

# Effects of stress and sulfur dioxide on Spectra<sup>®</sup>

J. Coates, K.L. DeVries\*

*Department of Mechanical Engineering, University of Utah, Salt Lake City, UT 84112, USA*

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## Abstract

Polymers are often subjected to aggressive environments where mechanical and chemical mechanisms may act synergistically to degrade the polymers. This research focused on the effects of stress and sulfur dioxide (SO<sub>2</sub>) environments on ultrahigh molecular weight polyethylene (UHMWPE) fibers (Spectra<sup>®</sup>). Spectra<sup>®</sup> yarn specimens were exposed to stress, SO<sub>2</sub>, and/or near ultraviolet (UV) light environments. Degradation, a decrease in tensile properties, was measured by tensile testing specimens immediately after exposure to the stress/environment conditions. Creep lifetime degradation of Spectra<sup>®</sup> single fiber specimens was also measured in SO<sub>2</sub> and/or near UV light environments. The Spectra<sup>®</sup> fibers were found to degrade due to the applied stress. This was evidenced by a decrease in the ultimate strength subsequent to an applied creep load and the short creep lifetimes. No chemical degradation was observed, nor were any mechanical–chemical synergisms observed due to the SO<sub>2</sub> and/or near UV light environments. The creep lifetimes of the Spectra<sup>®</sup> fibers, however, increased slightly in environments of SO<sub>2</sub> and/or near UV light. The degradation of the Spectra<sup>®</sup> fibers is consistent with their fibrillar morphology and was attributed to chain scission of the interfibrillar tie chains due to the applied creep load. Since no degradation of the Spectra<sup>®</sup> was observed in the SO<sub>2</sub> and/or near UV light environments, it was concluded that it is relatively insensitive to environmental attack from SO<sub>2</sub> and/or near UV light. The increase in the creep lifetimes of the Spectra<sup>®</sup> fibers suggests that the SO<sub>2</sub> and/or near UV light does affect the Spectra<sup>®</sup> fibers. Based on this and the work of other researchers, it is hypothesized that the SO<sub>2</sub> and/or near UV light are, to a limited extent, capable of crosslinking or branching linear polyethylene molecules. Such crosslinking or branching appears to be minimal, altering only the creep lifetimes and leaving the other tensile properties largely unaffected. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Polymers are increasingly being used in structural applications with potentially aggressive environments where mechanical and chemical mechanisms may act to degrade the polymers. Although chemical inertness is a property associated with many polymers, it has been demonstrated that common industrial atmospheric pollutants such as nitrogen dioxide (NO<sub>2</sub> or NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), and ozone (O<sub>3</sub>), as well as ultraviolet (UV) light, can have deleterious effects on some polymers. For nylon and Kevlar<sup>®</sup> fibers, a synergistic effect between applied stress and NO<sub>x</sub> has been observed. [1–3] A similar synergistic effect between applied stress and SO<sub>2</sub> has been reported for Spectra<sup>®</sup> fibers. [4] The present research considers interactions of mechanical, SO<sub>2</sub> pollutant gas, and photochemical degradation of Spectra<sup>®</sup> fibers. Tensile property degradation was examined, and over a longer time period, creep lifetime degradation was examined.

Degradation is recognized to be accelerated by increases in normal environmental conditions such as applied stress, pollutant gas concentration, or UV light intensity. To conduct real time tests on polymers under combinations of these conditions is excessively time consuming and, therefore, accelerated testing is frequently used. The accelerated test conditions in this research were an attempt to simulate a polluted SO<sub>2</sub> environment using high concentrations of SO<sub>2</sub> and increased near UV light intensity. The UV light was used to excite the SO<sub>2</sub> molecules into more reactive states and not to introduce photodegradation. The excited states of SO<sub>2</sub> are thought to be responsible for many of the harmful effects of SO<sub>2</sub>.

A principle behind combined mechanical and pollutant gas degradation is that stress and/or strain can assist in overcoming the activation energy for breaking backbone bonds. This principle has been used to explain the synergistic behavior between stress and pollutant gas for some polymers. For example, NO<sub>x</sub> is known to break backbone bonds in nylon. [5] For combined stress and NO<sub>x</sub> degradation of highly oriented nylon fibers, the effects are synergistic. The behavior has also been investigated on a

\* Corresponding author. Tel.: +1-801-581-7101; fax: +801-585-1467.

*E-mail address:* larry.devries@dean.eng.utah.edu (K.L. DeVries).

molecular level. A significant portion of the load carrying capacity of oriented polymers is attributed to their primary bonds. It is believed that in nylon fibers a synergistic effect is observed because the primary bonds are strained and are more susceptible to  $\text{NO}_x$  attack. A similar phenomenon was thought to occur with Spectra<sup>®</sup> fibers under stress in  $\text{SO}_2$ .

### 1.1. $\text{SO}_2$ photochemistry

$\text{SO}_2$  is a colorless, moderately toxic, pollutant gas with a pungent odor. A primary source of  $\text{SO}_2$  in the environment is from coal combustion. Daily average  $\text{SO}_2$  concentrations in cities may be 0.5 ppm, and hourly average  $\text{SO}_2$  concentrations may be as high as 1.5 ppm. [6] Once in the atmosphere,  $\text{SO}_2$  may undergo several photochemical reactions. In the presence of near UV light,  $\text{SO}_2$  may be excited into its singlet ( $^1\text{SO}_2$ ) or triplet ( $^3\text{SO}_2$ ) states. The singlet state occurs near a UV wavelength of 294 nm, while the triplet state occurs near a UV wavelength of 388 nm. [7] Both these states are highly reactive, and it has been postulated that an excited  $\text{SO}_2$  molecule ( $^{1,3}\text{SO}_2$ ) is capable of liberating hydrogen from polyethylene. [8] Furthermore, in the atmosphere,  $\text{SO}_2$  may react with oxygen and water to form ozone and sulfuric acid. It is the formation of acid rain from sulfuric acid, which may damage vegetation, that is a major driving force for  $\text{SO}_2$  pollution control.

### 1.2. $\text{SO}_2$ degradation of polyethylene

Dainton and Ivin [9] studied the effects of  $\text{SO}_2$  on hydrocarbons, which may be considered low molecular weight polyethylene. Sulphinic acids were found to form on the end groups of the hydrocarbons.

Jellinek et al. [10] performed chemical degradation studies using cast low-density polyethylene (LDPE) film. They exposed the LDPE film to combinations of  $\text{SO}_2$  and near UV light for 10-h periods. The  $\text{SO}_2$  was 7% by volume, and the UV light was generated from a high-pressure mercury vapor lamp with the most intense wavelength at 366 nm. Based on viscosity measurements, Jellinek et al. concluded that LDPE film did not degrade in the presence of  $\text{SO}_2$  alone, nor in the presence of UV light alone. However, they concluded that the LDPE film was highly crosslinked in the presence of both  $\text{SO}_2$  and UV light.

### 1.3. Combined stress and $\text{SO}_2$ degradation of polyethylene

Igarashi [11] examined the combined effects of stress and  $\text{SO}_2$  on commercial HDPE film, HDPE fibers, and HDPE rod. He concluded that there was no apparent significant degradation in the strength of the HDPE film, HDPE fibers, or HDPE rod.  $\text{SO}_2$  concentrations of up to 12% by volume were used with exposure times up to 120 h.

Salisbury [4] measured the degradation in tensile properties for Spectra<sup>®</sup> fibers that were exposed to combinations of stress and  $\text{SO}_2$ . He concluded that there was a synergistic degradation caused by the combination of applied stress and

the  $\text{SO}_2$ . For his research, the applied stress ranged from 20 to 80% of the ultimate strength, and 4%  $\text{SO}_2$  by volume was used. The exposure times were up to 144 h.

Perry [12] performed photoacoustic spectroscopy experiments on Spectra<sup>®</sup> fibers that were exposed to stress and  $\text{SO}_2$ . Sulfate groups ( $\text{C}-\text{O}-\text{SO}_2-\text{O}-\text{C}$ ), along with alkene ( $\text{C}=\text{CH}_2$  or  $\text{C}=\text{C}$ ), ether ( $-\text{O}-$ ), and carboxylic acid groups ( $\text{COOH}$ ) were evidenced. Perry asserted that the alkene, ether, and carboxylic acid groups were new end groups formed during chain scission degradation, and that these findings agreed with Salisbury's conclusions that stress and  $\text{SO}_2$  degraded Spectra<sup>®</sup>.

### 1.4. Photodegradation of polyethylene

The effects of UV light on polyethylene have been researched extensively. [13,14] It is reported that UV light may lead to crosslinking, chain scission, or a combination of both, depending on the environment. After long exposure to UV light in an inert environment, chain scission and hydrogen abstraction may occur. Hydrogen abstraction may lead to crosslinking and the evolution of hydrogen gas or to chain scission with a stable end group and a free radical end. The free radical end may continue to react with neighboring chains. In the presence of oxygen, crosslinking and chain scission may still occur, with the ratio of crosslinking to chain scission depending on the oxygen concentration. In addition, some of the crosslinks may contain ether linkages ( $-\text{O}-$ ).

## 2. Experimental

To investigate the effects of stress and  $\text{SO}_2$  environments on Spectra<sup>®</sup>, two types of experiments were performed: tensile property degradation experiments and creep lifetime degradation experiments. The tensile property degradation experiments involved subjecting Spectra<sup>®</sup> yarn specimens to a constant creep load in environments of  $\text{SO}_2$  and/or near UV light for fixed time duration. The specimens were then removed from the environment and tested to failure in a uniaxial tensile testing machine. The creep rupture experiments consisted of subjecting Spectra<sup>®</sup> single fiber specimens to a constant creep load in environments of  $\text{SO}_2$  and/or near UV light. The specimens were left in the environment until creep failure.

### 2.1. Material and specimen preparation

The material that was used in this research was Spectra<sup>®</sup>-1000 (Spectra<sup>®</sup>) fibers that were provided by AlliedSignals Inc. Spectra<sup>®</sup> fibers are highly oriented UHMWPE fibers that are manufactured by surface growth solution spinning. UHMWPE has a very linear structure with little side branching and a molecular weight that ranges from 1,000,000 to 6,000,000 g/mol. [15] The Spectra<sup>®</sup> yarn contained 68 individual fibers and had a linear density of 42 tex. The average

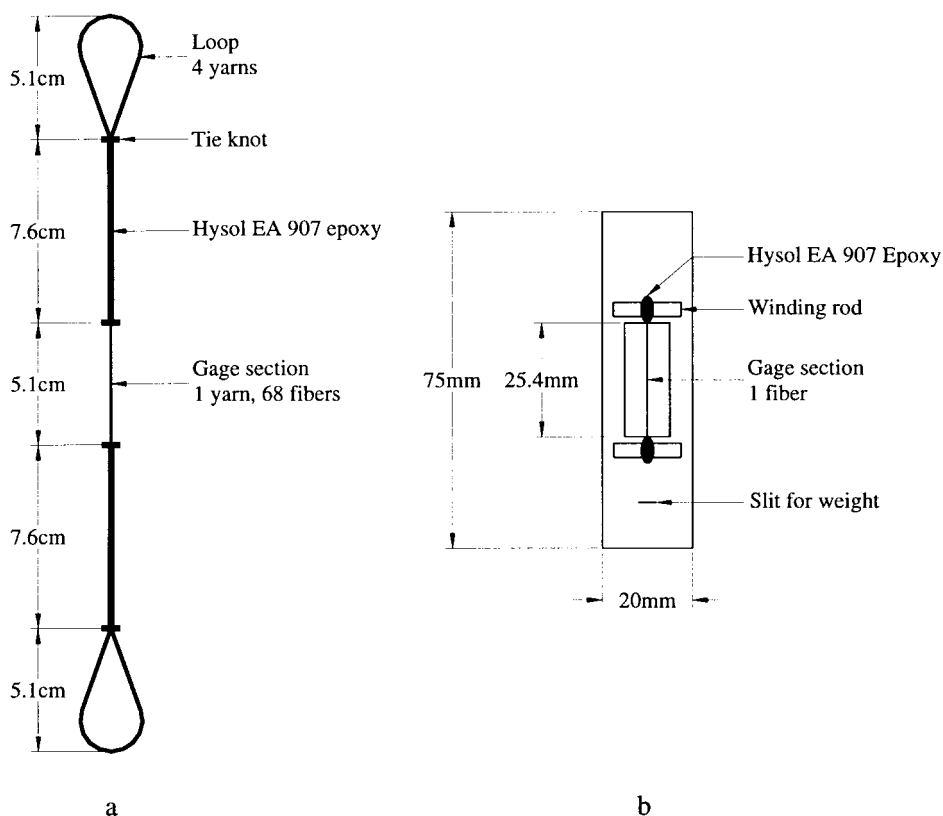


Fig. 1. Spectra<sup>®</sup> specimens: (a) yarn tensile specimen; (b) single fiber creep specimen.

fiber diameter was 28  $\mu\text{m}$ . The fiber diameter and the linear density were calculated from density considerations. A density of 0.97  $\text{g}/\text{cm}^3$  was measured for the Spectra<sup>®</sup> using Archimedes method with ASTM 3800-79 as a guide.

Spectra<sup>®</sup> yarn specimens were prepared in the form of fiber bundle “dogbones”. The gage section of the specimens consisted of one yarn that was 5.1 cm long. The average area corresponding to one yarn, 68 fibers, was used to determine the specimen’s tensile properties. The yarn specimens are illustrated in Fig. 1a.

Spectra<sup>®</sup> single fiber specimens were prepared using ASTM-D3379-75 as a guide. The gage section consisted of a single fiber that was 2.54 cm long. The average area corresponding to one fiber was used to determine the specimen’s tensile properties. The single fiber specimens are illustrated in Fig. 1b.

## 2.2. Stress/environmental exposure apparatus

Stress was applied to the yarn specimens using a lever arm apparatus with lead weights. Stress was applied to the single fiber specimens by hanging lead weights directly from the specimens.

Stressed and unstressed specimens were exposed to  $\text{SO}_2$  and/or near UV light inside glass chambers. The chambers were constructed of 6.35 mm plate glass. The chambers had

removable lids and bases to allow access to the specimens and were sealed with a bead of vacuum grease.

For the environmental exposure, the chambers were purged with dry air to remove moisture in order to prevent sulfuric acid formation. This was done to maintain  $\text{SO}_2$  gas in the chamber. A given volume of  $\text{SO}_2$  was then measured and injected into the test chamber using a 1.5 l piston-cylinder device. During the injection of the  $\text{SO}_2$ , a small vent port of the environmental chamber was temporarily left open to allow the pressure in the chamber to remain at atmospheric pressure in order to prevent a pressure build up that might burst the chamber seals. All the experiments involving  $\text{SO}_2$  were carried out under a fume hood.

When the UV light was used, it was placed on the outside of the glass chambers, 7.6 cm away from the yarn specimens and 15.2 cm away from the single fiber specimens. The UV light source was placed at the elevation of the gage length of the specimens. The near UV light source that was used for the experiments had a wavelength of 365 nm with an intensity of 1000  $\mu\text{W}/\text{cm}^2$ , as reported by the manufacturer.

To measure the tensile property degradation of the yarn specimens, the specimens were broken in an Instron uniaxial tensile testing machine within 30 min after the stress/environmental exposure. A 25 kN load cell was used with a crosshead speed of 12.7 mm/min. For the creep lifetime degradation experiments, the creep lifetimes

Table 1  
Fraction of the baseline ultimate strength of Spectra® fibers under various stress/environment conditions. Each table entry is the average of three data points

Stress/environment	Exposure time (h)		
	24	48	72
No stress, 5% SO <sub>2</sub>	0.96	0.95	0.99
No stress, UV	1.02	1.02	0.99
No stress, 5% SO <sub>2</sub> , UV	0.99	1.04	0.98
20% $\sigma_U$	0.98	0.98	1.01
20% $\sigma_U$ , 5% SO <sub>2</sub>	0.96	0.97	0.99
20% $\sigma_U$ , UV	1.02	0.98	0.99
20% $\sigma_U$ , 5% SO <sub>2</sub> , UV	0.98	0.99	1.02
40% $\sigma_U$	0.98	0.96	0.95
40% $\sigma_U$ , 5% SO <sub>2</sub>	1.00	0.93	0.96
40% $\sigma_U$ , UV	1.02	0.98	0.92
40% $\sigma_U$ , 5% SO <sub>2</sub> , UV	0.95	0.96	0.94

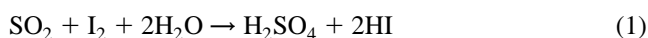
were measured using a Fluke® data logger that recorded data in discrete time intervals. The data logger was connected to electrical circuits inside the test chamber. When a specimen broke, the weight dropped, and a tethered magnet was pulled from a reed switch that was part of the electrical circuit. This sent a signal to the data logger, thereby allowing the creep lifetimes of the specimens to be measured. The data logger time intervals were adjusted on a daily basis so that all the measured creep lifetimes were accurate to within  $\pm 5\%$ .

### 2.3. Environmental verification

For this research, humidity in the chambers, SO<sub>2</sub> concentration in the chambers, and UV light penetration into the chambers were of concern. Although the initial concentration of SO<sub>2</sub> is known with reasonable certainty, the concentration of the SO<sub>2</sub> as a function of time after it is injected into the chambers is less well known. If moisture is in the chambers, the SO<sub>2</sub> may react to form sulfuric acid. Furthermore, the SO<sub>2</sub> may react with the specimens, the chamber seals, or with the load frames. The SO<sub>2</sub> may also diffuse through the chamber seals. In addition, during the SO<sub>2</sub> injection, some of the SO<sub>2</sub> may escape through the open vent port.

To eliminate moisture in the chambers, they were purged with dry air. A hygrometer was placed in the chambers to measure the humidity as a function of time. Immediately after the purges, the humidity at the bottom of the chambers was less than 1%. After 24 h, the humidity had increased to 10% and remained near that level for the remainder of the tests. This trend was independent of the humidity in the laboratory.

One method of directly measuring the SO<sub>2</sub> concentration in the chambers is through titration. SO<sub>2</sub> reacts with iodine and water to form sulfuric acid and hydrogen iodide (Reaction 1). [16]



In order to measure the SO<sub>2</sub> concentration in the chamber, iodometric titration was performed using a solution of iodine in potassium iodide. The solution was 0.01 M of iodine in 0.01% by weight potassium iodide. For the titration, 10 ml of the iodine in potassium iodide solution and a few drops of a starch indicator solution were measured into a flask. A volume of SO<sub>2</sub> was removed from the chamber with a syringe and then injected into the iodine solution. During the injection, the solution was shaken vigorously until the end point of the titration was reached when the color of the solution changed from dark blue to clear. Since the volume of the SO<sub>2</sub> and the amount of iodine were known, the concentration of SO<sub>2</sub> in the chamber was calculated using reaction (1).

Although 5% SO<sub>2</sub> by volume was injected into the chambers, a maximum concentration of 3.1% SO<sub>2</sub> by volume was measured. The concentration decreased with time in a relatively linear manner reaching 2.7% SO<sub>2</sub> by volume after 10 days. The titration results showed that a considerable amount of SO<sub>2</sub> was present in the chambers for the duration of the tests.

The near UV light source that was used for the experiments had a wavelength of 365 nm, and plate glass has a transmissivity that drops from 0.92 to 0 near this wavelength. [17] In order to determine if the UV light would penetrate into the chamber, the transmissivity of the glass was measured for the UV light source. The transmissivity is the ratio of the transmitted intensity to the incident intensity, and was measured with a Newport Optical Power Meter. A transmissivity of 0.9 was measured indicating that most of the UV light did penetrate the glass.

## 3. Results and discussion

### 3.1. Baseline tensile strength

The baseline tensile strengths for the Spectra® yarn specimens and the Spectra® single fiber specimens were  $3.1 \pm 0.1$  and  $3.5 \pm 0.7$  GPa, respectively. The baseline tensile properties of the yarn and the single fibers were determined from 12 and 48 specimens respectively and are reported as an average with a standard deviation. Allied-Signals Inc. reports the ultimate strength for Spectra® yarn as 3.0 GPa. [18] For the yarn specimens, the measured ultimate strength agreed very well with that reported by Allied-Signals Inc. The results show that the ultimate strengths of the single fibers have more variation than those of the yarn. This may occur because the single fibers have different diameters, and the single fiber specimens are more susceptible to damage than the yarn specimens. The results also show that the average ultimate strength of the single fibers is higher than the average ultimate strength of the yarns. This phenomenon is as predicted by the micromechanical model of Daniels [19]. The tensile properties that relied on displacement measurements, such as the ultimate strain

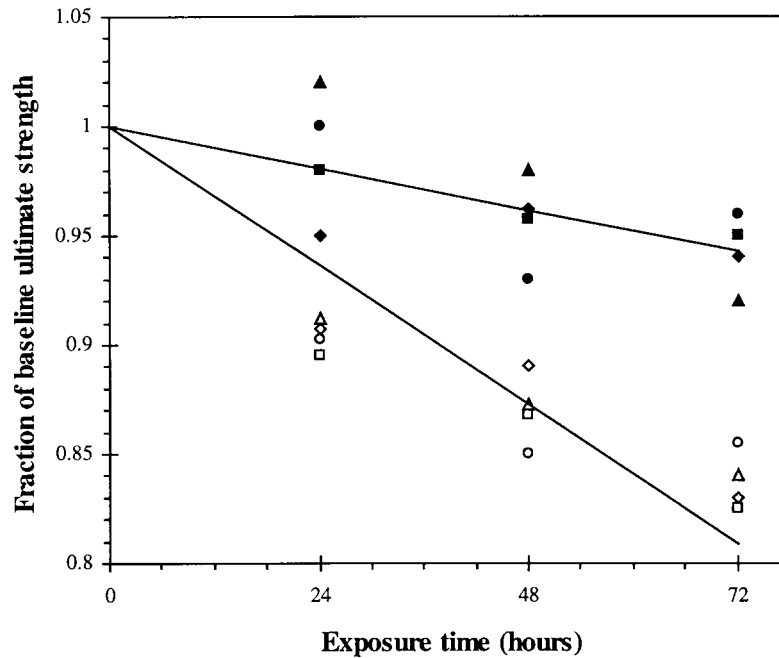


Fig. 2. Degradation of stressed Spectra<sup>®</sup> fibers subsequent to a 40%  $\sigma_U$  (solid symbols) and 50%  $\sigma_U$  (open symbols) creep load versus exposure time in environments of dry air ( $\square$ ), dry air with 5%  $\text{SO}_2$  ( $\circ$ ), dry air with near UV light ( $\Delta$ ), and dry air with 5%  $\text{SO}_2$  and near UV light ( $\diamond$ ). Each point in the figure is the average of three data points.

and the modulus, were not consistent and hence are not reported. One reason for this is associated with the poor bonding of the Spectra<sup>®</sup> fibers to the epoxy that caused the fibers to slip during the tensile testing. Despite this, the ultimate strength and the creep lifetimes of the Spectra<sup>®</sup> specimens are reliable and consistent because the load was carried by the fibers in the gage section, and the initial cross-sectional area of the gage section was accurately known.

### 3.2. Tensile property degradation

Table 1 contains the results for the tensile property degradation experiments of the Spectra<sup>®</sup> yarn. The results are reported as a fraction of the baseline ultimate strength as determined from tensile tests on the as received material. On a percentage basis, the standard deviation for the ultimate strength was 5%. All the data points except two are within 5% of the baseline ultimate strength. The remaining data points are within 8% of the baseline ultimate strength and occur for specimens exposed to stress for longer periods of time.

Fig. 2 demonstrates that applied, sustained stress degrades the ultimate strength of the Spectra<sup>®</sup> fibers. Shown is a comparison of results for environments of dry air, dry air with  $\text{SO}_2$ , dry air and near UV light, and dry air with  $\text{SO}_2$  and near UV light. Linear curve fits are shown on the plot to illustrate the trends. The ultimate strength decreased with increasing creep load and increasing exposure time. For example, the ultimate strength decreased by approximately 18% after a 72-h exposure to a creep load of 50%  $\sigma_U$ .

Table 1 and Fig. 2 show that the sustained mechanical stress decreased the ultimate strength of the Spectra<sup>®</sup> fibers, while the presence of  $\text{SO}_2$  and near UV light environments had no detectable effect on them. For the Spectra<sup>®</sup> fibers, no chemical degradation was observed, nor were there any observable mechanical–chemical synergisms.

### 3.3. Creep lifetime degradation

During the tensile property degradation experiments, relatively short creep lifetimes were observed for the

Table 2  
Weibull statistics for the creep lifetimes of Spectra<sup>®</sup> single fibers

Creep load/environment	<i>n</i>	<i>b</i>	$\phi$ (min)	$B_{10}$ (min)	$B_{50}$ (min)	$B_{90}$ (min)
60% $\sigma_U$	24	0.74	256	12	156	788
40% $\sigma_U$	44	1.01	2187	237	1522	4986
40% $\sigma_U$ , 5% $\text{SO}_2$	44	0.85	4447	313	2886	11,895
40% $\sigma_U$ , UV	40	0.93	4349	384	2929	10,692
40% $\sigma_U$ , 5% $\text{SO}_2$ , UV	42	0.88	2846	218	1872	7382

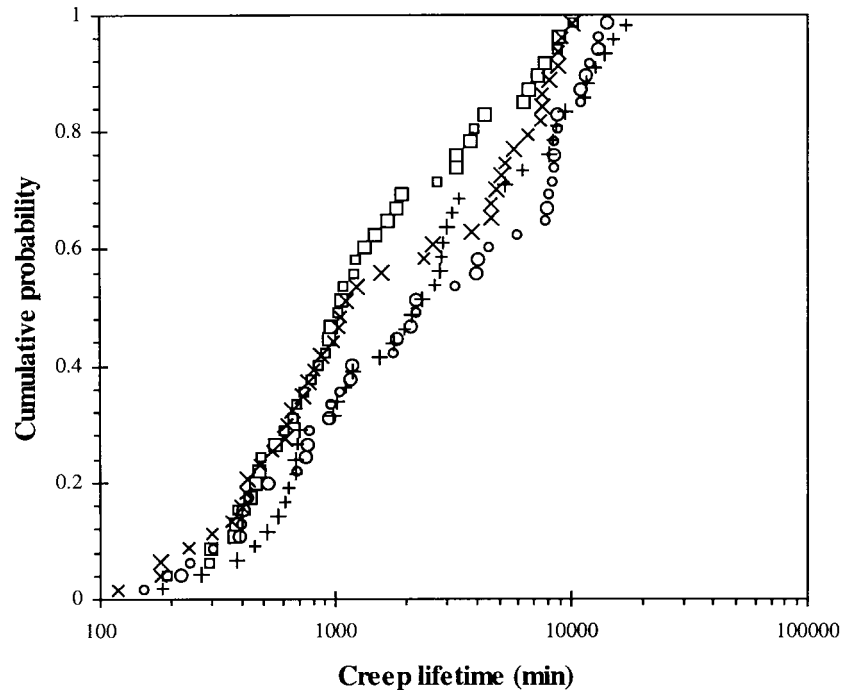


Fig. 3. Creep lifetime distributions of Spectra<sup>®</sup> single fibers loaded with a 40%  $\sigma_U$  creep load. The environments were dry air ( $\square$ ), dry air with 5%  $\text{SO}_2$  ( $\circ$ ), dry air with near UV light (+), and dry air with 5%  $\text{SO}_2$  and near UV light ( $\times$ ). The different sized points indicate different creep rupture tests.

yarns. Only a few data points were obtained for the yarn specimens. Therefore, single fiber creep rupture experiments were undertaken to gather a large number of data points in order to develop a higher confidence level in the results.

The data for the creep lifetimes were analyzed using the Weibull distribution, and Table 2 contains statistics for these creep lifetimes. For comparison, Table 2 includes the number of specimens ( $n$ ), the shape parameter ( $b$ ), the characteristic life ( $\phi$ ), the 10% life ( $B_{10}$ ), the 50% life ( $B_{50}$ ), and the 90% life ( $B_{90}$ ). Fig. 3 is a cumulative probability plot that illustrates the range of the creep lifetimes in the various environments.

For the single fiber creep rupture tests, the creep load was based on the average ultimate strength as determined from tensile tests. That is, the reported creep loads are represented as fractions of the average ultimate strength. Single fibers with a 60%  $\sigma_U$  creep load were found to fail rapidly, and, therefore, a lower creep load of 40%  $\sigma_U$  was chosen for the bulk of the creep rupture tests. This was done to give the specimens a longer exposure time in the different environments. It was thought that, with rapid failure times, the applied stress would dominate, and that longer exposure times would allow the effects of the environments to be more reliably observed. An examination of Fig. 3 shows that early failures occur near the same time regardless of the environment, whereas, for longer creep lifetimes, the results depend on the environment. Presumably, this occurs because the smaller diameter fibers are more highly stressed and therefore fail earlier than the larger diameter fibers.

Table 2 and Fig. 3 show that the  $\text{SO}_2$  and/or near UV light have the effect of slightly increasing the creep lifetimes. The combination of  $\text{SO}_2$  and near UV light increases the creep lifetimes, but not as much as either the  $\text{SO}_2$  or the near UV light alone. The data indicates that when used separately,  $\text{SO}_2$  and near UV light are strengthening the Spectra<sup>®</sup> fibers. The excited  $\text{SO}_2$  molecules may have no effect or they may be causing some degradation, while the  $\text{SO}_2$  and near UV light, acting alone, are strengthening the Spectra<sup>®</sup> fibers. For all the environments considered, the creep lifetimes were increased. In contrast to the degradation of nylon and Kevlar<sup>®</sup> in  $\text{NO}_x$ , [1–3] there is no degradation of Spectra<sup>®</sup> in  $\text{SO}_2$ . The increase in the creep lifetime represents an improvement.

### 3.4. Scanning electron microscopy

After the degradation experiments were performed, the fractured specimens were examined under a scanning electron microscope. Since no degradation had been observed, an objective was to confirm this on a microscopic level. Another objective was to examine the differences between the fracture surfaces of the fibers that failed in a tensile test and the fibers that failed in creep.

Fig. 4 contains scanning electron microscopy (SEM) images of the fracture surfaces of fibers from both the yarn and the single fiber specimens. No differences due to the stress/environment conditions were observed on the fiber fracture surfaces. No surface damage, such as pitting or scarring, and no potential fracture nucleation sites caused by chemical attack were observed either along the fiber

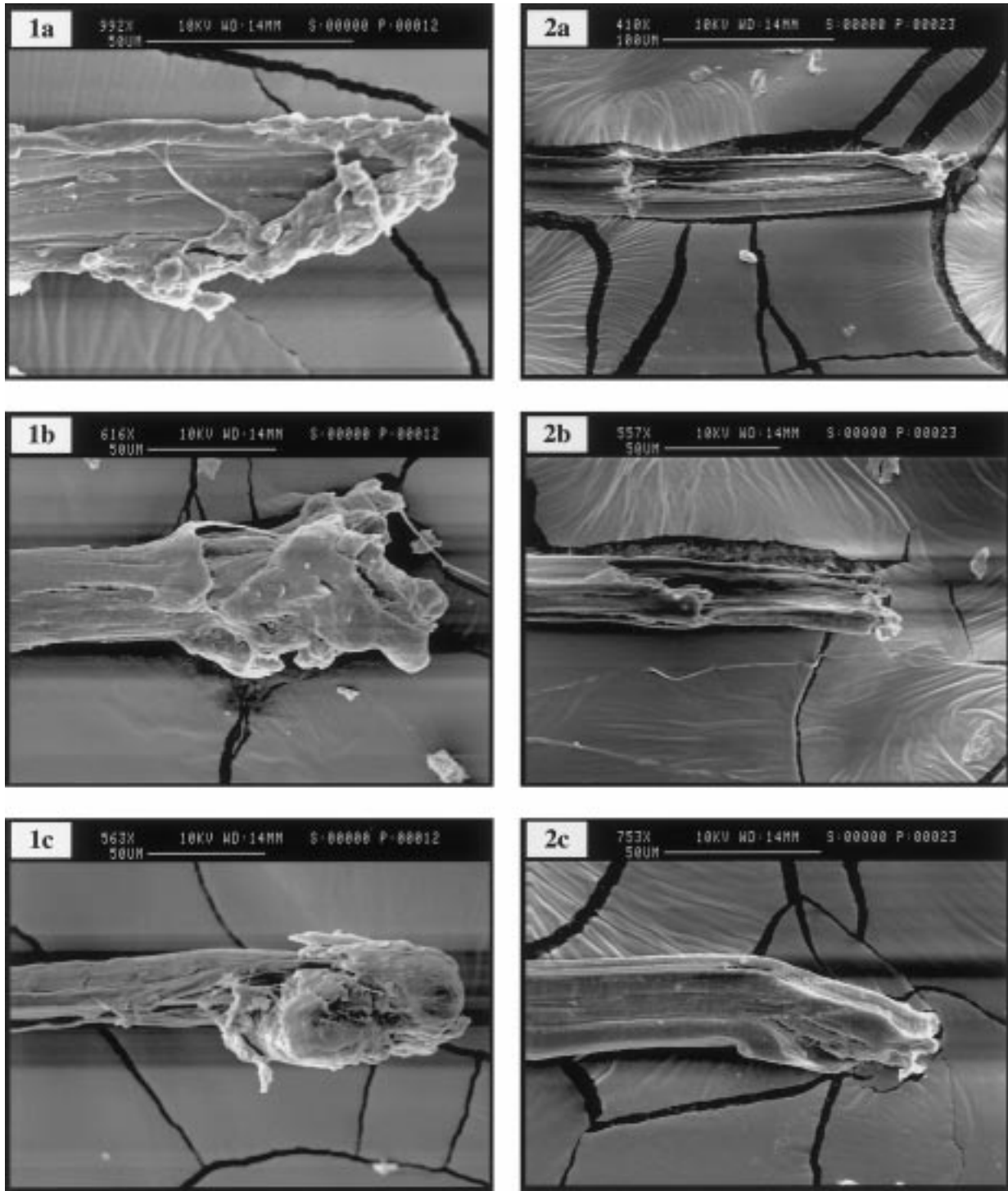


Fig. 4. SEM images of Spectra<sup>®</sup> fiber fracture surfaces after: (1) tensile testing subsequent to a 72 h 40%  $\sigma_U$  creep load, (2) creep testing with a 40%  $\sigma_U$  creep load in environments of (a) dry air, (b) dry air with SO<sub>2</sub>, (c) dry air with SO<sub>2</sub> and near UV light.

lengths or on the fiber fracture surfaces. For the fiber fracture surfaces, no differences in fracture trends, such as fibrillated fracture versus blunt fracture, were observed. All samples that had been exposed to the environments exhibited similar ranges of fracture surfaces that included blunt, tapered, and fibrillated features.

However, differences in fracture surfaces were observed between fibers from the yarn and the single fiber specimens. Fracture surfaces of fibers from the yarn specimens exhibited rounded and curled ends with an appearance of almost having melted during fracture. Fracture surfaces of fibers from the single fiber specimens generally exhibited much

more blunt features. The differences were attributed to the different tensile test strain rates. For the yarn specimens, a high strain rate, which developed a high stress over a short period of time, was used. A stress may be considered a negative pressure and may have the effect of lowering the temperature at which significant flow occurs. The stress may lower the temperature to the point where the fiber almost appears to melt at room temperature. In comparison, in the single fiber specimens, which were loaded at lower strain rates or creep loaded, blunt fracture surfaces were typically observed.

### 3.5. Discussion

Sustained applied stress caused considerable mechanical degradation of Spectra<sup>®</sup> fibers. The degradation of the Spectra<sup>®</sup> was evidenced in a decrease in the ultimate strength and the relatively short creep lifetimes. Only the Spectra<sup>®</sup> that was creep loaded at 20%  $\sigma_U$  did not show any degradation due to the applied stress for the time periods examined. It is, however, believed that longer exposure times at the lower stress level might also cause the Spectra<sup>®</sup> yarns to degrade. The data also indicates that the SO<sub>2</sub> and/or near UV light environments have little or no effect on the Spectra<sup>®</sup> fibers because no chemical degradation was observed nor were any mechanical–chemical synergisms observed. This lack of degradation in strength indicates that the linear polyethylene molecules of UHMWPE are not susceptible to attack. The creep lifetime data indicate that the SO<sub>2</sub> and/or near UV light, to a limited extent, enhance the properties of Spectra<sup>®</sup>.

The decrease in ultimate strength subsequent to an applied creep load and creep rupture may be interpreted in terms of a molecular phenomenon. Creep loading apparently results in the rupture of interfibrillar tie chains, consequently causing the decrease in the ultimate strength and the consequent creep failure. Salisbury [4] provided evidence of this in Spectra<sup>®</sup> using Electron Spin Resonance (ESR) techniques. Samples were pulled to failure while passing through the ESR cavity. As the failure stress was approached, a rapid production of free radicals that increased somewhat exponentially up to fracture was observed. The free radical production is evidence of homolytic chain scission. It was observed that for samples held under constant creep conditions, the extent of free radical production during the subsequent loading to failure in the ESR cavity was significantly less than that for the as received material. The decrease in free radical density at fracture was concomitant with the observed decrease in the ultimate strength. This may be explained as follows: Bonds broken during the sustained loading need not be broken in the subsequent tensile test, nor are the tie chains associated with the broken bonds available to contribute to the material's load carrying capability; hence the decrease in strength. Creep rupture occurs when sufficient bonds are broken and the material can no longer sustain the load. It is

noted that the free radicals associated with the chain scission are inherently unstable entities that decay rather rapidly. ESR, therefore, provides no direct measure of the bond rupture that occurs during the sustained loading. Rather it measures the accumulation of free radicals during the short time involved in the final loading to failure. The bonds ruptured during creep are represented by the deficit in the final accumulation.

This research was originally intended to further quantify the degradation of Spectra<sup>®</sup> in SO<sub>2</sub> that was originally reported by Salisbury [4]. However, since no degradation was found due to the SO<sub>2</sub>, the research was expanded to include SO<sub>2</sub> and near UV light environments to examine the effects of excited SO<sub>2</sub> on Spectra<sup>®</sup>. However, again, no degradation was observed. The creep rupture experiments were conducted to examine more subtle degradation mechanisms. It was considered possible that the SO<sub>2</sub> could act as a plasticizing agent and allow the polyethylene molecules to flow past each other more easily without causing chain scission. This may have increased the creep rate and decreased the creep lifetimes while not significantly changing the tensile properties. The creep rupture experiments did indicate that the SO<sub>2</sub> and/or near UV light affect the Spectra<sup>®</sup>. However, the effects were strengthening rather than degrading.

We would like to briefly discuss why the findings of this research differ from those of Salisbury [4]. Salisbury's research was the main reason for undertaking this research as he reported that stressed Spectra<sup>®</sup> degraded rapidly in the presence of SO<sub>2</sub>. Salisbury performed tensile property degradation experiments and based his conclusions on specimens that failed early due to creep. Of his specimens that failed in creep in SO<sub>2</sub>, two specimens failed early while seven of the specimens failed with creep lifetimes that were similar to those observed in air. The results provided evidence for concern about the degradation of Spectra<sup>®</sup> in SO<sub>2</sub> and a reason to more thoroughly evaluate the effects of SO<sub>2</sub>. We now question that these limited data indicate rapid degradation of stressed Spectra<sup>®</sup> in the presence of SO<sub>2</sub> because other factors, such as specimen damage, could have caused these early failures.

Some explanation of the results of this research is required to bring it into qualitative agreement with the findings of Jellinek et al. [10] They reported that unstressed LDPE film was highly crosslinked in the presence of SO<sub>2</sub> and UV light, while separately, SO<sub>2</sub> and UV light had no effect on the LDPE film. In this research, because of the increased creep lifetimes, it is speculated that the Spectra<sup>®</sup> fibers may have been lightly crosslinked or branched. There was no strong indication of crosslinking or branching as might have been expected from the findings of Jellinek et al. There are several reasons for the different results. Most importantly, the LDPE studied by Jellinek et al. has more potential branch points than the UHMWPE in the Spectra<sup>®</sup> fibers. The methyl end groups (–CH<sub>3</sub>) on the branches may provide sufficient sites for crosslinking or branching to



occur. If crosslinking or branching occurs at the end groups, UHMWPE would be expected to exhibit little crosslinking or branching because UHMWPE has comparatively few end groups. Unfortunately, such limited crosslinking or branching in UHMWPE is well below the level of detection by swelling measurements or other analytical measurements available for this research. Jellinek et al. also used a high-pressure mercury vapor lamp that had a peak at 366 nm but with a broad spectrum. The UV lamp used in this research was concentrated at a 365 nm wavelength. It is possible that, in the research of Jellinek et al., the broad spectrum of the UV light was responsible for the excited SO<sub>2</sub> molecules and the consequent crosslinking.

Finally, a plausible explanation of the results of this research is offered. For the Spectra<sup>®</sup> fibers, the sustained stress breaks the interfibrillar tie chains and causes a reduction in strength and ultimately creep rupture. The SO<sub>2</sub>, the near UV light, and the SO<sub>2</sub> with near UV light may cause a small number of chemical reactions in the polyethylene. It is suggested that the chemical reactions include chain scission and crosslinking or branching with the crosslinking or branching being the dominant reactions. The only indication of these reactions was in the creep rupture experiments. This explanation is consistent with the results of Jellinek et al [10] if the differences between LDPE and UHMWPE are considered. The explanation is also consistent with the findings of Igarashi [11] who reported that the strength of HDPE film, fibers, and rod did not degrade in SO<sub>2</sub>. It is also consistent with Salisbury's [4] data although not with his conclusions. It is consistent, too, with the results of Perry's [12] photoacoustic spectroscopy experiments on Spectra<sup>®</sup>. The sulfate and ether groups are consistent with crosslinking, while the alkene, and carboxylic acid groups are consistent with chain scission. Lastly, the explanation is consistent with research on the photodegradation of polyethylene since crosslinking is known to occur in polyethylene. [13,14]

#### 4. Conclusions

Significant mechanical degradation was observed in the Spectra<sup>®</sup> fibers. The degradation observed in the Spectra<sup>®</sup> fibers was manifested by a decrease in the ultimate strength subsequent to a constant creep load, which decreased with increasing exposure time and increasing creep load. The degradation was also apparent in the short creep lifetimes. The degradation of the Spectra<sup>®</sup> fibers is consistent with their fibrillar morphology in which applied stress breaks the interfibrillar tie chains resulting in a reduction in strength.

For the Spectra<sup>®</sup> fibers, neither any chemical degradation nor any mechanical–chemical synergisms were observed due to the SO<sub>2</sub> and/or near UV light environments. The

results for the Spectra<sup>®</sup> fibers indicate that linear polyethylene molecules do not degrade in the presence of SO<sub>2</sub> and/or near UV light. The creep rupture experiments, however, indicate that the Spectra<sup>®</sup> fibers are slightly affected by SO<sub>2</sub> and/or near UV light environments since the creep lifetimes were increased. It is hypothesized that the SO<sub>2</sub> and/or near UV light are, to a limited extent, capable of crosslinking or branching linear polyethylene molecules. The amount of crosslinking or branching appears to be minimal, altering only the creep lifetimes and leaving the other tensile properties largely unaffected.

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