

# UV Photo-Stabilization of Tetrabutyl Titanate for Aramid Fibers via Sol–Gel Surface Modification

Yanjun Xing,<sup>1</sup> Xin Ding<sup>2</sup>

<sup>1</sup>College of Chemistry and Chemical Engineering, Donghua University, Shanghai 200051, China

<sup>2</sup>College of Textiles, Donghua University, Shanghai 200051, China

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**ABSTRACT:** Tetrabutyl titanate was used as sol–gel precursor of a nanosized TiO<sub>2</sub> coating to improve the photo-stability of aramid fibers. The nanosized TiO<sub>2</sub> coating was characterized by XRD and XPS. The influence of the TiO<sub>2</sub> coating on photo-stability of aramid fibers was investigated by an accelerated photo-ageing method. The photo-stability of aramid fiber showed obvious improvement after coating. After 156 h of UV exposure, the coated fibers showed less deterioration in mechanical properties with the retained tensile strength and elongation at break greater than 36 and 50% of the original values, respectively, whereas the uncoated fibers degraded completely

and became powdery. SEM analysis showed no significant surface morphological change on the coated fiber after the exposure, while some latitudinal crack fractures appeared on the uncoated aramid fiber. The effect of the nanosized TiO<sub>2</sub> coating was also well demonstrated by examining the difference of distributions of C1s in XPS deconvolution analysis on the surface of uncoated/coated fibers with increasing UV exposure time. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3113–3119, 2007

**Key words:** aramid fibers; photo-stabilization; TiO<sub>2</sub> coatings; sol–gel surface modification

## INTRODUCTION

Aramid fibers are being used increasingly in a wide range of application due to low density, high specific strength, high modulus, and high thermal resistance of aramid.<sup>1</sup> The long-term service in hostile environments is required when used in aviation and space engineering. However, aramid fibers are subject to UV photodegradation with the consequences such as increase in brittleness, loss of brightness, change of color and opacity, formation of surface cracks, etc. Therefore, special care must be taken to improve the UV photo-stability of aramid fibers.

It is reported that aramid fibers are very sensitive to ultraviolet (UV) radiation with a wavelength of about 310 nm, leading to severe bond breakages.<sup>2</sup> Reports are also given that the ultrafine or nanoparticle titanium dioxide has been used as photo-stabilizer for a number of polymers subject to UV lights of shorter wavelengths (300–400 nm).<sup>3–5</sup> Unfortunately, aramid fibers have poor interfacial bonding with most of the

commercially available photo-stabilizer used for polymers, including titanium dioxide.

Oxide or oxide-based coatings have been deposited on various substrate materials using sol–gel techniques.<sup>6–9</sup> There are several potential advantages of sol–gel technique for providing aramid fibers with photo-protective coating films, such as low costs in both the coating equipments and the precursors, low temperature and low pressure processing conditions, fast throughput and no damage to the substrate materials, etc. Moreover, large area films can be made easily during the processing because the sol–gel method is a liquid-phase process.

In the present research, nanosized TiO<sub>2</sub> was prepared using tetrabutyl titanate as precursor and coated onto the surface of aramid fibers by sol–gel method to improve the photo-stability of the fibers. Tensile properties of both uncoated and coated aramid fibers were tested under an accelerated photo-ageing procedure following the standard method by ISO 4892 (part 3)<sup>10</sup> to investigate the effect of TiO<sub>2</sub> coating on photo-stability of aramid fibers. Microscopic scale analyses including SEM and XPS were conducted to make further investigation on the tensile testing results at microcosm.

## EXPERIMENTAL

### Materials

Tetrabutyl titanate was purchased from Shanghai Chemicals and Medicals Co., Ltd. The aramid fiber

Correspondence to: Dr. Y. J. Xing (yjxing@dhu.edu.cn) or Prof. X. Ding (xding@dhu.edu.cn).

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used is commercial 1.47 dtex Kevlar 49 staple fiber by DuPont (Richmond, VA). The tensile strength of the fiber is 27.21 cN, elongation at break 3.4% and elastic modulus 648.7 cN/dtex (DIN EN ISO 527-1-1996). Before TiO<sub>2</sub> coating, the aramid fibers were extracted by acetone and deionized water for 3 h in sequence to eliminate organic impurity on the fiber surface. The fibers were then dried in a vacuum oven.

### Preparation of TiO<sub>2</sub> coating

The homogeneous mixture of tetrabutyl titanate (TBT) and acetic acid was added dropwise to a mixture of water and hydrochloric acid under vigorous stirring for 10 min at room temperature. The chemical composition of the inchoative alkoxide solution was TBT : HAc : H<sub>2</sub>O : HCl = 1 : 4 : 150 : 0.6 in molar ratio. The solution was dispersed by ultrasonic (SK2200H, 90 W, 59 kHz, Kudos, Shanghai) for 10 min to obtain a suspending solution of sol ready for coating.

To treat the surface of aramid fibers by sol-gel method, the fibers were dipped in TiO<sub>2</sub> sol solution and ultrasonic-treated at room temperature for 30 min, and then dried and annealed in a vacuum oven at 80°C for 30 min.

### UV exposure conditions

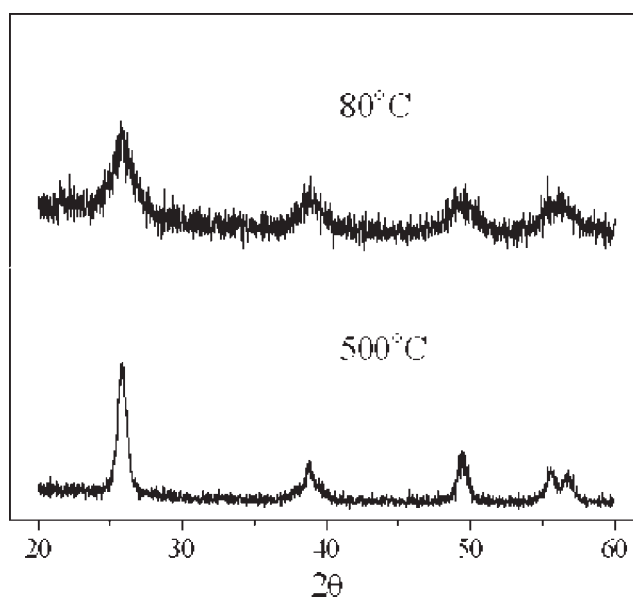
The uncoated and coated aramid fibers were exposed following the accelerated photo-ageing procedures<sup>10</sup> (UV lamp: 400 W, 280–340 nm, Hualun, Shanghai; Filter: 280 nm ≥ 50%, 313 nm ≥ 81%, 405 nm ≤ 1.0%, Shanghai Seagull Colored Optical Glass). The experiments were conducted continuously (24 h/day) at room temperature. The mechanical properties and microscopic analyses of fibers were tested regularly at predetermined UV exposure times.

### Fiber tensile test

Fiber tensile properties were tested on a Model XQ-1 fiber tester (Lipu, Shanghai) with a 25-N load cell. The gauge length was 20 cm and the loading speed was 5 mm/min. The pretension was 0.2 cN. The test was carried out at (20 ± 2)°C and (65 ± 5)% RH. Every tensile value was averaged from 50 tests. All the test data were statistically analyzed at 95% confident level and the difference in tensile properties between the uncoated and coated fibers is then examined. Since Young's modulus is normally not affected by photo-oxidation,<sup>2,11</sup> it is not recorded in the present study.

### Microscopic analysis

The size of TiO<sub>2</sub> particles in the sol was measured by Zetasizer Nano 300 (Malvern, UK). The composition of the crystal phase and size of crystal grains were



**Figure 1** XRD patterns of nanosized TiO<sub>2</sub> baked at different temperatures for 2 h.

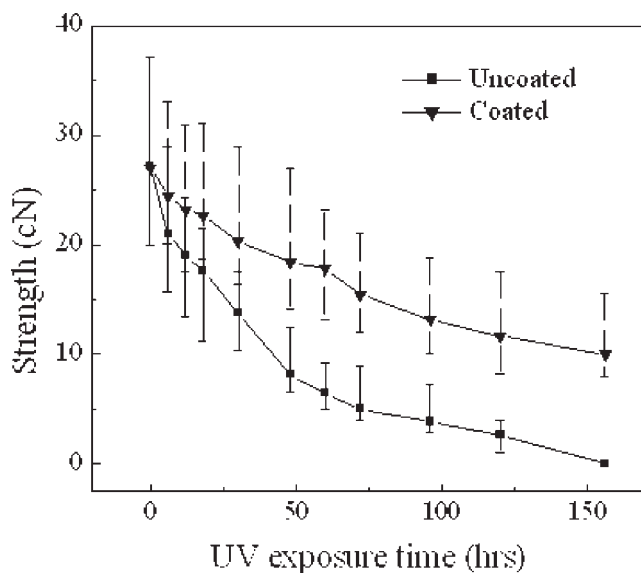
analyzed by X-ray diffraction (XRD) with a diffractometer (D/max-RA model, Rigaku, Tokyo, Japan) employing Cu K $\alpha$  radiation. The nanoscopic damage on the fiber surface was examined with a scanning electron microscope (SEM, JSM-5600, JEOL, Japan). The chemical composition of the fiber surface was analyzed with a SCALAB MK-II XPS spectrometer (VG, UK). The X-ray source was Mg K $\alpha$  and the take-off angle was 45°. The pressure in the chamber was  $7 \times 10^{-9}$  mbar. XPS signals were taken with step width 0.05 eV and pass energy 20 eV.

## RESULTS AND DISCUSSION

### Preparation and characterization of nanosized TiO<sub>2</sub> coating

Acetic acid was used as stabilizer to form complexes with titanium atoms in this experiment. The hydrolysis of tetrabutyl titanate was consequently slow and the preparation of nanosized TiO<sub>2</sub> with desired crystalline structure and shapes was also easy to control.<sup>12,13</sup> No other organic solvent was used in the preparation of nanosized TiO<sub>2</sub>. This would be convenient and safe for the large-scale industrial production.

The size of the TiO<sub>2</sub> particles in sol was about 25 nm, examined by the photon correlation spectroscopy (PCS) method. The crystal shape of the TiO<sub>2</sub> coated on the surface of aramid fibers was characterized by X-ray diffraction (XRD). Compared with the film baked at 500°C, the broad and sawtooth peaks of the TiO<sub>2</sub> coating baked at 80°C indicate an anatase TiO<sub>2</sub> structure ( $2\theta = 25.3^\circ$ ), although a small amount of amorphous content could still be noticed (Fig. 1).



**Figure 2** Tensile strength of aramid fibers as a function of UV exposure time.

The mean crystallite size (25 nm) of the  $\text{TiO}_2$  in the coating is calculated by Scherer equation and it agrees well with the size of the  $\text{TiO}_2$  particles in sol.

The  $\text{TiO}_2$  layer on aramid fiber was formed by dip-coating method. Ultrasonic treatment was used to improve the wettability of  $\text{TiO}_2$  coating on aramid fibers.<sup>14</sup> The coated substrates were annealed at  $80^\circ\text{C}$  for 30 min. The low temperature annealing process allowed for the preservation of aramid fibers and the reduction of possible crack formation in the sol-gel coatings due to the difference in thermal expansion coefficients of titanium oxide and aramid fibers. The sol-gel network undergoes an extensive collapse leading to the formation of a dense and compact film upon removal of solvent during drying. The compact  $\text{TiO}_2$  layer would play an important role in the prevention of oxygen penetrating into the internal of fiber, which is also an important factor in the photo-oxidation of aramid fibers.<sup>15</sup>

### Tensile properties of aramid fibers

The tensile properties of both uncoated and coated aramid fibers were examined to show the effect of  $\text{TiO}_2$  coating on the photo-stability of aramid fibers. Compared with the uncoated fibers, there is no significant loss of tensile strength in the coated ones before UV exposure, indicating little damage to the fibers by sol-gel treatment.

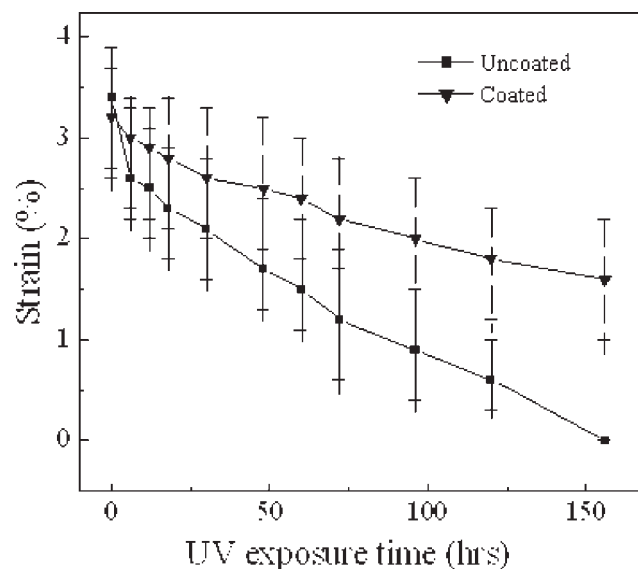
As shown in Figures 2 and 3, the tensile properties of both uncoated and coated aramid fibers show a decrease with respect to UV exposure time. The tensile strength and elongation at break of uncoated fibers suffer a greater deterioration than that of the coated

ones under the same conditions of UV exposure. After 156 h of UV exposure, the uncoated fibers degraded completely and became powdery. On the contrary, more than 36% tensile strength and 50% break elongation of the coated fibers still remained. The improvement of tensile properties of aramid fibers can be attributed to the photo-stabilization of the nanosized  $\text{TiO}_2$  particles in the coating, which improved the durability of the organic bonding in aramid fibers to UV radiation by absorbing the UV light under  $400\text{ nm}$ .<sup>5</sup>

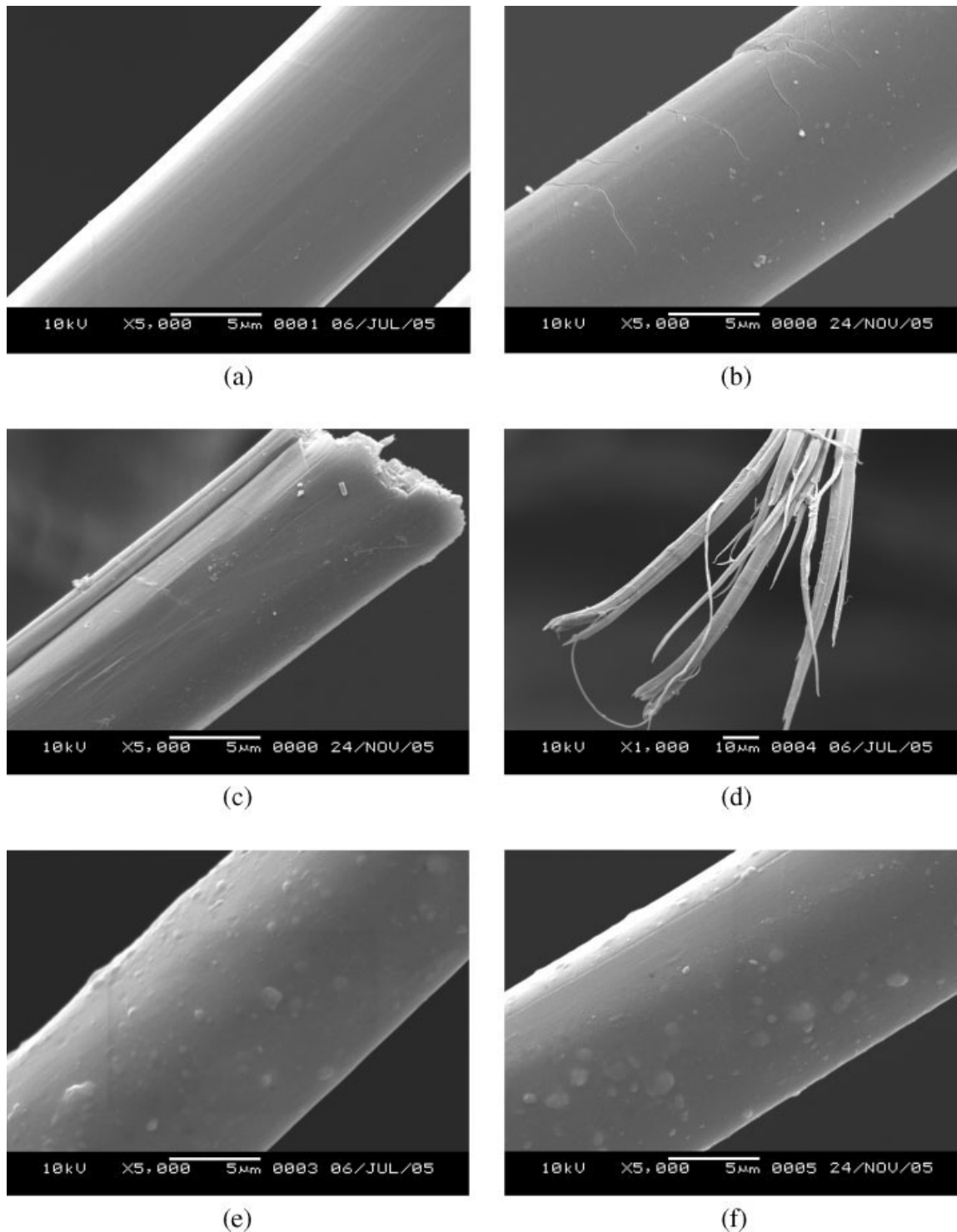
However, the decrease of the tensile properties of fibers is still obvious even after the sol-gel surface treatment. This could be attributed to the negative influence of coexisted photo-catalysis of nanosized anatase  $\text{TiO}_2$ . The free radicals produced by photo-catalysis could degrade the aramid fibers and weaken the photo-stabilization of  $\text{TiO}_2$  layer. It is expected that the nanosized rutile  $\text{TiO}_2$  by modified sol-gel hybridization should have higher photo-stabilization and lower photo-catalysis than nanosized anatase  $\text{TiO}_2$ .<sup>5</sup>

### Analysis of fracture surface morphology

The fracture surface of uncoated aramid fibers before UV exposure was observed by a scanning electron microscope [Fig. 4(a)]. Typical longitudinal fibril structure can be noticed in the uncoated samples, indicating that fiber molecules align along the fiber axis or longitudinal direction.<sup>16</sup> Under a long-time (156 h) UV exposure, brittle latitudinal cracks appeared on the fiber's surface [Fig. 4(b)], which would facilitate molecule chain scission. High magnification observation on the fracture surface of the fragment sample [Fig. 4(c)] gives the impression that the latitudinal cracks are dif-



**Figure 3** Tensile strain of aramid fibers as a function of UV exposure time.

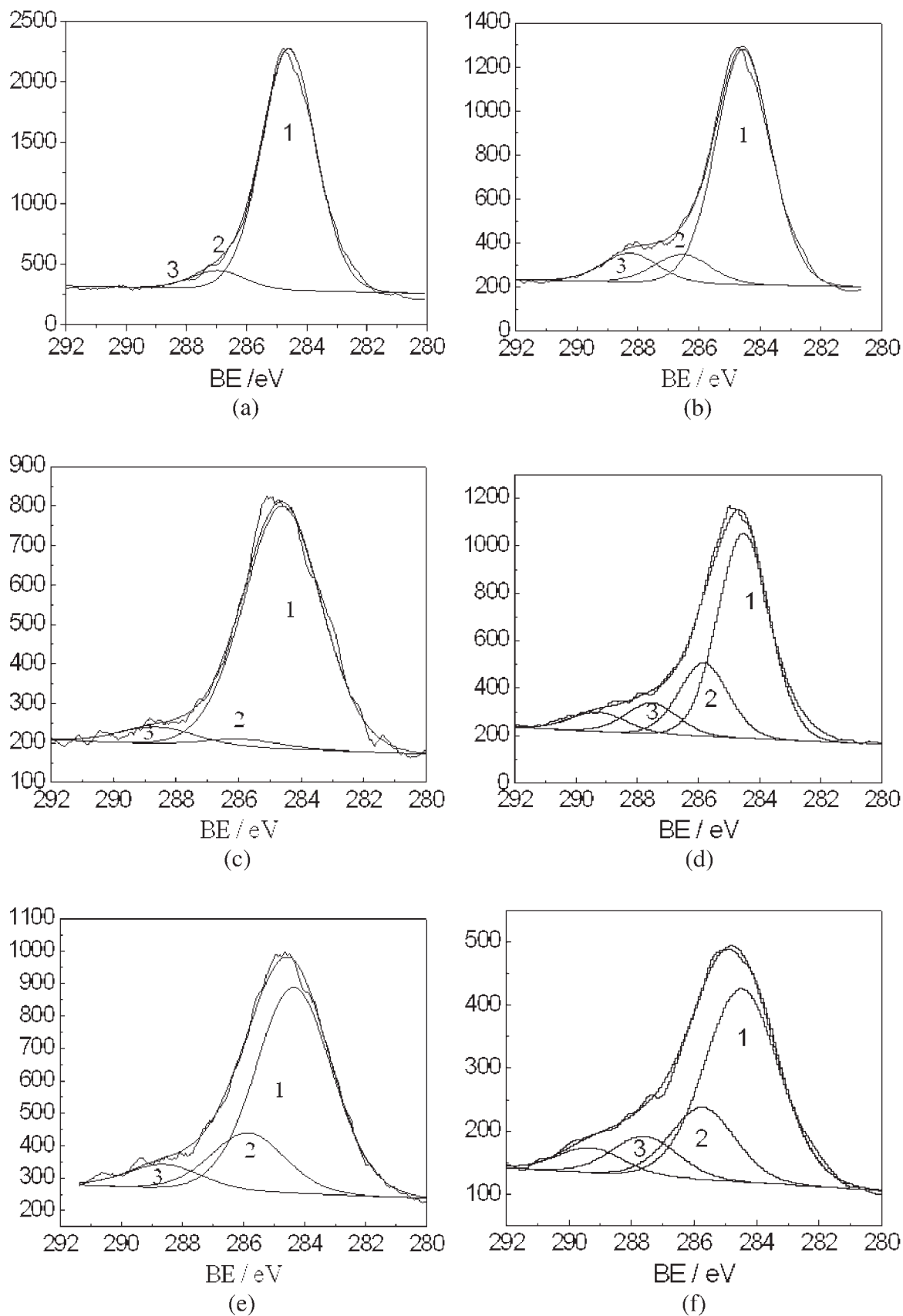


**Figure 4** SEM images of surface of aramid fiber. (a) uncoated, exposure for 0 h; (b) uncoated, exposure for 156 h; (c) uncoated, exposure for 156 h (the latitudinal crack fracture); (d) fiber fracture after tensile test, before exposure; (e) coated, exposure for 0 h; (f) coated, exposure for 156 h.

ferent from the surface cracks formed during tensile tests [Fig. 4(d)]. It is clear that the crack on the fiber's surface caused by UV exposure should be the main reason for the decrease of tensile properties.

As shown in Figure 4(e), the surface of coated fiber is smooth and a number of small titanium dioxide

clusters adhere to the fiber surface. No negative effect by sol-gel surface modification on the tensile properties of the fiber should be expected here because there is no etching found on the surface of the fibers. This is consistent with the tensile test data. After exposed for 156 h, no significant change could be observed in the



**Figure 5** XPS spectra of C1s in surface of aramid fibers. (a) uncoated, exposure for 0 h; (b) uncoated, exposure for 48 h; (c) uncoated, exposure for 156 h; (d) coated, exposure for 0 h; (e) coated, exposure for 48 h; (f) coated, exposure for 156 h.

SEM micrograph of the coated fibers compared with those before UV exposure [Fig. 4(f)]. On the other hand, no delamination or lifting of TiO<sub>2</sub> coating from the fibers is observed in Figure 4(f). It is thus suggested that the nanosized TiO<sub>2</sub> coating is still chemically stable and remains good adhesion after long-time UV exposure.

### XPS analysis

The chemical composition changes on the surface of aramid fibers were examined by XPS. The appearance of free acid (—COOH) peak in C1s deconvolution analysis in both uncoated and coated aramid fibers after exposure, shown in Figure 5 and Table I, indicates breakage of the acylamide bond in aramid.<sup>17</sup> However, the ratio of the free acid in uncoated fibers increases faster than that in the coated counterparts with the increase of UV exposure time. This result indicates that the molecular chain scission caused by UV photo-oxidation is weakened by the nanosized TiO<sub>2</sub> coating.

The XPS spectra also give information of titanium in the coating layer, which shows a doublet at 458.40 eV (Ti 2p<sub>3/2</sub>) and 464.00 eV (Ti 2p<sub>1/2</sub>), as indicated in Table II. The peak areas give a 1 : 2 ratio and the binding energy gap between them is about 5.6 eV, which is in good agreement with the pure TiO<sub>2</sub>.<sup>18</sup> This means that tetrabutyl titanate used in the surface modification has all been transferred to the nanosized TiO<sub>2</sub> after coating process.

### CONCLUSIONS

It has been demonstrated that the photo-stability of aramid fibers has been effectively improved by the nanosized TiO<sub>2</sub> coating from tetrabutyl titanate by sol-gel.

1. A new method for the photo-stability coating by nanosized TiO<sub>2</sub> for aramid fibers is studied.

**TABLE I**  
Deconvolution Analysis of C1s Peaks for Uncoated and Coated Aramid Fibers

Sample	Functional group ratio (%)			
	C—C	C—O	C=O	COOH <sup>a</sup>
Uncoated fiber, 0 h	77.0	3.1	2.7	0
Uncoated fiber, 48 h	57.1	6.7	2.6	7.0
Uncoated fiber, 156 h	44.5	15.1	6.7	11.1
Coated fiber, 0 h	58.4	3.9	3.9	4.0
Coated fiber, 48 h	42.1	11.6	4.7	4.7
Coated fiber, 156 h	33.55	10.99	6.07	9.9

<sup>a</sup> For coated fibers, the ratio also includes the free acetic acid used in the preparation of TiO<sub>2</sub> sol.

**TABLE II**  
XPS Spectra of Ti 2p Region for Coated Aramid Fibers with Various UV Exposures

Sample	Binding energy (eV)		
	Ti 2p <sub>3/2</sub>	Ti 2p <sub>1/2</sub>	Gap
Coated fiber, 0 h	458.4	464.0	5.6
Coated fiber, 48 h	458.9	464.5	5.6
Coated fiber, 156 h	459.2	464.9	5.7

2. The nanosize and anatase crystal shape of TiO<sub>2</sub> particles in the coating is characterized by PCS and XRD.
3. Upon accelerated UV radiation, both coated and uncoated aramid fibers show deterioration in tensile properties. However, significant improvement of photo-stability is observed for the coated fibers, of which more than 36% tensile strength and 50% break elongation still remained after 156-h UV exposure. On the contrary, the uncoated fibers degraded completely and became powdery.
4. As inferred from the SEM micrographs, it is apparent that the TiO<sub>2</sub> coating protects aramid fibers from latitudinal cracks caused by UV exposure. The TiO<sub>2</sub> coating is also chemically stable and has good adhesion on the surface of aramid fibers.
5. The chemical composition on the surface of the fibers investigated by XPS shows that the TiO<sub>2</sub> coating slows down the breakage of the acylamide bond and consequently retards the formation of the free acid in aramid molecular chain.
6. The sol-gel surface treatment is a gentle processing method for aramid fibers. No indication of tensile properties and etching damage to the fibers after the treatment has been detected in the present study.

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