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RESEARCH ARTICLE

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Properties of partially hydrolyzed PAN fibers

Abstract The properties of base PAN (polyacrylonitrile) fibers and their partially hydrolyzed PAN-COOH fibers were characterized by means of a Fourier transform infrared spectrophotometer, elemental analyzer, specific surface area analyzer etc. The main factors that can affect the strength of the base PAN fibers and how the hydrolysis reaction happens in alkaline conditions are discussed. Acidic hydrolyzed PAN-COOH fibers, having a strength of 9.6 cN/dtex, capacity of 0.26 mmol/g, BET area of 0.58 m^2/g (calculated on dry basis) were prepared. The conversion rate from –CN to –COOH, the ways that groups of –COOH array on the surface of the fibers and the possible maximum amounts of –COOH are discussed in detail.

Keywords polyacrylonitrile, fiber, hydrolysis, ion-exchange fiber

Generally, there are two kinds of ways to produce ion-exchange fibers [1]: (i) Monomers or polymers, which have ion-exchange groups or have groups that can be transformed into ion-exchange groups, polymerize or blend with monomers or polymers to form the resins which can be spun into fibers, and then process the resins to get the needed ion-exchange fibers; (ii) Modify the natural or synthesized fibers by means of functional-group-transforming, grafting, chemical-gel-coating etc. to get the functional ones. The former is suitable for large quantity production, and the latter is much more economical for preparation of small amounts of special or specific application under the condition that the strength of the original fibers can be conserved after the necessary steps of chemical treatments. There are many commercial synthesized fibers, such as polyester, nylon, polypropylene, polyacrylonitrile (PAN) *etc*., and one of them—the PAN fiber—should be most feasible for modification.

The groups of –CN on the surface of PAN fibers have great potential to be modified to get functional fibers: (i) to produce chelating fibers by reaction with hydroxylamine reagents [2–5]; (ii) to prepare PAN-COOH ion-exchange fibers through direct hydrolysis [6–8]; (iii) to form PAN-PEI ion-exchange fibers by gel-coating PEI (polyethyleneimine) on the exterior surface of hydrolyzed PAN-COOH fibers [9,10]. The main factors that can affect the strength and exchange capacity of the new functional fibers prepared using the aforesaid methods using commercial PAN fibers as base include the manufacturing process, the chemical composition, crystal structure, and the surface properties of the base fibers.

In the study described below, the key factors that affect the strength and thermo stability of base PAN fibers are discussed on the basis of PAN's super molecular crystal structure; the FTIR spectra of both the PAN fibers and the partially hydrolyzed PAN-COOH fibers are measured and discussed; the hydrolysis reaction equation in alkaline condition is deduced and proved; the amount of –COOH groups on the hydrolyzed fibers is determined; the production rate of –CN to COOH and the possible maximum amount of –COOH on the hydrolyzed fibers are discussed on the condition that the base fibers are designated and the strength of the base fibers should be conserved during the process.

1 Experiments

1.1 Materials and reagents

PAN fibers, short fibers (Provided by Qinhuangdao Alight Anrylic Fiber Co. Ltd). All reagents used were AR grade.

1.2 Apparatus and equipment

Nicolet 550 Fourier transform infrared spectrophotometer (U.S.), ASAP 2010 specific surface area-role diameter tester (U.S.), Elementar Vario EL elemental analyzer (Germany), XJ 103 stelometer fiber strength Instrument (Shanghai, China).

1.3 Preparation of the partially hydrolyzed PAN fibers

15 mL pure water, 12 g sodium hydroxide and 285 mL ethanol were added into a 500 mL round flask which was

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shaken till sodium hydroxide dissolved completely; 4 g PAN fibers that had been previously cut into one centimeter-long pieces were placed in the flask to perform the hydrolysis solution. The reaction mass was refluxed for 4 h at 85°C on a constant temperature water bath shaker with moderate shaking speed. After finishing the reaction the fibers were picked out, washed with ethanol till no free sodium hydroxide was observed, and the PAN-COONa ion-exchange fibers were obtained. The PAN-COONa ion-exchange fibers were soaked in a solution of 1M HCl for transfer into the PAN-COOH ion-exchange fibers.

1.4 Characterizations of the fibers

The amounts of –COOH groups in the PAN-COOH ion-exchange fibers were determined according to the national standard of GB/8144-87 (Method for determination of exchange capacity of cation ion resins).

The base PAN fibers and partially hydrolyzed PAN-COOH ion-exchange fibers were characterized by FTIR, elemental analyses and specific surface area analyses.

2 Results and discussion

2.1 Choice of base fibers

Strength and thermostability are the main consideration factors in choosing the kind of base fibers. Normally, the strength and thermostability of PAN fibers are determined by their crystallization and orientation. The commercial PAN fibers are mainly processed through three methods—melt-spinning, dry-spinning and wet-spinning; their super molecular structure orientations are 76.0%, 78.9%, 75.8%, respectively, and their crystallizations are 32.9%, 35.4%, 33.9%, respectively [11].

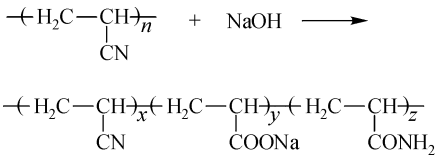
The degrees of orientation and crystallization of the PAN fibers processed by the dry-spinning method are higher than those of the PAN fibers processed by the other two methods, hence their strength and thermostability are the best.

Dry-spinning fibers manufactured by Qinhuangdao Alight Anrylic Fiber Co. Ltd were chosen as the base fibers in this paper.

2.2 Hydrolysis reaction on the surface of PAN fibers

Experimental results showed that the hydrolysis reaction of PAN fibers took place so violently that it was difficult to control the conditions for obtaining good shape and strength of fibers either in acidic—or in alkaline-water solution environment. In this paper, PAN-COOH fibers with good shape and strength were prepared in sodium hydroxide-water-ethanol solution with ethanol as main solvent and water as assistant solvent refluxed on a shaker at moderate speed.

The groups of –CN on the PAN fibers can be transformed into amide ($–CONH_2$) and carboxylic sodium (–COONa) groups after being hydrolyzed in alkaline conditions and co-polymerized fibers have formed; the reaction equation is represented by Eq. (1):



(1)

In order to verify the reaction Eq. (1), infrared spectra of the base PAN fibers and the partially hydrolyzed PAN-COOH fibers were measured and are shown in Fig. 1 and Fig. 2.

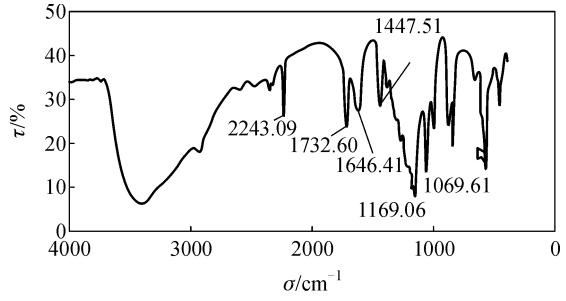


Fig. 1 Infrared Spectrum of Base PAN Fibers

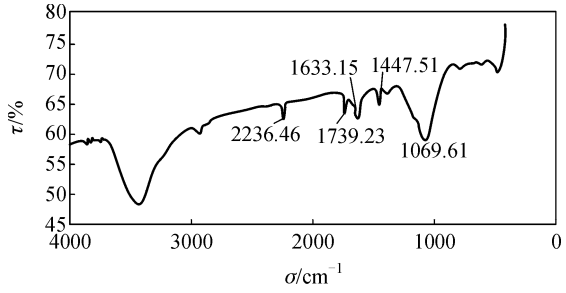


Fig. 2 Infrared spectrum of partially hydrolyzed PAN-COOH Fibers

In Fig. 1, the specific peak (2243 cm^{-1}) of the –CN groups was strong and sharp, showing that the base PAN fibers have large amounts of –CN groups, and the peak (1732 cm^{-1}) was attributed to the specific stretching absorption of –CO groups of the second and third ingredients (esters).

Comparing Fig. 1 and Fig. 2, it can be seen that: (i) the solvents and other components in the base PAN fibers were leached out after being refluxed in sodium hydroxide-water—ethanol solution, and so the spectra of the hydrolyzed fibers was much "simpler" and "cleaner"; (ii) the relative intensity of the specific peak (2240 cm^{-1}) of the –CN

Table 1 Comparison of properties of base PAN fibers and partially hydrolyzed PAN-COOH fibers

fibers	*W*/%			Diameter/μm	Surface area /($m^2 \cdot g^{-1}$)	Pore-volume /($m^3 \cdot g^{-1}$)	Broken strength cN/dtex	Rate of broken stretch/%
	C	*H*	*N*					
PAN	66.80	6.19	23.28	16 (dry)	0.188	0.026	9.6	6.91
PAN-COOH	66.35	6.18	22.26	10 (dry), 12 (wet)	0.580	0.051	8.3	5.62

groups of the hydrolyzed PAN-COOH fibers was much weaker than that of the base PAN fibers, suggesting that the ratio of the –CN groups was reduced; (iii) the specific peak (around 3400 cm^{-1}) of the active hydrogen of the hydrolyzed PAN-COOH fibers was strong and sharp, indicating that there were large amounts of –COOH groups in the fibers; (iv) the peak (around 1633 cm^{-1}) was the specific absorption of the $–NH_2$ groups in the $–COONH_2$ groups, showing that part of the groups of –CN on the surface of the base fibers transformed into $–COONH_2$ groups after the hydrolysis reaction, and also proved that reaction Eq. (1) took place after hydrolysis.

2.3 Characterization of the fibers

A batch of partially hydrolyzed PAN-COOH fibers with 0.260 mmol/g of –COOH groups (on dry basis) was prepared, and the main properties are shown in Table 1; for comparison, the relative values of the original base PAN fibers are listed too.

From Table 1, it can be seen that: (i) the mass fraction of element *N* in the base PAN fibers was 23.28%; if all of the *N* atoms were in –CN groups, then the mass fraction of acrylonitrile in the base PAN fibers would be 88.13%, and that of the other component, as the second and third ingredients, would be 11.87%; (ii) Compared to the base PAN fibers, the broken strength and the rate of broken stretch of the reduced hydrolyzed PAN-COOH fibers are not significant; (iii) the pore volumes of both the base PAN fibers and the hydrolyzed PAN-COOH fibers were very small, suggesting that their specific surface areas were mainly contributed by the exterior surface.

2.4 Conversion ratio

The elemental composition of the hydrolyzed PAN-COOH fibers (Table 1) decreased by 1.02% of *N* compared to that of the base fibers. Provided that all the reduced *N* atoms are transformed into NH_3 and released, and that equal molar groups of –COONa were obtained in the mean time, the amount of –COOH groups in the partially hydrolyzed PAN-COOH fibers should be 0.728 mmol/g (on dry basis). The experimental results (Table 1) show that the quantity of –COOH groups in the fibers were 0.260 mmol/g (on dry basis) only. The reaction conversion ratio of –COOH groups from the groups of –CN was 36%, and the other reacted *N* atoms should exist in the forms of $–CONH_2$ and other intermediates.

2.5 Possible maximum hydrolysis amount

To estimate the possible maximum hydrolysis amount of the –COOH groups, the following assumptions were made: (i) the –CN groups on the surface of the base PAN fibers will transform into the –COOH groups after hydrolysis; (ii) to maintain the strength of the base PAN fibers during hydrolysis, the crystal structure of the fibers should not be damaged, and the exterior surface area should be the same; the amount of the specific surface area of the hydrolyzed PAN-COOH fibers is the determining factor for the amount of the –COOH groups.

Here, we set *m*(–COOH), $mmol \cdot g^{-1}$ as the molar concentration of the –COOH groups (on dry basis) of the hydrolyzed PAN-COOH fibers, *S* as the specific surface area of the fiber, and S_c as the cross-sectional area of the –COOH group. The relationship equation among them can be represented as Eq. (2):

$$m(\text{–COOH}) = S/(S_c \times L) \quad (2)$$

In this equation, *L* stands for Avogadro's constant, 6.02×10^{23} mol^{-1}.

Provided that the density of the –COOH group is 1 g/cm^3, the volume of one single –COOH group is 7.46×10^{-29} m^3.

Provided that the –COOH groups array on the exterior surface of the hydrolyzed PAN-COOH fibers as balls and as columns, of which the diameters are the bond lengths of C–O (0.143 nm) and the diameter of the O atom (0.132 nm), respectively, the maximum molar amounts are listed in Table 2.

Table 2 Possible maximum amounts of –COOH on partially hydrolyzed PAN-COOH fibers

Array forms of –COOH groups on fiber surface	*s*/m^2	*m*(–COOH)/($mmol \cdot g^{-1}$)
Balls (*D*, 0.522 nm)	2.14×10^{-19}	0.0045
Columns (*D*, 0.143 nm)	1.61×10^{-20}	0.0602
Columns (*D*, 0.132 nm)	1.37×10^{-20}	0.0703

The data (Table 2) shows that: (i) if the –COOH groups array on the surface of hydrolyzed PAN-COOH fibers in a

ball shape, the difference between the calculated possible maximum amount and the experimental results is significant; (ii) Provided that the –COOH groups stand tightly on the surface of hydrolyzed PAN-COOH fibers in the shape of columns, the theoretical amount is about 3/10 of the experimental result.

The surface area value used in Table 2 was that of PAN-COOH fibers on dry basis. In fact, PAN-COOH fibers will swell when soaked in water, and will become longer and thicker (the diameter of the wet fiber was 1.2 times larger than that of the dry one, as shown in Table 1), and will also have more grooves and slots, therefore the specific surface area of the wet fibers will be larger than that of the dry ones, therefore the possible maximum amount of –COOH groups is mainly determined by the specific surface area of the wet PAN-COOH fibers under the condition that the strength of the fibers can be conserved.

3 Conclusion

(1) The specific surface area of the hydrolyzed PAN-COOH fibers is the essential factor that determines the amount of –COOH groups.

(2) The specific surface areas of both base PAN fibers and hydrolyzed PAN-COOH fibers are mainly composed of their exterior surfaces, so it is necessary to decrease the diameter of the fiber if a larger specific surface area is needed.

(3) Limited by the specific surface area of the wet fibers, excessive hydrolysis can not achieve a larger exchange capacity and will, on the contrary, cause a loss of strength of the fibers and trouble in further treatment and use.

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