Study of flame-resistant acrylic fibers reinforced by poly(vinyl alcohol)

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ABSTRACT: Acrylic fibers [polyacrylonitrile (PAN) fibers] have excellent flame-retardant properties after they are modified by hydrazine hydrate and metal ions; however, their widespread applications are restricted because of poor mechanical properties. To improve the mechanical properties of these modified PAN fibers, poly(vinyl alcohol) (PVA) was added to the spinning solution of PAN as an effective reinforcing agent. The structure of the fibers before and after modification was studied by Fourier transform infrared spectroscopy, scanning electron microscopy, energy-dispersive spectroscopy, and wide-angle X-ray diffraction. The mechanical properties and flame resistance of the fibers after treatment were also tested by a single-fiber tensile tester and a limiting oxygen index (LOI) analyzer, respectively. We found that the LOI of the modified fibers was reduced from 54.7 to 29.1 after the introduction of 50 wt % PVA; however, the tensile strength was dramatically improved from about 1.50 cN/dtex to more than 4.00 cN/dtex. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43006.

INTRODUCTION

The flame-retardant modification of acrylic fibers [polyacrylonitrile (PAN) fibers] has been widely studied because of the flammability and toxicity of these fibers during burning.[1–4] Halogenated compounds are the most widely used flame retardants because of their excellent flame resistance; they have been adopted to improve the flame resistance of acrylic fibers; the resulting fibers are known as *modacrylics*.[5–9] However, because of the toxicology, or assumed toxic effects and environmental concerns, of halogenated additives and/or of their synergists (e.g., antimony trioxide and zinc substances), there has been a movement from traditional halogenated flame retardants toward nonhalogenated alternatives.[10,11]

Many researchers, therefore, have used metal-based flame retardants to improve the flame resistance of PAN fibers.[4,12–15] Most of their approaches have been to treat the acrylic fiber with hydrazine hydrate (HHA) followed by alkali hydrolysis, neutralization, and subsequent treatment with metal salt to impart flame-retardant properties. It has been reported that the PAN fibers modified by these methods had superior flame-retardant properties.[4,16–18] Their limiting oxygen index (LOI) values were between 39 and 45 and were, thus, higher than that of the two widely known inherently flame-retardant fibers, namely, polyphenylene sulfide fiber and Nomex. Moreover,

these modified PAN fibers exhibit considerable inertness to heat. When exposed to a naked flame, the fibers degrade with negligible output of smoke and toxic gases and form stable chars without melting and shrinking. The chief decomposition products of these fibers are CO_2, H_2O, and NH_3 with traces of HCN, HCl, and NO_2.[12,19]

However, there are common disadvantages for most modified flame-resistant fibers, for instance, low mechanical properties, and the addition of flame retardants or flame-resistant post-treatment processes lowers the tensile strength of the fibers inevitably. Similarly, the mechanical properties of those modified PAN fibers are also quite poor; this severely handicaps their applications. The reported tensile strength of these fibers is only about 1.15–1.50 cN/dtex.[15–18] The low tensile strength makes these fibers mainly useful in nonwoven form for heat insulation as fire barriers and in composites as a very effective way to enhance the fire and heat insulation properties.[17,18]

Recently, we reported a convenient two-step method for obtaining flame-retardant acrylic fibers.[19] With shorter processing procedures, the tensile strength of the fiber was improved slightly. Empirically, to be used in woven form, the tensile strength of the fiber should be above 2.50 cN/dtex. Therefore, it is still necessary to improve the mechanical properties of these metal-based flame-retardant-modified PAN fibers. Because of the

unavoidable damage to PAN fibers during modification, the addition of a reinforcing agent to the PAN fibers may be an effective way to improve the mechanical properties. It has been reported that many fillers (e.g., carbon nanotubes and graphene oxide) can be used to enhance PAN fibers,[20,21] but the improvement of these fillers was not sufficient because the PAN matrix was seriously destroyed during modification. Actually, the significant reinforcement of the PAN fibers has been less documented; only Kim et al.[22] used polyurea to improve the mechanical properties of PAN fibers, and they found that polyureas were quite effective in improving the high-temperature modulus of PAN fibers, but unfortunately, the tensile strength and breaking elongation of the fibers decreased.

With an excellent spinnability, high tensile strength, and acid/alkali resistance, poly(vinyl alcohol) (PVA) has been widely used to improve the mechanical properties of many natural polymer fibers, such as alginate fibers and chitosan fibers, by blend spinning, and it was found that the tensile strength of these natural polymer fibers was greatly improved by PVA.[23–26] However, the use of PVA to improve the mechanical properties of PAN fibers has rarely been studied. Most of the studies of PAN/PVA composite materials focused on the reinforcement effect of PAN on PVA-based membranes or polymeric networks.[27–29] The high hydrophilicity of the PVA membranes or networks made their wet breaking strength quite low; therefore, the addition of hydrophobic PAN was favorable for the improvement of their mechanical properties. Desphande et al.[29] studied the structural, morphological, and mechanical aspects of PAN-reinforced PVA-based polymeric networks in detail recently. They found that the presence of PAN not only imparted strength to the materials but also decreased the tensile strength and breaking elongation. The tensile strength and elasticity of the specimens with the highest PVA content were the largest. This may suggest that PVA can improve the tensile strength of PAN for its flexibility and stretchability. So, it would be interesting to study the impact of PVA on the mechanical properties of PAN fibers. Fortunately, PVA is easy to dissolve in dimethyl sulfoxide (DMSO), a commonly used solvent for preparing PAN fibers; this makes it possible to obtain blend fibers of PAN and PVA.

In this study, PVA was chosen to be added to a spinning solution of PAN as an effective reinforcing agent. Neat polyacrylonitrile (NPAN) and blend polyacrylonitrile (BPAN) fibers were modified by the methods reported in our previous work,[19] and the impact of the flame-resistant modification on the structure, appearance, morphology, and mechanical properties of the PAN fibers was investigated in detail by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), wide-angle X-ray diffraction (WAXD), and tensile strength testing.

EXPERIMENTAL

Materials
HHA, DMSO, and sodium hydroxide (NaOH) were analytically pure and were used as received. PAN, a commercial product, composed of 92.6 wt % acrylonitrile, 6.3 wt % methyl acrylate, and 1.1 wt % sodium vinyl sulfonate, was kindly provided by Ji Lin Chemical Industrial Co., Ltd. (China). PVA, with an alcoholysis degree of 99% or greater, a syndiotactic content of about

Table I. Shrinkage and Mass Loss of the BPAN Fibers in Boiling Water for 1 h

Sample	Shrinkage (%)	Mass loss (%)
BPAN-30%	0.67	0.67
BPAN-40%	1.00	0.79
BPAN-50%	1.67	1.11

52%, and a weight-average polymerization degree of 1700 ± 50, was kindly supplied by Sichuan Vinylon Works, SINOPEC (Chongqing, China).

Preparation of the NPAN Fibers
The spinning solution was prepared by the dissolution of 137.5 g of PAN powder in 500 mL of DMSO at 80°C, and it was used for spinning after deaeration. A mixture of DMSO and water was used as the coagulating bath. The as-spun fibers were stretched in hot water and thermoformed at 160°C, and then, the NPAN fibers were finally obtained.

Preparation of the BPAN Fibers
To improve the mechanical properties, certain amounts of PVAs were added to the DMSO solution of PAN to prepare PAN/PVA blend fibers by wet spinning; this process was similar to the preparation of the NPAN fibers. The total polymer content of the spinning solution was 20 wt %. Cold methyl alcohol was used as the coagulating bath. The BPAN fibers were finally achieved after hot stretching and thermoforming at 215°C. They are denoted as BPAN-wt %, where wt % is the mass fraction of PVA.

It is worth noting that PAN was partially oxidized and cross-linked during thermoforming at 215°C;[30,31] this improved the hot-water resistance of the BPAN fibers and prevented PVA from dissolving in hot water during flame-resistance treatment. The low shrinkage and mass loss of the BPAN fibers, shown in Table I, indicate that the BPAN fibers were stable in boiling water and could be used for flame-retardant modification.

Flame-Retardant Modification
The NPAN and BPAN fibers were treated with HHA and then followed by alkali hydrolysis to acquire flame retardancy, as mentioned in our previous work.[19]

In the first step, the fibers were treated in the 40 wt % aqueous solution of HHA at 95°C for 1 h and then treated in the 0.5 mol/L NaOH aqueous solution at 95°C to introduce the sodium ions to the fibers. The fibers were stretched during modification in NaOH aqueous solution with about 3% elongation.

The solid–liquid ratio of the reaction system of each step was 1:20, and after each stage of treatment, the fibers were washed to neutral with distilled water and dried in oven at 80°C.

Experimental Techniques
IR spectra were recorded with a Nexus-560 Fourier transform infrared spectrophotometer (Nicolet) on fiber powders by transmittance methods. The samples were prepared by the grinding of the fiber powders with KBr to form a thin film. The wavenumber resolution was 2 cm^{-1}, and the scan region was from 4000 to 400 cm^{-1}.
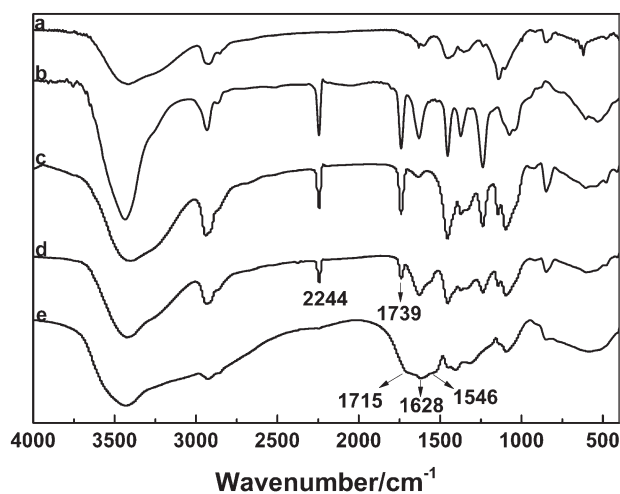
Figure 1. Fourier transform infrared spectra of the PVA, NPAN, and BPAN-40% fibers: (a) PVA, (b) NPAN, (c) BPAN-40%, (d) BPAN-40% after treatment in an HHA solution, and (e) BPAN-40% after treatment in an NaOH aqueous solution.

The mechanical properties were measured with 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 with a crosshead velocity of 20 mm/min and a gauge length of 20 mm. All of the tensile tests were carried out at a constant temperature of 25°C and a relative humidity of 70%. Twenty single-fiber specimens were measured to make the average.

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

The microcalorimetry (MCC) tests were conducted on an FTT0001 microcalorimeter instrument (FTT, United Kingdom). The dried powdered fiber samples, placed in 40-μL alumina crucibles, were heated from 100 to 750°C at a heating rate of 1°C/s in a stream of nitrogen flowing at 80 mL/min. Then, the volatile anaerobic thermal degradation products and nitrogen gas stream was mixed with a 20 mL/min stream of oxygen gas before placement in a 900°C combustor.
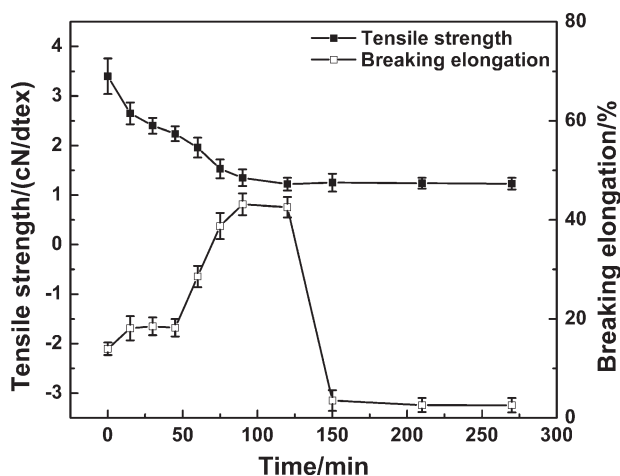

Figure 2. Tensile strength and breaking elongation of NPAN during modification in an NaOH aqueous solution for different times.
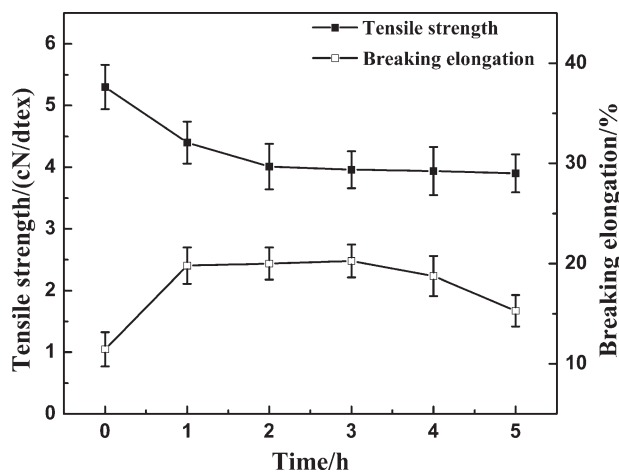

Figure 3. Tensile strength and breaking elongation of BPAN-50% during modification in an NaOH aqueous solution for different times.

SEM micrographs of the fibers before and after treatment were obtained by a JSM-5900LV scanning electron microscope (JEOL) to determine the extent of destruction of the fiber. Cross sections of the fibers were prepared to determine the extent of penetration of the sodium ions into the fibers. The EDS analysis of these cross sections was performed with at least three different areas of the sample. The accelerated voltage was 20 kV.

WAXD measurements of the PAN fibers before and after modification were performed at room temperature on a X'Pert Pro (Philip) X-ray diffractometer operating in the 2θ range of 5–40° at a scanning rate of 12°/min with nickel-filtered Cu Kα radiation. The software MDI Jade 5.0 was used to analyze the WAXD results and to calculate the degree of crystallinity.

RESULTS AND DISCUSSION

Characterization of the Molecular Structure

The Fourier transform infrared spectra of PVA, NPAN, BPAN-40%, and BPAN-40% after each stage of treatment are given in Figure 1. The absorption peaks of 2931 and 2859 cm^{-1} were due to the stretching vibrations of —CH$_2$ in the molecular chain of PVA and PAN. The broad peak from 3600 to 3200 cm^{-1} was the characteristic absorption of —OH in PVA. The peaks at 2244 and 1739 cm^{-1} were ascribed to the stretching vibrations of —CN and C=O of the carboxyl groups in PAN, respectively. As shown in Figure 1(c), BPAN-40% showed the characteristic

Table II. Tensile Strength (%) Retention of the NPAN and BPAN Fibers after Treatment in an NaOH Aqueous Solution for Different Times

Sample	Treatment time in NaOH aqueous solution				
	1 h	2 h	3 h	4 h	5 h
NPAN	53.3	33.2	33.0	33.0	–[a]
BPAN-30%	56.9	54.5	52.3	48.5	48.1
BPAN-40%	73.6	69.4	67.8	63.9	60.9
BPAN-50%	79.1	72.1	71.2	70.9	70.1

[a] The tensile strength and breaking elongation of the sample were too low to test.

Table III. LOI Values of the NPAN and BPAN Fibers before and after Treatment

	LOI value (%)		
Sample	Before treatment	After treatment in HHA for 1 h	After treatment in NaOH for 2 h
NPAN	18.5	19.0	54.7
BPAN-30%	19.0	19.5	40.0
BPAN-40%	19.0	19.5	34.0
BPAN-50%	19.0	19.6	29.1

Table IV. MCC Test Results

Sample	$pHRR_1$ (W/g)[a]	$pHRR_2$ (W/g)[b]	THR (kJ/g)	T_{max1} (°C)[c]	T_{max2} (°C)[d]
1	225.9	76.1	16.6	352.1	423.5
2	155.2	101.4	15.9	371.2	422.3
3	98.9	54.4	11.1	359.0	467.7
4	52.7	49.4	9.4	350.0	476.4
5	45.4	54.6	8.4	349.6	483.3
6	4.5	36.0	3.3	293.9	474.6

The samples were as follows: (1) BPAN-50% before treatment, (2) BPAN-50% after treatment in HHA for 1 h; and (3–6) BPAN-50%, BPAN-40%, BPAN-30%, and NPAN fibers after treatment in an NaOH solution for 2 h, respectively.
[a] First peak of HRR.
[b] Second peak of HRR.
[c] Temperature at the first peak of HRR.
[d] Temperature at the second peak of HRR.

absorption peaks both of PVA and PAN. The peaks of —CN and C≡O decreased after treatment in HHA solution, and the absorption at 1628 cm^{-1}, attributed to the stretching vibrations of C≡N of the amidrazone groups, increased simultaneously. The hydrolysis in NaOH aqueous solution led to the disappearance of the peaks of —CN and C≡O and the rise of peaks at 1546 and 1715 cm^{-1}; this indicated the presence of —COONa and —CONH$_2$ groups in the modified fibers.[32] We concluded that PAN in the BPAN-40% fibers took part in the reaction during modification, as reported in our previous work,[19] and PVA tended not to be involved in the reaction with the HHA and NaOH aqueous solution.
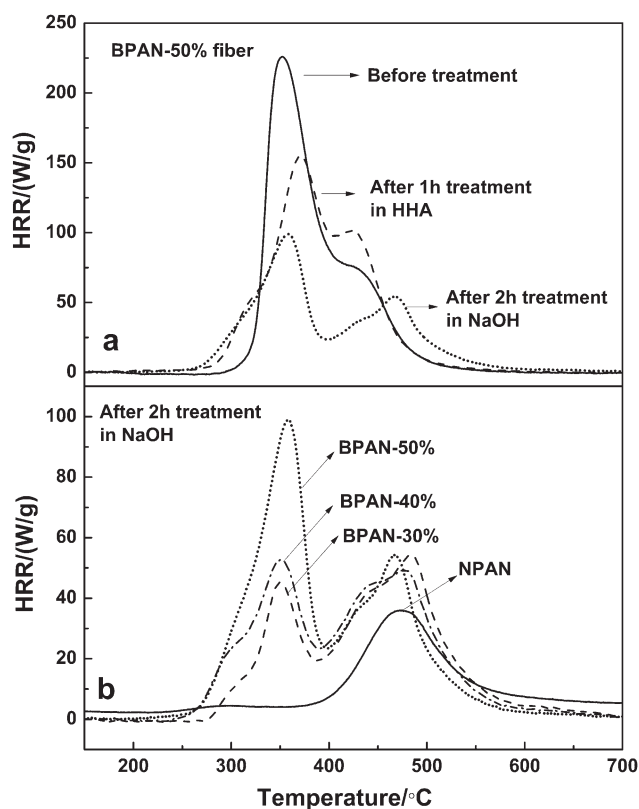
Figure 4. HRR curves of the fibers tested by MCC: (a) BPAN-50% fibers before and after modification and (b) BPAN-50%, BPAN-40%, BPAN-30%, and NPAN fibers after modification in NaOH for 2 h.

Mechanical Properties

We reported in our previous work that the tensile strength of the PAN fiber decreased dramatically after flame-retardation modification, and the decrease in the tensile strength was mainly ascribed to the second step, namely, the treatment in NaOH solution.[19] Thus, in this study, we mainly examined the changes in the fiber structure during treatment in NaOH solution. Figure 2 shows the tensile strength and breaking elongation of NPAN fibers during treatment in NaOH solution for different times to give the fibers flame resistance. We found that the tensile strength of the fiber decreased sharply from 3.43 to 1.96 cN/dtex after 60 min of treatment and to only about 1.20 cN/dtex after 120 min of treatment. Also, the shorter process in NaOH may have helped us obtain fibers with a higher tensile strength. However, the shorter treatment meant a low flame resistance, which was also discussed in our previous work,[19] and actually, the fiber should be treated for at least 60 min to become self-extinguishing under air conditions. In addition, the breaking elongation of the fiber first rose and then dropped sharply during treatment in NaOH; this may have been caused by the deorientation of the molecular chains at the beginning of the hydrolysis reaction and resulted in the slight shrinkage of the fibers. However, the longer hydrolysis time may have caused structural damage to the fibers and then made the breaking elongation of the fibers decrease sharply.

Figure 3 shows the tensile strength and breaking elongation of the BPAN-50% fiber during modification in NaOH solution. Compared with the NPAN fiber, the tensile strength of BPAN-50% also decreased during modification in NaOH. However, the tensile strength of the BPAN-50% fiber even after 5 h of modification in NaOH solution was still as high as about 4.00 cN/dtex; this was much higher than that of the NPAN fiber after the same modification. In addition, the retention of the tensile strength after modification was also highly improved by the introduction of PVA, and the tensile strength retention increased with increasing PVA content, as shown in Table II. For example, only 53.3% of the tensile strength of NPAN remained after 1 h of treatment in NaOH solution, and only
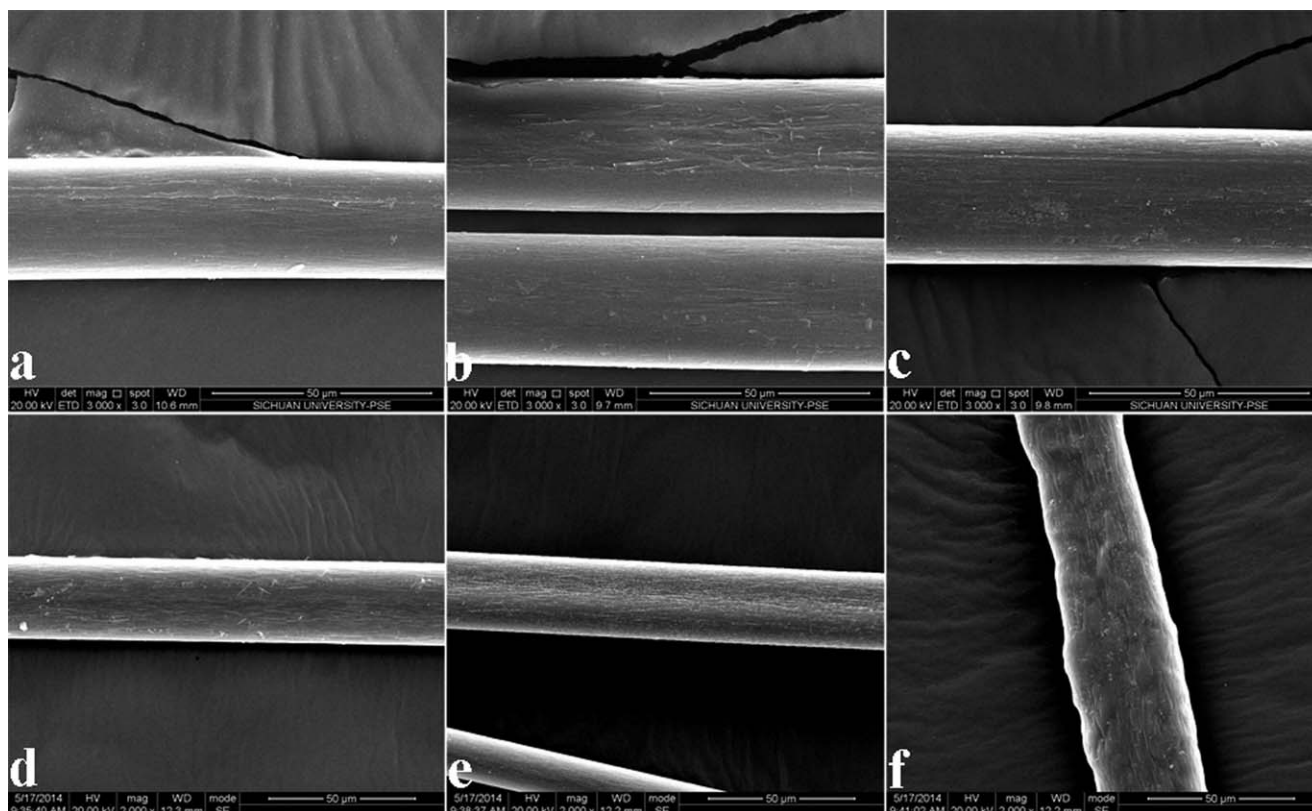
Figure 5. SEM images of the NPAN fibers during modification: (a–c) NPAN after treatment in HHA for 1, 2, and 4 h, respectively, and (d–f) NPAN fibers after further treatment in an NaOH aqueous solution for 30, 60, and 90 min, respectively.

about 33% was obtained after further treatment. However, the tensile strength retention after 1 h of treatment was improved to 56.9% through the introduction of 30 wt % PVA, and this was further improved to 73.6% after the amount of PVA was increased to 40 wt %. Moreover, even after 5 h of treatment, the tensile strengths of BPAN-40% and BPAN-50% still remained above 60%. We concluded that the introduction of PVA not only improved the tensile strength of the fibers but also improved the tensile strength retention during modification. Thus, the introduction of PVA improved the mechanical

properties of the PAN fiber effectively. However, as discussed, PVA did not react with HHA and NaOH aqueous solution during modification, and the addition of PVA may have led to the decrease in the flame-retardant performance of the fibers after modification.

Flame Resistance

To clarify the influence of PVA on the flame-retardant performance of the fibers, the LOI values of the NPAN and BPAN fibers before and after modification were tested and are given in Table
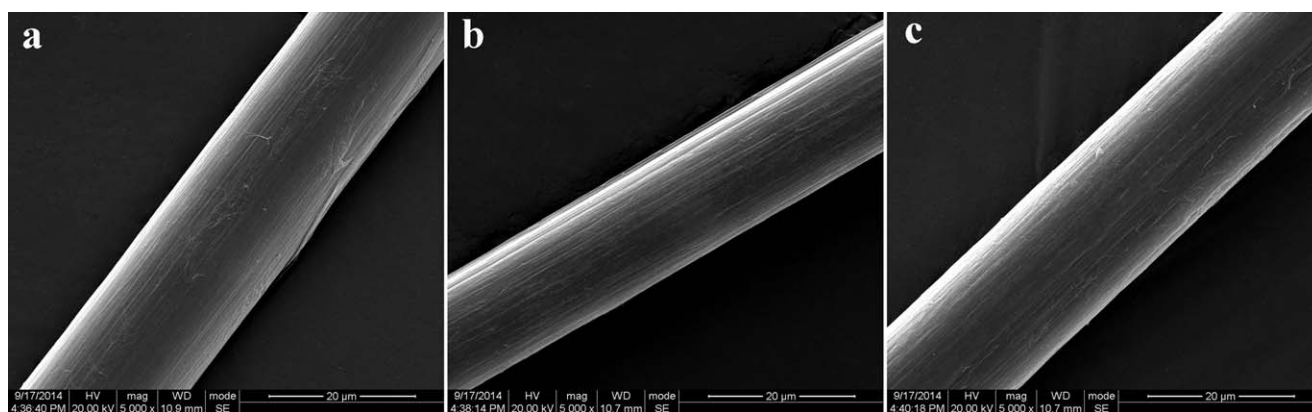

Figure 6. SEM images of the BPAN-50% fibers during modification: (a) before treatment, (b) after treatment in HHA for 1 h, and (c) after further treatment in an NaOH aqueous solution for 2 h.
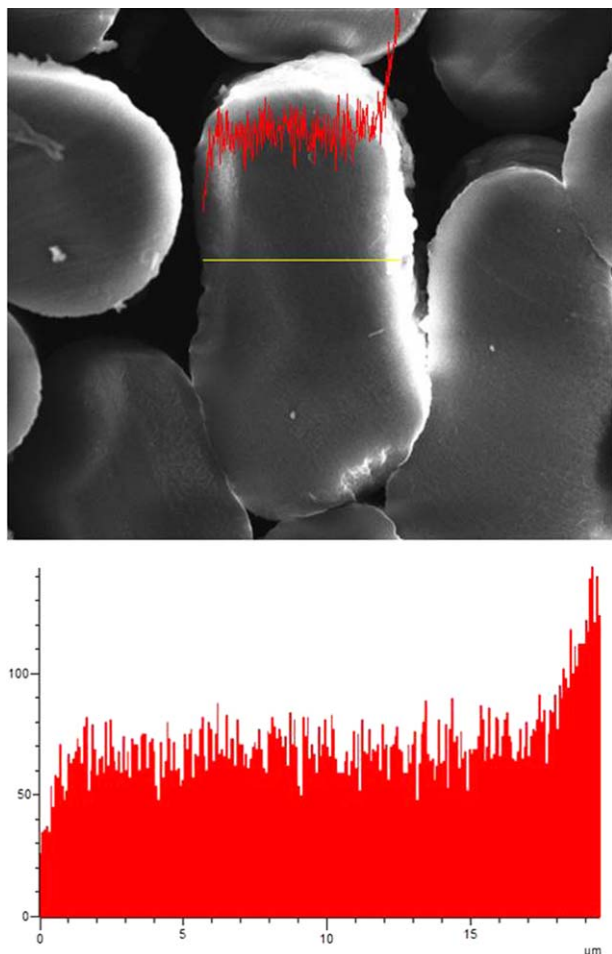
Figure 7. SEM micrograph of a cross section of the NPAN fibers after treatment in HHA for 1 h and after further treatment in an NaOH aqueous solution for 90 min and distribution of sodium ions on the cross section as detected by EDS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

III. We observed that the LOI values of the NPAN and BPAN fibers before treatment both ranged from 18.5 to 19.0; this indicated they are quite easy to burn in air. After treatment in HHA for 1 h, the LOIs of the NPAN and BPAN fibers improved from about 19.0 to 19.5; that is, the fibers were still very combustible. However, their LOI values improved greatly after hydrolysis in the NaOH aqueous solution, and the fibers become self-extinguishing when they were removed from the igniting flame. It also is also shown in Table III that the LOI of the modified fibers decreased with increasing PVA content; for example, the LOI of NPAN after 2 h of modification in an NaOH aqueous solution was 54.7 and decreased to 40.0 after the addition of 30 wt % PVA. It further decreased to 34.0 after the PVA content was increased to 40 wt %. The flame-retardant mechanisms of acrylic fibers after this two-step method modification were reported in our previous work, and we found that the flame resistance of the acrylic fibers relied mostly on the content of sodium ions.[19] After the introduction of PVA, the content of reactive groups in the modified BPAN fibers was reduced; therefore, the flame-resistant performance decreased

with increasing PVA content. However, the LOI value of BPAN-50% after modification was 29.1; this was still higher than that of Nomex, and the fiber was self-extinguishing under air conditions. In summary, the introduction of PVA greatly improved the mechanical properties of the fibers and also led to some decrease in the flame resistance. The mechanical properties and flame resistance of the fibers could be controlled by the adjustment of the content of PVA.

Heat-Release Behavior

MCC testing is a useful bench-scale method for investigating the combustion properties of polymer materials.[33] The peak heat release rate (pHRR), total heat release (THR), and temperature at the peak heat release rate (T_{max}) can be obtained by MCC testing. Low values of pHRR are an indication of low flammability and low full-scale fire hazard.[33–35] THR is characterized as the total energy released by the combustion of the gases generated in the material decomposition process; this is another important parameter for fire hazard evaluation.[33] Figure 4 presents the curves of the heat release rate (HRR) of the fibers before and after modification, and the corresponding experimental data are summarized in Table IV.

As shown in Figure 4(a) and Table IV, BPAN-50% fiber without treatment created much combustible gases during heating, with a THR as high as 16.6 kJ/g and a pHRR of 225.9 W/g. After modification in HHA for 1 h, the THR of the BPAN-50% fiber decreased slightly to 15.9 kJ/g, but pHRR decreased sharply to 155.2 W/g; this indicated that modification of HHA did not reduce the generation of combustible gases significantly, but it was effective in slowing the release of combustible gases during heating. The lower pHRR meant that the fire hazard of BPAN-50% fiber was reduced after treatment with HHA. Moreover, the THR and pHRR of BPAN-50% fiber after modification in NaOH solution for 2 h were 11.1 kJ/g and 98.9 W/g, respectively; this illustrated that the further treatment in NaOH solution led to a dramatic decrease in HRR and also prevented the generation of combustible gases.

As also shown in Figure 4(b) and Table IV, the pHRR and THR values of the modified BPAN fibers decreased with decreasing PVA contents; this indicated that the introduction of PVA to improve the mechanical properties of the fibers reduced the flame retardancy of the modified fibers simultaneously; this was consistent with the result of the LOI tests.

Surface Morphology

The mechanical properties of fibers are mostly based on their structure. To directly observe the changes in the structure of the fibers during modification, the SEM micrographs of NPAN fiber before and after modification are shown in Figure 5. It was obvious that the NPAN fiber before treatment was intact, as is shown in Figure 5(a), and it was still smooth with few defects after it was reacted with the HHA solution even for 4 h; this explained quite well why the tensile strength of the NPAN fiber remained high after modification in HHA. However, there appeared a lot of corrosion on the surface of the NPAN fiber during modification in the NaOH aqueous solution; this indicated that NaOH had an apparent etching effect on the NPAN fiber. The structure of the NPAN fiber was seriously destroyed,
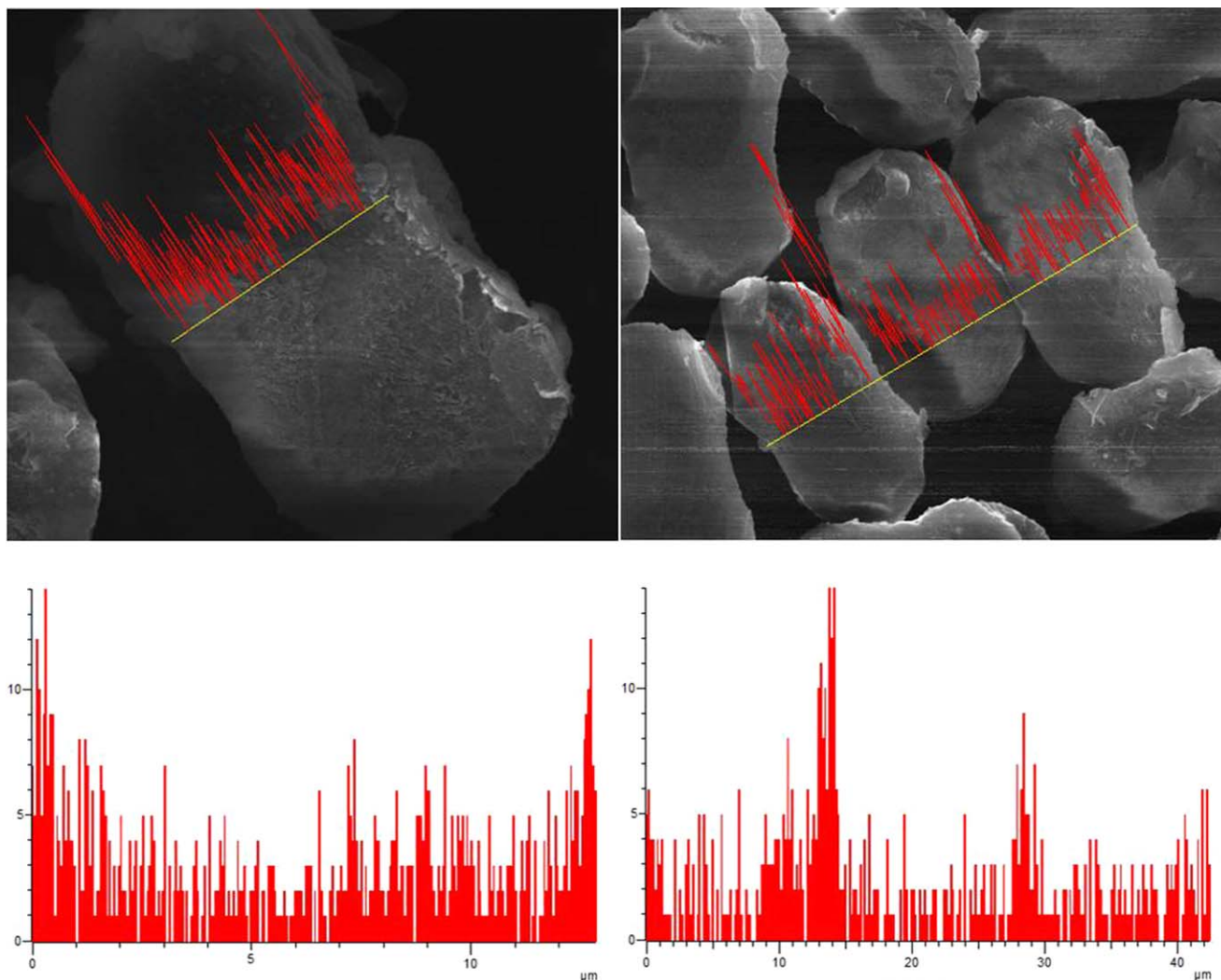
Figure 8. SEM micrograph of a cross section of BPAN-50% fibers after treatment in HHA for 1 h and after further treatment in an NaOH aqueous solution for 2 h and distribution of sodium ions on the cross section as detected by EDS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and the fiber became uneven in thickness after it was treated in NaOH aqueous solution for 90 min, as shown in Figure 5(f), so its mechanical properties decreased sharply. Figure 6 shows the SEM micrographs of the BPAN-50% fiber before and after modification. We observed that the fiber was still smooth and intact, even after 2 h of treatment in NaOH solution; that is, the addition of PVA improved the alkali resistance of the fiber. With fewer defects, its mechanical properties remained higher than that of the NPAN fiber.

Elemental analyses were performed on the treated fibers with an awareness that it had no quantity value but could be used as a useful medium to better understand the distribution of sodium ions in the modified fibers, and the results are shown in Figure 7 (modified NPAN fiber) and Figure 8 (modified BPAN-50% fiber). It is clear in Figure 7 that the content of sodium ions was almost the same from the surface of the modified NPAN fiber to its interior; this indicated that the fiber was highly hydrolyzed from the outside to the inside, and the structure of the fiber was seriously destroyed. However, after even longer

treatment, the sodium ions were mainly distributed around the surface of the modified BPAN-50% fiber, as shown in Figure 8. It was obvious that the sodium ions in the interior of the fiber were fewer than at its surface; this indicated that the interior of the fiber was mildly hydrolyzed. With a low degree of damage, its mechanical properties remained high. Simultaneously, because of the reduction of flame-resistant groups, the flame resistance of the modified BPAN fiber was not as good as that of the modified NPAN fiber.

The results of EDS also raise the prospect that the NPAN fibers may also have had flame retardancy after being hydrolyzed only around its surface in NaOH aqueous solution by a decrease in the hydrolysis time. The flame resistance of this low-hydrolytic-degree NPAN fiber may not be as good as that of the high-hydrolytic-degree NPAN fiber but could be similar to that of BPAN-50% with many sodium ions distributed around its surface as well. It is true that only the surface of the NPAN fiber was hydrolyzed at the very beginning of the hydrolysis reaction in NaOH aqueous solution; however, these low-hydrolytic-
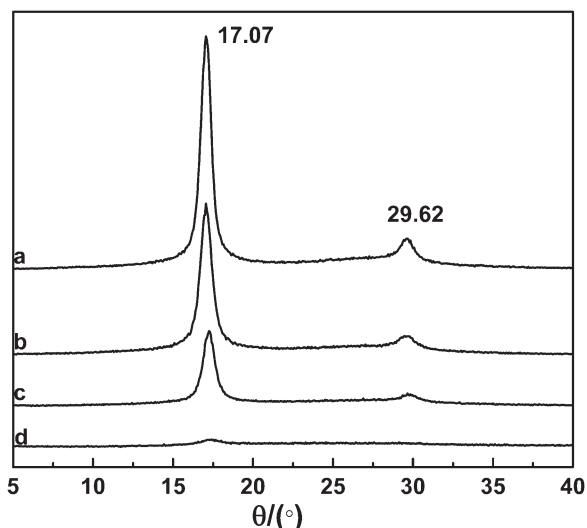
Figure 9. WAXD spectra of NPAN before and after modification: (a) before modification, (b) treated in HHA for 1 h, (c) treated in HHA for 1 h and then further treated in an NaOH aqueous solution for 30 min, and (d) treated in HHA for 1 h and then treated in an NaOH aqueous solution for 90 min; "θ" is diffraction angle.

degree NPAN fibers were non-self-quenching in air conditions. To improve its flame resistance, the treatment time needed to be longer, and actually, the fiber should have been treated for 60 min at least to become self-extinguishing, as mentioned previously. With more and more hydrophilic groups generated during treatment, the fiber became swollen, and the interior of the fiber was hydrolyzed quickly. However, PVA in the BPAN fiber was not hydrolyzed, and this prevented the fiber from swelling during modification.

Crystalline Structure

WAXD was used to observe the changes in the crystalline structure of the fibers during modification. Figure 9 shows the WAXD results of the NPAN fibers. The peaks at 17.07 and 29.62° were attributed to the lattice planes (100) and (2$\bar{1}$0), respectively, as reported by many researchers.[36–38] We found that the intensity of the diffraction peaks decreased with increasing treatment time; this indicated that the crystalline structure of the fiber was destroyed during modification. Furthermore, it was clear that the diffraction peaks of the NPAN fiber after treatment in NaOH aqueous solution for 90 min

Table V. Crystallinity Degree (%) of the Fibers Calculated with Jade 5.0

Sample	Before treatment	Treatment in HHA for 1 h	Further treatment in NaOH	
			30 min	120 min
NPAN	71.99	68.01	61.00	—[a]
BPAN-50%	81.02	80.31	—[b]	74.88

[a] The crystal structure was seriously destroyed after a 90-min treatment in an NaOH aqueous solution, and the intensity of the diffraction peaks was too weak to calculate its crystallinity degree.
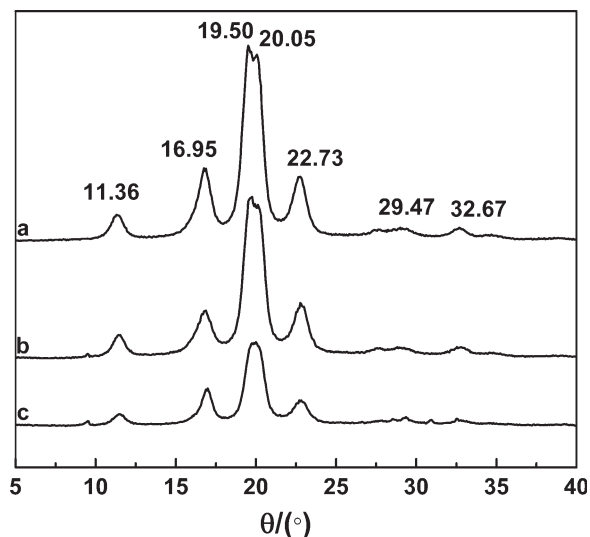[b] Not done.

Figure 10. WAXD spectra of BPAN-50% before and after modification: (a) before modification, (b) treated in HHA for 1 h, and (c) treated in HHA for 1 h and then further treated in an NaOH aqueous solution for 2 h; "θ" is diffraction angle.

[Figure 9(d)] was quite weak, and this demonstrated the low crystallinity. Jade software was used to analyze the WAXD results and calculate the crystallinity degree of the fibers, and the analysis results are shown in Table V. The crystallinity degree of the NPAN fiber decreased from 71.99 to 68.01% after 1 h of treatment in HHA and further decreased to 61.00% after 30 min of treatment by the NaOH aqueous solution. Moreover, after 90 min of modification by the NaOH aqueous solution, the crystal structure was seriously destroyed, and the intensity of the diffraction peaks was too weak to calculate its crystallinity degree. Figure 10 shows the WAXD spectra of BPAN-50% during modification. The diffraction peaks of PAN and PVA appeared independently. The peaks at 16.95 and 29.47° were ascribed to the lattice planes (100) and (2$\bar{1}$0) of PAN, and the peaks at 11.36, 19.50, 20.05, 22.73, and 32.67° belonged to the lattice planes (100), (10$\bar{1}$), (101), (200), and (002) of PVA, respectively.[39] It has been reported that the peak at $2\theta = 20°$ (101) is due to the intermolecular interference between PVA chains in the direction of the intermolecular hydrogen bonding, and the increase in the intensity of the (101) diffraction corresponds to the increase in the number of PVA chains packing together.[40] Thus, the high intensity of the (101) diffraction indirectly suggested the high orientation of the fiber. As shown in Figure 10, the intensity of the (101) diffraction decreased with increasing treatment; this indicated that the flame modification did some damage to the oriented structure of the BPAN-50% fiber. However, compared with those of the NPAN fiber, the diffraction peaks of BPAN-50% after modification in the NaOH aqueous solution for 2 h were still apparent; this means that its crystal structure remained greater than that of NPAN after the same treatment. The crystallinity degree of BPAN-50% before modification was 81.02%, as calculated by MDI Jade 5.0, as is shown in Table IV, and after 2 h of treatment in NaOH aqueous solution, it still remained at 74.88%. With less destruction during modification and a higher initial tensile strength, the

mechanical properties of the PAN fibers were highly improved after the introduction of PVA.

CONCLUSIONS

In this study, PVA was used to enhance the mechanical properties of flame-retardant PAN fibers. It was found that the flame resistance of the fibers decreased with increasing PVA content. However, the LOI value of the BPAN-50% fiber after modification remained at 29.1; this was still higher than that of Nomex. Importantly, the mechanical properties of the fiber were highly improved after the introduction of PVA. For example, the tensile strength of the NPAN fiber after flame-retardant modification was only about 1.96 cN/dtex, and it was improved to 2.72, 3.02, and 4.01 cN/dtex after the introduction of 30, 40, and 50 wt % PVA, respectively. The high tensile strength made the blend fibers possible to be used as woven fabrics not only as fiber fillers. SEM, EDS, and WAXD were used to observe the structures of the fibers during modification, and we found that the structures of the blend fibers were less damaged after the same modification than the neat one. With less destruction during modification and a higher initial tensile strength, the mechanical properties of the PAN fibers were highly improved after the introduction of PVA.

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