

Accelerated Ultraviolet Aging Study of the Vectran Fiber

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ABSTRACT: Aging behavior of Vectran fiber exposed to ultraviolet (UV) radiation was investigated. Vectran fiber was subjected to UV-accelerated degradation environment. Tensile strength of Vectran fiber was determined at room temperature using a two-parameter Weibull distribution. The average tensile strength loss was 42.75% when the irradiation time reached 186 h. The surface morphology of the degraded fiber was examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

X-ray photoelectron spectroscopy (XPS) and ¹³C-NMR were used to provide a molecular characterization of fibers. SEM and AFM showed that UV exposure result in microvoids on the surface of fibers. The results of the XPS and ¹³C-NMR indicated that the UV radiation could lead to chain scission of fiber surface layer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3286–3292, 2012

Key words: Vectran fiber; UV aging; tensile strength; XPS

INTRODUCTION

In the recent years, there has been increased interest in high altitude, lighter-than-air (LTA) systems. LTA applications at high altitudes (stratosphere) impose significant challenges for the system flexible materials. The material must also be designed to resist the harsh stratospheric environment, high ozone concentration, intense ultraviolet (UV), and extremely low temperature.¹

Thermotropic liquid crystalline polymer (Vectran) is a new family member of high-performance fibers compared to lyotropic liquid crystals polymer (aromatic polyamide, Kevlar), providing unique properties such as high strength and modulus, heat resistant, waterproof, and flame retardance, which can be exploited in the design of the high-altitude airship envelope materials.^{2–6}

High performance fibers, however, are known to degrade upon exposure to light. They tend to lose significant strength upon exposure to UV radiation.⁷ Some studies on this subject were motivated by the applications for high performance fibers and also by the great effect of UV radiation on their mechanical and other properties. Some studies for Kevlar, PBO, Kermel fibers, and other fibers have indicated that the deterioration in the mechanical properties of fibers was due to the photolytic degradation when exposed to UV irradiation.^{8–10} Said et al.⁷ reported

the results of an investigation of the resistance of four commercial high strength fibers (Vectran, Spectra, Kevlar, and PBO) to UV exposure. Vectran showed the highest loss in strength after 144 h of exposure to UV. Some synthetic polymers, for example, aromatic polyesters and polyamides, have inherent absorption of UV light, which gives excitation, radical formation, oxygen addition, splitting off of small molecules, and chain scission.¹¹ Wei Wang et al.¹² found that the photodegradation process of PET film samples takes place in two steps: a very rapid initial step followed by a normal step. The relation between the molecular weight and the mechanical properties of the irradiated PET demonstrates that the decrease in molecular weight is one of the main origins causing the deterioration in the mechanical properties.¹³

High performance fibers undergo severe degradation upon exposure to UV radiation, hence there is a need to protect them from getting degraded and thereby increase the life of the airship envelope materials. But there are far few investigations that focus on the effects of UV radiation on the degradation of Vectran fibers.

The purpose of this project was to study the photodegradation of Vectran fiber. The tensile properties were measured using a two-parameter Weibull distribution. The surface degradation behavior is evaluated using XPS and ¹³C-NMR techniques. Surface morphologies of the fibers were examined using atomic force microscopy (AFM) and scanning electron microscope (SEM).

EXPERIMENTAL

Vectran fiber

The Vectran fiber (HT) T-126 was purchased from Shanghai Rock-firm Interconnect Systems Corp.

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TABLE I
Properties of Vectran Fiber

Properties	Unit	Value
Density	g/cm ³	1.41
Decomposition temp.	°C	>400
Tensile strength	kg/mm ²	330
Breaking elongation	%	3.8
Initial modulus	kg/mm ²	7610

Typical properties are shown in Table I. Its chemical structure is shown in Figure 1.

UV exposure

Accelerated artificial ultraviolet (UV)-aging was conducted with an UVA high-pressure mercury lamp (100 W) that provided radiation at wavelengths of 280–380 nm. The intensity of the lamp was about 60 MW/cm², and the wavelength of about 60% of the UV radiation was 365 nm. The specimens were then placed under the UV lamp. The sample to lamp distance used was 10 cm. The specimens were removed after 20, 80, 140, and 186 h of exposure.

Tensile strength measurement

The tensile strength of single-filament specimens was tested on a universal testing machine. The gauge length was 2.00 cm, and the loading speed was 10.0 mm min⁻¹. The test was carried out at (20 ± 2)°C. A single filament was mounted onto slotted testing cardboard tabs, with the fiber aligned along the center of the tab. The side portions of the tab were fastened with fixture just before application of the load. Every tensile value was averaged from 50 tests. The diameters of the fibers were determined by SEM.

Atomic force microscopy

The surface morphology of Vectran fibers was characterized by a Nanoscope III PIMENSION 3100 atomic force microscope (AFM). Morphology images were recorded for each fiber on various scanned areas.

Scanning electron microscopy

Scanning electron images for Vectran fibers were taken using a HITACHI S-4700 microscope. The sample was mounted on an adhesive carbon layer stuck onto an aluminum stub and sputtered with a thin layer of gold. The acceleration voltage was 15 kV.

X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) analysis was conducted using a PHI 5700 ESCA System with

a monochromated Al K α X-ray source (1486.6 eV) operated at 15 mA emission current and 10 kV anode potential. Vectran fiber sample was carefully mounted on the spectrometer probe tip by means of double-sided adhesive tape. Survey spectra in the range of 0–1400 eV were recorded for each sample with a pass energy of 187.85 eV and a step of 0.5 eV, followed by high resolution scanning over C1s range with a pass energy of 29.35 eV and a step of 0.1 eV.

Solid-state NMR

The ¹³C {¹H} cross-polarization magic-angle spinning (CP/MAS) spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4-mm standard bore CP/MAS probe head whose X channel was tuned to 100.62 MHz for ¹³C, and the other channel was tuned to 400.18 MHz for broad band ¹H decoupling, using a magnetic field of 9.39 T at 297 K. The dried and finely powdered samples were packed in the ZrO₂ rotor closed with Kel-F cap, which were spun at 12 kHz rate. The $\pi/2$ pulse for proton and carbons were found to be 11.3 μ s and 4 μ s at power levels of 120 and 8 dB, respectively. The experiments were conducted at a contact time of 2 ms. A total of 10,000 scans were recorded with 6-s recycle delay for each sample. All ¹³C-CP/MAS chemical shifts are referenced to the resonances of Adamantane standard ($\delta = 29.5$).

RESULTS AND DISCUSSION

Tensile strength

The strength of Vectran fibers is determined by the statistical distribution of flaws in the material. The tensile strength of Vectran fibers is generally analyzed on the basis of the well-known Weibull statistics,¹⁴ expressed by the empirical equation:

$$F(\sigma) = 1 - \exp[-(\sigma/\eta)^\beta] \quad (1)$$

where $F(\sigma)$ is the survival probability of an individual fiber at an applied stress of σ , η is the scale parameter, and β is the shape or flaw dispersion parameter. β is constant for a given material. Equation (1) can be rearranged as

$$\ln \ln \{1/[1 - F(\sigma)]\} = \beta \ln \sigma - \beta \ln \eta \quad (2)$$

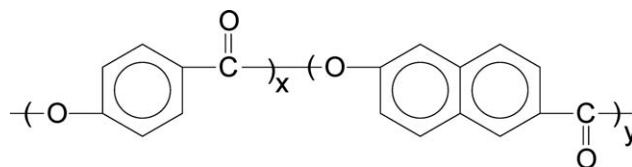


Figure 1 Chemical structure of Vectran fiber.

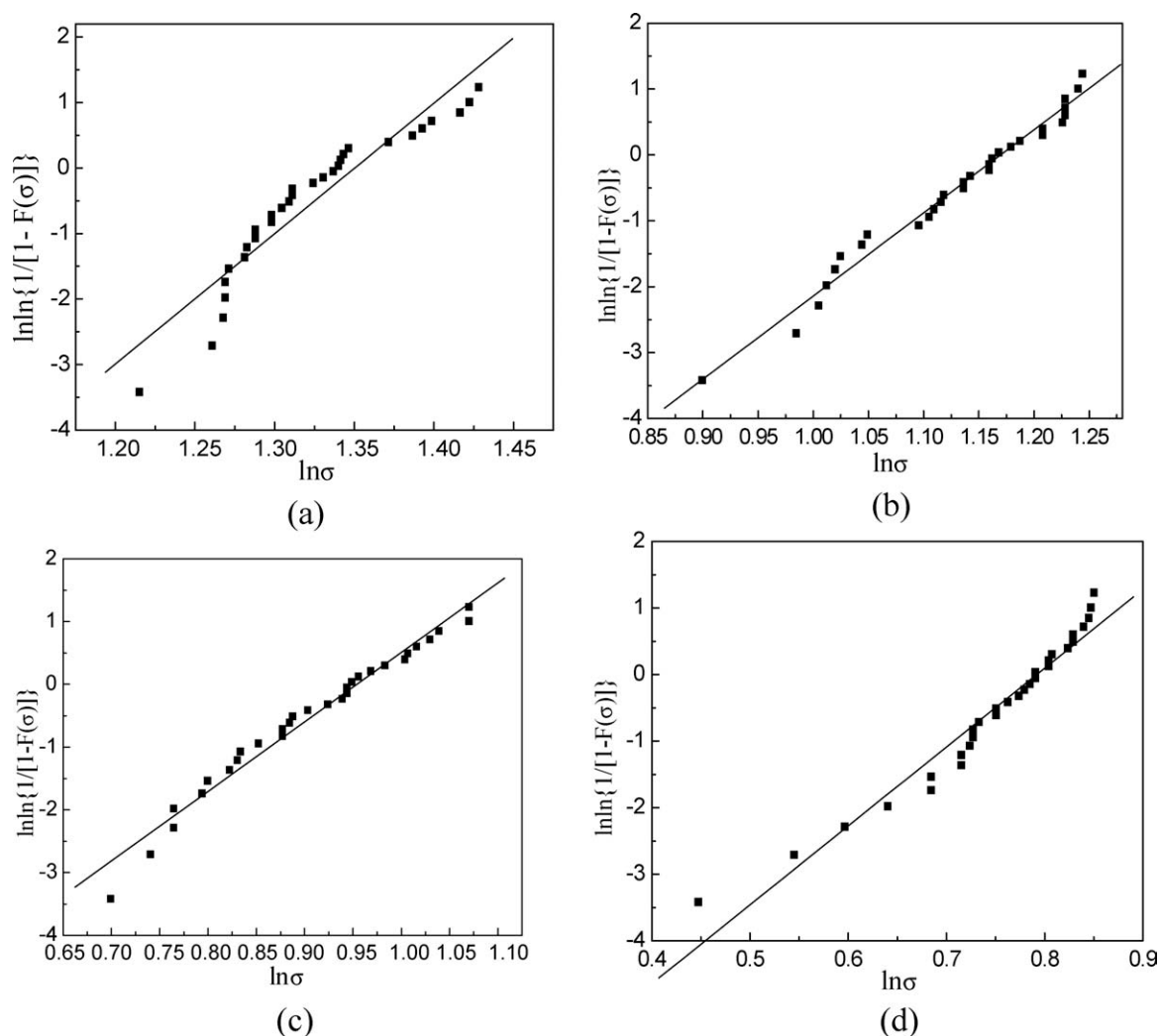


Figure 2 Weibull probability plots for room temperature tensile strengths of UV-treated Vectran fibers with different irradiation time: (a) 0; (b) 20; (c) 80; (d) 186 h.

The experimental data can be ranked in ascending order of strength values, and the cumulative probability $F(\sigma)$ can be assigned as

$$F(\sigma) = n/(N + 1) \quad (3)$$

where n is the rank of the tested fiber in the ranked strength tabulation and N is the total number of fibers tested. A least-square linear regression analysis can then be applied to a plot of $\ln\ln\{1/[1 - F(\sigma)]\}$ versus $\ln\sigma$. The slope of this analysis is the Weibull modulus β .

The $\ln\ln\{1/[1 - F(\sigma)]\}$ versus $\ln\sigma$ Weibull probability plots for virgin Vectran fibers and those fibers were exposed to UV for 20, 80, and 186 h are shown in Figure 2. Values of Weibull parameters obtained from linear regression analysis for Vectran fibers are given in Table II. It can be seen that the increase in irradiation time results in obvious decrease in the tensile strength of fibers. The average tensile strength of virgin fiber is 3.86 GPa. After exposure to UV radi-

ation for up to 186 h, the loss in tensile strength was 42.75%. As a result, the UV irradiation causes great loss to the tensile strength of Vectran fiber. So, it can be concluded that the UV exposure may cause the scission of main chain of Vectran fibers.

Atomic force microscopy

Surface morphologies of Vectran fibers were examined by atomic force microscopy (AFM). Figure 3

TABLE II
Weibull Parameters for Room Temperature Tensile Strengths of Virgin and UV-Treated Vectran Fibers

Irradiation time (h)	Average strength (GPa)	Weibull modulus (β)
0	3.86	19.91
20	3.22	12.62
80	2.59	11.08
186	2.21	11.85

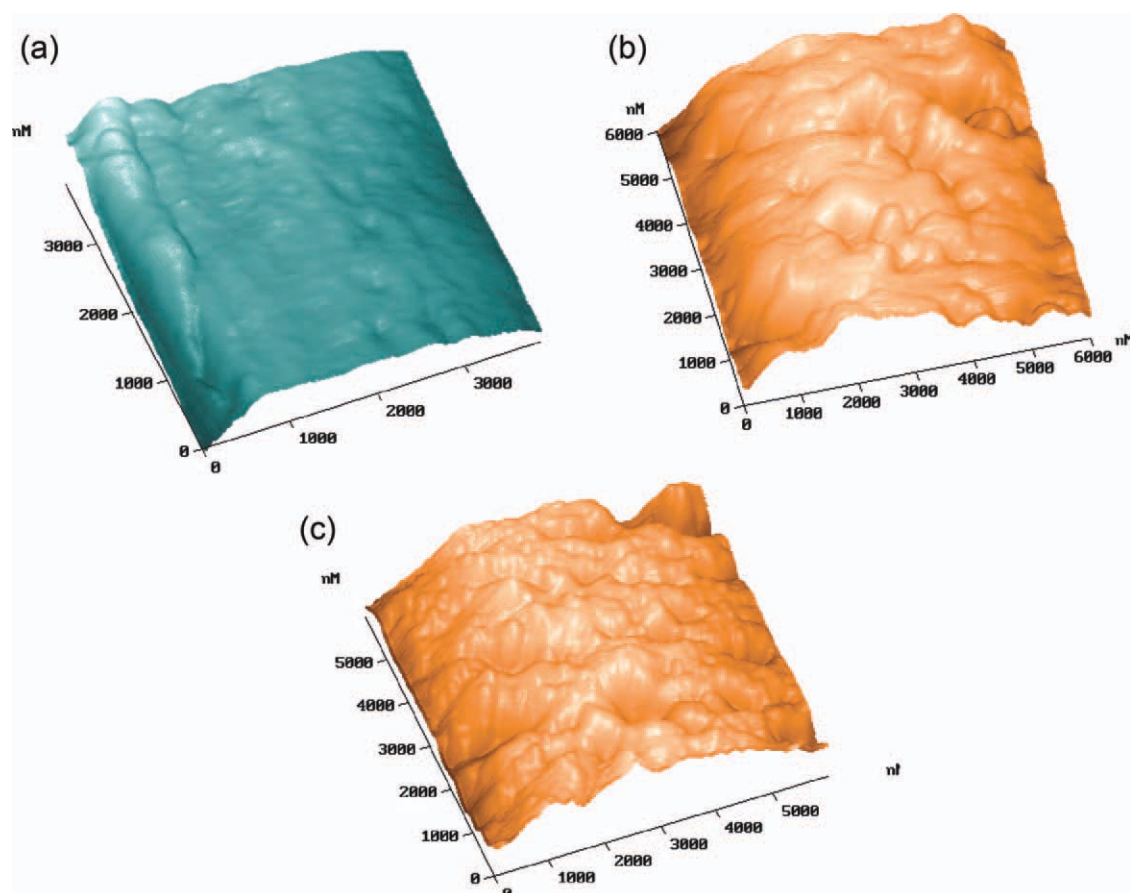


Figure 3 AFM micrographs of UV-treated Vectran fibers with different irradiation time (a) 0; (b) 80; (c) 110 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

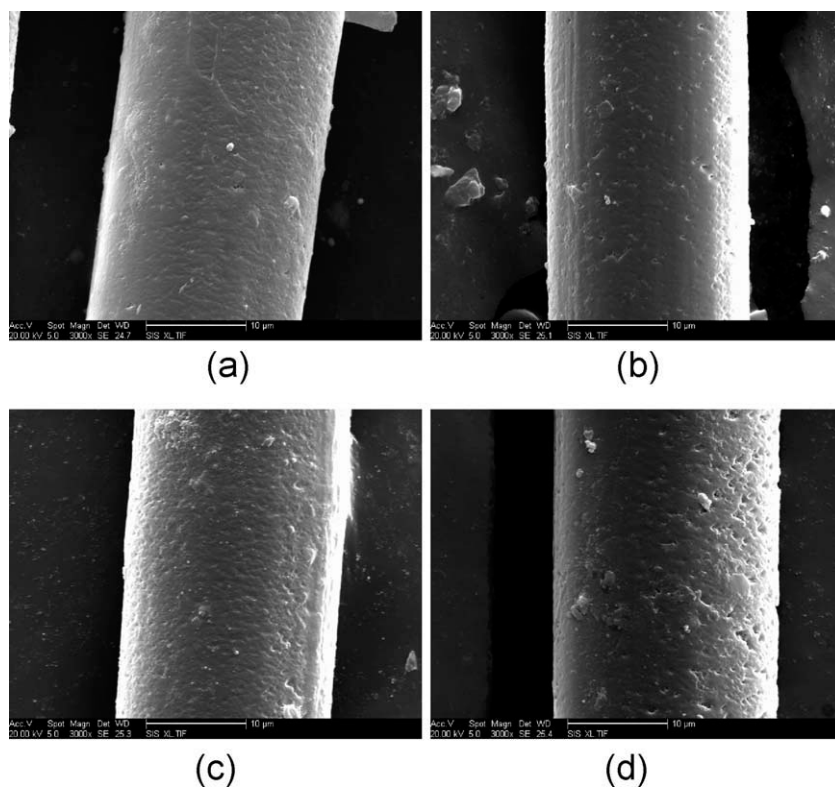


Figure 4 SEM images of UV-treated Vectran fibers with different irradiation time: (a) 0; (b) 80; (c) 110; (d) 186 h.

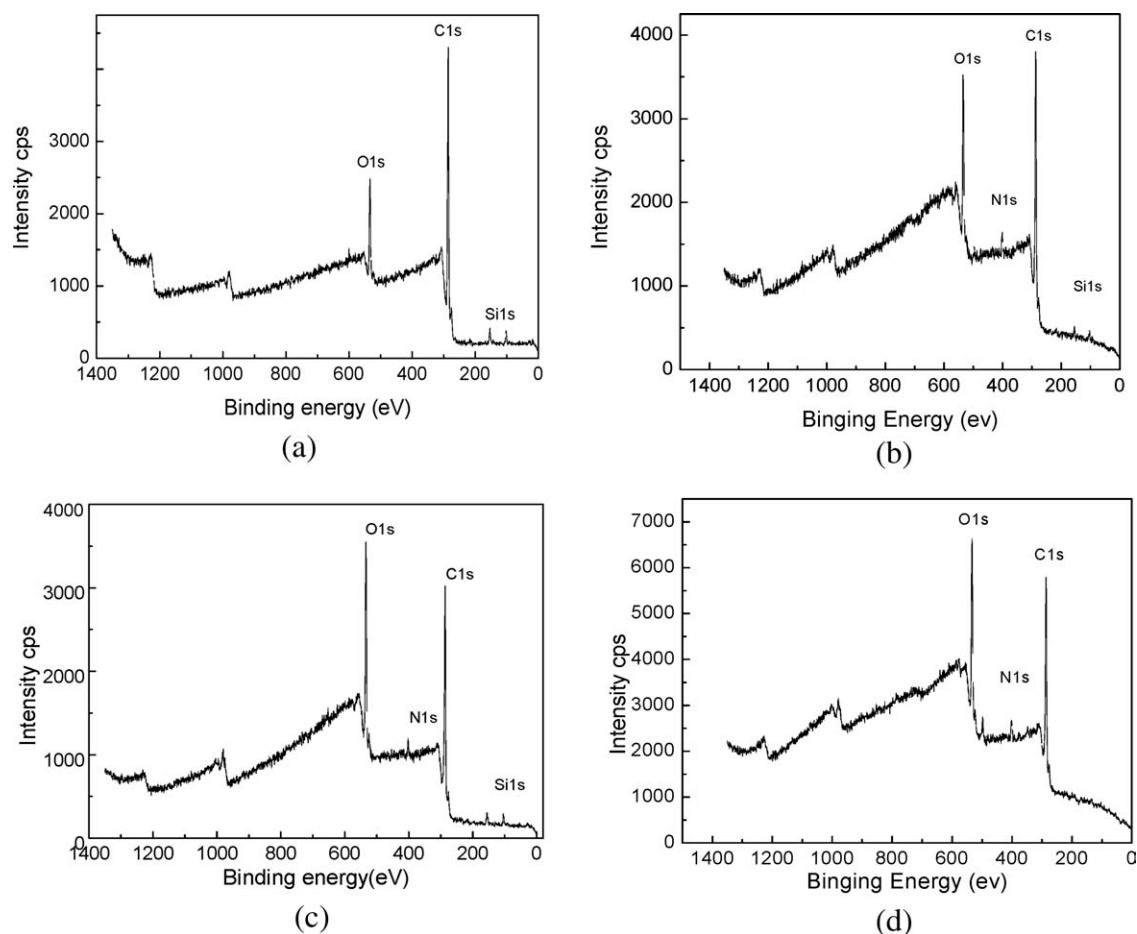


Figure 5 XPS wide scan spectra of UV-treated Vectran fibers with different irradiation time: (a) 0; (b) 80; (c) 110; (d) 140 h.

shows a comparison of AFM images of virgin and UV-treated fibers, respectively. The effects of UV radiation lead to significant material deterioration. It could be seen that the surface of fiber became rough after exposure to UV radiation.

Scanning electron microscopy

The scanning electron micrograph (SEM) shows a smooth surface of virgin Vectran fiber, but some streak flaws and spots can be seen in the scope of the observation [Fig. 4(a)], whereas the UV-treated fibers created the new features on the fiber surface as shown in Figure 4(b–d). It can be clearly observed that some microcracking and microvoids structures form on the fiber surface. It is evident that UV irradiation treatment has a visible effect on the skin layer of Vectran fibers, which would facilitate molecule chain scission. It is clear that the crack on the surface of fiber caused by UV exposure should be the main reason for the decrease of tensile properties.

X-ray photoelectron spectroscopy

A low-resolution scan was run to determine the percentages of the elements present at the surface. Figure 5 shows X-ray photoelectron spectroscopy (XPS) survey spectra for Vectran fibers. The relative elemental compositions of the samples before and after exposure to UV radiation are presented in Table III. The major element is carbon, with the second most concentrated element being oxygen. The fibers also

TABLE III
XPS Surface Element Analysis Data of Vectran Fiber Before and After Exposure to UV Radiation

Irradiation time (h)	Surface composition (%)				
	C	O	Si	N	C : O
0	88.18	16.23	1.88	0.00	5.04
20	77.14	17.84	4.27	0.75	4.32
50	73.67	21.25	3.50	1.58	3.47
80	69.54	25.58	1.69	3.18	2.72
110	66.78	28.46	2.48	2.28	2.35
140	65.86	30.03	—	4.11	2.19
186	62.51	32.30	1.81	3.37	1.94

TABLE IV
Surface Functional Components Obtained from the Deconvolution of C 1s Peaks After Exposure to UV Radiation

Irradiation time (h)	C—C		C—OH		C=O		—COOH	
	Peak (eV)	Area (%)	Peak (eV)	Area (%)	Peak (eV)	Area (%)	Peak (eV)	Area (%)
0	284.80	72.73	286.56	7.99	287.89	1.68	289.20	2.49
20	284.94	87.18	286.55	6.32	287.86	3.46	289.34	3.04
50	284.93	82.27	286.45	8.26	287.86	5.53	289.32	3.94
80	284.91	60.60	286.55	12.37	287.70	4.37	289.26	4.37
140	284.89	33.73	286.55	43.51	287.90	13.81	289.26	8.94
186	284.59	62.33	286.55	15.00	287.90	6.16	289.00	7.52

exhibit some minor elements such as nitrogen and silicon, nitrogen possibly arising from the absorption during the UV radiation process in air atmosphere, and the N/C ratio increased with increasing radiation time, while silicon is from the original surface treatment agent of the fiber. A C/O atomic ratio was calculated as an initial indication of surface oxidation. An increase in the concentration of oxygen atoms occurred after exposure to UV radiation. The

C/O ratio has decreased from 5.04 to 1.94 after the UV radiation, indicating that the surface of the material had oxidized.

To quantitatively characterize the change of the concentrations of various functional groups due to the UV radiation, a high-resolution scan was conducted on the C1s region for unexposed fibers and fibers exposed to UV radiation for 80, 140, and 186 h to determine the types and amounts of chemical

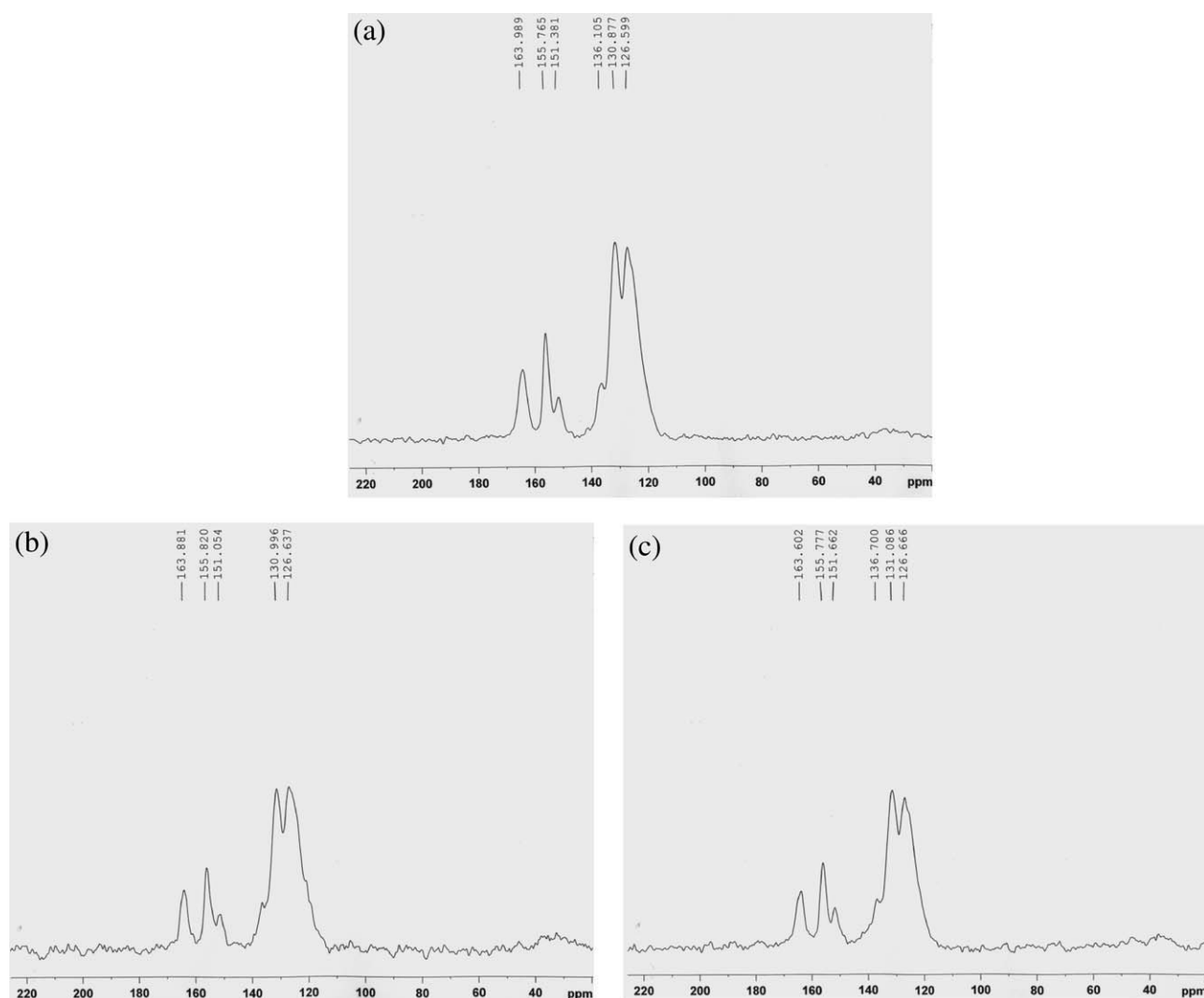


Figure 6 Solid-state ^{13}C -NMR spectra of UV-treated Vectran fibers with different irradiation time: (a) 0; (b) 80; (c) 186 h.

bonds present. The concentrations of the correlative functional groups on the surface of Vectran fiber are shown in Table IV.

The deleterious effects of weathering on polymers generally have been ascribed to a complex set of processes in which the combined action of UV light and oxygen is predominant.¹⁵ A drop in the peak area of C—C group indicated a decreased concentration of unoxidized carbon atoms. Because there has been an overall increase of O, this suggests that the new oxygen is in the form of —COOH, C—OH, and —C=O. The oxygen from air reacts with radiation-induced radicals and gives rise to —C=O and —OH bonds,¹⁶ and —OH group may also increase because of the hydration.¹⁷ Because chain scission may occur during exposure, it can be concluded that UV exposure might lead to the escape of small molecule like CO₂.¹⁸ Our results indicate that chain scission may have occurred upon exposure and that the number of chain scissions increased with the increase of exposure time.

Solid-State NMR measurements

Figure 6 shows the ¹³C CP/MAS spectra for virgin fiber and fibers exposed to UV radiation for 80 and 186 h. The spectra are very simple and only these five peaks were observed. In Figure 6(a), peak at 163.99 ppm was assigned to carbon of C=O group, whereas the peaks at 151.3 and 155.77 ppm were assigned to aromatic carbons vicinal to O. The broadening of the resonance signals of aromatics at 126–131 ppm was assigned to carbons of benzene and naphthalene.

The spectrum for fibers exposed to UV radiation, as shown in Figure 6(b,c), and no significant changes were observed in the line shapes and chemical shift values for any of the carbon signals. The solid-state NMR results demonstrated that the primary structure was unchanged after UV exposure. These results show that the strongest degradation takes place at the exposed surface, and the degradation rate decreases with increasing the distance.¹⁹ Therefore, the solid-state NMR analysis of the bulk of Vectran fibers could not provide enough evidence for surface degradation.

CONCLUSIONS

An UVA high-pressure mercury lamp that can simulate accelerated aging on Vectran fibers was used in

this study. Regarding the tensile strength, the experimental data revealed that it decreased significantly after UV exposure. The average tensile strength loss was 42.75% when the irradiation time reached 186 h. In addition, SEM and AFM results showed that UV exposure resulted in surface microcracks compromise. The results from the XPS measurements showed that the oxygen content of the surfaces of the Vectran fibers increased significantly due to the accelerated degradation conditions, the surface degradation of UV exposed Vectran fibers is dominated by the abrupt increase of carbonyl, carboxyl, and hydroxyl groups as main chains are oxidized. The UV degradation of Vectran fiber suggests that to improve the ability of fibers within a thin surface layer to resist UV radiation is the key factor to protect them. Therefore, the UV stabilizers should form coatings on the surface of fiber to protect them against UV light in the next step of study.

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