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Optical Spectroscopic Monitoring of Parachute Yarn Aging

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Optical Spectroscopic Monitoring of Parachute Yarn Aging

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Abstract

Optical spectroscopic techniques were evaluated as nondestructive monitors of the aging of parachutes in nuclear weapons. We analyzed thermally aged samples of nylon and Kevlar webbing by photoluminescence spectroscopy and reflection spectroscopy. Infrared analysis was also performed to help understand the degradation mechanisms of the polymer materials in the webbing. The photoluminescence and reflection spectra were analyzed by chemometric data treatment techniques to see if aged-induced changes in the spectra correlated to changes in measured tensile strength. A correlation was found between the shapes of the photoluminescent bands and the measured tensile strengths. Photoluminescent spectra can be used to predict the tensile strengths of nylon and Kevlar webbing with sufficient accuracy to categorize the webbing sample as above rated tensile strength, marginal or below rated tensile strength. The instrumentation required to perform the optical spectroscopic measurement can be made rugged, compact and portable. Thus, optical spectroscopic techniques offer a means for nondestructive field monitoring of parachutes in the enduring stockpile.

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Introduction

The parachute-retarded nuclear weapons currently in stockpile were developed for low-altitude aircraft delivery, also known as the "laydown" mode. The parachutes in these weapons experience large transient stresses as they slow the weapon from supersonic aircraft speeds to ground impact velocities of 50-100 feet per second. The two weapons systems still employing parachutes, the B61 and the B83, are approaching 30 and 15 years, respectively, in stockpile. Aging of the parachute materials, potentially leading to loss of tensile strength, has become a concern. While few parachutes have thus far shown evidence of significant strength degradation, prudent stewardship of the stockpile to the extended lifetimes now proposed should include regular monitoring of the parachutes in the B61 and B83 weapons systems.

The concept of parachute delivery systems for nuclear weapons originated in the 1950's to address two concerns: safe escape of aircraft after delivery of high-yield nuclear weapons (high altitude retarded delivery mode); and aircraft penetration of increasingly sophisticated air defenses (low altitude laydown delivery mode)¹. In the 1950's parachute development for nuclear weapons was carried out by the Department of Defense at Wright-Patterson Air Force Base (with Sandia Labs involvement and parallel development programs). Responsibility for the parachute program was transferred to a Sandia Laboratories organization in 1975. Parachute delivery systems were developed for the B28, B43, B53, B57, B61 (some versions) and the B83. Of these weapons systems, only the B61 and the B83 will exist in the enduring stockpile. The parachutes used in the B61 and the B83 are composed of ribbon and tape patterns rather than a "solid" cloth canopy, which would not survive the high inflation loads present in a nuclear weapon laydown environment. Ribbon parachute technology was developed in Germany before and during World War II and was brought to the United States after World War II by German scientists. The webbing (ribbons and tapes) in the B61 and B83 parachutes is composed of woven strands (yarns) of nylon or Kevlar filaments and is designated by the its width and its rated tensile strength. Thus, a "1" x 4000 lb" Kevlar webbing is one inch wide and has a rated tensile strength of 4000 pounds. Nylon webbing used in these parachutes ranges from 0.625" wide to 2" wide and from 1000 lbs to 10000 lbs in rated tensile strength. Kevlar webbing ranges from 0.5" wide to 2" wide and from 550 lbs to 15000 lbs in tensile strength.

The goal of this work was to investigate the potential for optical spectroscopic techniques to nondestructively monitor aging of parachutes in nuclear weapons. To this end we analyzed thermally aged samples of nylon and Kevlar webbing by photoluminescence (light-induced fluorescent emission) spectroscopy and reflection spectroscopy. Some infrared analysis was also performed to help understand the degradation mechanisms of the polymer materials in the webbing. The photoluminescence and reflection spectra were analyzed by chemometric data treatment techniques to see if aged-induced changes in the spectra correlated to

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changes in measured tensile strengths. As will be shown in this report, the correlation between the spectra and the measured tensile strengths is strong enough that the spectra can be used to predict the tensile strengths of nylon and Kevlar webbing with sufficient accuracy to categorize the webbing sample as above rated tensile strength, marginal or below rated tensile strength. The instrumentation required to perform the optical spectroscopic measurement can be made rugged, compact and portable. Thus, optical spectroscopic techniques offer a potential means for nondestructive field monitoring of parachutes in stockpile.

Aging and Tensile Strength Measurements

Nylon and Kevlar webbing received from Bally Ribbon Mills in 1993 and 1991, respectively, was aged in two batches during 1995 and 1996-1997 in ambient Albuquerque, NM, atmosphere. The following table shows aging conditions for both batches. A sample of each type of webbing for each batch, which was not exposed to elevated temperature (referred to as "0 days aged" or "baseline"), was analyzed in conjunction with the aged webbing samples. Samples of all of the aged webbing, except those nylon and Kevlar samples aged for 260 days during 1995, were available and were analyzed by optical spectroscopic techniques. The webbing types were selected as representative of those in stockpile.

Table 1 - Parachute Webbing Aging, 1996-1997

Webbing Type	Aging Time Period	Aging Temperature, °C	Aging Time (days) at Each Temperature
Nylon, 1" x 1000 lb	1996 - 1997	70, 100 and 130	29, 58, 114 and 230
Nylon, 1" x 1000 lb	1995	130	29, 58, 116 and 260
Kevlar, 1" x 4000 lb	1996 - 1997	90, 130 and 170	29, 58, 114 and 230
Kevlar, 1" x 4000 lb	1995	170	29, 58, 116 and 260

Tensile strength measurements (performed by personnel of organization 9116) for the nylon and Kevlar webbing are plotted versus aging time in Figures 1 and 2. The measurements were performed in triplicate, an average was obtained, and the averaged data were converted from absolute (pounds) units into percentages of rated tensile strength. The per cent standard deviations of the tensile strength measurements (performed in triplicate) averaged about 4% for the nylon webbing and about 2% for the Kevlar webbing.

For the nylon webbing samples (Figure 1) at the lowest aging temperature of 70°C, there is a significant increase in tensile strengths for the two shortest aging times. A similar increase in tensile strength was observed for webbing samples aged (in ambient conditions) at several stockpile locations for 12 and 24 months². Even some 12-year-old stockpile samples show tensile strengths higher than unaged material. This increase in tensile strength is probably related to an effect of delayed "curing", i.e. a

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slow reaction occurring in the polymer filaments after their manufacture, which completes or enhances the polymerization of the nylon. We have noted what we suspect are similar effects in polyurethane foams used in weapons applications³, suggesting that delayed curing may be an effect more generally encountered in polymeric materials. For the short term, delayed curing clearly enhances the tensile strengths of the nylon webbing. However, the effects of delayed curing could distort estimates of the useful lifetimes of nylon webbing. Lifetime estimates based optimistically on short-term (years to a decade?) tensile strength measurements could result in unjustified estimates of the long term stability of nylon webbing once the "curing" stage ends and degradation mechanisms begin to affect the webbing's tensile strength. With 130°C aging the tensile strengths of the nylon webbing degrade well below the rated strength. But the amount of degradation is significantly different for the two batches of webbing aged at 130°C. We currently have no explanation of why two batches of webbing, aged at nominally the same conditions, should degrade to such different extents.

Figure 1. Aging of Nylon Parachute Webbing (1" x 1000lb)

Figure 2 plots the tensile strengths versus aging time for the Kevlar webbing samples. At the lowest aging temperature (90°C) and shortest aging time (29 days) the

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tensile strength remains essentially constant before slowly decreasing with continued aging. For the higher exposure temperatures, the tensile strength decreases relatively quickly for the shorter aging times, then at a slower rate at the longer aging times. The fast initial decrease may be due to the loss of an additive, a slip agent designed to enhance tensile strength and believed to be present in webbing rated at tensile strengths of 4000 lbs and above². The aging conditions degraded the Kevlar webbing to a lesser extent than the nylon webbing.

Figure 2. Aging of Kevlar Parachute Webbing (1" x 4000lb)

Optical Spectroscopic Measurements

Photoluminescence and reflectance measurements were obtained on small (two to three centimeter) pieces of the webbing samples. The webbing samples were stored in the dark when not being analyzed, and they were handled using forceps or tweezers to avoid contamination from skin contact. There was no preparation of the samples for analysis, other than mounting in a holder. Light from a 150 watt xenon lamp, as filtered through a small, double monochromator, was focused onto the webbing sample using an off-axis mirror. The light impinging on the webbing sample was focused to a curved

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line one to two millimeters long by a fraction of a millimeter wide. The intensity of the light irradiating the webbing sample was of the order of microwatts. Light emitted from (photoluminescence) or scattered from (reflectance) the webbing samples was collected by a lens system and transferred to a 0.6-m spectrograph operated at a resolution of 2 nm and a bandpass of 300 nm. A charge-coupled-device detector simultaneously detected all the wavelengths in the bandpass of the spectrograph. Data acquisition for a single webbing sample typically required a minute or less, after which the recorded spectrum was transferred to a personal computer to be corrected for instrumental response and, subsequently, for chemometric analysis.

In photoluminescence, photons of wavelengths resonant with an absorption band of the irradiated material are absorbed by the material and emitted at longer wavelengths. Usually a narrow band of wavelengths (5 nm) is used for irradiation. In our experimental arrangement, the wavelength filtering action of the double monochromator on the broad band xenon lamp output provides this narrow band of wavelengths, which is wavelength tunable by rotating the gratings in the monochromator.

Using ultraviolet excitation wavelengths from 230 nm to 390 nm, photoluminescence spectra were obtained of the baseline (ambient exposure only) webbing and each of the thermally aged nylon and Kevlar webbing samples. Using these series of spectra, we selected an excitation wavelength for nylon and for Kevlar which maximized the differences in the photoluminescence between the aged and the baseline samples. For nylon this excitation wavelength is 270 nm. For Kevlar it is 380 nm. The photoluminescence of the nylon webbing samples shifted its peak intensity to longer wavelength with thermal aging. Its overall intensity increased for shorter aging times and lower temperatures but decreased at the longest aging times and highest temperatures. Examples of the photoluminescence of baseline and aged nylon are shown in Figure 3. The photoluminescence peak of Kevlar webbing samples also shifted to longer wavelength with thermal aging, but the magnitude of the shift is less than that observed in aged nylon webbing. The overall intensity of Kevlar photoluminescence decreased with aging. . Examples of the photoluminescence of baseline and aged nylon are shown in Figure 4.

Reflectance spectra were obtained by illuminating webbing samples with a broad range of wavelengths, collecting the reflected light using fiber optics and analyzing the collected light with the spectrograph and charge-coupled-device detector combination. Illumination of the webbing samples was provided by the xenon lamp as transmitted through the double monochromator with its gratings set a zero order. At zero order a grating acts as a mirror rather than diffractive element, and all wavelengths impinging on it can be passed simultaneously to the exit slit of the monochromator. Spectra so obtained were converted to reflectance values by ratioing to a reference spectrum obtained from a magnesium oxide disk, which emulates a diffuse, non-absorbing scatterer.

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Figure 3. Photoluminescence of Baseline and Aged Nylon Webbing (270 nm excitation)

Figure 4. Photoluminescence of baseline and aged Kevlar Webbing (380 nm excitation)

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Reflectance spectra of baseline and aged Kevlar are shown in Figure 5. Reflectance values greater than 1.0 are present in some of the spectra because the partially transparent filaments in the webbing, to a certain extent, refract light rather than acting as diffuse scatterers. The blue/ultraviolet reflectance band of Kevlar progressively broadens into the green and red visible regions with thermal aging. Reflectance spectra of baseline and aged nylon webbing were also obtained, but changes in their reflectance spectra do not correlate strongly with thermal aging.

Figure 5. Reflectance spectra of baseline and aged Kevlar Webbing

Chemometric Analysis of the Photoluminescence and Reflectance Spectra

Multivariate (also known as "full spectrum") chemometric analyses were carried out on the photoluminescence and reflectance spectra of baseline and thermally aged webbing, both nylon and Kevlar. The "PLSIQ" routines in the GRAMS/32 (version 4.11) software package were employed. In multivariate analysis the entire spectrum is correlated to an observable parameter, in this case the tensile strength of the webbing. Using complex algorithms involving linear (matrix) algebra, a type of regression analysis is employed which decomposes the spectra into a set of "loading vectors", or partial representations of the spectra from which all of the spectra can be reconstituted. Matrices of the weighting factors (called "scores") used to scale the loading vectors (which are summed to reconstitute the spectra) are correlated to the observable parameter. The process has a superficial resemblance to quantum theory, in which a

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wave function is represented by a linear combination of weighted basis functions. Indeed, similar terminology is sometimes used in multivariate analysis as in quantum theory, but multivariate analysis is a purely empirical, as opposed to a theoretical, analysis.

In our multivariate data treatments entire spectra, as shown in Figures 3 - 5, were used in the analysis. The spectra were pre-processed by mean centering. In mean centering, the average of all the spectra in a "training set" (i.e., a set of spectra of webbing samples with known tensile strengths, which is used to establish the correlation or calibration curve) is obtained, and the processing algorithms deal with the differences between the average spectrum and the individual spectra. This approach somewhat simplifies the mathematics involved. It was found that area normalization (scaling the spectra to achieve a constant integral under the spectroscopic curve) of the photoluminescence spectra significantly improves the correlation between the spectra and the tensile strengths. Normalization of the spectra during multivariate processing actually provides an experimental advantage, since data acquisition will not need to incorporate techniques which reproduce absolute luminescence intensities. Both partial least squares (PLS) and principal component regression (PCR) approaches to the multivariate analysis were compared. Results are presented from the approach which, for the data set used, appears to have better predictive capability. In addition, cross-validation was employed in all analyses. In cross-validation one of the spectra is left out of the calculations, and its tensile strength is predicted on the basis of the calibration derived from the remaining spectra in the training set. Thus, the results of the multivariate analyses are plotted in terms of tensile strengths predicted by cross-validation versus the measured tensile strengths. The squared correlation coefficient (R^2) shown with the plots is one measure of how well the analysis relates the spectra to the tensile strengths.

Figure 6 shows the predicted versus measured tensile strengths (in % rated strength) of the baseline and thermally aged nylon webbing samples. The data is from a cross-validated partial least squares (PLS) analysis using mean-centered, normalized photoluminescence spectra. Nylon webbing samples aged at 70, 100 and 130°C during 1996-1997 are represented by triangles. Those aged at 130°C during 1995 are represented by squares. The plot shows a strong correlation between trends in the photoluminescence spectra and the tensile strengths of the nylon webbing samples. The data points from the nylon webbing samples aged during 1995 fit within the distribution of the overall training set, even though these samples degraded significantly less than samples aged during 1996-1997 under nominally the same conditions (see Figure 1). This consistency of the correlation between the photoluminescence spectra and the tensile strength data for all the samples, despite differences in aging, suggests that changes in the spectra and the tensile strengths are related to the same aging mechanism.

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Figure 6. PLS cross-validation of photoluminescence from Nylon webbing aged at 70, 100 and 130°C

Figure 7 shows the predicted versus measured tensile strengths of the baseline and thermally aged Kevlar webbing samples. The data is from a cross-validated partial least squares (PLS) analysis using mean-centered, normalized photoluminescence spectra. Kevlar webbing samples aged at 90, 130 and 170°C during 1996-1997 are represented by triangles. Those aged at 170°C during 1995 are represented by squares. A strong correlation between the photoluminescence spectra and the tensile strengths is present for the Kevlar webbing samples as well as the nylon webbing samples, although the squared correlation coefficient (R^2) for the plot of the Kevlar data is lower. The correlation of the photoluminescence spectra to the tensile strength data does not depend on aging temperature nor does it appear to be affected by differences in aging for the two batches (1995 and 1996-7, see Figure 2) subjected to nominally the same aging conditions.

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Figure 7. PLS cross-validation of photoluminescence from Kevlar webbing aged at 90, 130 and 170°C

Figure 8 also shows the predicted versus measured tensile strengths of the baseline and thermally aged Kevlar webbing samples, but the correlation in this plot is based on reflectance spectra (380 - 680 nm). The data is from a cross-validated principal components regression (PCR) analysis using mean-centered spectra. Kevlar webbing samples aged at 90, 130 and 170°C during 1996-1997 are represented by triangles. Those aged at 170°C during 1995 are represented by squares. The Kevlar reflectance spectra correlate to the tensile strengths nearly as well as the photoluminescence spectra. The correlation does not show a dependence on aging conditions.

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Figure 8. PCR cross-validation of reflectance spectra from Kevlar webbing aged at 90, 130 and 170°C

The correlations between photoluminescence spectra and tensile strength data for the nylon and Kevlar webbing samples and between the reflectance spectra and the tensile strength data for the Kevlar webbing samples suggest that optical measurements may provide a means of nondestructively monitoring the aging of parachute webbing. From the cross-validation for nylon shown in Figure 6 we calculated a standard error of cross validation (SECV) of 8% (in % rated strength units) for the photoluminescence measurements of aged nylon. The SECV, also referred to as the standard error of prediction, is an estimate of the precision with which tensile strengths may be predicted from photoluminescence spectra. The SECV is analogous to the standard deviation calculated from a distribution of data points (rather than spectra, as here). For Kevlar, using photoluminescence spectra (Figure 7) and reflectance spectra (Figure 8), the SECV is 5% (in % rated strength units). The precision indicated by the SECV's should be sufficient for the use of optical

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measurements as a screening technique to categorize webbing as, for example, good ($\geq 110\%$ of rated strength), marginal (90 to 110% of rated strength) or failed ($< 90\%$ of rated strength). The calibration data shown above could be used directly to predict the tensile strength of nylon (1" x 1000lb) and Kevlar (1" x 4000lb) webbing in stockpile. The ability to predict tensile strengths for these webbing weaves could be tested if a set of samples were removed from stockpile, their tensile strength measured and their spectra recorded. Photoluminescence spectra have been obtained for stockpile samples of other weave types (different widths and rated tensile strengths), and the spectra appear to fit within the envelopes defined by the spectra shown in Figures 3 and 4. The calibration data shown in Figures 6 - 8 could also be used to predict tensile strengths of these other webbing weaves, but a bias factor would have to be applied. The bias factor will be needed to account for differences in rated tensile strengths (even per cent rated tensile strengths) between different weaves. For example, a population of newly manufactured 1" x 1000 lb nylon weaves appears to test at about 130% rated strength (Figure 1), but a population of newly manufactured 2" x 10000 lb weaves might test at, say, 110% rated strength. In other words, the ratio of the average tensile strength of a newly manufactured weave to what the manufacturer defines as the rated tensile strength is not necessarily the same for all weaves. However, the evidence to date leads us to believe that optical spectra measure the state of aging of a webbing independent of the type of weave and that the actual tensile strength of the webbing could be obtained by applying a weave-specific bias factor to the tensile strength prediction obtained from optical spectra. The bias factors could be determined by ratioing tensile strengths measured for unaged samples of a given weave to the manufacturer's definition of "rated" tensile strength for that weave.

Field Monitoring of Parachutes

It is possible to construct a field portable instrument of shoe box size (plus computer) to monitor the aging of parachute materials in stockpile. This instrument would use the optical methods, photoluminescence and reflectance, described in this report. It could probably be constructed for less than \$20K. It may be possible to design such an instrument to run off battery power. The instrument would consist of a small source of broad band ultraviolet and visible light, possibly a pen lamp, a fiber optic and sampling head assembly to deliver light to a parachute and to collect the emitted or reflected light and a small spectrograph and imaging detector to disperse and detect the emitted/reflected light. The detector would be a charge-coupled device, thermoelectrically cooled, if necessary, to increase sensitivity. Acquisition of entire spectra, such as those shown in Figures 3, 4 and 5 could be accomplished on the time scale of seconds. Spectra would be transferred to a portable computer pre-loaded with the calibration model. On the time scale of tens of seconds, the computer would estimate a tensile strength value for the parachute webbing sampled. Figure 9 shows a schematic diagram of a prototype instrument.

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Prototype Instrument for Field Monitoring of Parachutes

Figure 9. Prototype Instrument for Field Monitoring of Parachutes

As noted in the above discussion, these optical techniques should be capable of predicting parachute webbing tensile strengths so as to classify the parachute materials as good (significantly above rated strength), marginal or likely to fail tensile strength testing. This classification will provide a basis for deciding whether to retain the parachute in stockpile, replace it or put it under increased surveillance.

Infrared Absorption Analysis

Infrared absorption measurements using attenuated total reflectance (ATR) were performed on baseline and thermally-aged nylon and Kevlar webbing. These measurements were intended to complement diffuse reflectance infrared absorption studies², which correlated the increase in the intensity of a (carbonyl) infrared band with thermal aging. These changes in the infrared spectra are related to aging-induced oxidation of the polyamide structures in the polymer filaments which compose the webbing. Raman spectra of aged Kevlar webbing also show the development of oxidized molecular groups in the form of acid anhydride species. Since acid anhydrides hydrolyze in the presence of moisture, these species are believed to be forming inside the webbing filaments, where they would tend to be isolated from ambient conditions.

In infrared spectroscopy using ATR sampling, the infrared beam is propagated through a transparent, high refractive index plate in the shape of a trapezoid (typically 50mm by 20 mm by one-to-two millimeters thick). The beam is propagated through the plate at angles which result in 10 to 50 reflections at the plate/air interface. At each reflection an "evanescent" wave of the propagating beam penetrates a fraction of its

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wavelength beyond the plate. Thus, a piece of webbing pressed in contact with the plate is sampled by the propagating beam at multiple points along the length of the plate, yielding an infrared absorption spectrum characteristic of the webbing sample. This spectrum will be more characteristic of species on the surface of the webbing filaments than the diffuse reflectance spectrum, which samples more deeply into the bulk. A ZnSe ATR plate was used to obtain the spectra shown in this report.

Figures 10 and 11 show infrared absorption spectra, obtained by ATR, of baseline and thermally aged nylon and Kevlar webbing samples. The spectra of both types of webbing show the development, with aging, of infrared bands in the N-H stretching region (near 3400 cm^{-1}) and in the O-H stretching region (near 3200 cm^{-1}). The intense infrared band peaking near 3300 cm^{-1} in all the spectra of Figures 10 and 11 is due to the N-H stretch of amide linkages ($-\text{NH}-\text{CO}-$), which are intrinsic to polyamide filaments such as nylon and Kevlar. Other differences between the spectra of the ambient and thermally aged webbing occur in the carbonyl ($\text{C}=\text{O}$, near 1730 cm^{-1}) stretching region for both nylon and Kevlar and in the carbonyl bending region ($1100 - 1300\text{ cm}^{-1}$) for Kevlar. These changes in the infrared spectra are due to the presence of degradation products whose build-up was accelerated related by thermal exposure.

Webbing which was exposed to elevated temperatures (but not the baseline webbing exposed only to ambient conditions) left residues on the ATR plate. We obtained infrared spectra of these residues after the thermally aged webbing samples were removed from contact with the ATR plate. As can be seen in Figure 12, prominent bands in the residue spectra correspond to features which develop in the spectra of the webbing as they are aged at elevated temperatures (Figures 10 and 11). The residue spectra from the thermally aged nylon and Kevlar webbing are similar. Differences between the nylon and Kevlar residue spectra are primarily in the $1500 - 1600\text{ cm}^{-1}$ region and are related to aromatic structures present in Kevlar but not in nylon. The residue spectra are consistent with those of amino-substituted carboxylic acids. The presence of amino and carboxylic acid groups in the residues suggests that decomposition of the amide linkages in the nylon and Kevlar polymers is occurring by hydrolysis (reaction with water). In addition to the oxidative degradation mechanism, which was revealed by diffuse reflectance infrared and Raman spectroscopies, there appears to be degradation of the webbing by hydrolysis on the filament surfaces. Since the rate of a hydrolysis reaction depends on ambient humidity, it may be that the differences in tensile strengths of webbing aged under the same conditions of temperature and time (Figures 1 and 2) are due to differences in ambient humidity.

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Figure 10. Infrared absorption spectra of baseline and thermally aged Nylon webbing; spectra obtained using attenuated total reflection sampling.

Figure 11. Infrared absorption spectra of baseline and thermally aged Kevlar webbing; spectra obtained using attenuated total reflection sampling

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Figure 12. Infrared Spectra of Residues on attenuated total reflection plate after contact with aged Nylon and Kevlar webbing.

Yet another degradation mechanism appears to be occurring in the Kevlar webbing. Kevlar webbing with rated strengths of 4000 lb and above is believed to have a slip agent present on the filament surfaces as a strength enhancer. Peng² has identified this slip agent as a polyvinyl butyral. We subtracted spectra of thermally aged Kevlar webbing from that of the baseline material. The resulting difference spectra showed a band pattern which is most obvious when the spectrum of the most extensively aged Kevlar webbing is subtracted from the spectrum of the baseline webbing (Figure 13). The band pattern of this difference spectrum is similar to that of library spectra of polyvinyl butyrals. Thus, the suspected slip agent (polyvinyl butyral) is lost during thermal aging of the Kevlar webbing. Some evidence of loss of slip agent is apparent in difference spectra between the baseline Kevlar webbing and even the Kevlar webbing aged least extensively (shortest time at lowest temperature). The ATR sampling technique enhances our ability to detect the loss of slip agent because of its sensitivity of to surface coatings. Loss of slip agent may be responsible for the initial, relatively large decrease in tensile strength of the Kevlar webbing with elevated temperature aging (Figure 2) and may also be responsible for some of the observed changes in the photoluminescence and reflectance spectra.

Figure 13. Difference spectrum obtained by subtracting the infrared spectrum of thermally aged (230 days @ 170°C) Kevlar from that of baseline Kevlar; spectra obtained by attenuated total reflectance sampling.

Summary

Thermal aging of parachute webbing eventually causes significant loss of tensile strength, but there tends to be a interim period in which the tensile strength remains constant or even increases slightly. This behavior seems to be due to delayed completion of polymerization ("curing"). While this "curing" effect results in enhanced short term parachute performance, it could lead to overly optimistic predictions of parachute lifetime, since the tensile strength eventually decreases at a faster rate than shorter term measurements would indicate.

Photoluminescence spectra of nylon parachute webbing and photoluminescence and reflectance spectra of Kevlar parachute webbing show changes in peak shape, position and intensity as the webbing is aged by elevated temperature exposure. Chemometric analysis of the optical spectra using multivariate techniques indicates that a strong correlation exists between the optical spectra and the webbing tensile strengths. It appears that optical spectra are able to predict tensile strengths with

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sufficient precision to be used as an in-situ screening technique for stockpile surveillance. It is possible to design and construct a small, field-portable instrument which is capable of estimating the tensile strength of a localized area of the parachute on the time scale of tens of seconds.

Infrared absorption measurements using attenuated total reflectance sampling have identified surface degradation mechanisms in parachute webbing complementary to the bulk oxidation identified by diffuse reflectance infrared and Raman spectroscopies. Both nylon webbing and Kevlar webbing develop, with accelerated aging, amino-carboxylic acids on the surfaces of their filaments. These amino-carboxylic acids are most likely products of the scission of amide polymer chains by a hydrolytic mechanism, i.e. attack by absorbed water. Thus, humidity, in addition to temperature, is an important variable to control in aging experiments as well as in stockpile. In addition, Kevlar webbing shows at least some loss of slip agent under all accelerated aging conditions. This loss of slip agent is probably responsible for the initial, relatively fast loss of tensile strength during thermal aging.

Measurements on webbing samples aged in stockpile will be necessary to confirm the viability of using optical spectra to screen parachutes in the field. It appears that humidity, in addition to temperature, is a variable whose effect on the degradation of nylon and Kevlar should be investigated. Additional efforts along these lines should be undertaken in order to ensure the reliability of that portion of the weapons stockpile which has parachute-mediated delivery modes.

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Optical Spectroscopic Monitoring of Parachute Yarn Aging

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