

아라미드 종이의 특성에 대한 표면 개질 과정 조건의 영향

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Effect of Surface Modification Process Conditions on Properties of Aramid Paper

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Abstract: Surface modification of meta-aramid fibers was performed by phosphoric acid treatment. Surface morphology and element composition of untreated and treated fibers were analyzed by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). Effects of surface modification on the mechanical strength of aramid papers made from meta-aramid fibers and fibrid were investigated. Surface modification conditions were optimized by response surface analysis (RSA). Results show that phosphoric acid treatment increases the surface roughness and oxygen content of aramid fibers. They improve the interface bonding strength between aramid fibers and fibrid, which improves the tensile strength of aramid papers. The results of response surface analysis indicate that the tensile strength of aramid papers increases by 47.5% and reaches the maximum when meta-aramid fibers are treated with 21.1wt% phosphoric acid solution at 39.3 °C for 36.7 min.

Keywords: aramid fiber, phosphoric acid, surface modification, aramid paper, tensile strength.

Introduction

Aramid papers are widely used as electrical insulation, high temperature filter material, high temperature protective clothing, cellular structural material and the radar antenna because of their excellent mechanical properties and their heat-resistant electric insulating property.¹⁻⁵ For example, DuPontTM Nomex[®] paper Type 410 is the typical insulation paper, available in 11 thicknesses (0.05 to 0.76 mm) and is used in almost every known electrical sheet insulation application all over the world. Nomex[®] Type 411 is the uncalendered precursor of Nomex[®] Type 410, which is available in 5 thicknesses (0.13 to 0.58 mm) with a lower density of 0.3 g/cm³ and correspondingly lower mechanical properties.

Aramid papers are made from poly(m-phenylene isophthalamide) (PMIA) short fibers and PMIA fibrid. The two components share the same chemical structure unit, as shown in Figure 1. However, PMIA fiber and fibrid have distinct physical forms. PMIA fiber is very stiff, high strength and heat

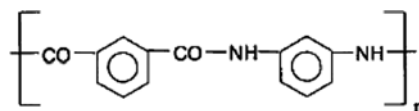


Figure 1. Chemical structure of PMIA fiber and fibrid.

resistance^{6,7} but it cannot make conglutination with each other to form paper due to its smooth and inert surface. PMIA fibrid is a differential product of PMIA fiber, it is a ribbon-like fiber with many microfibrils on its surface, which is more flexible and likes as wood fiber.⁸

In aramid paper, PMIA fibers function as the reinforcer in a composite material and it determine the physical strength of aramid paper while a function of aramid fibrid is binder, determining the overall strength and electrical properties of aramid paper.⁹ Because the surface of PMIA fibers is very smooth and lack of active groups, the interfacial bonding strength between PMIA fibers and fibrid is limited during papermaking process, which is unfavorable for having mechanical strength of aramid papers.

Surface modification is an important way to improve the interfacial bonding strength of aramid fiber-reinforced composite materials.¹⁰⁻¹² It works by introducing hydroxyl groups,

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carboxyl groups and other active groups on the surface of aramid fibers or by improving the roughness of fiber surface through etching. It can increase the surface tension and wettability of aramid fibers which improves the interfacial bonding strength between aramid fibers and matrix. Surface modification is carried out by various physical methods (plasma modification,¹³⁻¹⁶ ray radiation modification,^{17,18} ultrasonic modification,^{19,20} etc.) or chemical methods (surface etching modification,^{21,22} surface grafting modification,²³⁻²⁷ coupling agent modification,²⁸ etc.). In this paper, phosphoric acid solution was used as modifying agent. The effects of fiber surface modification on the mechanical strength of aramid papers were investigated on the mechanical strength. Also, the processing condition of surface modification was optimized and the strengthening mechanism was discussed.

Experimental

Materials. Aramid short fibers and fibrid were supplied by Yantai Tayho Advanced Materials Co., Ltd. Aramid fibers were obtained by low temperature solution polycondensation and wet spinning. Aramid fibrid was obtained by precipitating a solution of aromatic polyamide in a fibridding apparatus and was sheared during precipitation. Aramid short fibers were non-overdrawn fibers with low initial modulus, a length of 5-6 mm and a denier of 1.5. The aramid fibrid is a kind of ribbon-like particles with beating degree of 36° SR, having an average length of 1.02 mm. Phosphoric acid (PA, analytical pure) on 85% was purchased from market.

Single-factor Experiments of Fiber Surface Modification. Phosphoric acid (85% solution) was diluted to 10, 20, 30, 40, 50 and 60 wt% by water, respectively. Six groups of aramid fibers of 15 g were separately soaked in phosphoric acid solution of different concentration at room temperature for 30 min, then they were washed completely and dried thoroughly. Aramid fibers of 15 g were soaked in phosphoric acid solution of different concentration for 30 min at the temperature of 10, 20, 30, 40, 50 and 60 °C, respectively. Thirty-six groups of aramid fibers of 15 g were separately soaked in phosphoric acid solution of different concentration at room temperature for 10, 20, 30, 40, 50 and 60 min. Surface modified aramid fibers were washed and dried completely.

Response Surface Analysis. According to the results of single-factor experiments, three factors and three levels response surface analysis experiments were designed, and 15 groups of experiments were carried out. When the mass per-

Table 1. RSM Experimental Factors and Levels

Levels	X ₁ (%)	X ₂ (°C)	X ₃ (min)
-1	10	30	25
0	20	40	35
1	30	50	45

cent concentration of phosphoric acid solution X₁ (wt%), reaction temperature X₂ (°C) and reaction time X₃ (min) are assigned to independent variables, the tensile strength of aramid papers are measured by the response values (Y). The factors and levels are shown in Table 1.

Surface Morphology and Element Composition Analysis of Aramid Fibers. Scanning electron microscope (SEM, HITACHI S-3400, Japan) was used to observe the surface morphology and microstructure of aramid fibers before and after phosphoric acid modification. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD, Japan) was used to study the surface element composition of aramid fibers before and after phosphoric acid modification. Fourier transform infrared (FTIR) transmission/absorption spectra of aramid fibers before and after phosphoric acid treatment were collected with a BULKER V70 IR Spectrometer.

Preparation and Tensile Strength Determination of Aramid Papers. The modified aramid fibers and fibrid were mixed in a mass proportion as 40:60 and were dispersed thoroughly in water to form a fiber suspension. Aramid papers of 45 g/m² were made on a standard sheet former, hot calendering was further carried out on a three-roller calender. The temperature and pressure of calendering were 200 °C and 100 kgf/cm², respectively. The tensile strength of the aramid papers were determined by Tappi standard method.²⁹

Results and Discussion

Surface Morphology of Aramid Fiber, Fibrid and Paper. The microscope pictures of aramid fiber and fibrid are shown in Figure 2(a) and Figure 2(b). The self-made aramid paper and Nomex 410 paper are shown in Figure 2(c) and Figure 2(d).³⁰

It can be seen from Figure 2 that PMIA short fiber is very stiff and has smooth surface, while the fibrid is ribbon-like, flexible and has larger specific surface area which is helpful to the strength of aramid paper. Aramid fibrid melted partly during hot calendering and wrapped around the fibers tightly, thereby forming high strength aramid paper.

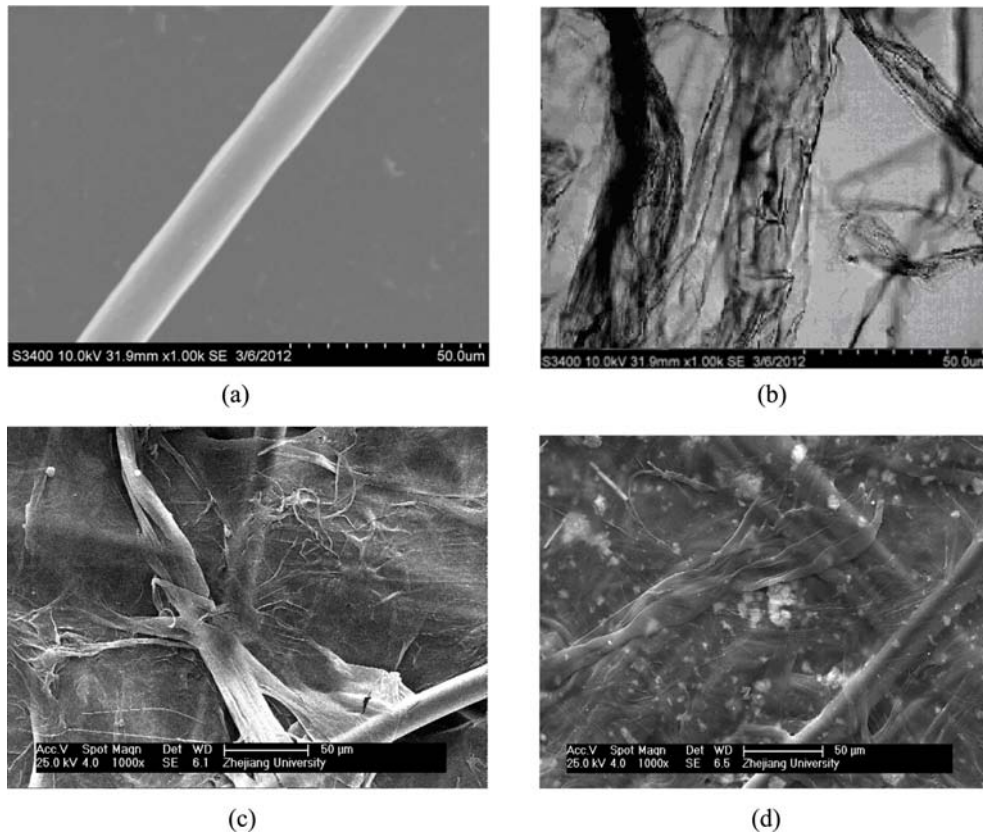


Figure 2. Pictures of (a) aramid short fiber; (b) PMIA fibril; (c) self-made aramid paper; (d) Nomex 410 paper ($\times 1000$).

Effects of Phosphoric Acid Modification on the Mechanical Strength of Aramid Papers. Effects of the concentration phosphoric acid solution on the tensile strength of aramid papers were shown in Figure 3. The treated temperature and time were 20°C and 30 min, respectively.

For paper with similar basis weight of 42 g/m^2 , the tensile strength of Nomex[®] Type 411 paper and Nomex[®] Type 410 paper are 1.8 kN/m (MD), 0.9 kN/m (CD) and 4.3 kN/m (MD), 1.9 kN/m (CD), respectively, where MD refers to machine direction and CD refers to cross-machine direction. Self-made paper is formed on standard sheet former rather than on Fourdrinier machine, fiber distribution in the paper is uniform in all direction, without having MD and CD.

It can be seen from Figure 3 that when the concentration of phosphoric acid solution is lower than 20 wt%, the tensile strength of aramid papers improve with the increase of the concentration of phosphoric acid solution. The tensile strength of aramid paper made from untreated fibers is 2.231 kN/m , which is lower than the average tensile strength of Nomex[®] Type 410 paper (average of MD and CD). Tensile strength of aramid paper made from fibers treated by 20 wt% phosphoric

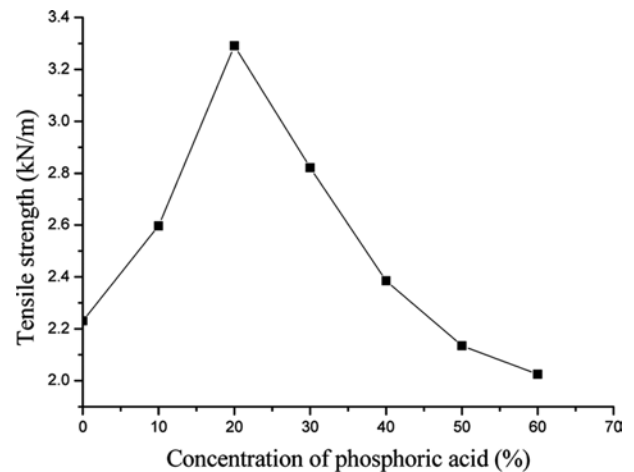


Figure 3. Effect of phosphoric acid concentration on tensile strength of aramid papers.

acid solution is 3.291 kN/m , which increases by 47.5%. It is higher than the average tensile strength of Nomex[®] Type 410 paper. However, when the concentration of phosphoric acid solution is higher than 20 wt%, the tensile strength of aramid papers gradually decreases with the increase of the concen-

tration of phosphoric acid solution. The tensile strength of aramid papers made from fibers treated by 60 wt% phosphoric acid solution is the lowest, which is even lower than that of aramid papers made from untreated fibers.

The effect of treated temperature on the mechanical strength of aramid papers were shown in Figure 4. Figure 4 shows that the highest value of the tensile strength of aramid papers reveal on the concentration of phosphoric acid solution at 20 wt%, and the lowest value of tensile strength occurs when the concentration of phosphoric acid solution is 60 wt%. The trends exist at different treated temperature, which indicates that the concentration of phosphoric acid solution is more important on fiber surface modification. In the same phosphoric acid concentration, the tensile strength of aramid papers improves with

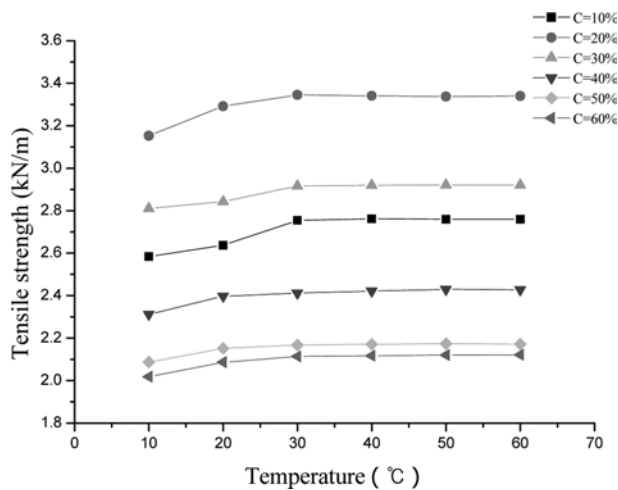


Figure 4. The effect of treated temperature on tensile strength of aramid papers (treated time: 30 min).

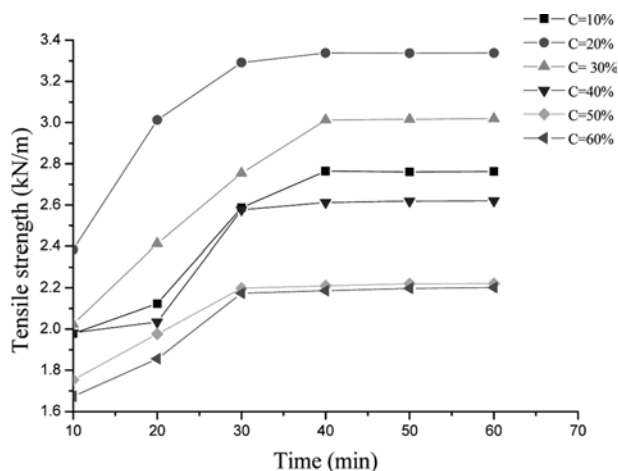


Figure 5. The effect of treated time on tensile strength of aramid papers.

the increase of treated temperature when the temperature is below 30 °C. However, when the temperature is higher than 40 °C, the changes in tensile strength of aramid papers are not obvious. The rate of chemical reactions speed up with the temperature, and when the temperature reaches about 40 °C, chemical reactions are completed basically, so further increase of temperature has little influence on the tensile strength of aramid papers.

The effect of treated time on the tensile strength of aramid papers were shown in Figure 5. The experiments were carried out at the room temperature. It can be seen from Figure 5 that if aramid fibers are treated in the same time, the aramid papers made from fibers treated by 20 wt% phosphoric acid solution have the highest tensile strength, while aramid papers made from fibers treated by 60 wt% phosphoric acid solution have the lowest tensile strength. The tensile strength of aramid papers increases with the extension of treated time. When the concentrations of phosphoric acid solution are 10, 20 and 30 wt%, and the treated time is more than 40 min, the tensile strength of aramid papers seems to be stable. However, when the concentrations of phosphoric acid solution are 40, 50 and 60 wt%, the tensile strength of aramid papers tends to be unchangeable when the treated time reaches 30 min. These indicate that the chemical reaction is completed basically in 30–40 min and extension of treated time has no obvious effect on the tensile strength of aramid papers.

Optimization of Phosphoric Acid Modification Processing Conditions. Box-Behnken method is effective to optimize process conditions and is widely used in biological, agricultural, food and papermaking field. It uses multiple quadratic regression equation to fitting the functional relation between factors and response value. Fewer tests and short cycle were required and the regression equation acquired from this test with high accuracy and can study the interaction between several factors. 15 groups of experiments were carried out in random order according to the Table 1. The response values of aramid papers' tensile strength were analyzed with Minitab software. The results were shown in Table 2.

After regression fitting with Minitab software, the response values of aramid papers' tensile strength can be expressed by a three-factor quadratic regression equation:

$$Y = 3.3510 + 0.1110X_1 - 0.0015X_2 + 0.0130X_3 - 0.5114X_1X_1 - 0.0264X_2X_2 - 0.0359X_3X_3 - 0.0203X_1X_2 - 0.0088X_1X_3 - 0.0008X_2X_3 \quad (1)$$

The optimum value can be obtained from the two-dimen-

Table 2. Box-Behnken Experimental Design and Results

Groups	X ₁	X ₂	X ₃	Y Tensile strength (kN/m)
1	0	0	0	3.351
2	1	0	1	2.912
3	0	0	0	3.351
4	-1	0	1	2.721
5	0	-1	1	3.292
6	1	0	-1	2.904
7	-1	-1	0	2.689
8	0	-1	-1	3.264
9	0	1	1	3.312
10	0	0	0	3.351
11	0	1	-1	3.287
12	-1	1	0	2.702
13	1	1	0	2.897
14	-1	0	-1	2.678
15	1	-1	0	2.965

sional map and the corresponding calculation. The response surface graphs were drawn with Minitab software and were shown in Figure 6. Each response surface depicted the common effect of two independent variables on the tensile strength of aramid papers. The third variable was kept at the optimum level. Figure 6 shows that if the treated temperature and time are kept at the optimum level, the tensile strength of aramid papers improves with the increase of phosphoric acid concentration in the range of 10~21.1 wt%. The tensile strength of aramid papers decrease with the increase of phosphoric acid concentration when it exceeds 21.1 wt%. If the concentration of phosphoric acid solution and treated time are kept at the optimum level, the tensile strength of aramid papers improves with the increase of treated temperature in the range of

30~39.3 °C. But when the temperature exceeds 39.3 °C, the tensile strength decreases with the increase of treated temperature. If the concentration of phosphoric acid solution and treated temperature are kept at the optimum level, the tensile strength of aramid papers improves with treated time prolonging in the range of 25~36.7 min. However, when the treated time exceeds 36.7 min, the tensile strength of aramid papers decreases with the extension of treated time.

According to the results of response surface analysis, the optimal concentration of phosphoric acid solution is 21.1 wt% and the optimal treated temperature and time are 39.3 °C and 36.7 min, respectively.

Effect of Phosphoric Acid Modification on the Surface Structure of Aramid Fibers. Aramid fibers were treated by phosphoric acid solution with the optimal processing condition described above and the SEM images of aramid fibers untreated and treated with 20, 40 and 60% phosphoric acid solution at room temperature for 30 min were shown in Figure 7.

It can be seen from Figure 7(a) that untreated aramid fiber is very stiff and has a smooth surface, however, after being treated by PA solution, the surface of treated fiber is very rough as shown in Figure 7(b). Their notches and grooves were produced on the surface of fibers by chemical etching. However, with the increase of the concentration of PA solution, as shown in Figure 7(c) and Figure 7(d), the surface of aramid fibers was damaged seriously and debris began to peel off from fiber surface, which decreased the strength of aramid fiber seriously. In short, treating aramid fibers with PA solution roughens and activates fiber surface. It improves the interfacial bonding strength among the fibers, but the concentration of PA solution should not be very high.

The surface element composition of aramid fibers before and after phosphoric acid modification were studied by XPS, and the results were shown in Table 3. It can be seen from Table 3 that the oxygen element content of aramid fibers first

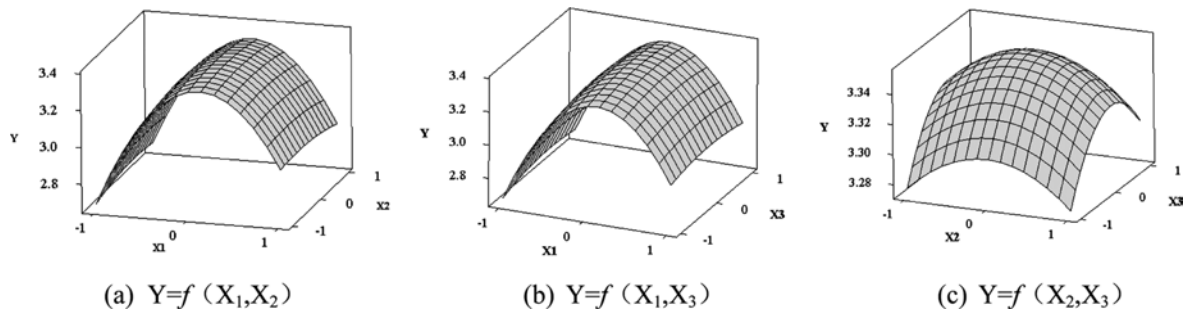


Figure 6. Response surface graphs.

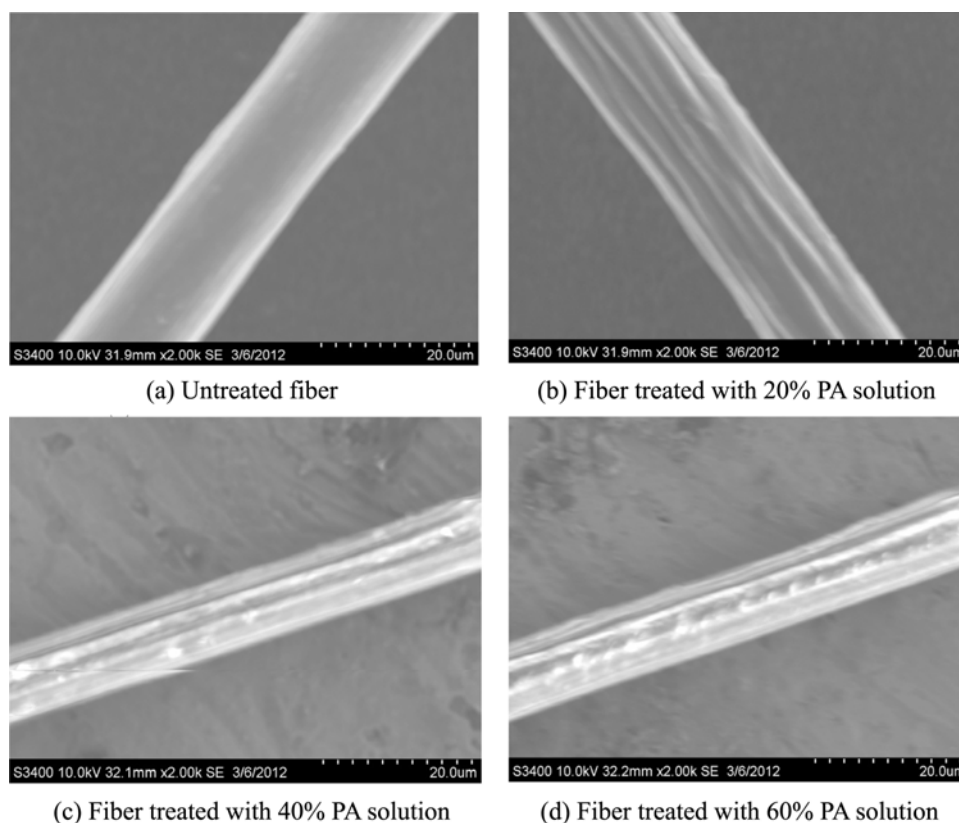


Figure 7. SEM images of aramid fibers before and after treatment ($\times 2000$).

Table 3. Elemental Contents of Aramid Fibers

Surface elements	Untreated fiber (%)	Fiber treated with 20% PA solution (%)	Fiber treated with 40% PA solution (%)	Fiber treated with 60% PA solution (%)
C	72.57	70.03	71.23	72.42
O	22.64	27.12	24.65	21.91
N	4.78	2.84	4.06	5.45
O/C	31.20	38.73	34.61	30.25

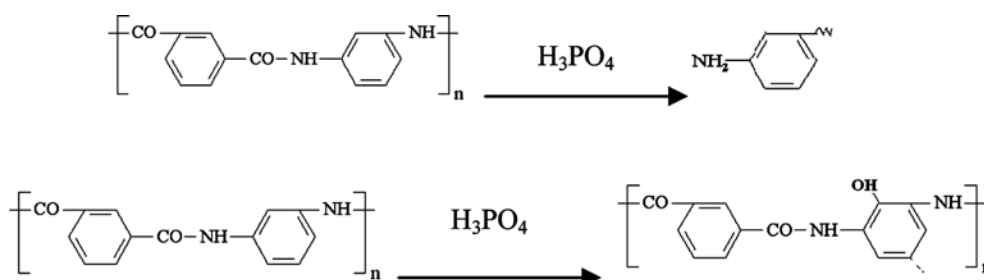


Figure 8. Scheme of the reactive progress.²¹

increases and then decreases with the increasing of phosphoric acid solution concentration. It reaches the maximum value when the concentration of PA solution is 20% and the ratio of oxygen/carbon increases from 31.20% to 38.73%. The increase

in oxygen element content maybe due to the increase of hydroxyl groups on fiber surface. Because the amide group ($-\text{CO}-\text{NH}-$) in aramid fibers is a strong electron-donating group, it can enhance the reaction activity of its meta-position

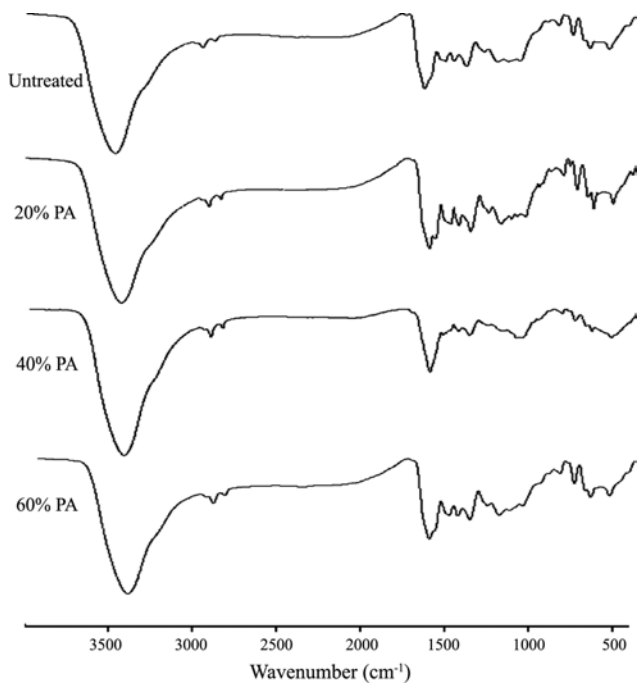


Figure 9. IR spectra of aramid fibers before and after PA treatment.

and ortho-position. Under the action of acid, it is easy to generate hydroxyl through electrophilic substitution^{31,32} which increases the surface oxygenic functional groups of modified aramid fibers. Meanwhile, under the action of phosphoric acid, the amide bond (-CO-NH-) on the surface of aramid fibers can also be hydrolyzed to generate strong polar amino group, which increases the interface bonding strength between aramid fibers and fibrils, thus improves the tensile strength of aramid papers. The reactive processes are shown in Figure 8:

IR spectra of untreated aramid fibers and aramid fibers treated with 20, 40 and 60% PA solution are shown in Figure 9. The IR spectra of aramid fibers treated with PA solution show the similar absorption bands as untreated aramid fibers. However, after PA solution treatment, the absorption band corresponding to N-H stretching (3435 cm^{-1}) shows a slight shift ($\sim 5\text{ cm}^{-1}$) to lower wavenumbers and the fact can be related to the increase of hydroxyl groups or hydrogen bonds.

Conclusions

Chemical modification with phosphoric acid etches the surface of aramid fibers which increases their surface roughness and activity. The modified aramid fibers have higher oxygen element content and polarity and they are helpful to improve the interfacial bonding strength between aramid fibers and

fibril in aramid papers.

The processing conditions of surface modification have considerable influence on the surface properties of aramid fibers and the mechanical strength of aramid papers. According to response surface analysis, the optimum modification technological conditions were obtained as following: phosphoric acid concentration 21.1 wt%, reaction temperature 39.3 °C, reaction time 36.7 min.

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