method used in our previous work [5,10]. Melamine, formaldehyde solution and distilled water were added into a 500 mL three-necked flask at 80 °C. The molar ratio of melamine to formaldehyde was 1:2 and the solid content of the system was 5%. Triethylamine was added to the solution to adjust the pH of the system to 9–10. The reactants were stirred until the products became homogeneous, and then the reaction continued for 12 h to obtain transparent homogeneous MF prepolymer solutions.

PVF-g-AA fibers were then put into the prepared MF prepolymer solutions at 80 °C for 1 h. The reaction between carboxyl groups which came from the surface of PVF-g-AA fiber and MF prepolymer is shown in Scheme 2. Then, glacial acetic acid was added into the reaction system to adjust the pH of the system under 6, and in that situation, MF prepolymer started to crosslink. After curing for 1 h, the fibers were taken out and washed with much water to remove the physically adsorbed MF resins. The mass fraction of MF resins was calculated as follows:

$$W=(m_2-m_1)/m_2 \times 100\%$$

$m_1$and m_2 are the weight of the fibers before and after reacting with MF resins, respectively.

2.4. Absorbing copper ions (PVF-g-AAMFCu fibers)

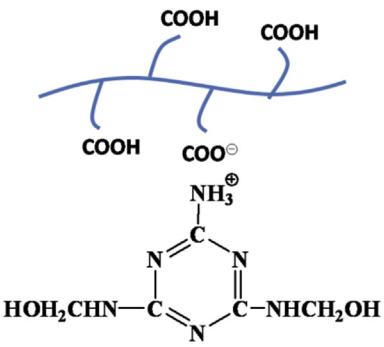
PVF-g-AAMF fibers were immersed into the 0.50 mol L^{-1} aqueous solution of copper sulfate for 1 h at 80 °C. The solid-liquid ratio of the reaction system was 1:40. Then, the fibers were washed with hot water for several times to remove the residual copper sulfates. The proposed structure of the PVF-g-AAMFCu fibers is shown in Scheme 3.

2.5. Preparation of model flame retardants (MFCu resins)

MF resin powders were immersed into the 0.50 mol L^{-1} aqueous solution of copper sulfate for 1 h at 80 °C. The solid-liquid ratio of the reaction system was 1:40. Then, the MF resins chelated with copper ions (MFCu resins) were finally obtained after washing with hot water for several times in the process of filtration.

2.6. Experimental techniques

Infrared spectra were recorded using a Nexus-560 (Nicolet, USA) Fourier transform infrared spectrophotometer (FTIR) on fibers powder by transmittance methods. The wave number resolution was 2 cm^{-1}, and the scan region was from 4000 cm^{-1} to 400 cm^{-1}.



Scheme 2. The proposed reaction between carboxyl groups and MF resins.