

Preparation of Sheath–Core Bicomponent Composite Ion-Exchange Fibers and Their Properties

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ABSTRACT: Based on sheath–core bicomponent composite ion-exchange fibers with modified polystyrene and modified polypropylene, composite fibers were further crosslinked and sulfonated with chlorosulfonic acid to produce strongly acidic cation-exchange fibers. The optimal technology of the obtained fibers was examined, and the structures of the fibers were investigated with Fourier transform infrared spectrophotometry, differential scanning calorimetry, and so forth. The properties were meas-

ured with chemical titration, filament strength instrumentation, scanning electron microscopy, and so forth. The results showed that cation-exchange fibers with better mechanical properties and a higher exchange capacity were obtained, and they had higher practicability. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 492–500, 2008

Key words: crosslinking; fibers; poly(propylene) (PP); structure

INTRODUCTION

Ion-exchange fibers have a bigger exchange capacity and faster rate of exchange and elution than ion-exchange resins. They can be applied in many kinds of forms, can be applied to various processes of exchange,^{1,2} and can be applied in many areas, such as environment protection, environmental monitoring, and resource exploitation.^{3–8} A sheath–core bicomponent composite ion-exchange fiber made from modified polystyrene (PS) as the sheath and modified polypropylene (PP) as the core has been successfully obtained, and it has some advantages, such as lower manufacturing costs, a simple process, and good use of the existing facilities, so it represents a new type of ion-exchange-fiber method with promising prospects. However, the compatibilization of the sheath–core fiber is so bad that its functions are different from those of the original fiber, and the poor mechanical properties of the fiber with its lower exchange capacity are not suitable for the needs of the posttreatment step.^{9–11} In this study based on the sheath–core bicomponent composite ion-exchange fiber with modified PS¹² and modified PP,^{13–15} we obtained a cation-exchange fiber with better mechanical properties and a higher exchange capacity; the properties of the fiber were probed, and it had high practicability.

EXPERIMENTAL

Materials

Self-made original sheath–core bicomponent composite fiber was made from modified PS as the sheath and modified PP as the core.^{16,17} PP was provided by Shanghai Petro-Chemical Co., Ltd. (Shanghai, China). Its characteristics commonly used for fiber spinning were as follows: number-average molecular weight = 1.7×10^5 , melt index (MI) = 39.0 g/10 min (230°C), density = 0.92 g/cm³, and polydispersity = 3.8. PS was provided by Shanghai Petro-Chemical. Its characteristics commonly used for fiber spinning were as follows: number-average molecular weight = 1.1×10^5 , MI = 31.0 g/10 min (260°C), and density = 1.08 g/cm³. The spinning machine was a general conjugate spinning machine that was composed of two extruders (length/diameter = 25, diameter = 20 mm) and gear pumps. Figure 1 illustrates the spinning system used for generating sheath–core bicomponent fibers.

Preparation of the sheath–core bicomponent composite ion-exchange fibers

Crosslinkage

The obtained sheath–core bicomponent composite fibers were cut into 0.5-cm staple fibers, and the staple fibers were cleaned with a detergent and methanol to remove oils and impurities on the surfaces of the fibers and then were dried fully in an oven. Some amounts of the original fibers were weighed, put into a bottle for sulfonation at 50–70°C for 2–6 h

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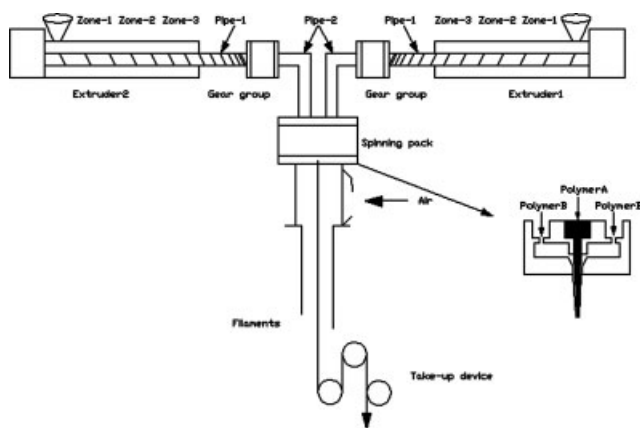


Figure 1 Schematic diagram for the bicomponent composite fiber spinning system.

while concentrated sulfuric acid,¹⁸ glacial acetic acid, and paraformaldehyde were added, and stirred during the process to obtain brown-yellow crosslinkage products.

Sulfonation

With the addition of concentrated sulfuric acid and 1,2-dichloroethane, the crosslinkage products were sulfonated for 1–4 h at constant temperatures of 75–90°C and stirred during the process to obtain the sulfonation products, which were diluted with sulfuric acid of a different density, then washed again and again with deionized water until the flushing water was neutral, and dried in air naturally to obtain the strongly acidic cation-exchange fiber.

Measurement of the static exchange capacity

After the sample of sheath–core bicomponent composite ion-exchange fibers was washed many times with deionized water, it was dried *in vacuo* to remove all water. The dried fiber (0.2 g) was weighed accurately and put into a 200-mL taper bottle; 30 mL of standard aqueous NaOH (0.1 mol/L) and 30 mL of distilled water were accurately added, the mixture was oscillated, the spirit attached to the fiber bubble was removed, and it was sealed completely for a certain time. Then, it was titrated with standard aqueous hydrochloric acid (0.1 mol/L), and according to the whole exchange capacity measurement method of cation-exchange resins on a wet subbase, the saturated ion-exchange capacity was calculated with the following equation:

$$Q_w = (V_0 - V_1) \times C/m$$

where Q_w is the adsorption capacity of the fiber (mmol/g), C is the concentration of standard aqueous hydrochloric acid (mol/L), V_0 is the physical

volume of aqueous hydrochloric acid that is consumed in the titration of the blank (mL), V_1 is the physical volume of aqueous hydrochloric acid that is consumed in the titration of the sample (mL), and m is the quantity of the fiber (g).

Measurement of the water absorption capacity

The stem fibers were placed in deionized water for 24 h and weighed after there was no water on the surface; then, the water absorption capacity of the fibers was calculated with the following equation:

Water absorption capacity (%)

$$= (W_1 - W_0)/W_0 \times 100\%$$

where W_0 is dry weight of the fibers, and W_1 is wet weight of the fibers.

Analysis of the chemical stability

The three parts of the sample of the sheath–core bicomponent composite ion-exchange fibers, which were soaked in 5M H₂SO₄, 5M HCL, and 2M NaOH for 24 h at room temperature, washed with deionized water until the flushing water was neutral, and soaked in a diluted 0.5M HCL solution to regenerate, were weighed accurately; then, the fibers were washed again and again with deionized water, and the saturated ion-exchange capacity of the fibers was measured with the aforementioned method.

Measurement of the regeneration performance

Some amount of the fibers, after being soaked circularly in 0.5M NaOH and 0.5M HCL, was weighed accurately; the fibers were washed with deionized water many times until the washing water was neutral, and it was circulated 10 times. The regeneration-exchange capacity of the fibers obtained was determined in documents. Then, the variety of the micromorphology, heat-proof performance, and chemical stability were examined.

Measurement of the strength of the fibers

After the fiber samples were sulfonated, the breaking elongation rate and fracture strength were determined with a filament strength instrument (PC/LLY-06) (Laizhou, Shangdong, China) with a descendent velocity of 5 mm/min and a prestrain of 200g.

Micromorphology observation

The fibers obtained under different conditions were made into samples, which then were gold-sputtered. The morphology and structure on the surface of the fibers were observed with a Quanta 200 scanning electron microscope (USA).

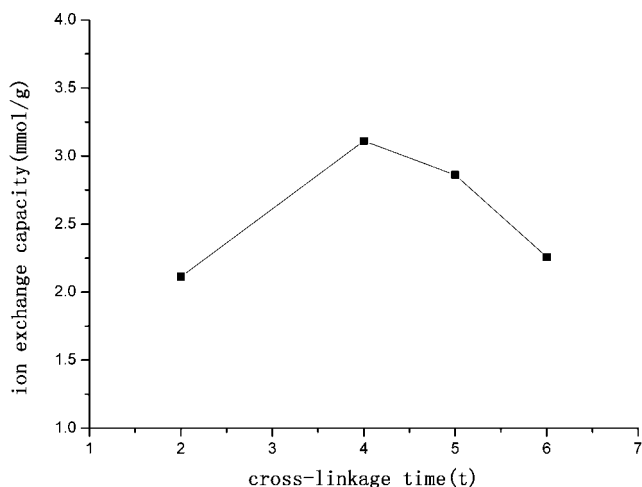


Figure 2 Effect of the crosslinking time on the capacity of the ion-exchange fiber.

Thermal analysis

For thermodynamic experiments, a PerkinElmer DSC-7 dynamic scanning calorimeter (Waltham, MA) equipped with a cooler was used under a nitrogen atmosphere. All the samples were heated from 0 to 250°C at 10°C/min.

RESULTS AND DISCUSSION

Influential factors in preparing the sheath-core bicomponent composite ion-exchange fibers

Effect of the crosslinkage time on the capacity of the ion-exchange fibers

The exchange fibers with different crosslinkage were obtained under the following conditions: 6 g of the fiber, 5 g of $(\text{CH}_2\text{O})_n$, 150 mL of H_2SO_4 (98%), 25 mL of CH_3COOH , 7.5 mL of $\text{C}_2\text{H}_4\text{Cl}_2$, crosslinking at 60°C, and sulfonation at 85°C for 2 h. Figure 2 shows that the capacity of the ion-exchange fibers increases first and decreases later with the prolongation of the crosslinkage reaction time; the exchange capacity attains its biggest value with better mechanical properties when the sulfonation time is 4 h or so. At less than 4 h, the fibers cannot gain an efficient crosslinkage degree, and this makes the sulfonated PS dissolve in water, so the fibers are damaged seriously, and the sheath appears to crack. However, if the crosslinkage reaction time is too long, it takes up the live position of the benzene wreath, and ion-exchange fibers with better mechanical properties but a lower exchange capacity are obtained.

Effect of the sulfonation time on the capacity of the ion-exchange fibers

Exchange fibers with different sulfonation times were obtained under the following conditions: 6 g of

the fiber, 5 g of $(\text{CH}_2\text{O})_n$, 150 mL of H_2SO_4 (98%), 25 mL of CH_3COOH , 7.5 mL of $\text{C}_2\text{H}_4\text{Cl}_2$, crosslinking at 60°C for 4 h, and sulfonation at 85°C. Figure 3 shows that the capacity of the ion-exchange fibers increases first and decreases later with the prolongation of the sulfonation time; the exchange capacity attains its biggest value with better mechanical properties when the sulfonation time is 2 h or so. At less than 2 h, ion-exchange fibers with better mechanical properties but a lower exchange capacity are obtained. However, if the sulfonation time is too long, they slag and even crack; the compatibilization is bad between the sheath and core of the fibers, so the strength of the fibers decreases.

Effect of the sulfonation temperature on the ion-exchange capacity of the fibers

Exchange fibers with different sulfonation temperatures were obtained under the following conditions: 6 g of the fiber, 5 g of $(\text{CH}_2\text{O})_n$, 150 mL of H_2SO_4 (98%), 25 mL of CH_3COOH , 7.5 mL of $\text{C}_2\text{H}_4\text{Cl}_2$, crosslinking at 60°C for 4 h, and sulfonation for 2 h. Figure 4 shows that the reaction temperature has a great impact on the ion-exchange capacity of the fibers mainly because the reaction will strengthen and expand inside the fiber in accordance with the temperature increasing; various side reactions will also increase when the reaction is strengthening in the sulfonated bodies. Thus, the fibers are harmed greatly, in that the strength of the fibers is reduced, but the surface of the fibers is shed easily. Therefore, we gain ion-exchange fibers with better mechanical properties and a higher exchange capacity when the temperature is 81°C.

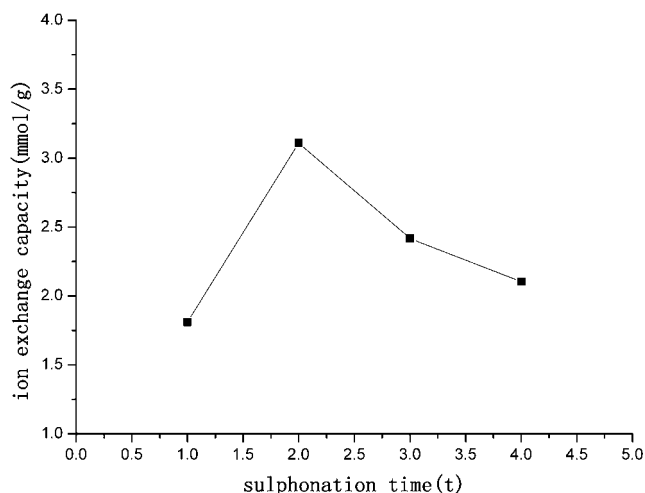


Figure 3 Effect of the sulfonation time on the capacity of the ion-exchange fiber.

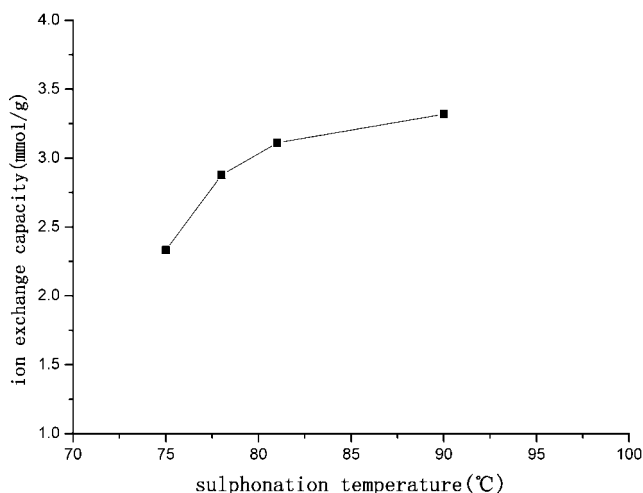


Figure 4 Effect of the sulfonation temperature on the capacity of the ion-exchange fiber.

Effect of the concentration of paraformaldehyde on the capacity of the ion-exchange fibers in the reaction bodies

Exchange fibers with different concentrations of paraformaldehyde were obtained under the following conditions: 6 g of the fiber, 150 mL of H_2SO_4 (98%), 25 mL of CH_3COOH , 7.5 mL of $C_2H_4Cl_2$, crosslinking at $60^\circ C$ for 4 h, and sulfonation at $85^\circ C$ for 2 h. Figure 5 shows that the capacity of the ion-exchange fibers increases first and decreases later with the increment of the paraformaldehyde; the exchange capacity attains its biggest value when the weight of paraformaldehyde is 5 g. The dose of paraformaldehyde has a great impact on the ion-exchange capacity of the fibers: a small dose of paraformaldehyde cannot make the fiber gain an efficient crosslinkage degree, and this makes the sulfonated

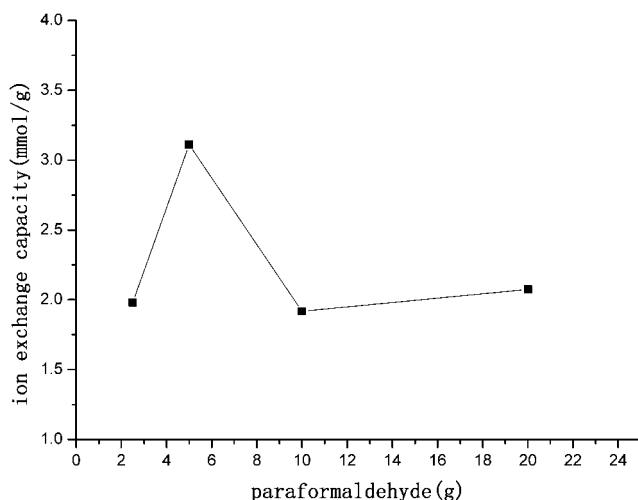


Figure 5 Effect of the dose of paraformaldehyde on the capacity of the ion-exchange fiber.

PS dissolve in water. Thus, both the sulfonation efficiency and ion-exchange capacity are reduced. An excessive dose leads to a crosslinkage degree that is too high; it not only takes up the live position of the benzene wreath but also makes the layer of fibers on the surface too tight, and this reduces the live positions in the sulfonation reaction to make the ion-exchange capacity decrease.

Effect of the concentration of glacial acetic acid on the capacity of the ion-exchange fiber in the reaction bodies

Exchange fibers with different concentrations of glacial acetic acid were obtained under the following conditions: 6 g of the fiber, 5 g of $(CH_2O)_n$, 150 mL of H_2SO_4 (98%), 7.5 mL of $C_2H_4Cl_2$, crosslinking at $60^\circ C$ for 4 h, and sulfonation at $85^\circ C$ for 2 h. Figure 6 shows that the capacity of the ion-exchange fibers increases first and decreases later with the increment of glacial acetic acid; the exchange capacity attains its biggest value with better mechanical properties when the dose of glacial acetic acid is 25 mL or so. With less or more than 25 mL, the capacity of the ion-exchange fibers decreases correspondingly, especially with less than 25 mL; the morphology of the fibers is so much worse that a crack appears on the sheath. With the addition of a small amount of acetic acid to the reaction bodies, it invades the amorphous phase of PS to extend the molecule crevice mutually as small organic molecules while reducing the concentration of sulfuric acid; this can promote the utilization ratio of paraformaldehyde. At the same time, an efficient crosslinkage degree can make the benzene wreath of the sheath connect together to improve the strength of the fibers.

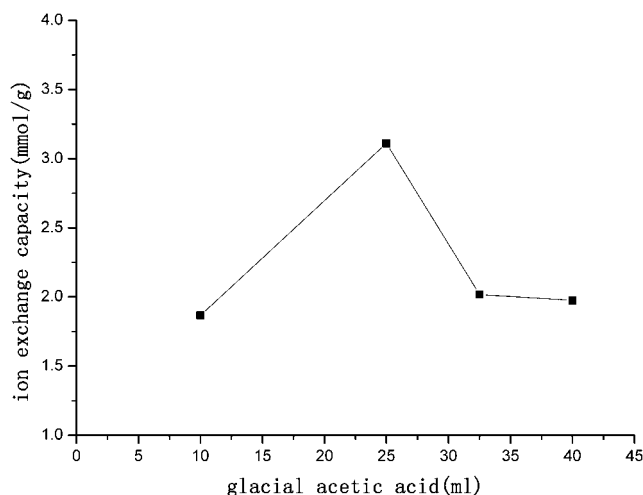


Figure 6 Effect of the dose of glacial acetic acid on the capacity of the ion-exchange fiber in the reaction bodies.

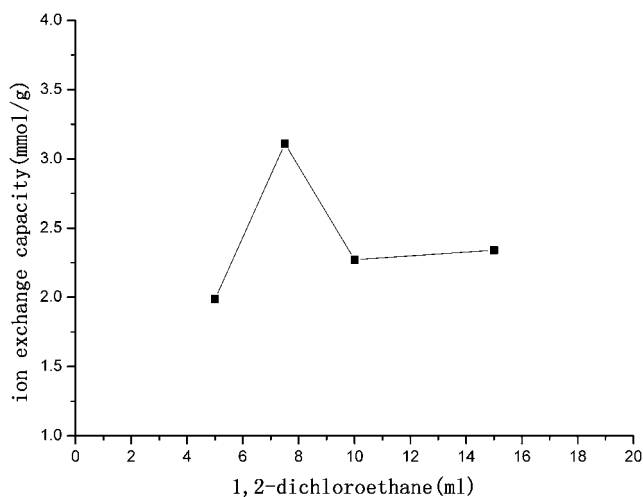


Figure 7 Effect of the dose of 1,2-dichloroethane on the capacity of the ion-exchange fiber in the reaction bodies.

Effect of the concentration of 1,2-dichloroethane on the capacity of the ion-exchange fibers in the reaction bodies

Exchange fibers with different concentrations of 1,2-dichloroethane were obtained under the following conditions: 6 g of the fiber, 5 g of $(\text{CH}_2\text{O})_n$, 150 mL of H_2SO_4 (98%), 25 mL of CH_3COOH , crosslinking at 60°C for 4 h, and sulfonation at 85°C for 2 h. Figure 7 shows that the capacity of the ion-exchange fibers increases first and decreases later with the increment of 1,2-dichloroethane; the exchange capacity attains its biggest value when the dose of 1,2-dichloroethane is 7.5 mL or so. When the dose is lower or higher than 7.5 mL, the capacity of the ion-exchange fibers decreases. Especially with more than 7.5 mL, the sheath of the fibers is damaged seriously because it is subjected to the influence of the swelling agent; it slags and even cracks, the compatibilization is bad between the sheath and core of the fibers, and the strength of the fibers decreases. However, with less than 7.5 mL, ion-exchange fibers with better mechanical properties but a lower exchange capacity are obtained. Therefore, we obtain ion-exchange fibers with better mechanical properties and a higher exchange capacity when the dose of 1,2-dichloroethane is 7.5 mL.

Structure of the sheath-core bicomponent composite ion-exchange fibers

Fourier transform infrared (FTIR) analysis

FTIR spectrophotometry diagrams of all the fibers are depicted in Figure 8. Figure 8(a-c) shows the FTIR curve of the sheath-core bicomponent composite fiber, the FTIR curve of the sheath-core bicomponent composite fiber with crosslinkage at 60°C for 4 h, and the FTIR curve of the sheath-core bicompo-

nent composite fiber with sulfonation at 85°C for 2 h, respectively. It is clear from Figure 8 that the broad and strong peak in the range of $1118\text{--}1221\text{ cm}^{-1}$ is the absorption peak of the sulfonic groups; it is explained that the fibers are sulfonated by sulfuric acids in the reaction. The absorption peaks situated at 695 and 755 cm^{-1} in infrared spectroscopy nearly disappear and change into the single peak at 834 cm^{-1} ; the fingerprint peak, which characterizes the substituted position of the benzene wreath, changes into a single peak from double peaks,¹⁹ and this shows that the *para*-substituted structure of the benzene wreath replaces the monosubstituted structure in the sulfonation reaction. That is, the *para*-benzene wreath is connected to sulfonic groups only because of the big steric hindrance of the *ortho*-benzene wreath. The absorption peak of styrene at 1026 cm^{-1} splits into double peaks at 1028 and 1001 cm^{-1} with the increment of the sulfonation degree because the in-plane rupture vibration of C—H in the benzene wreath is subjected to the influence of the symmetrical stretching vibration of S=O. The polar groups connected to PS in the sulfonation reaction make the fibers hydrophilic, and the water absorbency of the products is higher with the increment of the sulfonation degree. As shown in the diagram, a stronger and broader absorption peak appears at 3400 cm^{-1} because the interaction between the hydrogen bond and oxygen atom of the sulfonic groups in the water molecules makes the stretching vibration absorption peak of —OH displace in the direction of a low frequency.²⁰

Differential scanning calorimetry (DSC) analysis

DSC thermograms of all the fibers are depicted in Figure 9. Figure 9(a-c) shows the DSC curve of the sheath-core bicomponent composite fiber, the DSC curve of the sheath-core bicomponent composite

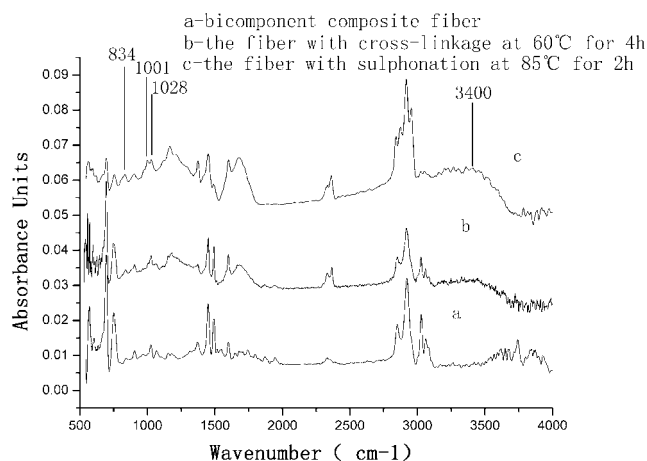


Figure 8 Infrared spectroscopy of the fibers.

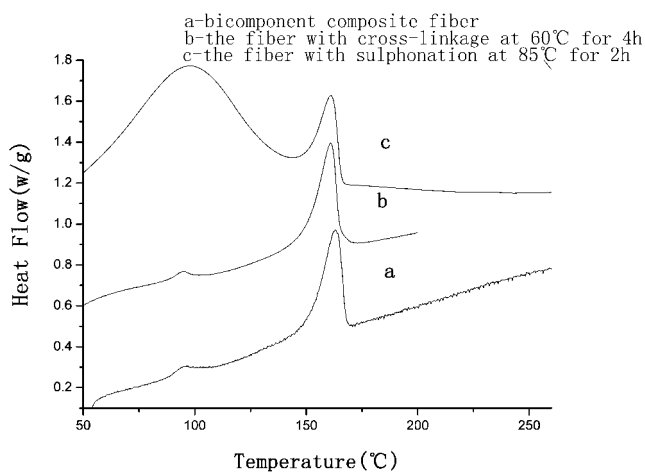


Figure 9 DSC diagrams of the fibers.

fiber with crosslinkage at 60°C for 4 h, and the DSC curve of the sheath–core bicomponent composite fiber with sulfonation at 85°C for 2 h, respectively. In a comparison of Figure 9(b) with Figure 9(a), the glass-transition temperature of PS shows no variation, and this shows that the fiber is not sulfonated but is crosslinked in the crosslinkage reaction. In a comparison of Figure 9(c) with Figure 9(b), a very strong peak appears from 47.31 to 142.37°C because the fibers are connected with very strong polar sulfonic groups to strengthen the hygroscopicity of the fibers. Moreover, the melting point of PP shows no variation, and this shows that the chemical stability of modified PP in the core of the fiber is very good and that it plays the role of skeleton support.

Function of the sheath–core bicomponent composite ion-exchange fibers

Water absorptivity of the fibers

The water absorptivity of a fiber is an important indicator of an ion-exchange fiber; its height is manifested as the utilization ratio of functional groups inside the fiber. Generally, the water absorptivity of fibers is stronger and the exchange capacity is higher with the increment of the sulfonation degree.²¹ The ion-exchange fibers were made from modified PS and modified PP in this experiment, C–H and C–C existing covalently only; as a result, the water absorptivity of the as-spun fibers was very bad. However, the fibers were connected with sulfonic groups with high hydrophilicity in the sulfonation reaction, so the fibers obtained were hydrophilic. Figure 10 shows the effect of the sulfonation temperature on the ion-exchange capacity of the fibers and water absorptivity; Figure 10(a) shows the variation of the ion-exchange capacity, and Figure 10(b) shows the variation of the water absorptivity. As we can see from Figure 10, both the ion-exchange capacity and

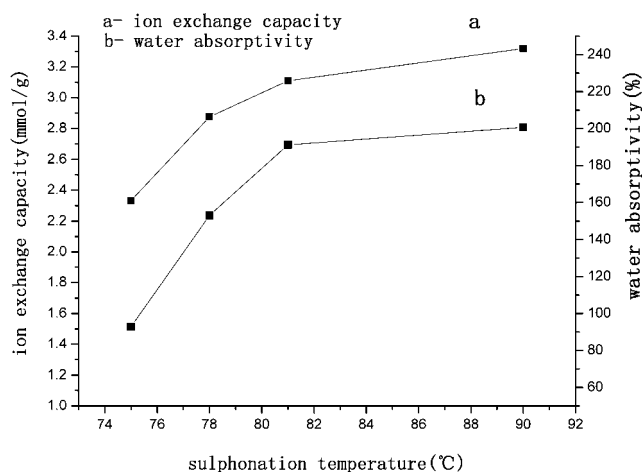


Figure 10 Effects of the sulfonation temperature on the capacity of the ion-exchange fiber and water absorptivity.

water absorptivity increase in accordance with the increment of the temperature, and the water absorptivity is in direct proportion to the ion-exchange capacity mostly. In the experiment, the water absorptivity of the fibers reached 200%, and this shows that the fiber can make good use of exchange groups to promote the utilization of function groups.

Acid and alkali corrosion resistance

After the ion-exchange fibers were used and regenerated 10 times, they were soaked in high concentrations of acid and alkali at room temperature, and the results are listed in Table I.

The results in Table I show that the exchange capacity varies a little, and some of the measurement values go up. It is likely that parts of groups of the inner fiber hydrolyze through the soaping treatment, and the morphology and strength of the fibers show no obvious variation; this shows that the strong acid and strong alkali had little influence on the fibers obtained.

Regeneration performance

Used as ion-exchange materials, ion-exchange fibers have higher practicability because of their many

TABLE I
Chemical Stability of the Bicomponent Composite Ion-Exchange Fibers

Category of soaking liquid	H ₂ SO ₄	HCl	NaOH
Concentration	5M	5M	2M
Exchange capacity before soaking (mmol/g)	3.110	3.110	3.110
Exchange capacity after soaking (mmol/g)	3.050	3.075	3.175
Exchange capacity variety	–1.9%	–1.1%	2.1%

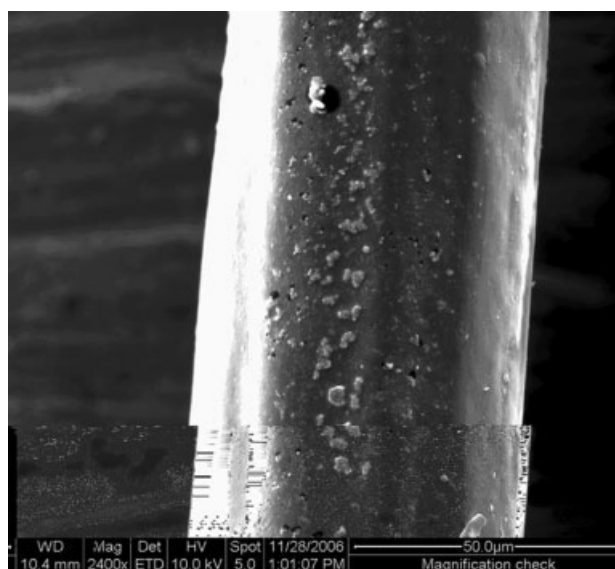


Figure 11 SEM image of sorption and desorption circulation (five times).

sorption and desorption circulations. To assess a material's stability, its adsorption ability and morphology variation are investigated through some sorption and desorption circulations. For this, we performed the experiment of sorption and desorption circulations 10 times, and the exchange capacity was measured; it decreased to 2.875 mmol/g from 3.110 mmol/g, and the repetition utilization rate of the fibers was 92.4%. Figures 11 and 12 present scanning electron microscopy (SEM) photographs (magnified 2400 \times) of sorption and desorption circulations (5 times and 10 times, respectively). The SEM results show that the fibers have no obvious variety, and

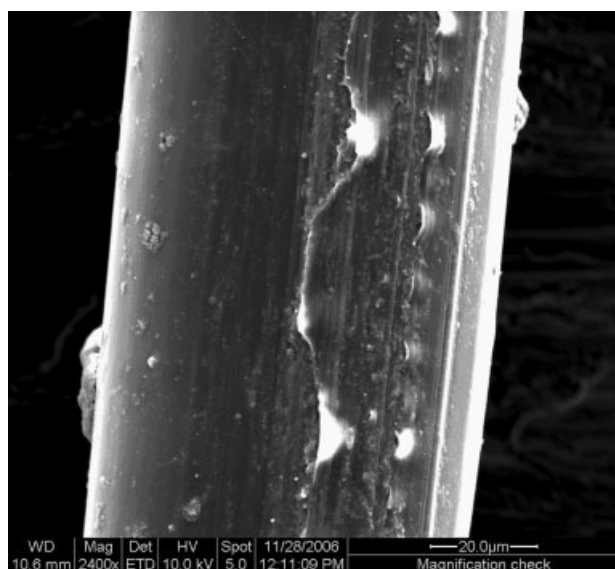


Figure 12 SEM image of sorption and desorption circulation (10 times).

TABLE II
Mechanical Properties of the Bicomponent Composite Ion-Exchange Fibers

Fiber category	Breaking elongation rate (%)	Fracture strength (cN/dtex)
Original fibers	20.56	1.199
Fibers obtained	7.60	0.666

crushing, crack, deformation, and so on do not appear; this shows that the fibers retain a good morphology.

Strength of the fibers

The obtained fibers were measured to determine the breaking elongation rate and fracture strength; the results are listed in Table II.

The results in Table II show that both the breaking elongation rate and fracture strength decrease significantly after the fibers are crosslinked and sulfonated, respectively, and this shows that the sulfonation reaction does great harm to the fibers. Compared with that of the original fibers, the fracture strength decreases about 44.5%, but the core of the fibers varies little and plays well the role of skeleton support to give the obtained fibers practical value.

Micromorphology of the fibers

The ion-exchange fiber is a new type of chemical adsorption material; a great deal of experimental data shows that the aggregation structure and morphology have a great influence on the mechani-

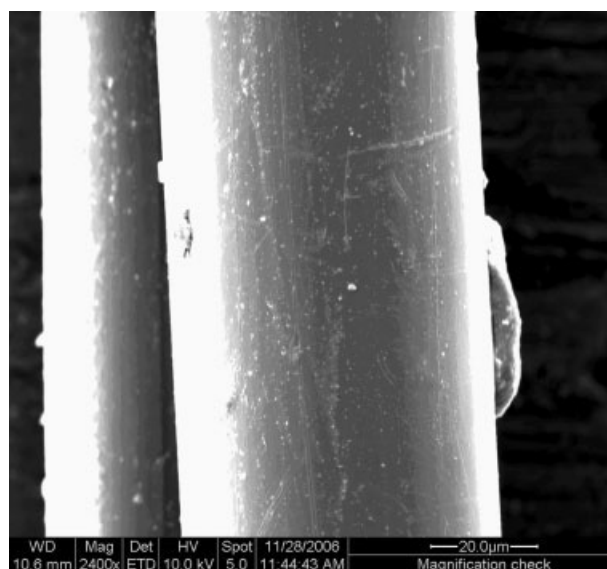


Figure 13 SEM image of the sheath-core bicomponent composite fiber.

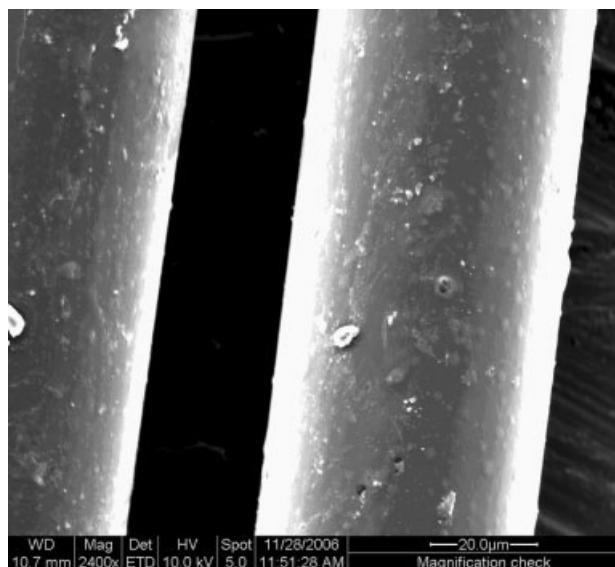


Figure 14 SEM image of the fiber crosslinked for 4 h.

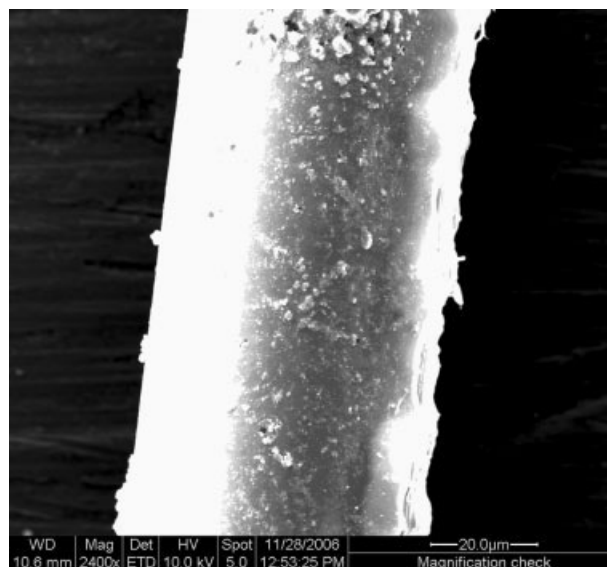


Figure 16 SEM image of the fiber exchanged with sodium.

cal strength, adsorption dynamics, and so forth. Figures 13–16 present SEM photographs (magnified 2400 \times) of the sheath–core bicomponent composite fibers, fibers crosslinked for 4 h, fibers sulfonated for 2 h, and fibers exchanged with sodium, respectively. A comparison of Figure 14 with Figure 13 shows that the crosslinkage fibers have very shallow scratches and bulges on the surface, their morphology is not different from that of the original fiber, and the obtained fibers retain good mechanical function. A comparison of Figure 15 with Figure 13 shows that the fiber morphology changes greatly: Its surface is much rougher than that of the original fiber, obvious scratches appear, the trenches on the

surface broaden and deepen, and the fiber diameter increases too. The aforementioned phenomenon shows that parts of the fibers are dissolved in the reaction, so it damages the structure of the fibers; it is shown that the sulfonation reaction has an important part in the reaction, which impacts on the mechanical function greatly. A comparison of Figure 16 with Figure 13 shows that rough spots appear on the surface of the fibers, and crushing, crack, deformation, and so on do not appear; this shows that the fibers have good stability in use and practical value.

CONCLUSIONS

The optimal technology for making sheath–core bicomponent composite ion-exchange fibers with better mechanical properties and a higher exchange capacity is as follows: 6 g of the fiber, 5 g of $(\text{CH}_2\text{O})_m$, 150 mL of H_2SO_4 (98%), 25 mL of CH_3COOH , 7.5 mL of $\text{C}_2\text{H}_4\text{Cl}_2$, crosslinking at 60 $^\circ\text{C}$ for 4 h, and sulfonation at 85 $^\circ\text{C}$ for 2 h. In particular, it is very important to control the crosslinkage temperature and the sulfonation temperature. The analysis of FTIR and DSC showed that the fibers were connected with very strong polar sulfonic groups. The sheath–core bicomponent composite ion-exchange fibers had a good adsorption property for Na^+ in aqueous solutions, and their static maximal exchange capacity could reach 3.110 mmol/g; no residues were left in the exchange column when the fibers were used several times. The fracture strength decreased about 44.5% from 1.199 to 0.666 cN/dtex, but the core of the fibers varied little, so the fibers obtained had practical value. The fibers had high hydrophilicity, good regeneration performance, and

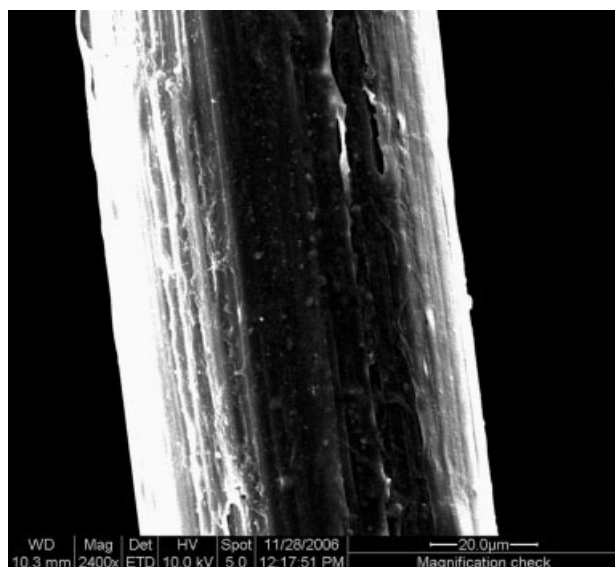


Figure 15 SEM image of the fiber sulfonated for 2 h.

good acid and alkali corrosion resistance; the water absorptivity of the fibers reached 200%, the repetition utilization rate of the fibers was 92.4% with 10 sorption and desorption circulations, the fiber exchange capacity varied little, and the SEM results showed that crushing, crack, deformation, and so forth did not appear for the fibers.

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