Study on the Acidic Hydrolysis Process of Poly(*N*-vinylformamide/acrylonitrile) Fiber

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ABSTRACT: A convenient method of preparing chelating fiber with amine groups on the fiber surface was developed. The precursor polymer of Poly(*N*-vinylformamide/acrylonitrile) (P(NVF/AN)) was synthesized via solution polymerization, using *N*-vinylforaimde as a functional monomer. The solution of P(NVF/AN) was spun through a wet spinning method and the precursor fiber was hydrolyzed in the hydrochloric acid solution to convert formamide moieties to the corresponding amine. The influence of hydrolytic conditions on hydrolysis degree, such as hydrolysis temperature, hydrolysis time, and hydrochloric acid concentrations were examined experimentally. The hydrolysis degree of the precursor fiber was evaluated by potentiometric and conductometric titrations.

The changes of the structure and properties of the fibers were characterized through infrared spectroscopy, scanning electron microscopy, and tensile strength tester. The results showed that the hydrolysis degree was limited in acidic hydrolysis because of the electrostatic repulsion among the cationic amine groups and proton. The hydrolysis degree of precursor fiber reached nearly 60%, and the chelating fiber remained the adequate mechanical properties under the suitable hydrolysis condition. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2636–2642, 2008

Key words: poly(*N*-vinylformamide/acrylonitrile); poly(vinylamine/acrylonitrile); acidic hydrolysis hydrolysis degree

INTRODUCTION

There has been an increased interest in chelating polymers recently because of their large adsorption capacity and higher selectivity to heavy metal ions than other absorbents. They have been widely used in many industrial branches, such as polymer catalyst, wastewater treatment, antibacterial and deodorizing fabric, and recovery of valuable metal ion traces, etc.[1,2] Among these polymers, polyvinylamine (PVAm) outstands significantly because it can form chelating complexes with diverse metal ions. Therefore, it has various applications in industries as papermaking, wastewater treatment, biological chemistry, petrochemical engineering, paint, and adhesive.[3–7]

PVAm cannot be synthesized directly from a vinylamine monomer because of its tautomerism. It is usually synthesized by alternative methods, like Hoffmann degradation of polyacrylamide or hydrolysis of vinylamine derivatives polymer. Considering practicability, the method of hydrolysis of PNVF is preferable. In this method, PNVF hydrolyzes under acidic or basic conditions to give poly(vinylamine/vinylformamide) copolymer.[8] PNVF hydrolysis under stoichio-metric acid conditions is 60–70% under typical conditions of 80°C/6 h, but hydrolysis slows down because of charge repulsion effects when pushed to high conversion.[9–11] Base hydrolysis suffers no such limitation and full hydrolysis is observed with near stoichiometric levels of hydroxide at 80°C/6 h.[12] Although not a problem in many applications, one issue with the two hydrolysis approach is the removal of hydrolysis byproducts. Except that, the latter is usually a more efficient approach for taking PNVF to PVAm. PNVF does not have spinnability and cannot be spun into fiber by using direct-spinning technique. PNVF can be made into PVAm in the forms of gel or hydrogel for application.

As a matter of fact, chelating fibers containing amine groups do have drawn intensive interests because of their effective applications in various cases recently. Hai et al., reported the preparation of a poly(vinylamine) based chelating fiber from a hydrolysate of poly(*N*-vinylformaide/acrylonitrile) copolymer.[13] In this copolymer, poly(acrylonitrile) was used as a fiber forming polymer and poly(*N*-vinylformamide) as a functional moiety which could be hydrolyzed to PVAm by a simple method. However, the hydrolyzed copolymer was of poor spinnability when the hydrolysis degree was high. The chelating fiber of P(VAm/AN) prepared by them had a average diameter of 80 μm, thus the linear density of the chelating fiber was too high for the usual uses.

Moreover, many studies have been carried out on the hydrolysis of PNVF under basic condition,[5] including the hydrolysis reaction conditions and kinetics. Nonetheless, investigations concerning hydrolysis under acidic condition and the hydrolysis of copolymer containing N-vinylformamide monomer are rarely reported.[13] The rarity of research on the latter is mainly because of its special difficulties, for example, the hydrolysis of PNVF always carries on with the hydrolysis of cyano group of PAN under alkaline conditions. The hydrolysis of PAN can be a complicated process and different types of hydrolyzed products such as acrylamide, sodium acrylate, and amidine from different stages of the hydrolysis will be generated.[14]

Our previous report described an alternative approach to prepare chelating fiber containing amine groups on fiber surface.[15] Briefly speaking, the preparation involved the solution copolymerization of N-vinylformamide and acrylonitrile, the spinning of the copolymer solution via a wet spinning method, and the hydrolysis of precursor fiber. The aim of this article is to report acidic hydrolysis conditions for the preparation of chelating fiber containing amine groups on the fiber surface, as well as to describe the effect of acid concentration, hydrolysis time, and temperature on tensile strength, structure and morphology of the copolymer fiber.

EXPERIMENTAL

Material and reagents

N-vinylformamide (NVF) monomer from Aldrich was distilled under vacuum at 70°C and stored at −15°C before polymerization. Acrylonitrile(AN), from Tianjin chemical reagent company of China, was refluxed with calcium hydride for 7 h and distilled twice at atmospheric pressure before use. 2,2′-Azobis(isobutyronitrile) (AIBN, Shanghai petrochemical) was recrystallized from ethanol. Dimethyl sulfoxide (DMSO) from Tianjin chemical reagent company of China was used for the solvent and reagent grade HCl and NaOH were used for hydrolytic catalyst. They were all used without further purification.

Instrument and apparatus

A home-manufactured wet-spinning apparatus was used for spinning the fibers. The mechanical properties of the fiber were tested by YG-001A fiber strength electronic tester (Taicang Textile Instrument). The morphology of the fiber was observed with a scanning electron microscope (SEM; JSM-5900LV). An infrared spectrophoto-meter (IR) (Nicolet FTIP 560) was used for recording the IR spectra in the wave number range 400–4000 cm^{-1}.

Fiber thin films were prepared by dissolving fiber in DMSO solution. The pH values of the buffer solutions were determined with the pH meter. The conductivity of electrolytic solution was measured by electrical conductivity instrument.

Preparing the fiber

Into a 250 mL four-necked flask equipped with a stirrer, a nitrogen inlet and a cooling tube, 159.6 g solvent containing 12 g NVF, and 28 g AN was added. After increasing the temperature to 60°C under stirring under nitrogen, 0.40 g AIBN was added. The resultant mixture was maintained under stirring at 60°C for 9 h to obtain a ropy solution that was used as spinning solution.

After filtered and deaired, the spinning dope was extruded through a spinneret with 200× Φ0.1 mm into the coagulation bath (50% DMSO in water, 35–40°C) to form nascent fiber. The courses aftermath included stretching, washing, winding and thermal treatment. The precursor fiber was washed thoroughly with distilled water and dried in a vacuum oven overnight at 50°C.

Acid hydrolysis of the fiber

An accurately weighed amount of fiber and distilled water were added into a 250 mL three necked bottle, and the mixture were then stirred under N$_2$ atmosphere for about 30 min until the temperature equilibrium was reached. Hydrochloric acid with certain concentration, preheated to the same temperature, was added into the bottle, and the mixture was stirred to be homogeneous. After being neutralized, the hydrolyzed fiber was washed with excess acetone to remove any residual monomer. The resulting fiber was dried under reduced pressure at 60°C for 12 h. The poly(VAm/AN) fiber with chelating function was collected for further characterization.

Determination of the residual hydrochloric acid in chelating fiber

The 10 mL of solution was taken from the reaction vessel in a time interval for determining the change of hydrochloric acid concentration. It was diluted to a certain volume with deionized water. With phenolphthalein as the indicator, the diluted solution was titrated by NaOH standard solution to red from colorless. This method was applied to determine the HCl residual content in the reaction solution.

Determination to the hydrolysis degree of fiber

Potentiometric and conductometric titrations were carried out for determining the hydrolysis degree.

Figure 1 Laboratory wet spinning line.

For each titration, 1.0 g hydrolyzed fiber and 200 mL distilled water were put into a 500 mL beaker. The beaker was then immersed in thermostat water bath with magnetic stirring device. After stirring for 1 h, 3 mL of 0.50 mol/L HCl solution was added to adjust the pH to 3. The solution was equilibrated at 25°C for 10 min. The forward titration was conducted using NaOH (0.5 mol/L) and stopped at pH 10.5, and HCl (0.1 mol/L) was then added and the back titration was stopped at pH 3.

RESULTS AND DISCUSSION

Hydrolysis and characteristics of fiber

By stoichiometrицly adding NVF and AN in the presence of azoinitiators to dimethyl-sulfoxide solvent and then by wet-spinning process(Fig. 1), the fiber containing stable primary amine functionality through hydrolysis under acid or base conditions was obtained. The process of forming the copolymer fiber is shown in Figure 2.

As to the copolymerization between NVF and AN in DMSO at 60°C, $r_1 = 0.26$ (NVF), $r_2 = 0.20$ (AN), the results suggested that the copolymerization was random but tends to yield alternative copolymers when raw material mole ratio was approximated to 45/55. The amino groups, from hydrolysis of PNVF, were one group with powerful potential chelating chelating metal ions function, so we should improve the proportion of NVF in material and keep good

Figure 2 Hydrolysis process of copolymer fiber in acid or alkaline condition.

Figure 3 Hydrolytic process of fiber.

spinnability of copolymer solution. A complete consideration to selection material ratio NVF/AN was 30/70. P(NVF/AN) copolymer fiber could be hydrolyzed in conventional basic conditions, transforming formamide into amino groups, cyano groups into amide groups, and even into carboxyl such hydrophilic groups, which was not beneficial to chemical modification of cyano groups so as to meet the requirement for practical application, furthermore the intensity of the fibers was badly decreased. The fibers could be readily hydrolyzed under acid conditions with high conversion degree because of the lack of strong charge repulsion between vinylamine groups in these strongly alternating copolymers. All amine groups would have a neighboring cyano group to react with. Unfortunately, in the direct base hydrolysis methods, or in the acid hydrolysis and then base neutralization, the amine groups would form amidine with neighboring cyano groups very rapidly, as shown in Figure 3, which was a block for further study on properties of modification of cyano groups.

Even if the fiber was hydrolyzed in acid conditions with relatively relaxative, the hydrolysate might contain multiple groups in different stages of the hydrolysis, such as amidine, formamide, cyano, amide, and carboxyl groups. The FTIR spectra of fiber (NVF/AN) before and after hydrolysis are shown in Figure 4.

Figure 4 FTIR spectra of fiber a: before hydrolysis; b: after hydrolysis.

From the FTIR spectra of poly(NVF/AN) before and after hydrolysis [Fig. 4(b)], The peak at 3347.99 cm^{-1} of $\gamma(N\text{---}H)$ became a double-peak. Poly (NVF/AN) fiber contained a secondary amino groups —NH on side chains, therefore there was only one absorption peak. But after the hydrolysis, poly(VAm/AN) fiber had a second —NH on side chain where it had used to contain the primary amine group (—NH$_2$). So at the original location the single absorption peak had split up into two, and the location was displaced towards higher wave number indicating hydrochloride salt has been formed by combination of NH$_2$ and HCl. —C≡N stretching (2242.90 cm^{-1}), —C=O stretching (amide I; 1667.2 cm^{-1}) and NH bending (amide II; 1529.2 cm^{-1}) absorption bands were detected before the hydrolysis. As the hydrolysis progressed, however, these bands decreased in proportion. The amino groups, formamide groups and cyano groups coexisted in hydrolysis products, which fully proved that partially hydrolyzed reaction of fibers occurred under acid conditions. The intensities of cyano groups peak slightly reduced, which showed they and their neighboring groups to taken part in cyclization side reaction.

Determination for hydrolysis degree of fiber

The fiber was hydrolyzed at 70°C in acid condition, then washed by water and dried as reserve. The hydrolysis degree of the fiber was determined by acid–base titration and electrical conductivity methods. The relationships between the NaOH addition quantities and the changes of pH value as well as electrical conductivity were shown in Figure 5.

The whole hydrolysis process was divided into three stages: At the first stage, the solution was titrated by NaOH according to neutralization rule of strong base to strong acid because of the existence of excessive HCl. At this stage NaOH was used directly for neutralizing HCl, which leaded to free electric charge reduction in the system. Conductivity accordingly reduced, and the pH value just increased slightly. Surplus HCl was gradually consumed with the increasing addition of NaOH. Then there came the second stage. The system at this stage contained following balance:

$$\text{---NH}_2\text{HCl} + \text{OH}^- \rightleftharpoons -\text{NH}_2 + \text{H}_2\text{O} + \text{Cl}^-$$
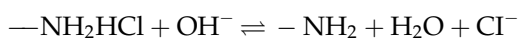
At the second stage, the aqueous NaOH solution was dropped continuously, and the balance moved to the right with increasing OH$^-$ ion concentration. In this case, the H$^+$ ions produced by NH$_2$HCl decomposition was gradually neutralized by OH$^-$ ions until all H$^+$ was completely consumed. Here the amount of alkali dropped into the solution was
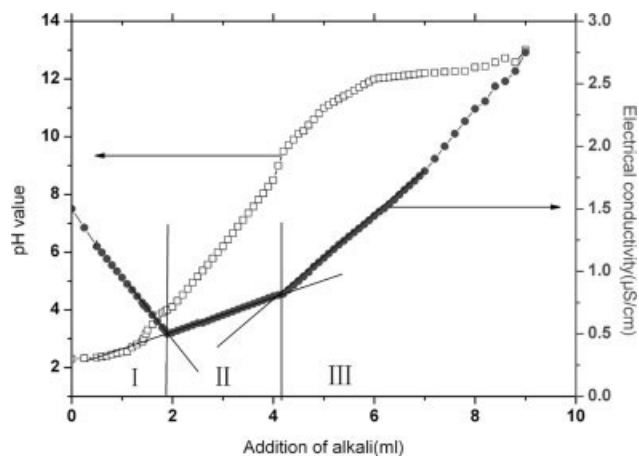
Figure 5 The relationships between NaOH addition quantity and pH value and Electrical conductivity.

sufficient for —NHCHO partly hydrolyzed into —NH$_2$. At this stage the pH value and electric conductivity of system varied with the changes of H$^+$ content. Once H$^+$ bonding onto —NH$_2$ were consumed by alkali solution, the system would come to the third stage. At this stage, addition of alkali dosages would cause the increasing of the ions concentrations in the solution. And the electric conductivity and pH value would increase, too.

Divisions between stages could be obtained by drawing (Fig. 5). The hydrolysis degree of fiber could be denoted by the alkali consumption between two stages and the theoretical values of formamide groups. The definition of the hydrolysis degree (ζ) could be expressed by formula:

$$\beta = \zeta/\text{p} = (x_2 - x_1)/p$$

Here:
ζ-the alkali consumption content of the second stage.
p-the theoretical values of formamide group.
x_1-the total alkali consumption content at the end of the first stage.
x_2-the total alkali consumption content at the end of the second stage.

Influence of temperature on the hydrolytic degree of fiber

The result showed that temperature had great influence on the hydrolytic degree of fiber as shown in Figure 6.. When the temperature was low, the hydrolysis reaction was slow and the degree was low. However, as temperature increases, the reaction activity was higher and hydrolytic degree gradually increased. At 75°C, hydrolytic degree of formamide groups was nearly 60%, but the mechanical properties of fiber decreased obviously. When the hydro-
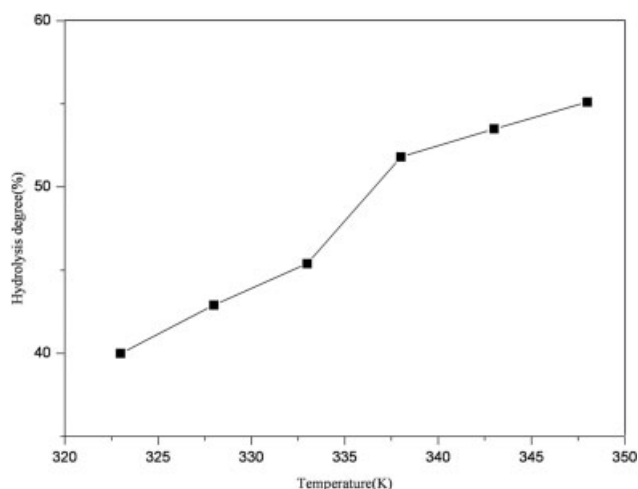
Figure 6 Influence of temperature on the hydrolytic degree HCl/formamide group molar ratios: 2.0; hydrolysis time: 10 h.

lytic temperature was higher than 80°C, deformation and even caking of the fiber would be observed. So the chosen hydrolysis temperature was 70°C in the actual operation.

Influence of hydrolysis time on hydrolytic degree of fiber

Reaction time had great influence on the hydrolytic degree of fiber (Fig. 7), the longer the reaction time was, the higher the hydrolytic degree of fiber was. On the early stage of reaction, the hydrolysis of fiber acutely occurred, and the hydrolytic degree increases comparatively fast. As time went by, the reaction slowed down and the hydrolytic degree had no obvious change after 8 h. This was because the hydrolysis of fiber started first on its surface. With the
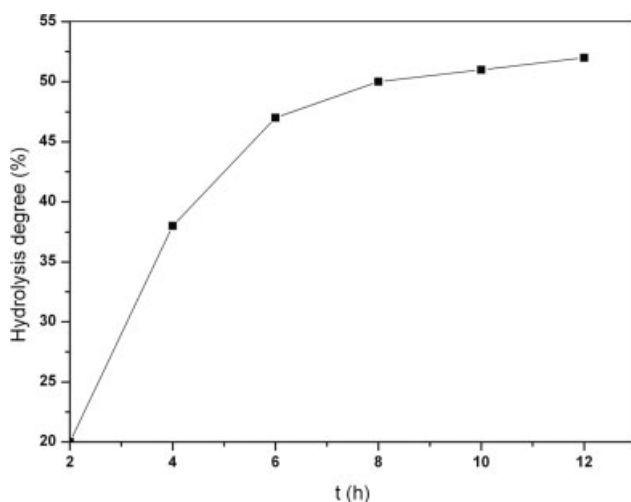
Figure 7 Influence of hydrolysis time on hydrolytic degree of fiber HCl/formamide group molar ratios: 2.0; hydrolysis temperature: 70°C.
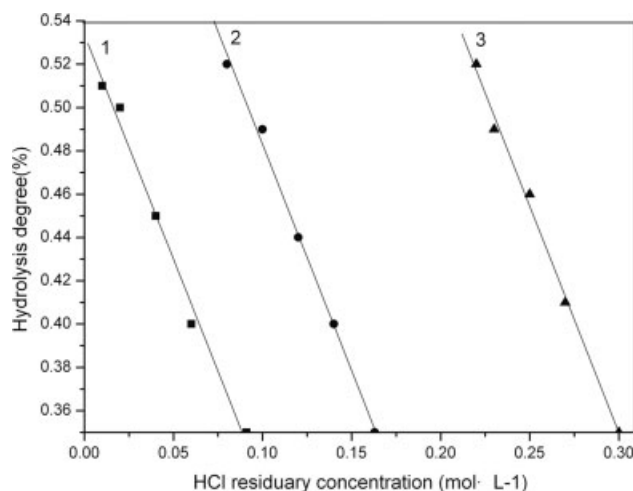
Figure 8 Effects of HCl residuary concentration on hydrolysis degree of fiber Hydrolysis temperature: 70°C; hydrolysis time: 10 h; HCl/formamide group molar ratios: (■)1 : 1; (●)2 : 1; (▲)3 : 1.

prolonging of hydrolysis time, HCl permeated into the interior of fiber continually. 8 h after hydrolysis started, the majority of the interior of fibers had been hydrolyzed and the micropore structures and amino groups had been formed in large portion, which improved the hydrolysis degree of fiber. Nevertheless, the regulation of shape and mechanical property of fiber turned worse with longer hydrolysis time. Most of the fibers had become yellow, rigid and even caking, losing necessary mechanical properties for functional fiber. When the molar ratio of HCl and formamide was 2 : 1 and hydrolysis temperature was 70°C, the optimal time of hydrolysis was about 10 h.

Influence of HCl concentration on hydrolytic degree of fiber

Effects of HCl consumption on hydrolysis degree of fiber were studied as following description. The temperature was 70°C and initial concentration of fiber was 0.1020 mol/L. The stoichiometrical molar ratio of HCl and formamide groups were 1 : 1, 2 : 1, 3 : 1 respectively, with tags of 1, 2, 3, separately as shown in Figure 8. After linear regression, the slopes of the straight lines were -2.07273, -2.08430, -2.09223, respectively. The results indicate that the stoichiometric molar ratio of HCl and hydrolysis degree was 2.08309, approximately equaling to 2. Also it could be concluded that the relation between HCl residuary concentration and hydrolysis degree of fiber was not susceptible to HCl concentration when HCl/formamide groups molar ratio over 1 : 1 because the three straight lines were approximately parallel. For the acid reaction condition, the reaction time should not last long, the selected HCl/formamide groups molar ratio was 2 : 1.
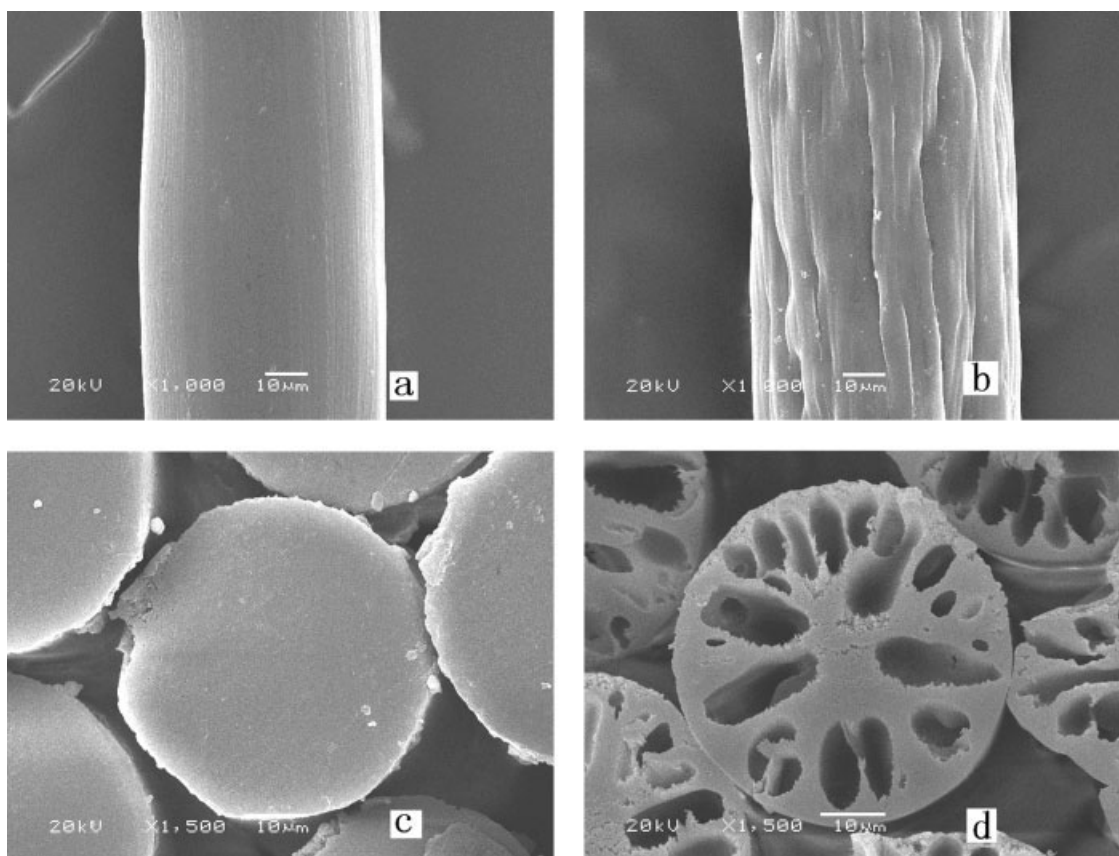
Figure 9 SEM images of the surface and cross section of poly(NVF/AN) and poly(VAm/AN) fibers.

Surface morphology changes of fiber before and after hydrolysis

Hydrolytic process not only changed the chemical structure of fiber, but also had a great influence on fiber's surface morphology. As shown in Figure 9, the SEM analysis of the fiber surface before hydrolysis showed that the surface was relatively smooth and uniform, while the surface of fiber had pores, grooves, and mounds after hydrolysis treatment, which indicated the considerable hydrolysis reaction occurred on the surface.

In terms of the cross sections of poly(NVF/AN) fiber, before hydrolysis they appeared elliptic, and nonporous. But they were laminated lotus root-shaped after hydrolysis with many irregular holes. The uneven structures of fiber surface and mutual breakthrough holes on the cross section enlarged the fiber's specific surface area, which effectively improved adsorption properties of fiber.

Tensile strength changes of fiber before and after hydrolysis

The test crosshead distance is 10 mm, and the effective data each groups was at least 10. The tensile strength of fiber before and after hydrolysis was 1.57 and 1.48cN/dtex, respectively. From this we could see that the tensile strength loss of fiber was very small, the reasons for these were perhaps to carry out hydrolysis reaction mainly on surface of fiber to form many grooves and mounds. This structure had increased specific surface area of the fiber and favorable for the application in chelating metal ions.

CONCLUSIONS

Determination of hydrolytic degree was feasible by conductometric and pH-metric methods that could obtain the precise value of formamide group hydrolytic degree. In the hydrolytic process temperature, time and HCl/formamide group molar ratio have a more tremendous influence to the hydrolytic degree. The experiment results showed that the optimum experimental conditions were as following: temperature: 70°C; time: 10 h; HCl/formamide group molar ratio: 2 : 1. From these conditions fibers with higher hydrolytic degree and decent mechanical properties could be obtained. Also, hydrolysis had great effects on the morphology structure of the fiber. After hydrolysis the surface of fiber appeared highly uneven, with abundant channels, mounds, and especially the interconnecting pores. These structures were advantageous to improve fiber's adsorption ability.

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