

NANO-ARAMID FIBER REINFORCED POLYURETHANE FOAM

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ABSTRACT

Closed cell polyurethane and, particularly, polyisocyanurate foams are a large family of flexible and rigid products the result of a reactive two part process wherein a urethane based polyol is combined with a foaming or “blowing” agent to create a cellular solid at room temperature. The ratio of reactive components, the constituency of the base materials, temperature, humidity, molding, pouring, spraying and many other processing techniques vary greatly. However, there is no known process for incorporating reinforcing fibers small enough to be integrally dispersed within the cell walls resulting in superior final products. The key differentiating aspect from the current state of art resides in the many processing technologies to be fully developed from the novel concept of milled nano pulp aramid fibers and their enabling entanglement capability fully enclosed within the cell walls of these closed cell urethane foams. The authors present the results of research and development of reinforced foam processing, equipment development, strength characteristics and the evolution of its many applications.

KEY WORDS: Aramid, Thermal Protection, Polyurethane Foams

NOMENCLATURE

Al = Aluminum
CEV = Crew Exploration Vehicle
CFC = Chlorofluorocarbon
CLV = Crew Launch Vehicle
HCFC = Hydrochlorofluorocarbon
HPLC = High Performance Liquid Chromatography
LEO = Low Earth Orbit
LH2 = Liquid Hydrogen
LOX = Liquid Oxygen
MDI = Diphenylmethane Diisocyanate
MSFC = Marshall Space Flight Center
N = Nitrogen
NDE = Non-Destructive Evaluation
OML = Outer Mold Line
O = Oxygen
RBV = Ratio by Volume
RBW = Ratio by Weight
TRL = Technology Readiness Level
TPS = Thermal Protection System

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I. Introduction

Urethane foam systems are utilized in a wide variety of commercial applications, including the roofing, boat building, automotive, medical, aerospace and defense industries. Its lightweight, conformability, great insulation qualities, relative high strength and ease of application technique make these foam systems a popular choice amongst designers. However, in aggressive environments these systems have their limitations even though their basic material characteristics are desired to be deployed. For instance, a more robust urethane foam thermal protection system (TPS) will enhance the functionality of the new Ares I Crew Launch Vehicle (CLV) Upper Stage by providing better margins, better resistance to hail & launch pad debris damage and reduced boil-off of cryogenics for loiter periods on the Ares V follow-on vehicle. Boat builders could possibly reduce laminate thickness, weight and labor costs for hulls with higher strength foam core systems. Roofing applications may experience longer life spans and resistance to damage in high wind areas.

At the onset, it was believed that the uniform incorporation of small, discrete fibers into foam systems could enhance the performance of the foam and result in a more robust material. Previous attempts to reinforce foams have failed for a variety of reasons not the least of which includes the novelty of the present solution to address nano scale effects during processing. It was postulated that the fiber would need to be fully incorporated into the cell walls, provide enhancing interfacial mechanistic effects with the cured polymer, compatible with existing spray techniques, not sacrifice the basic material characteristics and disperse enough to enhance heat rescission qualities. Kevlar® pulp was chosen to attempt to meet these requirements.

This paper discusses the results of NASA sponsored research from an Innovative Partnership Program (IPP) seed fund, cooperative efforts of E.I. DuPont in a Space Act Agreement and other suppliers contributing to this development of a materials process for introducing Kevlar® aramid fibers into foam systems in achieving robust foam while conserving the originally favored characteristics. Also, the research has revealed multiple discoveries relevant to the successful incorporation of fibers into one or both parts of urethane foam system raw materials to deliver robust final foam products.

II. Chemistry and Materials Behavior

“Rigid” urethane foams basically fall into two categories, polyurethane and polyurethane isocyanurate (PUIR) foams (e.g., polyethers and polyesters). “Flexible” urethane foam systems such as those used in the mattress industry and for car seats will not be discussed in this paper although their manufacture includes similar chemistries and processes and, if modified as for “rigid” foam systems, may lead to more robust products in this category. The foam “systems” are comprised of parts A & B from raw materials

originating from multiple sources. Part A is the isocyanate (typically a Diphenylmethane Diisocyanate or MDI) and Part B (or sometimes “R” for “resin”) is the polyol, catalysts, surfactants and the blowing agent. The Parts A & B are then proportionately sprayed or “poured” at a specified ratio onto a substrate such as aluminum in many cases or into a mold and in an exothermic reaction forms a protective closed cell foam insulation structure. Open cell foam systems are similarly manufactured and adaptable to this new material process, but are a subject of further investigation although some limited testing in this area was conducted during this research. The PUIR foams utilize an excess of isocyanate or higher isocyanate index (Part A/B ratio by weight) to create foams with better thermal stability and strength than the polyurethane foams.

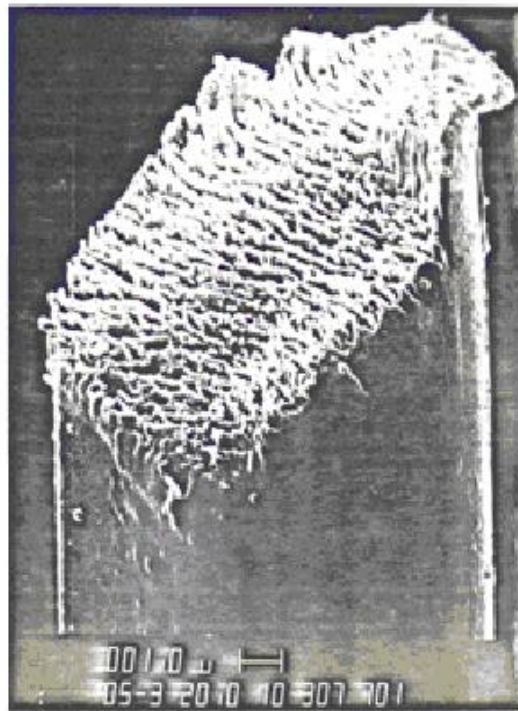
Polyurethanes contain carbamate groups, -NHCOO- , also referred to as urethane groups, in their backbone structure.¹ In general, urethane foams encompass both polyurethane and PUIR foams formed in the reaction of an isocyanate with a macro glycol, a so-called polyol based on polyethers, polyesters, or a combination of both. The stiffness associated with these foamed polymers is a product of the chemistry of the materials. In the realm of the solid state physicist and quantum chemist, the stiffness of these highly cross linked covalent bonded polymers can be estimated based on their chemical structure. Higher strength foams can be realized through higher functional polymeric isocyanates and higher functional polyols. These additional moieties increase the covalent cross link density and result in an increase in the Young’s modulus for the resultant foam. Additionally, cross linking is achieved through secondary reactions such as the trimerization of part of the isocyanate groups during formation of PUIR foams.

Kevlar® aramid fiber (poly para-phenyleneterephthalamide or PPD-T) was invented by DuPont in 1965. Kevlar® fiber was commercialized in 1970 followed by Kevlar® pulp in 1979. Kevlar® is a very unique material. It is a very soft, flexible fiber yet it has excellent mechanical and thermo-chemical properties. Its specific strength is 5x that of steel, has a very high modulus and a very low elongation, it is very tough, yet non-brittle, it has good wear resistance but is non-abrasive. The fiber is unaffected at cryogenic temperatures yet does not degrade until about 500° C. It has excellent radiation resistance and very good chemical resistance. Over the years Kevlar® has become a well known and well respected brand finding its way into a countless number of applications.

Kevlar® is a highly oriented fiber with a high level of crystallinity, which is surrounded by a weaker amorphous area. Its structure almost resembles a stalk of celery (See figure 1). This is an ideal structure to produce a pulp-like product which was introduced in 1979. Kevlar® pulp (See figure 2) is a short fiber having a length distribution with an average length of about 1 mm. Its diameter is still 12 μm , but it has submicron fibrils attached to the original fiber. By going from a fiber to a pulp the surface area was increased about 50x to about 9 m^2/g . This high surface area combined with the high degree of fibrillation provides for a very high effective aspect ratio and consequently an enormous amount of mechanical adhesion. As a result, Kevlar® pulp is widely used as reinforcement in brakes, automatic transmission papers, gaskets and elastomers for tires, belts, hoses, seals, etc. Kevlar® pulp is also used for rheology control and reinforcement in sealants, adhesives and coatings and for filter applications. However, there are certain

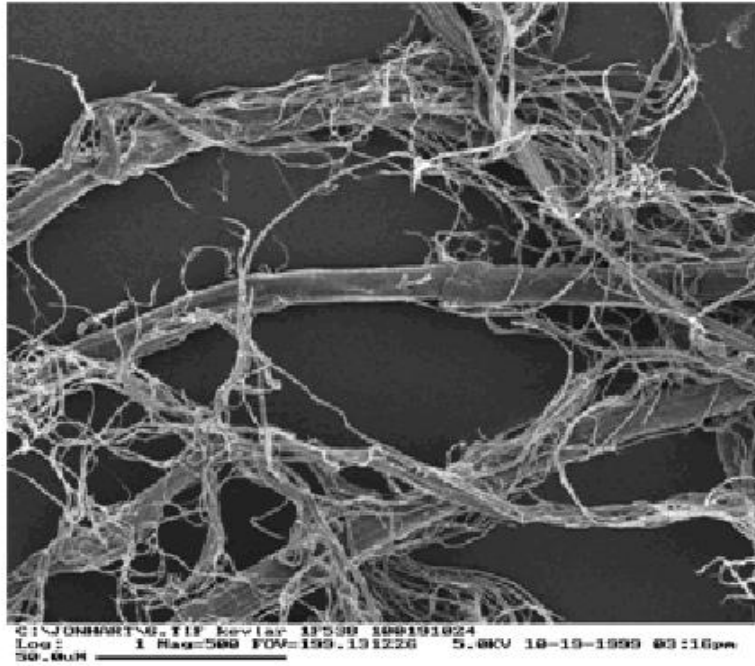
limitations with the commercial pulp forms, specifically; the fibers are too large and too coarse for some applications. These fibers can leave a textured surface on a coating, can plug in-line filters, can be difficult to spray and, are certainly too large to meet the intent of full incorporation into the cell walls of urethane foams.

Between 2000 and 2002, DuPont developed a new product form referred to as Kevlar® micro or nanopulp. This is really a family of very short film-like pulps. The size and shape are unique (See Figure 3, the circle superimposed on this figure represents a single Kevlar® filament with a 12 μm diameter), with surface areas up to 80 m^2/g . The average lengths of these fibers range from 100 μm down to about 0.1 μm and can be only a few nm or less in thickness dependent on application. These fibers typically provide better reinforcement and rheology control than the standard aramid pulps but with none of the limitations described earlier.



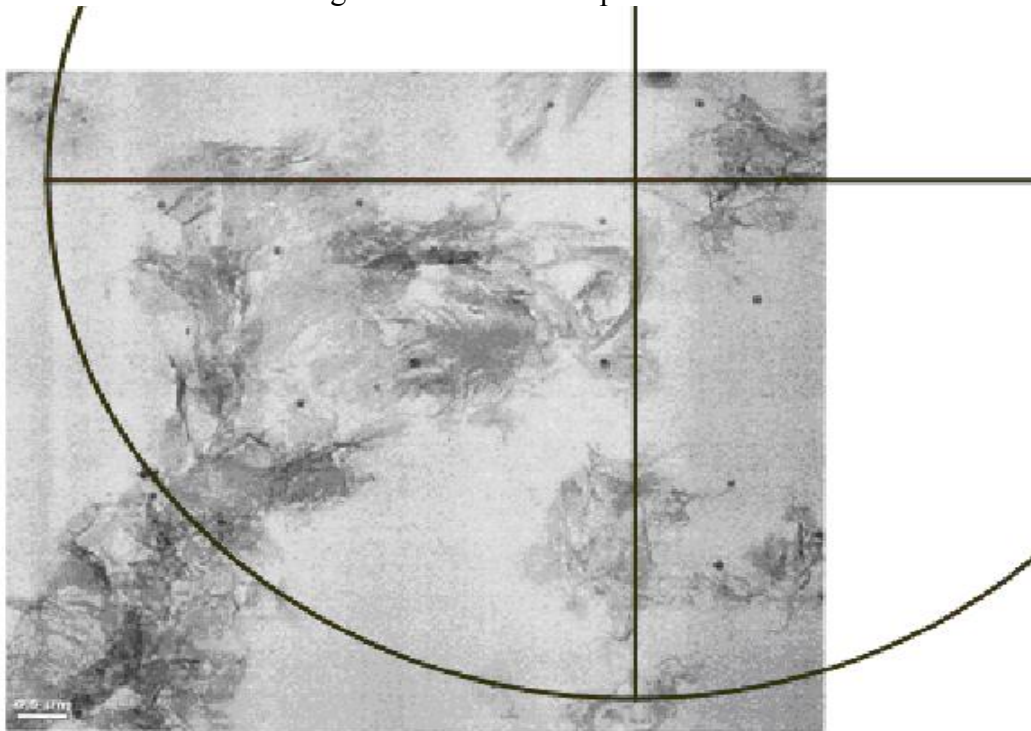
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Figure 1 – Kevlar® Cross Section



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Figure 2 - Kevlar® Pulp



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Figure 3 – Kevlar® Micro Pulp

However, there are still many trade-offs with regards to final chosen chemistry with or without the introduction of the relatively inert Kevlar® fibers. Catalysts are added to overcome acid impurities, enhance secondary linkage and control/balance the reactivity of the system. Surfactants are added to facilitate the formation of small bubbles necessary for a fine cell structure. Blowing agents have presented great challenges for the industry having to pursue non-CFC-11 versions. Alternative blowing agents such as HCFC's and HFC's have λ -values (m.W/m.K) of about 19.5 whereas CFC-11 blown foams have a value of 18.0 making the alternatives less efficient in their insulation performance due to the fact that the blowing agent accounts for 97% by volume of gas in these low density materials.¹ For instance, some formulations utilize a HCFC-141b and a little water which generate carbon dioxide as part of the blowing agent. Water affects the flow properties during the reaction period wherein the chemicals move from the low viscosity state of the original liquid mixtures to the polymerized foam. The configuration of the substrate can hinder the effective flow from initial "creaming" to the end of the rise during the foam expansion process and determines whether areas will be automatically sprayed, manually sprayed or poured. Similar to good chemistry, good flow is necessary to produce as close to an isotropic TPS material as possible. Introduction of Kevlar® fibers increases the viscosity of the raw materials and the deleterious effect on flow properties must be taken into consideration in any new application.

Closed cell urethane foams are a large family of flexible and rigid products the result of a reactive two part process wherein a urethane based polyol is combined with a foaming or "blowing" agent to create a cellular solid at room temperature. The ratio of reactive components, the constituency of the base materials, temperature, humidity, molding, pouring, spraying and many other processing techniques vary greatly. However, these conditions have a great impact on the final material properties. The cell wall thickness of typical rigid polyurethane foam is from 3 μ m at cell faces to 30 μ m at cell edges.² Figure 4 is an SEM photomicrograph view of typical polyurethane foam at the cell level (test sample produced during the course of this work).

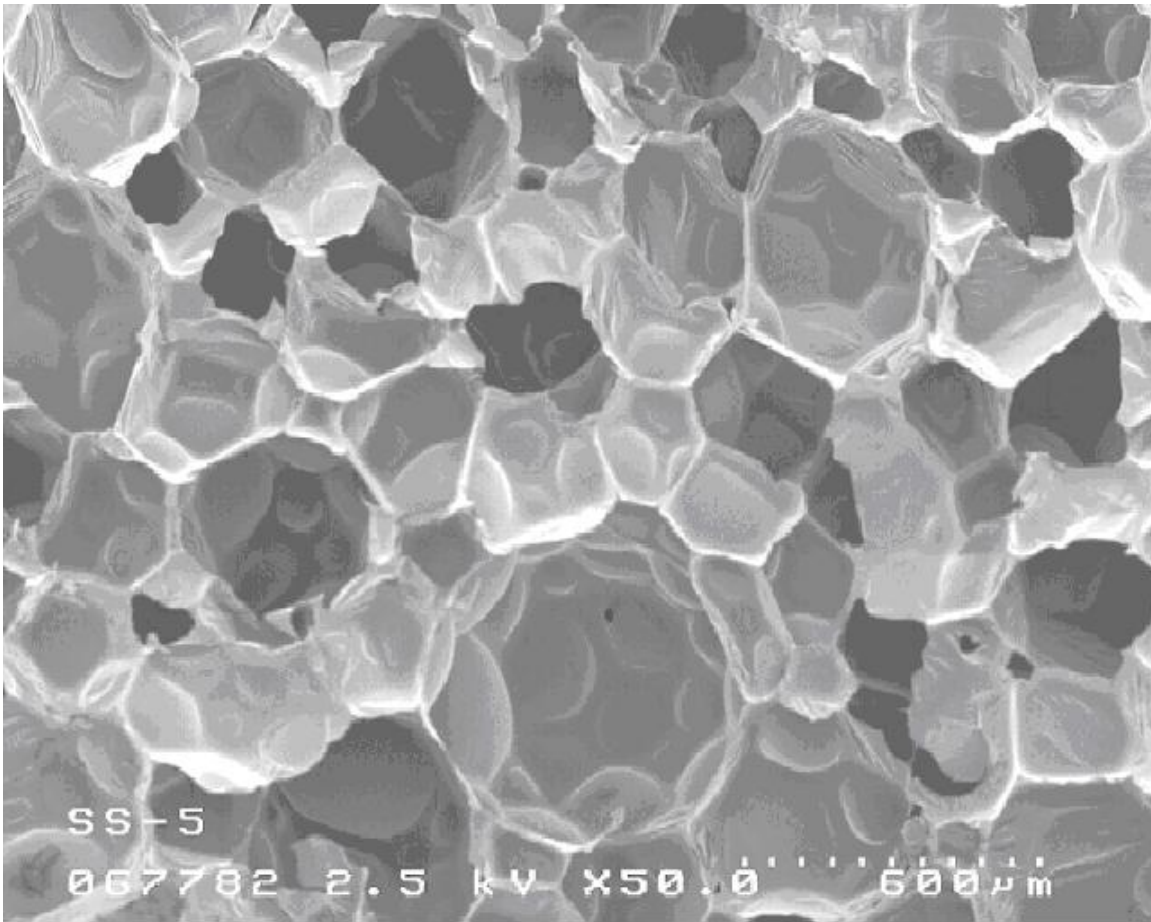


Figure 4 – Polyurethane Foam Cell Structure

Typically, the constituencies of closed cells in urethane foams are more than 90% throughout the foam material, but note the presence of voids of this early trial sample shown in Figure 4. Ideally, a foam cell structure exhibiting uniform spherical cell shapes, negligible voids and consistent cell wall thickness would provide a reliable engineering material. Recent research indicates that non-uniformity of cell shape in closed cell cellular solids decreases bulk Young's modulus and shear modulus.³ New NDE techniques might need to be developed should it be determined that sensitivity to cell shape or size becomes an important means of assessing the quality of foams. However, PUIR and polyurethane foams in practice exhibit reaction directional cell elongation, void agglomeration and variable cell wall thickness. These characteristics produce a foam structure of higher material mechanical properties in the foaming reaction rise direction than the transverse direction, higher gas pressures in "large" void locations and wide variances in material mechanical properties. Also, foam is sensitive to age and the exposed environment making baseline comparisons difficult without event driven data. Conventional engineering processes account for such naturally occurring variability by always maintaining positive margins and justify the need for more robust materials.

Extensive studies and testing provide great insight into how foam fails and other forensic observations. The initiating effect during space vehicle ascent triggering foam failure is the increase in temperature during aerodynamic heating. This increase in temperature decreases the strength of the foam cell walls while increasing the internal gas pressure until rupture of the cell wall occurs. These particles enter the boundary layer possibly creating downstream damage. In any case, the erosion accelerates exposing more irregular surfaces to aerodynamic viscous forces with an unpredictable path of degradation. It is conjectured that the loss in cell wall strength due to increased temperatures is irreversible and foam erosion continues well beyond maximum aerodynamic shear possibly more a function of thermal dissipation at that point.⁴ Polyisocyanurate and other urethane foams are susceptible to cracking, spalling, divots, pop corning and other forms of degradation under the harsh environmental conditions experienced during ascent of spacecraft to low earth orbit. In these critical applications as TPS for spacecraft, this type of degradation can lead to a loss in performance. NASA uses polyurethane foam as cryogenic insulation over fuel tanks. The foam is a good cryogenic insulator but has low mechanical strength. The foam is exposed to aero-heating and aero-shear during the launch. Due to its low mechanical strength the foam ablates and pops off the structural substrate.

The important take-away or lesson learned from this complex failure mode is dominance in strength of materials and load environments with regard to root cause failure. When actual stress becomes greater than that which the material will allow, failure occurs. “Structures” such as TPS designed without statistically relevant positive margins can and will fail. Where, when and how depends on which part of the equation becomes apparent first. Absent location specific stress/strain/temperature data and “A-basis” materials data, the significance of any materials improvements needed will remain not fully quantified. Stuckey in 1996 reported that at 0.0178 in/in strain to failure of tested NCFI 24-124 (current acreage foam on the shuttle) that this level was unimportant as “the ET (Shuttle External Tank) does not see strains to this level.”⁵ Design strain requirements for any new foam system or new product application are paramount to successful materials applications. For space vehicle applications, we find similar to Stuckey that strain values typically will not govern in acreage areas, but may control design for foam thermal protection system application in and around vehicle OML appurtenances. Commercial products may require multiple measures to meet economy of scale and to justify the cost of improvements. For instance, what is the trade-off for reduction in labor of hand lay-up laminate construction in the marine industry versus the cost of milling Kevlar® into component raw materials? Is there an optimum concentration level of fibers by weight to achieve a maximum average increase in strength? Material requirements must be properly assessed before proceeding with the decision to utilize the fiber reinforcement techniques presented herein.

A careful design of experiments approach including all variables in the current process, raw materials proportioning, mix ratios, substrate preparation and environment with specific attention to the respective change matrix sensitivities to strength, thermal, heat recession and other physical properties will result in a range of improvement solutions for each chosen foam system. However, the introduction of the relatively inert aramid fibers

completes the optimization process through reinforcement, added functionality and wide dispersion at the nano level. Figure 5 is a photomicrograph of standard Kevlar® pulp mixed into isocyanate. The amber colored area is isocyanate and the circular figure is a very tiny air pocket created during mixing. This test was done to prove the compatibility of the pulp fibers within raw isocyanate. Although the bulk of our research involved mixing and milling pulp fibers into the polyol or the Part “B” of the foam system, we have found that similar milling can be accomplished within isocyanate under stringent moisture controls and other applied equipment constraints.

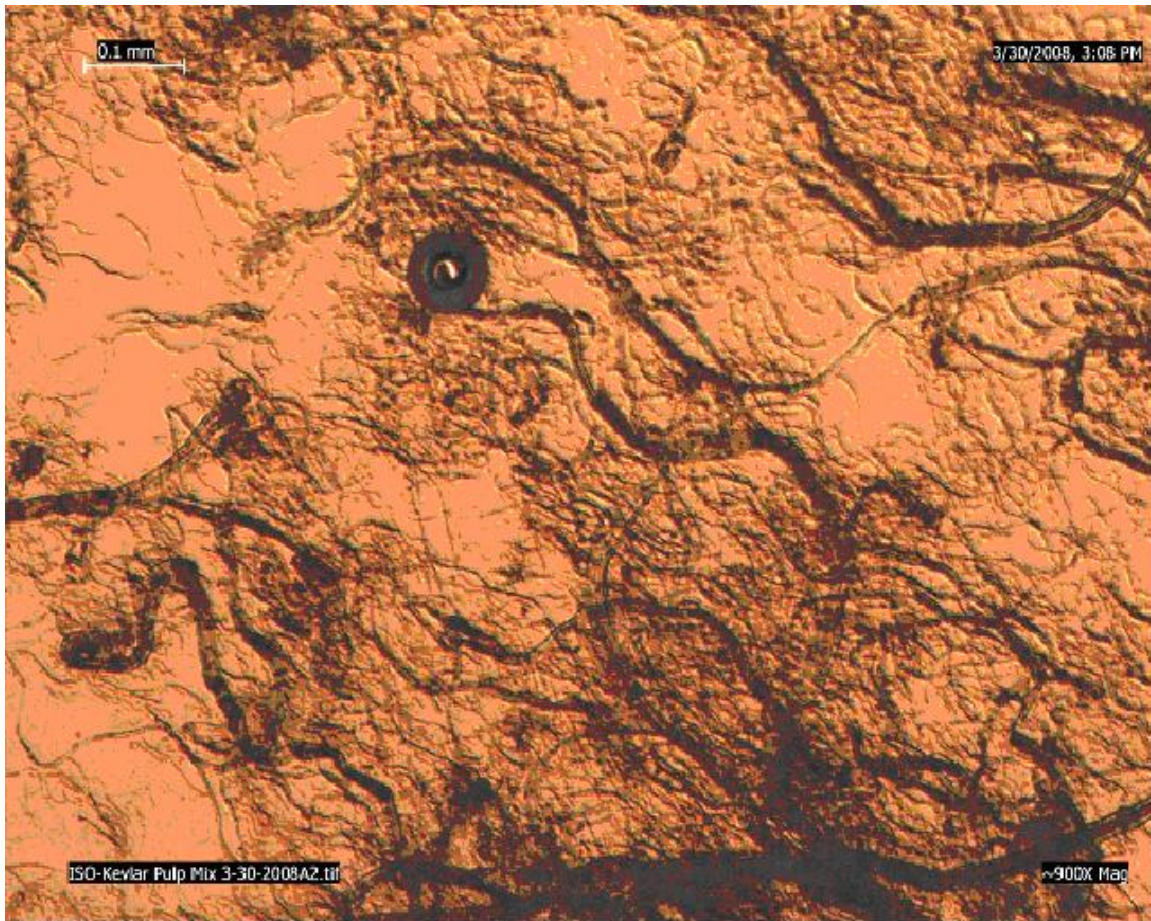


Figure 5 - Kevlar® Pulp “mixed” into Raw Isocyanate

The successful incorporation of aramid fibers into a foam system will include building on the current body of knowledge on polyurethane foams to optimize a formulation with high heat resistance and higher strength. Fiber reinforced foams offer a very high promise of being able to increase strength and performance. Future work should necessarily include strict process controls and data recording, sensitivity studies on fiber content and rise rates, volume fraction and chemical make-up.

Potential Ares V mission scenarios call for propellant systems to remain on orbit for extended periods (~90 days or more). This imposes unique and stringent requirements on

thermal insulation materials that protect these systems; the materials must maintain their strength and provide adequate thermal performance during long exposure to the on-orbit environments. At these higher altitudes, “pop-corning” of TPS is typically comprised of small pieces of foam liberated due to the less than threshold value voids reacting to a more extreme “vacuum” environment. Methods to reduce the number and size of voids are considered in the research being presented.

III. Research and Data

Even a 10% increase in the polyurethane foam's final mechanical properties can significantly extend the life of foam systems. The innovation of the technology lies in the incorporation of aramid fibers into one or both components of the polyurethane foam system while retaining ability to pour or spray it. The scope of this research incorporates a philosophy accepting variability of the materials and processes as is, but with the intent to establish statistically significant positive margins to meet requirements. The work included building on the current body of knowledge on polyurethane foams to optimize a formulation with high heat resistance and higher strength. At the outset, there was no known process for incorporating reinforcing fibers small enough to be integrally dispersed within the cell walls resulting in superior final products. Past attempts have included “long” glass fibers and other products not successfully integrated into the cell walls of the foam. The key differentiating aspect from current state of art resides in the many processing technologies to be fully developed from the novel concept of “nano-like” pulp aramid fibers, their potential added functionality and their enabling entanglement capability fully enclosed within these closed cell urethane foams. These aspects have been the fundamental premise driving this effort since as early as 2003.

The funded research was directed to a process for incorporating nano-pulp in the cell walls of urethane foams (e.g., polyurethane, polyisocyanurate). The cell wall thickness of typical rigid polyurethane foam is from 3 μ m at cell faces to 30 μ m at cell edges.² Ideally, the end product envisioned from this new foam formulation process will be a sprayed two part polyisocyanurate or polyurethane foam with aramid nano-pulp optimally dispersed (e.g., minimum fiber content producing complete interfacial enhancements) throughout the cell wall thickness only. Also, it is desirable that the “inert” aramid fibers combine with the chemical structure of either the polyol or isocyanate to form a higher functional material even if only partially. The resultant foam structure will provide better aging qualities, increased strength characteristics and enhanced thermal properties consistent with aramid’s superior mechanical reinforcement properties and full range of temperatures from cryogenic to 500°C. Such a family of rigid foam formulations can serve as the TPS for a wide variety of applications within the NASA mission framework and robust commercial products.

Initially, we intended to find a COTS system with a viscosity less than 1000 cps to better facilitate the raw introduction of Kevlar® nano-pulp avoiding any intermediate steps. A commercial marine product supplied by North Carolina Foam Industries (NCFI) was selected for our research. NCFI 15-010 is a water based foam system largely used in the marine industries. Per the company, “NCFI 15-010 is a two component, water blown, all PMDI based spray polyurethane foam system designed for use as a void fill, insulation

material or flotation material. NCFI 15-010 has been formulated to spray at 2.8–3.0 pcf depending on lift thickness. NCFI 15-010 is not ASTM E-84 flame spread rated and is not to be used in applications governed by building codes. This product meets USCG Title 33, Chapter 1, Part 183 for monohull boats under 20 feet in length.” This system was selected primarily for two reasons, 1) the polyol resin’s low viscosity rating of 500 cps and 2) its environmentally friendly water blown make up. The first batch of polyol was sent directly to DuPont’s Spruance facility in Richmond, Virginia for milling of the Kevlar® pulp in a phased milling and sampling process.

Incorporating Kevlar® nanopulp into a polymer system is not trivial. The nanopulp is a strange material and does not exist by itself. It must be made and consumed in a liquid. Since the polyurethane foam is made by reacting an isocyanate and a polyol, it was agreed that the nanopulp would be produced and supplied in the polyol at a concentration of 1% by weight, essentially limiting its concentration in the final foam to about 0.5%. Several series of nanopulp dispersions were produced by DuPont for NASA’s evaluation. The two series of samples described in this work were identified at NASA II and NASA IV. These samples are described in tables 1 & 2.

NASA II				
SAMPLE	KEVLAR®	MEAN LENGTH	MEDIAN LENGTH	WATER
	(%)	(microns)	(microns)	(%)
POLYOL RESIN				3.63
NASA II-1	1	6.2	10	2.15
NASA II-2	1	2.93	4.64	1.33
NASA II-3	1	0.76	1.69	1.08
NASA II-4	1	0.5	0.5	0.9
NASA II-5	1	0.26	0.26	0.76

Table 1 – NASA II Fiber Rich Polyol Samples

NASA IV					
SAMPLE	KEVLAR®	WATER	FINAL WATER*	FIBER LENGTH (µm)	
	(%)	(% of total)	(% in polyol)	MEAN	MEDIAN
POLYOL		3.60			
NASA-IV-1	1	1.77	3.70	4.54	8.16
NASA-IV-2	1	1.16	3.75	1.69	2.80
NASA-IV-3	1	0.92	3.66	0.72	0.31
*DI water added to get to this level					

Table 2 – NASA IV Fiber Rich Polyol Samples

After milling, four sets of various fiber length samples (NASA II-1, 2, 3 & 5) were sent to Marshall Space Flight Center (MSFC) for foam sample production and mechanical testing. Figure 6 is a photomicrograph view of the raw “nano” fiber rich polyol sample at the same magnification as Figure 5’s depiction of the pulp fiber resident in isocyanate.



Figure 6 – NASA II-5 Raw Polyol and Milled Kevlar® Pulp (Note the tiny dark spots of fiber as opposed to larger scale fibrils in Figure 5)

It was discovered that an adjustment for moisture content was necessary after milling to avoid affecting the blowing agent and resultant bubble nucleation process. This adjustment was made at MSFC for NASA II and at DuPont for NASA IV. Sample production for this first set of samples was performed manually using large “popcorn cups” and a paddle wheel mixer on a drill. Pours into aluminum molds were for the most part unsuccessful due to the quick rise time of the foam system. However, a sufficient number of ~50 X 50 X 25mm samples were cut from cup molds to be able to conduct several tension and compression tests. The results of tensile tests are shown in Figure 7 and compression results in Figure 8 (Note: Figure 8 Load and Stress are equal due to consistent sample cross sections).

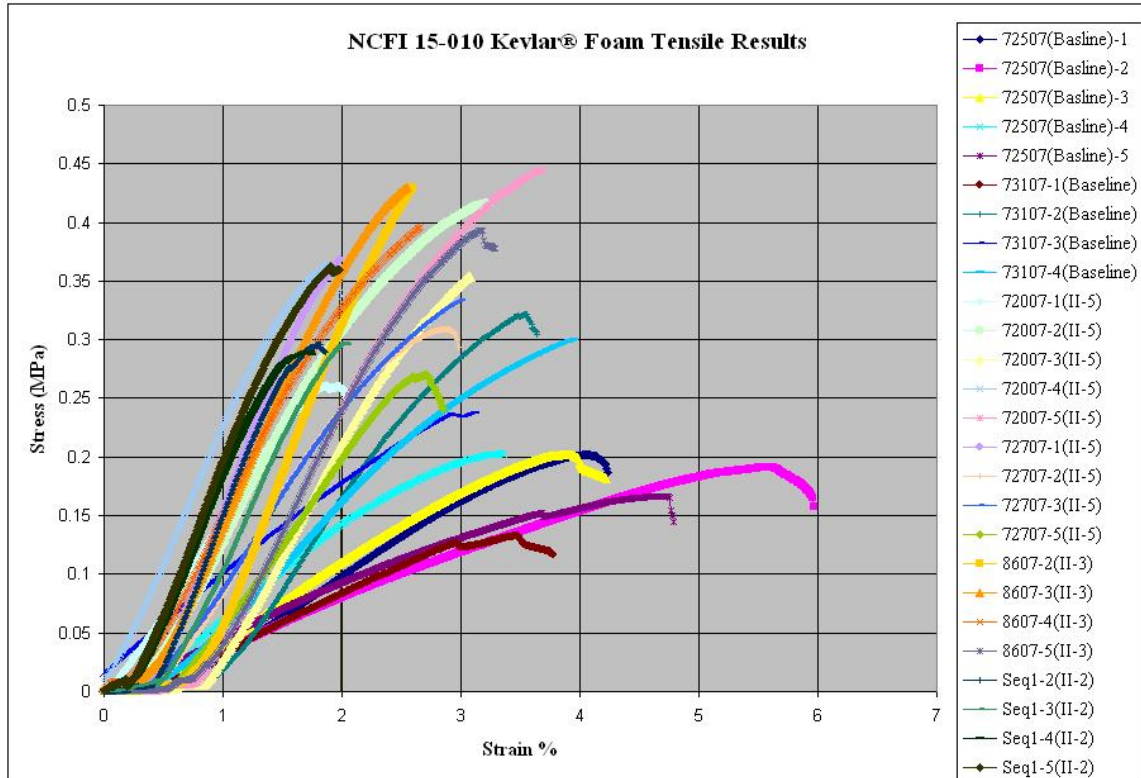


Figure 7 – Tensile Results (Steep curves represent fiber reinforced foam)

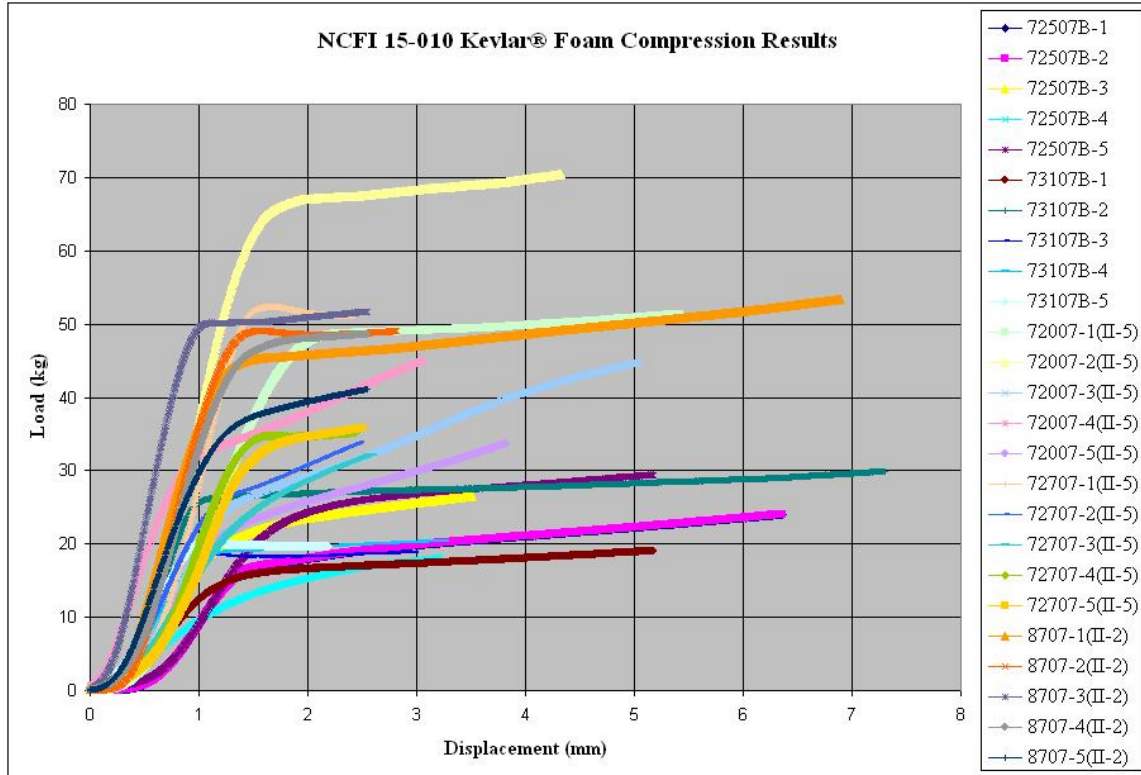


Figure 8 – Compression Results (Higher yield points represent fiber foam)

The average calculated tensile strength of all fiber length types was ~139% of the baseline and average compression results ~178% for the NASA II samples.

In early 2008, another batch of NCFI 15-010 was sent to DuPont for milling resulting in the production of three sets of various fiber length samples (NASA IV-1 thru 3) sent to MSFC for processing and testing. At this point, an Ashby Cross Company, Inc. Model #1125 VR foam dispensing machine had been setup for foam sample production. This single action machine with variable ratio meters, mixes and dispenses a wide range of two-part reactive resins. Its small shot capability makes it ideal for developing proper raw material mixes for reinforced foam systems. Several test were conducted upon receipt of materials to assure that the isocyanate index (weight of isocyanate to weight of resin was within specified range of the baseline NCFI 15-010 foam system). Between batches of materials the lines were purged with “dump shots” to insure homogeneity of the raw materials. A rise test was performed prior to each sample mold shot as a witness sample for isocyanate index, density consistency and post test checking. All batches proved to be within fractional ranges of the ~4.7 liter yield from the baseline NCFI 15-010. Two kinds of test samples were produced; 1) 50 mm diameter cylindrical samples, and 2) a rectangular sample. The cylindrical samples were the easiest to mount to the test blocks exhibiting very smooth, straight surfaces with only minor “rind” on the perimeter in most cases. It should be noted that “rind” is an area of high density typically found in most sprayed or poured foams at the interface with a large “heat sink” such as air, the wall of a mold or other areas wherein the foam fails to reach temperatures high enough for the blowing agent to create the correct bubble nucleation results. Samples exhibiting heavy “rind” were not utilized in calculation of the results. The samples were tested on a Mecmesin Model 5-i desktop mechanical test machine. The composite tensile results of these tests are shown in Figure 9 and the overall composite compression in Figure 10. On average, the NASA IV-3 samples exhibited 200% of baseline tensile results with NASA IV-2 and NASA IV-1 at 181% and 179%, respectively. The overall samples composite for compression reveals a predicted yield value 215% of the baseline value.

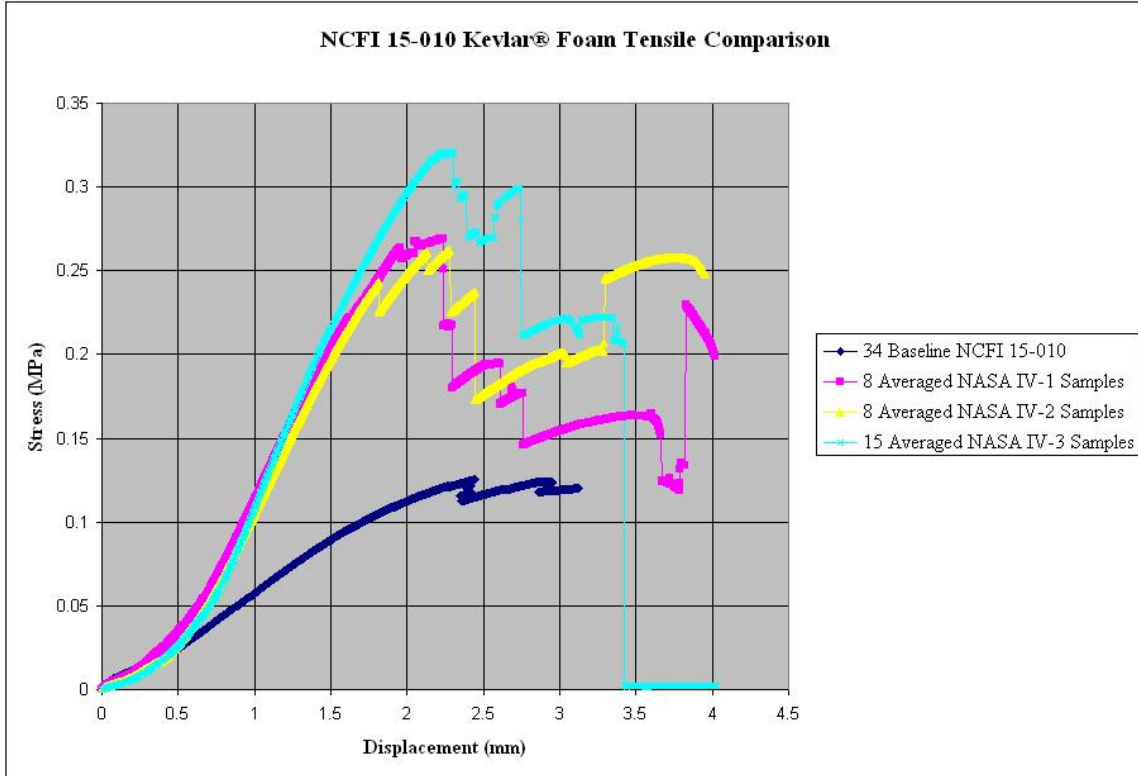


Figure 9 – Tensile Results

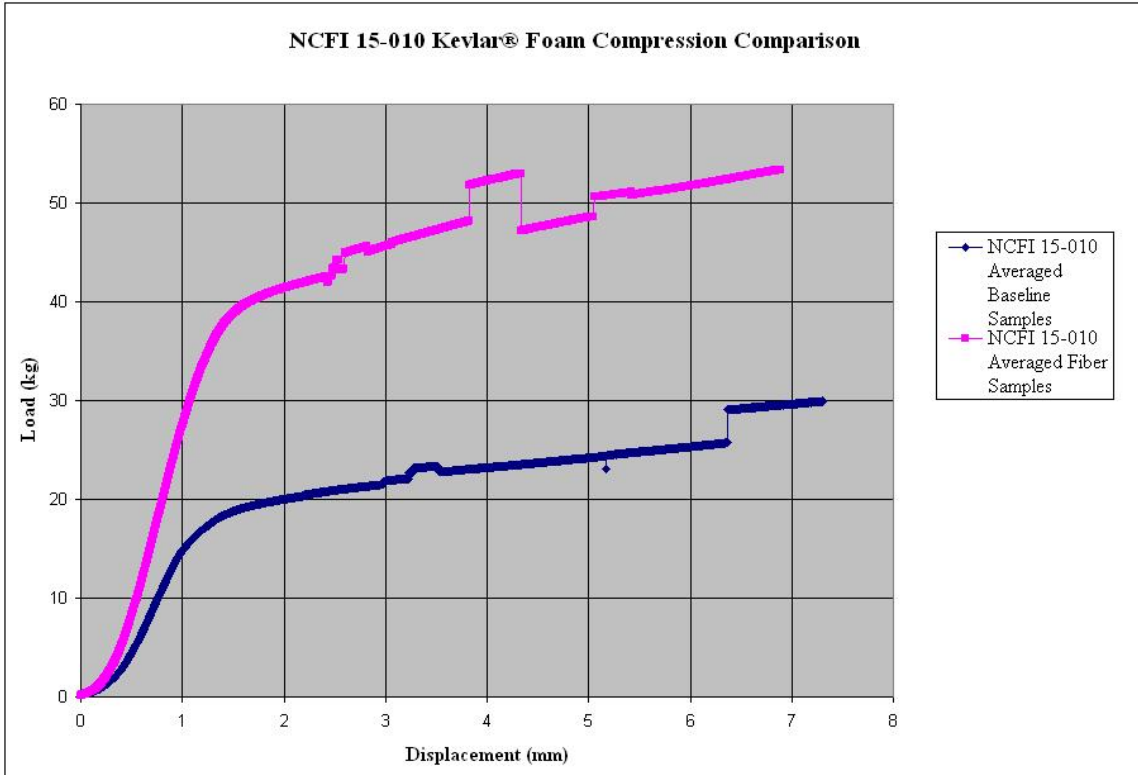


Figure 10 – Compression Results

The Ashby Cross dispensing machine was calibrated specifically for the NCFI 15-010 foam system to meter precisely a 1:1 ratio by volume (rbv) or 1.18 +/- 0.01 rbw (isocyanate index). These ratios were not only verified by the manufacturer, but validated in the lab at Marshall Space Flight Center with multiple dump shot tests. Witness samples and “rise” test proofs were established for fiber rich and baseline materials. The extensive mixing afforded by the Ashby Cross air motor shaft driven dynamic blades within the disposable mixer heads allows for an almost exact volumetric match in the “rise” proof tests. The positive displacement pumps and pressure fed reservoir feed system prove that the viscous fiber rich polyols can be easily delivered to a spray head @ only 4.14 bar. Also, final foam densities as low as 0.032 Mg/m³ (~2 lb/ft³) were produced with these viscous polyols. Interestingly, no good correlation could be made between strength and density or isocyanate index for the fiber rich or baseline materials. However, presence of high density “rind” revealed a two-fold increase in tensile strength as opposed to an adjacent rind removed sample. Directionality and orientation to rise direction of samples has a strong influence on results as does batch lot of materials. These parameters were kept under good control with statistically significant sample sizes, close monitoring of sample production and repetitive calendar attempts. Results were relatively consistent and within the family of the range of values commonly witnessed for the baseline materials.

One sample of the fiber rich foam, a “combined” mixture trial, was crushed inadvertently during testing to a 431 kg compressive load essentially flattening the sample. However, the tensile test was continued anyway to realize a maximum tensile stress of 0.41 MPa. Also, a ~1% by weight sample was produced and tested with results shown in Figure 11.

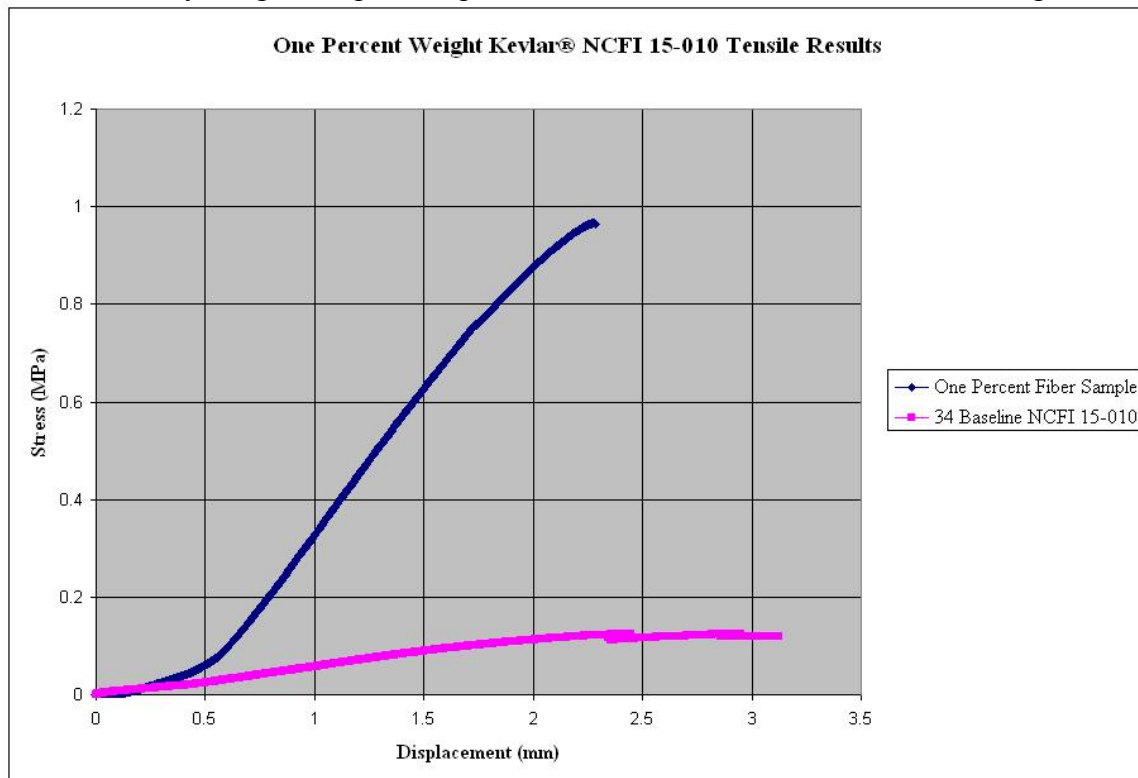


Figure 11 – One Percent by Weight Kevlar® Rich Foam Sample

At this concentration, the tensile results are 5-6X the average baseline value. Also, visual results of preliminary oven testing at 200°C has shown that the fiber rich foam exhibits less char and less rescission than the baseline material. This was expected and is consistent with previously published data on erosion rates of hypalon/kevlar fiber insulation.

IV. Conclusions & Summary

The test results clearly indicate the advantages of incorporating aramid fibers into a urethane foam system and far exceed our 10% minimum expectation level. The addition of ~0.5% Kevlar® results in an approximate two-fold increase in tensile and compressive strength without sacrificing density, thermal conductivity, processibility or any other key parameters. The addition of ~1.0% is even more dramatic as shown by the test data. This materials development can deliver robust functional design capabilities needed throughout the current NASA exploration mission such as insulation systems needed on the Crew Launch Vehicle (CLV), Crew Exploration Vehicle (CEV), lunar building blocks, inflatable structures and upper stages. The commercial uses are unlimited and may even prove to provide safer bedding materials in flexible foam systems.

The introduction of fibers into urethane foams can improve various material properties. These fibers successfully introduced into the cell walls of the urethane create a higher strength cell structure resulting in the capability to "bridge" areas weakened by variable spray application processes, materials composition and environmental factors. Many different fiber types, sizes, mixing techniques and % content can be optimized to realize the best urethane reinforcement combination. Further research is recommended from a nanotechnology perspective to fully characterize functional characteristics, increase fundamental knowledge of bubble nucleation effects, discovery of new assessment techniques and other key building blocks in this technology arena. However, the completed research is sufficient to begin full scale production of foam systems needing to be enhanced. The proven flow characteristics of the materials already tested, its compatibility with existing capital infrastructure and the initial results elevate this technology to a high TRL (technology readiness level). The authors are very confident that these techniques can be easily scaled up and introduced into a wide variety of urethane foam systems.

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Nano-Aramid Fiber Reinforced Polyurethane Foam

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MSFC, AL; A. Frances, E.I. DuPont
de Nemours and Company, Richmond, VA

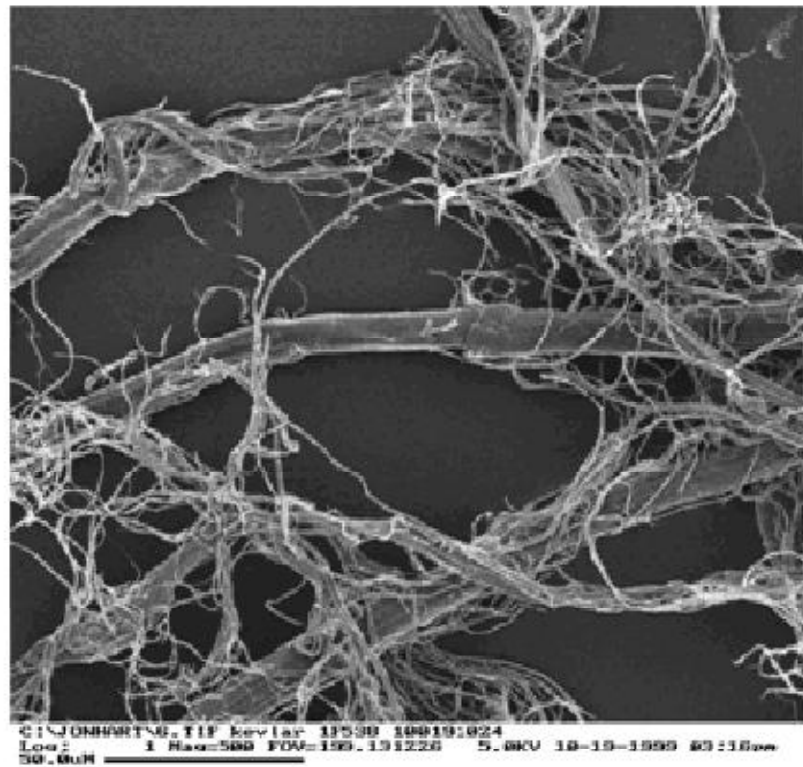
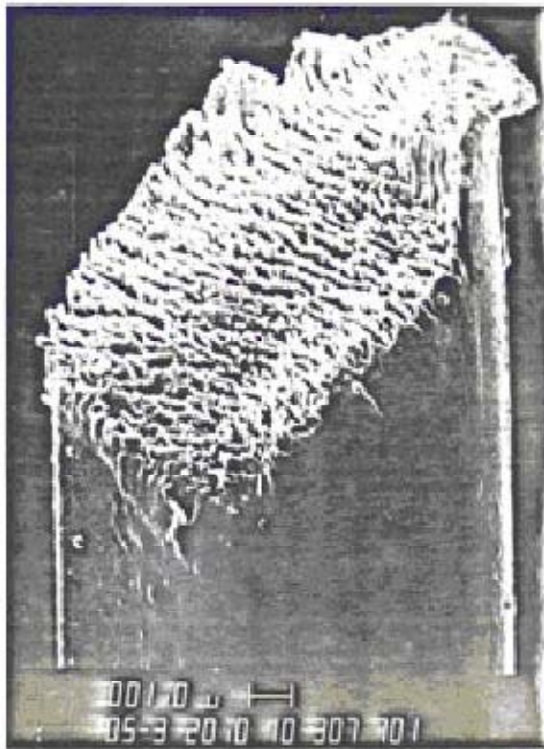


Research Objectives

- Material testing and proof of processing techniques for aramid fiber reinforced polyurethane rigid foams.
- The development of superior spray-on foam insulation can provide NASA with stronger insulation systems needed on Ares I and Ares V
- Higher strength, lightweight, FST and green friendly foams can lead to other innovative products with lower cost.

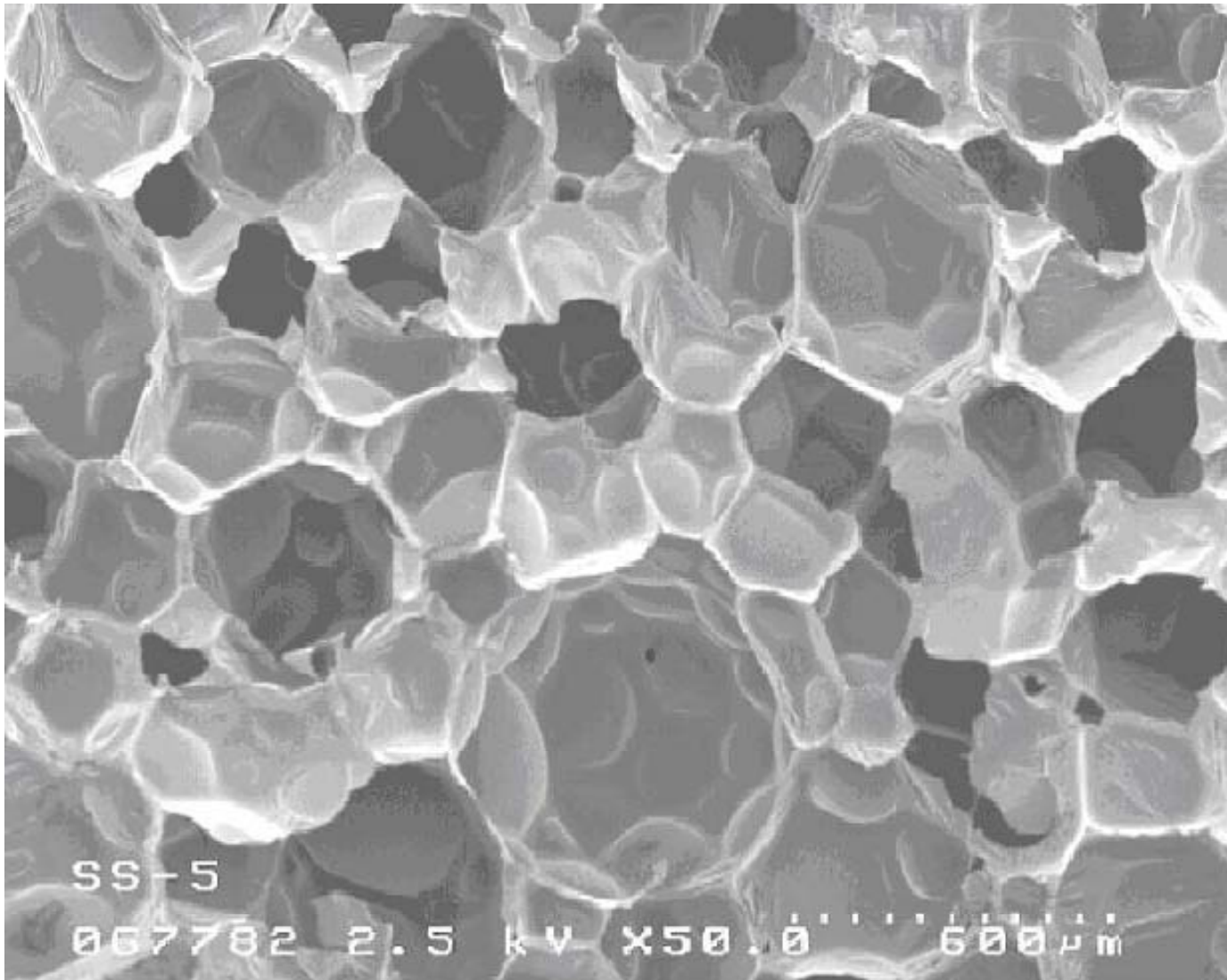


Kevlar® Fiber and Pulp



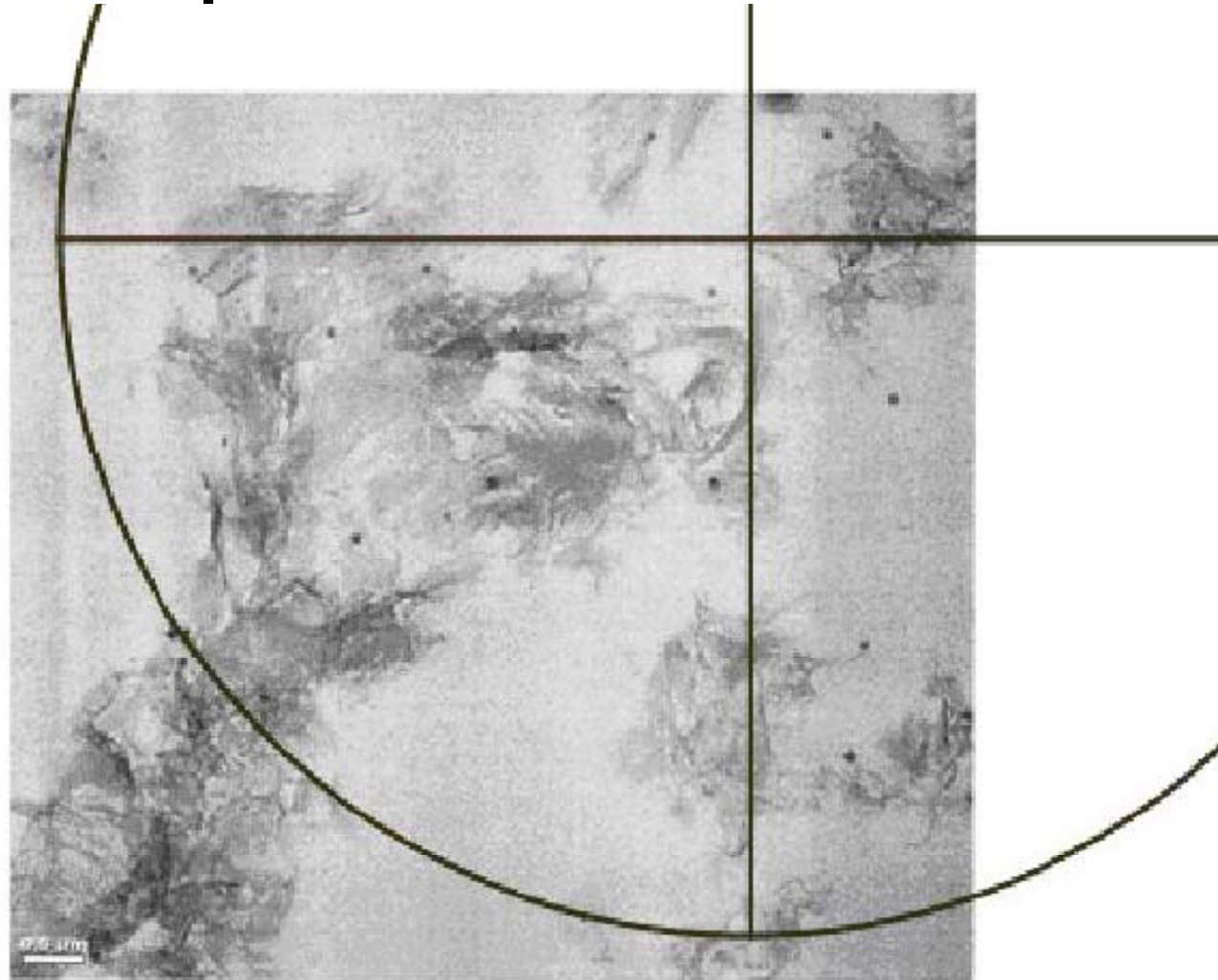


Cell Structure



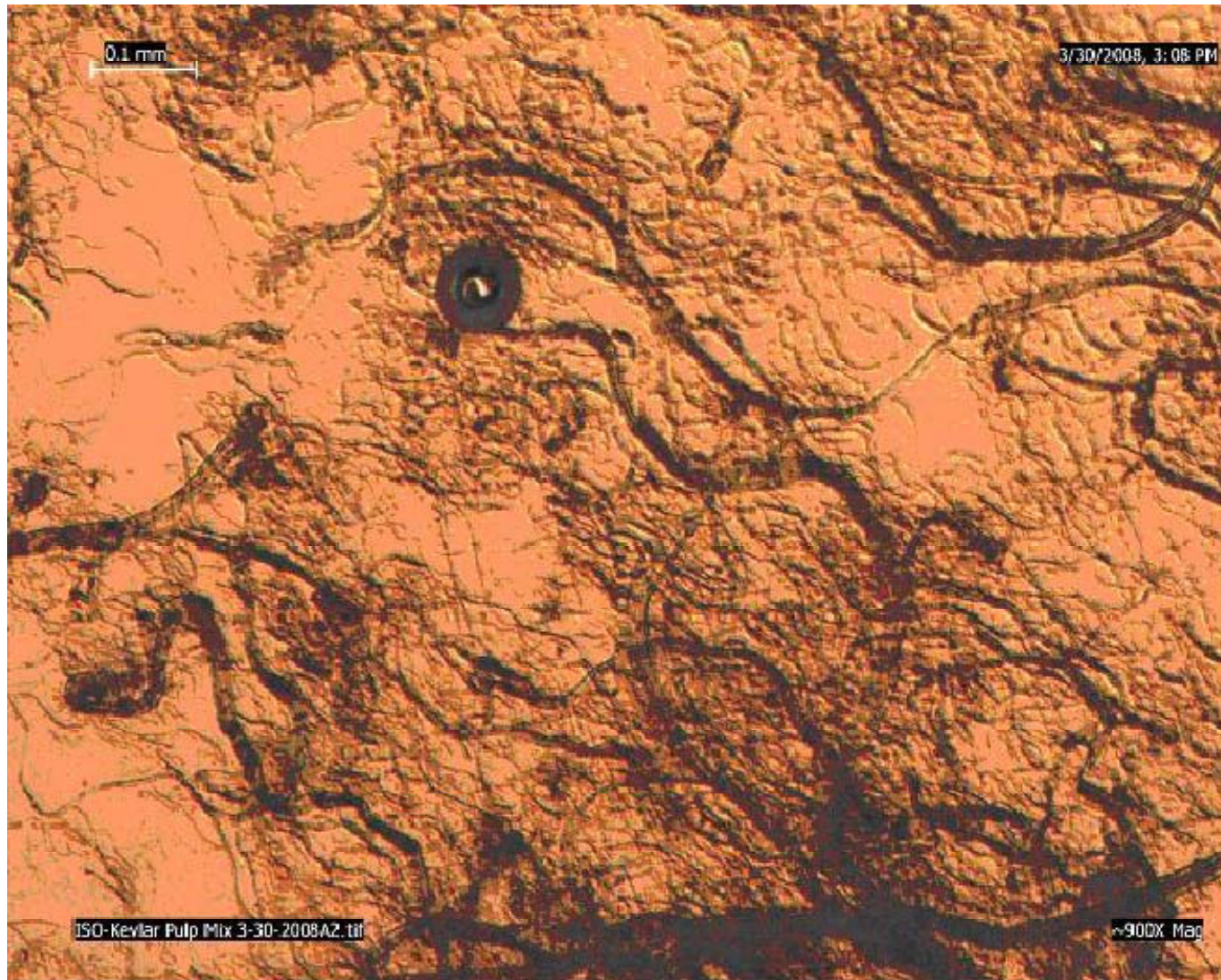


Pulp Size Reduction





Kevlar® Pulp “mixed” into Isocyanate





Polyol Milling Results

		NASA II		
SAMPLE	KEVLAR®	MEAN LENGTH	MEDIAN LENGTH	WATER
	(%)	(µm)	(µm)	(%)
POLYOL RESIN				3.63
NASA II-1	1	6.2	10	2.15
NASA II-2	1	2.93	4.64	1.33
NASA II-3	1	0.76	1.69	1.08
NASA II-4	1	0.5	0.5	0.9
NASA II-5	1	0.26	0.26	0.76

		NASA IV			
SAMPLE	KEVLAR®	WATER	FINAL WATER*	FIBER LENGTH (µm)	
	(%)	(% of total)	(% in polyol)	MEAN	MEDIAN
POLYOL		3.60			
NASA-IV-1	1	1.77	3.70	4.54	8.16
NASA-IV-2	1	1.16	3.75	1.69	2.80
NASA-IV-3	1	0.92	3.66	0.72	0.31
*DI water added to get to this level					

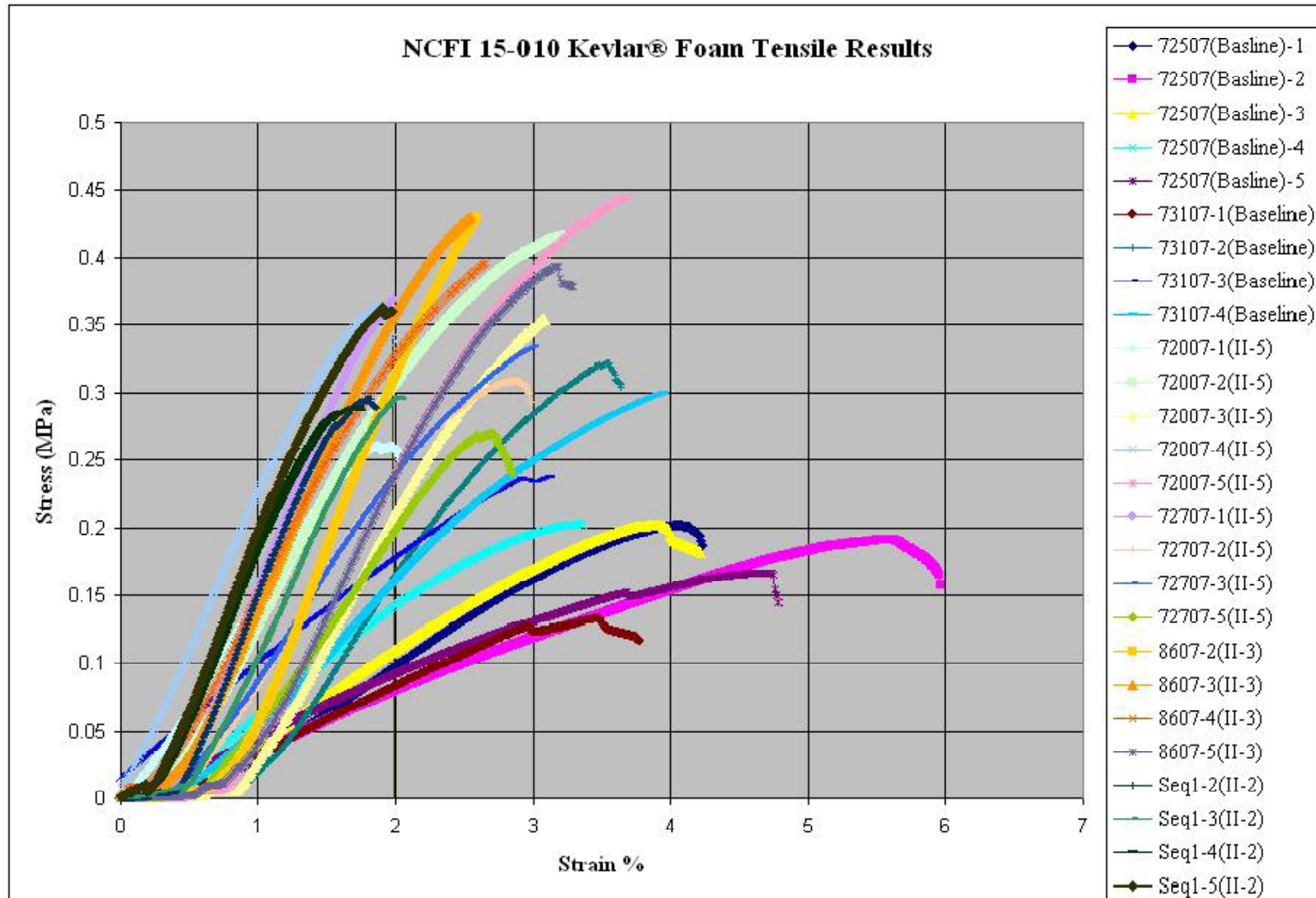


NASA II-5 Raw Polyol and Milled Kevlar® Pulp



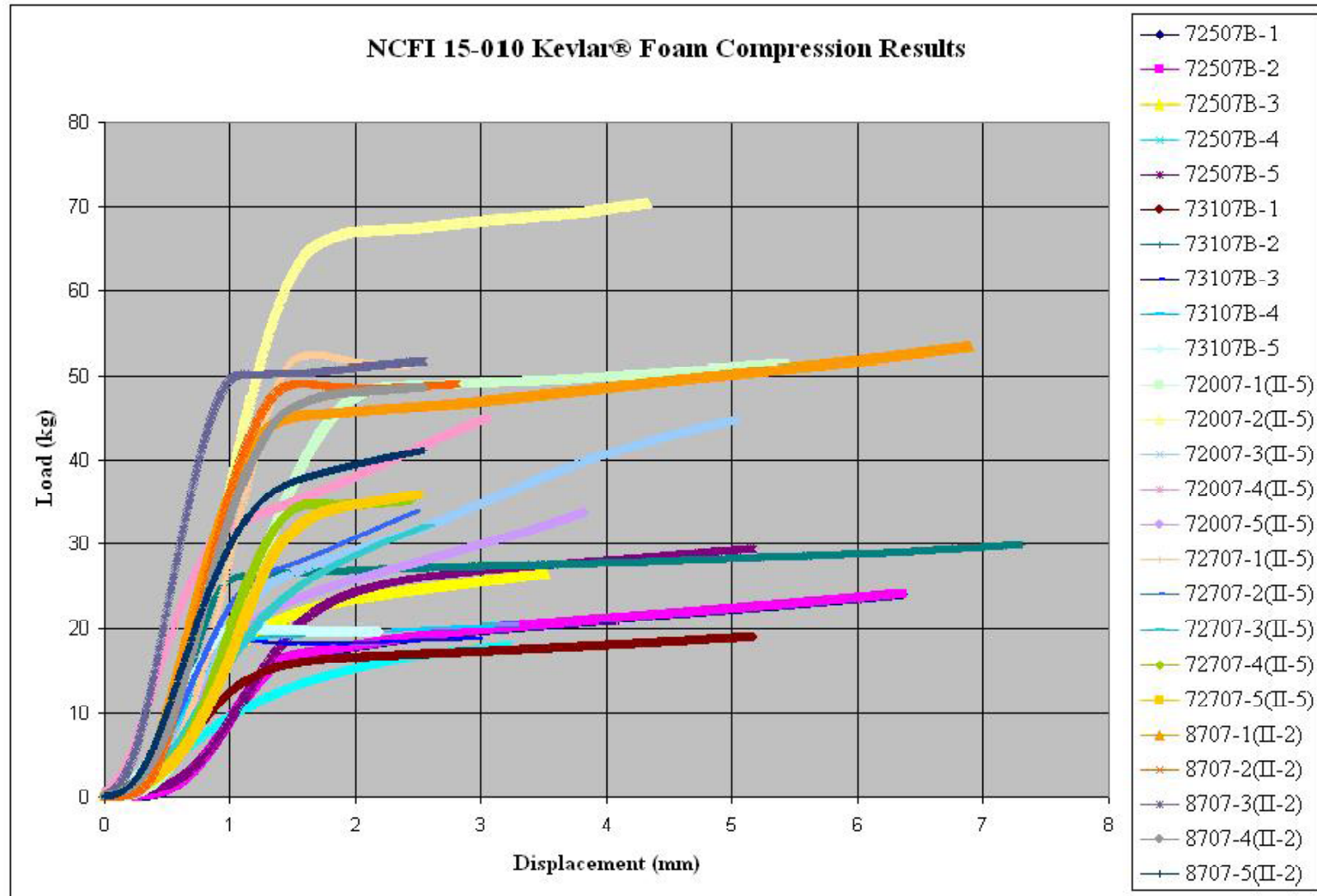


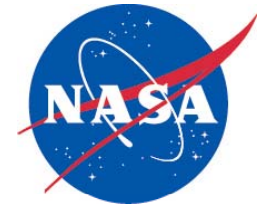
Tensile Results



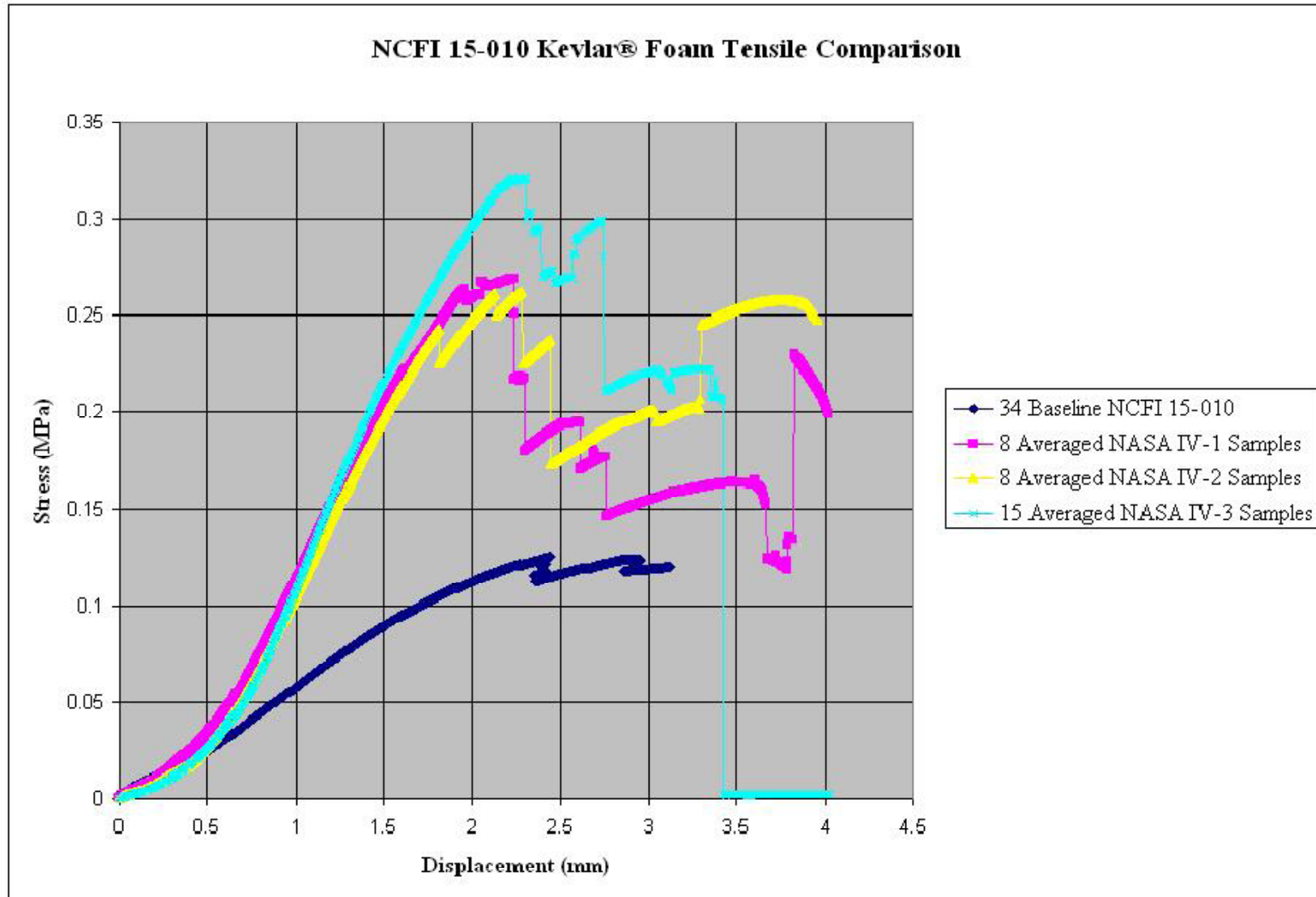


Compression Results



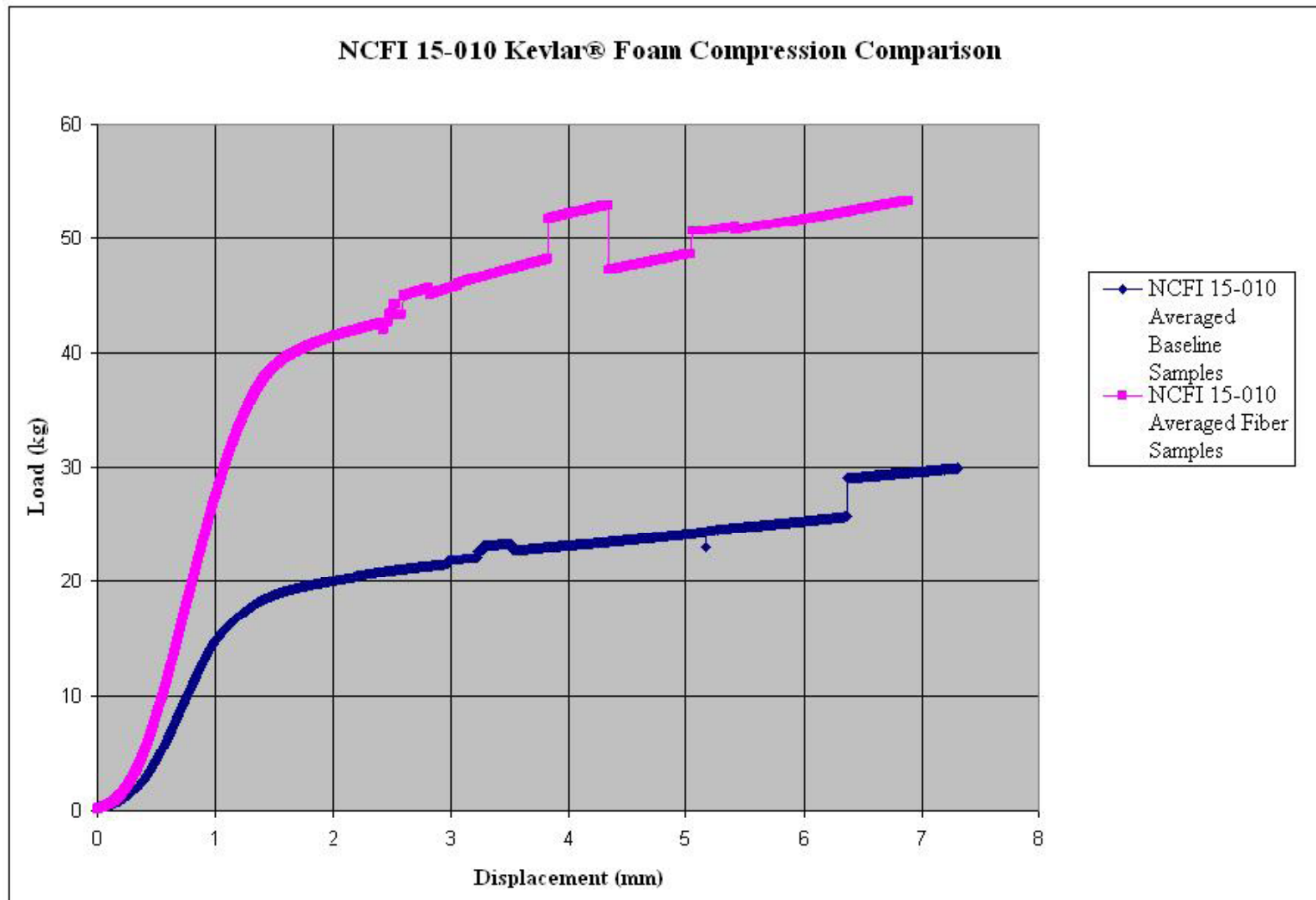


Tensile Results





Compression Results





One Percent by Weight Kevlar®





Summary

- All technical objectives of the research were met.
- TRL's are anticipated to be very similar in these systems due to the inert nature of Kevlar fibers, relevant flight experience, heritage systems certification processes and advanced knowledge in TPS.
- All technical performance characteristics anticipated to be equal or superior to baseline systems with respect to heat rescission, adhesion, thermal performance, producibility and automation.
- Spray equipment validation including nozzle design, higher viscosity pumping, temperature control and other key developments need timely implementation.
- Opportunities exist in correlating fiber interfacial interaction and other polymeric foams.