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Expancel® Foams: Fabrication and Characterization of a New Reduced Density Cellular Material for Structural Applications

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Expancel[®] Foams: Fabrication and Characterization of a New Reduced Density Cellular Material for Structural Applications

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Abstract

This study was initiated to produce a low-density centering medium for use in experiments investigating the response of materials to shock-loading. While the main drivers for material selection were homogeneity, dimensional stability, performance and cost, other secondary requirements included fine cell size, the ability to manufacture 5-10 cm-sized parts and an extremely compressed development time. We chose a non-traditional methodology using a hollow, expandable, polymeric microballoon material system called Expancel[®]. These microballoons are made from a copolymer of polyacrylonitrile (PAN) and polymethacrylonitrile (PMAN) and use iso-pentane as the blowing agent. The average diameter (by volume) of the unexpanded powder is approximately 13 μm , while the average of the expanded powder is 35-55 μm , with a few large microballoons approaching 150-200 μm .

A processing method was developed that established a pre-mixed combination of unexpanded and expanded Expancel[®] at a ratio such that the tap (or vibration) density of the mixed powders was the same as that desired of the final part. Upon heating above the tack temperature of the polymer, this "zero-rise approach" allowed only expansion of the unexpanded powder to fill the interstices between the pre-expanded balloons. The mechanical action of the expanding powder combined with the elevated processing temperature yielded free-standing and mechanically robust parts.

Although mechanical properties of these foams were not a key performance requirement, the data allowed for the determination of the best temperature to heat the samples. Processing the foam at higher temperatures enhanced both modulus and strength. The maximum allowable temperature was limited by dimensional stability and shrinkback considerations. Tomographic analysis of foam billets revealed very flat density profiles. Parts of any density between the low density expanded powder (approximately 0.013 g/cm³) and the higher density unexpanded powder (approximately 0.5 g/cm³) can be produced using this technique. The extremely wide range of accessible densities, ease of processing, relatively inexpensive materials, uniformity of the density, scaleable nature of the process should make this technology highly competitive for a variety of Defense Programs and commercial applications.

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Expancel[®] Foams: Fabrication and Characterization of a New Reduced Density Cellular Material for Structural Applications

Introduction

This study was undertaken after a series of discussions with LLNL staff regarding their need for a low density centering media for use in experiments investigating materials response to shock-loading. The initial plan was to use an aerogel derived resorcinol-formaldehyde material (Figure 1a) as the centering medium. While this cellular material had the required density, obtaining it in blocks that were large enough to machine the geometries of interest, without voids and cracks, was time consuming and expensive. However, the biggest disadvantage in using resorcinol-formaldehyde for this application was its inability to hold machining tolerances to ± 0.0025 cm. This was probably due to the high surface area, open cell nature of the material and its strong affinity for water. Solvent-blown polystyrene (Figure 1b) was also considered as a potential centering medium. In this instance, the source of the material was archival lots of foam from past Defense Programs. Large inhomogeneities in the macrostructure of this material, as seen in Figure 1b, were a principal deficiency. Early success with an alternate material, the subject of this report, resulted in solvent-blown polystyrene being removed from consideration.

While the main drivers for material selection were homogeneity, dimensional stability, performance and cost, other secondary requirements included fine cell size (1-3 μm), the ability to manufacture 5-10 cm-sized parts, and an extremely compressed development time. With regard to the latter, it was necessary to fabricate bulk material within a week of initiating this effort (in order to meet a pre-existing test schedule). In addition, it was desirable to identify a material and develop a process that could be scaled up to 18 cm-size parts using a commercially available material that had no high z elements (preferably only carbon and hydrogen). We were unaware of any commercially available foam or reduced density material that satisfied all of these requirements. However, recent experience with a hollow, expandable polymeric microballoon material called Expancel[®] suggested that we might be able to use it in a non-traditional way to satisfy most of the above requirements. Indeed, Figure 1c shows the resulting macrostructure of this microballoon material after it has been processed to form a self-supporting, low-density foam.

Figure 1. SEM images of (a) resorcinol-formaldehyde, (b) solvent blown polystyrene and (c) Expancel[®] Foam.

Expancel[®] microballoons are commercially produced as an inexpensive filler that expands its volume up to 50 times upon heating. This material is used in a wide range of applications including: printing inks, coatings, sealants, thermoplastic extrusions and injection moldings, shoe soles, stiffening agents for paper products, etc., but is not typically used to fabricate free-standing, structural forms. Expancel[®] powders are available wet or dry in the unexpanded and expanded forms.

Experimental

Materials Definition

Expancel[®] products are manufactured by Expancel, Inc. which is a sector of Casco Products, a business unit of the Dutch company, Akzo Nobel. To save on transportation costs, the unexpanded material is produced in Sweden and then shipped to their facility in Duluth, Georgia (1-800-786-4630) where it is expanded and then distributed through out the United States. The company makes a series of Expancel[®] products that cover a wide range of properties and processing characteristics to cover the variety of applications. Due to the program requirements listed earlier (mainly, no high z elements and as small of a cell size as possible) our selection options were very limited. Several of the available products contain vinyl chloride polymers that precluded their use due to the presence of chlorine, a high z element. Fortunately, Expancel, Inc. markets a line of products that are made from a copolymer of polyacrylonitrile (PAN) and polymethacrylonitrile (PMAN) and use iso-pentane as the blowing agent. These materials should have only carbon, hydrogen and nitrogen present, fulfilling requirement that the concentration of high z elements be minimized. Expancel, Inc. screens the unexpanded powder, producing several size fractions. By choosing the smallest size fraction, we have minimized the final cell size of the formed parts. The designation for the material used here is Expancel[®] 091DU and Expancel[®] 091DE. The “D” in the name indicates it is dry and the “U” and “E” indicate unexpanded and expanded, respectively.

The LLNL program supported the purchase of a 50 kg drum of Expancel[®] 091DU (lot #995032/19-24) for approximately \$950 and a box, containing 8 bags weighing 3 kg each, of Expancel[®] 091DE (lot #985193/194) for approximately \$1650. This purchase was made as a “program lifetime buy” to ensure uniformity of the starting material for several years. The pour, tap and vibration densities were determined for both Expancel[®] 091DU and DE and are shown in Table 1. The pour densities were determined by measuring the mass of the powder required to fill a 100 cm³ graduated cylinder. The tap densities were determined by tapping the 100 cm³ graduated cylinder 50 times on the counter and recording the reduced volume occupied by the powder. Vibration densities were obtained by recording the volume occupied by the powder after the time interval and power level (i.e., #4, #8, etc.) of the vibration table (Syntron, Model J-1) indicated in Table 1. Expancel, Inc. guarantees the performance of the Expancel[®] powders for at least one year when stored below 40°C. They also have anecdotal evidence that the material has shown no gross difference in performance when stored under 40°C for up to 5 years.

	091DU (44.68g)		091DE (0.97g)	
	Volume (cm ³)	Density (g/ cm ³)	Volume (cm ³)	Density (g/ cm ³)
Pour (graduated cyl)	100	0.45	100	0.010
Tap (50 times)	96	0.47	91	0.012
Vibrate (#4, 1 min)	93	0.48	78	0.012
Vibrate (#8, 2 min)	87	0.51	75	0.013
Vibrate (#8, 4 min)	86	0.52	74	0.013

Table 1. Pour, tap and vibration densities of unexpanded and expanded Expancel[®].

Physical Analysis

Particle size analysis¹ (Figure 2) of the unexpanded material was supplied by the vendor for the lot of material received. The graph in Figure 2 shows the particle size distribution (volume %). The average diameter (by volume) is approximately 13 μ m. This is consistent with Expancel[®] specifications indicating the average diameter of Expancel[®] 091DU is 10-16 μ m. This curve suggests that there are a large percent of small microballoons and this is confirmed by the data below showing that greater than 50% of the spheres are less than 6 μ m in diameter.

Number Statistics (Arithmetic)

Calculations from 1.345 μ m to 43.03 μ m

Number	38269				
Mean	6.813 μm		C.V.:	59.4%	
Median	5.920 μm				
% <	10	25	50	75	90
Size μm	2.240	3.459	5.920	9.540	12.62

Volume Statistics (Arithmetic)

Calculations from 1.345 μ m to 43.03 μ m

Volume	32.59e6 μm^3				
Mean:	12.35 μm		C.V.:	33.7%	
Median:	12.66 μm				
% <	10	25	50	75	90
Size μm	7.637	10.04	12.66	15.33	17.97

Figure 2. Particle size and number distribution of Expancel[®] 091DU (lot #995032).

Expancel, Inc. does not perform these same analyses on the expanded foam. However, company literature indicates that the average diameter (by volume) of Expancel® 091DE is 35-55 µm. Attempts were made to obtain particle size information on the expanded material, but proved unsuccessful. The expanded powder was mixed with an epoxy, degassed and allowed to cure at room temperature. The plan was to cut and polish a cross-section of the sample and perform image analysis on SEM images of the prepared surface. However, over the cure time of the epoxy, the microballoons floated to the top of the mixture with the larger balloons rising above the smaller balloons. Since there was no longer a random distribution of balloons within the epoxy mount, standard image analysis techniques could not be applied to the specimen.

Chemical Analysis

Samples of both Expancel® 091DU and 091DE were submitted to an analytical laboratory, (Galbreath Labs, Knoxville, TN) for elemental analysis. The samples were consolidated into monolithic specimens for ease of handling. Since the vendor-supplied information indicated that only polyacrylonitrile, polymethacrylonitrile and iso-pentane should be present, we were only expecting to see carbon, hydrogen and nitrogen present in the samples in non-trace amounts. Figure 3 shows both the chemical structure and empirical formulae for each of these components.

Figure 3. Chemical structures and empirical formulas of PAN, PMAN and iso-pentane.

The analytical results are summarized in Table 2. Oxygen was found at levels much higher than expected. However, this may be easily explained by the presence of surface adsorbed water, which is common for high surface area materials. The chlorine, sodium, calcium, iron, magnesium, strontium and zinc are all present as impurities, totaling about 1% of the mass for Expancel® 091DU and about 0.5% of the mass for Expancel® 091DE.

An empirical formula for Expancel® 091DE was calculated from elements present in concentrations greater than 1% of the composition as identified in the above Table (C, H, N and O). The formula derived from these elements was:

$$\text{C}_{3.7}\text{H}_{4.7}\text{N}_{1.0}\text{O}_{0.19} \quad (1)$$

Major Elements	Expancel® 091DU	Expancel® 091DE
Carbon	66.86%	66.83%
Hydrogen	8.15%	7.06%
Oxygen	4.05%	4.46%
Nitrogen	17.61%	20.79%
Chlorine	0.25%	0.47%
Sodium	0.63%	0.47%
Subtotal	97.55%	100.08%
Minor Elements		
Calcium	1019 ppm	1442 ppm
Magnesium	9233 ppm	4288 ppm
Strontium	20 ppm	28 ppm
Al, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Ga, Mn, Mo, Ni, P, Pb, Sn, Ti, V, Zn, Zr	<9 ppm	<10 ppm

Table 2. Elemental analysis (by weight) of Expancel® 091DU and DE performed by Galbreath Labs.

¹H NMR (Figure 4) was also used to determine an empirical formula for this material. The sample was dissolved in the solvent perdeutero dimethylformamide (DMF-d₇) and peaks were identified based on library comparisons. From the integration, we determined the ratio of PAN : PMAN : iso-pentane to be 3 : 1 : 0.1. When these ratios are multiplied by the empirical formulas (Figure 3) for each of the components and then summed, a formula,

Figure 4. ¹H NMR spectrum of Expancel® 091DE.

is obtained.² For comparison to the results from the elemental analysis (formula 1), formula 2 was normalized to the carbon stoichiometry of 3.7 by dividing formula 2 by 3.65, resulting in

Assuming the oxygen is due to adsorbed water, the hydrogen and oxygen ratios are increased by 0.4 and 0.2, respectively, for a formula of

This is in very good agreement with formula 1 derived from the elemental analysis of the Expancel[®].

Microballoon Structure

SEM images of the unexpanded powder is shown in Figure 5 and the expanded powder shown in Figure 6 illustrate the range of particles found in the material. These unexpanded microballoons have a rough surface and are puckered.

Figure 5. SEM images of Expancel[®] 091DU at (a) low and (b) high magnification.

After expansion, few if any of the spheres have puckered surfaces. As seen in Figure 6, there are several, very large microballoons approaching 150-200 μm in diameter. At this point, it is not known if or to what extent these larger spheres could cause local density gradients and affect overall homogeneity. If it is decided at some time in the future that these larger cells are undesirable, with considerable effort, the balloons could be sieved and the large diameter fraction separated. Such post-expansion handling is difficult due to the very low density of the expanded powder and the static charges that develop. One possible solution to this might be to incorporate the powder into a carrier fluid and use an ultrasonic sieve to fractionate the powder. Any of these options would be quite costly and would require substantial development efforts.

Figure 6. SEM images of Expancel® 091DE at (a) low and (b) high magnification.

Effect of Vacuum on Expancel® Structure

Certain parts fabricated from the Expancel® foam were required to withstand vacuum environments. Because of this, the effect of vacuum on the microballoons was examined. Expancel® 091DE was mounted on an aluminum stub using DAG (a mixture of powdered graphite and iso-propanol) and the diameters of several microballoons were first measured with an optical microscope at atmospheric pressure. The red numbers on top in Figure 7 indicate these measurements. The sample was then evacuated (7×10^{-3} torr) and sputter coated for the SEM followed by venting to atmospheric pressure. It was then placed in the SEM; vacuum was applied (5×10^{-6} torr) and the SEM image in Figure 7 was recorded. The sample was then vented to atmospheric pressure again and placed back under the optical microscope. The diameter of each balloon was then measured again (blue numbers on the bottom in Figure 7). The larger microballoon toward the middle of the micrograph, indicated by a star, had collapsed when viewed the second time in the optical microscope. When this sample was returned to the SEM for a second time the same microballoon re-inflated but was now distorted and oval shaped. As a general observation, many of the larger spheres were found to vent and shrink back after experiencing vacuum twice, while the smaller spheres tended to expand. The conclusion from this vacuum study was that the effect was only on the surface and would be acceptable for the application.

Figure 7. SEM image of Expancel® 091DE with measurements of the individual microballoons recorded before (top-red) and after (bottom-blue) in an optical microscope at ambient pressure.

Synthesis and Characterization of Foam Structures

Cylindrical Billets

Our original attempt to supply LLNL with machineable blanks was to place the neat, dry unexpanded Expancel® (no resin or binder) into a metal mold (sealed, but not airtight) and heat it above the polymer T_g, i.e. expansion temperature of the balloons. This would allow the internal pressure of the microballoon to expand the softened polymer. The unique aspect of this method is the absence of resin or binder. In this instance, we were relying on the pressure generated by the expanding microballoons in the fixed mold volume to tack the microballoons together while the polymer was above its T_g.

Figure 8. Synthetic scheme for first attempt to make monolithic Expancel® foam parts.

As shown schematically in Figure 8, the initial synthetic attempt involved loading a right circular cylindrical mold with enough unexpanded Expancel[®], such that after heating and expansion to fill the ullage, the final part would have the desired density of 0.18 g/cm³. The results from this first attempt were promising in that the balloon-to-balloon tacking was sufficiently strong to produce a monolithic billet with good mechanical integrity. However, x-ray tomographic reconstruction (Figure 9) revealed substantial density gradients throughout the part. The image shown in Figure 9 was obtained by recording multiple radiographs of the part, then using a computer to reconstruct the images in three dimensions. The reconstructed image is then interpolated to form a solid, 3D rendering of the part. The false color image shown in Figure 9 is a slice, normal to the cylindrical axis of the interpolated image. Red represents regions of low density while blue represents regions of high density. The trace shown at the top of Figure 9 is a density profile taken across the diameter of the image as indicated. These tomography results indicated that the perimeter of the billet had significantly lower density than the core.

This density gradient can be rationalized as follows: Initially upon heating, the Expancel[®] powder closest to the mold wall gets hot and expands, thereby insulating and constraining the less expanded interior microballoons. By the time the material in the center of the cylinder is above the T_g of the polymer, virtually all of the free volume is gone and the microballoons in the interior cannot expand as fully as those at the perimeter. This results in the observed lower density around the outer portion of the part and higher density in the middle.

Figure 9. X-ray tomographic reconstruction of first synthetic attempt.

Three potential solutions to this problem were suggested. The first idea was to heat the mold and Expancel[®] more slowly so there would be a smaller temperature gradient across the diameter of the mold – hopefully resulting in a smaller density gradient. A limitation associated with this

method is that if the Expancel[®] is heated too long, the microballoons will collapse and cause the sample to “shrinkback”. A second method involves rotation of the mold on at least two axes while heating. This mixing of the Expancel[®] powder while heating would ensure more uniform heat distribution and should result in smaller density gradients. Equipment to perform this type of procedure was available at LLNL (not at SNL), but this option was not examined due to success with the last, less elaborate approach. The third, and ultimately preferred approach (Figure 10), was to combine unexpanded and expanded Expancel[®] at a ratio such that the tap (or vibration) density of the mixed powders was the same as that desired of the final part. This “zero-rise approach” has the effect of completely filling the mold volume with powder and therefore, upon heating allows only expansion of the unexpanded powder into the interstitial regions between the pre-expanded balloons.

Figure 10. “Zero-rise approach” to monolithic Expancel[®] foam parts.

Many parts were made for testing and evaluating this process. Cylindrical parts ranging from 70 mm diameter by 100 mm high (Figure 11a) to 130 mm diameter by 150 mm high were prepared. Cylinders were prepared having uniform densities that ranging from 0.013 to 0.5 g/ cm³. These cylinders were examined via x-ray tomography similar to the analyses shown above in order to characterize density uniformity, sectioned for SEM analysis and machined into parts for LLNL testing.

Figure 11. Picture of the various parts prepared using the “zero-rise approach”. (a) cylinders, (b) disks and (c) top hats.

A simple, hollow metal cylinder sitting on a metal plate formed the sides and bottom of the mold for cylindrical parts. After filling the mold with the mixture of expanded and unexpanded powder, another metal plate was placed on top and the assembly clamped together to prevent the Expancel[®] from pushing the lid off the mold as it is heated. The mold was then placed in a forced-air oven, typically for 1 hour at 150°C. These parameters were varied and their effects on shrink back and mechanical properties examined. It was found that the mold must be allowed to cool to below 80°C before the clamp can be removed to prevent the Expancel[®] from further expanding.

Tomographic analysis of two billets made by this procedure are shown in Figures 12 and 13. In Figure 12, the starting 0.20 g/cm³ cylinder (130 mm diameter, 150 mm long) had been mechanically cut in half and the two resulting cylinders placed side by side with the cut ends facing up, for radiography, thus allowing exposure and analysis of two locations of the cylinder at one time. The false color images shown in Figure 12 illustrate the uniformity in the density at four locations along the cylindrical axis of the cylinder while the associated line graphs show the x-ray attenuation (which is directly related to density) along the line traces in each of the images to the left. The tomographic analyses indicate very flat density profiles at both the half height (Figure 12a) and near the cast ends of the cylinder (Figure 12b). Figure 13a-e show the results of a similar tomographic analysis of a smaller (70 mm diameter by 100 mm long) and lower density (0.16 g/cm³) billet at five locations along its cylindrical axis. Here too, the results indicate very flat density profiles across the diameter of cylinder at each location, as well as little variation in the density along its length.

These billets were delivered to LNL for subsequent testing. Indeed, this “zero-rise approach” proved so successful, that it was used to make all of the subsequent parts discussed in this report. Parts of any density between the low density expanded powder (approximately 0.013 g/cm³) and the higher density unexpanded powder (approximately 0.5 g/cm³) can be produced using this

technique. The extremely wide range of accessible densities, ease of processing, relatively inexpensive materials, uniformity of the density, scalable nature of the process and the fundamental understanding of this material we have gained in this project should make this technology highly competitive for a variety of applications. Sandia is pursuing a patent on this technology.

Figure 12. Tomographs of “zero-rise approach” for a 130 mm diameter cylinder with a target density of 0.20 g/cm^3 . The red line in the graphs represents the data for the half cylinder located in the top portion of each figure. Tomographic virtual “slices” at: (a) 13 mm from the saw cut middle of the cylinder and (b) 19 mm from the cast ends.

Figure 13. X-ray tomographs of “zero-rise approach” for the 70 mm diameter cylinder with a target density of 0.16 g/cm^3 . Tomographic virtual “slices” are (a) 1.9 cm, (b) 3.8 cm, (c) 5.7 cm, (d) 7.6 cm and (e) 9.5 cm up from the bottom of the 100 mm long cylinder.

Before making a part, the unexpanded and expanded powders needed to be thoroughly mixed. This mixing was accomplished by placing predetermined amounts of each powder into a 4-liter, wide-mouth polybottle fitted with baffles. The bottle was sealed and the contents were mixed on a paint can roller for 3-5 hours. The baffles were found to be necessary to ensure good mixing due to the slippery nature of the powders on the smooth inside surface of the polybottle. The desired density of the final part and the density of the starting powders shown in Table 1 determined the ratio of the pre-expanded to unexpanded powders. An example of how this ratio

and the amounts of each material are determined is shown in Figure 14. The selection of the appropriate density (pour, tap or vibration) is determined by the method used to load the mixture of powders into the mold (pour, tap or vibration).

$$\begin{aligned}
 &\text{Density of final part} = 0.20 \text{ g/cm}^3 \\
 &\begin{array}{cc} \text{Expancel}^{\text{®}} & \text{Vibration densities (\#8, 4 min)} \\ 091\text{DE} & 0.013 \text{ g/cm}^3 \\ 091\text{DU} & 0.52 \text{ g/cm}^3 \end{array} \\
 &\text{Batch size} = 500 \text{ cm}^3, \text{ therefore } 100 \text{ g total of both powders} \\
 &\text{Ratio calculation for density} = 0.20 \text{ g/cm}^3 \\
 &x = \text{volume \% } 091\text{DE} \\
 &0.013x + 0.52(1-x) = 0.20 \\
 &x = 0.63 \text{ or } 63\% \text{ of the volume is } 091\text{DE} \\
 &\text{and } 37\% \text{ of the volume is } 091\text{DU} \\
 &0.63 \times 500 \text{ cm}^3 = 315 \text{ cm}^3 \\
 &0.013 \text{ g/cm}^3 \times 315 \text{ cm}^3 = 4.10 \text{ g of } 091\text{DE} \\
 &0.37 \times 500 \text{ cm}^3 = 185 \text{ cm}^3 \\
 &0.52 \text{ g/cm}^3 \times 185 \text{ cm}^3 = 95.9 \text{ g of } 091\text{DU}
 \end{aligned}$$

Figure 14. Example of calculation to determine the ratio and amounts of each powder to mix for a given density and batch size (0.2 g/cm³ and 500 cm³ in this example).

Alternative Geometries

Smaller disk shaped parts (Figure 11b) were prepared for certain high-rate experiments performed on a two-stage gas gun at LLNL. These disks were 4 cm diameter and either 0.3 or 0.5 cm high. A total of approximately 35 disks were prepared at densities of 0.08, 0.20 and 0.45 g/cm³. The molding assembly for these disks was similar to that of the cylinders discussed above, except that more care was given to machining the end plates and the metal ring that formed the sides of the mold. Because these parts were intended to be molded to shape with no additional machining, size, dimensional stability and surface finish were considered critical. Initially, machined aluminum plates were used to form the ends of the mold. However, upon gold coating, LLNL personnel noted the presence of shallow concentric grooves on the surface of the Expancel[®] foam disks. Closer inspection of the aluminum end plates revealed that the foam had reproduce the machining marks formed during the polishing of the end plates. These aluminum plates were replaced with glass flats and no further problems with surface finish were encountered. A 2 mm thick silicone rubber pad was used on the outside of each glass end plate to help spread the load and prevent cracking or breaking from the metal clamp.

Top hat shaped parts (Figure 11c) were also fabricated for testing in the same two-stage gas gun, to determine the equation of state of the Expancel[®] foam material. The fabrication procedure was the same as for the disks and used the same glass flats as end plates. The larger diameter of the top hat was 2.5 cm and the smaller diameter was 1.2 cm. The thickness of the larger

diameter portion was 0.3 cm and the smaller was 0.25 cm. These top hats were prepared at the same densities as the disks. All 35 attempts to fabricate these parts were successful giving a yield of 100%.

To see if parts could be molded to more complex shapes and still hold dimensional tolerances, a large hollow hemispherical, aluminum mold (Figure 15) with an OD of 16.6 cm and an ID of 9.6 cm was machined. This mold was used to prepare parts having a density of 0.20 g/cm^3 . The mold was designed with three fill holes, six closure bolt holes and three removal (jack) holes. Much of the bulk of this mold was removed to aid uniform heat transfer to the microballons. The timing and order of disassembly of the mold was found to be important. If the mold was allowed to completely cool prior to removal of the inner hemisphere, the relative differences in the coefficients of thermal expansion between the polymer and the metal mold caused the foam to shrink down on the mold. It was virtually impossible, then, to remove the molded form without causing substantial damage. A procedure was developed to obviate this problem. A thermocouple was placed inside one of the unused jack holes and used to monitor the temperature of the inner surface of the top of the hemisphere. When the inner surface temperature cooled to 80°C the top half of the mold could be removed. At this temperature the Expancel[®] foam was dimensionally stable and held the required tolerances. The molded foam and the bottom half of the mold were then allowed to cool to room temperature. It was found that the cooled foam part could then be easily removed from the hemispherical mold. This last step should be performed gently, allowing the vacuum that is formed between the mold and the part to be released as the part is removed.

Figure 15. Large hemispherical mold and a 0.2 g/cm^3 Expancel[®] foam part produced from the mold.

Characterization of Net-Shape Parts

Microscopy has been very helpful in providing insight into the macrostructure of these novel foam materials. Early in the development of these procedures, a concern was expressed that a thin, low density zone may exist around the outer portion of every molded part. Such a skin could form due to the hot metal mold prematurely expanding the Expancel[®] powder at the mold-balloon interface. SEM images of a fracture surface of a monolithic foam part (Figure 16a) revealed that the cell size distribution was uniform from the bulk right up to and including the microballoons at the edge of the part. Figure 16b shows morphology of the microballoons that contacted the surface of the mold. The micrograph shows that the balloons retain their equi-axed shape, flatten as they assume the shape of the mold surface. This flattening results in the exclusion of nearly all of the initial interstitial space at the surface yielding a part that has essentially a smooth, unbroken skin.

Figure 16. SEM image of (a) fracture surface at a cast surface edge and (b) cast surface.

SEM analysis of the fracture surface of a large hollow hemisphere is shown in Figure 17. The images were recorded at the locations indicated in the center of the figure. These images clearly show that the individual microballoons near mold surfaces (a, b and d) are much more likely to tear as a part is fractured than those located near the interior. We believe that this observation is related to the effect of the hot mold on the microballoons in close proximity to the metal surfaces. The microballoons located closer to the surfaces of the part heat more quickly than those in the interior (they may also get hotter than those nearer to the interior). Because they are at a temperature longer, they tack together more effectively. Upon fracture of the part, these microballoons are more likely to tear rather than separate. This observation could also help explain some of the density gradients (discussed later) observed in this part. One possible solution to this “time-at-temperature” problem is to heat the mold and powder up to just under the expansion temperature and hold it there to allow the temperature to equilibrate throughout the part. The filled mold could then be slowly heated above the expansion temperature of the Expancel[®] taking care not to heat too slowly or for too long (which will cause the microballons to deflate). One way to monitor this process to help determine an optimum temperature profile is to incorporate a pressure transducer on the part to diagnose the internal pressure and the degree of shrinkback.

(a)

(b)

(c)

(d)

Figure 17. SEM images of a fracture surface of a large hollow hemisphere foam part. Locations are as indicated in center figure.

As discussed earlier, the effect of vacuum on the cell structure was of interest. Figure 7 showed the effect on the starting powder, but in Figure 16, for example, it is very difficult to discern if the vacuum is causing any distortion of the part. The surface of the part shown in Figure 16b appears to be quite flat, as expected for a cast surface. However, when the sample is tilted to an observation angle of approximately 30° in the SEM (Figure 18), the effect of the vacuum can clearly be seen. The surface microballoons are puffed out and the surface is rippled, not flat as we had thought from the other SEM images recorded at an observation angle of 90° .

(a)

(b)

Figure 18. (a) SEM image of cast surface of an Expancel[®] foam part showing the effect of vacuum on the microballoons. (b) Orientation of the sample in the SEM.

Uniformity of Net Shape Parts

Density gradients in the hemispherical parts were characterized using x-ray tomography as described earlier. The density gradient through one plane of the hemisphere is shown in the false color image, Figure 19. The density profile shown in Figure 19b is taken along the trace indicated in Figure 19a. This data indicates that lower density material is present around the exterior of the part with higher density zones toward the middle. This is consistent with heating the part too rapidly.

Figure 19. (a) X-ray tomographic reconstruction of and (b) density profile of slice through a large hollow hemispherical foam part.

In an attempt to determine the low-density limit of this technology, a cylindrical part was made using only expanded Expancel[®]. The expectation was that the microballoons would experience some small, additional thermal expansion and be tacky enough to form a monolith with sufficient mechanical integrity to support its own weight. Indeed, this was observed. The cylindrical part could be handled carefully without damaging the foam. However, more foam surface attrition was observed on these low density foams as poorly bonded microballoons are transferred during handling. The SEM image (Figure 20) of this low density foam shows that the microballoons are barely tacked together. There is little or no distortion and flattening of the contact points. These observations are consistent with the fragile nature of this foam. Tomographic slices were recorded at 2.0cm, 4.0 cm, 6.0 cm, and 8.0 cm from the bottom of the cylinder as shown in Figure 21. The density profiles at these locations appear to be quite flat, although there may be some fall off at the edges indicating a small lower density region on the outside of the part. Unfortunately, due to the noise associated with measuring the x-ray attenuation of a very low-density sample, the extent of a density gradient in this sample is not clear.

(a)

(b)

Figure 20. SEM image of low-density (0.013 g/cm^3) Expancel® foam. (a) High magnification. (b) Low magnification.

Figure 21. X-ray tomographic images and density profiles at slices located at (a) 2 cm, (b) 4 cm, (c) 6 cm and (d) 8 cm from the bottom of the low-density (0.013 g/cm^3) cylinder.

Mechanical Properties of Expancel® Foam

The mechanical properties of these foams were of general interest but were also key to determining the optimum mold temperature for part fabrication. Strength and modulus are typical mechanical properties that are used to characterize foams. Usually, high strength and modulus are desirable properties in free-standing foam monoliths. Given the nature of the "zero-rise approach", processing the foam at higher temperatures ought to enhance these properties. Of course, the maximum allowable temperature is limited by dimensional stability and shrinkback considerations. To investigate this, disk shaped samples were prepared for mechanical testing. These samples were 0.3 cm thick and 4 cm in diameter. The mechanical property data shown in Figure 22 are for two specimens having the same density but processed at 130°C and 150°C respectively. Tests were performed on a servomechanical test frame at a displacement rate of 1.3×10^{-2} mm/sec. It is clear from Figure 22 that, processing temperature has a significant effect on strength. The strength for this 0.2 g/cm^3 foam more than doubled by increasing the processing temperature from 130°C to 150°C. Less apparent is the effect of processing temperature on the modulus of the foam. For the specimens shown in Figure 22, the modulus increased by a factor of two as well.

Figure 22. Quasi-static uni-axial compression stress-strain curves for various density foams at either 130°C or 150°C for 1 hour.

Figure 23 shows the effect of processing temperature on the modulus of the Expancel® foam. Notwithstanding the limited data, it is clear that the higher processing temperature yields foams of higher modulus, especially at the lowest density. Note that in this figure, density is normalized to the estimated solid polymer density ($\rho_0 = 1.2 \text{ g/cm}^3$). The figure also compares the density dependence of the Expancel® foam modulus with previous data obtained on

conventionally processed, water-blown, rigid polyurethane foam (PUR)^{3,4}. The figure shows that the density dependence of the Expancel[®] foam modulus is consistent with that measured for the PUR foams over a wide range of density.

Figure 23. Graph of modulus vs. density for Expancel[®] foams heated at either 130°C or 150°C for 1 hour and comparison to other polyurethane foam.

Summary

Relatively inexpensive, commercially available starting materials were combined in a non-traditional way to prepare a new class of rigid foams. These foams are resin-free, using environmentally friendly, polymeric microballoons (Expancel[®]) that expand and tack together upon heating. No expensive post-processing (curing, extraction, etc.) is required. These Expancel[®] foams are easily processed, requiring only a roller mixer, a vibration table, a scale and an oven—a minimal capital investment. The resulting robust foams are quite uniform and can be prepared with densities ranging from 0.013 g/cm³ to 0.5 g/cm³. The mechanical properties of these foams are both predictable and comparable to other structural polymer-based foams. Monolithic foams with complex geometries and near net-shape have been prepared using this process. If desired, the foams can be readily machined with tolerances less than ± 0.0025 cm. With respect to the initial project definition, components were delivered to LLNL personnel on schedule that met or surpassed all of their experimental requirements.

Footnotes

1. Technical Bulletin Number 3, Expancel, Inc. Duluth, Georgia.
2. $3 \times (\text{C}_3\text{H}_3\text{N}) = \text{C}_9\text{H}_9\text{N}_3$
 $1 \times (\text{C}_4\text{H}_5\text{N}) = \text{C}_4\text{H}_5\text{N}$
 $\frac{0.1 \times (\text{C}_2\text{H}_{12})}{\text{C}_{13.5}\text{H}_{15.2}\text{N}_4} = \text{C}_{0.5}\text{H}_{1.2}$
3. Goods, S.H.; Neuschwanger, C.L.; Henderson, C.C.; Skala, D.M. *J. Appl. Polym. Sci.* **1998**, 68, 1045.
4. Goods, S.H.; Neuschwanger, C.L.; Whinnery, L.L.; Nix, W.D. *J. Appl. Polym. Sci.* **1999**, 74, 2724.

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