2015

Improving high-altitude UV–Vis resistance of PBO braided tendons of NASA's super pressure balloons

Rahul Vallabh
North Carolina State University, rvallab@ncsu.edu

Ahmed H. Hassanin
Alexandria University

Magdi A. Said
NASA Wallops Flight Facility, Wallops Island, VA

Abdel-Fattah M. Seyam
North Carolina State University

The Journal of The Textile Institute, 2015
http://dx.doi.org/10.1080/00405000.2015.1077021

Improving high-altitude UV–Vis resistance of PBO braided tendons of NASA's super pressure balloons

Rahul Vallabh[a]*, Ahmed H. Hassanin[b], Magdi A. Said[c] and Abdel-Fattah M. Seyam[a]

[a]*College of Textiles, North Carolina State University, Raleigh, NC, USA;* [b]*Textile Engineering Department, Alexandria University, Alexandria, Egypt;* [c]*NASA Wallops Flight Facility, Wallops Island, VA, USA*

(*Received 10 April 2015; accepted 18 June 2015*)

Super pressure balloons (SPBs) are used by the National Aeronautics and Space Administration (NASA) for ultra-long duration ballooning (ULDB) missions which carry various scientific explorations to support space and earth sciences research activities. The resistance to photo-degradation of load-bearing braided tendons of SPBs is critical to the success of ULDB missions. Recognizing the critical need to improve UV and visible light (UV–Vis) protective performance of *p*-phenylene-2, 6-benzobisoxazole (PBO) braids, North Carolina State University and NASA's Balloon Program collaborated to investigate the effectiveness of sheath extrusion method in improving the UV–Vis resistance of tendons. This study included two PBO tendon types – 48,000 (48k) denier tendons and 72,000 (72k) denier tendons. Using a sheath extrusion method, the tendons were covered with UV protective sheath of low-density polyethylene containing two types of UV inhibitors – TiO_2 rutile nanoparticles and PolyOne PE White CC®. Bare and sheathed tendons were subjected to artificial UVB exposure in the lab as well as to both high altitude and ground exposure during flight missions conducted by NASA. Protection against radiation exposure was evaluated by determining the loss of tensile strength after exposure. UV–Vis protection of tendons improved with an increase in sheath thickness as well as UV inhibitor content in the sheath. The results also showed that 72k denier braids had higher resistance against UV degradation compared to 48k denier braids. In-flight exposure results confirmed the comparative UV protective performance of tendons exposed to accelerated artificial UVB exposure in lab. 72k denier tendon covered with sheath containing 10% PE White CC® (sheath thickness of 0.37 mm) experienced the lowest strength loss among all tendon samples to high-altitude exposure during flight missions. The study has also utilized UV–Vis transmittance of the sheath covering the braids as a method of evaluating the performance of the protective sheaths.

Keywords: PBO; UV–Vis resistance; photo-degradation; high-altitude UV exposure

Introduction

Zylon® belongs to the "aromatic heterocyclic" class of high-performance polymers and consists of rigid-rod chain molecules of poly (p-phenylene-2, 6-benzobisoxazole) or PBO (Toyobo Co Ltd., 2005). It has the highest specific strength and specific modulus among the commercially available high-performance fibers (Toyobo Co Ltd., 2005; Yang, 1989). The superior mechanical properties including high creep resistance (Said, Seyam, Vallabh, & Bolin, 2013) makes the PBO fibers especially suitable for the braided tendons used as the primary load-bearing structural component of giant scientific balloons, such as super pressure balloons (SPBs) used in ultra-long duration ballooning missions (Sterling, 2003).

One of the critical requirements of tendons used in SPB is their ability to retain strength after exposure to ultraviolet and visible light (UV–Vis) radiations. Photo-degradation is a common phenomenon in polymers and polymeric materials including PBO which is known to be very susceptible to photo-degradation (Liu & Yu, 2005; Orndoff, 1995; Said et al., 2006; Toyobo Co Ltd., 2005). The presence of moisture and oxygen has also been found to accelerate photo-degradation (Song et al., 2012). PBO yarn when exposed to 340 nm wavelength light for 450 h lost 98% of its original tensile strength (Orndoff, 1995). In another study, PBO yarn was subjected to accelerated aging in a weatherometer which simulated the daylight through window pane. PBO yarn lost about 55 and 80% of its strength after 24 and 96 h of UV exposure in the weatherometer, respectively. After 144 h of exposure, PBO yarn lost about 86% of its strength (Said et al., 2006). Results published by Toyobo Co Ltd. have also shown that Zylon® yarn lose about 70% of its strength after 500 h (about 21 days) of exposure, while in an outdoor test, Zylon® yarn lost about 65% of its strength after 6 months (about 180 days) of exposure (Toyobo Co Ltd., 2005). PBO yarns have been reported to lose about 65% of its original strength after 160 h of exposure to simulated sunlight (Liu & Yu, 2005). The disparity among the strength loss results reported in these studies is suspected to be due to the different exposure condition used for weathering and material thickness.

The critical issue of photo-degradation in PBO fibers has been addressed by several studies, however most

*Corresponding author. Email: rvallab@ncsu.edu

studies have failed to achieve the level of protection which would make the PBO tendons maintain the load-bearing capabilities of long-duration high-altitude SPB missions. Protective coatings such as thin flexible amino silicone film-containing UV absorber/blocker (Gupta, 2005), nano-ZnO hybrid sizing (Zhang, Huang, Yuan, & Zhang, 2011), and multiple coating of polyhedral oligomeric silsesquioxanes and nano-TiO_2 (Song, Meng, & Huang, 2013) have been used with limited success. Lack of durability of the coating materials and the lack of uniform coverage and penetration in case of yarns and braids are also issues of concern. Other methods including chemical modification by introduction of binary hydroxyl groups (Zhang, Jin, Yang, Li, & Jiang, 2011) and 2,6-naphthalene groups (Wang, Yoon, & Min, 2015) into the PBO macromolecular chain have also been used. Other methods involving electrospun polyurethane nanofibrous protective sheath (Seyam & Won, 2013) and porous polyurethane protective film-containing UV absorbers/blockers have also been studied with promising results, however commercial use of these method for the protection of PBO braids remains a challenge. It is also important to mention that all the studies so far have used lab exposure conditions (including simulated exposure) to evaluate the effectiveness of various methods used to reduce photo-degradation in PBO. The extent of degradation due to real-time high-altitude photo-degradation which is critical to the real flight missions has not been investigated in these studies.

To address the lack, a suitable method to achieve adequate protection against photo-degradation of PBO-braided tendons of SPB during high-altitude flight missions, National Aeronautics and Space Administration (NASA) and North Carolina State University, College of Textiles have jointly investigated a commercially viable approach to achieve the desired level of UV–Vis protection in PBO-braided tendons. The effectiveness of this method which involves covering the PBO braids with an extruded polymer sheath contain UV inhibitors has been investigated to understand the effect of material properties such as braid denier, sheath thickness, UV inhibitor type, and content. Recognizing the lack of investigation on the photo-degradation caused by real-time UV–Vis exposure at high altitude, strength loss in PBO braids flown on actual SPB missions as well as those exposed in lab have been studied. Comparative analysis between the strength loss associated with lab exposure and exposure during flight missions is expected to serve as a guidance for determining the parameters of simulated lab exposure. The study also investigates the correlation between the UV–Vis transmittance of the sheath covering the braids and the strength loss caused by photo-degradation. The knowledge gained in this study would be beneficial in improving the UV resistance of ropes, cables, mooring lines, parachute cords, bulletproof vests, and other high-performance products used outdoors.

Material and sheathing method

This study included two PBO-braided tendon types – 48,000 (48k) denier tendon and 72,000 (72k) denier tendons. The 48k and 72k denier tendons were formed on a 16-carrier braiding machine with 2 and 3, 1500 denier yarns per carrier, respectively. Both tendons had a 2×2 braiding pattern. Using a sheath extrusion method, the tendons were covered with a UV protective sheath of low-density polyethylene (LDPE) containing two types of UV inhibitors – TiO_2 rutile nanoparticles (cylindrical particles with 10 nm diameter and 40 nm length) and PolyOne PE White CC®. Sheathed PBO tendons with different sheath thickness and UV inhibitor contents (add-on %) were produced as listed in Tables 1 and 2.

UV protection performance of tendons

Bare and sheathed tendons were subjected to artificial UV–Vis exposure in lab as well as subjected to both ground and high-altitude exposure during flight missions conducted by NASA. Protection against radiation exposure was evaluated by determining strength of the braids before and after exposure.

Artificial and in-flight exposure

Bare and sheathed tendons were subjected to accelerated exposure to UV–Vis light in the Ci3000 Weather-Ometer equipped with a xenon lamp jacketed in quartz inner and outer filters to simulate high-altitude conditions. The tendons were also subjected to accelerated UVA and UVB exposure in the QUV/Se Weather-Ometer. In order to subject the samples to actual exposure during a flight, the samples were flown in two separate Balloon-borne Large-Aperture Sub-millimeter Telescope (BLAST) flight mission and one The Cosmic Ray Energetics and Mass (CREAM) mission.

Two packages containing 48k denier tendons were flown on two Antarctica flight missions – BLAST mission launched on December 27, 2010 (BLAST1) and CREAM mission launched on December 21, 2010 (CREAM). Each package contained three 48k denier samples with clear LDPE sheath (48k-1), sheath containing 12% PE White CC® (48k-2), and sheath containing 10% TiO_2 (48k-4). The 72k denier (72k-0 and 72k-4) samples were flown in the 2012/2013 BLAST flight mission (BLAST2). Flight duration and recovery time (duration between flight termination and package recovery) of the three flight missions are shown

Table 1. Experimental design for 48k denier tendons.

Sample ID	UV inhibitor	UV inhibitor add-on (%)	Sheath thickness (mm)
48k-0 (control)	na (bare tendon)	na	na
48k-1	na (clear LDPE)	na	0.41
48k-2	PE White CC®	12	0.36
48k-3	TiO_2	5	0.39
48k-4	TiO_2	10	0.41

Table 2. Experimental design for 72k denier tendons.

Sample ID	UV inhibitor	UV inhibitor add-on (%)	Sheath thickness (mm)
72k-0 (control)	na (bare tendon)	na	na
72k-1	PE White CC® +TiO_2	6 + 6	0.35
72k-2	PE White CC® +TiO_2	6 + 6	0.43
72k-3	PE White CC®	10	0.26
72k-4	PE White CC®	10	0.37
72k-5	PE White CC®	10	0.43
72k-6	TiO_2	13	0.35

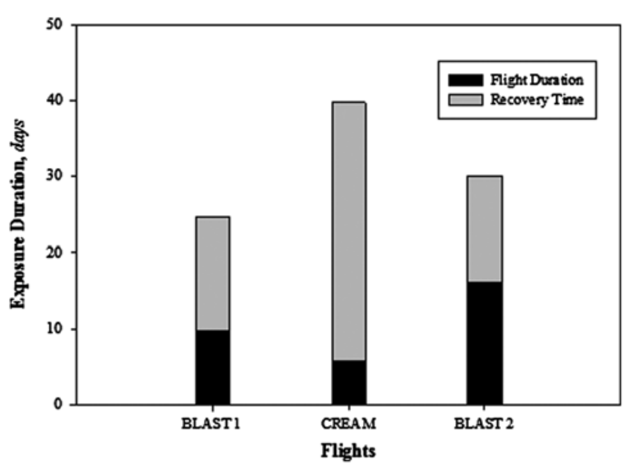

Figure 1. Flight duration and package recovery time.

in Figure 1. Flight trajectories of the three missions are shown in Figure 2.

In each package, the tendons were sandwiched between two layers of 1.5-mil polyethylene film (shown Figure 3). Individual tendons were separated by heat seals along the length of the package to form pockets. The two ends along with two other locations along the length of the package were then reinforced with 4-inch wide wooden strips on the back side, this was done to ensure that the packet stays flat during the flight and the tendons get equal exposure. The ends of each package were sealed with duct tape to prevent contamination with moisture and ice during the mission. The sample packages were mounted on the ladder of the SPB flight train (Figure 4).

Tensile testing of braids was performed using Instron 8800 Servo-Hydraulic system with 22.24-kN (5000 lbs) load cell. All tendons were spliced to 157.48 cm (62 inches) eye to eye. The eyes were 12.7 cm (5 inches) and each bury was 45.72 cm (18 inches). The actuator displacement was set to operate at a rate of 2.54 cm/min (1 inch/min). For sheathed tendons, the sheaths were removed before testing the tensile strength of the braids.

Strength loss percent

Strength loss percent was used as the performance metric to evaluate the effect of radiation exposure on tendons. Strength loss percent is defined as the strength lost by the braid (due to radiation exposure) expressed as percent of the original strength of the unexposed bare braid.

$$\text{Strength loss\%} = \frac{\text{Unexposed bare braid strength} - \text{Braid strength after exposure}}{\text{Unexposed bare briad strength}} \times 100. \quad (1)$$

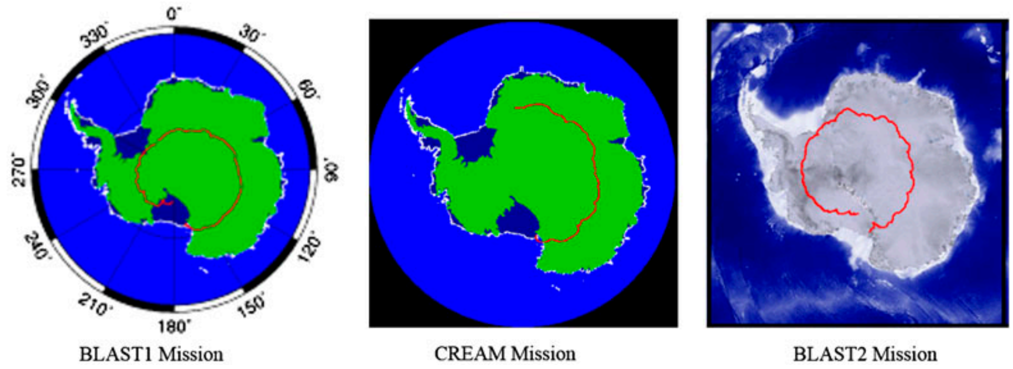

Figure 2. Flight trajectories of the three missions.

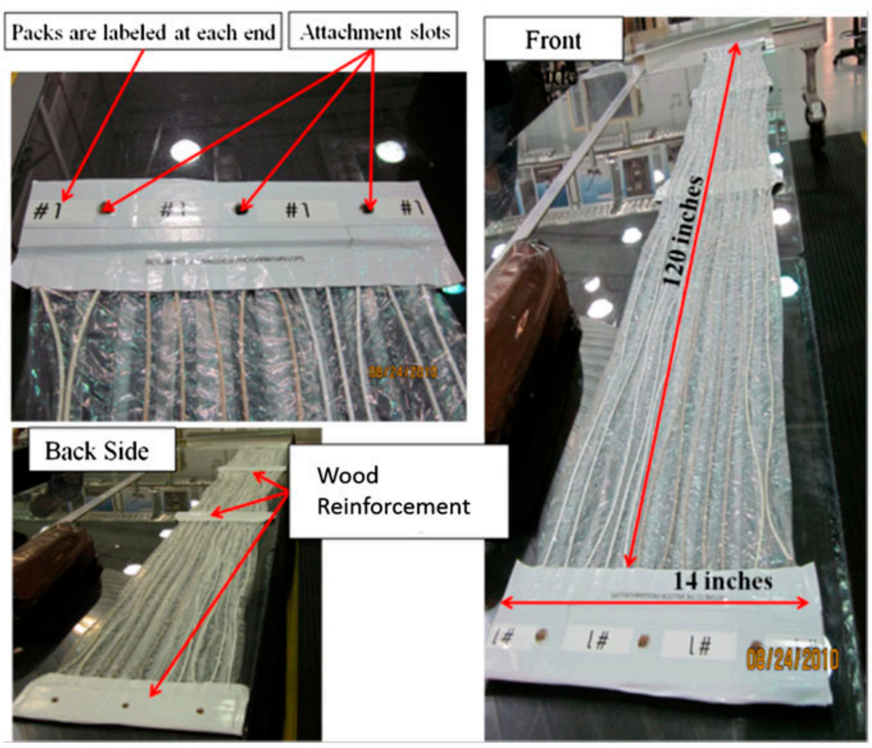

Figure 3. Description of the package containing PBO-braided tendon samples.

UV–Vis transmittance

UV/Visible spectroscopy analysis was performed using Cary 3E Ultraviolet-Visible Spectrophotometer to determine the UV–Vis transmittance for LDPE films. LDPE sheath was stripped off the braid and cut open to form film. Specimen of size 20 mm × 20 mm was mounted in the integrating sphere (DRA-CA-301) attached to the spectrophotometer.

Transmission electron microscopy (TEM)

TEM images were taken by Hitachi HF2000 using acceleration voltage 200 kV to assess TiO_2-nanoparticles dispersion. Samples with thickness of 100 nm were sliced using ultra microtome.

Results and discussion

Strength loss in 48k denier bare and sheathed tendons after 6 days of accelerated UV–Vis, UVA, and UVB exposure is shown in Figure 5. When exposed to the full spectrum of UV and visible light, both bare and sheathed tendons lost almost twice as much strength as when exposed to UVA or UVB alone. Bare tendons and tendons with a sheath of clear LDPE showed the highest strength loss after 6 days of exposure to UV–Vis, UVA,

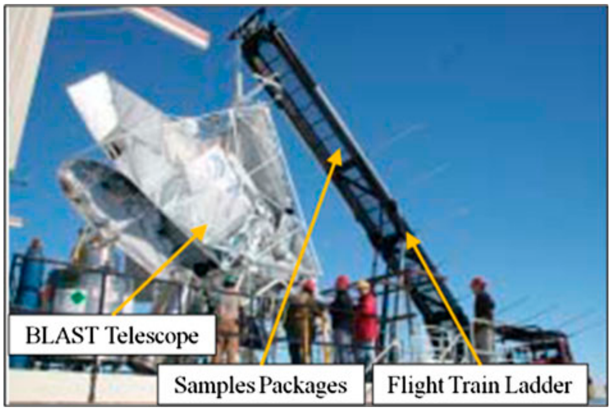

Figure 4. Sample packages mounted on flexible ladders attached to the super pressure balloon (2010 BLAST flight mission).

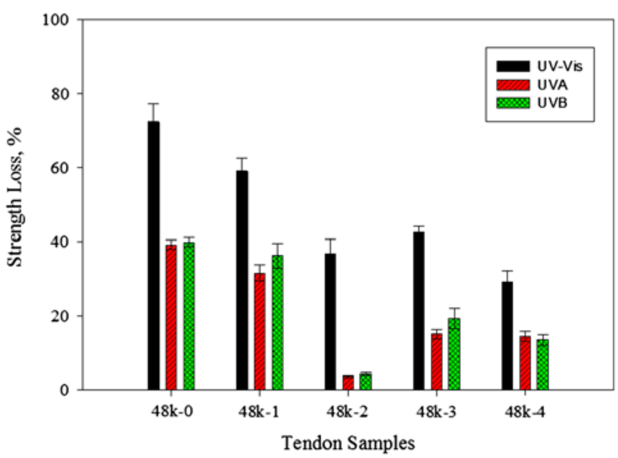

Figure 5. Strength loss in 48k denier tendons after 6 days of UV–Vis, UVA, and UVB exposure in lab.

or UVB. Tendons covered with a sheath with 10% TiO_2 exhibited lower strength loss when compared to tendon covered with 5% TiO_2. This can be attributed to the increased blocking of UV–Vis by larger amount of TiO_2 nanoparticles present in the sheath. The spectral transmittance through various sheath samples is shown in Figure 6. UV–Vis transmittance through sheath and as well as tendon strength loss due to UVA and UVB exposure were found to be the lowest in case of sheath with 12% PE White CC®, however, unlike other tendon samples, tendon covered with sheath with 12% PE White CC® showed much higher strength loss on exposure to UV–Vis compared to the corresponding strength loss due to exposure to UVA or UVB. This is also reflected in the comparison between UV–Vis transmittance and strength loss shown in Figure 6. Despite lower transmittance, sheath with 12% PE White CC® resulted in relatively higher tendon strength loss. Other results including the strength loss after UVA, UBV, and in-flight exposure (shown in Figure 9) showed lower strength loss in tendons covered with sheath containing 12% PE White CC®. It is therefore suspected that the samples in question could have been exposed to light due to improper handling during transportation, packaging, and/or sheath extrusion process.

Comparison between 72 and 48k denier tendon samples

72k denier and 48k denier bare and sheathed tendons were exposed to UVB to compare their strength performance. Results of tendon strength loss after 6 days of UVB exposure in lab are shown in Figure 7. 48k denier and 72k denier bare (unprotected) tendons (48 and 72k-0) showed a large loss in strength due to UVB degradation, however, the damage was significantly less

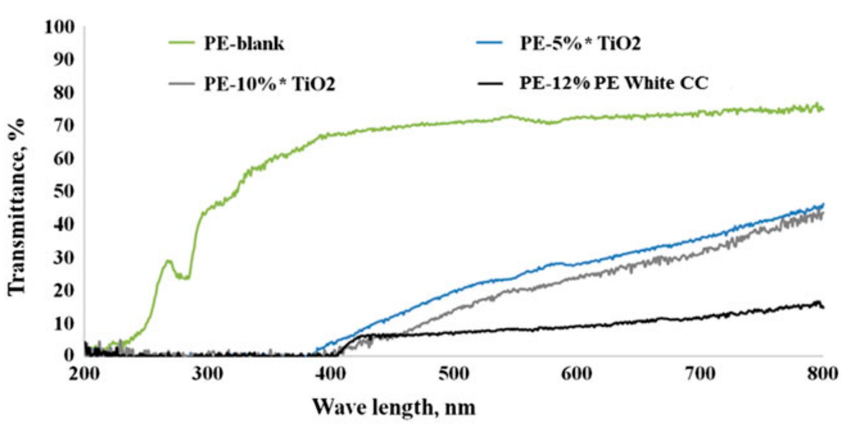

Figure 6. Spectral UV–Vis transmittance for different PE sheaths.

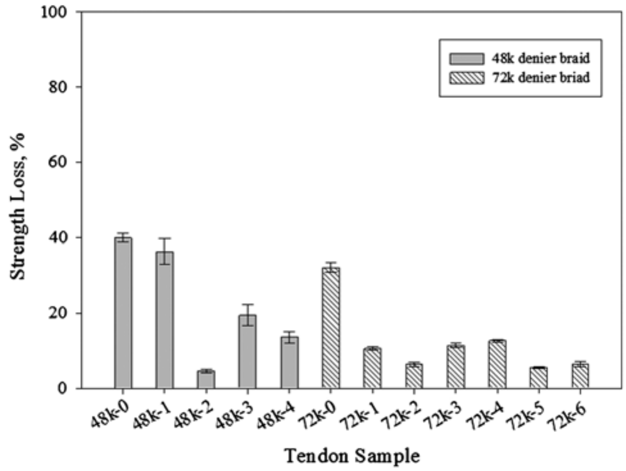

Figure 7. Strength loss in 48k denier and 72k denier tendons after 6 days of UVB exposure in lab.

in bare 72k denier tendon. Fibers on the outer surface of braid act like sheath to protection of fibers in the core. In 72k denier tendon, a larger proportion of fibers in the core are shielded from the UVB radiations, thereby resulting in a lower overall strength loss as compared to 48k denier bare tendon. 48k denier tendon covered with 0.36 mm sheath containing 12% PE White CC® (48k-2) was the only 48k denier sample that showed lower strength loss compared to all sheathed 72k denier samples. The improved protection can be attributed to higher content of PE White CC® in the sheath.

Effect of sheath thickness on strength loss performance of 72k denier tendons

Comparison between 72k denier tendons with different sheath thickness showed that UVB protection improved with the increase in sheath thickness. Increasing the thickness of the sheath containing 6% PE White CC® and 6% TiO_2 from 0.35 (72k-1) to 0.43 mm (72k-2) lowered the strength loss from 10.57 to 6.31%. Improvement in UVB protection due to increase in sheath thickness was also seen in case of sheaths containing 10% PE White CC®.

Effect of UV inhibitor content on strength loss performance of 72k denier tendons

Comparison of protection provided by sheaths covering 72k denier tendon with thickness close to 0.35 mm (72k-1, 72k-4, and 72k-6) showed that adding 13% TiO_2 to the sheath provided better protection compared to adding 6 or 10% PE White CC® and 6% TiO_2 to the sheath, respectively. Among the sheaths (covering 72k denier tendon) with thickness close to 0.42 mm, 10% PE White CC® provided better protection than that provided by 6% PE White CC® and 6% TiO_2. The results showed that UVB resistance of the tendons improved with increase in sheath thickness as well as UV inhibitor content in the sheath. The level of UVB protection provided by a sheath containing UV inhibitors is directly influenced by its ability to hinder UVB transmittance. An increase in sheath thickness and/or UV inhibitor content increases the areal coverage provided by UV inhibitor particles, which reduces UVB transmittance through the sheath.

Structural integrity of sheath

Another important factor that determines the performance of a sheathed tendon is the structural integrity of the sheath. After exposure to radiations, sheaths containing TiO_2 nanoparticles turned brittle and developed cracks which would lead to uninhibited transmission of UV radiations to the PBO braids. Development of cracks also adds the risk of puncturing the polyethylene film enveloping the tendons which cause the balloon to fail in the middle of a flight mission. The high content of TiO_2 and the agglomeration of TiO_2 nanoparticles in the sheath (seen in the TEM images of LDPE sheath shown in Figure 8) is a contributing factor in the development of cracks in the sheath.

Performance of tendons after in-flight exposure

Strength loss in the tendon samples as a result of UV–Vis exposure during the flight mission were found to be consistent with the lab exposure results. 72k denier tendon covered with sheath containing 10% PE White CC® showed the lowest strength loss among all tendons including 48k denier tendons, despite the longer flight duration of BLAST2 mission compared to BLAST1 and CREAM missions. The results also confirm the findings from the lab results that the 72k denier braids are inherently more resistant to damage caused by UV–Vis exposure. The in-flight strength loss in 48k denier tendons was also found to be consistent with the corresponding lab results of UV–Vis transmittance.

Strength loss due to the exposure to UV–Vis during flight missions is shown in Figure 9. Even though the flight duration of CREAM mission was shorter than BLAST1 mission, the 48k denier tendon samples flown in CREAM flight mission lost more strength compared to the corresponding 48k denier tendon samples flown in BLAST1 flight mission. The higher strength loss in tendons flown on CREAM mission can be attributed to the fact that the recovery of sample packages took much longer after flight termination than that of BLAST1 (Figure 1), resulting in longer duration of UV–Vis exposure.

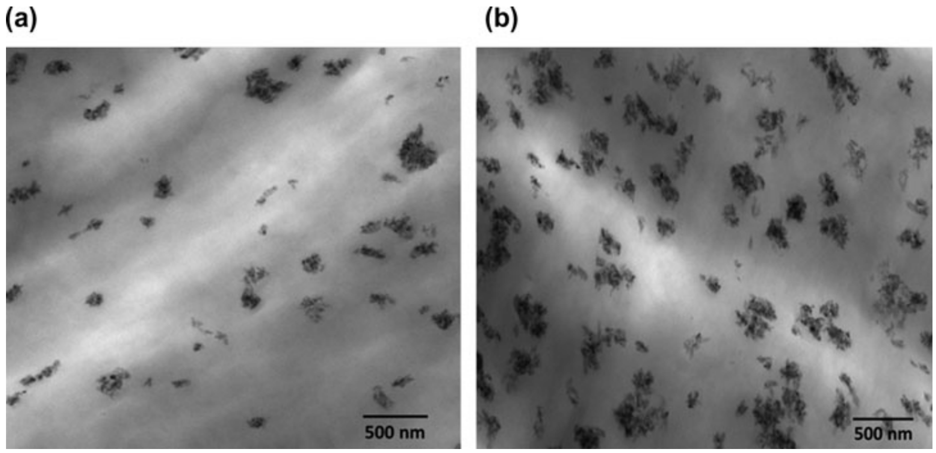

Figure 8. TEM images of 100 nm thick LDPE sheath with 5% (a) and 10% (b) of TiO_2 add-on weight.

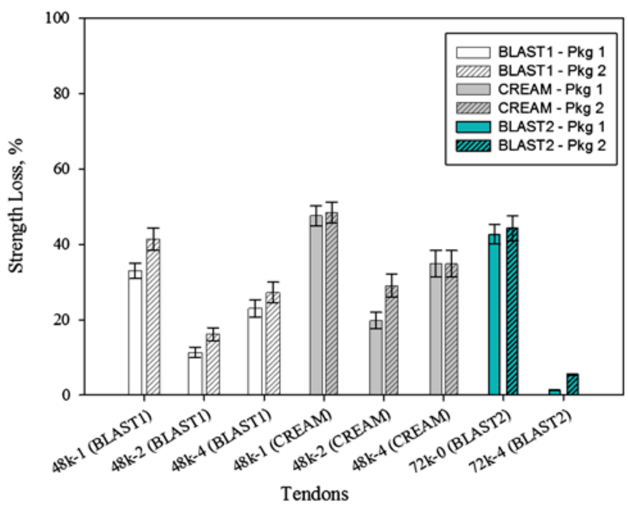

Figure 9. Strength loss in tendons after UV–Vis exposure in flight mission.

It was also found that the two packages flown in each mission experienced different strength loss. This can be attributed to several factors such as the location of packages on the flight, sun angle, and pre/post flight sample handling and exposure on ground. Upon flight termination, the ground exposure on the ice shelf can vary significantly due to folding, crumpling, shielding, as well as, recovery duration period that can extend to days or weeks. These factors can contribute to total exposure time and significantly affect the degree of strength loss.

Conclusion

Photo-degradation of PBO-braided tendons was evaluated by determining the loss of tensile strength in the braided tendons exposed to UV–Vis radiations under simulated lab condition as well as during SPB flight missions that were conducted in Antarctica. Covering PBO braid with a protective LDPE sheath containing UV inhibitors was found to be highly effective in improving the UV–Vis resistance of PBO braids. The photo-degradation was found to be lower compared to the other methods reported in the literature. It was also found that the extent of photo-degradation caused during the flight missions was consistent with that associated with simulated lab exposure (including lab exposure duration) used in this study. Good agreement was also seen between UV–Vis transmittance results and the tensile strength loss due to lab and in-flight exposure. The transmittance measurement of the sheath can therefore serve as quick and effective guide in evaluating the performance of the protective sheaths. The results also showed that 72k denier braids inherently provided higher resistance against UV degradation compared to 48k denier braids. UV protection of tendons also improved with an increase in sheath thickness as well as UV inhibitor content in the sheath. 72k denier tendon covered with sheath containing 10% PE White CC® showed the lowest strength loss among all tendons samples which were flown in the flight missions. Both PE White CC® and TiO_2-nanoparticles were found to be effective UV–Vis inhibitors, however, sheaths containing TiO_2 nanoparticles turned brittle and developed cracks which would potentially further damage the braid and significantly increase the risk of failure of flight missions. The shortcomings of using TiO_2 nanoparticles can be overcome through a better dispersion of nanoparticles in the sheath, which would achieve same or better UV–Vis protection with lower TiO_2 content.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by North Carolina State University; NASA, Balloon Research and Development Laboratory [grant number NNX10AE26G].

References

Gupta, A. (2005). *Improving UV resistance of high strength fibers*. North Carolina State University, Rayleigh.

Liu, X., & Yu, W. (2005). *The degradation of PBO fiber by heat and light*. In Proceedings of 2005 International Conference on Advanced Fibers and Polymer Materials (ICAFPM 2005), Vol 1 and 2: NEW CENTURY, NEW MATERIALS AND NEW LIFE, Shanghai, China, 343–348.

Orndoff, E. (1995). *Development and evaluation of polybenzoxazole fibrous structures: Technical memorandum 104814*. Houston: TX.

Said, M. A. A., Dingwall, B., Gupta, A., Seyam, A. M. M., Mock, G., & Theyson, T. (2006). Investigation of ultra violet (UV) resistance for high strength fibers. *Advances in Space Research, 37*, 2052–2058.

Said, M. A., Seyam, A. M., Vallabh, R., & Bolin, C. (2013). *Characterization of the UV Protection and creep upture of the super pressure balloon tendon*. In the Proceedings of the 22nd American Institute of Aeronautics and Astronautics Conference, Daytona Beach, Florida.

Seyam, A.-F. M., & Won, J. (2013). Development of UV protective electrospun layers for high performance fibres for high altitude applications. *Indian Journal of Fibre & Textile Research, 38*, 121–125.

Song, B., Fu, Q., Ying, L., Liu, X., Zhuang, Q., & Han, Z. (2012). Study on photoaging of poly(p-phenylene benzobisoxazole) fiber. *Journal of Applied Polymer Science, 124*, 1050–1058. doi:10.1002/app.35178

Song, B., Meng, L., & Huang, Y. (2013). Preparation and characterization of $(POSS/TiO_2)_n$ multi-coatings based on PBO fiber surface for improvement of UV resistance. *Fibers and Polymers, 14*, 375–381.

Sterling, J. (2003). *Material properties analysis of structural members in pumpkin balloons*. In AIAA's 3rd annual aviation technology, integration, and operations (ATIO) forum. Reston, Virigina: American Institute of Aeronautics and Astronautics. doi:10.2514/6.2003-6777

Toyobo Co Ltd. (2005). Zylon. Retrieved from http://www.toyobo-global.com/seihin/kc/pbo/

Wang, Q. W., Yoon, K. H., & Min, B. G. (2015). Chemical and physical modification of poly(p-phenylene benzobisoxazole) polymers for improving properties of the PBO fibers. I. Ultraviolet-ageing resistance of PBO fibers with naphthalene moiety in polymer chain. *Fibers and Polymers, 16*(1), 1–7.

Yang, H. H. (1989). *Aromatic high strength fibers* (1st ed.). New York, NY: Wiley-Interscience.

Zhang, C.-H., Huang, Y.-D., Yuan, W.-J., & Zhang, J.-N. (2011). UV aging resistance properties of PBO fiber coated with nano-ZnO hybrid sizing. *Journal of Applied Polymer Science, 120*, 2468–2476.

Zhang, T., Jin, J., Yang, S., Li, G., & Jiang, J. (2011). UV accelerated aging and aging resistance of dihydroxy poly (p-phenylene benzobisoxazole) fibers. *Polymers for Advanced Technologies, 22*, 743–747.