

Preparation and Characterization of PVC/PS Composite Cation Exchange Fibers and Their Adsorption Properties on Aniline

Zhi-Jia Ding,^{1,2} Lu Qi,¹ Jian-Zhong Ye¹

¹Research Institute of Biologic and Spinning Materials of Tianjin Polytechnic University, The Key Lab of Functional and Modified Fiber of Tianjin, Tianjin Polytechnic University, 63 Chenglin Road, Hedong District, Tianjin 300160, China

²Bosideng International Holding Co., Ltd, Bosiedng Industrial Zone, Changshu City, Jiangsu Province 215532, China

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ABSTRACT: Based on the composite fibers made from polyvinylchloride (PVC) and polystyrene (PS), the composite fibers obtained were further crosslinked and sulfonated with 50% oleum to produce the acidic cation ion exchange fibers. The optimal technology of the fibers obtained were discussed, the structures of the fibers thus obtained were investigated by using Fourier transform infrared (FTIR) spectrophotometry, thermogravimetry analysis (TG), differential thermogravimetry analysis (DTG), and scanning electron microscope (SEM) etc. Their properties were measured using chemical titration, filament mightiness instrument, etc. The absorption kinetics and the main factors affecting absorption capacity on aniline were studied, and their regenerating properties were

probed. The results indicated that the cation exchange fibers with better mechanical property and higher exchange capability were obtained. The fibers had bigger hydrophilicity, better ability of acid, and alkali corrosion resistance, so they had better practical application value. This type of ion exchange fibers had faster absorption property and better working stability to aniline and could be used repeatedly, so they were applied for treatment of waste water containing aniline with a promising prospect. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1914–1923, 2010

Key words: composite fibers; crosslinking; sulfonation; ion exchange; absorption

INTRODUCTION

Ion exchange fiber had bigger specific surface area, faster rate of exchange and elution, higher regeneration performance, lower consumption, and smaller fluid resistance than that of ion exchange resin.^{1–3} It could be applied in many kinds of forms, such as fiber, cloth, nonwoven, etc, and could be applied to various of exchange processes.^{4,5} The manufacturing methods and applications about ion exchange fibers had some development since recent 20 years.^{6–10} However, the existing ion exchange fibers had some defects, such as the lower capacity, poor fracture strength, lower efficiency in the usage progress, and new pollution, etc.^{11–16} Their performance could not play the role adequately and could not be suitable for the needs in the practical application. Only few studies have been reported on the ion exchange fibers of polyvinyl chloride (PVC). In this article, based on the self-made composite fibers with PVC and polystyrene (PS), we gained the cation exchange fibers with better mechanical property and higher exchange capability. The ion exchange

fiber obtained had some advantages, such as lower manufacture cost, simple process, good usage of the existing facilities, etc, so it was a new type of ion exchange fiber method with promising prospects. The treatment of the industrial waste water containing aniline needs attention as an environmental problem. The literature hitherto had some treatment methods for aniline at home and abroad, such as biochemical oxidation, extraction, incineration, electrolysis, ultrasonic degradation and membrane filtration, etc.^{17–21} However, the studies on the treatment for aniline by using the ion exchange fibers had been reported very less. The ion exchange fibers were suitable for the adsorption separation of organic pollutants and the selective concentration of trace element because of their faster exchange and elution rate, so they were applied as higher efficient adsorption separation materials.^{22–26} In the article, the treatment for aniline by using the ion exchange fibers was carried out. The aim is that it consequently could establish certain foundation for their applications in correlated fields.

EXPERIMENTAL

Materials

Self-made original PVC/PS composite fibers. The diameter of the composite fibers is 5–15 dtex, the

Correspondence to: L. Qi (dingzhijia611@sina.com).

TABLE I
The Concentration of the Standard Solution of Aniline

	1	2	3	4	5
C_0 (mg/L)	42.44	72.20	114.50	159.20	198.70
A	0.135	0.190	0.272	0.378	0.465

Fitting equation $(C) = -17.6704 + 469.0223A$; coefficient $(R) = 0.9989$.

fracture strength is about 1.426 cN/dtex, and the elongation at break is about 166.82%, respectively. The proportion of PVC and PS in the composite is 100/15. PVC was provided from Shanghai Petro-Chemical Co. (Shanghai, China). Its characteristics commonly used for fiber spinning were as follows: number-average molecular weight = 8.2×10^4 , Melt index (MI) = 45.61 g/10 min (200°C), density = 1.38 g/cm³. PS was provided by Shanghai Petro-Chemical Co., China. Its characteristics commonly used for fiber spinning were as follows: number-average molecular weight = 1.1×10^5 , MI = 4.32 g/10 min (200°C), and density = 1.08 g/cm³. POM was purchased from Tianjin Bodi Chemical Co.,(China). Glacial acetic acid (HAC) was purchased from Tianjin Huadong Reagent Plant (China). Oleum (50%) was purchased from Shanghai Zhenxin No.2 Chemical Plant Co., (China). Aniline was purchased from Tianjin Guangfu Fine Chemical Research Institute (China). All other chemicals concerned are commercially available products of reagent and used as received.

The preparation of PVC/PS composite ion exchange fibers

Crosslinking

The self-made composite fibers were cut into staples with 5 cm, and the staple were cleaned by detergent and methanol, respectively, so as to remove oils and impurities on the surfaces of fibers, then they were dried adequately in oven. Some amounts of original fibers were crosslinked at 40–80°C for 1–5 h with addition of paraformaldehyde (POM), 98% sulphuric acid (H₂SO₄), and HAC, respectively.

Sulfonation

With addition of the mixed swelling agent (the equivalent volume ratio of 1,2-dichloroethane to isopropanol) and 50% oleum, respectively, the cross-linking products were sulfonated for 1–5 h at constant temperatures of 60–100°C, then the sulfonation products were diluted with different density sulphuric acid, and washed repeatedly using deionized water until the flushing water showed neutral, dried in the air naturally to gain the acidic cation exchange fibers.

Measurement of the static capacity on aniline

The values A of ultraviolet absorption on different concentration aniline from Table I were measured at about 300 nm by using ultraviolet spectrophotometer. The calibration curve between C and A is fitted from data in Table I, which is shown in Figure 1.

Measurement of the capacity on different concentration aniline

0.1 g dried fibers were put into 250 mL taper bottle with addition of the accurate 100 mL aniline solution (C_0 mg/L) at the temperature of 283K for 4 h, respectively. The equilibrium concentration C_e (mg/L) of aniline was measured by using ultraviolet spectrophotometer, and adsorption equilibrium capacity was calculated using the following equation:

$$Q_e = (C_0 - C_e)V/W$$

where Q_e is adsorption equilibrium capacity of the fiber (mg/g), C_0 is the concentration of aniline before adsorption (mg/L), C_e is the concentration of aniline after adsorption (mg/L), V is the solution volume (L), W is the weight of the fibers (g).

Measurement of adsorption kinetics for aniline

Dried fibers (0.2 g) were put into 250 mL taper bottle with addition of 100 mL aniline solution (198.70 and 301.50 mg/L) at the temperature of 288 K, respectively. The concentration C_t (mg/L) of aniline at the certain time was measured by using ultraviolet spectrophotometer, the instantaneous adsorption capacity was calculated using the following equation:

$$Q_t = (C_0 - C_t)V/W$$

where Q_t is adsorption capacity at t time (mg/g), C_t is the concentration of aniline at t time (mg/L),

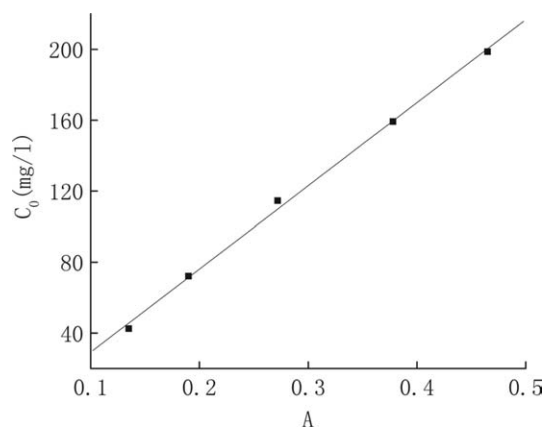


Figure 1 The standard work curve of aniline.

V is the solution volume (L), W is the weight of the fibers (g).

Measurement of 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:

$$\text{Water absorption capacity (\%)} = \frac{(W_1 - W_0)}{W_0} \times 100\% \quad (1)$$

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

Analyses of chemistry stability

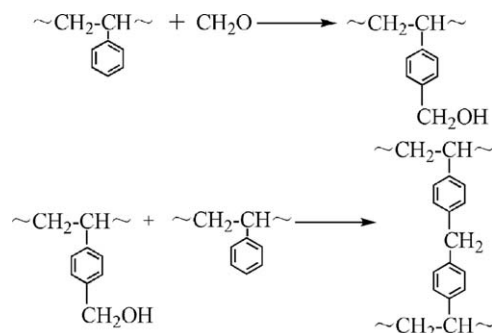
Three parts of the samples of composite ion exchange fibers were soaked in 5 mol/L H_2SO_4 , 5 mol/L HCl, and 2 mol/L NaOH for 24 h at room temperature, respectively, and washed using deionized water until the flushing water showed neutral, then, soaked in 0.5 mol/L HCl diluted solution to regenerate, and washed the fibers repeatedly using deionized water, the saturated ion exchange capacity of the fibers was measured using the aforementioned method.

Measurement of the strength of the fibers

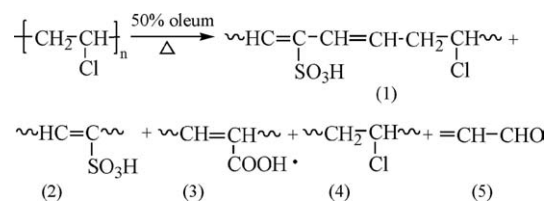
After the fiber samples were sulfonated, breaking elongation rate and fracture strength were determined using filament mightiness instrument (PC/LLY-06) with the descendent velocity of 5 mm/min, and prestrain was 200 g.

FTIR measurements

The obtained composite ion exchange fibers were characterized with a VECTOR-22 Fourier transform infrared (FTIR) spectrometer.



Scheme 1 The crosslinking reaction route.



Scheme 2 The sulfonation reaction formula.

Thermogravimetry measurements

For the thermogravimetry experiment, a NETZSCH TG-209 thermogravimetric analyzer equipped with a cooler was used under a nitrogen atmosphere. All the samples were heated from 20 to 600°C at 10°C/min.

Micromorphology observation

The fibers obtained in different conditions were goldsputtered, and the morphology and structure on the surface of the fibers were observed with a Quanta 200 scanning electron microscope.

RESULTS AND DISCUSSION

Reaction mechanism

Crosslinking mechanism

The crosslinking reaction formula is as follows (Scheme 1):

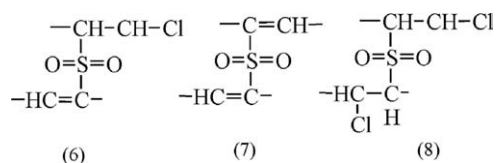
The crosslinking reaction can be enhanced by increasing the acid concentration, but when the acid concentration is too high, some side effects occur, such as sulfonation etc.

Sulfonation mechanism

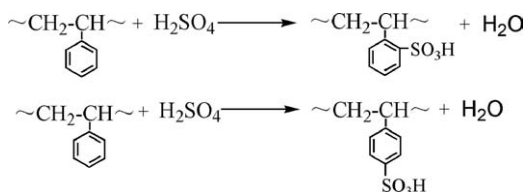
In the experiment, oleum was adopted as sulfonating agent, and the sulfonation reaction formula is as follows (Scheme 2):

The structures are generated between oxidation products and sulfonation products by the crosslinking as follows (Scheme 3):

The aforesaid reaction mechanism shows that the main Chain of PVC/PS fibers remove HCl to form the structure (1), and the new gas HCl accelerate the speed of the removal HCl again. The double bond



Scheme 3 The generated crosslinking structures between oxidation and sulfonation products.



Scheme 4 The other sulfonation reaction formula.

C=C in the structure (1) is oxidized to form carboxyl and aldehyde, then, the structure of (2)–(5) are generated. It is shown that the fibers have both strong acid sulfonic group and weak acid carboxylic group after they are sulfonated, that is demonstrated from FTIR analysis of Figure 11, too. Furthermore, the capacity of the ion exchange fibers decreases because of the formation of sulfone group crosslinking structures (6)–(8).

In addition, the other sulfonation reaction may occur, and their reaction formula is as follows (Scheme 4):

The affected factors of preparing PVC/PS composite ion exchange fibers

The affected factors of crosslinking

Effect of the content of POM on fracture strength (Fs) and ion exchange capacities (Q) of the PVC/PS fibers. Figure 2 shows that the variation of capacity is a little. The fibers get the efficient crosslinkage degree with the increment of content of POM, thus the fracture strength is improved. The excessive POM lead to much lower crosslinkage degree because the substituted alkyl are donating electron groups, so the fracture strength decreases contrarily. However, if the fibers were crosslinked effectively, POM took up the live position of the benzene ring, and the action reduced the live positions in the sulfonation reaction so as to make the ion exchange capacity decrease.

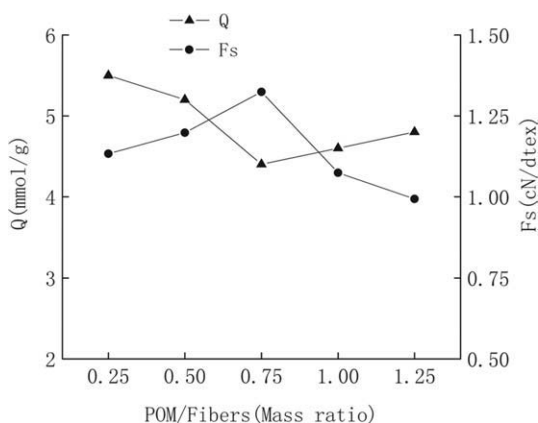


Figure 2 Effect of the content of POM on fracture strength (Fs) and ion exchange capacities (Q) of the PVC/PS fibers.

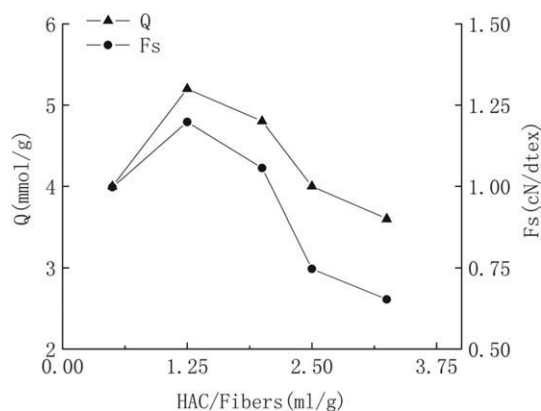


Figure 3 Effect of the content of HAC on Fs and Q of the PVC/PS fibers.

Effect of the content of HAC on Fs and Q of the PVC/PS fibers. Figure 3 shows that the trend of Q and Fs increases firstly and decreases later with the increment of HAC. Q can be decreased owing to the formation of sulfone group crosslinking structures while the content of HAC is lower, and it can be also decreased owing to the decreasing oxidizability of sulfonating agent while the content of HAC is excessive. The proper content of HAC can improve the crosslinking efficiency, and Fs is improved correspondingly. But the crosslinking efficiency decreases because of the lower activity of alkylation reaction while the content of HAC is excessive.

Effect of the crosslinking temperature on Fs and Q of the PVC/PS fibers. The crosslinking temperature has a great impact on Fs. Friedel-Crafts reaction is an exothermic reaction, so the higher temperature is not suitable for the reaction. In addition, the higher temperature can help to sulfonation reaction. Therefore, the two aforesaid factors cause the lower crosslinking efficiency to make Fs decreased greatly.

Effect of the crosslinking time on Fs and Q of the PVC/PS fibers. The trend of Fs always increases with the

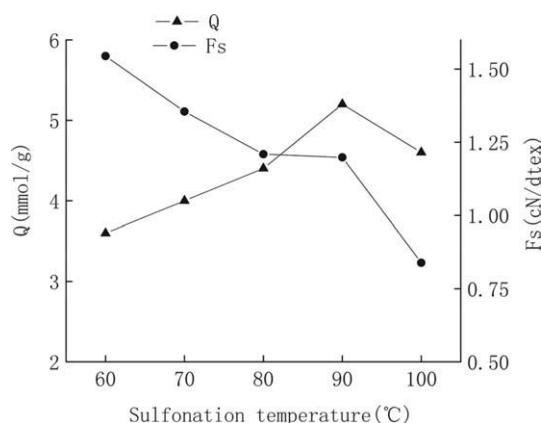


Figure 4 Effect of the sulfonation temperature on Fs and Q of the PVC/PS fibers.

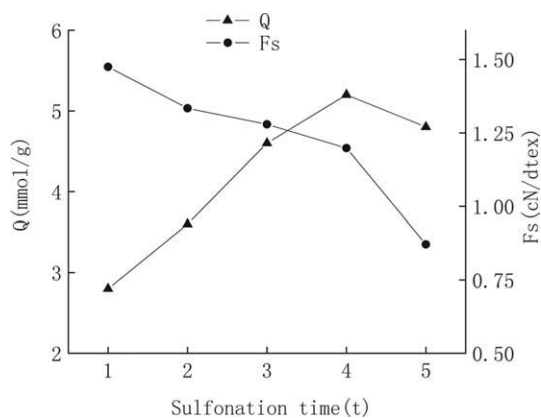


Figure 5 Effect of the sulfonation time on Fs and Q of the PVC/PS fibers.

increment of the crosslinking time, especially the variation is obvious before 3 h. The reason is that the crosslinking efficiency is not sufficient owing to the saturated benzene ring until the fibers are crosslinked for 3 h.

The affected factors of sulfonation

Effect of the sulfonation temperature on Fs and Q of the PVC/PS fibers. As showed from Figure 4, the temperature has a great impact on the sulfonation reaction. when the temperature exceeds 90°C, Q can be decreased owing to the formation of sulfone group crosslinking structures because the side reaction is enhanced. On the other hand, the strong oxidizability of oleum can damage the fibers at the higher temperature, so Fs is decreased because of the chain scission.

Effect of the sulfonation time on Fs and Q of the PVC/PS fibers. As showed from Figure 5, the sulfonation time has a great impact on Q and Fs. Fs decrease while the sulfonation time exceeds 4 h. The reason is that the side reaction is enhanced with the prolonged time, and the strong oxidizability of oleum can damage to fibers at the higher temperature, so Fs is decreased, too. While the sulfonation time exceeds 4 h, the variation of Q is a little because the sulfonation reaction is almost stopped.

Effect of the swelling agent on Fs and Q of the PVC/PS fibers. The swelling agent DCE and IPA were added in the sulfonation reaction, and they can extend molecule crevice mutually, so the action could promote the sulfonation efficiency, and Q is increased. However, while the content of swelling agent is excessive, the fibers are damaged seriously because they are subjected to the influence of swelling agent.

Effect of the sulfonating agent on Fs and Q of the PVC/PS fibers. When the content of sulfonating agent is excessive, the variation of Q is a little but Fs decreases greatly. The reason is that the oxidizability of sulfonating agent is enhanced owing to the higher

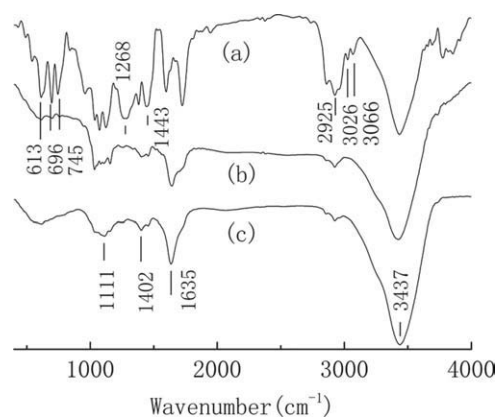


Figure 6 FTIR spectra of (a) the PVC/PS fibers, (b) the crosslinked fibers, and (c) the sulfonated fibers.

concentration of it, Q can be decreased because of the formation of sulfone group crosslinking structures. On the other hand, the strong oxidizability of oleum can damage to fibers at the higher temperature.

The structure of PVC/PS composite ion exchange fibers

FTIR analysis

FTIR spectrophotometry diagrams of extracted samples are depicted in Figure 6. As shown in the Figure 6(a), the stretching vibration bonding (C—C1) is situated at 613 and 696 cm^{-1} in the original PVC fibers. The characteristic absorption peak of C—H out-of-plane bending vibration in the monosubstituted benzene ring is nearly situated at 745 cm^{-1} , and the stretching vibration bonding (C—H) of aromatic ring is situated at 3026 and 3066 cm^{-1} . The stretching vibration peaks of methylene (—CH₂—) are situated at 1443 and 2925 cm^{-1} . In a comparison of Figure 6(b) with Figure 6(a), the infrared spectrum of crosslinking fibers has no obvious changes, and just the vibration peak of benzene ring situated

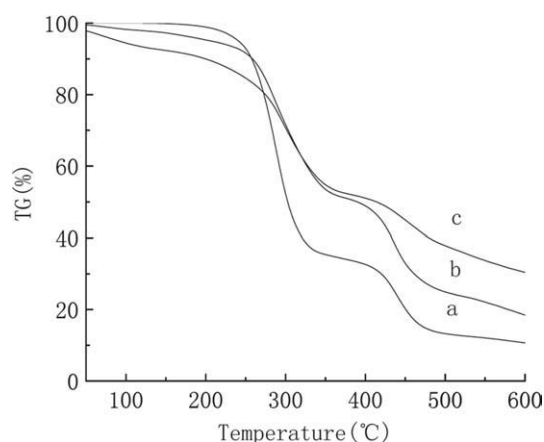


Figure 7 TG diagrams of (a) the PVC/PS fibers, (b) the crosslinked fibers, and (c) the sulfonated fibers.

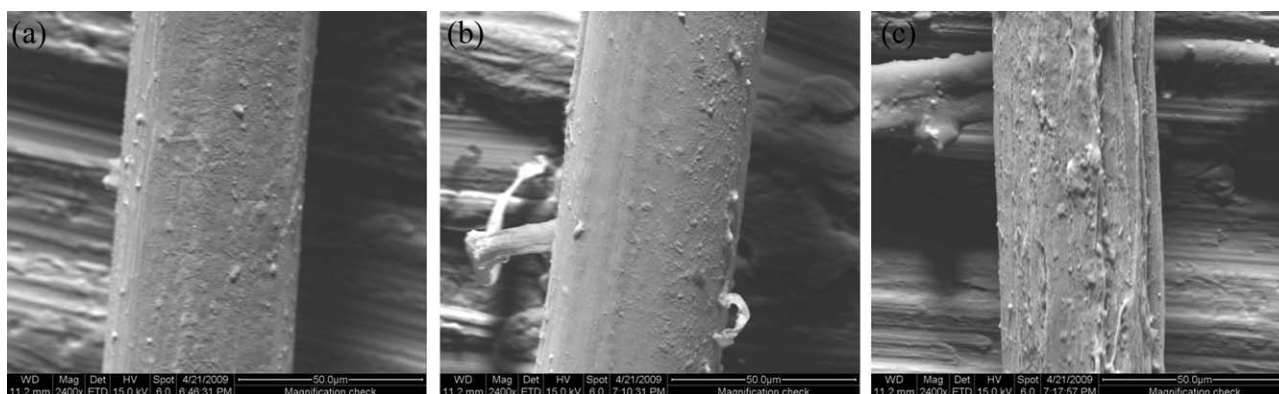
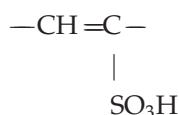
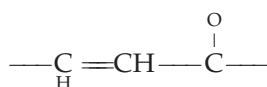


Figure 8 SEM image of (a) the original PVC/PS composite fibers, (b) the fibers crosslinked for 3 h, and (c) the fibers sulfonated for 4 h.

at 745 cm^{-1} disappears, it is demonstrated that PS are crosslinked with POM so as to take up substitution position of benzene ring, and the sulfonation is not obvious in the crosslinking reaction. In a comparison of Figure 6(c) with Figure 6(a), the stretching vibration (C—S) in the structure of



is situated at 1111 cm^{-1} . The asymmetrical stretching vibrations (SO_2) of sulfonic group and sulfonyl group are situated at 1402 cm^{-1} . The stretching vibrations (C=O and C=C) in the structure of



are situated at 1635 cm^{-1} , it further demonstrates the aforesaid sulfonation mechanism. The strengthening stretching vibrations (—OH) of carboxylic acid and sulfonic group are situated at 3437 cm^{-1} , the reason is that the interaction between hydrogen bond and oxygen atom of sulfonic groups in water molecules makes the stretching vibration absorption peak of —OH displace in the direction of low frequency.

Thermogravimetry analysis

Thermogravimetry analysis (TG) diagrams of fiber samples are depicted in Figure 7. As shown in

TABLE II
Mechanical Properties of PVC/PS Ion Exchange Fibers

	Fracture strength (cN/dtex)	Elongation at break (%)
Original fibers	1.426	326.82
Ion exchange fibers	1.198	9.12

Figure 7(a), the original PVC/PS fibers are rapidly decomposed when the temperature exceeds 286°C , which is mainly the decomposition of PVC, and their thermo gravimetric loss is 65.76%. Further, when the temperature exceeds 436°C , the diagram has also a mutation, which is mainly the decomposition of PS. In a comparison of Figure 7(b) with Figure 7(a), the TG mutation temperature of crosslinking fibers is ratherish higher than that of the original fibers, and its thermo gravimetric loss is 48.91%, which is obviously lower than that of the original fibers, it is demonstrated that the structure of fibers is compact and the thermal stability is improved. In a comparison of Figure 7(c) with Figure 7(b), the TG mutation temperature of sulfonation fibers is still higher than that of the crosslinking fibers, and its thermogravimetric loss is only 40.18%, it is demonstrated that the thermal stability of sulfonation fibers is still better than that of crosslinking fibers. The reason is that the fibers are grafted on the strong polarity sulfonic groups, then the intermolecular interactions are enhanced.

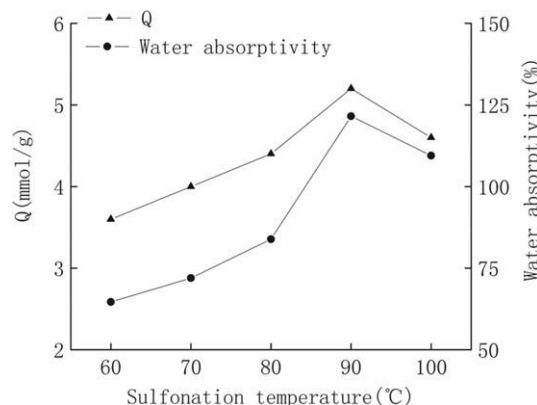


Figure 9 Effects of sulphonation temperature on Q and water absorptivity, respectively.

TABLE III
Chemistry Stability of Fibers

	Q_0 (mmol/g)	Q_1 (mmol/g)	ΔQ (%)
5 mol/L H_2SO_4	5.22	5.04	-3.4
5 mol/L HCl	5.22	5.11	-2.1
2 mol/L NaOH	5.22	5.47	4.8

Micromorphology of the PVC/PS fibers

The ion exchange fibers are new type of chemistry adsorption materials, a great deal of experiment data have shown that their aggregation structure and morphology had great influence on mechanical strength and adsorption dynamics, etc. Compared with Figure 8(a,b) shows that the surfaces of crosslinking fibers are smooth and compact, it is demonstrated that the crosslinking fibers keep good mechanical function. In a comparison of Figure 8(c) with Figure 8(a), the fibers morphology change greatly: Their surfaces are much rougher than original fibers and their specific surface areas increase, which can be suitable for ion exchange reaction, whereas the surfaces have some obvious scratches, and the trenches on the surface broaden and deepen. It is explained that the structure of fibers are damaged, but there is no phenomenon, such as crack and deformation, etc. In the experiment, the fibers obtained could satisfy the requirement of practical application owing to the improvement of mechanical properties (as listed in Table II) in the crosslinking reaction.

The fundamental properties of PVC/PS composite ion exchange fibers

Mechanical properties of the fibers

The fibers obtained were measured to gain the elongation at break and the fracture strength, the results are listed in Table II. The results show that the elongation at break decreases significantly but fracture strength decreases slightly after the fibers are cross-linked and sulfonated, respectively, it is demonstrated that the sulphonation does harm to fibers. However, compared with that of the original fibers, the fracture strength loses only about 16% because of the effective crosslinking, so the fibers obtained still have better practical application value.

Static and dynamic ion exchange capacity

The static ion exchange capacity of the H-type fibers obtained can be steadily kept at 5.0–6.0 mmol/g, and the dynamic ion exchange capacity can be kept at about 3.09 mmol/g, the reason is that the efficiency of dynamic ion exchange reaction is much lower in a short time.

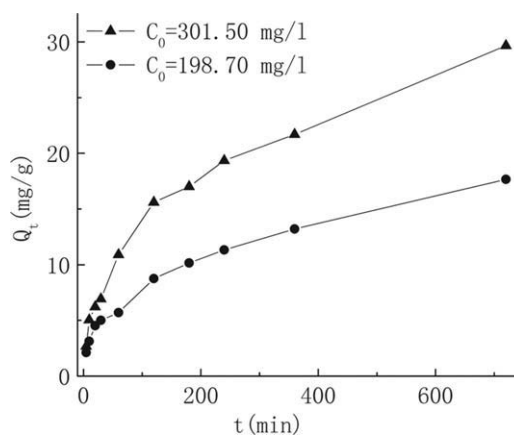


Figure 10 The variation of absorption kinetics for aniline with different concentrations.

Water absorptivity of the fibers

Water absorptivity is an important indicator of the ion exchange fibers, their height manifest the utilization ratio of functional groups inside the fibers. The fibers obtained are connected with sulfonic groups with big hydrophilicity in sulphonation reaction, which makes the fibers hydrophilic. Figure 9 shows that the effect of sulfonation temperature on capacity and water absorptivity, respectively. Both capacity and water absorptivity increase in accordance with the increment of temperature, and water absorptivity is in direct proportion to capacity mostly. In the experiment, the biggest water absorptivity of fibers obtained reaches 121%, it is demonstrated that the fiber may make good use of exchange groups to promote utilization of functional groups.

Ability of acid and alkali corrosion resistance

The ion exchange fibers were soaked in high concentration acid and alkali at room temperature, respectively, and the results are listed in Table III. The

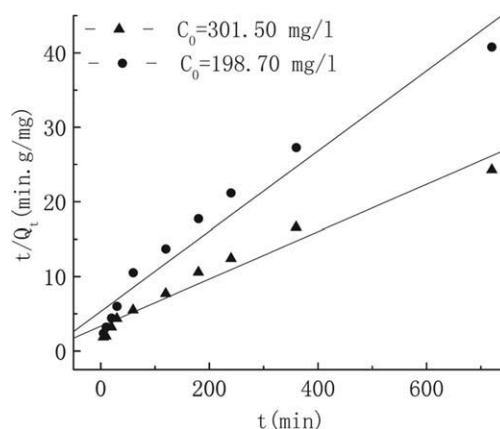


Figure 11 Measurement of adsorption rate coefficient for aniline with different concentrations.

TABLE IV
The Adsorption Kinetics Parameters for Aniline with Different Concentrations

C_0 (mg/L)	Q_e (Calculated values) (mg/g)	Q_e (Measured values) (mg/g)	Error (%)	$k \times 10^{-4}$ (L/(mg min))	R
198.70	18.61	17.66	5.10	5.42	0.977
301.50	31.51	29.67	5.84	3.05	0.981

results show that the variation of capacity is little, and part of the measurement value is increased owing to the hydrolysis of inner fiber groups via the soaping treatment, but the variation of morphology and strength are not obvious, it is demonstrated that the strong acid and the strong alkali take little influence on the fibers obtained.

The absorption properties of PVC/PS composite ion exchange fiber on aniline

Absorption kinetics for aniline

The variations of absorption kinetics for different concentration aniline are shown in Figure 10. The composite ion exchange fibers have faster absorption rate for aniline on the preliminary stage of adsorption, and the absorption rate gets slower gradually until they reach adsorption equilibrium capacity, the both adsorption efficiency in 5 h are better.

The curves can be fitted from data in Figure 10 with trial and error method based on pseudohyperbolic equations of second order reaction kinetics. According to the second order reaction kinetics, the equation is usually described in the following form:

$$\frac{dQ_t}{dt} = k(Q_e - Q_t)^2$$

And a new equation is obtained by integrating the aforesaid equation as follows:

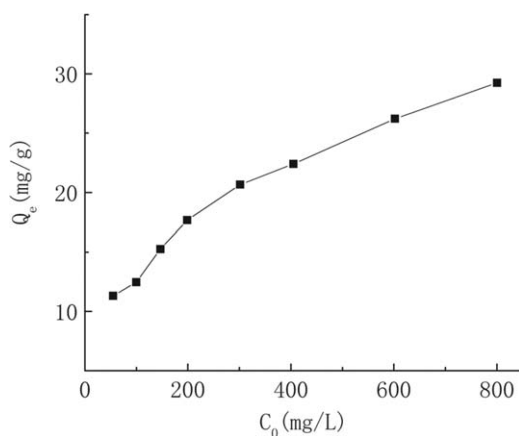


Figure 12 Effect of initial concentration on adsorption capacity on aniline.

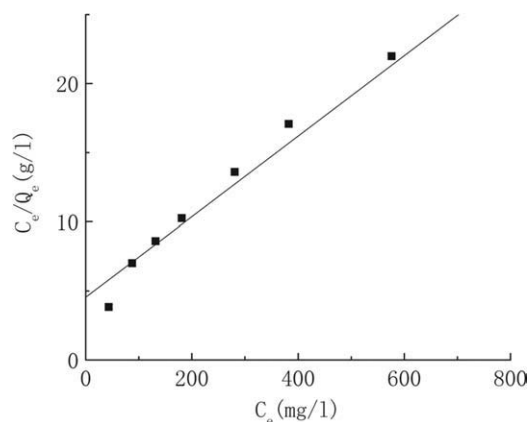


Figure 13 Langmuir isothermal curve of adsorption on aniline.

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{1}{Q_e}t$$

where k is the second order rate constant (l/(mg min)), Q_e is the adsorption equilibrium capacity (mg/g), Q_t is the capacity on aniline at t time (mg/g).

Q_e and k can be obtained by fitting the data between t/Q_t and t . The plots at the given time from the experiment are shown in Figure 11 and the parameters are listed in Table IV, respectively. It is clear from Figure 11 that the better straight lines between t/Q_t and t are shown. The correlation coefficient R are 0.977 and 0.981, respectively, it is demonstrated that the absorption of the composite ion exchange fibers on aniline can be described by the second order reaction kinetics. The errors of the calculated equilibrium capacities are less than 6.00% comparing with that of measured equilibrium capacity.

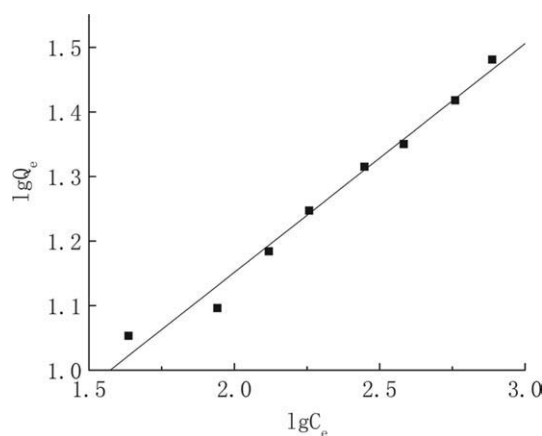


Figure 14 Freundlich isothermal curve of adsorption on aniline.

TABLE V
The Parameters of Langmuir and Freundlich Equations

Parameters	Q_m (mg/g)	b	$1/n$	k
Value	34.341	156.159	0.354	2.772

Effect of initial concentration on adsorption capacity

The curves are fitted from data in Figure 12 based on Langmuir and Freundlich adsorption isothermal equation of the simulation solution in common use, which are usually described in the following forms, respectively.

$$C_e/Q_e = C_e/Q_m + 1/Q_m b$$

$$\lg Q_e = \lg C_e/n + \lg k$$

where Q_e is adsorption equilibrium capacity (mg/g), C_e is equilibrium concentration (mg/L), Q_m is saturated adsorption capacity (mmol/g), b is adsorption equilibrium coefficient, meaning the adsorption ability of the fibers obtained on aniline, k , $1/n$ are Freundlich coefficients, respectively.

The plots of the given concentrations from the experiment are shown in Figures 13 and 14, respectively. The parameters of Q_m , b , $1/n$, and k are obtained by the linear regression, respectively, and the results are listed in Table V.

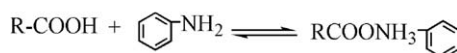
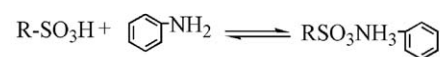
The Langmuir fitting equation obtained is $C_e/Q_e = 4.5474 + 0.0291C_e$, and the Freundlich fitting equation obtained is $\lg Q_e = 0.4428 + 0.3543 \lg C_e$. Their correlation coefficients R are more than 0.98 and 0.99, respectively, which is demonstrated that the process of isothermal absorption can be described by Langmuir and Freundlich adsorption isothermal equation, especially Freundlich adsorption isothermal equation is better. The biggest adsorption capacity Q is close to Q_m within the scope of concentration in the experiment, and the parameter $1/n$ means difficulty coefficient of reaction, the value is less than 0.5, so it is demonstrated that the adsorption reaction on aniline is very easy in the dynamics.

Effect of different counterion on adsorption capacity

The adsorption capacities on aniline (281.61 mg/L) of Na-type and H-type cation exchange fibers are listed in Table VI. The results indicate that the adsorption capacity of H-type is higher than that of Na-type. The reason is that the adsorption of Na-

TABLE VI
The Effect of Counterion Form on Adsorption Capacity

Counterion form	H ⁺	Na ⁺
Absorption capacity (mg/g)	92.18	21.69



Scheme 5 The acid–base neutralization reaction formula of H-type fibers with aniline.

type is mainly physical adsorption, but H-type fibers have a acid–base neutralization reaction with aniline besides the physical adsorption, their chemical reaction mechanism is as follows (Scheme 5):

Elution and regeneration performance of fibers

In the experiment, the adsorbed aniline (281.61 mg/L) by the fibers could be desorbed by using 5% concentration hydrochloric acid solution, and the results are listed in Table VII. The results indicate that the adsorption capacity of the regeneration fibers vary little, it is demonstrated that the function groups on the fibers obtained are stable on the process of sorption and desorption, and the regeneration rate is more than 96% with sorption and desorption circulations for 10 times. Therefore, the fibers obtained are ideal materials for treatment of the waste water containing aniline.

CONCLUSION

The static exchange capacity of the PVC/PS composite ion exchange fibers obtained can reach 5.0–6.0 mmol/g, their fracture strength can reach 1.198 cN/dtex, but the studies on mechanical property of ion exchange fibers had little been reported in documents. The fibers have bigger hydrophilicity, better regeneration performance and better ability of acid and alkali corrosion resistance, so they have better practical application value. The composite cation exchange fibers obtained have faster absorption rate for aniline, the process of isothermal absorption on aniline can be described by Langmuir and Freundlich adsorption isothermal equation. The utilization of function groups on the fibers is much higher and is close to theoretical value on the process of

TABLE VII
Elution and Regeneration Performance of Fibers

Regeneration times	Adsorption capacity for Aniline (mg/g)	Regeneration rate (%)
0	92.18	–
1	91.83	99.62
2	91.47	99.23
3	91.07	98.78
10	88.53	96.04

adsorption for aniline, so they are ideal materials for treatment of the waste water containing aniline.

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