

POLYIMIDE FOAMS FROM FRIABLE BALLOONS

Erik S. Weiser and Brian W. Grimsley
NASA Langley Research Center
Hampton, VA 23681

R. Byron Pipes
University of Akron
Akron, OH 44325

Martha K. Williams
NASA Kennedy Space Center
Kennedy Space Center, FL 32899

ABSTRACT

Recent advancements in high temperature polymeric materials at NASA Langley Research Center have led to the development of new polyimide foam systems with attractive properties. These foam materials have application as insulation for the cryogenic fuel tanks for the next generation reusable launch vehicles, commercial and defense marine ships and commercial aircraft. While the first foaming process developed consisted of thermal cycling the polymer precursor residuum and allowing the inflation of the particles to interact to create the foam. An innovative foaming process has been developed that begins with partially inflated microspheres with incomplete polymer molecular weight gain. Termed, "friable balloons," this new precursor form can be poured into a mold to "foam in place" the desired geometry. In addition, the new foaming concept produces a wide range of foam products with varying degrees of open and closed cell structure, compressive strength and tensile strength. Foamed in place Nomex^{®#} honeycomb core materials are tested to evaluate the enhancements achieved by the addition of this new polyimide foam to the core material. The addition of the polyimide foam to the Nomex[®] honey comb resulted in an increase in compressive strength by as much as 25% over the unfilled core.

Key Words: Polyimide, Foam, High Temperature, Insulation

[#] The use of trademarks or names of manufacturers in this report is for accurate reporting and does not constitute an official endorsement, either expressed or implied, of such products or manufacturers by NASA.

1. INTRODUCTION

Foamed plastics, also known as cellular plastics or plastic foams, have been important since primitive man began to use wood, a cellular form of the polymer cellulose [1]. Cellulose is derived from the Latin word *cellula*, which means very small cell or room, and the polymer in its natural form exists mostly in its cellular form as seen in wood and straw. The first commercial cellular polymer was sponge rubber, introduced between 1910 and 1920 [1]. Low density porous materials, otherwise known as foams, were first developed in the United States and Europe in the mid-to-late 1930's [2]. The term polymer foams or cellular polymers refers to a two-phase gas-solid system in which the solid polymer is continuous and the gaseous cells are dispersed throughout the solid [3]. Open-celled foams allow interconnecting gaseous cells while a closed-celled foam has discrete cells. Polymeric materials are foamed to meet various application needs, such as weight-reduction, insulation, buoyancy, energy dissipation, conveyance, and comfort. These polymeric foams can be produced by several different methods including extrusion, compression molding, injection molding, reaction injection molding, and solid state methods.

Despite the outstanding properties of common polymeric foams, such as excellent thermal and acoustic properties, high strength-to-weight ratios, cost effectiveness, and availability in various forms (rigid, semi-rigid, flexible, and reinforced), these materials suffer from certain disadvantages [2]. Early polymeric foams have been limited in their use temperature, poor fire resistance (flammability and toxic fume generation), dimensional stability, thermal aging and degradation, friability, and susceptibility to thermal cycling and UV light [1].

Based on a need for more fire resistance, less smoke generation, and higher operating temperatures, foams of polyimides, polybenzimidazoles, polyprones, polyureas, polyphenylquinoxalines, and phenolic resins were developed [2]. However, due to their high cost only the polyimide and phenolic foams have seen any commercial success.

One of the earliest polyimide foam patents is credited to E I DuPont de Nemours, Inc. (DuPont) in 1966. DuPont's patent describes a process whereby a solution of a polyamic acid (e.g. from oxydianiline and pyromellitic dianhydride) in a suitable solvent (N,N-dimethyl formamide) is prepared [4]. To this solution a dehydrating agent, alone or in combination with an amine, is added together with a gas-generating acid that, in the presence of an anhydride / amine mixture, produces carbon monoxide bubbles. The gas bubbles produced are uniformly dispersed mechanically in the solution. The solution can be foamed as a wet film on a moving belt or it can be injected into a mold and cured to form a shaped object.

Several Patents followed through the 60's and 70's leading up to the development of the most common polyimide foam Solimide [5-9]. Solimide[®] foam manufactured by Inspec Corp. is one of the only commercially available polyimide foams. Solimide[®] foams have many of the outstanding properties sought after by Industry, but they are limited to very low closed cell contents and low densities, 0.008 gm/cc, which in combination are not

suitable for use as an insulation on future reusable launch vehicles. As reported in the literature NASA Langley Research has developed a novel polyimide foam from the reaction of a unique polyimide precursor residuum [10]. These foams could be manufactured to densities ranging from 0.008 gm/cc to 0.32 gm/cc and had all the beneficial properties of other polyimide foams. However these foams did not meet the requirements of being nearly 100 percent closed cell.

As a result NASA Langley Research Center utilizing the novel polyimide precursor residuum in a modified form developed a intermediate precursor termed 'friable balloons'. The resultant friable balloons on the order of 200 micrometers could be placed in a contained space and foamed to a density ranging from 0.016 gm/cc to 0.128 gm/cc. These new foams have the added benefit of being highly closed cell. In the present work initial physical properties of these unique foams from friable balloons will be investigated.

2. EXPERIMENTAL

2.1 Friable Balloon Fabrication The salt-like foam precursor is synthesized by mixing monomer reactants of a diamine with a foaming agent (tetrahydrofuran) in methanol at room temperature. The diamine (e.g., ODA, 227g – 1.1 moles) is dispersed in a mixture of tetrahydrofuran (THF-1120g) and 280 g of methanol (MeOH) at room temperature. To the stirring 3,4'ODA solution, a dianhydride (e.g., ODP, 176g – 0.57mol) is added gradually at 15°C to yield a homogenous solution. To this solution, 197 g (0.57mol) of ODP-tetraacid is added gradually and the mixture is stirred for 24 hr at 30°C to yield a homogenous precursor solution. Solid contents and viscosity of the resulting solution are 30wt% and 0.2 poise, respectively. The solution is then charged into a stainless-steel vat and treated at 70°C for 14 hours in order to evaporate the solvent (THF and MeOH). The resulting material is cooled and crushed into a fine powder (2 to 500µm). The polyimide precursor solid residuum is then treated for an additional amount of time (0 to 300 minutes) at 80°C to further reduce the residual solvents to about 1–10 wt % depending on the final foam density desired. Residual amounts of THF are determined by measuring proton NMR spectra of the powders. The polyimide precursor powders are further treated at 100°C to expand the powders without thermal imidization so that the apparent density of the precursor is decreased without thermal imidization and friable balloons resulted. [Figure 1](#) shows a flow chart of the process to fabricated the precursor solid residuum.

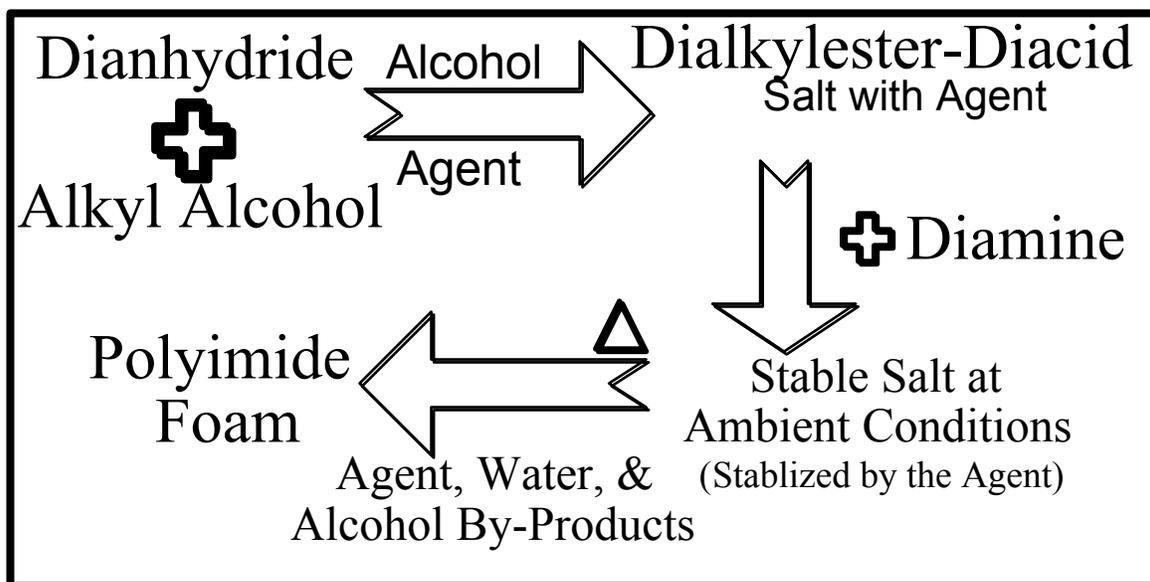


Figure 1 Flow Chart of Polyimide Precursor Residuum Formation

2.2 Friable Balloon Foaming Process The process of foaming the friable balloons into a solid neat piece of foam or a foam filled honeycomb is accomplished by a closed mold foaming technique. The cartoon represented by figure 2 displays the method by which the friable balloons are placed in a mold containing a piece of honeycomb core. The mold, core, and friable balloons are sealed on the top surface by a porous piece of graphite and placed in an oven for curing. In order to obtain a specific density from the friable balloons a simple back calculation is utilized. The desired density is multiplied by the mold volume and a specific weight is obtained. To this weight an additional twenty percent is added to account for solvent removal and water formation during precursor imidization.

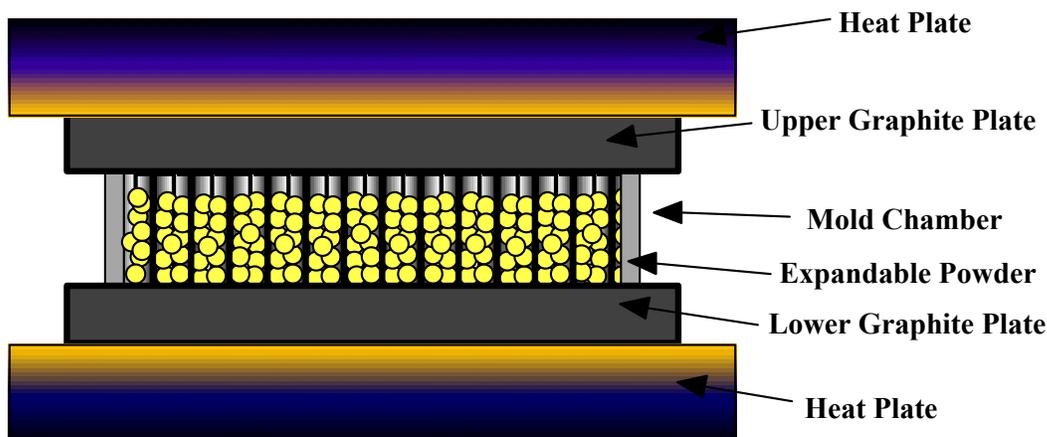


Figure 2 Cartoon of Friable Balloon Processing Lay-up

Figure 3 shows the cure cycle used to fully imidize the friable balloons and form a well-consolidated piece of foam filled core insulation. The entire process is performed in an air convection oven. The mold is placed in the oven and restrained with weights on the top surface. The oven is raised in temperature to 250°C and held for one hour. After the first hold, the temperature is raised for a second hold at 300°C. Once the second one-hour hold is complete, the oven is cooled to room temperature and the mold is removed. Modifications to the basic foaming cycle are utilized when the friable balloons are used to fill honeycomb cores with lower use temperatures. In this work the Nomex[®] core that is utilized has a cell size of 0.318 cm. and a density of 0.048 gm/cc. The maximum use temperature of the core is 235°C and thus a modification to the process cycle is necessary to efficiently process the friable balloon precursor. In this situation the core and foam are held at 230°C for two hours in a nitrogen environment to minimize damage to the core. The final foam filled part including Nomex[®] core has a density of 0.088 gm/cc.

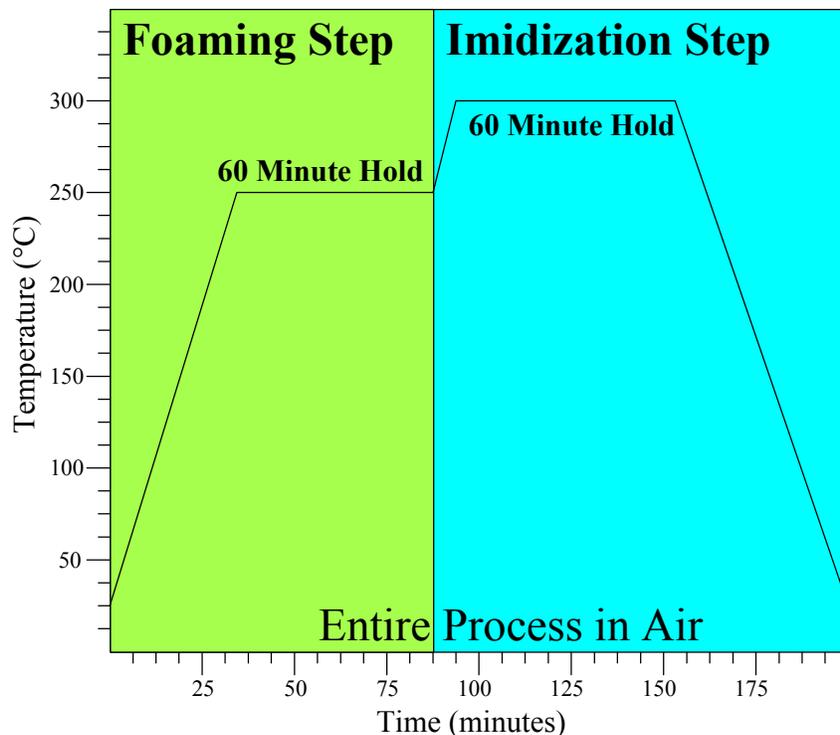


Figure 3 Cure Cycle for Polyimide Friable Balloon Foams

Figure 4 displays samples of the foam filled honeycomb from the friable balloon precursor. Visual inspection of foam specimens indicated a uniform cellular structure for all foam specimens until the density approached 0.08 gm/cc. In order to obtain densities higher than 0.04 gm/cc, friable balloons are crushed to reduce the initial volume which they occupy. The fragmented friable balloons allow more material to be filled into the mold before the entire cavity is filled. The balloon shards are uniformly mixed to ensure a homogeneous size distribution during processing. However, inspection of foams fabricated at densities above 0.04 gm/cc indicated the formation of a multi-density layer

within the foams. Further study into the fabrication of high-density foams from the friable balloons is necessary to alleviate this multi-density layer.

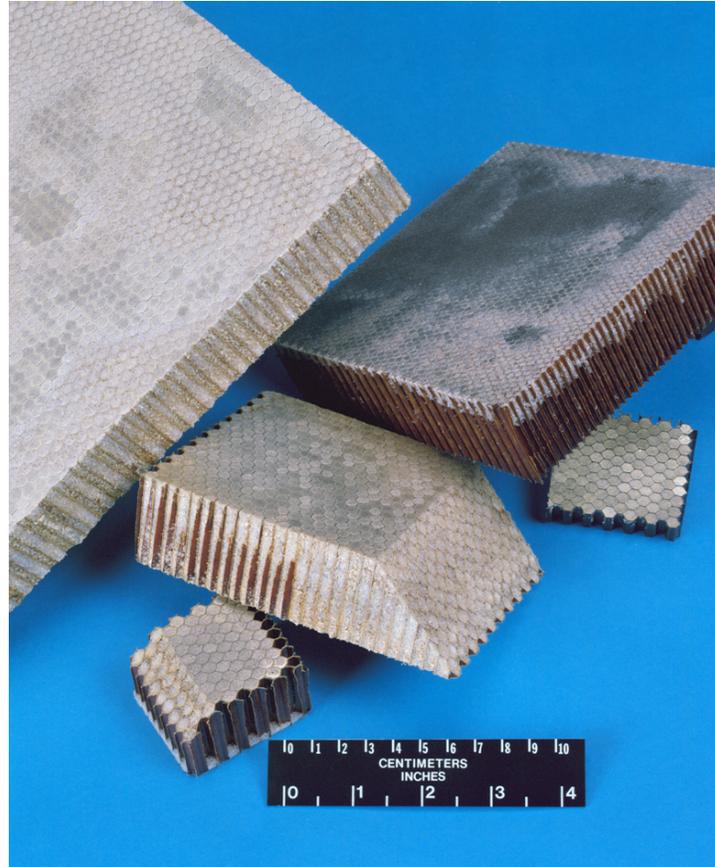


Figure 4 Photograph of Several Foam Filled Honeycomb Specimens

2.3 Closed Cell Content Testing The proportion of closed to open cells in a given foam material is important because it quantifies its resistance to the flow of gases through the foam and thereby its insulation characteristics. Further, “cryopumping” that occurs when thermal cycling acts to pump fluids into the foam and condense to the gas phase as the temperature rises to ambient. This increase in temperature can damage the foam structure, however it is retarded by the percentage of closed cells within a foam.

Closed cell content measurements were performed according to ASTM D - 6226 utilizing a Quantachrome UltraFoam 1000. Closed cell measurements are determined by obtaining the open cell content from Boyle’s Law. Boyle’s law states that the volume of a gas at constant temperature is inversely proportional to its pressure ($V=1/P$). Therefore, if a known volume is pressurized in a contained chamber the decrease in pressure can be correlated to the actual volume and simple mathematics will allow the open cell content to be determined. Once the open cell content is determined, the closed cell content can be

obtained. Measurements were performed on seven different polyimide friable balloon foams with densities ranging from 0.020 gm/cc to 0.096 gm/cc.

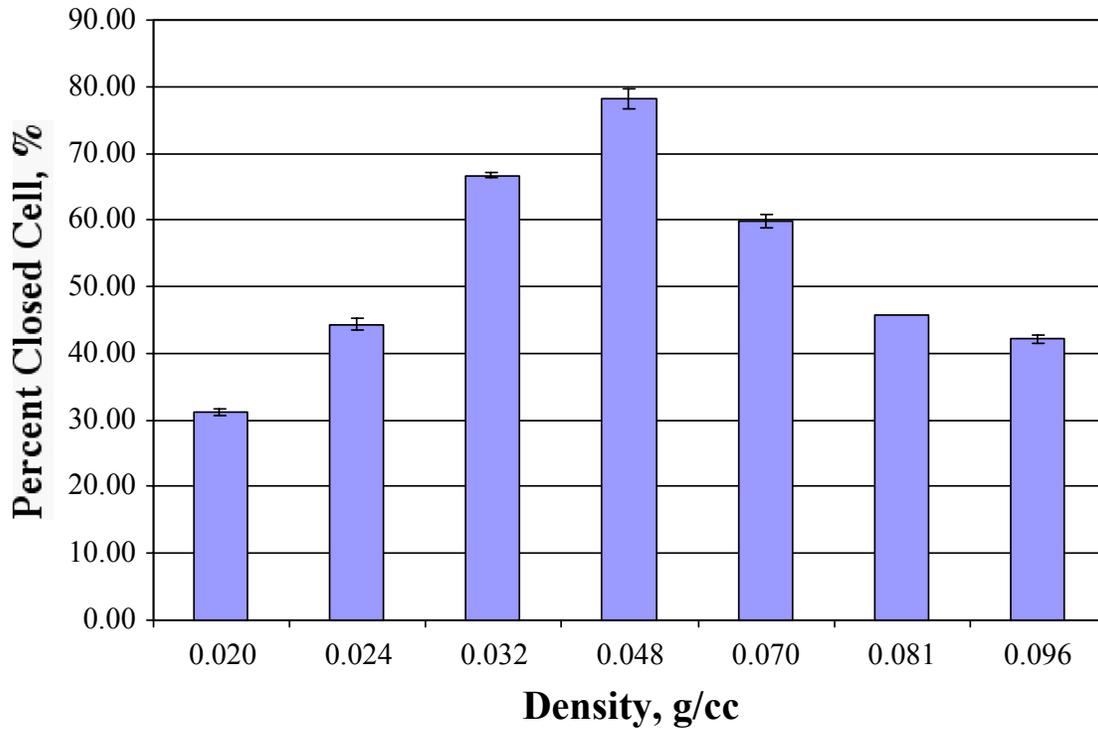


Figure 5 Closed Cell Content of Friable Balloon Foams

Figure 5 shows that, as the density is increased from 0.02 to 0.048 gm/cc, the closed cell content of the foams increases from 32% to a maximum of 78%. The low closed cell content at 0.02 gm/cc can be explained in part by the lack of sufficient material present to completely fill the interstitial voids and thus a lower closed cell value is obtained. As the density is increased, more material is present and a greater percentage of the interstitials are filled. Figure 5 also shows that as the density of the foam is further increased from 0.048 to 0.096 gm/cc, the closed cell percentage decreases from 78% to 42%. Thus, the greater the foam density, the greater the open cell percentage. This result is likely due to the kinematics of the foaming process. For the lowest density foams, the friable balloon experiences the largest degree of expansion. Given that the initial shape of the friable balloon is near spherical, as the multiple friable balloons inflate, the balloon shape changes as multiple inflation paths intersect. At the point the spherical elements first touch, the space not filled by the balloon is open cell space. As the balloons further expand, the closed cell space increases and the open cell regions decrease. Therefore, the closed cell fraction is proportional to the degree of friable balloon inflation and thereby, inversely proportional to foam density.

2.4 Mechanical Testing of Neat Foam Specimens Foam filled specimens are fabricated at several densities to be tested for mechanical properties under tensile and compressive loads. Flatwise tensile specimens are tested according to ASTM D-1623. The specimens are cut to a dimension of 5.08 cm x 5.08 cm x 2.54 cm. and are then adhesively bonded to aluminum blocks utilizing Hysol EA9394. [Figure 6](#) depicts the specimen lay-up and mounting blocks. The specimens are allowed to cure for a minimum of 24 hours at room temperature under load to ensure intimate contact between the testing blocks, the adhesive, and the foam. The foam specimens are then loaded into an instron test fixture and tested to failure.

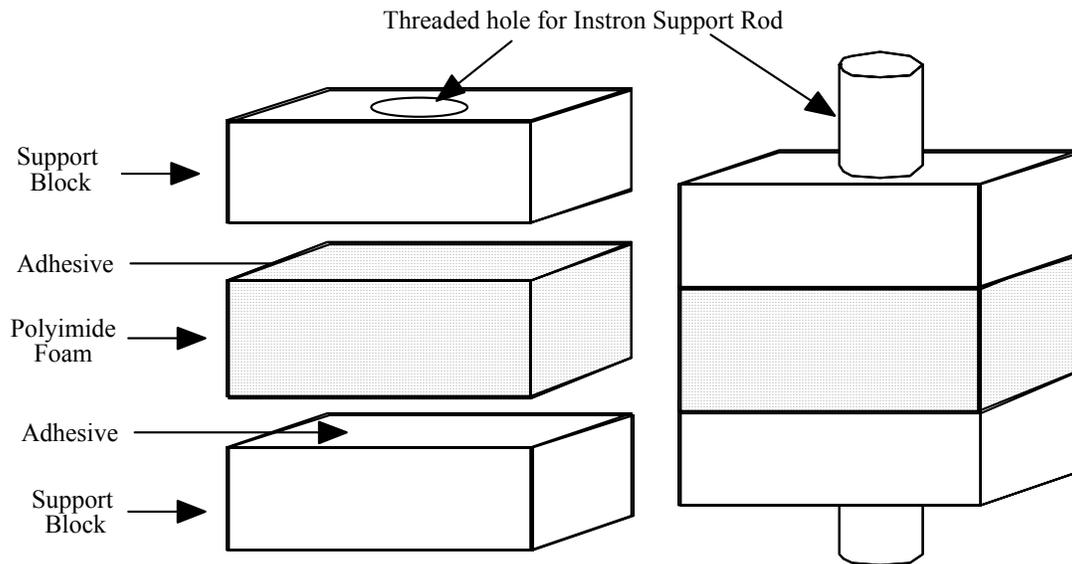


Figure 6 Cartoon of Flatwise Tension Specimen Set-Up

The foam tensile strengths are shown in [Figure 7](#) for foams ranging in density from 0.040 to 0.11 gm/cc. The tensile strength is shown to be greatest for the 0.074 and 0.081 gm/cc foam density at 0.88 MPa. A photomicrograph of the 0.107 gm/cc foam is shown in [Figure 8](#). The foam density clearly varies within the specimen from 0.080 to 0.155 gm/cc. The failure is clearly shown to occur at the interface between the two density regions and may have resulted from a stress concentration. Thus, the tensile strength test results for the 0.107 gm/cc foam should not be taken as representative. It is also notable that the foaming process can lead to a laminar structure wherein layers of different foam densities are developed near the surfaces.

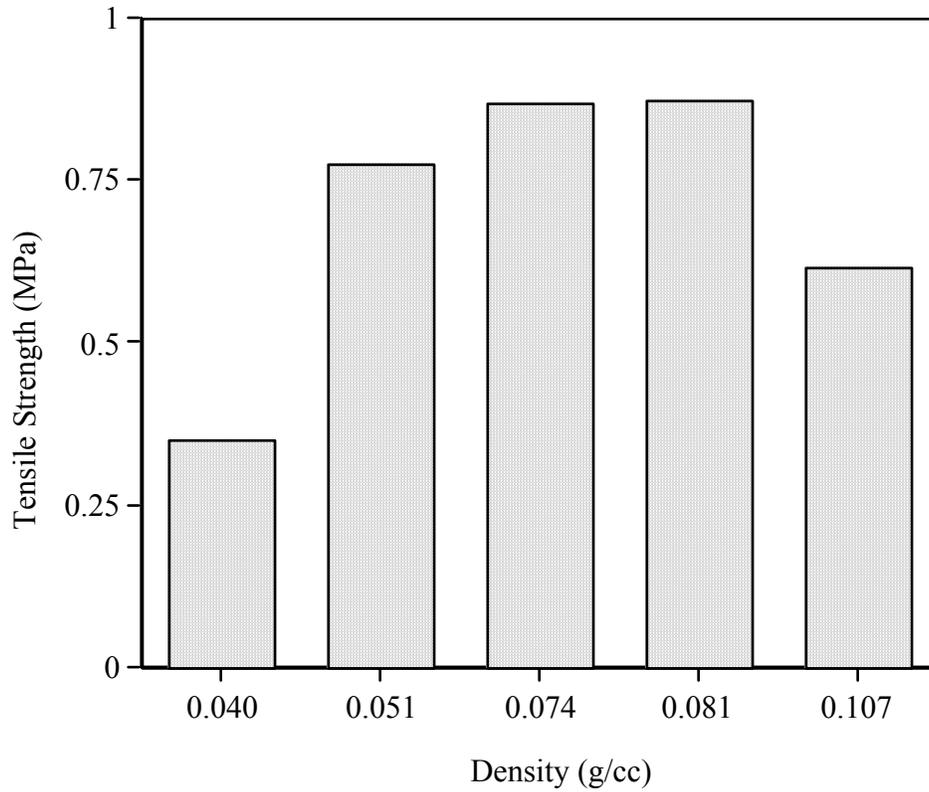


Figure 7 Flatwise Tensile Strength

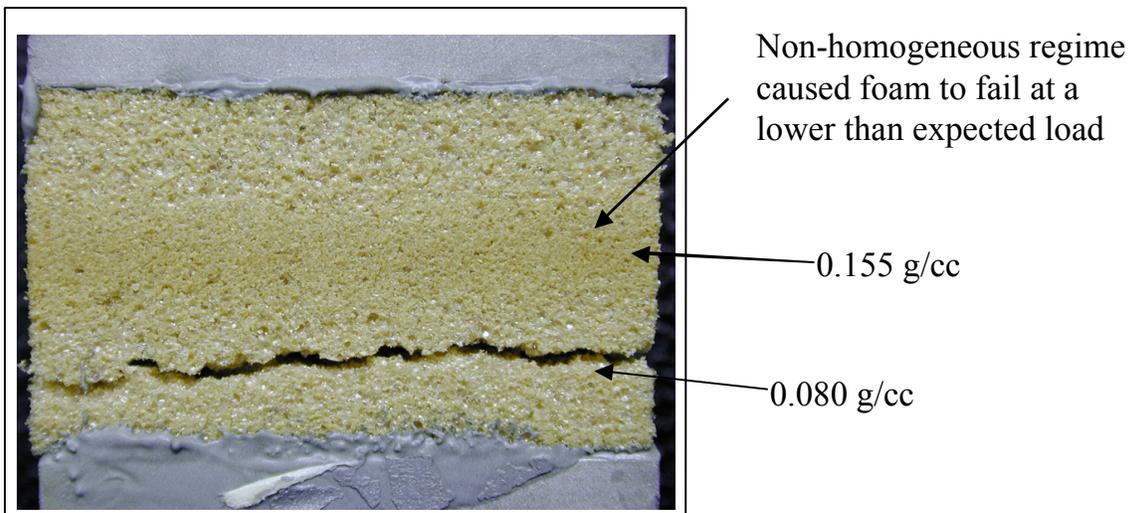


Figure 8 Photomicrograph of TEEK Friable Balloon Foam at 0.107 gm/cc

Friable balloon foam specimens at several different densities are tested in compression according to ASTM D3574. Compressive specimens are cut to a dimension of 5.08 cm x 5.08 cm x 2.54 cm and placed in a Unitech testing fixture. The foam specimens are

compressed at a rate of 0.1 cm/s until a 50% deflection is obtained and compressive strength measurements are taken and reported.

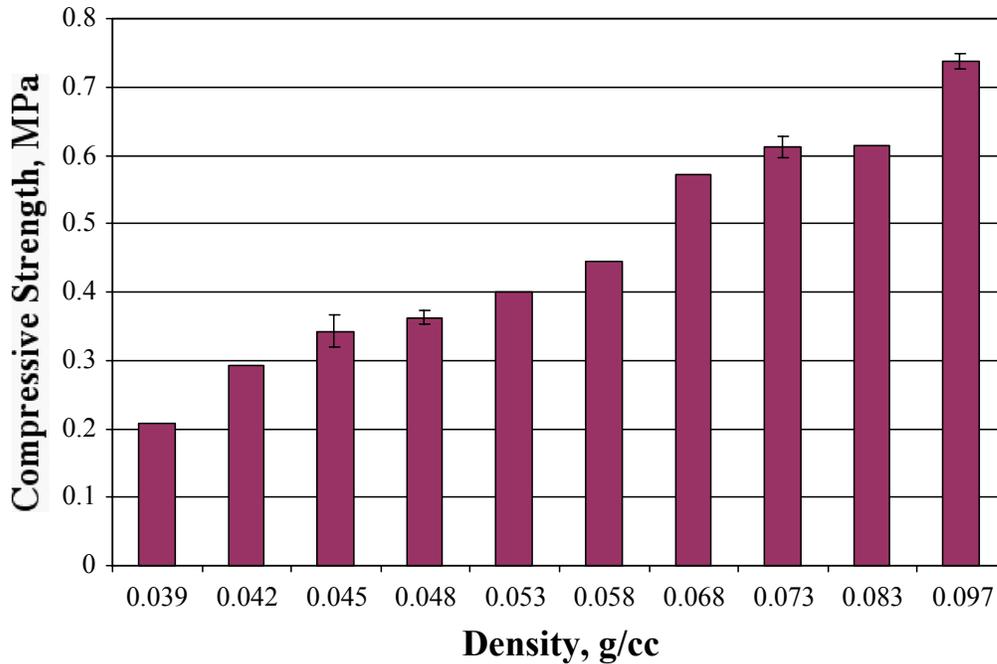


Figure 9 Flatwise Compressive Strength (50% Deflection)

Figure 9 displays the compressive strength data. The compressive strength properties are measured for samples of ten different densities, ρ , ranging from 0.039 to 0.097 gm/cc. These results show that as the density is increased, the compressive strength, X_c also increased. A linear fit to these data would provide the following relationship:

$$X_c = -0.17 + 9.26 \rho$$

This result shows a linear relationship between foam compressive strength and density as opposed to the results obtained by Gibson et al. [11] where foam strength is shown to be a cubic function of density. Values were obtained on foam specimens with densities ranging from 0.039 gm/cc to 0.097 gm/cc. In all cases, the 50% deflection strength increased with increasing density from a lower value of 0.21 MPa to a higher value of 0.74 MPa.

2.5 Mechanical Testing of Foam Filled Honeycomb Specimens Compression testing was performed for the foam filled honeycomb specimens as described in section 2.4. Foam specimens are cut to a 5.08" x 5.08" x 2.54" dimension and adhesively bonded to steel mounting blocks. Three different specimens are tested in compression; the empty core, foam filled core with a 0.159 cm gap on either side, and a completely foam filled specimen. The gap specimen was tested to verify the improved adhesive bond line possible through filleting / wicking of the adhesive down the core wall. This type of

specimen is advantageous when testing in tension but the effects in compression were unknown.

Table 1 Foam filled Honeycomb – Compressive Strength and Modulus

Specimen	Stress (MPa)	St. Dev.	Modulus (GPa)	St. Dev.
Nomex [®] Core	2.0684	---	0.1379	---
Foam / Nomex [®] – Gap	2.2865	0.0538	0.166	0.0012
Foam / Nomex [®] – No Gap	2.4945	0.1173	0.1753	0.0032

Table 1 displays the results of the compression testing to 50% deflection of the Nomex[®] core and Nomex[®] foam filled cores. The data indicates the introduction of the foam into the honeycomb cells improves both the strength and modulus of the system. This is to be expected due to the restriction on buckling of the cell walls by the foam. The foam filled Nomex[®] with a gap is only 10% lower in strength and modulus than the completely foam filled systems. This result is significant when utilizing the foam filled core systems not only in compression but tension where the filleting / wicking can enable much higher tensile loads than completely filled core can. Data to support this concept is in test.

3. CONCLUSIONS

The results of this preliminary study provide an insight into the methods by which polyimide foams can be fabricated with high closed cell content with a polyimide friable balloon precursor. The maximum closed cell content achieved is for a foam of density of 0.048 gm/cm³ with a closed cell content approaching 80%. Optimization of the friable balloon content to achieve maximum interstitial void filling and maximum closed cell content is discussed. A Gaussian distribution in balloon size is suggested as one approach to increase closed cell content.

Experimental data are presented for both compression and flatwise tensile strength for polyimide foams fabricated from friable balloons and of various densities. The tensile strength is shown to increase with density. An anomaly at a density of 0.107 gm/cm³ is observed wherein the foam density varied significantly though its thickness and the measured tensile strength is lower than expected. Further research is needed to develop methodologies to produce uniform density in foams for all densities required. Experimental results for the foam compressive strength showed a linear increase with density. These results are in contradiction with the cubic relationship between density and compressive strength proposed by Gibson et al [11]. Finally, foam filled Nomex[®] honeycomb is tested in compression and found to exhibit 25% greater strength than the unfilled honeycomb core. When a small gap in thickness of the honey comb core is left unfilled by the foam, the increase in tensile strength over unfilled core is 10%.

4. REFERENCES

1. Cellular materials Encyclopedia of Polymer Science and Engineering **1985** vol. 3 (New York: Wiley) pp. 1-59
2. NASA Contractor's Report **1994** NASA Contract No. NASW-4367, Research Triangle Institute, North Carolina.
3. Cellular materials Encyclopedia of Polymer Science and Technology **1965** vol. 3 (New Yor: Wiley) pp. 80-130
4. U.S. Pat. 3,249,561 (May **1966**) "Forming a Foamed Polyimide Article," W. R. Hendrix.
5. U.S. Pat. 3,310,506 (Mar. **1967**) "Cellular Polyimide Product," L. E. Amborski et.al.
6. U.S. Pat. 3,483,144 (Dec. **1969**) "Process for the Preparation of a Polyimide Foam," E. Lavin et.al.
7. U.S. Pat. 4,296,208 (Oct. **1981**) "Method of Preparing Polyimides and Polyimide Precursors (Spray Drying Polyimide)," J. Gagliani et.al.
8. U.S. Pat. 4,305,796 (Feb. **1982**) "Method of Preparing Polyimides and Artifacts Composed Thereof (Polymerization Using Microwave Radiation)," J. Gagliani et.al.
9. U.S. Pat. 4,439,381 (Mar. **1984**) "Methods of Preparing Polyimides and Artifacts Composed Thereof (Microwaves Develop Cellular Structure)," J. Gagliani et.al.
10. E. S. Weiser, et.al. High Temperature Polyimide Foams for Aerospace Vehicles, Journal of High Performance Polymers, March **2000**, Vol. 12, 1, 1-12.
11. L. J. Gibson and M. F. Ashby, Cellular Solids - Structures and Properties, 2nd Edition, Cambridge University Press, New York, NY., **1997**, pp. 183-224.