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STORAGE LIFE OF PARACHUTES -- LONG TIME MATERIAL DEGRADATION

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Abstract

This study considers the long-time storage of singleuse nylon and Kevlar[®] parachutes. We present data from a 29-year-old nylon parachute, and nylon and Kevlar[®] test samples stored 14 years under ambient conditions in the absence of sunlight. We compare the results with existing predictions of parachute material degradation and other aging data. X-ray photoelectron spectroscopy analyses were preformed on Nylon and Keylar[®] fabrics that were degraded by elevated temperature aging. The results suggest that this technique should be further examined as a "nondestructive" method of detecting degradation.

Introduction

Parachute applications usually require some storage of a packed system before deployment and between Successful deployments require that the reuses. materials and parachute structural elements meet one of the following two conditions.

- The as-manufactured properties must stay the same throughout the intended system life.
- Design factors of safety must take into account predictable decreases in properties.

Unexpected degradation, the modification of a material by its environment or service history, if severe enough can cause system failure. Degradation processes can involve various combinations of chemical, physical and mechanical attack. The extent and importance of all the mechanisms depend on the type of material and application. If the system under consideration contains more than one material type, the definition of degradation must also include modifications resulting

from material interactions (compatibility). All of these degradation processes can take place to some extent in polymeric-fiber-based parachute materials.

Parachute applications are diverse so that the relative importance of the degradation processes varies significantly from one system to another. In a broad sense, the applications may be grouped into those involving one-time deployments versus those involving multiple uses. Examples of single-use conditions include space missions and some weapon delivery applications. Military troop, civilian-sport, forest service and space shuttle applications involve multiple uses and varying lengths of time between uses. Information about storage of these latter systems applies to single-use conditions if effects associated with multiple deployments can be separated out. The age/service-life criteria for U.S. personnel parachutes historically have been based on somewhat arbitrary but generally conservative requirements¹. The service life of nylon personnel parachutes was increased over the years to 12 years service plus 3 years storage. This 15-year life remains as today's time criteria even though it is well known that this number of years of service will not present any hazard.²

Other constraints for single-use systems such as those combining different materials and extremely long storage times require specialized studies to establish specifications for storage life, The present study focuses on aspects of parachute degradation relevant to single-use applications where storage times may exceed 30 years. An important question is how long may this storage time be?

The present study considers parachute aging involving the following conditions.

- Long time ambient temperature storage in the 1. absence of sunlight but with exposure to atmospheric moisture and pollutants.
- 2. Short time high and low temperature excursions within the temperature range -50C (-60F) to +70C (160F).

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3. Relatively high pack densities.

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- 4. One-time deployment with multiple packing cycles to allow for reefing line cutter changeout.
- 5. Possible degradation caused by marking inks and polymer materials used to assist in fabrication (antifray coatings, etc.).

Degradation of the chemical, mechanical and physical properties of the parachute materials defines the allowable stockpile life of a parachute system. Fabric tensile strength is the main property usually considered in defining the storage life of a parachute under the conditions enumerated above. Changes in the parachute such as porosity and dimensional changes that can arise from shrinkage are also pertinent degradation mechanisms. We will not consider processes such as photodegradation that are clearly excluded by the above environmental and storage parameters. We also exclude from the present discussion factors that also affect system life and reliability such as reefing line cutter behavior and possible damage that could occur during the unpack/repacks that are required for cutter changeout or quality assurance audits.

A technology that is related to prediction of material life is periodic testing for unexpected material degradation. It is generally agreed within the US personnel parachute community that "the risk is not with an average condition, but rather with the exceptional case.^{3,4}. Tensile testing of samples from a packed parachute is a destructive test. Most other direct measures of material strength such as tear or burst tests involve some material expenditure, or cause enough damage to require repairs to the tested region. These latter techniques are not applicable to high strength ribbons and webbings for the applications considered here. Spectroscopic or other material analyses techniques can provide indirect measures of material strength. These indirect techniques frequently require so little material that they can be considered non-destructive. Such procedures have been considered previously but none are currently in use. The most promising non-destructive technique for monitoring aging in nylon involves measurement of optical absorbance^{5,6}. Shortcomings of this technique are the need for zero-time reference data and the use of hazardous solvents. We are evaluating some new material analyses and data reduction techniques that might detect aging in nylon and Kevlar[®] fabrics. One in particular, X-ray photoelectron spectroscopy (XPS), has been used to detect photochemical changes in Nomex fibers⁷. Because of some similarities between

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Nomex and Kevlar[®] chemistry, this technique may be promising for monitoring aging in Kevlar[®].

This paper presents material strength and dimensional data from a nylon parachute manufactured in June 1965 and strength data from nylon and Kevlar[®] material samples that have been stored for 14 years. Preliminary results from XPS analyses of elevated temperature aged samples of nylon and Kevlar[®] are also described.

Results and Discussion

Materials from a stored parachute

We tested materials from a 12.5 foot diameter nylon ribbon parachute that was manufactured in June 1965. The storage conditions fell in the envelope of parameters described above. The testing and inspection looked for information concerning possible:

- 1. Strength changes of the nylon fabric
- 2. Mechanical damage at creases and folds
- 3. Nylon compatibility with marking ink
- 4. Material shrinkage
- 5. Sewing degradation

Table 1 contains a summary of the data. As is usually the case with old parachutes, material strength data from the time of manufacture are not available. Two observations provide some interpretation of the strength data. First, the measured strengths exceed the Mil Spec minimum strengths for each material. Second, all of the measured strengths exceed the specified minimum strength by amounts that are consistent with usual narrow fabric production conditions. The ribbon data is even more conservative since the test samples included radial and mini-radial stitching (but no ribbon joints). Some reduction in strength relative to unstitched material is, therefore, reflected in the test data in Table 1. While these observations can be considered only qualitative, they suggest that the fabrics have not undergone significant strength degradation by aging processes.

Tadios³ summarized the results of earlier tests conducted on 25-year old nylon solid canopy and ribbon parachutes. The present data set clearly showed strength values above the specified values while some of the parachutes evaluated by Tadios showed strength losses up to about 8% below the specified values. A significant point is that we are not aware of any data on 20-30 year old parachutes that show consistently low strength values for all of the materials. We revisit this point in the next section of this paper.

	Suspension Lines	Ribbons	Ribbons with Markings	Ribbons	Ribbons
Specified Strength (lbs)	9000	1000	1000	2000	3000
Measured Strength (lbs)	11040	1233	1230	2189	3410
Specified Width (in)		2.00 +/- 0.06		2.00 +/- 0.06	2.00 +/- 0.06
Range of Measured Widths (in)		1.94 - 2.06		1.98 - 2.05	1.94 - 2.06
Average Measured Width (in)		1.98		2.01	2.00

Table 1: Strength and dimensional data from a 29-year-old parachute.

Yarn shrinkage leading to reduction in ribbon width can alter the geometric porosity of a ribbon parachute. If this change is sufficiently large, some parachute performance conditions can be can be adversely affected. The data shown in Table 1 indicate that the ribbon widths in this parachute are unchanged relative to the values in the material specifications.

A routine quality-assurance evaluation of nylon ribbons in test-deployed parachutes revealed degradation in strength of ribbons in areas containing blue-ink identification markings. The tested ribbons with ink markings were three to eight years old. A follow-on accelerated-aging study of the effects of inks and chemicals used to coat fabrics in parachute construction on tensile strengths⁹ was not able to duplicated the levels of strength loss observed in the naturally aged parachutes. Because of lingering concerns that some ink components might interact with nylon and cause localized reductions in strength, it is important to check for any signs of degradation. Table 1 summarizes strength data from marked and unmarked material in the 29-year-old parachute--inkinduced degradation is not detected.

We were also unable to detect any strength changes associated with the remaining two areas enumerated above--damage at creases and folds, and sewing degradation. Ideally, both creased and uncreased samples from the same fabric should be tested. The crease density in a packed parachute usually makes it impossible to obtain truely uncreased material. In the present case, an attempt was made to determine if breaks could be associated with creased areas in the suspension line webbings. No correlation was found. This, and the relatively high strength of the suspension lines, suggests little, or more likely, no fold degradation has occurred. For sewing, there is no zero-time data to reference for the strength of joints. Test data showed values typical of those found on currently manufactured joints of similar material. As noted above some strength reduction because of stitching is expected--our point is that we could not find any indication of effects that might have been caused by aging of either the narrow fabrics or the sewing threads.

Real Time Aging Data

The data reported in this section are the most recent from a program initiated 14 years ago to expose nylon and Kevlar[®] ribbon parachute materials to local ambient temperature and environmental conditions, at four locations representing arctic (Elemendorf AFB), tropic (Barksdale AFB), desert (Nellis AFB) and industrial environments (Los Angeles). Another set of samples is stored at Sandia National Laboratories in Albuquerque. The aging tests started before parachutes using Kevlar[®] went into production so that periodic sampling could provide a lead time to make system changes if unpredicted aging were detected in this material. The early data from this program is described previously¹⁰. Figure 1 illustrates representative sets of ribbon and webbing data from the 14 year time span of this program. The data points shown in the figures are an average of at least three strength measurements.

Except for two webbing types that are discussed later, all of the data points like those in Figure 1 fall within strength levels that exceed specified minimum strengths. The range of individual strength values for a given test condition is relatively large. Preliminary analyses of the data indicate that most of the differences between average data points in Figure 1 are not statistically significant. We have not detected any trends in the data that suggest any systematic reduction in strength with location, exposure time, or fabric construction.

In a previous report¹⁰ we pointed out that the 2 inch-1000 lb Kevlar[®] ribbon (bottom left plot in Figure 1) has exhibited more variability in strength than most narrow fabrics. This observation is based on production lot sampling, testing of material from deployed parachutes and after various environmental exposures. (See Figure 2 in Reference 8 for a summary of the data). In this study we see a slight decrease in strength of the aged samples relative to the short time data but this change is small compared to some found under conditions reported in Reference 8.

Figure 2 shows composite plots of all the nylon and Kevlar^{\circ} data as percent of rated strength vs. aging time. One set of data, the low values at 168 months are from 0.625 inch - 2250 lb nylon tubular webbing.

For this fabric, pronounced curvature and preferential loading of some warp yarns induced premature failure. Excluding the tubular webbing data, the plots in Figure 2 do not indicate any decrease in strength with time that would indicate aging of the nylon or Kevlar^{\circ} fiber. Statistical analyses support this observation.

The data points that fall below 100% of rated strength on the Kevlar[®] plot are all from samples of 1.75 inch -15000 lb Kevlar[®] webbing. Even though this material has lower than specified strength, the strength does not change with time. Figure 3 shows the 1.75 inch-15000 lb Kevlar[®] webbing data. The strength of materials tested after 12 months at the remote storage locations are significantly different from the strength of the control samples. We cannot explain these differences except that this fabric construction seems to have more strength variability than most constructions. This material has tested low in some cases when production lots of Kevlar[®] were sampled.



Figure 1: Aging data for representative ribbon and webbing samples



Figure 2: Composite plots of all the Nylon and Kevlar[®] real time aging data



Figure 3: Aging data for a 15000 lb Kevlar[®] webbing

Auerbach¹¹ studied the kinetics of tensile strength degradation of nylon and Kevlar[®] yarns using data from an experimental study by Mead et al¹². Most of the experimental data were obtained from samples maintained at temperatures above 110 C for nylon and 130 C for Kevlar[®] over a six month period. The experiment matrix included aging atmospheres of varying humidity, smog and ozone contents, however, Auerbach considered only the effect of humidity in his kinetic study. Half of the samples in the test matrix were knotted to provide some simulation of conditions in a tight parachute pack. Auerbach¹¹ also examined some short time data for Kevlar[®] from Dupont¹³ and nylon data from Mikolajewski et al¹⁴. The kinetic modeling of the data extrapolated to 25 years at 25 C predicted less than 10% degradation. Accelerated tests are fraught with problems because of the possibility of accelerating trivial processes at the expense of more important degradation processes or even completely altering the degradation mechanism.¹⁵ Because of the uncertainties of predictions from accelerated aging data it is important to have real time data for comparison. The 29 year nylon parachute data reported above suggests that the predictions of Auerbach may be conservative.

Not all aging data for nylon are consistent with the low levels of degradation indicated by the present data. Husain¹⁶ reported strength data for nylon fabrics stored indoors (not exposed to light) under temperature and humidity conditions that varied with the seasons (this study was carried out in India). Husain's data indicates strength losses for undyed fabrics of about 10% after 10 years. If the nylon used in the present study was degrading at the rate suggested by Husain's data we should have detected lower strength levels. Differences in data like this underscore the difficulties of making the aging predictions that are pointed out in the introduction. It is possible that different antioxidant stabilizers were used in the material tested by Hussain. The nylon strength data used by Auerbach for his kinetic modeling was obtained from nylon used in U.S. parachutes. This material was obtained at about the same time that the materials for the real time aging experiments were woven. Similar manufacturing times suggest the same stabilizer contents. We do not know if the stabilizers present in the material used in the 29 year old parachute are the same as those used in the more current material.

Non-destructive Techniques for Monitoring Degradation

We used elevated temperatures to accelerate the aging process in nylon and Kevlar[®] to provide samples with known amounts of degradation that we could compare with unaged material. Failure loads for the series of aging conditions are shown in Table 2. X-ray photoelectron spectroscopy (XPS) analyses indicate

that the chemical state of the aged materials is different from that of the unaged material. These results are encouraging since a prerequisite for a technique to monitor aging is the ability to detect chemical or other changes that arise from mechanisms that influence material strength. The XPS data from the aged samples show some similarities to that reported by Hamilton et al⁷ for photodegraded materials. Before the potential of XPS can be defined for monitoring parachute materials, however, further evaluations of samples aged in inert and other environments are required. If further work can establish that XPS can detect degradation products that are not present in as-produced materials, this technique could have the potential for detecting the onset of degradation without requiring data from materials at the time of production.

While the present data suggests that 30-year-life for parachutes is a conservative time we still do not have an estimate of the time when significant degradation might be expected under ambient storage conditions. It continues to be difficult to maintain the resources for the long-time, moderate temperature-tests that are required to make reliable long-time strength extrapolations and to support studies to understand the degradation mechanisms. With the rapid advances currently being made in material analyses techniques, and the difficulty of maintaining a large-enough test matrix to support all of the material and environmental variables that must be considered, it is possible that our best progress in guaranteeing the reliability of parachutes that are stored for long periods of time will come through development of "nondestructive" techniques. Even if advances are made in this area, however, some applications, such as systems for long-

Table 2: Elevated temperature air-aging of nylon

	1 inch - 4000 lb Kevlar®	1 inch 1000 lb Nylon	
Aging Temperature (°C)	170	130	
Aging Time (days)	Failure Load (lbs)		
0	4747	1315	
29	3685	1171	
58	3571	1042	
116	3241	712	

time space missions will continue to require better predictive data.

Summary

Mechanical property and dimensional data from a 29year-old nylon parachute revealed no strength loss, shrinkage or other evidence of degradation. This data supports previous estimates of storage life degradation that indicate minimal strength loss for parachutes stored 25-30 years. Fourteen-year data on nylon and Kevlar[®] fabrics stored in four different climatic zones also show no evidence of material degradation. The results of preliminary x-ray photoelectron spectroscopy analyses on degraded Nylon and Kevlar[®] fabrics suggest that this technique should be further examined as a "non-destructive" method of detecting aging.

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References

¹ R. W. Rodier, E. A. Wuester and J. E. Hall, "Personnel Parachute Age/Service Life Criteria", Proceedings, AIAA 10th Aerodynamic Decelerator Systems Technology Conference, Cocoa Beach, FL, April 18-20, 1989.

² R. J. Coskren and E. A. Wuester, "Investigation of the Service and Age Lives of U. S. Army Personnel Parachutes", Proceedings, AIAA 10th Aerodynamic Decelerator Systems Technology Conference, Cocoa Beach, FL, April 18-20, 1989.

³ J. W. Gardella, "Service Age Life Study of Parachute Components", U. S. Army Natick Research and Development Laboratories, Clothing, Equipment and Materials Engineering Laboratory, Report No. 104, June 1981.

⁴ R. W. Coskren, N. J. Abbott, and E. A. Wuester, "Investigation of the Service and Age Lives of U.S. Army Troop Parachutes", TR.-87/019L, Natick Research, Development, and Engineering Center, Natick, MA, November 1986.

⁵ C. L. Renschler and F. B Burns, "Monitoring of Degradation in Thermally Aged Nylon 6,6 I. UV--

Visible Absorption Spectrophotometry", Journal of Applied Polymer Science, Vol 29, 1125-1131, 1984.

⁶ C. L. Renschler, "Optical Absorption for the Detection of Thermal Ageing in Nylon 6,6", Journal of Material Science Letters, Vol 4, 707-710, 1985.

⁷ L. E. Hamilton, P. M. A. Sherwood and B. M. Reagan, "X-Ray Photoelectron Spectroscopy Studies of Photochemical Changes in High-Performance Fibers", Applied Spectroscopy, Vol. 47, No. 2, 1993.

⁸ E. L. Tadios, "Summary of Aging Effects on 25-Year Old Nylon Parachutes", Proceedings, AIAA 10th Aerodynamic Decelerator Systems Technology Conference, Cocoa Beach, FL, April 18-20, 1989.

⁹ I. Auerbach, L. D. Whinery, D. W. Johnson, K E. Mead and D. D. Sheldon, "*Effects of Parachute-Ribbon Surface Treatments on Tensile Strength*", Proceedings, AIAA 9th Aerodynamic Decelerator Systems Technology Conference, Albuquerque, NM, October 7-9, 1986.

¹⁰ R. H. Ericksen, W. B. Pepper and L. D. Whinery, "Preliminary Results of the Effects of Sewing, Packing and Parachute Deployment on Material Strength", Proceedings, AIAA 8th Aerodynamic Decelerator Systems Technology Conference, Hyannis, MA, April 2-4, 1984

¹¹ I. Auerbach, "Kinetics for the Tensile Strength Degradation of Nylon and Kevlar Yarns", J. Appl. Polym. Sci., 37, 2213-2227 (1986).

¹² J. W. Mead, K. E. Mead, I. Auerbach, and R. H. Ericksen, "Accelerated Aging of Nylon 66 and Kevlar 29 in Elevated Temperature, Elevated Humidity, Smog, and Ozone", I&EC Product Research and Development, 21, 159-163 (1982).

¹³ DuPont Textile Fibers Dept., "*Characteristics and Uses of Kevlar 29 Aramid*", Report No. 371, September. 1976.

¹⁴ E. Mikolajewski, J. E. Swallow, and M. W. Webb, J. Appl. Polym. Sci., 8, 2067-2093 (1964).

¹⁵ "Degradation", Encyclopedia of Polymer Science and Engineering, Vol. 4, pp 630-696, Wiley-Interscience, NY.

¹⁶ I. Husain, "Degradation of Nylon Canopy Fabrics Due to Ageing", Proceedings, AIAA 10th Aerodynamic Decelerator Systems Technology Conference, Cocoa Beach, FL, April 18-20, 1989.