

# UV Aging Resistance Properties of PBO Fiber Coated with Nano-ZnO Hybrid Sizing

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**ABSTRACT:** In this article, we focus on the ultraviolet (UV) shielding efficiency for poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) fiber with zinc oxide (ZnO) nanoparticle/epoxy hybrid coating. ZnO nano particles were initially functionalized with silicon coupling agent for improving their dispersion and surface reactivity, and then they were hybridized with epoxy resin by grafting on the ZnO nano particles. The hybrid reactions have been indicated by means of Fourier transform infrared spectrometer (FT-IR). Its UV light shielding effect of the hybrid coating on PBO fiber properties has been studied

using ultraviolet spectrum, tensile test, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). Results showed that the surface topographic, the surface polymer structure, and the tensile strength of coated PBO fiber were less declined than that of uncoated fiber by UV light. From these results, the nano-ZnO hybrid sizing had good UV-aging shielding efficiency for PBO fiber. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2468–2476, 2011

**Key words:** aging; coatings; fibers; tension

## INTRODUCTION

Photo-degradation of polymeric materials was a common phenomenon that led to changes in their chemical, physical, and mechanical properties. Solar light especially ultraviolet (UV) light irradiation was a frequently encountered factor that could induce photo-degradation of polymers under outdoor service environment.<sup>1,2</sup> Poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) fiber as a sort of synthesis material has become prominent in high strength applications such as body armor, ropes and cables, and recreational equipment.<sup>3</sup> However, PBO fiber, like other high strength organic fibers, was generally sensitive to light exposure and susceptible to UV degradation. It tended to lose significant strength upon exposure to UV irradiation. Such UV degradation posed a serious challenge for the development of the PBO-based products. In an attempt to quantify the UV vulnerability of PBO fiber,<sup>4,5</sup> new methods for protecting the PBO fibers from the environmental effects are needed.

ZnO nano-particles were extensively used as agents to attenuate (absorb and/or scatter) the ultraviolet radiation. ZnO was a direct wide band-gap 3.3 eV material and could absorb the light of wavelength as 384–410 nm.<sup>6–8</sup> As a result, nano-ZnO as UV absorber could offer unique benefits in protecting coatings and coated substrates from being degraded by UV radiation.<sup>9</sup>

In recent years, organic/inorganic hybrid materials, which combined the advantages of organic polymers with the benefits of inorganic components, has received a great deal of attention.<sup>10,11</sup> Benzoate had the properties of shielding and absorbing UV light.<sup>12</sup> In the present study, nano-ZnO/benzoic acid/epoxy resin hybrid sizing has been used to improve the performance of the PBO fiber UV aging resistance. The application of specially formulated finishes and their effect on fiber protection would be addressed in a future publication.

## EXPERIMENTAL

### Materials

PBO fiber was provided by Toyobo. The shape of fiber cross section was circular, and its average diameter was 11.0  $\mu\text{m}$ . The measured tensile strength and tensile modulus were about 6.5 and 260 GPa, respectively. Bisphenol A diglycidyl ether

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epoxy resin was supplied by Wuxi Resin Plant, China. Nano-ZnO, was provided by Beijing Nachen, silicon coupling agent, HK560 was provided by Chenguang Silane Chemistry. The diameter of nona-ZnO particles was 10 nm, and the purity was more than 99.9%. Benzoic acid was supplied by Tianjing Chemistry Com.

#### Preparation of hybrid sizing and coating on the fiber surface

ZnO nano-particles were modified first with HK560 at 100°C and on the pH value of 3.6 for 2 h according the ratio of nano-ZnO, HK560, water, and ethanol in the weight of 4 : 2 : 95 : 3. The modified ZnO nano-particles were filtered and washed with distilled water three times and washed with ethanol one time and dried at 100°C for 6 h in a vacuum system to remove the solvent.

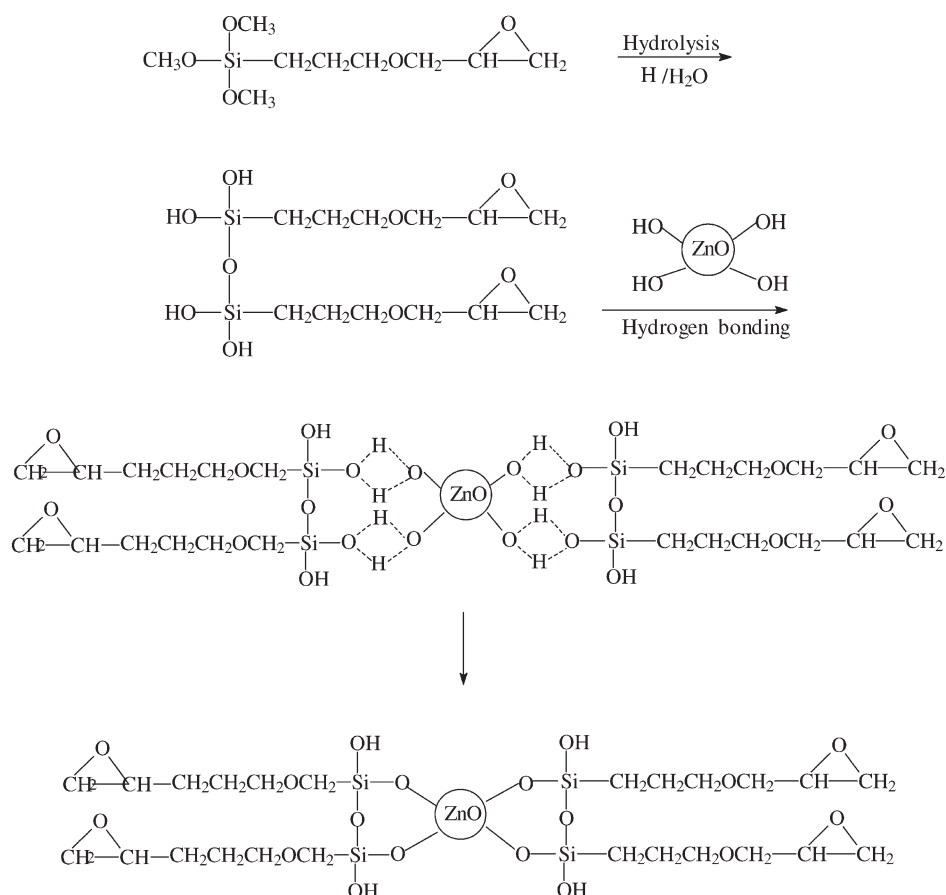
The modified ZnO nano-particles were added in a solution of the epoxy resin modified by benzoic

acid and acetone according to the weight ratio of 1(ZnO) : 3(epoxy resin) : 96 (acetone). The particles were dispersed by using quick stirring and ultrasonic vibration for 60 min; the hybridization reactions were carried at temperature of 90°C for 2 h, acetone was added into the hybrid materials and a series of hybrid sizing at the concentration of ZnO nano-particles for 0.5, 1.0, and 2.0 wt % was produced.

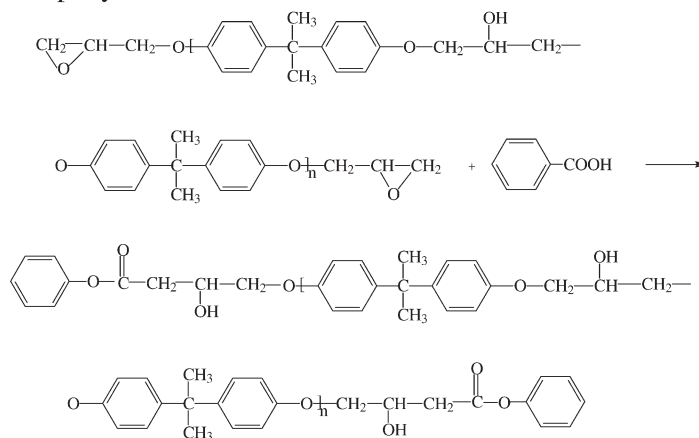
PBO fibers were extracted using acetone for 48 h to remove the size on the surface of fiber before being treated with nano-ZnO hybrid coatings. The hybrid sizing with different concentration (mass %) of were prepared to control the coating thickness about 100 nm. PBO fibers were immersed in the prepared solution at the temperature of 70°C for 6 h to coat nano-ZnO hybrid sizing on fiber surface, and then the fibers were dried at the temperature of 150°C for 2 h.

The hybrid grafting reaction was shown as follows:

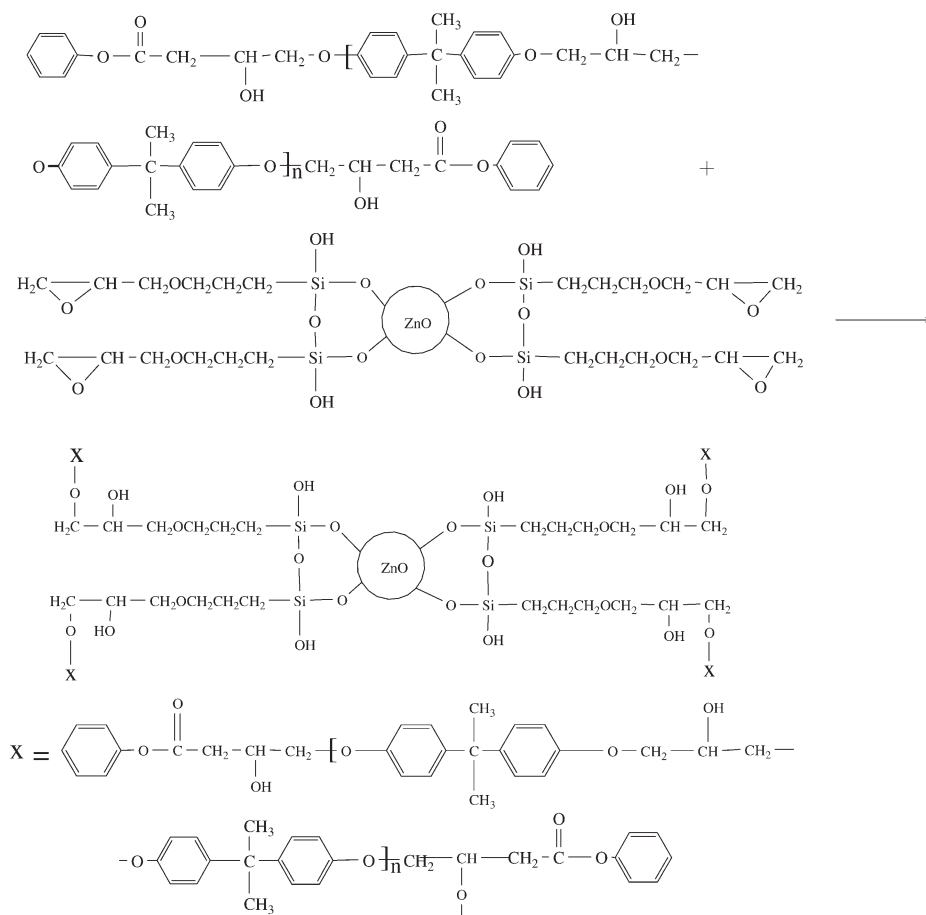
#### □ hydrolysis reaction of HK560 on the surface of ZnO nano-particles



## ② reaction of epoxy resin and benzoic acid



## ③ hybrid grafting reaction of ZnO nano-particles and epoxy resin



### FT-IR analysis and UV absorption of the nano-ZnO hybrid sizing

Fourier transform infrared spectra (FT-IR) of the nano-ZnO hybrid sizing were carried out on a Thermo Nicolet Nexus 670 spectrometer with samples pressed into KBr pellets.

An ultraviolet absorption spectra for the nano-ZnO hybrid sizing were determined employing a 1 m, single beam, vacuum monochromator equipped with UV and vacuum UV photomultipliers, a deuterium light source, analog to digital circuitry, a computer controlled stepping motor drive for

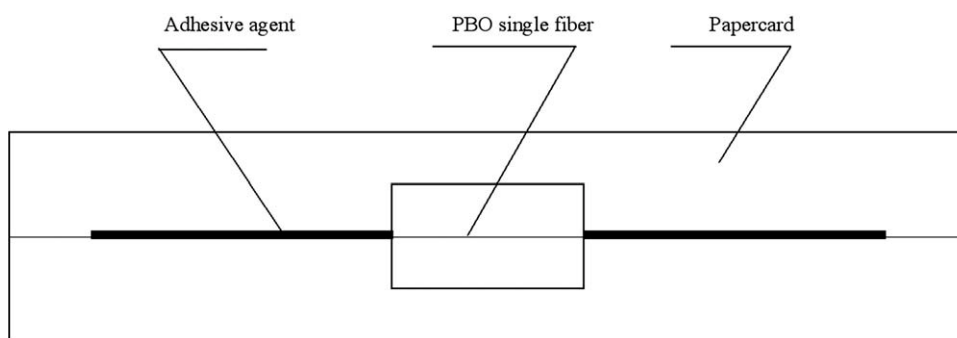


Figure 1 Single fiber specimen of tensile test.

wavelength control, and computerized data acquisition.

### UV exposure test

The samples of UV exposure test were made of the coated and uncoated fibers. The form of exposure samples was the same as tensile samples. Tensile sample of PBO fiber was shown in Figure 1. An individual fiber was mounted across holes (20-mm length) on the centerline in the middle of a plotting paper frame and was fixed using room cured epoxy resin. The fiber samples were exposed to UV radiation using a xenon lamp weatherometer which has a 1500 W Xenon lamp emitting UV rays at 380 nm and 250–765 W m<sup>-2</sup>. The current setting, exposure time of 1 h in the Weathering tester equals exposure time of 20 h in the sun at land in Harbin.<sup>13</sup> The samples were attached to a metal frame holder and the samples were exposed for 10, 20, and 30 h, respectively. After being exposed to the UV radiation, the samples were removed and subjected to surface morphology analysis, surface chemical analysis, and tensile testing.

### Fiber surface topography analysis by AFM

Atom force microscope (AFM) measurements were performed with a NanoscopeIII instrument manufactured by Digital Instruments. A single PBO fiber was fastened to a steel sample mount using the tapping mode. Roughness analysis was carried out from the images obtained over a 3 μm × 3 μm area.

### Tensile testing

The strength of single filament was studied by tensile testing. Tensile testing of yarns was carried out in accordance with ASTM D2256-02 "standard test method for tensile properties by the single-strand method" using an Instron 1121 mechanical testing machine.

The exposed samples from the Weatherometer were taken out and made ready for tensile testing. The paper card was mounted between the two grips of the test machine; the exposed region was placed in the middle of the jaws. Two rubber pieces were

put in between the grips of the jaws to prevent the samples from slipping. The paper edges were cut and the load displacement curves were recorded on chart paper. The universal test frame was equipped with a 5N load cell, and cross-head speed was 10 mm min<sup>-1</sup>. The test was measured at 20°C and 65% relative humidity. The diameter of each selected fiber was measured by AFM. The tensile strength was calculated using eq. (1).

$$\sigma_t = 4 \frac{F_b}{\pi d^2} \times 10^{-9} \quad (1)$$

where  $\sigma_t$  was the single fiber tensile strength (MPa),  $F_b$  was the tensile force recorded at the moment of rupture (N),  $d$  was the diameter of single fiber (μm). The value of test was more than 50 successful measurements.

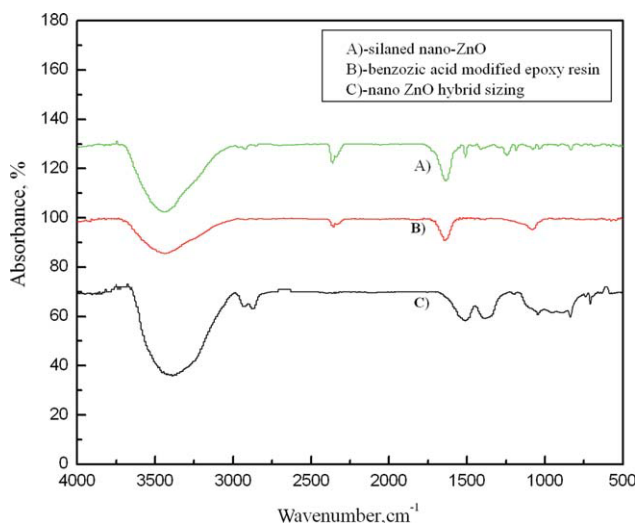
### Surface chemical analysis of PBO fiber

Surface chemical analysis of the fiber before and after irradiation treatment are carried out by X-ray photoelectron spectroscopy (XPS) on a Shimadzu ESCA 750 X-ray photoelectron spectrometer using MgK X-rays at power of 240 W. The instrument is calibrated by Ag 3d spectrum which has a peak half width and height of 1.15 eV and 350 kcp, respectively. The voltage and current for the excited state of MgK are 8 kV and 30 mA. Different functional groups are evaluated by curve fitting spectrum using Caussian-Lorentzian distribution.

## RESULTS AND DISCUSSION

### Result analysis of hybrid grafting reaction

Fourier transform infrared (FT-IR) spectroscopy was adopted to examine the intermolecular hydrogen bonding of epoxy resin with ZnO nano-particles. This technique is often helpful in extracting specific chemical changes and providing information on the formation and depletion of specific functional groups. Figure 2 shows the FT-IR spectra of nano-



**Figure 2** IR spectra of nano-ZnO hybrid sizing. (A) Silanated nano-ZnO; (B) benzoic acid modified epoxy resin; (C) nano-ZnO/benzoate/epoxy resin hybrid sizing. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ZnO hybrid sizing (ZnO nano-particles percentage composition was 1 wt %). A blank benzoic acid and epoxy resin solution was taken as reference. In Curve A, the peaks observed at  $1000\text{--}1200\text{ cm}^{-1}$  for Si—O—Si bonds,  $780$  and  $1260\text{ cm}^{-1}$  for epoxy ring,  $1540\text{ cm}^{-1}$  for ZnO,  $1680\text{ cm}^{-1}$  for carbonyl, and  $2850\text{ cm}^{-1}$  for methylene are assigned to the vibrations of above functional groups, respectively.<sup>14</sup> It indicated that silicon coupling agent was grafted on the surface of ZnO nano particles.

The absorption peak of  $780\text{ cm}^{-1}$  for epoxy ring characteristic vibration disappeared and the peaks of  $1190$  and  $1680\text{ cm}^{-1}$  for ester carbonyl appeared in Curve B, indicating at least the partial epoxy ring reacted with the carboxylic groups of benzoic acid. The deconvoluted C=O zone, in Curve C, showed that the hydroxyl group (—OH) in ester group produced with the incorporation of ZnO. The vibration frequency of carboxyl group (—C=O) and —OH shifts from  $1680$  to  $1428\text{ cm}^{-1}$  and  $3450$  to  $3375\text{ cm}^{-1}$ , respectively, indicating the occurrence of hydrogen bonding between —C=O and —OH. This may be either due to the intermolecular hydrogen bonding between —C=O, ester —OH with the surface —OH group of ZnO. The above deconvolution result suggested that the hydroxyl on the surface of ZnO nano-particles had reacted with epoxy ring of modified epoxy resin. The above result suggested that the ZnO nano-particles were inserted into the resin matrix.

#### UV absorption of the nano-ZnO hybrid sizing

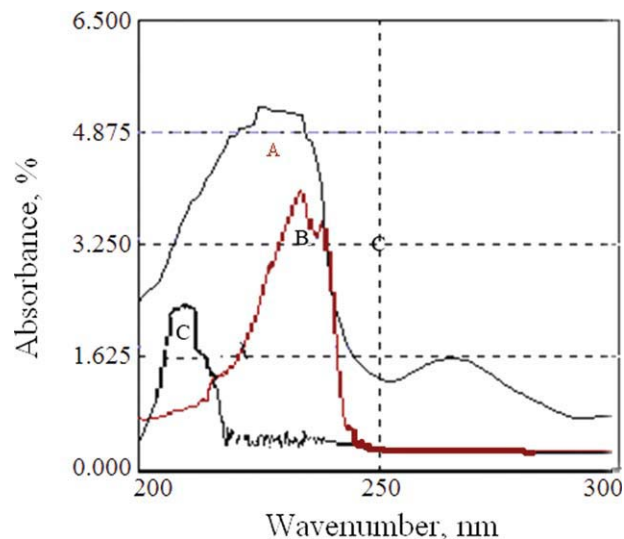
ZnO nano-particles could be used as agents to shield UV aging because of its good absorption and scattering properties of UV band. The UV absorption spec-

tra of PBO polymer, ZnO nano-particles of 10 nm and its hybrid solution were presented in Figure 3. There are strong absorb peak in the wavelength range of 200–300 nm for benzobisoxazole structure in PBO polymer in Curve A, it indicated that PBO fibers were very susceptible to UV. Photo-degradation of PBO fiber would occur by the chain scission at double bond N=C in benzobisoxazole structure of PBO polymer by UV photons irradiation.

ZnO nano-particles and its hybrid sizing also had intensive absorption in the range 200–300 nm in Curve B and C; they had added advantages of scattering effect within an applied coating. The explanation is as follows: UV light absorption spectra consist of two contributions by ZnO/UV light absorption and light scattering. As light transmits in an inhomogeneous medium (like hybrid sizing) where the refractive index varies at different locations, light scattering would occur<sup>15</sup>; when ZnO nano-particles grow and agglomerate, UV light scattering will play a larger role in shielding. It thus can be deduced that ZnO nanoparticles play an important role in stabilizing the PBO molecules and delay the photo-degradation process by acting as screens.

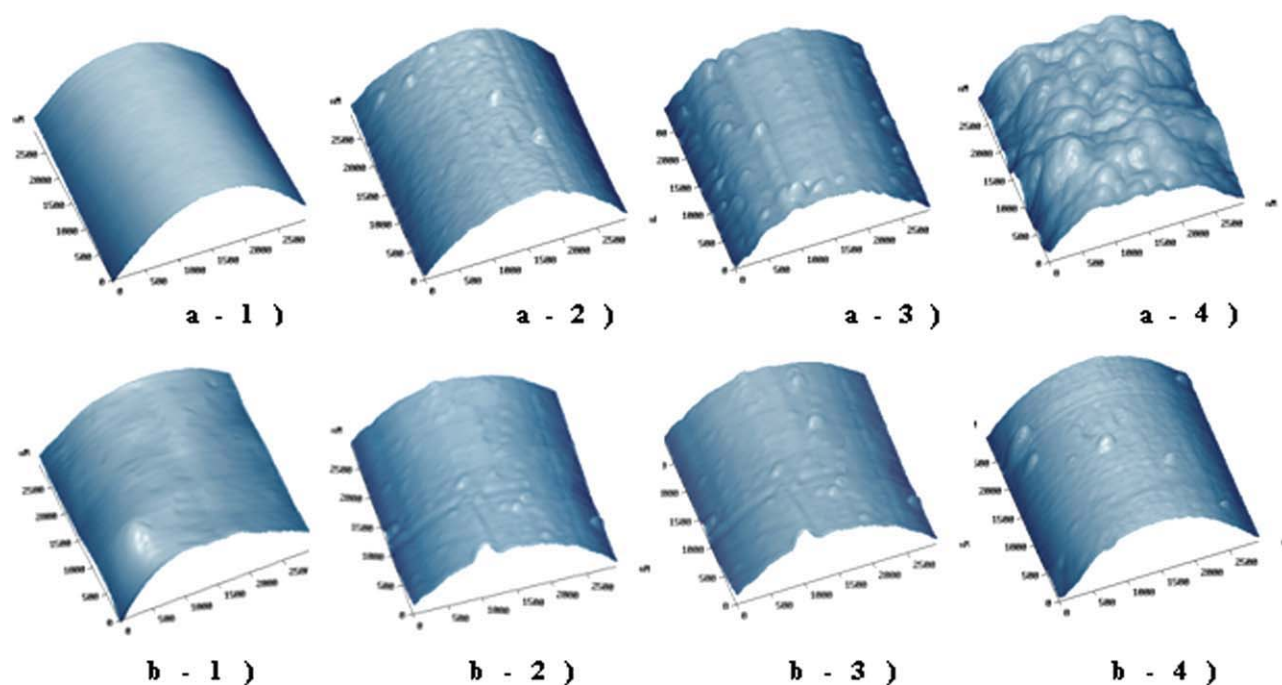
#### Effect of UV aging on fiber surface morphology

To further explore UV aging resistance effect of nano-ZnO hybrid sizing on the surface of PBO fiber, AFM was performed. The AFM surface topographic images of various PBO fibers are shown in Figure 4. It was found that there were a series of bulges and projections on fibers' surface after UV aging, and the size of these bulges and projections was magnified with the increase of UV irradiation time. Surface



**Figure 3** UV absorption spectra of: (A) PBO fiber; (B) ZnO nano particle (crystal size of 10 nm); (C) ZnO nano particle hybrid sizing. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 4** AFM images of PBO fibers before and after UV aging (a-1) before aging; (a-2) 10 h aging; (a-3) 20 h aging; (a-4) 30 h aging of noncoating fiber; (b-1) before aging; (b-2) 10 h aging; (b-3) 20 h aging; (b-4) 30 h aging of fiber coated 1 wt % sizing. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

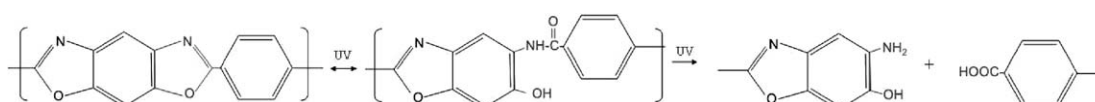
roughness value ( $R_a$ ) is an important parameter of fiber surface morphology. The calculated values of PBO fiber surface roughness from the AFM for uncoated and coated with 2.0 wt % nano-ZnO hybrid sizing during UV aging treatment were shown in Table I. The  $R_a$  of the uncoated PBO fiber increased more significantly than that of the coated PBO fiber with the increasing of UV irradiation time. The  $R_a$  of the coated fibers was only 29.134 nm when the irradiation time is 30 h; it was 63.2% lower than that of the uncoated ones. The morphological change indicated that the nano-ZnO hybrid sizing physically modified the UV aging resistance properties of PBO fiber.

#### Effect of UV aging on uncoated PBO fiber surface chemical structure

The interaction between the surface properties of materials and the X-ray photoelectron spectroscopy provides valuable information on the molecular structure of organic materials. The spectroscopy peaks of surface chemical structure of uncoated PBO fiber are shown in Figure 5. Changes in the inten-

sities or binding energy of observed spectral peaks can be used to elucidate changes in the molecular structure of the compound.

The surface atom composition, chemical structure, the values of the binding energy (BE), and full width at half maximum (FWHM) of uncoated PBO fiber before and after UV aging are given in Tables II and III, respectively. Noticeable changes are observed with the surface atom composition, oxygen percentage increases with the increasing UV radiation time. The oxygen content of the aged fiber is 22.5% higher than that of the untreated ones when the radiation time is 30 h. The chemical structure of the polymer molecule on PBO fiber surface has also changed, carboxyl group and amino group are produced, and the content of the groups from the area of Peak 4 increases with the increasing UV radiation time. The reason may be that the bond-break actions of benzoxazole to benzamide have arisen in low molecular weight compounds in the procedure of UV radiation, *N*-(2-phenylhydroxybenzamide) is first formed, *N*-(2-phenylhydroxybenzamide) is then further broken up to 2-aminophenol and benzoic acid, respectively, as follows:



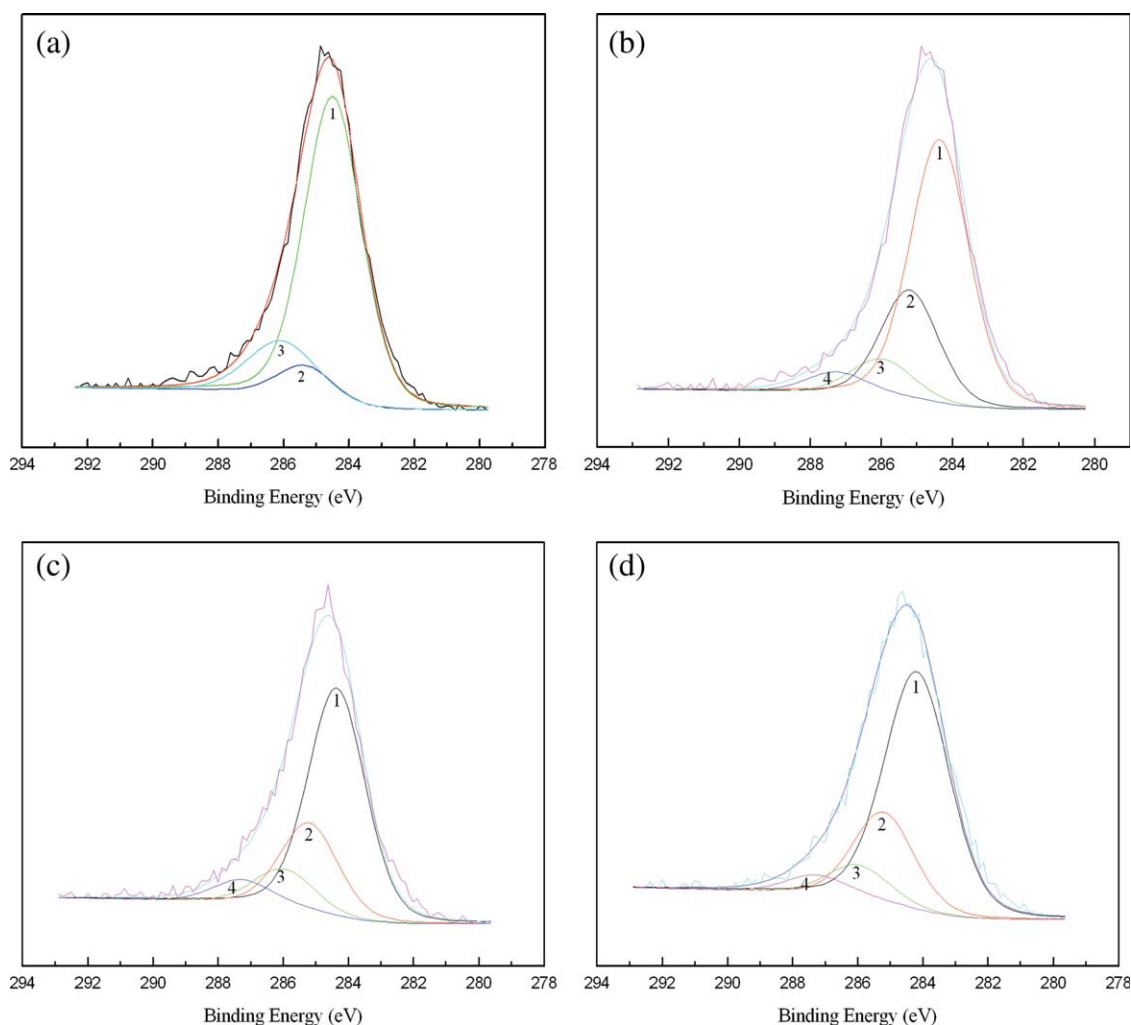
**TABLE I**  
Calculated Surface Roughness Value of PBO Fibers by AFM

Aging time	Calculated surface roughness value							
	0 h		10 h aged		20 h aged		30 h aged	
	Uncoated PBO fiber	Coated PBO fiber	Uncoated PBO fiber	Coated PBO fiber	Uncoated PBO fiber	Coated PBO fiber	Uncoated PBO fiber	Coated PBO fiber
Apparent surface area ( $\mu\text{m}^2$ )	9.0258	9.1256	9.0258	9.1256	9.0258	9.1256	9.0258	9.1256
Real surface area ( $\mu\text{m}^2$ )	9.1093	9.2123	9.2103	9.6212	9.3564	9.5421	9.6051	9.4687
Surface roughness value (nm)	19.109	20.156	25.936	23.623	33.337	25.560	47.548	29.134

As a result, carboxyl group and amino group made from the bond-break actions of the polymer molecule on PBO fiber surface increase proportionately with the increasing of UV radiation time, the degradation of chemical structure may induce fiber surface roughness.

### Tensile behavior of PBO fibers

Figure 6 shows the tensile strength of the PBO fibers subjected to UV radiation aging as a function of exposure time. It can be found that the tensile strengths of both coated and uncoated PBO fiber



**Figure 5** (a) XPS C1s spectra of PBO fiber coated 1 wt % sizing (a) unaging (b) XPS C1s spectra of PBO fiber coated 1 wt % sizing (b) 10 h aging (c) XPS C1s spectra of PBO fiber coated 1 wt % sizing (c) 20 h aging (d) XPS C1s spectra of PBO fiber coated 1 wt % sizing (d) 30 h aging. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

**TABLE II**  
Results of Uncoated PBO Fiber Surface Composition by XPS

Element content (%)	C	O	N
Unaging	75.78	15.84	8.38
10-h aging	76.04	17.00	6.96
20-h aging	75.67	17.56	6.77
30-h aging	73.44	19.40	7.16

were decreased with the increase of UV aging time, but for PBO fiber coated with ZnO hybrid sizing, the tensile strength is higher than uncoated PBO fiber at all aging time in our test, and it is increased with the increase of concentration of ZnO hybrid sizing. As shown in Figure 7, the tensile strengths of the coated with 2.0 wt % nano-ZnO hybrid sizing was 109% higher than that of uncoated, 66% higher than that of coated 0.5 wt % hybrid sizing and 33% higher than that of coated 1.0 wt % hybrid sizing after 30-h UV aging. The difference between the tensile strengths of the coated fiber and uncoated fiber by UV aging is attributed to effect of nano-ZnO hybrid coating.

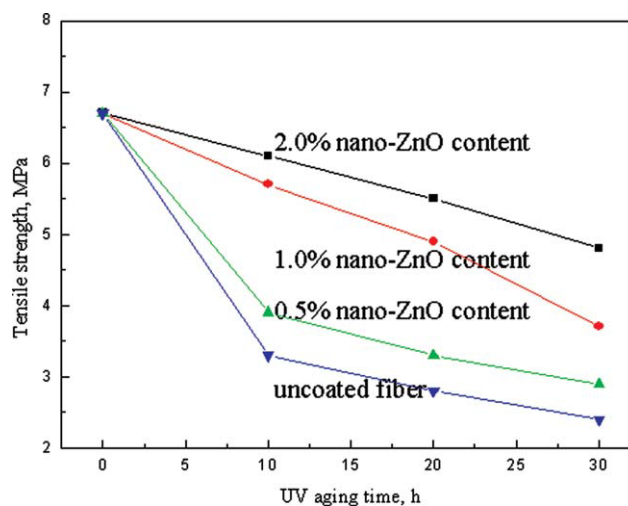
During the tensile testing of PBO fiber, it was observed that, occasionally, the fibers break at the hole's edge regions of a plotting paper frame. That occurred with a sharp break all times. The results clearly illustrated that the nano-ZnO has provided UV protection to PBO fiber, nano-ZnO particles were more prone to be anchored in the surface of fibers. So, as the results herein illustrate, they were effective for much longer exposure periods.

## CONCLUSIONS

Nano-ZnO particles/epoxy resin hybrid sizing is successfully prepared by using modified nano-ZnO

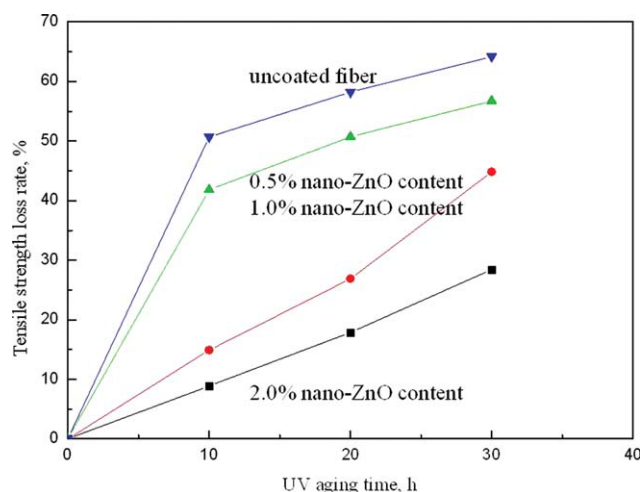
**TABLE III**  
Results of  $C_{1s}$  Spectra Fitting Curve of Uncoated PBO Fiber by XPS

	Peak	BE (eV)	Area	FWHM	Correlative structure
Unaging	1	284.22	2447	2.18	-C-C-C-
	2	285.33	522	2.31	-C-O-
	3	286.06	357	3.92	-C=N-
10 h UV aging	1	284.35	1845	1.95	-C-C-C-
	2	285.20	737	1.90	-C-O-
	3	286.00	264	2.04	-C=N-
	4	287.27	149	2.00	-COOH, -C-NH <sub>2</sub>
20 h UV aging	1	284.35	1554	2.07	-C-C-C-
	2	285.20	601	2.10	-C-O-
	3	286.00	261	2.14	-C=N-
	4	287.27	158	2.10	-COOH, -C-NH <sub>2</sub>
30 h UV aging	1	284.18	1587	2.35	-C-C-C-
	2	285.20	601	2.20	-C-O-
	3	286.00	210	2.24	-C=N-
	4	287.27	179	2.20	-COOH, -C-NH <sub>2</sub>



**Figure 6** Effect of UV aging time on PBO fiber tensile strength. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and epoxy resin *in situ* grafting reaction. The analyses of AFM and tensile test suggested that the hybrid sizing had good UV light shielding effect on PBO fiber properties. It could protect the surface of PBO fiber from deterioration by UV, the tensile strength of the coated PBO fiber was significantly higher than that of uncoated PBO fiber at all UV aging time, the retention rate of tensile strength of coated fiber was significant increased with the increase of the content of nano-ZnO in the hybrid sizing. The tensile strength of PBO fiber coated 2.0 wt % nano-ZnO hybrid sizing reached 4.8 GPa after 30-h UV radiation, it was 109% higher than that of uncoated. Nano-ZnO/epoxy hybrid sizing had good UV aging resistance properties for PBO fiber.



**Figure 7** Effect of UV aging time on the tensile strength loss rate of PBO fiber. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



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