

THE EFFECTS OF OXYGEN UPON STRENGTH DEGRADATION OF PBO CORDAGE

E. Lee Rainwater^{*}, Raven Industries, Inc., Sulphur Springs, Texas USA

Joe McLaughlin[†], Raven Industries, Inc., Sulphur Springs, Texas USA

Loren G. Seely[‡], Raven Industries, Inc., Sulphur Springs, Texas USA

ABSTRACT

The Ultra-Long Duration Balloon (ULDB) platform is made viable by the availability of tendons braided of PBO (p-phenylene-2,6-benzobisoxazole). This material, manufactured by Toyobo Co., LTD of Japan under the trade name Zylon[®], possesses a strength-to-weight ratio unattainable by other materials. PBO has one disadvantage in that its strength is severely degraded by exposure to visible and UV radiation¹. Current ULDB platforms circumvent this characteristic by the use of pigmented polyethylene sleeves which shield the tendons from visible and UV radiation. These sleeves, however, add significant weight to the balloon, as well as introduce complications in the sealing process due to the TiO₂ pigment.

Research conducted by Raven Industries, Inc., has shown that the strength degradation of PBO when exposed to visible and UV light is significantly lessened or eliminated when placed in a rarefied oxygen environment. This very significant discovery suggests that the need to shield PBO tendons may be greatly reduced or eliminated in the rarefied atmosphere encountered at the float altitude of a typical scientific ballooning platform. Presented in this paper are details, results, discussion, and potential ramifications of this study.

BACKGROUND

Poly (p-phenylene benzobisoxazole) (PBO) fiber is believed to be the strongest commercially-available synthetic polymer fiber. It was selected for use as tendon cordage for the ULDB program due to its superior mechanical properties, thermal stability, and excellent strength-to-weight ratio. However, one significant drawback in the use of PBO is its tendency to degrade in strength when exposed to visible or UV light; in some instances, the strength degrades to less than 50% of its nominal value. The means by which the material degrades is reported to be a free-radical breakdown mechanism². It is speculated that this mechanism is facilitated by oxygen-carried free radicals, leading to a

breakdown of the carbon-carbon bond between the phenylene and benzobisoxazole groups. For this reason, it was postulated that the breakdown could be mitigated by lower concentrations of atmospheric oxygen.

When used as meridional tendons in the ULDB, the PBO is shielded against visible and UV light by the use of a pigmented polyethylene sleeve. However, this sleeve adds significant weight to the balloon vehicle, thereby compromising its performance envelope. However, if the degradation is influenced by the presence of atmospheric oxygen, then the rarefied atmosphere that is present during much of the ULDB mission could negate the need for light shielding.

TEST PROCEDURE

Three sets of five tendons were prepared as test and control samples. Tendons of Set #1 were placed in bags equipped with fittings to allow the introduction of helium as a purging media. Tendons of Set #2 were placed in an unsealed bag for use as an exposed control set. Both sets of tendons were stored in the dark prior to installation in the UV light box. Set #3 was prepared and stored in the absence of light until step 5 below. The test procedure for evaluating the effects of oxygen exposure is as follows:

1. Set #1 was placed in the UV light box and purged with helium. The helium flow through the bag was regulated at 0.3+/-0.1 SCF/hour. All tendons were placed to be optimally exposed to the UVA radiation.
2. Set #2 was placed in the UV light box, exposed to ambient air. All tendons were placed to be optimally exposed to the UVA radiation.
3. Set #1 and Set #2 were then exposed to 340 nm UVA at 40 °C for 600 hours.
4. At the conclusion of UVA exposure, specimens of both Set #1 and Set #2 were examined for visual degradation.

^{*} Engineering Manager, Member AIAA

[†] Senior Consultant

[‡] Plant Manager, Senior Member AIAA

- Specimens from all three sets were then destructively tested on an Instron-type tensile test machine to determine their ultimate tensile properties. The crosshead speed was 2 in/min (50 mm/min).

significant color change as compared to Set #3. The color change is best described as a change from caramel to light yellow. Tendons in Set #1 did not exhibit any visual change as compared to Set #3. Results of ultimate tensile strength (UTS) testing are graphically presented in Figure 1 and detailed in Table 1.

RESULTS

The UVA-exposed tendons that were subject to ambient atmosphere during UVA exposure (Set #2) exhibited a

Ultimate Tensile Strength Comparison

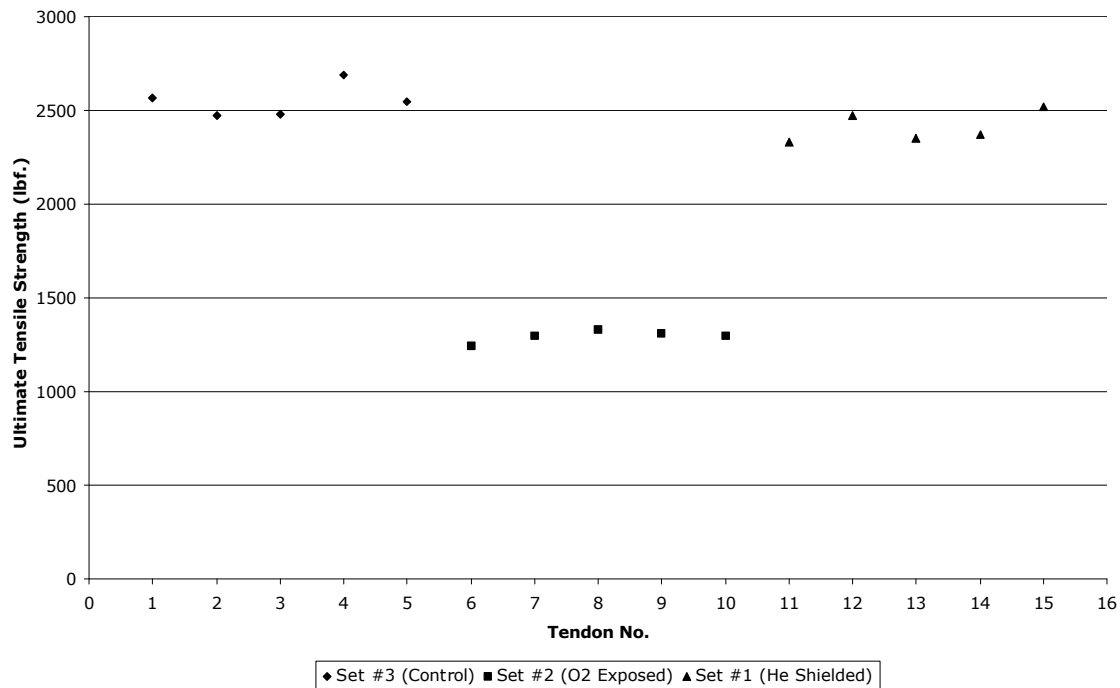


Figure 1—Comparison of Ultimate Tensile Strength of Aged and Non-aged Specimens

DISCUSSION

The effect of eliminating O₂ exposure to light-exposed PBO is dramatic, with Set #1 retaining over 94% of the average strength of the control set (See Table 1). By contrast, the tendons that were exposed to both light and ambient oxygen lost approximately half of their original tensile strength.

Conditions at Float

The atmospheric density at a typical ULDB float altitude of 110K ft is approximately 1/120 of that at sea level. The mixing ratio of free radicals and oxidizers, however, varies with altitude. For example, the concentration of O₃ increases from approximately 20 ppb by volume at sea level to 7.5 ppm by volume at 30 km, a factor of 375. When considering the lower atmospheric

Table 1—Ultimate Tensile Strength Results

Set	Min. (lbf)	Max. (lbf)	Mean (lbf)	% of Control Mean
Set #1 (He Shielded)	2330	2520	2409	94.40%
Set #2 (O ₂ Exposed)	1240	1330	1296	50.78%
Set #3 (Control)	2470	2690	2552	100.00%

density at that altitude, the molecular concentration of O_3 in the stratosphere remains about three times that at sea level. Obviously an understanding of which free radicals provide the mechanism for strength degradation is necessary to predict the behavior of unshielded PBO at float altitude.

CONCLUSION

It has been well-known that PBO fiber-based material suffers significant degradation in tensile strength when subjected to long-term light exposure. This degradation is thought to be the result of an oxygen-carried free-radical mechanism. This experiment has shown that the strength degradation is significantly lessened by shielding the specimens from ambient laboratory atmosphere. Whether this discovery will eliminate the need for light shielding for applications in the rarefied near-space environment is contingent upon confirming the actual mechanism of degradation and evaluating the activity of this mechanism in the environment of interest.

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¹ Toyobo Product Literature, *Technical Information, PBO Fiber-Zylon*, Bulletin F0461K(2001.9), Toyobo Co., LTD, 2001.

² Communication between Loren Seely, Raven Industries, Inc., and Toyobo Co., LTD., 2000.