Polyimide x-ray filter substrates optimized for cryogenic temperatures

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ABSTRACT

New generation x-ray instruments for spacecraft such as ASTRO-E and CONSTELLATION-X have very specialized requirements, notably operation at cryogenic temperatures. Luxel Corporation, under a NASA Phase I SBIR contract, undertook demonstrating feasibility of producing polyimide films suitable for use as x-ray filter substrates specifically optimized for cryogenic applications. 5000Å thick polyimide films were processed using different cure cycles, and burst pressure (tensile strength) analyses were performed at 293, 77, and 4 Kelvin (K). Test data showed that polyimide films are inherently stronger at cryogenic temperatures than at room temperature (20.5% at 4K). Through cure modification, film strength was increased an additional 9% at 4K over that of the standard cure clearly showing the feasibility of film optimization.

Keywords: X-ray filters, cryogenic, polyimide, thin films, microcalorimeters, bolometers, NIF

1. INTRODUCTION

Based on previous research, it is believed that for x-ray filter substrates, polyimides have the highest strength of the polymers available. Figure 1 clearly demonstrates the higher strength afforded by polyimide over the previous standard polymer, Lexan. Considering that x-ray filters are extremely thin (on the order of 500Å to 5000Å thick) any improvement in strength results in filters that are more robust and better able to survive the environments associated with spacecraft launch. Stronger films will also be more reliable for long-term operation in space. For the newest concept high-throughput, high-resolution x-ray instruments, this means survival of launch acoustic and vibrational loads as well as long-term operation at temperatures in the milliKelvin range. Structural integrity of the filters used in these missions is critical. Damage of the thin foil filter during launch or operation could compromise the mission, potentially swamping the detectors with stray radiation, thermally overloading the cryogen and/or critical loss of instrument cryogen through leakage.

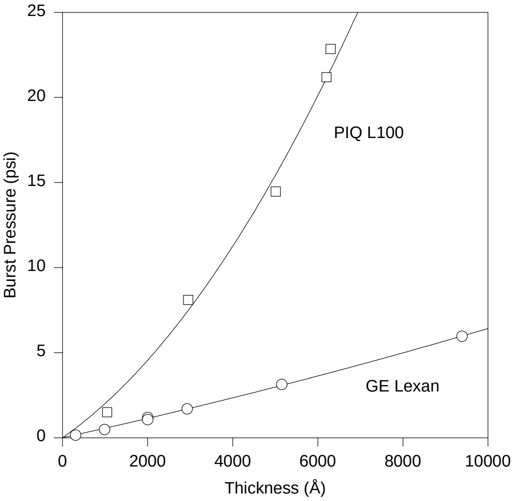

Figure 1. Burst pressure vs. thickness for polyimide and Lexan. Prior to the development of ultra thin freestanding polyimide films for x-ray applications, Lexan was the polymer most often chosen as a rugged filter substrate.

Luxel Corporation has developed unique manufacturing processes to produce thin polyimide filters for x-ray applications[1]. These polyimide films were developed for a broad range of applications. The success of this work has led to the selection of five polyimide-supported blocking filters for NASA Goddard's X-Ray Spectrometer (XRS), part of the ASTRO-E mission. These filters prevent ultraviolet and infrared radiation from reaching the detector, while not overly attenuating the x-ray radiation. The operating temperatures for these filters range from 6mK to 270K depending on the location of the filter[2].

Cryogenic applications for thin films have been increasing. Applications such as new detectors operating in the milliKelvin temperature range and inertial confinement fusion targets for the National Ignition Facility are pushing the limits of currently manufactured thin film materials.

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The focus of this project is to explore the feasibility of developing polyimide films specifically engineered for operation at cryogenic temperatures. Films optimized for this temperature regime will be incorporated into filters needed for high-resolution x-ray spectroscopy using microcalorimeters.

Polyimide has proven a reliable filter substrate time and again. However, further research is needed to ensure continued dependability for the new cryogenic detectors. The mechanical behavior of polyimide changes radically as temperature drops below 100K.

Mechanical properties

Polyimide exhibits a ‘typical’ stress-strain behavior at temperatures above 100K; a linear elastic region, yield point, plastic deformation region and ultimately sample failure are observed. As temperature decreases, however, both the inter polyimide chain and intra polyimide chain bond lengths decrease, increasing bond/film strength. With decreased thermal energy, the conformity of the polymer chains becomes increasingly fixed. As the chains become more rigid, failure tends to be more brittle with only slight yielding observed at 77K and effectively none observed at 4K[3].

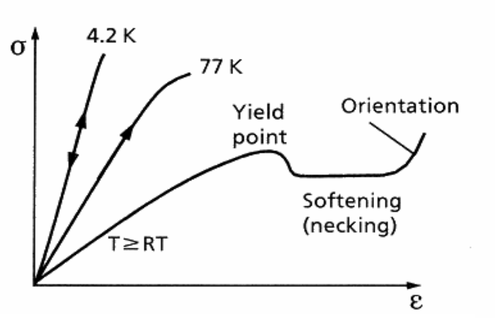

Figure 2. Stress-strain curve at different temperatures[5].

Though significant testing has been performed on bulk polyimide, thin film properties can vary significantly from those of the bulk material. As an example, the shear stress required to cause plastic deformation can be estimated by the relationship $\tau = \mu b / l$, where *b* is the Burgers vector and *l* is the distance between dislocation pinning points in the material. Substituting film thickness for *l* shows film strength varies inversely with film thickness[4]. Film thickness has also been shown to have a direct effect on the film’s coefficient of thermal expansion[5] (CTE).

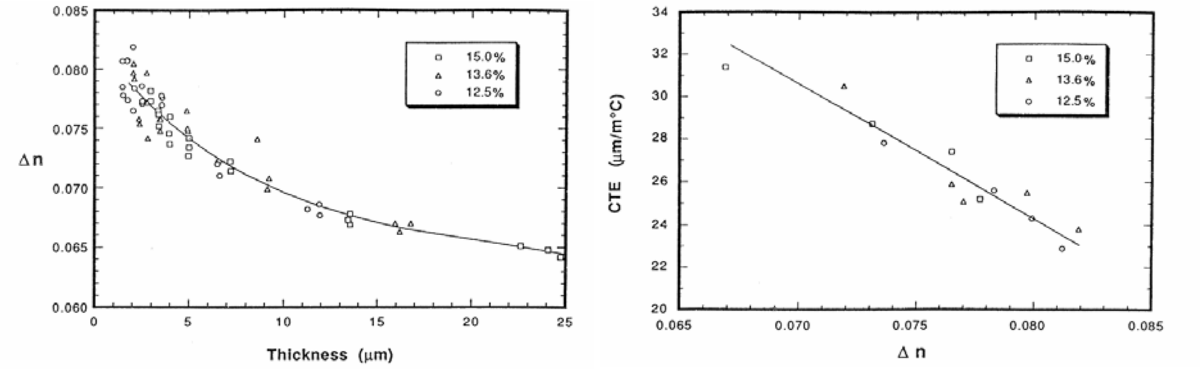

Figure 3. Effect of film thickness on CTE form PMDA/ODA.[5]

Methods of measuring mechanical properties such as stress, strain and various moduli in bulk materials are relatively simple and are commonly used. Most materials (including polyimide) have been extensively tested and characterized.

When sample thickness drops into the sub-micron range, the problems associated with sample production, handling, mounting and measurement render the standard techniques impractical.

One method of testing thin film properties is the bulge test. In bulge testing, the target film is epoxied to a test frame with an aperture of a known size. The sample is then placed in a pressure test fixture and pressure is applied to cause a deflection. The pressure and corresponding film deflection are then measured. The film’s stress and strain can be derived by the relations:

$$\sigma = \frac{pa^2}{4ht} \qquad \varepsilon = \frac{2h^2}{3a^2}$$

where *p* is the applied pressure, *a* is the aperture radius, *h* is the height of deflection, and *t* is the target film thickness.

Because no significant yielding is expected in the cryogenic temperature range and due to the difficulties of measuring deflections at 77 and 4K, it was deemed appropriate to use a burst pressure test as a relative measure of film strength. The burst pressure test employs the same target filter setup as bulge testing, but only the pressure at film failure is recorded. This pressure is then used directly to compare film strengths.

2. TESTING

The initial feasibility study was guided by three primary questions:

- What is the effect of ambient temperature on the burst pressure (tensile strength) of standard polyimide films?
- Can the burst pressure be altered by changes in the cure treatment?
- Can the strength of the polyimide be optimized for cryogenic operation?

Original plans called for the use of a vacuum dewar to perform testing at 77K, 15K, and 4K. Due to the relatively high overhead (both in time and money) associated with cryogenic testing, initial estimates from the subcontractor, Ball Aerospace, projected that approximately 18 tests could be conducted using their facilities during the feasibility study.

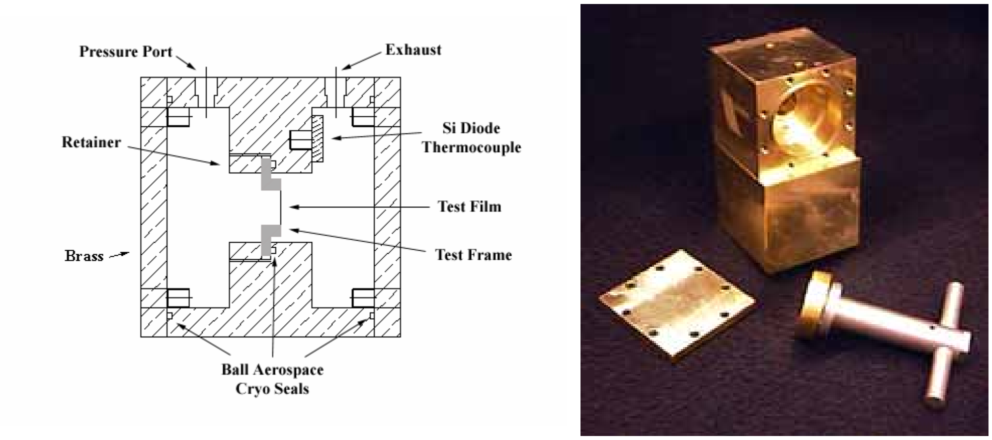

Figure 4. Burst test fixture.

Through the help of Ball Aerospace, a burst test apparatus was designed that could be immersed directly in the cooling medium, greatly reducing test cycle time and expense associated with complex vacuum dewar systems (see **Figure 4**).

The test fixture was machined from a solid block of brass, with an additional block of brass attached to the base as a heat sink. The test film/frame are secured in the test fixture by a threaded brass retainer. A soft metal gasket seals the fixture and frame. Once assembled, the chambers on both sides of the film are evacuated to prevent condensation on cooling. An equalizing valve is used between the chambers to prevent a differential pressure across the film during evacuation. Once evacuated, the fixture is immersed in cryogen, either liquid nitrogen (LN_2) or liquid helium (LHe). After the fixture temperature (as indicated by a Si diode thermocouple) stabilizes, the equalizing valve is closed and helium gas is admitted to the chamber upstream of the film. Helium pressure is increased and the maximum differential pressure is recorded.

The direct immersion technique precluded testing at 17K and also introduced the potential problem of different cool-down rates from the different cryogens. After careful consideration, it was decided that increasing the number of sample tests would provide a greater benefit to proving feasibility outweighing the drawbacks mentioned above. The more stringent controls obtainable through the use of the vacuum dewar will be employed in later stages of this research.

Due to the efficiency of the direct immersion testing, a total of 42 cryogenic tests were conducted, more than double the initial estimate.

2.1 Effect of ambient temperature on burst pressure.

Based on bulk properties research, it was expected that the yield strength (as indicated by burst pressure) would increase with a decrease in burst temperature (See **Figure 5**). Though LN_2 and LHe burst pressures were higher than those obtained at ambient temperatures (as expected), burst pressures obtained during LHe testing were unexpectedly lower than the LN_2 results (see **Figure 6**).

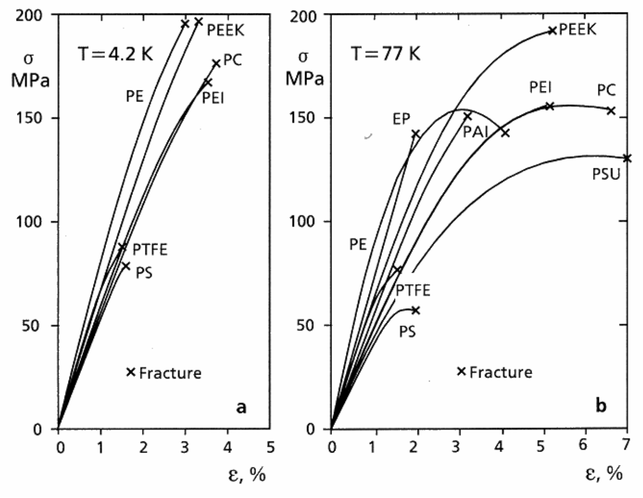

Figure 5. Stress-strain curves of several polymers at 4.2K and 77K[3].

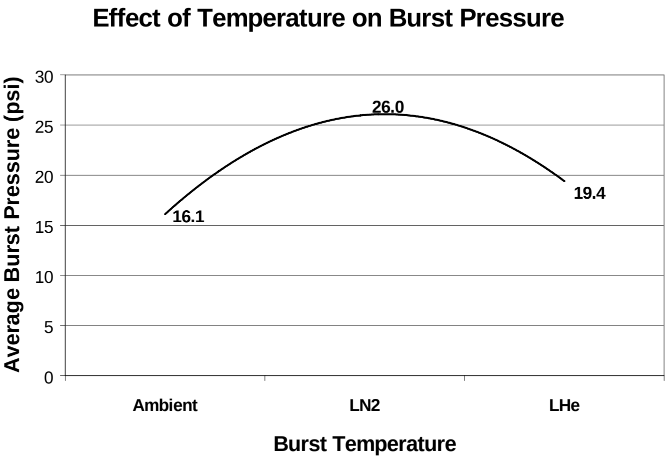

Figure 6. Burst pressure as a function of burst temperature.

It is unclear whether the LHe burst pressures are lower than the LN_2 pressures because of a fundamental property of the polyimide film or due to external influences. The effect of factors such as additional stresses due to the mismatch in CTE between the frame and film materials between 77K and 4K, or the difference in cool-down rate between immersion in LN_2 and LHe, have not been evaluated. Though every attempt was made to minimize experimental error through randomization and repeatability, the additional apparatus required to consistently control cool-down rate to 77K and then to 4K were beyond the scope of this phase of the project.

One other observation worthy of note is in the area of yielding. As stated above, no yielding is expected in films tested at 4K. Once the films burst, they typically are carried away in the exhaust piping. One film, however, remained intact after a burst at 4K showing a surprising degree of yielding (see **Figure 7**). Localized yielding may occur at high strain rates due to adiabatic heating. If the strain rate is sufficiently high, heat production may exceed removal rate, enhancing plastic deformations[3]. Though this behavior has been noted at 77K, the effect of localized heating was not thought capable of producing sufficient temperatures to allow deformation of this magnitude at 4K. This effect is largely unexplained at this point in time and is the subject of ongoing research.

Researchers have performed cryogenic characterization of many types of polyimides. Overall response trends may be extrapolated from bulk material behavior. However, it is clear from the initial results that thin films can behave in unique and unexpected ways. A significant portion of the ongoing research will focus on characterizing polyimide thin film cryogenic properties including *in-situ* stress strain measurements.

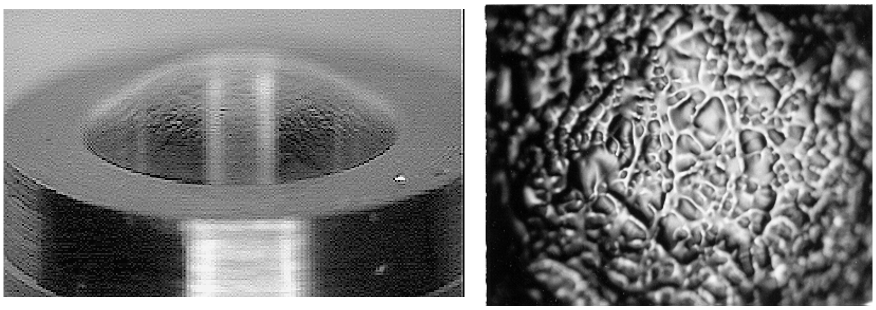

Figure 7. Images of a relatively intact film after burst at 4K showing a) the extent of overall film bulge and b) film surface showing the microscopic pattern of yielding.

2.2 Effect of cure process on burst pressure.

Various processes of polyimide thin film production are well known and widely used. For this project, semi-crystalline BPDA/PPD polyimide films were produced by spin casting and subsequent thermal imidization. The way in which the polyimide is imidized contributes greatly to the mechanical properties of the film.

To determine the effect of cure treatment on the strength of thin polyimide films at cryogenic temperatures, the cure process currently used by Luxel was evaluated. Four parameters were identified as basic to the polyimide cure cycle: heat-up rate, maximum cure temperature, duration of cure, and rate of cooling to ambient. Heat-up rate affects the degree of stress produced in the film due to the mismatch in CTE of the polyimide and the substrate. Ultimate cure temperature and cure time affect the degree of imidization. Cool-down rate affects the degree of crystalinity of the semi-crystalline BPDA/PPD[5]. It was not the purpose of this research to quantify each of these factors individually but to evaluate their combined affect on the resulting strength of the film.

Given the limited number of samples that would be available, to properly address the questions of feasibility with such a limited database, it was essential to develop an efficient test matrix. A factorial design approach was adopted to make as efficient use as possible of the data that could be obtained within the limitations of the project. In the factorial design each of the cure process variables is assigned a high (+) and low (-) state. During testing, all combinations of the variables are explored simultaneously. One of the primary benefits of the factorial design is efficiency. As well as evaluating the effects of the primary variables, the factorial design evaluates interactions between the variables being tested. For example, in addition to showing how the ultimate cure temperature or heat up rate affects burst pressure, the degree to which heat-up rate contributes to the effect of ultimate cure temperature is also determined. The factorial test matrix used for this work required 16 tests, in contrast to the 64 tests that would be required to achieve the same accuracy with standard test schemes[6,7].

Testing states for the four variables were selected both to cover a statistically significant range and also to produce viable films. The original statement of work called for production of 1000Å films cured to 450°C. Luxel has produced polyimide films below 500Å, however, 1000Å films imidized at temperatures above Luxel's standard cure temperature could not be recovered from the casting substrate. Through trial and error, it was determined that 5000Å films could be produced with cures as high as 400°C. The final cure values selected are shown in **Table 1**. Test films were produced using all possible combinations of these states.

	Parameter Values		
Test Parameters	Min.	Nominal	Max.
Heat-up rate (°C/min)	3.125	6.25	6.25
Ultimate cure temp. (°C)	300	325	400
Cure time (minutes.)	30	40	60
Cool-down rate* (°C/min.)	1	2.25	2.25

Table 1. Factorial test parameters.

Treatment	Test Order	Cure Profile				Test Results		
		Heat –up rate (a) °C/min	Cure Temp (b) °C	Cure Time (c) Min	Cool-down rate (d) °C/min	Ambient Burst psid	LN_2 Burst psid	LHe Burst psid
1	8	3	300	30	1	13.30	19.82	13.90
2	13	6.25	300	30	1	11.45	14.75	14.20
3	3	3	400	30	1	16.90	19.76	18.30
4	4	3	300	60	1	13.38	18.17	14.40
5	9	3	300	30	2.25	13.61	19.35	11.60
6	6	6.25	400	30	1	18.43	32.67	22.80
7	5	6.25	300	60	1	14.32	18.99	14.40
8	12	6.25	300	30	2.25	12.83	18.62	14.00
9	1	3	400	60	2.25	17.34	28.40	20.60
10	2	3	400	30	1	19.27	34.53	26.70
11	7	3	300	60	2.25	11.80	18.20	15.10
12	10	6.25	400	60	2.25	17.96	29.56	17.50
13	15	6.25	300	60	1	11.88	18.98	7.90
14	16	3	400	60	2.25	17.79	30.99	19.60
15	11	6.25	400	30	2.25	20.35	25.74	22.20
16	14	6.25	400	60	2.25	16.84	23.63	21.50

Table 2. Imidization profile test matrix. Results shown are normalized to 5000Å

2.3 Optimizing the strength of polyimide for cryogenic operation

Analysis of the factorial design results confirms that ultimate cure temperature is the preeminent factor controlling burst pressure. Increasing the cure temperature from 300°C to 400°C produced an average burst pressure increase of 53% and 61% on films tested at 77K and 4K respectively (See **Figure 8**.)

	Percent Effect	
Test Parameters	LN_2+/-2.5	LHe+/-1.4
Heat-up rate (°C/min)	-0.8	-0.7
Ultimate cure temp. (°C)	9.8	8.0
Cure time (minutes.)	0.2	-1.6
Cool-down rate* (°C/min.)	1.0	0.3

Table 3 Primary effect contributions

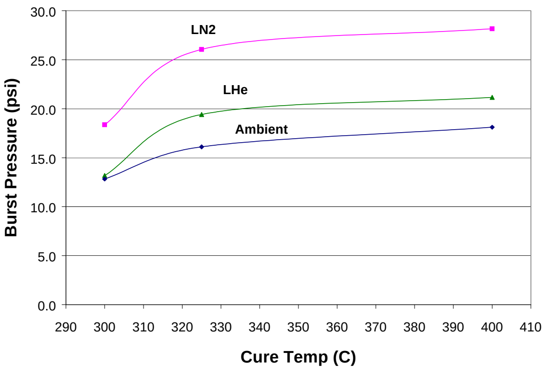

Figure 8 Testing shows burst pressure increase as a function of ultimate cure temperature

What was unexpected was how little apparent effect the other process parameters had on the final film properties. The relative contributions of the primary variables are tabulated in **Table 3**. Contributions of both the primary variables and their secondary interactions are shown in **Figure 9**. Second to ultimate cure temperature, cool-down rate contribution should be significant due to its effect on crystalinity. Crystalinity has been shown to have a significant effect on CTE below 70K^3. Changes in film crystalline content should result in a thermal stress on cooling to 4K and an attendant change in ultimate tensile stress. Two possible reasons no significant effect from varying cool-down was observed are a) cool-down rate may simply have no appreciable effect on cryogenic burst pressure or b) the lack of effect may be due to insufficient range in the cool-down rate states. Further testing is being conducted to verify the cool-down rate contribution.

3. CONCLUSIONS

Initial research results indicate that it is feasible to improve the mechanical characteristics of polyimide for operation at cryogenic temperatures. Film strength was improved by modifying the current polyimide production process (see **Figure 10**). On average, films cured at 400 °C were 9% stronger than those cured using the standard process (when burst at 4 K).

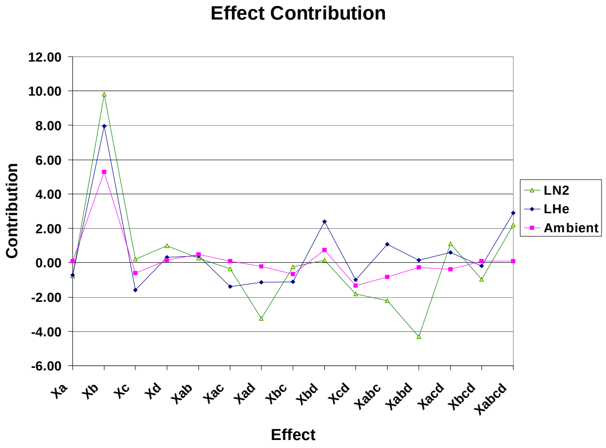

Figure 9. Relative effect of cure parameters on burst pressure

The positive result of strength enhancement with altered cure is very encouraging, but more extensive research is called for and is the focus of ongoing research. The data indicate that further increase in cure temperature should result in further enhancement in strength. One important result from the initial study is that present film processing techniques proved ineffective for producing ultrathin films cured at or above 400 °C because the films would not release from the casting substrate. Specifications for instruments such as the XRS for ASTRO-E specify filter substrates as thin as 750 Å for use at temperatures as low as 4mK. Therefore, significant work is required to develop new release agents and methods capable of producing the thinner films at elevated cure temperatures.

The XRS on ASTRO-E will fly a calorimeter detector with five x-ray filters. This mission has already procured flight filters that utilize Luxel's standard polyimide films as filters. The current design employs five thin foil filters in front of a calorimeter detector operating at 0.065 K. The Next Generation X-ray Observatory now incorporated into a NASA future mission CONSTELLATION-X will also employ a calorimeter array and will require x-ray filters. The baseline design for CONSTELLATION-X calls for major improvements in resolution and throughput over XRS. Improvements in the strength of the polyimide will allow the use of thinner filters and this will increase the mission throughput. As in the XRS, aluminum coating on the polyimide can still be used to control and reduce the head load.

Normally when an instrument is designed, the physical specifications of the film are derived from the band pass requirements of the instrument. These requirements are balanced against results from previous filter designs, and the films are produced. Once the films are fabricated, they are tested and the design is adjusted as necessary. In the absence of hard engineering data, this process is necessarily iterative. Researchers have performed cryogenic characterization of many types of polyimides. Overall response trends may be extrapolated from bulk material behavior. However, it is clear that thin films can behave in unique and unexpected ways. A significant portion of subsequent research is focusing on characterizing polyimide thin film cryogenic properties. The investigation of material properties such as Young's modulus, tensile strength, film creep, fatigue strength, strain rate sensitivity, and failure mode is an extensive process with many technical hurdles to be overcome. During instrument development, each design iteration adds cost and time to the design process. In this age of constricting budgets and shorter concept-to-flight times, the addition of comprehensive film characterizations to the design engineers' repertoire is potentially a *very* beneficial windfall of this continuing project.

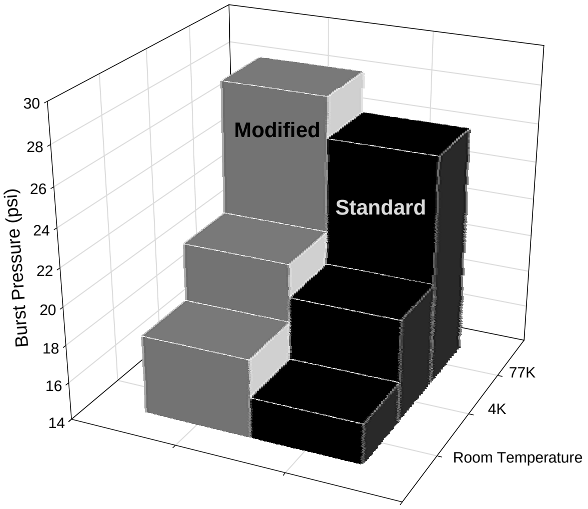

Figure 10. Enhanced cryogenic performance of modified polyimide films compared to standard process.

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