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Investigation of ultra violet (UV) resistance for high strength fibers

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Abstract

Ultra long duration balloons (ULDB), currently under development by the National Aeronautics and Space Administration (NASA), requires the use of high strength fibers in the selected super-pressure pumpkin design. The pumpkin shape balloon concept allows clear separation of the load transferring functions of the major structural elements of the pneumatic envelope, the tendons and the film. Essentially, the film provides the gas barrier and transfers only local pressure load to the tendons. The tendons, in the mean time, provide the global pressure containing strength. In that manner, the strength requirement for the film only depends on local parameters. The tendon is made of *p*-phenylene-2,6-benzobisoxazole (PBO) fibers, which is selected due to its high strength to weight ratio when compared to other high performance, commercially available, fibers. High strength fibers, however, are known to degrade upon exposure to light, particularly at short wavelengths. This paper reports the results of an investigation of the resistance of four commercial high strength fibers to ultra violet (UV) exposure. The results indicate that exposing high strength fibers in continuous yarn form to UV led to serious loss in strength of the fibers except for Spectra® fibers. The adverse changes in mechanical behavior occurred over short duration of exposure compared to the 100 day duration targeted for these missions. UV blocking finishes to improve the UV resistance of these fibers are being investigated. The application of these specially formulated coatings is expected to lead to significant improvement of the UV resistance of these high performance fibers. In this publication, we report on the mechanical behavior of the fibers pre- and post-exposure to UV, but without application of the blocking finishes.

Keywords: Scientific balloons; Pumpkin design; High strength fibers; UV degradation

1. Background

Current scientific ballooning capabilities worldwide are generally limited to large and mid-size payload capacity zero-pressure balloons. Although these balloons are capable of maintaining their float altitude over the polar regions for extended durations and up to a record of 41 days; they, however, can only maintain float altitude for only few days at mid latitudes. Historically, however, small payload capacity super-pressure balloons with worldwide long duration capacity have been successfully flown for several months. In response to the growing needs of the scientific community, the NASA Balloon Programs Office is pursuing the development of significantly improved high altitude scientific balloon platforms that will be capable of maintaining float altitude for long duration flights worldwide with a load carrying capacity that is comparable to current zero-pressure balloons. This is an improvement by almost two decades in payload capacity relative to current super-pressure balloons.

The proposed flight duration for these new balloon platforms is 100 days and thus labeled as ultra long duration balloons (ULDB). The enabling technologies are improved lightweight membrane materials, high strength, high stiffness, light weight tendon and a design concept, the pumpkin shape balloon that has been

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discussed since the 1970s (Smalley, 1970; Rougeron, 1978; Yajima, 1998) but only analytically proven for large structures since 1999 (Schur, 1999).

The pumpkin shape balloon concept allows clear separation of the load transferring functions of the major structural elements of the pneumatic envelope, the tendons and the film. Essentially, the film provides the gas barrier and transfers only local pressure load to the tendons. The tendons, in the mean time, provide the global pressure containing strength. In that manner, the strength requirement for the film only depends on local parameters. The selected tendon, a key member of the structure is made of *p*-phenylene-2,6-benzobisoxazole (PBO) which was first developed by Dow Chemical Company and latter commercialized by Toyobo Co. Ltd. (www.toyobo.co.jp/e/seihin/kc/pbo/technical.pdf) under the commercial name Zylon®. The high performance characteristics of PBO stem from its high stiffness, high strength when compared to other high performance fibers such as Kevlar®, Dyneema® and Vectran® (www.Vectran®fiber.com).

Zylon® and other high strength fibers are generally sensitive to light exposure. They tend to lose significant strength upon exposure to ultra violet (UV) radiation. Such UV degradation poses a serious challenge for the development of the ULDB in order to achieve its target duration of 100 days. To improve the mission performance of the ULDB, new methods for protecting the tendons from the environmental effects need to be developed. The National Aeronautics and Space Administration (NASA) and North Carolina State University College of Textiles are undertaking a research program to address these issues to provide protection coatings to extend the service life of the fibers while maintaining their physical characteristics (Said et al., 2004).

Previous studies have reported results on UV degradation of thick ropes (Allen et al., 1992). Currently, the tendons used for ULDB are braided thin structure, essentially like a tape of about 1 cm in width. The UV degradation of such thin structures is expected to be more severe as compared to thick structures like cables and ropes and hence pose greater threat to the survivability of the balloon. The purpose of this part of our study is to evaluate high strength fibers in single continuous yarn form so as to quantify their strength loss with UV exposure in a more realistic fashion to that experienced in an actual balloon.

The UV stability of Kevlar® has been described in the literature (Yang, 1989). Since Kevlar® is self-screening, its light stability depends on the thickness of the exposed item. Very thin Kevlar® 49 fabric, if exposed directly to very high intensity sunlight for an extended period, will loose about half its tensile strength within few days. In thicker items, such as a half-inch diameter rope, the outer layer protects the majority of the rope and strength loss is minimized. The strength loss progression for the Kevlar® rope is given in Table 1. The data show that Kevlar® offers some inherent stability to UV radiation, this effect will be reduced in case of a thin braided structure. Limited data on light exposure are also available for Vectran®, Zylon®, and Spectra® in their respective web sites, but mainly concerned with thick structures rather than single yarns.

In this paper, we will report on the changes in mechanical behavior pre- and post-exposure to UV for four commercially available high strength fibers. The application of specially formulated finishes and their effect on fiber protection will be addressed in a future publication.

2. Methodology

2.1. Materials

Four high strength yarns were selected for this study. Table 2 shows the yarns specifications along with the suppliers. Zylon® is Toyobo's commercial name for *p*-phenylene-2,6-benzobisoxazole (PBO). A polymer that was originally commercialized by Dow chemicals and latter successfully spun into fiber by Toybo, under a joint agreement. Zylon is characterized by its higher strength and stiffness compared to currently available high performance fibers. Vectran® was developed by Kuraray in cooperation with Celanese with full-scale production started in early 1990. Vectran® is an aromatic polyester. Kevlar® aramid fibers were introduced to the commercial market by DuPont company in the early 70's. Kevlar® is an aromatic polyamide with structural repeat

Table 1
Effect of UV radiation on the strength of Kevlar® rope

Product	Break load	Strength retained (%)
[Rope 1/2 in. diameter (13 mm), three strand] unexposed	14,400 lb (64,100 N)	–
Florida Sun, 6 months	13,000 lb (58,000 N)	90
Florida Sun, 12 months	11,600 lb (51,600 N)	81
Florida Sun, 18 months	9950 lb (44,300 N)	69
Florida Sun, 24 months	9940 lb (44,200 N)	69

Table 2
Yarn specifications and source

Yarn type	Denier/No. of filaments	Manufacturer
Zylon® HM	1500/996	Toyobo
Vectran® T-97	1500/300	Celanese Corp.
Kevlar® 49	1420/NA	Du Pont Textile Fibers
Spectra® 1000	1300/240	Honeywell Specialty Fibers

unit of *p*-phenylene terephthalamide. Spectra® fibers are made from extended chain polyethylene molecules. Spectra® was first commercialized by Honywell's Allied Signal in early 1985. Kevlar®, Vectran® and Zylon® molecules contain rigid covalent bonds in the main chain of the structure resulting in almost rod-like structure. This rod-like behavior arises from the fact that all three polymers, contrary to Spectra®, contain aromatic rings in their backbone structure. These polymers have the tendency to form crystallites in the liquid state and hence marked as liquid crystalline polymers.

2.2. UV exposure

The four yarns were exposed to UV radiation using a Xenon lamp Weatherometer (Atlas Hi 3 Sun Weatherometer) using (AATCC 16E) standard test procedure. The filters used are ''outer-borosilicate'' and ''inner-soda lime'', which simulate the daylight through window pane. The current setting, exposure time of one hour in the Weatherometer equals exposure time of 0.583 h in the sun at sea level. Yarns are wrapped over a black panel, 20 cm long, which is attached to a metal plate holder. The holder is then hung onto the rack of the Weatherometer, which then rotates around the Xenon lamp. The yarns were exposed in the Weatherometer, which has a Xenon lamp emitting UV rays at 340 nm at an irradiance of 1.1 W/m^2. The samples after being loaded in the Weatherometer are shown in Fig. 1. Samples were exposed for different durations then removed and subjected to tensile testing. The yarns were treated at different exposure times. After being exposed to the

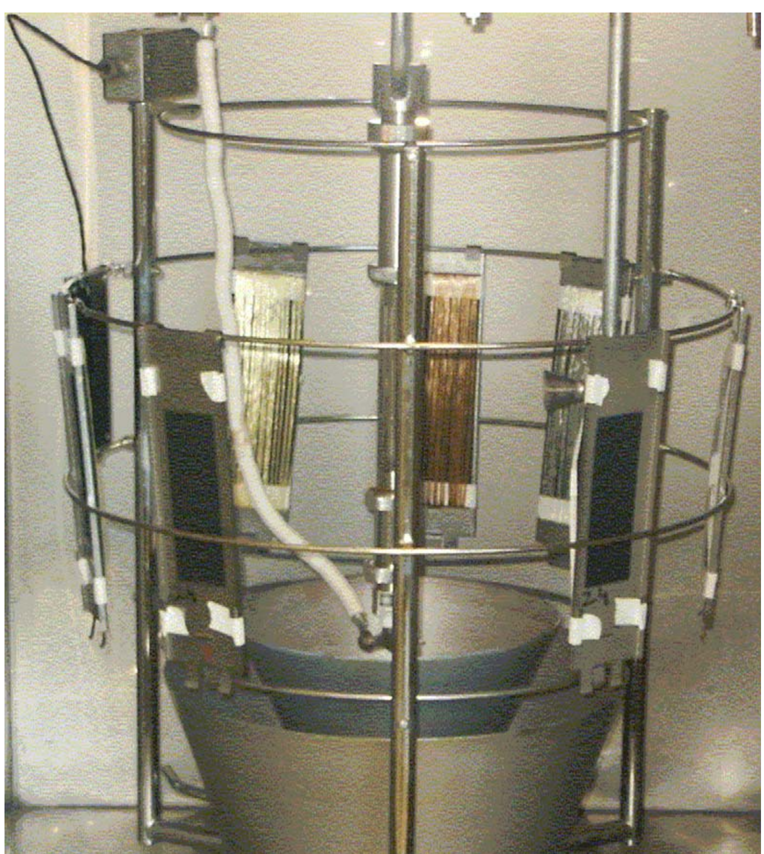

Fig. 1. Rack of the Atlas 3 Sun Weatherometer with samples loaded and ready for exposure to UV radiation.

UV radiation, the samples were taken out and tested for tensile strength.

2.3. Tensile testing

The yarns tensile testing was performed according to (ASTM D 2256) using SINTECH tensile tester. Yarn denier, gauge length, cross head speed, break sensitivity, and grip pressure are typical inputs in the data acquisition "Testworks" software. The tester is calibrated before each run. The exposed samples from the Atlas 3 Sun tester are taken out and the exposed regions are marked (Fig. 2) and made ready for tensile testing. The yarn samples are then removed from the frame carefully ensuring no entanglements between filaments of adjacent strands and mounted on the jaws of the SINTECH. Fig. 3 shows the yarn sample mounted on the machine and ready for loading, the exposed region is placed in the middle of the jaws. In order to prevent the yarns from slipping rubber pieces are put in between the grips of the jaws. Zylon®, Vectran® and Kevlar® require these rubber pieces along with 1–2 wraps and 551,580 Pa (which is different from the normally used 413,685 Pa) grip pressure. Spectra® is a very smooth yarn and requires many wraps to minimize slippage upon loading.

3. Results and discussion

Figs. 4–7 show the effect of UV exposure duration on the strength and elongation of the four yarns in the study. The results indicate that there is a significant difference in behavior of strength loss among the four yarns with Zylon®, Kevlar® and Vectran® following a clear decreasing trend. Spectra®, however, did not exhibit a clear trend. It is likely that, Spectra® while being exposed, it is also cross-linking. The asymmetric behavior may reflect the rate at which the two mechanisms are occurring. This can be confirmed by the fact that Spectra® was the only fiber to break outside the marked exposed region in the tensile tester. It was also observed that some slippage took place during the test, which may have contributed to the inconsistency behavior shown in the results.

The strength loss of Spectra® and Kevlar® yarns is the least among the four yarns with Kevlar® being better than Spectra®. While untreated/unexposed Zylon® yarn is initially the strongest among the four yarns; it became weaker after exposure to UV. Only later on, after 72 h of exposure, it was stronger than Vectran® but still weaker than Spectra® and Kevlar®. Vectran® and Kevlar® are always weaker than Spectra® at all exposure times while unexposed and untreated Vectran® is stronger than Kevlar®, it became weaker than Kevlar® as exposure time increased. Vectran® showed the highest loss in strength (about 86% reduction in strength) after 144 h of exposure to UV. Kevlar® shows a leveling effect in loss of strength suggesting some kind of stabilization with respect to UV exposure which is not present in any of the other three yarns. However, Spectra®, being polyethylene in terms of basic chemistry, should not be at all affected by UV radiation. In order for UV light to cause photolysis of a polymer, it must first be absorbed which requires a chromophore (e.g., structures containing carbonyl group) and since polyethylene is one of those several polymers which do not contain a chromophore (Allen et al., 1992) in the repeat structure, it should not undergo photolysis. A possible explanation for this behavior is the presence of some carbonyl groups in the chains formed as a result of oxidation. Another possible reason is that it is quiet possible that the

Fig. 2. Sample ready for tensile testing, degraded region marked in black.

Fig. 3. Yarn sample ready for loading.

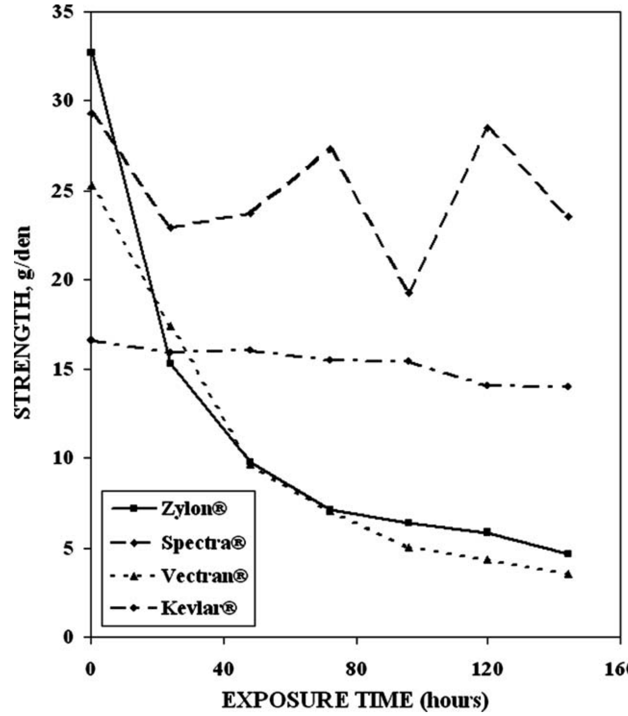

Fig. 4. Effect of UV exposure on the tensile strength of the four yarns.

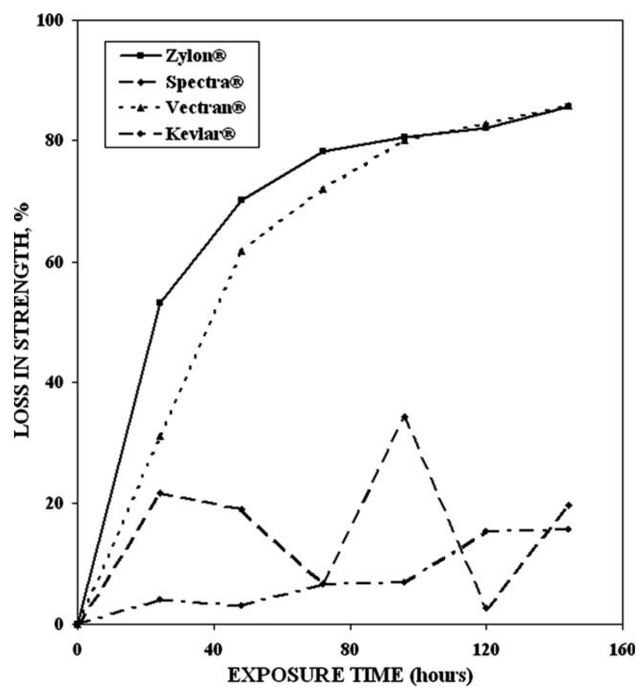

Fig. 5. Effect of UV exposure on the loss in tensile strength of the four yarns.

Spectra® has a spin finish or other lubricant which is actually acting as a photo degradation initiator. Hence we suggested that gloves be used while preparing samples for UV exposure so that the yarns can be prevented from any contaminants which might have initiators of photo degradation. For Spectra® the results of tensile testing are not dependable for reasons discussed later. Similarly, Zylon® and Vectran® both showed an unusual behavior during their tensile testing which will be discussed later.

The results also indicate that in general the % strain at peak load decreases with increasing exposure time. Similarly, the loss in % strain at peak load shows increasing behavior with Vectran® showing an initial decrease with subsequent increase.

4. Critical observations during tensile testing

During the tensile testing of Spectra® one important observation was made, that is, almost all the samples broke in the unexposed region. An immediate conclu-

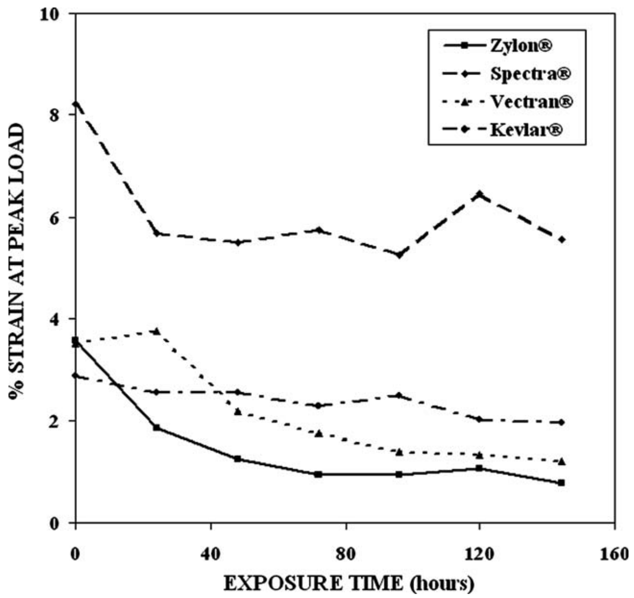

Fig. 6. Effect of UV exposure on the % strain at peak load of the four yarns.

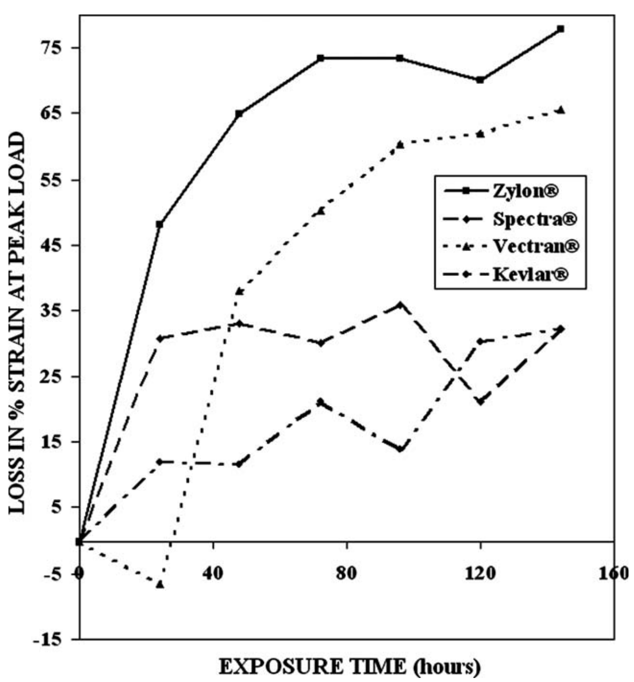

Fig. 7. Effect of UV exposure on the loss in % strain at peak load of the four yarns.

sion that comes to mind was that UV exposure is actually making Spectra® stronger rather than degrading it, likely due to favorable conditions for cross-linking that may exist due to the exposure. It was also observed that the break in the unexposed region was actually taking place exactly at the lower edge of the jaws, suggesting that it is that 90° edge, which causes a stress concentration at that point, and causes the break. Corrective measures were taken to resolve this matter. It is also recommended that yarn preparation for UV exposure test must be redesigned to allow producing continuous yarn with full exposure length of much longer than the gauge length used for tensile testing.

Similarly, during the tensile testing of Zylon® and Vectran® it was observed that, occasionally, both fibers break at the junction of the exposed and the unexposed regions. That occurs sometimes with a sharp break and other times with little or more intermeshing of filaments. For Vectran® this might not be a very big problem because there was consistency among the values of yarns breaking normally and those breaking near the junction. For Zylon®, however, this consistency was not followed with samples breaking near junction showing strength values about 60–70% of those breaking normally. Sometimes the samples showed a sharp break and sometimes the ends were intermeshed. Again, redesigning the holding frame to allow exposure of long specimens to UV will result in more uniform specimens that will likely eliminate these inconsistencies.

5. Conclusions

Four high performance fibers have been selected for this research investigation. These are Vectran®, Spectra®, Kevlar®, and PBO (Zylon®). From the above results it is clear that these high strength 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 load tendons of the balloon. For this purpose four tracks have been identified to prepare finishes that are believed to enhance the resistance of high strength fibers to UV. These tracks are: (a) self-polymerizing, (b) diffusion application, (c) polymer-filled with 30–40% UV absorber, and (d) combination of dyeing plus surface application.

We are currently investigating the formulation of various finishes and their effectiveness in protecting the yarns from the adverse effects of light exposure while maintaining proper yarn to yarn friction, yarn stability at float altitudes, and good finishes coverage uniformity of yarn and individual filaments.

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