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Improving the Photo-stability of High Performance Aramid Fibers by Sol-gel Treatment

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Abstract: Although high performance fibers possess higher thermal resistant properties, they show very low sunlight stability. In this paper, a new sol-gel treatment method was used to enhance their light-resistant properties. Their mechanical property retention ratios (tenacity, extension, modulus) of fibers treated with titanium hydrosol were higher than those of the original Kevlar®129, PBO, and Kermel® fibers after light irradiation. Moreover, Kermel® fiber showed the highest improvement among the three kinds of fibers.

Keywords: High performance fiber, Photo stability, Sunlight, Tensile, Morphology, Sol-gel treatment

Introduction

Since high performance fibers show super high tenacity, high modulus, and high temperature-resistant property, they are widely used in the aerospace, military, structural composites, and so on [1-6]. However, even though they show favorable thermal properties [7-14], they exhibit very low resistance to sunlight exposure [15-21]. Accordingly, based on our former research work, a kind of new method was herein put forward to improve the sunlight resistant property of high performance fibers.

The sol-gel was firstly used in the silicate production [22-24] and the process is based on the hydrolysis and subsequent condensation of metal alkoxide compounds. The chemistry of the sol-gel process can be described as hydrolysis and condensation [25] shown in equations (1), (2), and (3).

$$M(OR)_x + H_2O \rightarrow M(OR)_{x-1}OH + ROH \quad (1)$$
$$2M(OR)_{x-1}OH \rightarrow (OR)_{x-1}M\text{-}O\text{-}M(OR)_{x-1} + H_2O \quad (2)$$
$$M(OR)_{x-1}OH + ROH \rightarrow (OR)_{x-1}M\text{-}OR + H_2O \quad (3)$$

where M is a metal species (Ti, Si, Al, Zr, etc.) and R is an alkyl group (methyl, butyl, ethyl, etc.). These reactions generate an oxide skeleton in the solution. Upon exposure to atmosphere or heating, the solution gels and becomes rigid.

In our previous research, the sol-gel technology was used in the textile finishing such as water-repellent, antistatic, UV-blocking, etc [26-31]. The transparent, strong adhesive metal or non-mental oxidative film, which might change the properties of textile greatly can be formed on the textiles by the sol-gel process.

In this paper, the sol-gel technology was adopted to improve the photo-stability of three kinds of high performance fibers (Kevlar®129, PBO, and Kermel®). Acidic aqueous tetrabutyl titanate solution was used as a precursor of titanium oxide film formed on the fiber surface after sol-gel treatment. The xenon weather tester is used to simulate the sunlight to irradiate these samples.

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Experimental

Samples

Three kinds of filaments were used in this experiment, one is Kevlar®129 filament from Dupont company of USA, another is Zylon® AS (PBO) from Tory company in Japan, and the other is Kermel® filament from Kermel company, France. Their chemical structures are shown in Table 1. Kevlar® belongs to para-aramid and PBO is a kind of aromatic heterocyclic polymer composed of rigid-rod molecules.

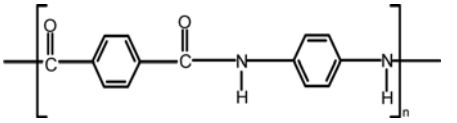
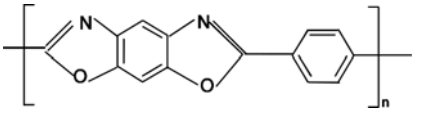
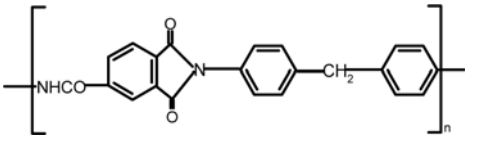
Preparation of Titanium Hydrosol

Tetrabutyl titanate was used as a precursor, acetic acid was used to retard the hydrolysis and condensation of tetrabutyl titanate, and hydrochloric acid was used as a catalyst for the hydrolysis. Tetrabutyl titanate was dissolved in the acetic acid at a certain molar ratio and the solution was agitated until homogenization was reached, then the solution was slowly added to an aqueous hydrochloric acid solution and stirred strongly for 3 h in a three-necked bottle at ambient temperature. Titanium hydrosol of 2.0 % concentration, so called hydrosol, was thus obtained.

Sol-gel Treatment

The filament samples were dip-and-nipped twice in the hydrosol with a pick up of 40~50 %. The treated samples were dried at 70 °C for 5 min, and then rinsed with distilled water for 30 s to remove excessive hydrochloric acid and acetic acid to avoid the damage of filaments when cured at higher temperature. Subsequently the treated samples were dried and cured at 150 °C for 3 min.

Table 1. Sample and specification

Sample	Density (dtex)	Tenacity (cN/dtex)	Extension (%)	Modulus (cN/dtex)	Chemical structure
Kevlar® 129	1.68	23.17	4.24	621.5	
PBO	1.67	32.73	4.12	892.6	
Kermel®	1.7	3.55	14.91	32.12	

Experimental Tester

The particle size distribution of titanium hydrosol was measured by Nanosizer from Malvern Instruments Ltd., UK. The ATLAS 150S+ of xenon arc light was used to simulate sunlight. The testing conditions in the chamber are as follows; wavelength of light : 300 nm~800 nm, chamber temperature : 60 °C, and relative humidity : 20 %. Samples were continuously irradiated for 24, 72, 120, and 168 h, and then the tensile properties were tested.

The mechanical properties of single fiber, including tenacity, modulus, and extension to break, were recorded on an XQ-1 single filament tensile tester, where adopted was tester yarn-gripping attachment with a nominal gauge length of 20 mm (from the upper edge to the lower edge of the grippers), and the crosshead speed was set 10 mm/min. All tensile tests were carried out at ambient conditions, with constant temperature (20 °C) and humidity (65 %); the sample size of every test was chosen to ensure ±10 % variance at 90 % confidence level.

Finally, the SEM photographs of fibers after exposure to light were observed with the JSM-5600 LV.

Results and Discussion

Characterization of Titanium Hydrosol

The size of hydrosol was measured by Nanosizer as shown in Figure 1, which described the relation between the statistical number and the diameter of titanium hydrosol particles.

From Figure 1, it can be seen that the titanium hydrosol particles become very small via the hydrolysis of tetrabutyl titanate. 95 % of the sols are less than 5 nanometer in particle diameter, which indicates that the hydrolysis of tetrabutyl titanate is thoroughly complete and uniform. Thus it is very advantageous to form the thin and compact film on the surface of fibers by sol-gel treatment as shown in Figure 2, where (a) and (b) are for the pristine Kevelar® 129 samples and (c) and (d) are for the samples treated with titanium hydrosol. Especially the photo (d) displayed clearly the film on the surface of Kevlar fiber after sol-gel treatment.

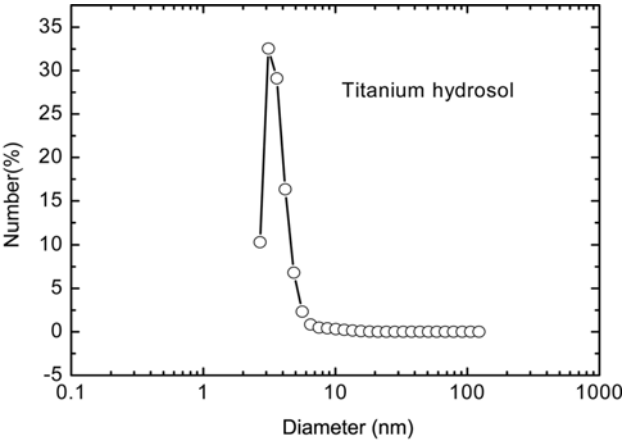


Figure 1. The particle size distribution curve of titanium hydrosol.

The Mechanical Property of the Pristine and Titanium Hydrosol Treated Fibers Exposed to Simulated Sunlight

The mechanical properties of original and treated fibers after light irradiation are illustrated as in Figure 3. The figure shows the relation between their mechanical property retention ratio and the irradiation time. The mechanical properties retention ratios of samples treated with titanium hydrosol are obviously enhanced compared with the untreated samples after light exposure.

The moduli of Kevlar® and Kermel® fibers increase with increasing irradiation time up to 20 h, after which they decrease slightly. However, even after 168 h irradiation, the

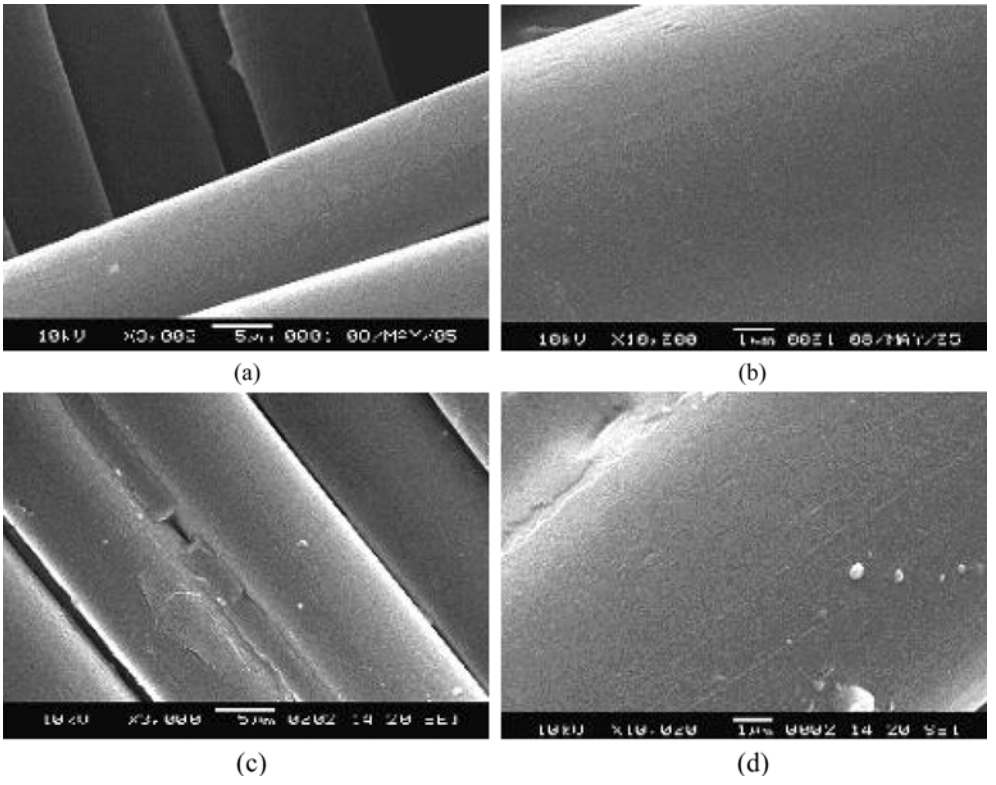


Figure 2. SEM photographs of pristine Kevlar®129 ((a), (b)) and sol-gel treated one ((c), (d)).

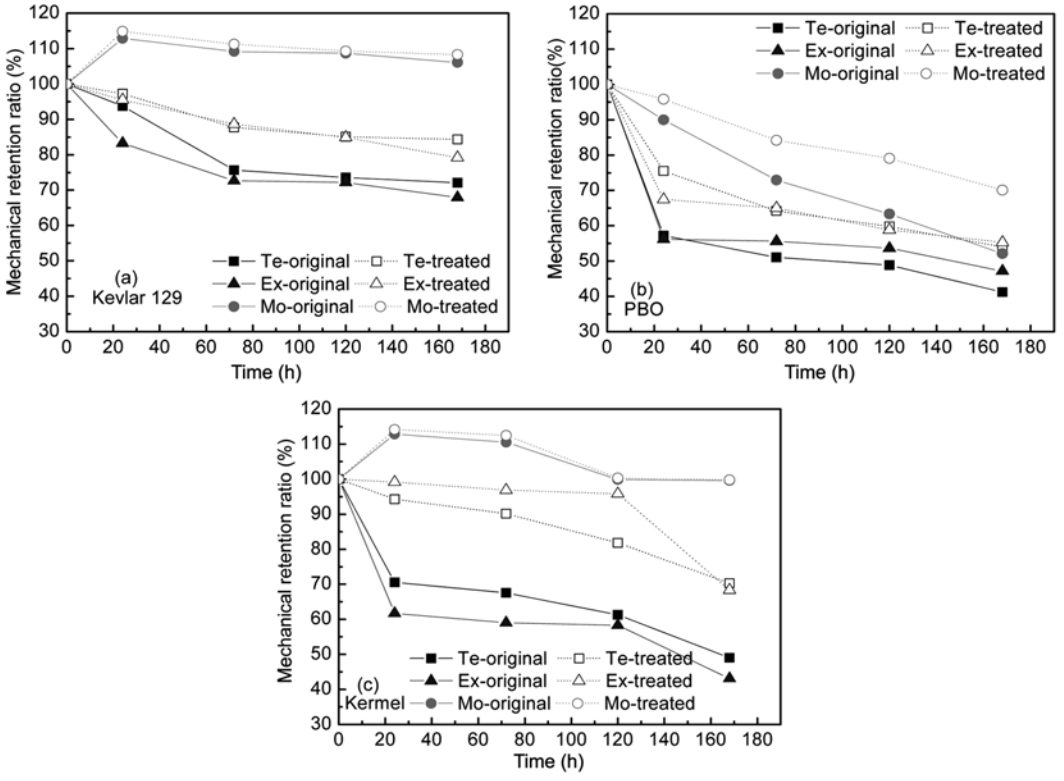


Figure 3. Changes in mechanical properties retention percentage of the original and titanium hydrosol treated samples as a function of irradiation time under simulated sunlight. Te: tenacity, Ex: extension at break, Mo: modulus.

modulus retention ratio is still above 100 % for Kevlar® and Kermel® fibers. This may be because the light irradiation energy can make improvement in the overall axial orientation, crystal perfection, and lateral order of the two fibers, even though the mechanism is not elucidated yet.

When comparing the original and treated samples, Kevlar® and PBO fibers treated with sol-gel method have only about 12 % increase of retention ratio in their tenacity and extension after 168 h irradiation. However, Kermel® fiber shows much higher increase of retention ratio after sol-gel treatment. After being irradiated for 168 h, sol-get treated Kermel® fiber shows not only the tenacity retention ratio increasing from 49 % to 70 %, but also the extension retention ratio increasing from 43 % to 68 %. Kermel® is a smooth-surface fiber with an almost circular cross-section. This shape as well as its modulus makes it comfortable and very pleasant to touch Kermel® fiber like cotton. It has been reported that the sol-gel treatment shows the best UV-blocking ability for cotton fiber [30]. Since the titanium hydrosol has a good affinity to Kermel® as in the case of cotton, the film formed on Kermel® fiber is more compact than on the other two fibers and consequently the highest improvement is shown naturally.

These results imply that the photo stability properties of high performance fibers could be obviously improved because the titanium dioxide thin film was formed on the surface of high performance fibers by sol-gel treatment, which can effectively block the ultraviolet rays so that the inner aramids avoid being damaged strongly and the light degradation of aramids is retarded.

The Rupture End Morphology of High Performance Fibers Exposed to Simulated Sunlight

The fracture end morphology of Kevlar®129, PBO, and Kermel® fibers from the tensile test after exposure to simulated sunlight for 168 h can be seen in Figures 4, 5, and 6. From the rupture end morphology of Figure 4(a) and (b), the original Kevlar®129 sample shows more splitting and broken partly when extended to the rupture after sunlight irradiation. On the other hand, the sol-gel treated Kevlar®129 samples (seen in Figure 4(c) and (d)) show higher rupture consistency and their inner fibrils don't separate obviously, which implies that the treated fiber has higher light-resistant property than the untreated one.

When the original and treated PBO fibers are compared under the same light condition (seen in Figure 5), the treated PBO fiber shows flatter fracture end than the original, which predicts that the treated PBO fiber has higher mechanical property.

Referring to the rupture end of original Kermel® fiber, it displays brittle broken characters and the interior fibril spacing can be found in their inner structure (Figure 6(a) and

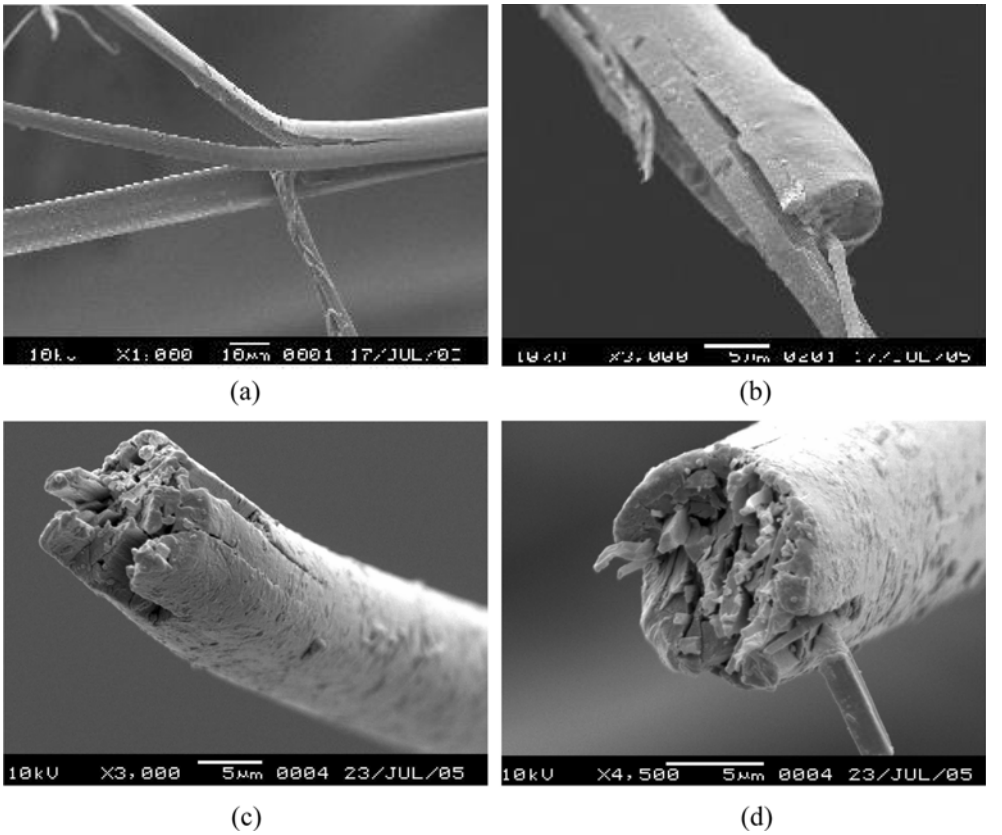


Figure 4. SEM photographs of rupture ends of pristine Kevlar®129 ((a), (b)) and sol-gel treated one ((c), (d)) after light irradiation for 168 h.

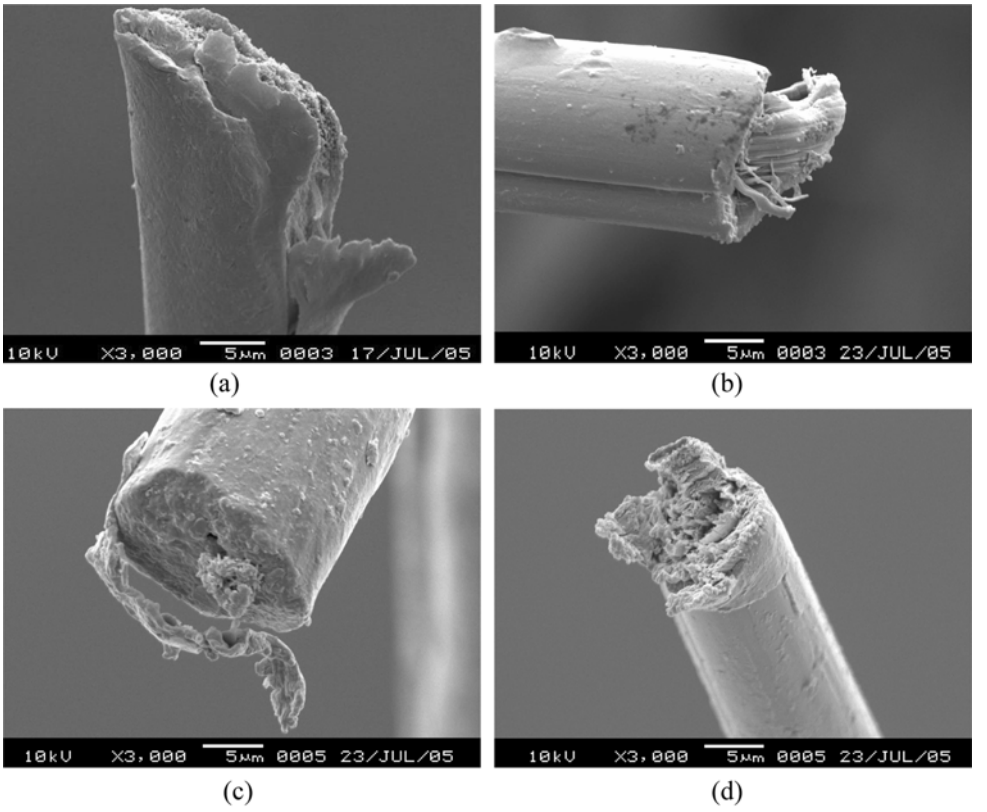


Figure 5. SEM photographs of rupture ends of pristine PBO ((a), (b)) and sol-gel treated one ((c), (d)) after light irradiation for 168 h.

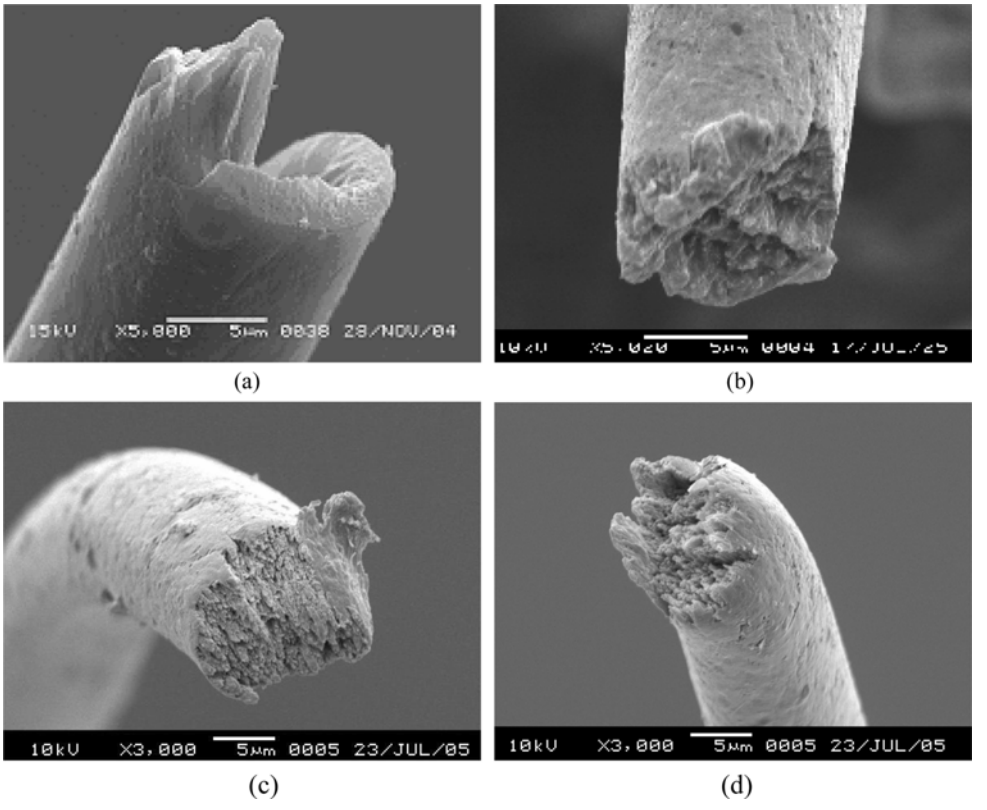


Figure 6. SEM photographs of rupture ends of pristine Kermel® ((a), (b)) and sol-gel treated one ((c), (d)) after light irradiation for 168 h.

(b)). On the other hand, the treated Kermel only shows little peeling in the cortex with almost no obvious damage in its interior fibril.

According to differences in the fracture end of the original and treated fibers, it can be concluded that there is a layer protection film on the surface of three kinds of high performance fibers after sol-gel treatment, which can prevent aramids from being damaged after long exposure to the light.

Conclusion

High performance fibers, Kevlar®129, PBO, and Kermel® treated with titanium hydrosol, showed higher mechanical properties retention ratio than the untreated counterparts. Kermel® fiber treated with titanium hydrosol showed the highest retention ratio of mechanical properties among the three fibers.

High performance fibers treated with titanium hydrosol show more uniform rupture when observed from their fracture end morphology after light irradiation. The reduction of mechanical properties after long exposure to the light has become much smaller through the treatment with titanium hydrosol. This is because the gel particles on the high performance fiber surface tightly link together with interconnected -Ti-O-Ti- bonds to form an inorganic network by sol-gel process and thus this kind of film can effectively block the UV-visible light.

Although the modification effect is not the best to date, it shows bright future of high performance fibers resistant to sunlight irradiation. Therefore more suitable precursors and processes can be considered to optimize in future to develop the highly UV-resistant aramid and aromatic amide-imide fibers.

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