

Flame retardant modification of acrylic fiber with hydrazine hydrate and sodium ions

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ABSTRACT: The sodium ions were introduced into the acrylic fibers by post-treating the fibers with hydrazine hydrate and aqueous sodium hydroxide to improve the flame resistance of the fibers. The molecular structure of the modified acrylic fibers was characterized by FTIR spectra. The flame resistance of the acrylic fibers was significantly increased after post-treatment and was relied mostly on the content of sodium ions. The flame-retardant mechanism of the modified fiber was studied in details. The micro calorimeter tests showed that the total heat release and the peak heat release rate were largely reduced after post-treatment. Photographs of the char residues and the results of TGA and TG-IR technique revealed that the flame retardance of the modified acrylic fiber was provided through the combination effect of the gas phase and condensed phase. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41996.

KEYWORDS: fibers; flame retardance; thermal properties; thermogravimetric analysis (TGA)

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INTRODUCTION

Acrylic fiber is one of the major categories of synthetic fibers, which is widely used in many fields, such as apparel, home furnishings and biomedicine materials, because of its excellent performance and low price. However, the limiting oxygen index (LOI) of the commercial acrylic fiber is only about 18,^{1,2} belonging to the highly flammable fiber, which believed to be a potential fire risk/hazard. Therefore, it is necessary to improve the flame resistance of acrylic fibers.³ Most of the reported methods used to improve the flame resistance of acrylic fibers are based on *modacrylics*, which are the copolymers of acrylonitrile and vinylchloride/vinylidene chloride.^{4–8} Although the flame retardancy of the *modacrylics* is sufficient, the fibers cannot be declared to be safe due to their toxicity while burning.³ As a result, there is renewed effort to investigate and develop new classes of flame resistant acrylic fibers with nontoxic and smokeless. The phosphorus-containing compounds and sulfur-containing compounds then were introduced to acrylic fibers by copolymerization, blending, post-treating and many other methods.^{9–13} Although, the phosphorus flame retardants are effective to improve the flame resistance of the acrylic fibers, the commercial use of the phosphorus flame retardants for acrylic fibers are few reported yet for many reasons, such as poor thermal resistance, complex architecture and high additive amount to acquire the good flame retardant property.

The metal-based flame retardants (metal oxide/salts and complexes), which are environmental-friendly and cheap, have

shown some effectiveness in reducing polymer flammability.^{14–18} Although metal-based flame retardants have been studied by a lot of researchers and applied in many areas, only a few of metal-based flame retardants have been studied in details.¹⁹ The transition metal-based flame retardants also have been used for acrylic fibers by many researchers.^{3,20–22} Xu *et al.* modified the acrylic fibers with aqueous hydrazine hydrate and metal acetate solution in sequence and the obtained fibers had excellent flame-retardancy.²¹ Bajaj *et al.* reported the treatment of acrylic fiber with hydrazine hydrate and HCl solution, followed by treating with $Ti_2(SO_4)_3$ solution to improve the flame resistance.²² However, application of the alkali metal compounds in improving the flame resistance of fibers has been few documented and studied. Gao *et al.* immersed the cellulosic fibers into potassium formate and sodium formate for 2 h respectively, and it was found that the alkali metal ions (Na^+ and K^+) effectively improved the flame resistance of cellulosic fibers.²³ Moreover, the approaches many researchers used to introduce the transition metal ions were to treat the acrylic fiber with hydrazine hydrate followed by alkali hydrolysis, neutralization, and subsequent treatment with metal salt.^{3,21,22} These four-step methods may affect the structure and surface appearance of the acrylic fibers seriously, the reported tensile strength of these fibers is only about 1.15–1.50 cN/dtex.^{3,24} The low tensile strength makes these fibers mainly used in non-woven form for heat insulation as fire barrier and in composites as a very effective way to enhance the fire and heat insulation properties.

Table I. Code of Modified Acrylic Fibers and Treating Time

Sample		Treating time in HHA/min	Treating time in NaOH/min
O-PAN		—	—
H-PAN	H1	10	—
	H2	20	—
	H3	30	—
	H4	40	—
	H5	50	—
	H6	60	—
Na-PAN	N61	60	10
	N62	60	20
	N63	60	30
	N64	60	40
	N65	60	50
	N66	60	60
	N67	60	120
	N68	60	240
	N69	60	360

Compared with the transition metal ions, the alkali metal ions can be introduced into the acrylic fibers during the hydrolysis reaction, which can shorten the total processing procedures. Therefore, it is interesting to investigate the influence of alkali metal ions on the combustion behavior and thermal stability of acrylic fiber.

In this article, the convenient two-step method was proposed to prepare the low-flammability acrylic fibers, that is, the flame-retardant acrylic fibers were obtained by treating with hydrazine hydrate and sodium hydroxide in sequence. The aim of the present work is to study the flame retardant properties of the original and treated acrylic fibers comprehensively, and to discuss the flame retardant effect of Na^+ on the acrylic fibers.

EXPERIMENTAL

Materials

Hydrazine hydrate (HHA, $\geq 80\%$), sodium hydroxide ($\geq 98\%$), and diethyl ether ($\geq 99.5\%$) (all from Ke Long Co., Ltd., Chengdu, China) were analytically pure and used as received. Polyacrylonitrile (PAN) fiber, a commercial product, composing of 92.6 wt % acrylonitrile, 6.3 wt % methyl acrylate, and 1.1 wt % sodium vinylsulphonate, was kindly provided by Ji Lin Chemical Industrial Company Ltd., China.

Preparation of H-PAN Fibers

The received PAN fibers were washed in a Soxhlet extractor with diethyl ether at 35°C for 24 h to remove the finishing oil. Then, the original PAN (O-PAN) fiber was modified in a consecutive two-stage process to prepare the flame retardant acrylic fibers. In the first stage, the H-PAN fiber was obtained by treating the O-PAN fiber in the 40 wt % aqueous solution of HHA at 95°C for different time. The solid–liquid ratio of the reaction system was 1 : 20.

Preparation of Na-PAN Fibers

In the second stage, the Na-PAN fiber, which contained Na^+ in the molecular structure, was obtained by treating the H-PAN fiber in the 15 wt % aqueous sodium hydroxide at 95°C for different time. The solid–liquid ratio of the reaction system was 1 : 20.

After each stage of treatment, the fibers were cooled, washed with distilled water until the washings were neutral and then dried in a vacuum oven at 80°C . The code of modified acrylic fibers and treating time are summarized in Table I.

Measurements

Infrared spectra were recorded using a Nexus-560 (Nicolet, USA) Fourier transform infrared (FTIR) spectrophotometer on fiber powders by transmittance methods. The samples were prepared by grinding the fiber powders with KBr to form a thin film. The wavenumber resolution was 2 cm^{-1} and the scan region was from 4000 cm^{-1} to 400 cm^{-1} .

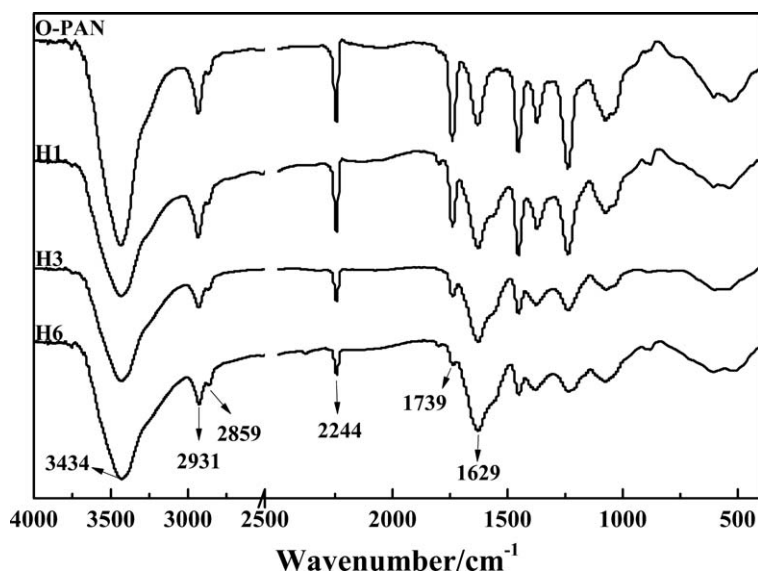


Figure 1. FTIR spectra of the O-PAN, H1, H3, and H6 fibers.

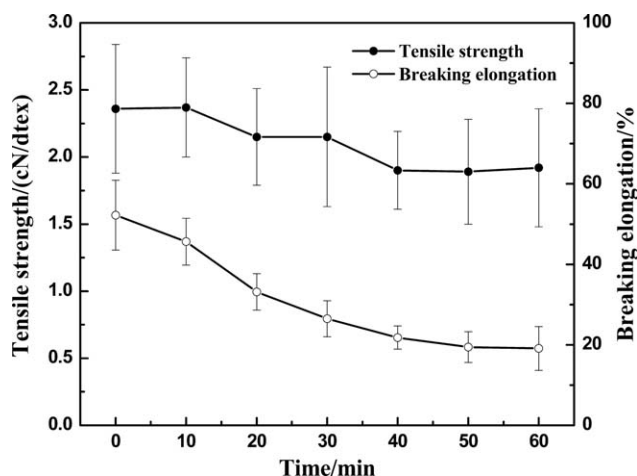


Figure 2. The tensile strength and breaking elongation of the O-PAN fibers before and after modified with HHA for different time.

Mechanical properties were measured using a single fiber tensile tester (Model LLY-06, Laizhou Electron Instrument Co., Ltd., China) with a 10 cN load cell. Tests were conducted on single fiber specimens using a crosshead velocity of 20 mm/min and a gauge length of 20 mm. All the tensile tests were carried out at the constant temperature of 25°C and relative humidity of 70%. Twenty single fiber specimens were measured to make an average.

The LOI values were measured on an LOI analyzer (Model JF-3, Jiangning Co., China) according to ISO 4589-2. An average of at least five replicas was adopted.

The photographs of the thermal decomposition residue of the fibers were taken by a TK-C921EC model digital camera (JVC, Japan). The acrylic fibers, placed in a glass tube, were thermal decomposed in a muffle furnace at different temperature for 30 min.

Scanning electron micrographs of the combustion residue were obtained by a JSM-5900LV scanning electron microscope (JEOL). The accelerated voltage was 20 kV. The sample for SEM

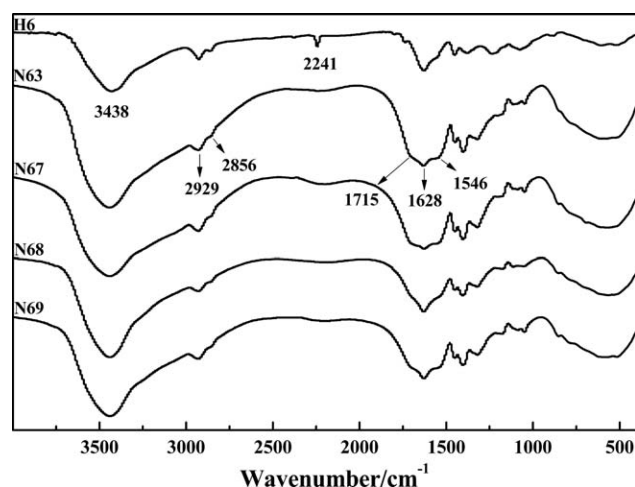


Figure 3. FTIR spectra of the H6, N63, N67, N68, and N69 fibers.

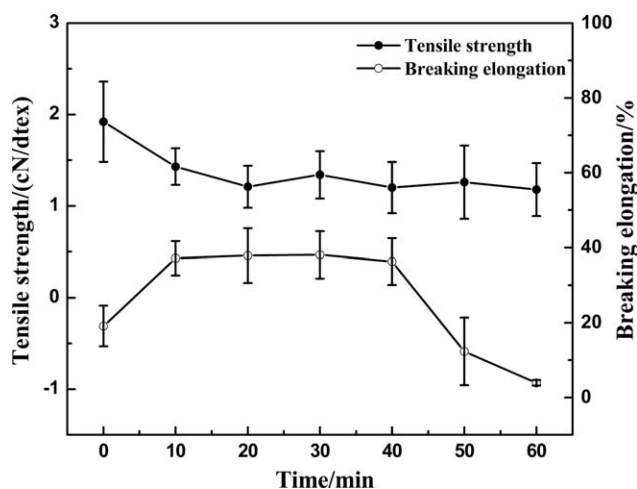


Figure 4. The tensile strength and breaking elongation of the H6 fibers before and after modified with NaOH aqueous solution for different time.

was the residue left after burning in air. All the samples were coated with a conductive gold layer.

Thermal gravimetric analysis (TGA) was carried on a TA instrument Q600. The fiber samples were cut into powder and dried in a vacuum oven at 80°C for 12 h. The measured temperature was varied from 100°C to 700°C at a heating rate of 10°C/min under nitrogen atmosphere.

Thermal gravimetric analysis/infrared spectrometry (TG-FTIR) was performed to analyze the volatilized products after the pyrolysis of samples under a nitrogen flow of 35.0 mL/min. All samples were approximately 10 mg and were kept at 100°C for 5 min first to remove the absorbed water, then were heated up to 700°C at a heating rate of 10°C/min.

The microcalorimetry (MCC) tests were conducted on a FTT0001 micro calorimeter instrument (FTT, UK). The dried powdered fiber samples, placed in a 40 μ L alumina crucible, were heated from 100°C to 750°C at a heating rate of 1°C/s in a stream of nitrogen flowing at 80 mL/min. Then, the mixer of the volatile anaerobic thermal degradation products and

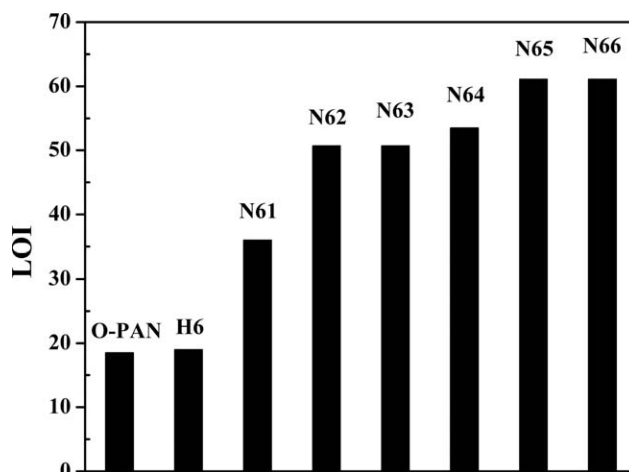


Figure 5. The LOI values of the O-PAN, H-PAN, and Na-PAN fibers.

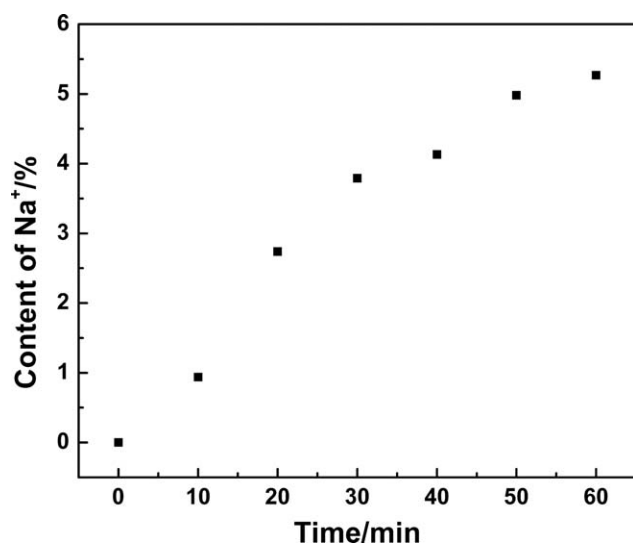


Figure 6. Uptake amount of Na⁺ in the H6 fiber versus treating time in NaOH aqueous solution.

nitrogen gas stream was mixed with a 20 mL/min stream of oxygen gas before entering to a 900°C combustor.

The content of sodium ion in the Na-PAN fibers was determined by an ICPS-8100 inductively coupled plasma emission spectrometer (Shimadzu, Japan). The fiber samples were immersed into the concentrated sulfuric acid for 48 h at 25°C with stirring so that all the Na⁺ of the fiber samples were replaced by H⁺ and released to the solution. Then, the content of Na⁺ in the acid solution was tested by ICP.

RESULTS AND DISCUSSION

Characterization of the Molecular Structure and Mechanical Properties of H-PAN fibers

The H-PAN fiber was obtained by treating O-PAN fiber with HHA and the FTIR spectra of the fiber before and after treating were given in Figure 1. The absorption peaks of 2931 cm⁻¹ and 2859 cm⁻¹ are due to the stretching vibration of -CH₂ in the molecular chain. The peaks at 2244 cm⁻¹ and 1739 cm⁻¹, which are ascribed to the stretching vibration of -CN and C=O of the carboxyl groups respectively, decrease with the increase of reaction time notably. The absorption at 1629 cm⁻¹, which attributed to the stretching vibration of C=N of the amidrazone groups,²⁵ increases simultaneously. In addition, the H-PAN fiber cannot be dissolved in the solvents of O-PAN fiber, such as dimethylsulfoxide, dimethylformamide, and tetramethylene sulfone, even under heating conditions. These changes indicate that partial nitrile and ester groups of the O-PAN fiber reacted with HHA and formed the cross-linked structure. The changes of the mechanical properties of the acrylic fibers, as is shown in Figure 2, also suggest the formation of a cross-linked structure. The breaking elongation of the fibers reduces from 52% to 27% after 30 min treatment and to 20% after 60 min treatment in HHA because the cross-linked network will embrittle the fibers. It also can be seen from Figure 2 that the tensile strength of the fibers reduces slightly with increasing the treating time in HHA.

Characterization of the Molecular Structure and Mechanical Properties of Na-PAN Fibers

The H-PAN fiber was further modified by NaOH aqueous solution for introducing Na⁺. Figure 3 shows the FTIR spectra of the H6 fibers before and after modification in NaOH aqueous solution. It can be seen from the spectra that the absorption peak of nitrile groups is quite weak, that means, most of the nitrile groups in the fibers have been hydrolyzed. Additionally, the C=O peak of ester groups at 1739 cm⁻¹ is disappeared due to the chemical reactions of the ester groups with NaOH aqueous solution. The hydrolysis leads to the arising of peaks at 1546 cm⁻¹ and 1715 cm⁻¹, which indicates the presence of -COONa and -CONH₂ groups in the modified fiber.²⁶ Figure 4 shows the tensile strength and breaking elongation of the H6 fibers before and after modification with NaOH aqueous solution for different time. It can be seen that the breaking elongation of the fibers first rises and then drops, because of the deorientation of the molecular chains at the beginning of

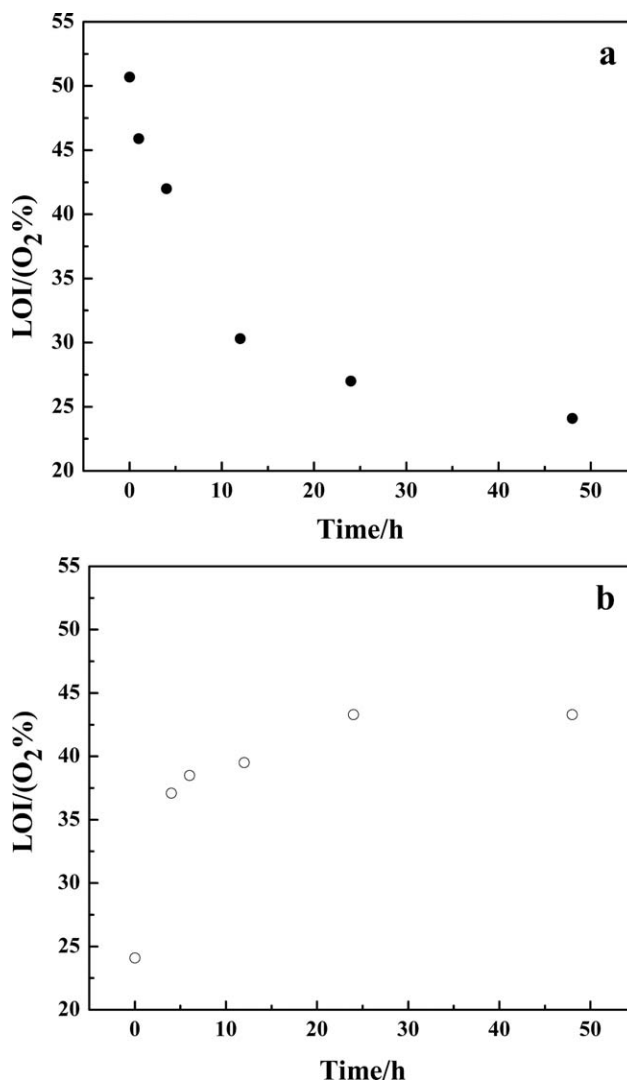


Figure 7. The LOI of the N63 fibers; (a) immersed in dilute sulphuric acid for different time; (b) further immersed in dilute sodium hydroxide solution for different time.

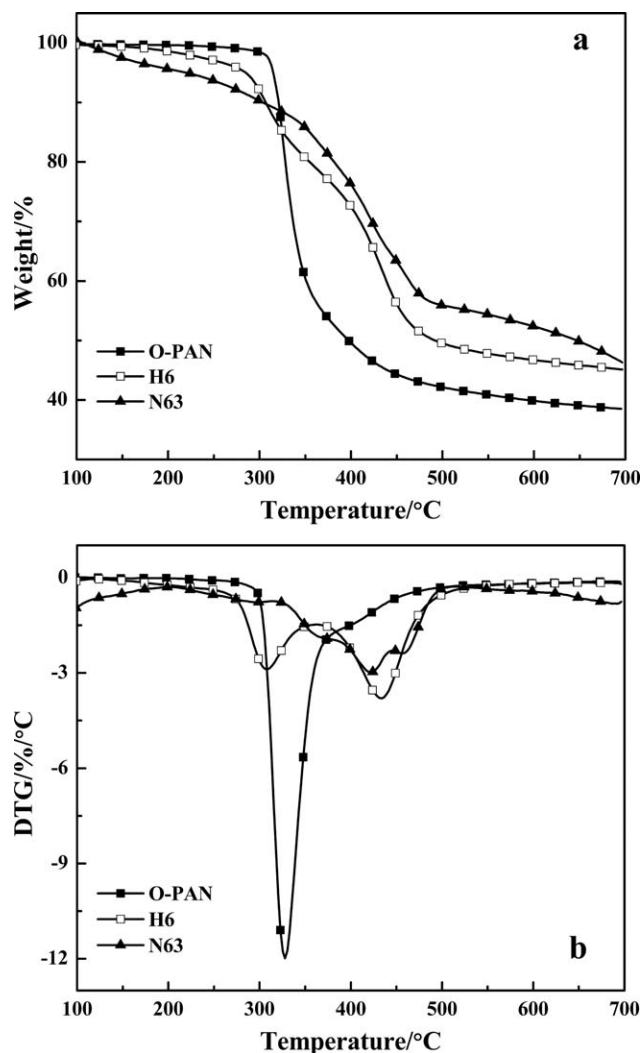


Figure 8. The TG and DTG curves of O-PAN, H6, and N63 fibers.

hydrolysis reaction, which results in the slight shrinkage of the fibers. However, the longer hydrolysis may cause structural damage of the fibers, so the breaking elongation of Na-PAN fibers sharply decreased at last. At the same time, the tensile strength of the Na-PAN fibers further decrease with increasing the treating time in NaOH aqueous solution. Therefore, the treating time should keep as short as possible under the precon-

Table II. TG Data of O-PAN, H6, and N63 Fibers

Sample	T_{on}^a (°C)	T_{max1}^b (°C)	T_{max2}^c (°C)	Weight of char residue at 700°C (%)
O-PAN	312	328	—	38.5
H6	284	309	434	45.1
N63	219	297	423	46.3

^a T_{on} is the temperature of 5% weight loss.

^b T_{max1} is the maximum-rate degradation temperature of the first stage.

^c T_{max2} is the maximum-rate degradation temperature of the second stage.

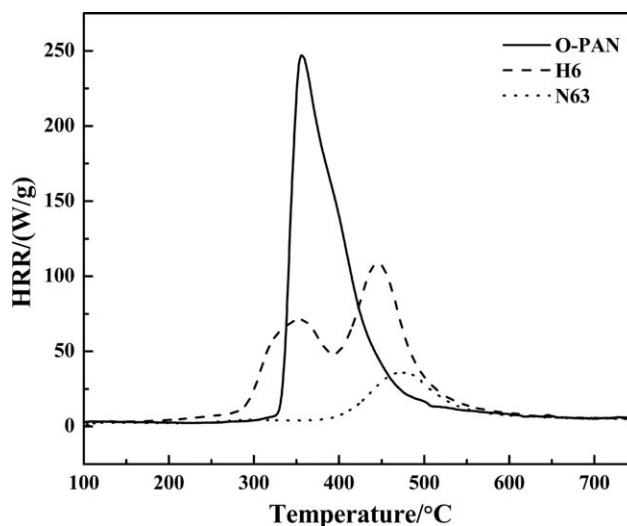


Figure 9. The HRR curves of O-PAN, H6, and N63 fibers.

dition of insuring the flame retardance of the modified acrylic fibers. Compared with the transition metal ions modified acrylic fibers, its tensile strength retention was a little higher because of the shorter processing procedures.³ From the results of FTIR spectra and the changes of mechanical properties, it can be concluded that the Na^+ is firmly fixed on the fiber and the acrylic fibers are modified as expected.

Flame Resistance

Figure 5 shows the limiting oxygen index (LOI) of the O-PAN, H-PAN, and Na-PAN fibers. The LOI of the O-PAN fiber shown here is 18.5, which is consistent with the previously reported values.^{1,2} After treated with HHA for 60 min, the LOI of H6 fiber improves to 19.0, but still quite easy to burn in air. Actually, the fibers accomplish the flame resistance after modified by NaOH aqueous solution. It can be seen from Figure 5 that the LOI of the fibers is largely improved even after only 10 min treatment in NaOH solution and increases to more than 60 after 50 min treatment. As reported by many researchers that the LOI values of the transition metal ions modified acrylic fibers are about 30–45,^{3,21,24,27} which are higher than that of the widely known inherently flame-retardant meta-aramid fibers (Nomex). Compared with those transition metal ions modified acrylic fibers, the fiber modified by Na^+ here possesses even higher LOI. This may due to the higher content of sodium ions after treatment.

It also can be found from Figure 5 that the LOI of the fibers increases when increase the treating time, which may be expressed by the increasing of Na^+ content in fibers during treatment in NaOH aqueous solution, because the process of

Table III. MCC Test Parameters of O-PAN, H6, and N63 fibers

Sample	pHRR/(w/g)	THR/(kJ/g)	T_{max} (°C)
O-PAN	243	17.2	356.3
H6	104.6	14.2	444.6
N63	31.7	3.3	460.3

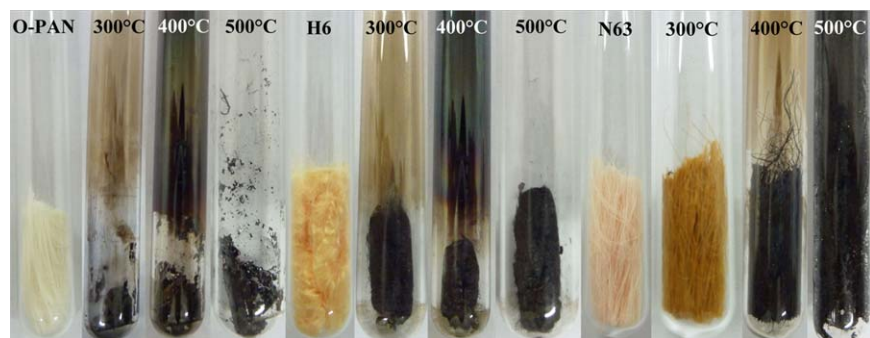


Figure 10. The representative char residues for the O-PAN, H6, and N63 fibers before and after 30 min oxidative pyrolysis in muffle furnace at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

treatment of H-PAN fiber in NaOH solution is a hydrolysis reaction, in which Na^+ is attached to fibers. The content of Na^+ in fibers versus the treatment time in NaOH aqueous solution is shown in Figure 6. It can be seen that the content of Na^+ increases along with the increasing of treating time as expected. To observe the influence of content of Na^+ in fibers on LOI value of fibers, N63 fibers were immersed in the dilute sulphuric acid (0.1 mol/L) at low temperature (15°C) to remove the Na^+ in the fibers by the replacement of H^+ in the solution, and the N63 fibers were collected at different duration of replacement reaction to test the LOI value. Figure 7(a) shows that the LOI of the N63 fibers drops rapidly after immersing in the dilute sulphuric acid. For example, the LOI of N63 fibers reduces from about 50.0 to 24.1 after 48 h immersion. Simultaneously, the content of Na^+ in the N63 fibers, which is determined by ICP, drops from 3.79% at the beginning to only 0.11% after 48 h immersion. It indicates that the flame retardant efficiency is relied mostly on the content of sodium ion. To prove the assumption, the N63 fibers after dipping into dilute sulphuric acid for 48 h were again immersed in 0.1 mol/L sodium hydroxide solution at 15°C to regain Na^+ . Figure 7(b) shows that the LOI of N63 fibers increases quickly after immersion in sodium hydroxide solution, i.e., the fibers show fire resistance again. For example, the LOI of N63 fibers increased from 24.1 to 43.3 after 48 h immersion in sodium hydroxide solution. Meanwhile, the content of Na^+ in the N63 fibers

increases from 0.11% to 2.40%, which means the content of Na^+ has an important effect on the flame retardant efficiency. Conclusion can be drawn from the above that the higher content of sodium ions gives the fibers better flame resistance, however, taking into account the decrease of mechanical property of fibers with treatment time, the treatment time of H-PAN fiber in NaOH solution should be limited to 30 min. Notably, it is the quantity not the kind of the metal ions affects the LOI of the fibers closely. The acrylic fiber after modified by KOH instead of NaOH shows the similar flame retardancy, and the flame resistance also relied mostly on the content of K^+ .

Thermal Stability

The TGA measurements can serve as useful indicators for polymer flammability.²⁸ Figure 8 shows thermogravimetric curves (TG curves) and differential thermogravimetric curve (DTG curves) of O-PAN, H6, and N63 fibers, and the main information of TGA results is summarized in Table II. Compared to O-PAN, H6 and N63 fibers show an obvious decrease in thermal stability below 300°C and a significant increase in thermal stability over 300°C [Figure 8(a)]. However, the thermal decomposition rates of H6 and N63 fibers are lower than that of O-PAN fiber [Figure 8(b)]. The low thermal decomposition rate is in favor to produce char and protect the polymer matrix.¹⁶ It can be also found from Figure 8(b) that the thermal degradation process of H6 and N63 can be divided into two stages. The

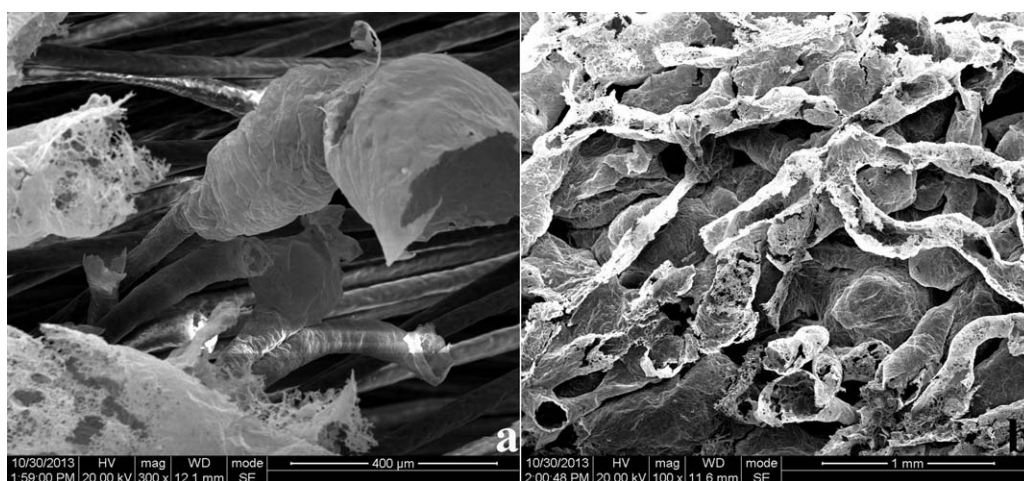


Figure 11. The SEM photos of the char residue of N63 fibers after burning in air.

weight loss of H6 and N63 fibers at the first stage below 300°C may ascribe to the decomposition of the long side chains, which generated in the reaction with HHA. The higher weight loss of N63 fiber than that of H6 fiber at the first stage is attributed to the loss of adsorbed water, because N63 fiber has the higher hygroscopicity after hydrolysis. The evaporation of the water will take away partial heat and increase the flame resistance in a certain sense.²⁹ On the other hand, the cross-linked structure of H6 and N63 fibers is beneficial to form compact char residue in the second stage of thermal degradation, which slows down the decomposition effectively. From Figure 8, it can be seen that the char residues of N63 fiber are higher than that of O-PAN fiber and H6 fiber in the temperature range of 400°C to 700°C, indicating that the combination modification of acrylic fiber in HHA and NaOH aqueous solution improves the amount of carbon residue.

Heat Release Behavior

MCC test is a useful method for investigating the combustion properties of polymer materials. Results including peak heat release rate (pHRR), total heat release (THR), and temperature at the peak heat release rate (T_{max}) can be obtained by MCC test. Figure 9 presents the curves of the heat release rate of O-PAN, H6, and N63 fibers and the corresponding experimental data were summarized in Table III.

It can be deduced from Figure 9 that O-PAN fiber creates more decomposed products after heating and HRR reaches a sharp peak with a pHRR of 243 W/g. After modified in HHA, the pHRR of H6 fiber is reduced remarkably to 104.6 W/g, indicating that modification by HHA is effective to reduce heat release rate. Furthermore, the pHRR of N63 fiber is only about 31.7 W/g illustrating that the further treatment of H6 fiber in NaOH solution will lead to a dramatically decrease of the heat release rate.

THR is characterized as the total energy released by combusting the gases generated in material decomposition process, which is another important parameter for fire hazard evaluation. The data listed in Table III show that the O-PAN has the highest THR value of 17.2 kJ/g. After treating in HHA, the THR value of H6 reduces to 14.2 kJ/g. The THR value of N63 fiber declined significantly to 3.3 kJ/g after treatment of H6 fiber in NaOH aqueous solution. The results indicate that more decomposition products of N63 fiber participated in the charring process, rather than formed into the flammable gases.^{30,31}

Besides, it can be also found from Table III that the T_{max} of acrylic fiber is highly improved from 356.3°C to 460.3°C after modification, which indicates that the thermal stability of the fibers is improved after modification. Generally speaking, the results of MCC tests declared that the modification is benefit to suppress the decomposition of the acrylic fibers.

Carbon Residue Morphology

To clarify the pyrolysis behavior of the fibers, the representative char residues for O-PAN, H6, and N63 fibers before and after oxidative pyrolysis in muffle furnace at different temperatures were collected and the optical microscopic photos are shown in Figure 10. It can be seen that the O-PAN fiber decomposes seriously at 300°C, and shrinks severely during pyrolysis, leaving an apparently

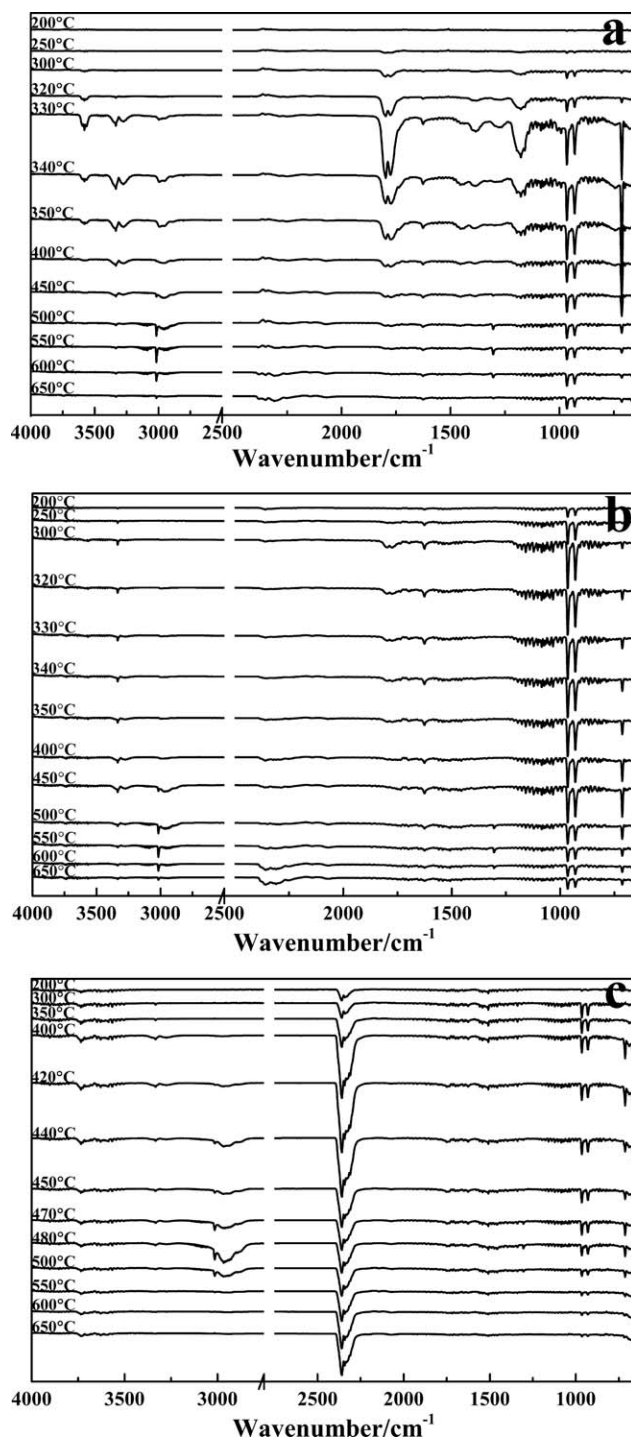


Figure 12. Volatile gases spectra measured by TG-FTIR for O-PAN (a), H6 (b), and N63 (c) fibers.

loose and random-shaped char residue. Though the H6 fiber also decomposes seriously at 300°C, the char residue of H6 fiber is considerably intact, and almost completely retains the fibrous structure. However, the N63 fiber just turns brown after 30 min decomposition at 300°C, indicating that N63 fiber occupies a better thermal stability. Moreover, the char residue of the N63 fiber starts to inflate and fills up the glass tube at 500°C, i.e., the intumescent char residue is generated in the course of pyrolysis.

To further study the intumescent char residues of the N63 fiber, SEM was used to observe the morphology of the char residue of N63 fibers after combustion in air. Figure 11(a) shows SEM photo of the transition area of N63 fiber during burning process. It can be seen that the diameter of the N63 fiber rapidly increases from about 40 μm to 365 μm after burning and then the inflated hollow carbon layer is formed. Figure 11(b) presents SEM photo of the final char residues of N63 fiber after combustion. It can be found that the inflated hollow carbon layer is broken at the end. This may be explained by the combustible gas generated during combustion. In the process of burning, the combustible gas is obstructed by the inflated carbon layer at first. However, with more and more gas generated, the carbon layer will be broken, so the char residue is cut into pieces at last, which leads to the consequent rapid combustion of the accumulated combustible gas.

It is interesting that the fibers modified by KOH generate the same intumescent char residues after burning. However, the char residues of the fibers modified by Cu^{2+} , Zn^{2+} , and Al^{3+} are compact, i.e., the effect of alkali metal ions (Na^+ and K^+) on the modified acrylic fibers seems different to that of the transition metal ions (Cu^{2+} , Zn^{2+} , and Al^{3+}). It may be because the alkali metal ions will form into alkali metal oxides during burning, which are instability and will further react to generate the strong alkalis (NaOH and KOH) and carbonates. However, the transition metal ions will produce stable transition metal oxides during combustion. So the formation of the intumescent char residues may have some concern with the strong alkalis formed during combustion and it still needs further study.

Analysis of Combustion Gases

Thermal gravimetric analysis/infrared spectrometry (TG-FTIR) technique was applied to study the flame-retardant mechanism in the gaseous phase and the results are shown in Figure 12. The TG-FTIR spectra of O-PAN fiber at different pyrolysis temperature are shown in Figure 12(a). The peaks at 966 cm^{-1} and 930 cm^{-1} are ascribed to NH_3 and the absorption peaks at 1798 cm^{-1} and 1774 cm^{-1} are assigned to the C=O of the flammable gas produced by pyrolysis. The peaks at 1798 cm^{-1} and 1774 cm^{-1} , first appear at 300°C, and become stronger with the increase of temperature, then reach the maximum at about 330°C, and then disappear at about 400°C, indicating the generation of combustible gases from 300°C to 400°C. These combustible gases make the O-PAN fiber easy to burn though a small amount of NH_3 generated concomitantly during the decomposition. The volatile gases analysis of H6 fiber [Figure 12(b)] shows weak absorption peaks at 1798 cm^{-1} and 1774 cm^{-1} , and strong absorptions at 966 cm^{-1} and 930 cm^{-1} , declaring that less combustible gases and more NH_3 are produced during the decomposition after modification with HHA. Compared with the spectra of O-PAN and H6 fibers, there appears an obvious absorption at 2350 cm^{-1} , which can be assigned to CO_2 in the spectra of N63 [Figure 12(c)], and the peaks of C=O disappeared. This indicates that the N63 fiber mainly decomposed into the nonflammable gases (CO_2 and NH_3) rather than the combustible gases under heating, which can well explain why the THR value of the N63 fiber is only 3.3 kJ/g, given in Table III.

It can be concluded from the results above that the flame retardance of the modified acrylic fiber was provided through the combination effect of the gas phase and condensed phase. After modified by HHA and aqueous sodium hydroxide, the thermal stability and char residues of the acrylic fiber are increased and the combustible gases decreased, simultaneously. Besides, the intumescent carbon residue of the modified fiber is also conducive to suppress the combustion.

CONCLUSIONS

In this article, the acrylic fibers with good flame resistance are prepared successfully by treating the fibers with HHA and NaOH aqueous solution. It has been proved that the flame retardance of the acrylic fibers mainly depended upon the content of Na^+ . The TGA results show that the thermal stability of the modified fibers is highly improved and the modification in HHA and NaOH aqueous solution both improve the amount of carbon residue. Moreover, the intumescent char residue of the N63 fiber was formed after burning, which acts as a strong flame shield for protecting the fiber from combustion. The non-flammable gases (CO_2 and NH_3) are mainly generated during combustion of the N63 fiber, which makes the THR of N63 fiber much less than that of O-PAN fiber. In summary, the flame retardance of the modified acrylic fiber is largely improved through the combination effect of the gas phase and condensed phase.

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