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Reliability Study of an Emerging Fire Suppression System

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ABSTRACT

Self-contained fire extinguishers are a robust, reliable and minimally invasive means of fire suppression for gloveboxes. Plutonium gloveboxes are known to present harsh environmental conditions for polymer materials; these include radiation damage and chemical exposure, both of which tend to degrade the lifetime of engineered polymer components. The primary component of interest in self-contained fire extinguishers is the nylon 6-6 machined tube that comprises the main body of the system.

Thermo-mechanical modeling and characterization of nylon 6-6 for use in plutonium glovebox applications has been carried out. Data has been generated regarding property degradation leading to poor, or reduced, engineering performance of nylon 6-6 components. In this study, nylon 6-6 tensile specimens conforming to the casing of self-contained fire extinguisher systems have been exposed to hydrochloric, nitric, and sulfuric acids. This information was used to predict the performance of a load bearing engineering component comprised of nylon 6-6 and designed to operate in a consistent

manner over a specified time period. This study provides a fundamental understanding of the engineering performance of the fire suppression system and the effects of environmental degradation due to acid exposure on engineering performance. Data generated help identify the limitations of self-contained fire extinguishers. No critical areas of concern for plutonium glovebox applications of nylon 6-6 have been identified when considering exposure to mineral acid.

Introduction

The most effective protection from radioactive materials is engineered barriers and has been incorporated through architectural and structural design.[1] Potential engineering controls include differential ventilation pressure zones, High-Efficiency Particulate Air filtration, radiation shielding, and gloveboxes. Gloveboxes used for radioactive materials are maintained at a lower pressure than the surrounding room atmosphere so that relatively small leaks result in air inflow rather than radioactive material release. In addition, they are constructed of stainless steel to provide structural stability.

However, seismic events present unresolved issues in designing gloveboxes. One of the most challenging accident scenarios is the post-seismic fire event. History has shown that glovebox fires can be extremely dangerous and may pose significant health hazards when the products of combustion include radioactive and toxic materials.[2]

As previously reported in this journal, self-contained fire extinguishers were demonstrated to be a robust, reliable and minimally invasive means of fire suppression for gloveboxes.[3] They can be mounted to the interior of the glovebox. One example of such a system is the Fire Foe™ system. This self-contained fire extinguisher employs a nylon tube that contains a jelled fire suppression media. The nylon tube is pressurized to 0.7 MPa at room temperature conditions, and the combination of thermally induced weakening of the nylon material associated with heat from the fire and expansion of the jelled fire suppression media causes the rupture and release of the fire suppressant.

The overall system reliability depends on the tube failing predictably for any given fire scenario. There will be variability in the time of release associated with

variations in the fire signature. As previously reported in this journal, methodology has been developed to predict fire induced wall failure in small scale compartments such as gloveboxes.[4] A small scale test apparatus has been developed to characterize tube wall temperature and breakage properties. In this experimental campaign, the thermal environment that causes a tube wall failure has been determined. The study shows that the heat release rate and heat flux has been accurately modeled since forward predicted temperatures closely matched the experimentally measured values.

Plutonium gloveboxes are known to be a harsh environment for polymer materials. Radiation, chemical exposure, inert atmosphere, and dry (low humidity) atmosphere have high potential to degrade the lifetime of engineered components.[5,6,7] In the Fire Foe™ system, the primary component of interest is the nylon 6-6 machined tube that comprises the main body of the system, as seen in Figure 1.

Figure 1. Self-Contained Fire Extinguisher Tube

The investigation of the remaining engineered components of the fire suppression system is beyond the scope of this study.

The reliability of nylon 6-6 due exposure to alpha radiation was recently studied.[8] The environment of a plutonium glovebox is such that the expected dose rate from radiological sources ranges to very high levels of over several Mrad per year in the worst case. In the worst case glovebox scenario, the plutonium radiation sources exist as a thick

plutonium oxide (PuO_2) dust which layers onto every surface within the glovebox. Methodology has been developed to predict radiation induced wall failure in small scale compartments such as gloveboxes. The data showed evidence of slight degradation in the nylon 6-6 material with increasing levels of alpha particle dose. Variations in the level of alpha particle dose applied to the nylon material show discolorations which may prove useful as a quick reference to age of self-contained fire extinguisher systems within gloveboxes. There appears to be a much higher level of degradation in the specimens under neutron irradiation. Data generated from radiation induced degradation studies help identify the limitations of self-contained fire extinguishers.

Besides high levels of radiation, plutonium gloveboxes are also exposed to high levels of mineral acids. The goal of this report is to create a model by which the effects of mineral acids on nylon 6-6 could be quantified and from which conclusions on the shelf life and reliability of the self-contained fire extinguisher systems could be drawn. The effect of mineral acid induced mechanical property changes on failure mode and lifetime are also characterized.

In the following study, a literature review of material properties of nylon 6-6 was conducted to provide a fundamental understanding of the engineering performance of the fire suppression system and the effects of environmental degradation. Engineering analysis and material testing in nylon 6-6 were conducted that measures the performance of the material under acid induced degradation. This information will be used to aid in the assessment of the performance of a load bearing engineering component comprised of nylon 6-6 and designed to operate in a consistent manner over a designated time period.

Definitions

- **Creep (sometimes called cold flow)** The time dependent tendency of a solid material to move slowly or deform permanently under the influence of mechanical stresses, despite stresses being below the yield stress of the material.
- **Hardness** The measure of the materials resistance to deformation and is related to the yield stress and fracture toughness of the material.

Literature Review

An article by Thanki and Singh provided an excellent review of nylon 6-6 degradation from photooxidative, thermal, radiative and sensitized degradation.[9] Degradation of properties is identified as an irreversible process stemming from small structural changes within the polymer induced by the environment. A second review article, by Fairgrieve, provided insight into the background of nylon 6-6 properties and degradation.[10] This article summarized the history, the degradation properties, stabilization, and recycling of nylon 6-6. The chemistry behind the material is described as well as the reactions that take place during the degradation process. Early stages of research showed that nylon 6-6 was susceptible to heat and light. This observation is consistent with observations with glovebox glove polymers reported in this journal.[11] The degenerative process was characterized as a discoloration followed by loss in physical properties. Photooxidative degradation is also apparent in nylon 6-6.

Brown et al. studied the effect of sulfuric acid on nylon 6-6.[12] In this study the diffusion rate of sulfuric acid was studied in nylon 6-6 at various concentrations and

temperatures. The pH concentrations ranged from distilled water to 1.0 M sulfuric acid. The temperatures tested ranged from 20 to 90 °C. The degradation of the material was based upon yield stress, flexural modulus, and inherent viscosity.

The yield stress of the material was then compared with the saturation temperature at different concentrations. Water and 0.1M Sulfuric Acid were shown to slightly increase the yield strength of the material with increasing saturation temperature. Although at higher temperature, the acid present showed signs of degradation. Higher concentrations showed a significant decrease in the yield strength of the material as the saturation temperature was increased. A similar trend was found for the flexural modulus for given temperatures and concentrations. In conclusion it was stated that nylon 6-6 will show significant degradation at higher concentrations, but at concentrations approaching that of distilled water, the effect of low-acid-concentration will be minimal.

Vachon et al. studied oxidative degradation of nylon.[13] In this study the exposure to oxidative aqueous environments was studied in nylon 6-6 filaments. Both chemical and physical properties were studied as a function of exposure. The rate and extent of degradation was also related to the pH of the environments. Studies were conducted on both drawn and undrawn nylon filaments.

By studying the viscosity data, the degradation of the nylon filaments was determined to be strongly dependent on the pH at oxidation. It was shown that little to no degradation was apparent for a pH of less than 5. For a pH of greater than 5, it was shown that there was rapid degeneration, with a maximum around a pH of 8. At higher pH values, the rate of degeneration decreases. These results came from experiments in oxygen-water systems at 80 °C. It was also noted that the undrawn filaments degrade

more rapidly, which was attributed to the slower diffusion of oxygen into the oriented filaments. The temperature dependence of degeneration was also examined at 60, 70, and 80 °C. It was shown that at a given pH, the rate of degradation increases with temperature. This was true for all pH values. This study also determined whether the oxygen absorption was dependent on pH once oxidation was initialized.

Nair et al. studied the effect of solutions on the creep rate of nylon 6-6.[14] The creep behavior of nylon 6-6 was characterized in dry and wet environments (water or zinc chloride) in this study. To study this, the strain recovery was measured for specimens exposed to the different environments. Creep strain was characterized by looking at the strain rate versus creep strain graphs. It was shown that water and zinc chloride affect the strain development. Plasticization of the molecules was used to explain the increase in creep rate for both the water and zinc chloride environments. The zinc chloride mist environment was shown to have a greater influence than water on the creep rate.

George et al. studied the creep strain development in warm and wet environments.[15] It was concluded in this study that increased annealing temperature during processing decreased the weatherablility of the nylon 6-6. It was also shown that lower annealing temperatures resulted in higher creep rates at the same applied load. Annealed samples showed a greater resistance to creep that the quenched samples. This was explained by the differences in crystalline structures within the materials. It was also noted that samples exposed to higher UV radiation showed a greater resistance to creep than the shelter specimens. This work has relevance to the plutonium glovebox operations due to the combined effects of the radiation and chemical exposure which will

limit the ductility of the material. This limited ductility would mimic that of the UV radiation and increase the resistance to creep.

Radiation effects of all types, including gamma, UV, and electron beam, have been studied for nylon 6-6. These studies have been performed in multiple ways, but have consistently shown a degradation of mechanical properties. A sample of these reports is included below.

Aytac et al. studied the effect of gamma radiation in nylon 6-6 used for automotive tires.[16,17] The motivation for the study was radiation used for pre-vulcanization of the tires. Treated and untreated cords were tested at different twist levels and radiation doses and the changes in mechanical properties were measured. The cords were irradiated at ambient temperature in air using a 0.13 kGy/hr and an 11.5 kGy/hr source. The tensile properties of the Nylon 6-6 cords were tested at several different radiation levels.

It was shown that the tensile strength of the cords was decreased with increasing dose. The effect of irradiation on nylon 6-6 was shown to not be dependent on twist levels. The dose rate was also shown to only slightly effect the change in mechanical properties of the material, especially at higher doses. The elongation at breakage was also recorded, and it was shown that percent elongation slightly decreased with increasing radiation

These authors also looked at the effects on mechanical properties of untreated, treated, and calendared fabric specimens. Irradiation was supplied at 0.13 kGy/hr for gamma rays and 1.5 MeV-25 mA with 25 Gy/pass for the electron beam. Irradiation was carried out in air. The tensile property and viscosimetric measurements were taken at

various dosage levels. The nylon 6-6 showed a decrease in strength with increased radiation levels, for both gamma and e-beam radiation. The electron beam radiation caused less strength decrease as explained by the dosage rate difference. The treatment process used showed no protective effects against the oxidative degeneration. Elongation measurements at failure showed a general decrease in value as the radiation was increased. Limiting Viscosity Numbers were also examined at each radiation level and showed a decrease in this value as the dosage increases. This was attributed to the oxidative degeneration of the main chain which causes deterioration of the mechanical properties. In conclusion, both e-beam and gamma radiation caused degeneration of mechanical properties with gamma radiation causing more damage.

Ellison et al. studied radiation effects on nylon fibers.[18] In this study nylon 6-6 fibers were irradiated with cobalt-60 gamma radiation and high energy protons. Ultimate mechanical properties as well as fracture morphology were tested at room temperature for selected moisture contents. Tensile, torsional brittleness, and flexural fatigue tests were completed for several temperature and moisture contents. Gamma radiation was supplied at a rate of 1 Mrad/hr. for a period of 10, 20, 30, 40, 50, and 60 hrs. in air at 30% and 65% RH. High energy proton radiation was conducted in a vacuum to charge levels of 12, 24, 43, and 76 microcoulombs. Tensile tests of gamma radiated samples showed an initial decrease of 50% strength at 10 Mrad with a gradual decrease to 15% at 60 Mrad. This was independent of moisture content. Elongation at break showed little to no decrease from 10 to 40 Mrad with a steady decline to 35% at 60 Mrad after that for samples tested in air. Samples that were tested wet showed no decrease in elongation for any radiation level. The breaking twist angle was also shown to be affected by the

radiation. This value was initially 39° and increased to 52° at 10 Mrad. Increasing the dosage resulted in no further change in the angle. Flexural tests showed that the fatigue life was affected by both humidity and radiation levels. It was shown that increased radiation and increased humidity caused a decrease in the flex life of the fibers.

The results of high energy proton radiation were as follows. Both wet specimens and specimens at 65% Relative Humidity (RH) showed similar tensile properties with increasing exposure. There was an initial rapid decrease at 24 μC followed by a more gradual decrease to 76 μC. The wet specimens did show signs of weaker tensile properties, which were attributed to the interaction of the water with the interchain hydrogen bonds. The elongation at break decreased initially to about 60% at 24 μC with a gradual decrease to about 50% at 76 μC for both wet and 65% RH specimens. For the break angle test, the 65% RH specimens showed a large initial increase in angle followed by slight increases with increased dosage. The wet specimens showed more of a continuous increase with dosage.

Ellison continued this work and showed the effects of high energy radiation on the thermal properties and densities in nylon 6-6.[19] Specimens were irradiated in a similar manner to the previous study. Density, heat of fusion, and melting temperature were characterized with increasing dosage. The melting temperature for nylon 6-6 was shown to decrease continually for both types of radiation as the dose was increased.

Gee et al. also studied the effect of radiation on nylon 6-6.[20] In this study, measurements of thermal properties were taken on samples irradiated at different levels of cobalt-60 gamma radiation applied at room temperature. The measurements were

taken over a temperature range of 200-550 K and differential scanning calorimetry was used to make heat capacity measurements.

The melting temperature was taken as the maximum in the heat capacity versus temperature plot. Up to 200 Mrad there is a steady decrease in the melting temperature of nylon 6-6. After 200 Mrad is reached a second peak appears in the curve. With increasing dose, the lower temperature peak becomes more apparent while the higher temperature peak becomes less so. If the sample is heated above the melt crystallization temperature, a single peak can be observed that falls between the original two. The presence of the two peaks was explained by irradiation causing a new crystal structure to form in the nylon 6-6 that melts at a lower temperature. The single peak after melt crystallization was explained as an intermediate structure formed between the two. The glass transition temperature, enthalpy, and entropy of formation were also considered in this study.

Experiment

- **Material:** Tensile specimens of nylon 6-6 were cut from a square tile; 0.092 m^2 in area according to the standards given by ASTM for the testing of thin polymers (ASTM D638-10). The specimens were measured to be 0.0157 cm in thickness which corresponds to the thickness of the fire suppression system's nylon 6-6 tube casing.
- **Tensile Testing:** 60°C was given as the expected maximum operating temperature for which the Fire Foe™ tubes would be exposed in normal glovebox operations. To directly obtain tensile stress-strain data at the desired temperature, four nylon 6-6 dogbone specimens were heated and then quasi-statically tested in an Instron 5582 load frame at a strain rate of 0.003253 strain per minute.

- **Hardness and Chemical Attack Testing:** The American Society for Testing and Materials (ASTM) highlights three methods that are acceptable for hardness testing polymers, Vickers (ASTM E384), Rockwell (ASTM D785), and Shore Durometer (ASTM D2240-00). Vickers hardness testing uses a square based diamond pyramid with an apical angle of 136°, shown in Figure 2, and a variable load to make indentations in the specimen.

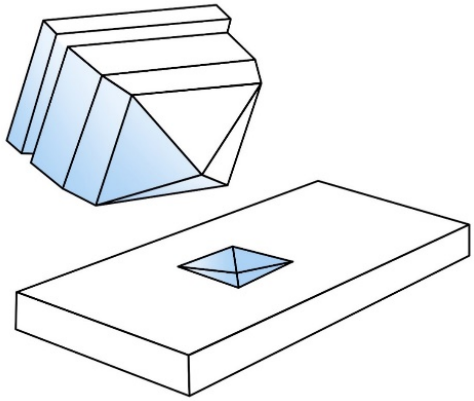

Figure 2. A Vickers Indentor, *Image courtesy of NewAge Industries*

The results are reported as kg/cm^2, the proportion of the applied load divided by the square of the diagonal of the indentation measured (ASTM E384). Rockwell hardness testing of polymers uses a spherical steel, or tungsten carbide, ball indenter, the diameter of which is dictated by the chosen scale. Typical Rockwell scales for testing plastic are Rockwell E, Rockwell M, and Rockwell R.

For the acid treated nylon specimens, Rockwell R, was chosen. The Rockwell R test uses a ½" ball indenter to first minor load of 10 kg being applied to the nylon , followed by a major load of 60 kg, and then returns to the minor load. The ASTM standard dictates the duration of the loads. The Wilson Rockwell testing machine used has a preprogrammed plastic testing mode that precisely follows the

loads and durations laid out by ASTM D785. The equation to calculate hardness uses the difference in height before and after the major load is applied and the diameter of the indenter. The Wilson Rockwell testing machine knows these values and handles the computation internally, simply outputting a hardness value at the end of the test cycle.

Acid effect testing was completed with Hydrochloric Acid (HCl), Nitric Acid (HNO_3), and Sulfuric Acid (H_2SO_4). Two chemical attack tests were performed to gain a better understanding of the severity of the chemical attack in the nylon. The first round of chemical attack tests consisted of soaking nylon samples directly in liquid acids. Six samples, approximately 1.27 cm by 1.27 cm by 0.635 cm were placed in beakers containing approximately 200mL of the three test liquids.

The second round of acid testing was intended to create a scenario in which the test coupons would be exposed to acidic vapor. The test consisted of a covered 600 mL beaker with an inverted 150 mL beaker inside it acting as a platform to support the nylon specimens above the level of the acid. For this test, approximately 150 mL of each acid was used. The acid was added to the larger beaker and the smaller beaker was placed inside. The larger beaker was tipped so that the smaller beaker would contain enough acid to overcome the buoyant force of the air trapped inside. Four samples of the same shape and size as used in the direct soak were placed on the glass platform with one of the 1.27 cm by 1.27 cm surfaces face down on the platform. The beakers were loosely covered and left to sit in a vent hood for 48 hours, at room temperature and atmospheric pressure (approximately 840 mb). After 48 hours the samples were rinsed with a large volume of water in a coarse filter until the

runoff water was neutral in pH. The samples were then tested in a Wilson Rockwell Tester, following ASTM D785.

- **Failure Analysis:** A failure analysis of the tube geometry was performed using both analytical and numerical techniques. The goal of the analysis was to determine the primary failure mechanism of the nylon system under the applied load of heat and pressure. This analysis was first considered using nominal properties of the nylon and then repeated using degraded properties of strength and toughness.
- **Finite Element Analysis:** To begin, the cross-section of the Fire Foe™ tube was created in a solid modeling package. The solid model of the tube exploited the radial line of symmetry of tube from the center of the reduced thickness area. The drawing was exported to the Finite Element Analysis program ANSYS. The symmetry is placed as a boundary condition in the ANSYS analysis, which reduces the number of nodes required for analysis and speeds the time to solution. Element type PLANE183 was used; this is a quarter-point element with midside nodes. To further streamline the Finite Element Analysis (FEA) model, a plane strain condition was imposed. The mesh sensitivity was checked and then that mesh geometry was used for all subsequent FEA.

Results

- **Tensile Testing:** The following testing results are focused on Vickers and Rockwell test procedures, as those methods are most suitable to the materials. As with most material tests, repeatability is good but generally includes a small amount of error. The Stress-Strain data for nylon 6-6 at 60°C, is plotted alone in Figure 3.

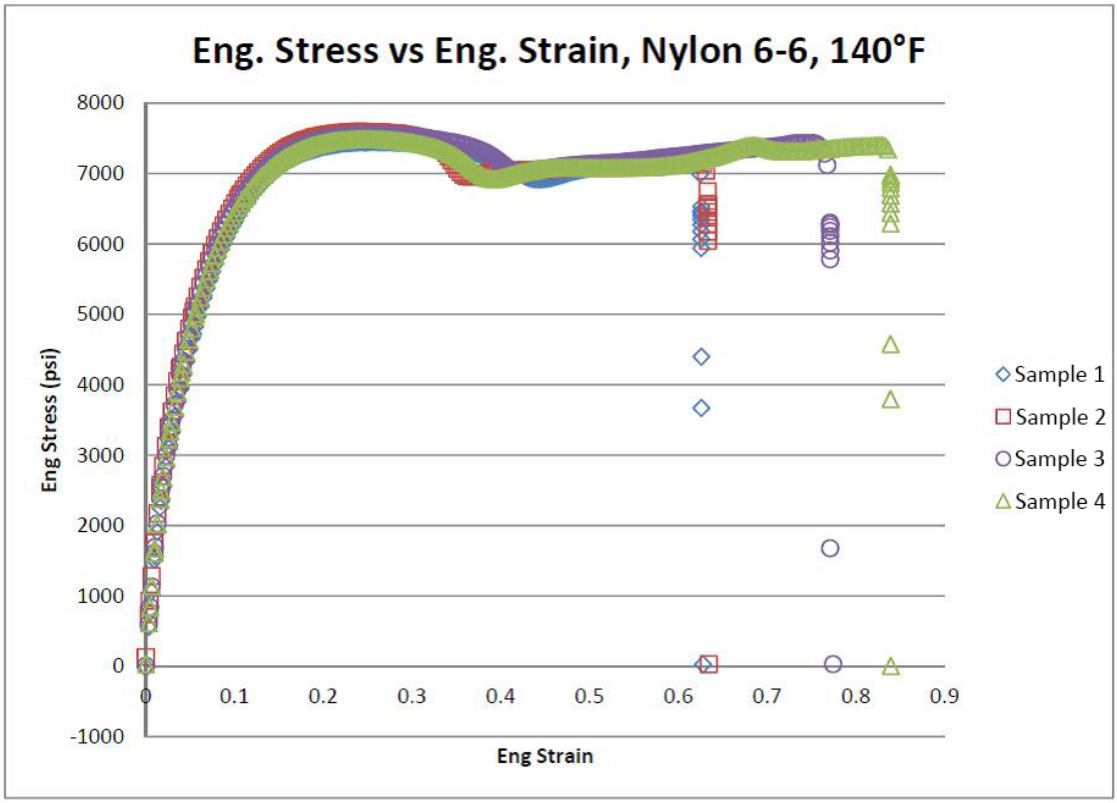

Figure 3: A Plot of Engineering Stress vs. Engineering Strain for Nylon 6-6 at 60°C.

- **Hardness and Chemical Attack Testing:** For this study, the hardness of nylon 6-6 samples were measured as a function of exposure to chemical attacks. The average hardness of virgin samples was 115.5 ± 0.34 HRR. After 48 hours, all samples soaked in acid were partially to completely gelled. In terms of observed severity, the nitric acid acted on the samples the fastest, gelling almost all samples after only 24 hours, followed by hydrochloric and then sulfuric. After 48 hours, the samples in the hydrochloric were completely gelled, and only small remnants of solid plastic remained in the sulfuric acid. This test method yielded no testable samples.

The test results of test coupons exposed to acidic vapor were tabulated and

shown in Table 1.

Table 1. Nylon 6-6, 48 Hour Acid Vapor Test.

	Hardness Scale = HRR					
	HCl (Wet)	HCl (5-Day Dry)	HNO3 (Wet)	HNO3 (5-Day Dry)	H2SO4 (Wet)	H2SO4 (5-Day Dry)
Glass Average	114.4	114.0	-*	114.9	115.2	114.9
Vapor Average	109.6	111.6	71.6	110.0	112.3	110.0
Vapor StdDev	3.38	2.14	27.2	8.47	3.28	3.30

*These samples were not tested due to the softness of the slides.

The samples exposed to nitric acid showed the most sensitivity, losing an average 38% of the original hardness, with a standard deviation of 27.25 HRR. Hydrochloric and sulfuric were the second and third detrimental acids tested, although they both had significantly less effect on the samples. These two acids exhibited a reduction in hardness of only 5% and 2.75%, respectively, from the virgin hardness.

Also, an important trend was shown in the recovery of hardness in the nylon after five days of open-air drying. The samples exposed to nitric acid vapor recovered an average of 48.46% of their hardness from the soaked hardness, with a standard deviation of only 8.47 HRR. That is a reduction in hardness of 8.03% from the virgin hardness—a substantial amount of recovery.

- **Stress Analysis of the Fire Foe™ Tube:** The Fire Foe™ system is innately simple in its design, and as such lends itself well to classic analytical pressure vessel theory. The analysis is further simplified by thin wall approximations. Thin wall

approximations are within 5% of exact values for thickness to radius ratio, $t/r_i < 0.1$. The following tube dimensions were used in all subsequent analyses:

$$Nominal\ OD = 1.500"\ (38.1\ mm)$$
$$Nominal\ ID, d_i = 1.370"\ (34.8\ mm)$$
$$Nominal\ Wall\ Thickness, t_n = 0.065"\ (1.65\ mm)$$
$$Reduced\ Wall\ Thickness, t_r = 0.055"\ (1.40\ mm)$$

$$\frac{t_r}{r_i} = \frac{0.055}{0.0685} = 0.08$$

It should be noted that slight variations exist in the wall thickness around the tube, in both the full-thickness and reduced-thickness areas of the tube.[3] The nominal reported thicknesses were used for all calculations and it should be noted that the minor variations have negligible effects on the stress calculations presented.

The critical area of the tube in terms of stress analysis is the activation strip, or reduced wall section, of the tube. The maximum tangential stress is calculated by[21]

$$\sigma_{t,max} = P \cdot \frac{d_i + t}{2 \cdot t} \quad [1]$$

The maximum axial stress is calculated by

$$\sigma_{x,max} = P \cdot \frac{d_i}{4 \cdot t} \quad [2]$$

where P is the internal pressure, t is material thickness and $(d_i + t) / 2$ is the average radius. At room temperature, the typical charge on the Fire Foe™ tube is listed as 698.4 kPa at 21.1°C. Therefore, the maximum stresses in the tube are:

$$\sigma_{t,max} = 9.03\ MPa$$

$$\sigma_{x,max} = 4.52\ MPa$$

At room temperature, the average ultimate tensile strength (UTS) of nylon 6-6 is listed as 70.3 MPa. Using max shear failure criteria, with thin-walled assumptions of negligible through-thickness stress, a safety factor against failure, X_{uts}, is calculated as

$$X_{uts} = \frac{\sigma_{uts}}{\sigma_{t,max}} = \frac{70.3}{9.03} = 7.79 \text{ at } 21℃ \quad [3]$$

The largest quantified degradation in ultimate strength is created from exposure to elevated temperature, from 70.3 MPa at 21°C to 20.7 MPa at 149°C. It is notable that the glass transition temperature, T_g, of nylon 6-6 is listed between 50°C and 75°C.[22] Analysis of the stress conditions at 150°C would be as follows:

Following the ideal gas law for a constant volume process,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad [4]$$

using absolute temperatures of 294 K and 423 K and the initial pressure of 698.4 kPa, the pressure in the tube, P_2, is 1.00 MPa, for a maximum tangential stress of

$$\sigma_{t,max} = P_2 \cdot \frac{(d_i + t)}{2 \cdot t} = 12.9\ MPa$$

Using the ultimate tensile strength of nylon 6-6 at 149°C of

$$\sigma_{uts}^{149℃} = 20.7\ MPa$$

A safety factor for ultimate failure is calculated as

$$X_{uts} = \frac{\sigma_{uts}}{\sigma_{t,max}} = \frac{20.7}{12.9} = 1.60 \text{ at } 149℃$$

With a safety factor still greater than 1, this analysis shows that reduction of the materials ultimate strength is not the driving mechanism for failure of the tube. Rearranging equation [1] to solve for the pressure at the ultimate strength of the material, the rupture pressure, yields

$$P = \frac{2 \cdot t \cdot \sigma_{uts}}{d_i + t} \qquad [5]$$

The resulting internal pressure required to rupture the tube, P_r, is

$$P_r = 5.44\ MPa \text{ at } 21℃$$
$$P_r = 1.60\ MPa \text{ at } 149℃$$

This represents an increase of 160% over the ideal temperature adjusted pressure at 149 °C. A cursory thermodynamic analysis of the DuPont materials contained in the Envirogel shows that the components are held in a supersaturated condition. A condition which would indeed undergo a rapid volumetric expansion as temperature is increased and a phase change occurs. An exact description of the thermodynamics of the Envirogel components is beyond the scope of this study; however, it is felt that the underlying failure mechanisms have been identified and influenced both by the Envirogel expansion and the tensile strength reduction.

- **Brittle Failure of the Fire Foe™ Tube:** The fracture toughness of a component is related to the geometry and loading of a part through the equation [6]

$$K_{IC} = F \cdot S_g \sqrt{\pi \cdot c_{critical}} \quad [6]$$

where F is a geometric factor, S_g is the applied normal stress, and $C_{critical}$ is the critical crack length for brittle fracture.

Setting F=1 for a center crack in a large plate (and best matching the tube geometry), equation [6] can be solved for critical crack length, $C_{critical}$, as seen in equation [7].

$$c_{critical} = \frac{K_{IC}^2}{\pi \cdot \sigma_{t,max}^2} \quad [7]$$

where the applied stress, S_g, becomes the largest component of normal stress $\sigma_{t,max}$. The critical crack length represents the largest crack the material can support before undergoing brittle failure. In the application of a thin walled pressure vessel, the critical crack length is compared with the material thickness to calculate a ratio commonly known as the leak-before-break safety factor, X_c. If $C_{critical}$ is larger than the material thickness, it is assumed the structure will leak from a small crack and thus remove the stress. If $C_{critical}$ is smaller than the material thickness it is predicted that the structure will fail in a brittle manner from rapid crack growth.

At room temperature, the *fracture toughness*, K_{IC}, of nylon 6-6 is reported to range from 1.5 – 3.0 MPa*m$^{1/2}$ [23,24,25,26] The Fire Foe™ system at room temperature under the tangential stress in the tube from equation [2] above (9.03 MPa) and K_{IC} = 1.5 yields a critical flaw size of *8.8 mm*. For a reduced wall thickness of *1.4 mm*, this provides a safety factor of

$$X_c = \frac{8.8}{1.4} = 6.3$$

Solving for the fracture toughness with a critical crack length equal to the material thickness, at standard pressure, results in

$$K_{IC} = 9.03\sqrt{\pi \cdot 0.0014} = 0.599\ MPa\ \sqrt{m}$$

This value of fracture toughness therefore represents the value against which experimental measurements should be compared. Above the glass transition temperature T_g, (50°C to 75°C),[25] Nylon fails in a ductile manner. Therefore these calculations do not need to be repeated for elevated temperature conditions.

- **Finite Element Analysis:** To begin this portion of the study, the cross-section of the Fire Foe™ tube was created in a solid modeling package. The solid model of the tube exploited the radial line of symmetry of the tube from the center of the reduced thickness area. The drawing was exported to the FEA program ANSYS. The symmetry is placed as a boundary condition in the ANSYS analysis, which reduces the number of nodes required for analysis and speeds the time to solution. Element type PLANE183 was used; this is a quarter-point element with mid-side nodes. To further streamline the FEA model, a plane strain condition was imposed. The mesh sensitivity was checked and the resulting satisfactory mesh geometry was used for all subsequent FEA runs. The internal pressure utilized in the analytical analysis was applied to the inner wall of the tube, and the Von Mises stress in the thin section of the tube wall was examined and is shown in Figures 4 and 5.

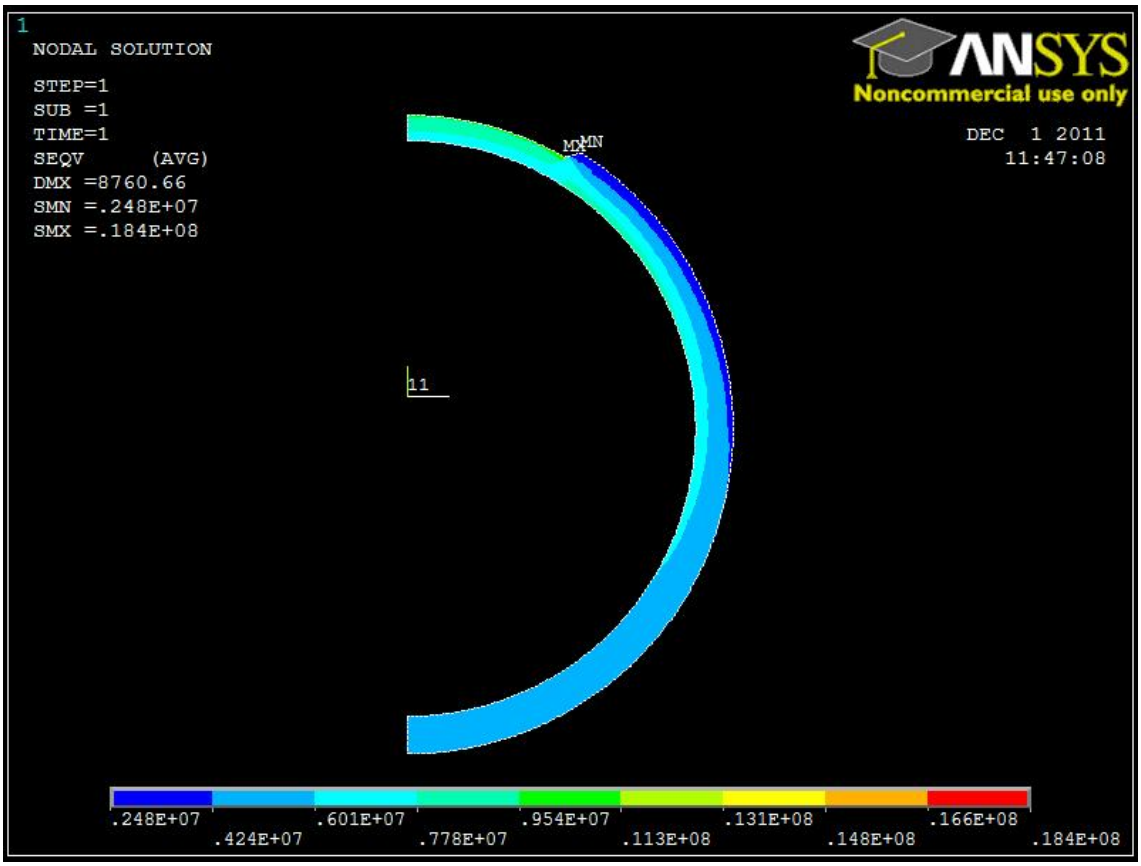

Figure 4. FEA Solution of the Fire Foe™ Geometry under a Pressure Loading of 698 kPa at 21 °C. Showing a Von Mises Stress Distribution.

It can be seen in Figure 4 that the reduced section (located at the top of the model shown) does indeed carry the highest stress level in the part. A close up of this region is shown in Figure 5.

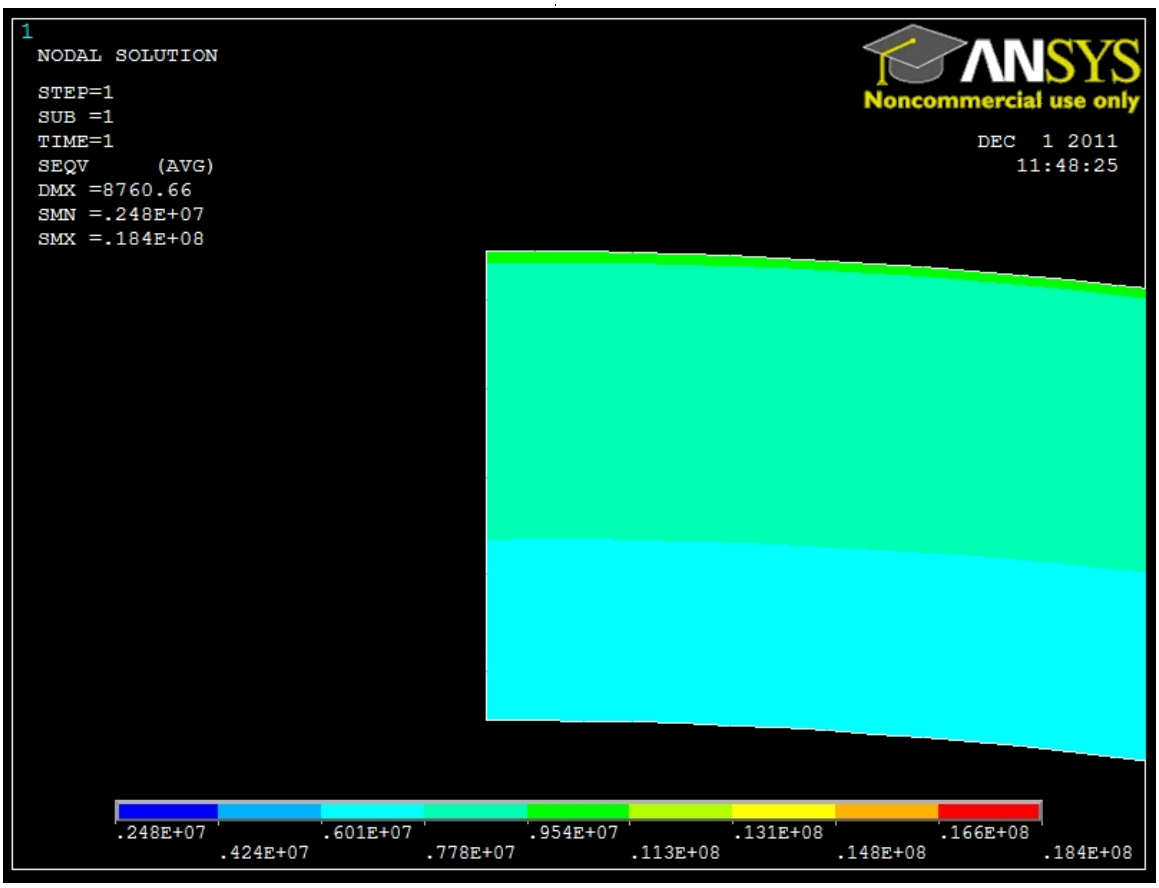

Figure 5. Close-Up of the FEA Solution Showing the Stress Distribution through the Thickness of the Reduced Section of the Tube.

Numerical stress values for the reduced thickness region are shown in Table 2 as function of location within the tube.

Table 2. FEA Predicted von Mises Stresses as a Function of Radius.

Radius (mm)	Stress (Mpa)
18.8	9.62
18.6	9.32
18.5	9.02
18.4	8.76
18.2	8.50
18.1	8.19
18.0	7.54
17.9	7.87
17.7	7.54

These values support the analytical solutions presented above utilizing the thin walled approximation. From these solutions, it was determined that more complex simulations were not necessary.

Discussion

No portion of this research was funded or directed by the vendor. After an extensive review of literature that exists on the properties of nylon 6-6, no critical areas of concern have been identified for the plutonium glovebox application of nylon 6-6.

Environmental effects listed in the above sections discuss the degradation of strength properties of nylon. Although few specifics are provided about the percentage of strength loss, a simple analysis shows that for failure to occur at static loading due to reduction of strength, the ultimate strength would have to be reduced 87.2% (from 70.3

MPa to 9.03 MPa). This percentage reduction is well beyond any reported values for environmental effects and is therefore considered a highly unlikely method of failure of the Fire Foe™ system.

The resulting internal pressure required to rupture the tube represents an increase of 160% over the ideal temperature adjusted pressure at 149 °C, and leads to the conclusion that the primary mechanism driving the activation of the Fire Foe™ tube is the dramatic increase in internal pressure associated with the phase change in the Envirogel components. A cursory thermodynamic analysis of the DuPont materials contained in the Envirogel shows that the components are held in a supersaturated condition, a condition which would indeed undergo a rapid volumetric expansion as temperature is increased and a phase change occurs. An exact understanding of the thermodynamics of the Envirogel components are not provided for this study; however, underlying failure mechanisms have been identified and influenced both by the Envirogel expansion and the tensile strength reduction.

Material failure can be broadly classified as either ductile or brittle in nature. Ductile failures are commonly accompanied by large plastic strains, and elongation, which can serve as an indicator for impending failure. This type of failure mechanism is most commonly seen in the nylon 6-6 at temperatures above the glass transition temperature, T_g, and a described in the previous section. Brittle fracture is identified by a sudden, or nearly instantaneous, failure of a material governed by uncontrolled crack growth through a material. The mechanical property associated with the crack growth is *fracture toughness*, K_{IC}. Fracture toughness is a term utilized in the field of Linear Elastic Fracture Mechanics (LEFM) and is based on an assumption of minimal plastic strain

prior to material failure. Additionally, fracture toughness can be defined as the ability of a material containing a crack to resist crack growth; and thus a rapid and uncontrolled fracture.

The tangential stress safety factor in the tube implies that for the tube to spontaneously fail in a brittle manner, the fracture toughness would have to significantly be reduced due to environmental degradation. At the expected maximum operating temperature for which the Fire Foe™ tubes would be exposed in nominal glovebox operations, the data between four samples at 60°C is satisfactorily consistent in ultimate stress, despite larger, but not anomalous, variations seen in failure strain, as shown in Figure 3.

The hardness of a material is a measure of the materials resistance to deformation and is related to the yield stress and fracture toughness of the material. Vickers hardness is suitable for thin materials, such as the wall of the Fire Foe™ tube. A critical drawback to the Vickers method is requirement of the surface finish to be very smooth. The Fire Foe™ tubes and virgin nylon dogbones were of acceptable surface finish; however, the acid treated specimens did not, and thus the Rockwell method was used on those samples.

Nylon 6-6 test coupons soaked in mineral acids showed that exposure to strong acids could be severely detrimental to nylon 6-6. The results of the vapor attack tests mimicked the results from the direct soak test. The large standard deviation in the samples exposed to nitric acid vapor is worthy of note as it indicates that even though all the samples experienced the same preparation and exposure, there was still substantial variance in hardness reduction, as shown in Table 1. The reason for this variance was beyond the scope of this investigation. However, the samples do regain a significant

amount of hardness after drying for five days. Nitric acid samples, which were reduced to 72% of their original hardness returned to 95% their original hardness after drying.

In metals, a decrease in hardness is often related to a decrease in the yield strength and an increase in ductility; however, this is a phenomenon not necessarily transferrable to polymer systems. Regardless, a decrease in polymer hardness due to acid exposure certainly should not be expected to result in an increase in yield strength. A decrease of strength should be anticipated, but the degree to which strength will decrease is not well-defined.

Without specific knowledge of acid concentrations to which the Fire Foe™ would be exposed, it is difficult state with absolute certainty that the product would perform as advertised. Furthermore, the test conditions created are not necessarily the worst case scenario. While the acids used were quite high in concentration, higher concentrations exist. The data would indicate that higher molarity solutions would only decrease the material properties of the nylon 6-6.

The stress analysis of the engineering component has identified a large safety factor in static failure of the Fire Foe™ system at least near room temperature. Even at 60ºC, the highest normal operating temperature anticipated by this study, the safety factor on ductile failure is 1.60. This means that material properties would need to significantly degrade before the system risks premature failure. It is supposed that any visual inspection procedure would identify such drops in material integrity. The analysis also shows that premature failure is the largest concern of long-term application, and not a change in the ability of the system to perform as designed. Stress analysis of the system shows that the deployment temperature is more likely driven by the internal stress

generated during a phase change of the Envirogel components than any material property reduction. Therefore, slight changes in glass transition temperature and fracture toughness will not significantly affect performance of the system.

The stress and failure analysis of the Fire Foe™ utilizes analytical and FEA techniques to determine the stresses and failure mechanisms of the nylon 6-6 system. The analysis identified that large reductions in both ultimate tensile strength and fracture toughness can occur without compromising the operational ability of the tube. It is also supported by calculations that do not predict failure with known material parameters. However, unknown changes of the tube's internal pressure are suspected to be the cause of tube failure when properly activated by temperature.

Questions still remain about the combined effects of material irradiation and environmental degradation. This study did not address these concerns; however, from the engineering analysis and data collected it is believed by the authors that combined effects will only alter the static strength of the system, and not affect the performance of the system regarding fire prevention. The static strength reduction implies that the system would become more prone to damage such as bumps and nicks within the glovebox environment.

Conclusions

The primary mechanism driving the activation of the Fire Foe™ tube is the dramatic increase in internal pressure associated with the phase change in the Envirogel components. Thin walled pressure vessel and Finite Element Analysis techniques identified a safety factor on material failure of 7.79. Therefore, large reductions in both

ultimate tensile strength and fracture toughness can occur without compromising the operational ability of the tube. It was observed that direct contact of the current model of Fire Foe™ tubes with strong acids would be highly catastrophic, causing premature failure due to gelling of the Nylon 6-6. Exposure to acidic vapors for 48 hours softened the material, although not to the point of gelling. Once the atmosphere was no longer acidic, the material hardened, returning to an average of 95% of the original hardness in the case of nitric acid vapor exposure. This suggests that short term exposure of the Fire Foe™ system to an acidic atmosphere would not impede the systems operation ability, particularly if the system is returned to a non-acidic atmosphere.

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References

1. Cournoyer, M.E.; et al. *J. Chem. Health Safety* **2014**, 10.1016/j.jchas.2014.09.014.
2. http://www.lm.doe.gov/land/sites/co/rocky_flats/closure/references/068-ORPs%20Report-2003-0011.pdf. Link verified September 14, 2015.
3. Rosenberger, M.S; et al. *J. Chem. Health Safety* **2014**, 20(6) 24-29.
4. Cournoyer, M.E. *J. Chem. Health Safety* **2014**, 21(4), 1-6.
5. Wilson, K.V.; et al. *Polymer Degradation and Stability* **2004**, 84(3), 439-449.
6. Cournoyer, M.E.; et al. *Royal Society of Chemistry*, Proceeding from Actinides 2005,

July 4-8, 2005, Manchester, England.

7. Cournoyer, M.E.; et al. *J. American Society of Mechanical Engineers*, Proceeding from WM'06, Tucson, Arizona, February 26 - March 2, 2006.
8. Milsap, D.W.; et al., "Evaluation of Nylon 6,6 in Use in Fire Foe™ Fire Suppression Systems within Plutonium Gloveboxes," *Nuclear Technology*, accepted for publication.
9. Thanki, P.N.; Singh, R. P. *J. Macromolecular Science-Reviews in Macromolecular Chemistry and Physics* **1998**, C38(4), 595-614.
10. Fairgrieve, S. *Plastics Engineering* **2008**, 64(7), 34.
11. Cournoyer, M.E. et al., *J. Chem. Health Safety* **2009**, 16(1), 4-10.
12. Brown, L.; et al. *J. Applied Polymer Science* **2005**, 97(6), 2476-2487.
13. Vachon, R.N.; et al. *Textile Research Journal* **1968**, 38(7), 716.
14. Nair, S.V.; Donovan, J. A. *J. Applied Polymer Science* **2001**, 81(2), 494-497.
15. George, G.A.; Oshea, M. S. *Polymer Degradation and Stability* **1990**, 28(3), 289-310.
16. Aytac, A.; et al. *Nuclear Instruments & Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **2007**, 265(1) 271-275.
17. Aytac, A.; et al. *Radiation Physics and Chemistry* **2010**, 79(3), 297-300.
18. Ellison, M.S.; et al. *Journal of Materials Science* **1984**, 19(1), 82-98.
19. Ellison, M.S.; et al. *Textile Research Journal* **1989**, 59(11), 657-660.
20. Gee, D.R.; Melia, T. P. *Polymer* **1970**, 11(4), 192.
21. Shigley, J.E. *Shigley's Mechanical Engineering Design, 8th ed.* McGraw-Hill: 2006.
22. Greco, R.; Nicolais, L. *Polymer* **1976**, 17(12), 1049-1053.
23. Averett, R.D.; et al. *Composites Science and Technology* **2006**, 66(11-12), 1671-

1681.

24. Chen, J.; et al. *Journal of Applied Polymer Science* **2010**, 115(1), 588-598.

25. Wyeth, D. J.; Atkins, A.G. *Engineering Fracture Mechanics* **2009**, 76(18), 2690-2697.

26. Yu, Z.Z.; et al., *Polymer International* **2004** 53(8), 1093-1098.