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Surface modification of Poly-p-phenylene benzobisoxazole fiber by dielectric barrier discharge for magnet reinforcement

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Abstract—**At present, Poly-p-phenylene benzobisoxazole (PBO) fiber is one of the most preferred reinforcement materials for magnet. However, the poor interface performance between the PBO fiber and resin matrix has become the bottleneck of the pulse magnetic field intensity improvement. Surface modification of the PBO fiber may be an effective way to solve this problem. In this paper, PBO fibers were treated by atmospheric dielectric barrier discharge (DBD) in air under different treatment time. It is found that when the discharge power density remained unchanged at 8.49W/cm2, the optimal treatment time is 60s. In this case, the shear strength of PBO fiber-resin interface increases up to 52.77% compared with the untreated, while the tensile strength of fiber monofilament only decreases 4.73%. The plasma treatment results in a large number of deep pits and protrusions on the surface of PBO fibers and a significant increase in roughness. The relative content of C element on the surface of PBO fiber decreases significantly, the content of O element increases obviously, and the content of N element increases slightly. Polar groups -O-C=N- and -C=O- are introduced through grafting copolymerization reaction, which enhances the chemical activity and wettability of the fiber surface. All of these contribute to the interfacial shear strength increase between the PBO fiber and the resin.**

Keywords—PBO fiber; surface performance; DBD; optimal treatment time

I. INTRODUCTION

Pulsed high magnetic field, as an extreme case technology, is widely used in the fields of magneto-optical, microwave conductivity, magnetization, specific heat and so on [1]-[3]. However, the mechanical strength of the pulsed magnet used to generate the pulsed strong magnetic field becomes the biggest obstacle of expanding of the magnetic field strength. The pulse magnet is mainly composed of wire winding, insulation layer and reinforcement layer. The early magnet is mainly made of high performance conductor materials such as copper wire, metal-based micro-composite copper/niobium alloy, copper/silver alloy.[4], [5] However, the conductivity of the conductor materials decreases with the tensile strength increasing. Besides, for pulsed magnets generating magnetic field intensity of more than 80T, the electromagnetic stress inside the magnet windings can reach 3~4GPa, which cannot be borne by current conductor materials. Luc Van Bockstal proposed layered reinforcement technology to optimize the stress of each layer of conductor windings, which greatly enhanced the mechanical properties of conductors without affecting their electrical conductivity [6]. Fiberglass reinforced resin matrix composite materials, carbon fiber, PBO fiber and other materials were used to strengthen pulse magnets. Because of fiberglass could not matching with copper/niobium alloy and copper/silver alloy well and poor insulation of carbon fiber, PBO fiber becomes the first choice for strengthening pulse magnets. [7], [8] However, smooth surface and poor chemical activity of the fiber make the resin matrix unable to infiltrate fully, which is not conducive to the internal reinforcement of pulse magnet [9], [10]. Therefore, it is necessary to modify the surface properties of the PBO fiber.

At present, the commonly used modification methods include using the chemical etching, coupling agent layer, copolymerization modification, radiation modification and low temperature plasma treatment [11]-[15]. Compared with other methods, low temperature plasma treatment has the advantages of no pollution, high treatment efficiency, low energy consumption and low cost, which has a good prospect of industrialization. [16]-[19] In this paper, an atmospheric DBD was used to conduct the surface modification of the PBO fiber in air condition. The single filament tensile strength (SFTS) and the interfacial shear strength (IFSS) between the fiber and the resin were tested under different treatment time. At the same time, the surface morphology, roughness and the compounds changing were all tested to address the related mechanism.

II. MATERIALS AND METHODS

A. Sample Preparation

The PBO fiber used in this paper is produced by Toyo Textile Co., LTD. The PBO fibers were divided into 30cm long fiber bundle and put into a stainless steel container with acetone. After soaking for 48h, the residual slurry and acetone were cleaned with ultra-pure water. Then, the PBO fibers were dried in a drying oven at 110℃ for 2h for the subsequent experiments.

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B. Expermental Setup and Treatment

An Atmospheric DBD was used to treat the PBO fiber in this study, and the ambient air is used as the working gas. The experimental system is shown in Figure 1. The system consists of DBD device, power monitoring system, emission spectrum measurement system and gas control system. The electrode in the DBD device is a round copper with a diameter of 30mm. Its surface is covered by a quartz glass sheet with a thickness of 1mm and a diameter of 80mm. The gap between the electrodes is fixed at 1mm. The DBD device was driven by a 20kHz frequency high voltage AC power supply. The discharge and fiber processing were carried out in a plexiglass chamber. The discharge image were shoot by digital camera Nikon D750 with 1/15s exposure time. The power density was mesured by using Lissajous method.

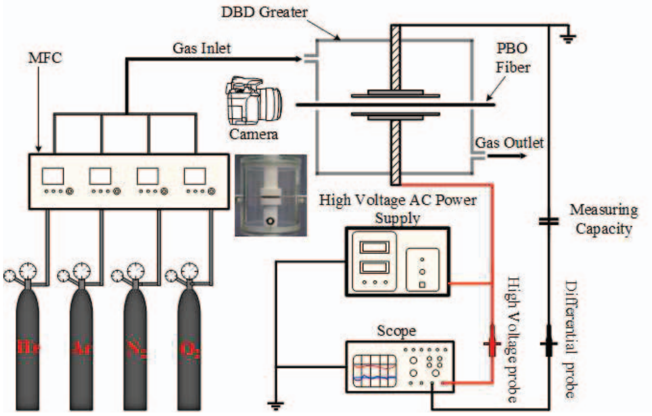

Fig.1. Experimental system.

The relationship between power density and input voltage is shown in Figure 2. As can be seen from the figure, the plasma discharge power density gradually increases with the increase of the input voltage.

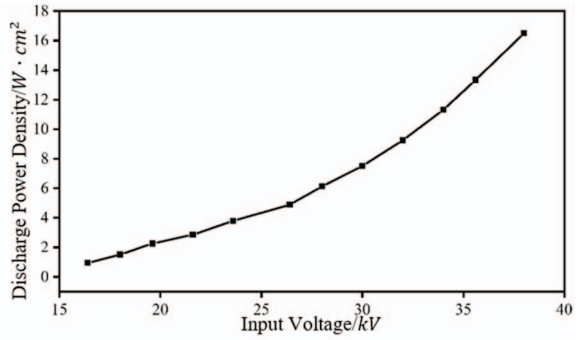

Fig.2. The Relationship between discharge power density and the input voltage.

Figure 3 shows the discharging images at different discharge power densities. The overall performance of the plasma is white and purple. Its luminescence intensity increases with the discharge power density and the discharge area shows a trend of expansion as the power density increases.

During treatment, the pretreated PBO fibers were placed in the middle of the discharge gap under atmospheric circumstances with the power source parameters of 20kHz frequency and $8.49W / cm^2$ power density for 20, 40, 60, 80 and 100s treatment, respectively.

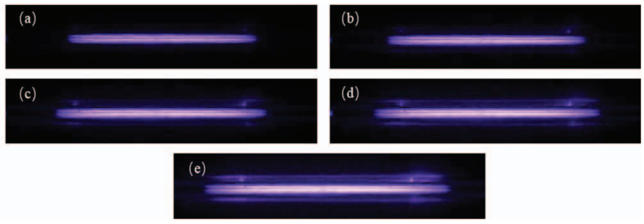

Fig.3. Air DBD plasma discharge picture at different discharge power densities. (a) $2.83W / cm^2$;(b) $5.66W / cm^2$;(c) $8.49W / cm^2$;(d) $11.32W / cm^2$;(e) $14.15W / cm^2$

C. Material Property Test

After plasma treatment, the physical and chemical characteristics of PBO fiber were tested, including scanning electron microscope (SEM, Sirion 200), atomic force microscopy (AFM, SPM9700) and X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600W). The mechanical properties and reinforcement performance of the fiber were also tested by single filament tensile strength (SFTS) and interfacial shear strength (IFSS) experiments with YG163 electronic microsphere debonding tester.

III. RESULTS AND DISCUSSION

A. The Effect of Plasma Treatment Time on Characteristics of PBO Fibers

The surface morphology of PBO fibers was observed by scanning SEM and AFM as shown in Figure 4 and Figure 5, respectively.

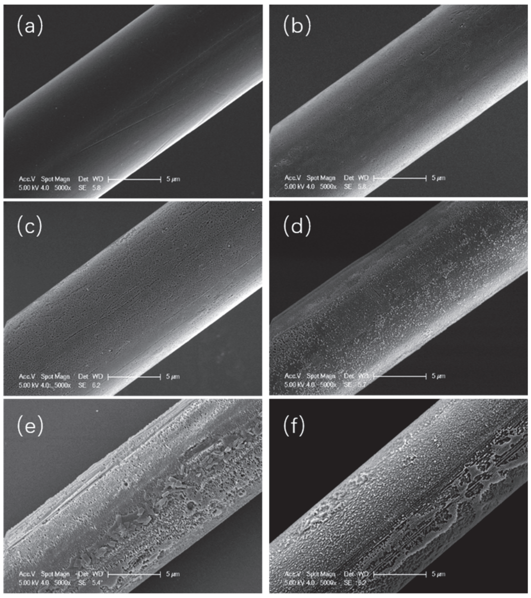

Fig.4 SEM results of PBO fiber under different plasma treatment time. (a) Untreated; (b) 20s;(c) 40s; (d) 60s; (e) 80s; (f) 100s.

The surface of the untreated PBO fiber is smooth and only a few shallow streaks and microprotrusions as shown in Figure 4(a). From Fig.4(b)-(f), it can be seen that as the plasma treatment increased from 20s to 40s, the surface became uneven, the notch shape expanded and small numbers of nicks were produced; with the treatment time up to 60s, many grooves and sediments appeared on the surface, and the uneven area extended to the entire surface; after the fibers were treated by 80s, the cortex was partially shed, forming deep grooves along the axial direction of the fibers and producing a large number of cortical fragments; with the treatment time extended to 100s, the cortex basically disappeared, the plasma directly acted on the core layer, roughness of the fiber surface increased significantly. The AFM results of three-dimensional morphology of fiber surface are consistent with the SEM image results.

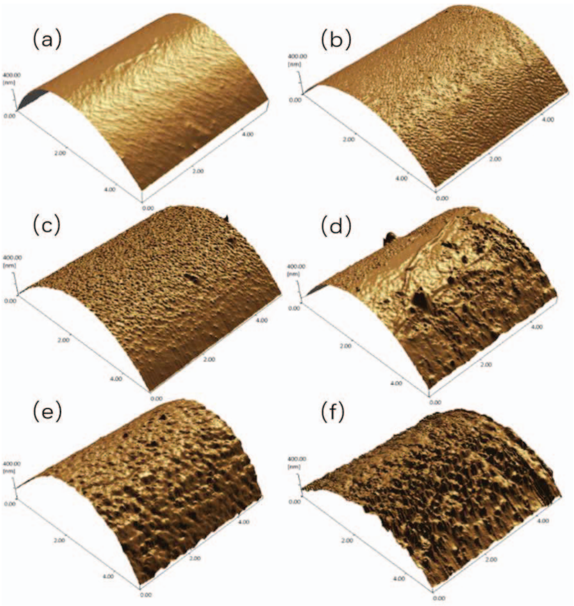

Fig.5 AFM results of PBO fiber under different plasma treatment time.(a) Untreated; (b) 20s;(c) 40s; (d) 80s; (f) 100s

In order to further quantitatively characterize the roughness of fiber surface, the roughness were calculated according to Equation (1) and (2). The results are listed in Table 1 and show that the surface roughness and the root mean square deviation roughness of the PBO fiber increased synchronically with the treatment time. With plasma treatment, the roughness increased from 141.943nm (untreated) to 273.195 nm (100s).

$$R_a = \frac{1}{N}\sum_{i=1}^{N}\left|Z_i - \frac{1}{N}\sum_{i=1}^{N}Z_i\right| \tag{1}$$

$$R_q = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(Z_i - \frac{1}{N}\sum_{i=1}^{N}Z_i\right)^2} \tag{2}$$

Table 1 The surface roughness of PBO fiber at different treatment time

Treatment time/s	***Mean Roughness/nm***	***Root Mean Square Deviation Roughness/nm***
Untreated	141.943	165.921
20	163.857	190.440
40	178.039	207.079
60	195.738	227.859
80	226.133	263.057
100	273.195	319.214

The chemical composition and content on the surface of the PBO fiber were obtained by XPS. The overall results are shown in Figure 6. The intensity of the characteristic spectral lines of each basic element changed significantly after plasma treatment. The relative content of each element was obtained by integrating the area enclosed by its characteristic peak and baseline, as shown in Table 2.

Table 2 Chemical composition and relative content of PBO fiber surface at different plasma treatment times.

Treatment time/s	***Relative Element Content***			***Element Content Ratio***	
	C	***O***	***N***	***O/C***	***N/C***
Untreated	79.3	16.0	4.7	0.2018	0.0593
20	75.0	18.8	6.2	0.25067	0.08267
40	71.3	20.2	8.4	0.28331	0.11781
60	64.8	25.7	9.5	0.3966	0.1466
80	68.0	23.2	8.8	0.34118	0.12941
100	70.9	21.7	7.4	0.30606	0.10437

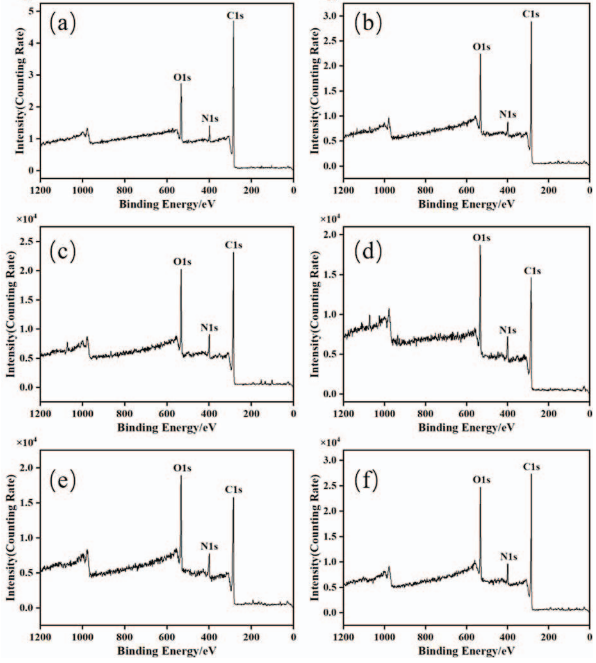

Fig.6 XPS Results of PBO fiber under different plasma treatment time. (a)Untreated; (b) 20s;(c) 40s; (d) 60s; (e) 80s; (f) 100s.

After 20s plasma treatment, the content of C element on the surface of PBO fiber decreased from 79.3% to 75.0%, and the content of O and N elements increased to 18.8% and 6.2%, respectively. The ratio of O/C and N/C were both higher than those of without treatment. With the extension of treatment time, the content of C element decreased significantly, the content of O element increased continuously, but the content of N element increased slightly. When the treatment time was 60s, the content of C element reached the lowest value, the content of O element and N element increased to 5.7% and 9.5%, and the ratio of O/C and N/C reached the maximum. As the treatment time continued to increase, the content of C element increased, while the content of O element and N element decreased. When the treatment time was 100s, the content of C element increased to 70.9%, the content of O element and N element decreased to 21.7% and 7.4%, but still higher than the original fiber level.

The C1s peak was scanned at high resolution and Gaussian Lorentz peak splitting fitting was performed to furtherly study the relationship between the changes of elements on the fiber surface and their chemical structure. The results are shown in Figure 7.

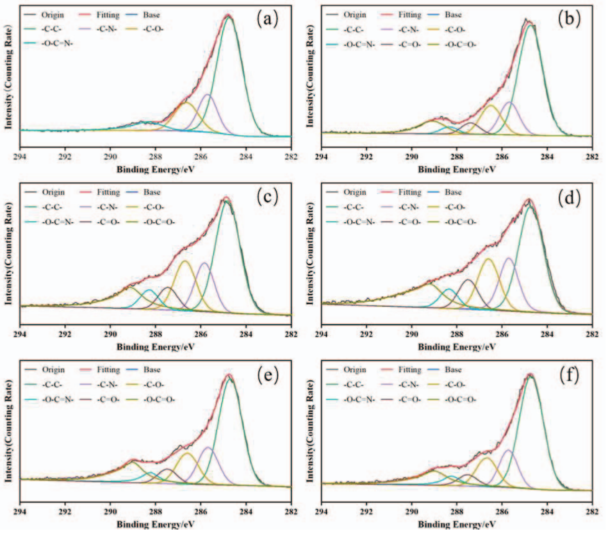

Fig.7 C1s split-peak fitting spectra of PBO fiber surface under different plasma treatment time. (a) Untreated; (b) 20s;(c) 40s; (d) 80s; (f) 100s.

After plasma treatment, six different carbon-containing groups existed on the fiber surface, including the four original groups -C-C-, -C-N-, -C-O- and -O-C=N- and two newly generated groups of -C=O- and -O-C=O-. The relative content were obtained by calculating the area between each functional group and the baseline, as shown in Table 3.

Table 3 The content of chemical groups on the surface of PBO fiber treated at different time.

Treatment time/s	***Relative Group Content***					
	-C-C-	***-C-N-***	***-C-O-***	***-O-C=N-***	***-C=O-***	***-O-C=O-***
Untreated	63.07	15.03	14.44	7.46	—	—
20	56.89	13.27	12.97	2.78	4.43	9.66
40	42.06	14.13	16.52	5.84	6.68	14.77
60	36.63	15.06	14.82	5.2	7.78	20.51
80	46.13	14.07	12.51	5.35	5.16	16.77
100	52.45	13.1	11.57	5.05	4.76	13.06

When the treatment time was 20s, the chemical bonds in the fiber molecular chains were broken, new active groups -C=O- and -O-C=O- were formed through grafting copolymerization, and the relative content of non-polar C-C- groups reduced to 56.89%. With the extension of the treatment time, the plasma etching effect was strengthened, the number of chemical bond breaks and the reaction degree increased accordingly. The content of polar groups -C=O- and -O-C=O- increased gradually, resulting in the decrease of the content of non-polar groups -C-C-. In addition, the content of –C-N- and -C-O- remained basically unchanged. When the treatment time increased to 60s, the content of non-polar group -C-C- decreased to the lowest level, while the content of polar group -C=O- and -O-C=O- reached the maximum. However, when the treatment time was further extended, the content of -C-C- group increased and the content of -C=O- and -O-C=O- group showed a downward trend. After plasma treatment for 100s, the content of polar groups -C-C- on the fiber surface increased to 54.45%, while the content of non-polar groups was slightly higher than that in 20s treatment group.

The influence on mechanical properties of PBO fiber monofilaments can be characterized by SFTS, and the results are shown in Figure 9. The tensile strength of single fiber shows a decreasing trend with the extension of treatment time. When the treatment time is 20s, 40s and 60s, the monofilament tensile strength decreased by 1.82%, 3.22% and 4.73%. When the treatment time reached 80s and 100s, the decrease rates of filament tensile strength were up to 7.39% and 10.52%, respectively.

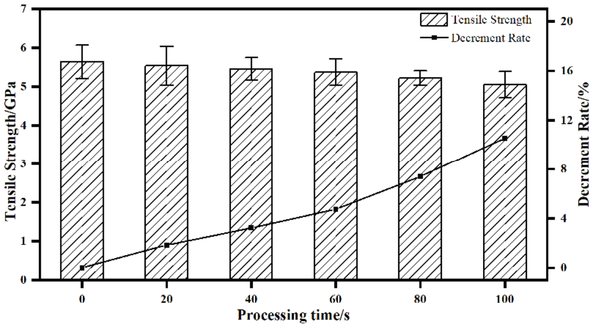

Fig.9 SFTS results of PBO fiber under different plasma treatment time.

In general, the physical and chemical characteristics on fiber surface and mechanical properties of the fiber had been changed after plasma modification. With the increace of treatment time, the degree of plasma etching and sputtering were improved. The grooves on the fiber surface were deepened and the nicks became obvious. A large number of protrusions and folds appeared, thus the roughness of the surface increased. The roughness improves the infiltration performance of the fiber surface, so that the fiber and the resin may establish stronger mechanical meshing, according to the Wenzel model theory.

As for the changes of PBO fiber’s chemical properties, active groups generated after plasma modification are conducive to the establishment of stronger chemical bonding between the fiber and the resin, so as to improve the interface bonding performance. Besides, polar groups on the surface of the fiber increases, which is beneficial for the infiltration of resin matrix. However, those favorable chemical groups decrease under excessive length of plasma treatment time. As for mechanical properties of the fiber, plasma only acts on the cortical area of the fiber surface in relatively short treatment time. Hence, the reduction rate of the filament tensile strength was relatively low and the damage degree of the fiber body mechanical properties is limited and could be ignored. However, long treatment time leads to significant decrease of the tensile strength of monofilament. This is caused by plasma etching touching the inner core layer of the fiber and damaging the overall structure, leading to strengthened stress concentration effect. In short, the treatment time should be limited within a reasonable range.

B. *Effect of Modified PBO Fibers at Different Time Scales on Reinforcement Performance*

IFSS can characterize the interfacial bond state between the fiber and resin, which can indirectly reflect the overall reinforcement performance of the fiber on pulsed magnet .The experimental results are shown in Figure 10.

When the treatment time was 60s, the interfacial shear strength further increased to 37.69MPa, with a growth rate as high as 52.77% compared with untreated fiber. However, when the plasma treatment time was extended to 80s and 100s, the shear strength of the fiber/resin interface was 36.10MPa and 31.27MPa, respectively, which was still lower than the value of 60s and decreased slightly, although it was improved by 46.33% and 26.74% compared with that of the untreated interface.

According to the previous results on PBO properties before and after the plasma modification, with the extension of the treatment time, the etching sputtering effect of active particles in the plasma was enhanced, and the surface roughness of the fiber and the number of active groups were also improved, which was conducive to the establishment of stronger mechanical meshing and chemical bonding between the fiber/resin, and the interface bond strength of the two was increased as well. Thus the interfacial shear strength grown with the plasma treating time. However, the growth rate of IFSS gradually decreased. This is because the degree of chemical binding between the active groups on the surface of the fiber and the resin was limited by surface roughness, and the contact area between the fiber and the resin cannot provide the newly generated polar groups with the number of matching bond position, resulting in the chemical bond cooperation cannot be effectively improved. Nevertheless, the IFSS decreased and the decrease rate went faster when the fiber were treated under excessive length of time. This is because the active groups generated in the early reaction were destroyed in long treatment time, leading to the weakening of chemical bond cooperation.

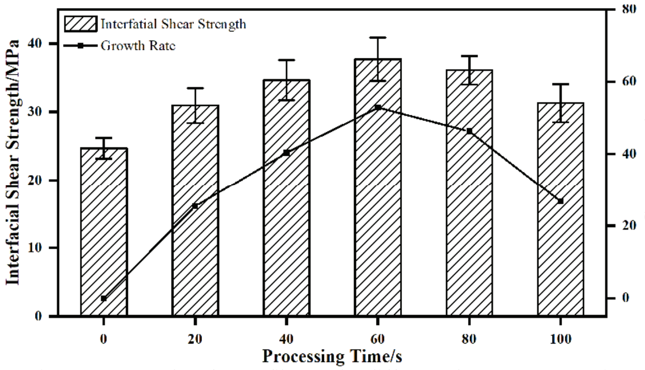

Fig.10 IFSS results of PBO fiber under different plasma treatment time.

In short, proper plasma treatment can effectively improve the interface bonding performance of the PBO fiber and resin, while long treatment time will have a negative impact on the interface bonding state of composite materials.

IV. CONCLUSION

The effects of air DBD treatment on the physical and chemical properties of PBO fiber surface as well as its mechanical properties were conducted in this paper. The mechanism of plasma action on the surface of PBO fiber and the mechanism of improving the bond strength of fiber-resin interface were discussed.

When the discharge power density remained unchanged at $8.49W / cm^2$, the optimal treatment time was 60s. In this case, the shear strength of the PBO fiber-resin interface increased up to 52.77% compared with the untreated. The surface roughness increased gradually with the extension of the treatment time, which enhances the mechanical meshing of the composite interface. The fiber surface chemical bond breaking introduced a variety of active groups through grafting copolymerization, which also improved the surface chemical activity and infiltration performance. However, long treatment time would destroy the polar groups generated in the previous reaction and damage the fiber structure. Within the appropriate treatment time, the mechanical properties of the fiber body were basically not affected.

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