

Ultraviolet resistance modification of poly(*p*-phenylene-1,3,4-oxadiazole) and poly(*p*-phenylene terephthalamide) fibers with polyhedral oligomeric silsesquioxane

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ABSTRACT: Octa-ammonium chloride salt of polyhedral oligomeric silsesquioxane (POSS) was synthesized by a hydrolysis reaction and introduced into poly(*p*-phenylene-1,3,4-oxadiazole) (*p*-POD) and poly(*p*-phenylene terephthalamide) (PPTA) fibers by a finishing method to enhance the UV resistance. The effects of the POSS concentration, treatment temperature, and time on the tensile strength of the fibers were investigated. The surface morphology, mechanical properties, crystallinity, degree of orientation of fibers, and intrinsic viscosity of the polymer solution were characterized in detail. The results indicate that the tensile strength retention and intrinsic viscosity retention of the fibers treated with POSS were much higher than those of the untreated fibers after the same accelerated irradiation time; this demonstrated that this treatment method was feasible. We also found that the efficacy of the protection provided by POSS was more beneficial to *p*-POD than PPTA because of the different structure. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42643.

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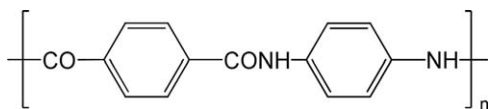
INTRODUCTION

Poly(*p*-phenylene terephthalamide) (PPTA) as a high-performance fiber exhibits excellent properties, such as a high strength and modulus, outstanding thermal stability, chemical resistance, and flame retardation. Therefore, it is widely applied in the areas of firefighting, aerospace, and national defense.^{1,2} Aromatic poly(1,3,4-oxadiazole) is a class of heterocyclic polymers with an excellent thermal stability, good chemical stability, high glass-transition temperature, low dielectric constant, and tough mechanical properties, which had been extensively studied for a long time.^{3,4} Poly(*p*-phenylene-1,3,4-oxadiazole) (*p*-POD) fiber, which is the most commonly used, can be used for heat-resistant composite materials, filtration fabrics, and protective working clothes, and the special membranes may be used for gas separation or reverse osmosis.^{5,6} These two polymers are sensitive to UV light and have presented weak UV resistance in the reported literature.^{7–10} Fully aromatic polymers with rigid chain structures, such as polythiophene, poly-*p*-phenylene benzobisthiazole, and poly(phenylene vinylene), degrade much faster than nonaromatic polymers under the same UV conditions. So, we need an effective and simple pretreatment method

to promote the UV stability of this series of polymers and fibers.

PPTA fibers are subject to UV photodegradation with consequences, such as increases in brittleness, losses in brightness, changes in the color and opacity, and the formation of surface cracks. It was reported that the most significant damage of PPTA fibers usually occurred after UV radiation with a wavelength of about 310 nm; this led to severe amide-bond breakages.⁷ Similar to PPTA fibers, the mechanical properties, such as the tensile strength, resilience, and fracture toughness, of *p*-POD fibers obviously decreased because the oxadiazole ring of the structural unit was partly opened and the tight aggregation structure of the fibers was gradually destroyed.^{9,10} Therefore, it is important to improve the UV resistance of the PPTA and *p*-POD fibers.

Xing and Ding¹² and Liu *et al.*¹¹ used tetrabutyl titanate as the sol-gel precursor of a nanosized TiO₂ coating to improve the photostability of PPTA fibers. However, the preparation of the homogeneous mixture of tetrabutyl titanate was difficult, and the stability of the solution was poor. For *p*-POD fiber, in our team, Yang¹³ added carbon black to the *p*-POD solution before



Scheme 1. Structural unit of PPTA.

spinning to prevent UV light from directly irradiating on the surface of the fiber. Although the UV resistance of the fiber increased, the control of the spinning process became difficult, and the yield of the qualified products decreased. Yang also selected poly(vinyl alcohol) 1799, cellulose acetate, and sodium carboxymethylcellulose as anti-UV agents to coat the *p*-POD film.¹³ However, the anti-UV effect of this method was not obvious. Furthermore, to improve the UV resistance, an azo group was introduced into the *p*-POD macromolecular chains through copolymerization and blending by Zhou *et al.*¹⁰ However, this method also increased the difficulty of the preparation of the spinning solution.

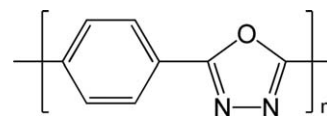
Polyhedral oligomeric silsesquioxanes (POSSs) are a type of organic–inorganic hybrid material;^{14,15} they embody a truly cage-like silsesquioxane architecture containing an inner inorganic framework made up of silicon and oxygen.¹⁶ POSSs have attracted considerable attention for dielectric, heat-resistant, and radiation-resistant paint and coatings because of the fact that the thermal degradation of POSS leaves behind a self-healing SiO₂ layer,^{17–19} which hinders the further propagation of both the oxygen and flame into the polymer surface layers. However, the POSS-containing hybrid polymers reported in most reports have been made from a one-pot copolymerization method, where POSS monomers and organic monomers are mixed together before the polymerization process.^{20–23} There have been no reports on POSS directly introduced into high-performance fibers with a finishing method.

To improve the UV resistance of *p*-POD and PPTA fibers, POSS was used as a colorless dye in a treatment for the selective adsorption of POSS for UV light at a specific wavelength. The effects of the POSS use, temperature, and time on the tensile strength retention of the fibers were examined, and the optimum treatment conditions were determined. To evaluate the possibility of the treatment method, the structural changes of the fibers were analyzed during the treatment and UV irradiation processes with inductively coupled plasma/atomic emission spectrometry (ICP–AES), intrinsic viscosity, X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy.

EXPERIMENTAL

Materials

γ -Aminopropyltrithoxysilane (from Debang New Chemical Materials Co., Ltd., Hubei, China) and formaldehyde, tetrahydrofuran, and hydrochloric acid (all from Ke Long Co., Ltd., Chengdu, China) were analytically pure and were used as received. PPTA fiber, a commercial product, was kindly provided by Chenguang Chemical Industry Institute (Chengdu, China). *p*-POD fiber was prepared in our laboratory and was described in our previous work.^{6,24} The PPTA and *p*-POD chemical formulas are shown in Schemes 1 and 2, respectively.

Scheme 2. Structural unit of *p*-POD.

To remove the oil and chemicals clinging to the fibers, they were scoured with acetone and ethanol at room temperature for 20 min, respectively, washed repeatedly with hot and cold deionized water, and dried under laboratory conditions.

Synthesis of Octa-Ammonium Chloride Salt of Polyhedral Oligomeric Silsesquioxane (POSS–NH₃Cl)

POSS–NH₃Cl was synthesized according to the procedures described in refs. 14 and 25. The resulting crude product was recrystallized with tetrahydrofuran. A white microcrystalline powder was obtained.

The yield was 34.20%.

IR (KBr, cm⁻¹): 3026 (–NH₃⁺); 2906, 2903 (–CH₂–); 1604, 1047 (–Si–C–); 1122, 1047 (–Si–O–Si–). ¹H-NMR (ppm, CDCl₃, room temperature, δ): 0.70 (m, –CH₂–, 16H), 1.75 (m, –Si–CH₂CH₂–, 16H), 2.91 (m, –Si–CH₂–, 16H), 8.19 (s, –NH₃⁺, 24H). ²⁹Si-NMR (ppm, CDCl₃, room temperature, δ): –57.9 (s, –Si–C–), –66.6 (s, –Si–O–).

The POSS chemical formula is shown in Scheme 3.

Treatment of the Fibers

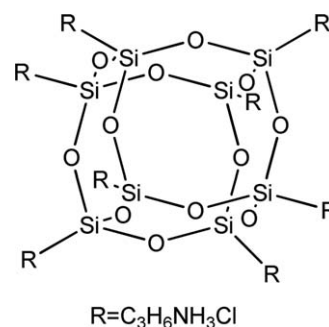
The fiber bundles were dipped in a POSS aqueous solution (concentration = 2–10 g/L) for 30 min at 30°C. The excessive solution was nipped. Then, the specimen was dried at 100°C for 30 min under shading conditions. Finally, the treated samples were cured at temperatures of 140–280°C for 0.5–8 min in the oven.

UV-Accelerated Aging

All of the *p*-POD and PPTA fibers were irradiated by an iodine–gallium lamp, whose emission wavelength was 200–450 nm. The irradiation power of the lamp was 800 W/m², and the distance between the sample and the lamp was 35 cm. The UV aging tests were conducted at 30 ± 0.5°C.

Measurement of the Tensile Strength

Tests were conducted on single-fiber specimens with a crosshead velocity of 20 mm/min and a gauge length of 20 mm. All of the tensile tests were carried out at a constant temperature of 25°C.

Scheme 3. Structure of POSS–NH₃Cl.

and a relative humidity of 70%. Twenty single-fiber specimens were measured to obtain the average.¹⁰

Silicon Content Measurement

Weights of 0.1000 g of dried and shredded fiber and 0.80 g of a mixture (anhydrous sodium carbonate/boric acid ratio = 2 : 1) were sufficiently mixed by a glass rod in a clean crucible and covered with the crucible cover. After the sample was melted for 12–15 min at 900–950°C in a muffle furnace, the mixed ash of the fibers was cooled to room temperature. Then, the mixture was put into a 250-mL beaker (with 80 mL of hot water and 20 mL of concentrated nitric acid inside), which was heated in an electric panel to digest the reaction until the sample was dissolved completely. Final, the volume of test solution was diluted with water to 200 mL in a volumetric flask. The Si content was analyzed with an ICP–AES spectrometer (Thermo Fisher).

Intrinsic Viscosity

The *p*-POD and PPTA fibers were dissolved with sulfonic acid as the solvent. The concentrations of the solutions were accurately prepared and ranged from 0.300 to 0.600 g/dL. The viscosity was measured with an Ubbelohde viscometer (diameter = 0.9–1.0 mm) at 30 ± 0.1°C under conditions where the kinetic energy effect was negligible.²⁶ The intrinsic viscosity value η_{sp} was obtained from the extrapolation of reduced viscosity η_{sp}/C to $C \rightarrow 0$ which made in accordance with Huggins' equation:^{27–29}

$$\eta_{sp}/C = [\eta] + k[\eta]^2 C \quad (1)$$

where $\eta_{sp} = (t/t_0) - 1$; t_0 is the flow time of the pure solvent; $[\eta]$ is the viscosity of the solution; C is the concentration of the solution; t is the flow time of the fiber solution; k is Huggins' constant.

SEM Analysis

An S-2150 scanning electron microscope (Hitachi, Ltd., Tokyo, Japan) was used for the morphological observation of the original and treated fiber surfaces. Before SEM observation, the surface of the specimen was coated with a thin layer of gold.³⁰

FTIR Spectroscopy

The FTIR spectra were obtained with an FTS3000 FTIR spectrometer (Digilab Co.). The wave-number scan range was from 4400 to 400 cm^{-1} with a resolution of 2 cm^{-1} . Samples of original and treated fibers were shredded to powders.

XRD Analysis

To determine the degree of crystallinity (%*K*), the integral area distribution method was used; it is suitable for a polymer having a limited number of crystalline peaks on its XRD pattern [$\text{intensity} = \text{function}(2\theta)$]. In this way, the sharp diffraction peak(s) of the crystalline region could be differentiated from the scattering of the amorphous ones. The testing fiber was wound on an opaque glass slide. %*K* was calculated with MDI Jade 5.0 software from the experimental data.^{31,32}

Degree of Fiber Orientation

Because the moisture content of a fiber has great impact on the test results of the orientation degree, the samples were laid under the conditions of constant temperature and humidity (23°C, relative humidity = 68%) for 24 h before the test. An

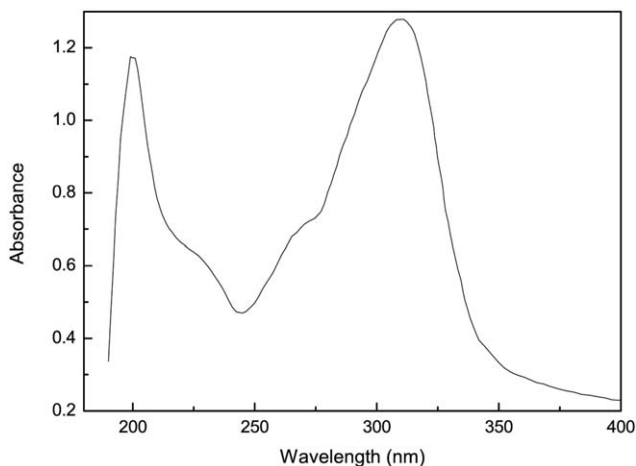


Figure 1. UV spectra of a POSS solution (1 g/L).

SOT-II velocity-oriented tester (Shandong Laizhou Electronic Instrument Co., Ltd., China) was used as the test instrument. Both ends of the fiber were fixed on the tester, and appropriate tension was applied to the test sample. After the sound wave through the fiber was stable, the value of the sonic speed on the display was recorded. Ten measurements for each sample were averaged to determine the value of sonic speed.^{33,34}

RESULTS AND DISCUSSION

UV Spectra of the POSS Solution

Figure 1 is the UV adsorption spectra of the POSS solution (1 g/L) at 20°C. In this curve, the two obvious adsorption bands were observed from 190 to 220 nm and from 280 to 340 nm. This result indicates that the POSS used in this research could effectively absorb UV light energy at some wavelengths. In the previous research, the intense absorption peaks of PPTA were from 280 to 320 nm, and that of *p*-POD was at 340 nm nearby.^{7,9,10,35} It is theoretically possible that the POSS solution could be used for UV protection of these two synthetic fibers.

Effect of the Treatment Condition on the Tensile Strength of the Irradiated Fiber

The effects of the POSS concentration on the tensile strength of the treated and irradiated PPTA and *p*-POD fibers are shown in Figure 2. As shown in the curves in Figure 2, the strength retention of both fibers increased with the POSS concentration up to 6 g/L. However, with the concentration further increasing to 8 g/L, the strength retention significantly declined. In the process of treatment, POSS was adsorbed and fixed on the fiber surface; this effectively adsorbed the specific wavelength of UV light and partially prevented the direct exposure of the UV light to the fibers. However, the overmuch POSS led to an excessively strong attractive force between the POSS molecules; this resulted in the aggregation of POSS molecules. This not only hindered the POSS fixed on the amorphous region of fibers but also decreased the UV absorption capacity of POSS.

Furthermore, the data points in this figure also demonstrated that the strength retention percentage of the *p*-POD fiber was higher than that of PPTA fiber. The differences may have been related to the supramolecular structure of the fiber. Because %*K*

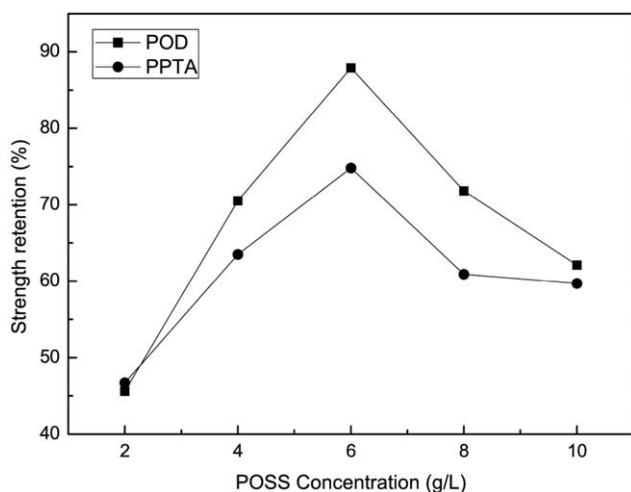


Figure 2. Effect of the POSS concentration on the strength retention of the irradiated fibers. The treatment conditions were 230°C and 2 min. The irradiation conditions were 30°C and 72 h in air.

of the PPTA fiber was higher than that of the *p*-POD fiber^{1,6,24,36} (see also Table IV), POSS could be more easily adsorbed and fixed on the *p*-POD fiber surface. The protective effect of POSS on the tensile strength of the *p*-POD fiber was more significant than that of the PPTA fiber.

As the results in Figure 3 show, the strength retention of the irradiated examples treated with POSS increased with increasing temperature. A higher temperature could not only increase the collision probability between the POSS molecules and fibers in the solution, which is beneficial to the adsorption and diffusion of POSS molecules on the fibers, but could also promote the thermal motion of the *p*-POD and PPTA macromolecular chain segments in the amorphous region of the fibers. This effectively increased the volume and quantity of the instantaneous gap in the amorphous region of the fiber, which was the main channel of POSS diffusion into the fiber.

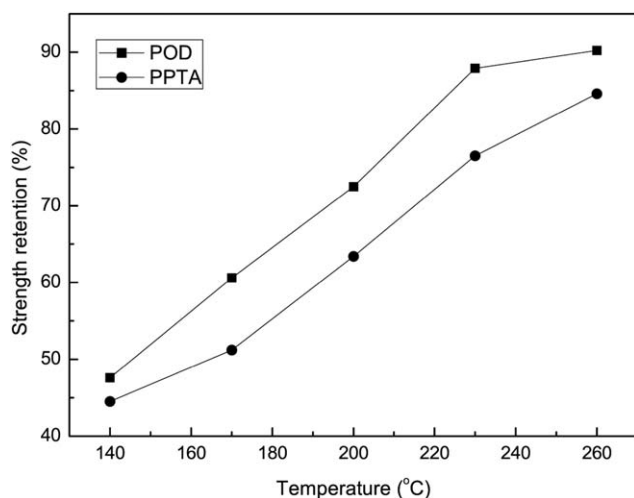


Figure 3. Effect of the treatment temperature on the strength retention of the irradiated fibers. The treatment conditions were POSS at 6 g/L and 2 min. The irradiation conditions were 30°C and 72 h in air.

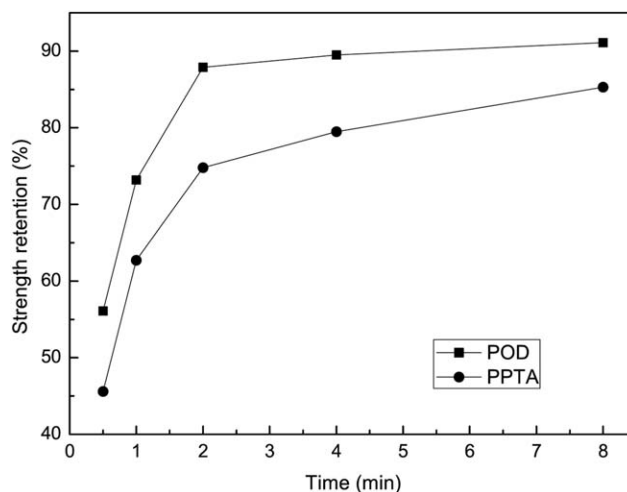


Figure 4. Effect of the treatment time on the strength retention of the irradiated fibers. The treatment conditions were POSS at 6 g/L and 230°C. The irradiation conditions were 30°C and 72 h in air.

Furthermore, the curves in Figure 3 indicate that at every treatment temperature, the value of the strength retention of the treated *p*-POD was higher than that of PPTA. One possible reason was that the surface of the PPTA fiber was smoother and denser than that of *p*-POD; this was not conducive to POSS adsorption. The other logical explanation was that the glass-transition temperature and decomposition temperature of *p*-POD were higher than those of PPTA,³⁷ so the effect of the higher temperature on the loss of strength of the *p*-POD samples was more limited than that of PPTA fibers. Taking into account the tensile strength of treated fibers and energy consumption savings, we used a treating temperature of 230°C.

As is well known, the adsorption and diffusion of the disperse dye on the synthetic fiber have time-dependent properties.³⁸ On the basis of previous conventional dyeing theory, Figure 4 shows that the strength retention of the treated and irradiated *p*-POD and PPTA fibers increased with increasing treatment time. However, after a treatment time of more than 2 min—in other words, when the diffusion equilibrium was reached; the effect of further increases in the treatment time on the amount of POSS on the fibers was not significant. Furthermore, the value differences of corresponding points between the two curves in this figure were similar to those in Figure 3. The specific reason for this phenomenon was almost the same, so we do not discuss it here. According to the previous results, an optimal treatment time of 2 min was selected.

Effect of the POSS Treatment on the Structure of the Fibers

ICP–AES. ICP–AES is a powerful analytical technique for trace elemental analysis. The technique is widely used for qualitative and quantitative elemental analyses on a routine basis.³⁹ On the basis of Bao *et al.*'s⁴⁰ and Wang *et al.*'s⁴¹ ICP–AES testing method, in this study, the accurate silicon element contents in the two samples treated with POSS were obtained by ICP–AES, listed in Table I; these were used to calculate the contents of POSS on the fibers.

Table I. POSS Contents of the Treated *p*-POD and PPTA Fibers

| Fiber | Silicon content ($\mu\text{g/mL}$) | POSS content (mg/1 g of fiber) |
|------------------------------------|--------------------------------------|--|
| Treated <i>p</i> -POD ^a | 3.006 | 0.315 |
| Treated PPTA | 2.302 | 0.241 |

^aThe treatment conditions were POSS at 6 g/L, 230°C, and 2 min.

The data in Table I indicate that silicon element was found from the testing of both ash samples; it mainly resulted from the POSS on the treated fibers. According to this, the mass of the POSS fixed on the fibers could be calculated approximately with the experimental values and the formula of POSS. The results demonstrate that it was technically feasible with the water-soluble POSS ammonium salt to treat the *p*-POD and PPTA fibers. Meanwhile, the content of silicon on the treated PPTA fiber was lower than that on the *p*-POD sample; this indirectly demonstrated that %K and degree of orientation of PPTA were higher than those of the *p*-POD fiber.

Intrinsic Viscosity. It is not easy to obtain a real relative molecular weight through ordinary methods for fibers that are difficult to dissolve or fuse. The determination of the intrinsic viscosity of a polymer solutions is a good alternative. In this study, the intrinsic viscosity was used to characterize the relative molecular weight of the *p*-POD and PPTA fibers. As the results in Table II show, the intrinsic viscosity of the treated and original samples all decreased after 72 h of UV exposure. However,

Table II. Intrinsic Viscosities of the *p*-POD and PPTA Fibers

| Fiber | Intrinsic viscosity (dL/g) | | Retention of intrinsic viscosity (%) |
|------------------------------------|----------------------------|----------------------------------|--------------------------------------|
| | Nonirradiated | Irradiated for 72 h ^b | |
| Original <i>p</i> -POD | 2.02 \pm 0.09 | 1.03 \pm 0.04 | 50.99 |
| Original PPTA | 9.18 \pm 0.15 | 5.68 \pm 0.11 | 61.87 |
| Treated <i>p</i> -POD ^a | 2.50 \pm 0.13 | 2.36 \pm 0.08 | 94.40 |
| Treated PPTA ^a | 9.37 \pm 0.04 | 8.36 \pm 0.09 | 89.22 |

^aThe treatment conditions were POSS at 6 g/L, 230°C, and 2 min.

^bThe irradiation conditions were 30°C and 72 h in air.

the retention of the intrinsic viscosity was obviously high for the treated fibers. This indicated that the degradation of the *p*-POD and PPTA fibers occurred in each process of UV irradiation, and the decline of the intrinsic viscosity was attributed to photodegradation.

Table II also shows that the intrinsic viscosity change of the *p*-POD solution was more significant than that of the PPTA solution with the introduction of POSS; this explained quite well why the strength retention of the *p*-POD fiber was much better than that of the PPTA fiber after UV aging. A reasonable explanation was that the deposition of POSS on the fiber surface effectively restricted the macromolecular chain from rupturing and the oxadiazole rings from breaking in oxygen.^{7,9,10,35}

SEM. Figures 5 and 6 show the surface SEM micrographs of all of the samples; they show the changes in the surface

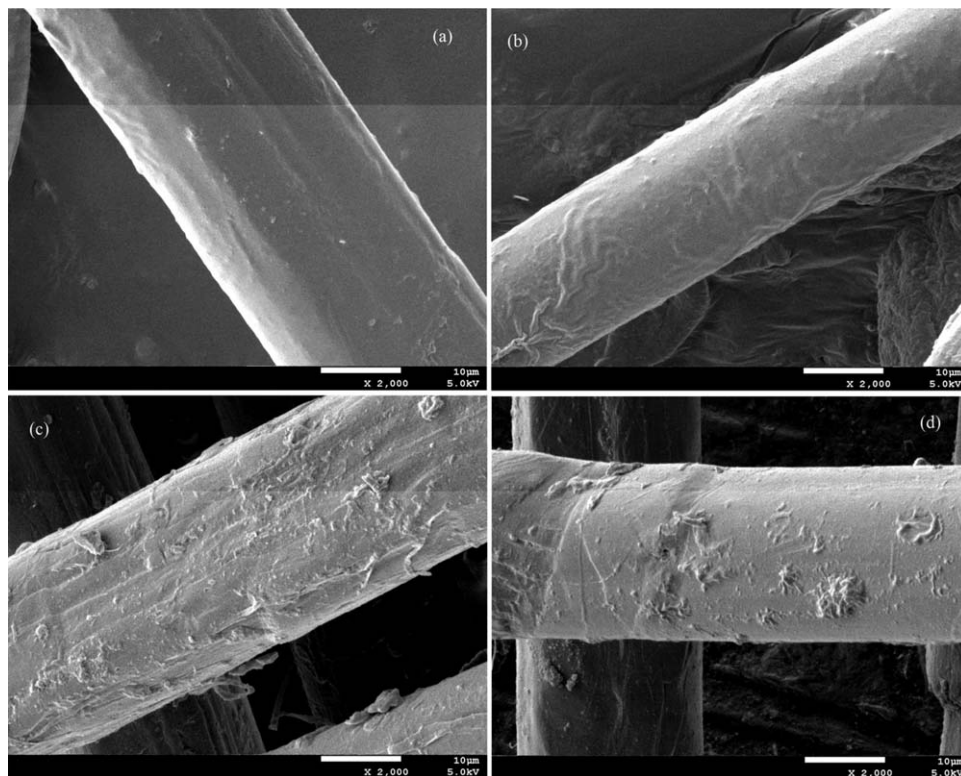


Figure 5. Surface SEM images of the *p*-POD fibers: (a) original *p*-POD, (b) POSS-treated *p*-POD (the treatment conditions were POSS at 6 g/L, 230°C, and 2 min), (c) irradiated *p*-POD, and (d) irradiated and treated *p*-POD (the irradiation conditions were 30°C and 72 h in air).

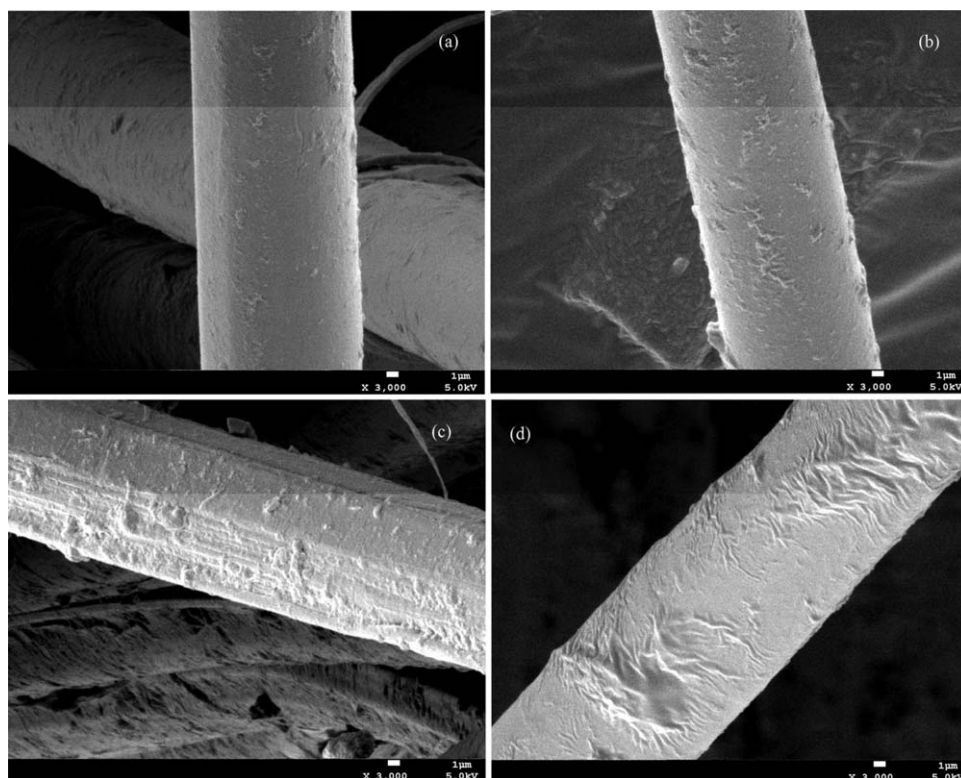


Figure 6. Surface SEM images of the PPTA fibers: (a) original PPTA, (b) POSS-treated PPTA (the treatment conditions were POSS at 6 g/L, 230°C, and 2 min), (c) irradiated PPTA, and (d) irradiated and treated PPTA (the irradiation conditions were 30°C and 72 h in air).

morphology during the treatment and irradiation processes. The fiber surface showed almost no significant change, and the soluble POSS particles, whose molecular size was on the nano-scale, were not observed. This phenomenon indicated that the effect of the treatment on the surface structure of the fibers was very limited. Axial streaks appeared on the original fiber surface, and parts of the skin began to roll up after 72 h of UV exposure. This showed that the damage of UV irradiation to the untreated fibers was very obvious. However, for the treated samples, the extent of damage to the epidermis was completely different. Only slight bulges and inconspicuous axial streaks were observed on the irradiated *p*-POD fiber surface. There were slight skin folds like water ripples on the PPTA surface.

Degree of Orientation. The basic principle of measuring the degree of fiber orientation with the sonic velocity method is that the orientation differences in the fiber macromolecular chains result in the anisotropy of sonic wave propagation. When sound waves propagate along the fiber axis, the speed of sound is the fastest; when sound waves propagate along the perpendicular direction of the fiber axis, it is minimal. Thus, a larger sonic speed value corresponds to a higher degree of orientation of the fiber.⁴² The data in Table III indicate that the sonic speed values for the *p*-POD and PPTA fibers decreased after 72 h of irradiation. Because the basic structural units of the two polymers were partly destroyed, the supramolecular structure changed; this disordered and created a loss in the arrangement of macromolecules. In other words, the orientation and %K of the fibers significantly declined.

The decrease in the speed values of the untreated samples was more evident compared to that of the treated samples after UV exposure. The phenomenon demonstrated that the POSS on the fiber surface effectively prevented UV light from accelerating the decrease in the degree of orientation, especially for the PPTA fibers. Furthermore, the orientation of the two fibers decreased slightly during the treatment process. This showed that the high temperature in the treatment process only had a small effect on the supramolecular structure, although the treatment temperature (230°C) is unbearable for general polymers.

XRD. The XRD pattern of a polymer reflects its crystalline structure. In Figure 7, the XRD patterns of original and treated fibers are compared. The shapes of the two XRD patterns of the treated fiber were very similar to that of the untreated sample,

Table III. Effect of the Treatment Process on the Degree of Orientation (Sonic Velocity) of the *p*-POD and PPTA Fiber

| Fiber | Sonic velocity (km/s) | | Loss ratio of sonic velocity (%) |
|------------------------------------|-----------------------|----------------------------------|----------------------------------|
| | Nonirradiated | Irradiated for 72 h ^b | |
| Original <i>p</i> -POD | 3.71 ± 0.13 | 2.92 ± 0.18 | 21.29 |
| Original PPTA | 2.55 ± 0.11 | 1.78 ± 0.06 | 30.20 |
| Treated <i>p</i> -POD ^a | 3.58 ± 0.16 | 3.03 ± 0.08 | 15.36 |
| Treated PPTA | 2.43 ± 0.09 | 2.02 ± 0.09 | 16.87 |

^a The treatment conditions were POSS at 6 g/L, 230°C, and 2 min.

^b The irradiation conditions were 30°C and 72 h in air.

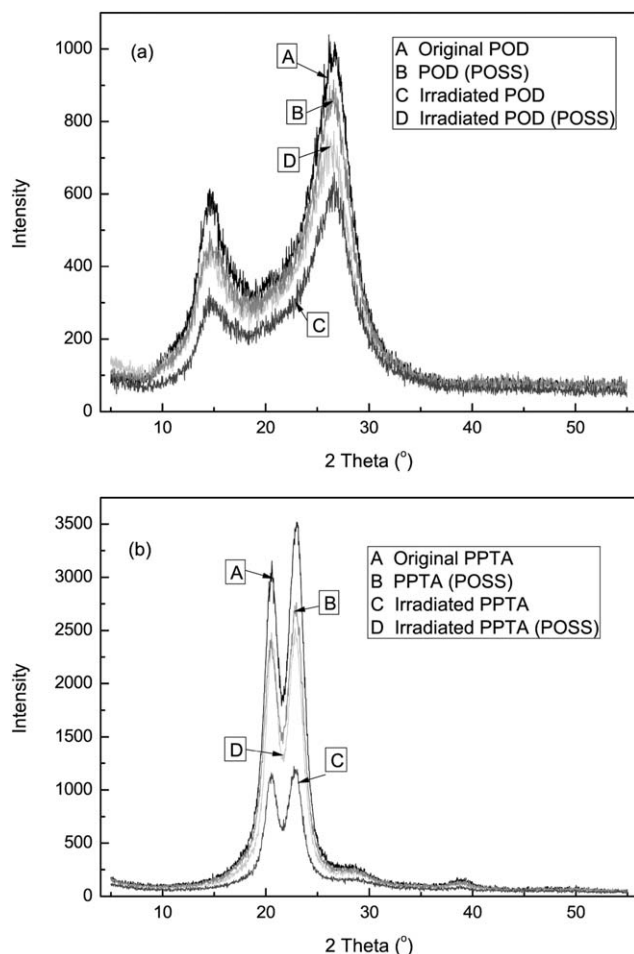


Figure 7. XRD patterns of the fibers. The treatment conditions were POSS at 6 g/L, 230°C, and 2 min. The irradiation conditions were 30°C and 72 h in air.

and the diffraction angles corresponding to the diffraction peak of the two sets of patterns were almost the same. The %K values of all of the samples are listed in Table IV by fitting and calculation with MDI JADE 5.0 software. The experimental data indicated that the treatment and UV exposure partially broke down the crystalline region of all of the samples. However, the main crystalline region structures of the *p*-POD and PPTA fibers after

Table IV. Effect of the Treatment Process on %K of the *p*-POD and PPTA Fibers

| Fiber | %K | | Loss ratio of the crystallinity (%) |
|------------------------------------|---------------|----------------------------------|-------------------------------------|
| | Nonirradiated | Irradiated for 72 h ^b | |
| Original <i>p</i> -POD | 51.2 | 25.0 | 26.2 |
| Original PPTA | 73.1 | 40.8 | 32.3 |
| Treated <i>p</i> -POD ^a | 45.0 | 34.4 | 10.6 |
| Treated PPTA | 58.6 | 54.8 | 3.8 |

^aThe treatment conditions were POSS at 6 g/L, 230°C, and 2 min.

^bThe irradiation conditions were 30°C and 72 h in air.

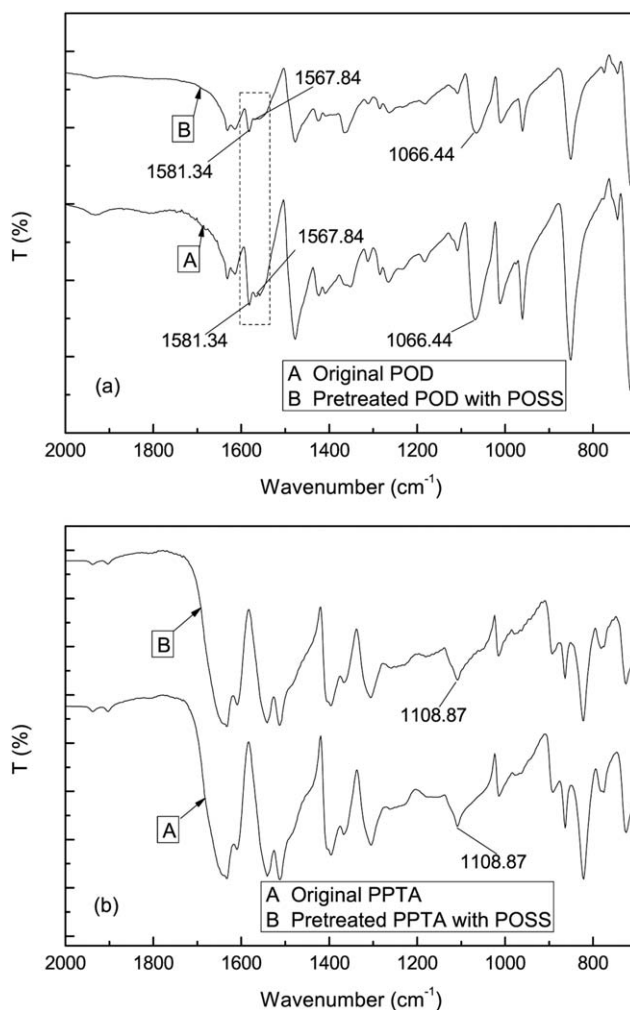


Figure 8. FTIR spectra of fibers before and after treatment with POSS. The treatment conditions were POSS at 6 g/L, 230°C, and 2 min.

treatment did not change significantly. This fundamentally confirmed the UV resistance of POSS.

There are obvious differences in the diffraction peak areas between the original and treated fibers after 72 h of UV exposure. The main peak at 27° was significantly lower after UV irradiation for the untreated *p*-POD. There was a small difference in the diffraction peak height for the treated *p*-POD. However, the change in the peak height of the original sample was still obvious, and the diffraction peak of the treated fiber showed almost no change at 15° after UV exposure. The special phenomenon indicated that for the treated *p*-POD fiber, the smaller size crystal, corresponding to a larger diffraction angle, was more easily damaged than the larger size crystal, corresponding to a smaller diffraction angle, during UV irradiation. The difference in the diffraction peaks in lines B and D in Figure 7(b) was also very small; this further proved that the UV resistance of POSS on the PPTA fiber was stronger than that on the *p*-POD fiber.

FTIR Spectra. Figure 8 shows the FTIR spectra of the *p*-POD and PPTA fibers before and after treatment with POSS. The

wave number and the intensity of the corresponding absorption peak of each sample showed almost no significant difference. The results indicate that the structural units of the macromolecules did not obviously change, and no new chemical groups were generated during the treatment, although stretching vibrations of Si—O—Si at 1030–1110 cm^{-1} ⁴³ were observed. However, the two adsorption peaks failed to show up because they were overlapped by a strong absorption peak of the corresponding characteristic groups of *p*-POD. Hofmann *et al.*⁴⁴ discovered that there are two different crystalline structures, the α and β forms, whose characteristic FTIR adsorption peaks are at 1568 and 1584 cm^{-1} , respectively. The adsorption intensity at 1568 cm^{-1} of the treated sample became weaker. It showed that the content of the α -form crystalline structure decreased.

CONCLUSIONS

p-POD and PPTA fibers were treated with POSS with a convenient method to retard UV photoaging. Under the treatment conditions of a temperature of 140–280°C and a time of 0.5–8 min, a higher temperature or a longer time was beneficial for increasing the fixed amount of POSS and prevent the UV-accelerated aging of both fibers.

This treatment process with POSS introduced silicon elements onto the fiber surface. Changes in the physical surface morphology and chemical composition were not obvious. After UV-accelerated aging, the degree of orientation and %*K* of the fibers and the intrinsic viscosity of the polymer solutions were well maintained. The supramolecular and macromolecular structures of the fibers were well protected. In general, POSS exerted a beneficial effect and protected *p*-POD and PPTA against UV-induced photodegradation in oxygen.

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