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Syntactic Foam Supports

By H. M. McIlroy

Published June 1980

Final Report

Prepared for the United States Department of Energy
Under Contract Number DE-AC04-76-DP00613.

Bendix **1** **Kansas City**
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SYNTACTIC FOAM SUPPORTS

By H. M. McIlroy

Published June 1980

Final Report
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**Kansas City
Division**

SYNTACTIC FOAM SUPPORTS

BDX-613-2425, Final Report, Published June 1980

Prepared by H. M. McIlroy

Foams consisting of blends of a polyimide resin and glass microbubbles were prepared to provide thermal protection and energy absorption. With the selected type of glass microbubble, tests were conducted to measure the effect of foam formulation, microbubble strength, and molding pressure on certain mechanical, thermal, and environmental properties.

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SUMMARY

Three support parts were designed to provide thermal insulation and energy absorption upon impact. Several resins and low density fillers were considered for this application. However, only foams made from Kerimid 601 polyimide resin and glass microbubbles (GMB) were evaluated.

The Kerimid 601 is a powdered solid that melts prior to curing to a highly crosslinked polymer. Since it is a fully imidized addition type polymer, no volatile by-products are evolved during the cure.

Glass microbubbles were selected as the low density filler to provide energy attenuation by crushing at a constant load level over wide deflections. An understanding of the packing of the GMB was considered important in providing reproducible and high quality foams. A literature review revealed that a limited amount of work had been done to characterize the packing behavior of materials with a distribution of particle sizes. Most of the investigations were concerned with discrete and monosized particles. Glass microbubbles consist of a continuous distribution of sizes from 10 to 200 μm in diameter. Most of the particles are spherical, but some small quantity of the GMB are broken. Although the system is relatively complicated with a distribution of sizes, densities, and a quantity of glass chips (from broken bubbles), simple tests are available to measure the average packing. The packing factor or volume fraction of GMB in a given volume is about 0.65 for B35D glass microbubbles. This means that in a foam, the maximum volume of glass microbubbles is 65 percent. Exceeding this volume will crush part of the bubbles.

The manufacturing procedure for the foam is uncomplicated. The powdered resin and glass microbubbles are combined as a dry mix in a twin shell blender. The dry mix is charged to a mold and heated to the melt temperature. When the resin has melted, pressure is applied to consolidate the foam. A study was made to evaluate different cure cycles.

During the preliminary evaluation, foams were made from the Kerimid 601 resin and six types of glass microbubbles. The foams selected for extensive testing were made from blends of the Kerimid 601 resin and B35D glass microbubbles. The goal was to learn how to manufacture a foam with a uniform density and predictable strength properties. Information was needed on the variables associated with molding the foam. These molding studies were separated into the major areas of foam formulation, glass microbubble strength, and molding pressure.

The crush strength data on test specimens machined from production type billets leads to a different conclusion than data obtained from individually molded test coupons or from specimens taken from small test blocks. The data from the molded coupons and small test specimens indicate that the strength depends upon the foam density and is independent of the foam formulation. The other series of data taken from molded billets indicate that the volume fraction of GMB in the formulation is the controlling factor, and that at a constant density, the formulation with the highest GMB content will be the strongest. Additional testing is required to clarify the apparent contradiction in data.

Certain mechanical, thermal, and environmental properties of the foams were measured. The crush strength was measured at four temperatures and up to 50 percent deflection. Shear strength and tensile strength were measured at room temperature. Thermal conductivity and thermal expansion were measured for different density foams. The effects of moisture on the crush strength of the foam and equilibrium moisture contents also were measured.

The normal procedure for preparing parts from syntactic foam is to mold a billet or block of foam, and in subsequent operations machine the part to final dimension. When this program was cancelled, a process was being developed to mold-to-size certain syntactic foam parts. By adjusting foam formulation, heat rates, and molding pressure, significant improvements were made in dimensional control of mold-to-size parts.

DISCUSSION

SCOPE AND PURPOSE

Structural foam parts for energy attenuation and thermal insulation were required. This project was to provide design data on the types of glass microbubbles available and to measure mechanical, thermal, and environmental properties of candidate foam systems.

PRIOR WORK

A series of foam materials were tested by Sandia Laboratories Livermore. The crush strength at room temperature, and at 149°C and the amount of deflection at room temperature were measured. Foam samples, made from Kerimid 601 polyimide resin and glass microbubbles submitted by Bendix Kansas City, performed well during these tests.

ACTIVITY

Resin

Five resins were considered as the binder for the syntactic foam support parts. These resins were Kerimid 601 and Kerimid 353, both polyimides, QR-4-3154, a silicone resin, Xylok 225, a phenolic resin, and Xylok 234C, an epoxy resin. The QR-4-3157 and Xylok 234C are liquid systems while the Xylok 225, Kerimid 601, and Kerimid 353 are powders that soften or melt prior to cure. The Kerimid 601 resin had been selected as the binder resin for a syntactic foam made with carbon microbubbles and was available for making preliminary test parts for this application. Because of the success of these early tests, Kerimid 601 was the only resin evaluated.

Kerimid 601 is an addition-type polyimide resin. The resin is made from maleic anhydride and methylene-dianiline (MDA) and is fully imidized when received from the vendor. Since it is a fully imidized addition polymer, no volatile by-products are evolved during the cure.

The small particle size allows the powdered resin to mix easily with the glass microbubble (GMB) filler and to fit between the individual GMB. Although a solid at room temperature, the Kerimid 601 melts at about 100°C and is a very viscous liquid for 30

to 60 minutes at 120°C. While the resin is in fluid form, it flows around the GMB prior to cure. During the cure the resin bonds adjacent GMB to each other and forms a low density, rigid foam. Physical and thermal properties of the Kerimid 601 resin are summarized in Table 1 and in References 1, 2, and 3.

Filler

Six types of glass microbubbles were used in the initial formulation study with Kerimid 601 resin as the binder. Particle size distribution, bulk density, tap density, true particle density, sinker/floater ratio, alkalinity (pH), and isostatic crush strength were measured on the different types or grades of GMB. The test results are shown in Table 2.

According to the vendor, the GMB are all made from a chemically similar borosilicate glass. Different strengths are achieved by modifications of the manufacturing process. The suffix B in B408B denotes a general purpose grade of GMB. The A series of bubbles is called a high strength bubble while the D series is super strength. In addition to the relative strengths of the microbubbles, the A and D series are called floated microbubbles. That is, the bulk of the broken bubbles are removed during processing and prior to shipment. Also, the A and D series have a coupling agent added to improve adhesion to organic resins. Although the pH of the GMB is 9.1 to 9.5 the bubbles are insoluble in water and caking or lumping of the bulk microbubbles is not a problem.

A typical particle size distribution is given in Figure 1. The type bubble shown in Figure 1 (B40A) is one of the highest density glass microbubbles. Low density bubbles such as the B18A or B22A tend to be slightly larger in diameter throughout the distribution. For the B18A GMB, the particle sizes range from 20 to 220 μm .

The bulk density test consists of pouring the GMB through a series of baffels into a container of known volume and weighing the GMB collected. The tap density is measured by placing a given weight of GMB into a graduated cylinder and shaking or tapping until a constant volume is obtained. True particle density is measured by liquid displacement and is the average density of an individual microbubble.

The tap density is the maximum density that can be obtained by packing the GMB as tightly as possible without breaking the bubbles. The packing factor is the ratio of tap density to the true particle density and is the volume fraction of glass spheres in a given volume.

Table 1. Typical Properties of Kerimid 601 Polyimide Resin.

Characteristic	Values
Appearance	Yellow powder
Density	1.3 g/cm ³
Melting Range	100 to 105°C
Thermal Stability	5 percent weight loss at 390°C
Coefficient of Thermal Expansion	49 $\mu\text{m}/\text{m}\cdot^\circ\text{C}$ between 0 and 300°C
Average Particle Size	8 to 10 μm
Compressive Strength	193 MPa at 25°C
Shrinkage	Less than one percent

Packing Study

Reproducible high quality syntactic foams require a consistent and known packing of the GMB with no crushing or at least with a controlled amount of crushing. Data are available based on theoretical and experimental studies of packing of particles.^{4,5} Most of the information available in the literature is concerned with the packing of discrete sizes of spheres rather than with real particulate systems with some type of continuous size distribution such as the B40A glass microbubbles shown in Figure 1.

A review of previous attempts to characterize particulate systems is included in Reference 4. That work basically is a theoretical study of two- and three-dimensional systems (circles and spheres) by computer modeling. Sohn⁵ lists 112 references concerned with packing of particles.

Slightly different values for maximum packing factor are obtained by different investigators, depending on the theoretical assumptions and the experimental techniques. Basically the packing of particles is classified as systematic packing or random packing. Also the systems are divided into uniform (one) size, a small number of discrete sizes, or a continuous size distribution.

Spheres of a uniform size can be stacked or arranged in five ways resulting in a theoretical packing factor (volume fraction) ranging from 0.536 to 0.7405. The value of 0.7405 is the closest possible packing of spheres with one size. These volume fractions of spheres could be obtained by carefully arranging each sphere one at a time. For a real system of randomly packed spheres all of one size, the packing factor obtained experimentally ranges from 0.631 to 0.641.

Table 2. Properties of Glass Microbubbles

GMB Type	Density			Floater (Percent)	Packing Factor	Alkalinity (pH)	Isostatic Crush Strength* (MPa)
	Bulk (g/cm ³)	Tap (g/cm ³)	True (g/cm ³)				
B18A	0.083	0.110	0.158	96.2	0.696		
B22A	0.100	0.130	0.188	98.0	0.691		
B35A	0.189	0.224	0.335	96.9	0.668		
B40A		0.242	0.370	99.3	0.654		6.89
B35D	0.179	0.214	0.318	98.6	0.673	9.5	13.79
B40B	0.195	0.248	0.329	89.9	0.754	9.3	2.41
B40BX	0.213	0.254	0.377	93.6	0.673	9.1	15.17
*Pressure to crush 10 percent by volume (vendor data).

Figure 1. Particle Size Distribution of B40A Glass Microbubbles

When spheres with different sizes are used, much larger packing factors or volume fractions of spheres are obtained. For binary systems, a theoretical packing factor of 0.87 is possible. This assumes no bridging or gaps in the mixture and an infinite diameter ratio. McGeary⁶ obtained a packing factor of 0.845 with a mixture of 7 mesh steel shot and 400 mesh tungsten balls with a ratio of diameters of 78:1. For a ternary mixture the maximum packing is 0.926, and for a mixture of five discrete sizes of spheres the maximum volume fraction is 0.949. Again, this assumes an infinite diameter ratio. Actual experimental values are somewhat less because of bridging and gaps between the spheres and of discrete sizes of spheres.

Little information is available on the packing of continuous particle size distributions. Lee⁷ used an idealized particle size distribution in the shape of a symmetric triangle and obtained a maximum packing factor of 0.663. The triangular distribution would only approximate the distribution in Figure 1 for GMB. However,

it does show that a continuous distribution will not have as high a packing factor as selected discrete sizes of spheres.

In real systems such as the seven types of glass microbubbles given in Table 2, the measured packing factor varied from 0.654 to 0.754. The GMB with the large packing factor also have a large amount of sinkers or broken GMB. For the B35D type of glass microbubbles, the packing factor varied from 0.600 to 0.660 for eight lots of GMB with about one percent broken microbubbles.

As mentioned previously the tap density is a random packing obtained by shaking or tapping until a constant volume is obtained. After the shaking process the GMB are so densely packed that they will not flow from a graduated cylinder and must be forced out by probing. The maximum expected packing factor or volume fraction of GMB in any given volume is 0.65 to 0.66. The addition of resin will tend to separate the individual GMB and reduce the overall volume percent of GMB. A volume loading in excess of 0.66 percent can be obtained only by crushing GMB.

B35D Glass Microbubbles

The B35D glass microbubbles were selected as the filler for syntactic foam application. Typical properties reported are given in Table 3. These values for thermal conductivity, thermal expansion, specific heat, and softening point are typical of all types of glass microbubbles.

For syntactic foam applications, the bubble properties of particle size distribution, crush strength, amount of broken bubbles, and density are important. Measured properties of 17 lots of B35D glass microbubbles are given in Table 4. Particle size distribution was measured on several of the first lots by Coulter Counter and micromerograph methods. Only gross changes in distribution can be measured by either of these methods. The other bubble properties such as density, packing factor, and sinkers will give an indication of gross changes in size distribution. Therefore, particle size distribution measurements were not made routinely on the B35D glass microbubbles.

The true particle density of the B35D GMB can vary between 0.30 and 0.35 g/cm³ with a nominal value of 0.325 g/cm³. All of the lots of B35D tested were within the allowed range of values. Packing factor and tap density were measured by ASTM-D-3101. The packing factor varies from a low of 0.600 to a high of 0.66 with most of the values between 0.65 and 0.66.

The crush strength was measured according to ASTM-D-3102. Although the typical value of 10 percent crush strength is reported as 13.8 MPa, only one lot of GMB had a 10 percent crush strength as low as 13.8 MPa. All of the other lots measured significantly

Table 3. Typical Properties of B35D GMB

Characteristic	Values
Particle Density	0.30 to 0.35 g/cm ³
Particle Size Distribution	90 percent between 20 and 80 μ m
Crush Strength	10 percent volume change 13.79 MPa
Thermal Conductivity	2.75×10^{-4} cal/cm $\cdot$ s $\cdot$ °C
Thermal Expansion	8.8 μ m/m $\cdot$ °C (60 to 440°C)
Specific Heat	0.27 approximate
Softening Point	615°C

higher. Two lots of GMB were tested four times for isostatic crush strength. The test values are given in Table 5. The standard deviation varies from about 1 to 10 percent of the measured values.

Stratification of the GMB during shipment and storage was considered a potential problem. The vendor indicated their tests had shown that the B35D did not separate during shipment. Two lots of GMB were tested at Bendix for stratification. These test results are given in Table 6 and show no separation or stratification of the GMB during shipment.

Processes

Blending

A twin shell blender provides an easy, efficient method of combining the powdered resin and the glass microbubbles. Since the resin particles are only slightly smaller than the GMB, the particles fit between the individual glass microbubbles. To prevent any resin rich areas caused by agglomeration, the resin is sieved before blending.

Molding

The three molding methods considered are sintering (no pressure), vacuum bag (low pressure), and compression (high pressure). The sintering method consists of simply charging a mold with dry blend and heating through the melt and cure temperature. The void content of the foam is high. That is, for a given formulation, the density of the cured foam is lower than for the other two methods because the GMB are not packed as close together.

Table 4. Lot to Lot Variation of B35D Glass Microbubbles

Lot Number	Particle Density		Packing Factor	Sinkers (Weight Percent)	Crush Strength (MPa) Percent	
	True (g/cm ³)	Tap (g/cm ³)			at 10	at 20
8131-3	0.319	0.214	0.673	1.45		
5960-5	0.333				28.3	40.0
7697-1	0.325				23.4	39.3
8581-7	0.350	0.21	0.600	0.80	24.8	35.2
8581-5	0.350	0.22	0.628	1.0	19.3	34.5
8907-1	0.315	0.206	0.654	0.6	23.4	30.3
8907-7	0.310	0.20	0.645	0.8	28.3	35.2
8907-2	0.300	0.197	0.657		24.8	31.0
8948-2	(0.327)				20.7	27.6
8581-8	(0.316)				29.6	37.9
8861-1	0.313	0.207	0.661		13.8	29.0
8866-2	0.313	0.205	0.655		25.5	34.5
8866-3	0.317	0.208	0.656		26.2	32.4
8866-4	0.315	0.208	0.660		31.0	39.3
2727-3	0.342	0.226	0.660			
3406-4	0.331	0.215	0.649		40.3	46.9
3406-7	0.351	0.228	0.650		37.7	49.3

The compression molding method consists of charging a certain weight of material to a constant volume mold. Then material is heated to melt temperature, and the mold is closed. Overall density of the molded block is determined by charge weight and mold volume. The closing pressure is not controlled; sufficient pressure is applied to close the mold. If the proper melt temperature is not achieved throughout the material, some of the glass microbubbles could be broken during molding.

Table 5. Expected Variation of Isostatic Strength
Within a Lot of B35D Glass Microbubbles

Test	Pressure to Collapse (MPa)	
	10 Percent	20 Percent
3406-4-1	39	47
-2	39	46
-3	40	47
-4	43	48
Average	40	47
Standard Deviation	±1.8	±0.49
3406-7-1	41	50
-2	43	53
-3	36	48
-4	31	46
Average	38	49
Standard Deviation	±4.6	±2.8

By the vacuum bag method, a constant low pressure, determined by the vacuum pump, is applied to the molding material. Block thickness and density are determined by the material formulation and temperature (melt) history. As the resin softens, the foam is compressed or packed to achieve a maximum packing factor. This method has the advantage of being gentle with the GMB and is used to evaluate cure schedules and material formulations.

Curing

The cure cycle for Kerimid 601 resin has been developed previously for small blocks of foam.⁸ The cure cycle used for all the test blocks is a melt of 120°C for 1.5 hours, a cure of 190°C for 2 hours, and a postcure of 250°C for 16 hours in a nitrogen atmosphere. A study was made to evaluate different cure cycles with a desire to reduce the total cure and postcure time. For this evaluation, syntactic foams were molded from 45/55 and 50/50 weight

Table 6. Stratification of B35D Glass Microbubbles

Sample*	Density** (g/cm ³)		Packing Factor	Particle Size Distribution*** Weight Percent Greater Than Diameter (μm)				
	Tap	True		10	20	40	70	100
3406-4-1	0.215	0.332	0.648	70	60	34	6	3
-2	0.217	0.334	0.650	95	87	52	6	0
-3	0.216	0.330	0.654	77	58	35	5	0
-4	0.214	0.329	0.650	72	49	28	5	1
-5	0.213	0.326	0.653	93	83	49	9	1
-6	0.217	0.333	0.652	97	94	69	10	3
Average	0.215	0.331	0.651	84	72	44	7	1
3406-7-1	0.227	0.346	0.656	94	86	56	10	0
-2	0.226	0.346	0.653	66	58	34	5	0
-3	0.226	0.348	0.649	78	71	44	10	3
-4	0.229	0.355	0.645	77	69	42	10	0
-5	0.232	0.359	0.646	98	94	66	12	1
-6	0.228	0.351	0.649	90	82	46	6	0
Average	0.228	0.351	0.650	84	77	48	9	0.5

*Samples taken from 100-pound containers of GMB as received from Vendor; Sample 1 taken at the top and Sample 6 taken at the bottom of the container.

**Values for tap and true densities are averages of three tests.

***Particle size distribution by Coulter Counter.

blends of resin/GMB and given various cures and postcures. The goal was to measure the effects of cure time, cure temperature, postcure time, postcure temperature, and postcure atmosphere on mechanical and thermal properties.

The actual mold cures tested were from 1.5 to 8 hours at 190 to 250°C, while the postcures were from 4 to 24 hours at 220 to 250°C in a retort with either air or argon atmospheres. Changing the cure and postcure conditions did not change the specimen density. The test specimens postcured in an air atmosphere did oxidize and darken, but any shrinkage or weight loss was not measurable.

The compressive and tensile properties of the foam are more a function of the foam density than of cure and postcure conditions. When tested at room temperature, even the green foams with a minimum cure of 1 hour at 190°C have the same crush strengths as the postcured foams. The 150°C compressive and the 25°C tensile tests did show the postcured foams to be stronger than green cured foam. However, the different postcure temperatures and times did not significantly influence the compressive or tensile properties.

Thermal properties were measured using Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA), Dielectric Spectroscopy (DS), and Thermogravimetric Analysis (TGA). By the TGA weight loss method, no change in foams was measured as a function of postcure. Dielectric spectroscopy was not effective with the foams because of the high GMB content. With the resin only, the cure times by DS measurements ranged from 1 hour at 250°C to 7 hours at 175°C. The TMA and DSC methods show that some time at 245°C is necessary to completely cure the resins. Cure times longer than 5 hours at 220°C would probably completely cure the resin, but no tests were made.

Syntactic foams made from Kerimid 601 resin develop strength and thermal resistance with only minimum cures. For the foam to develop full properties within reasonable times, a postcure is necessary. For the 150°C maximum use temperature of this application, a mold cure of 5 hours at 190°C without any postcure is adequate but does not take into account slight variations because of changes in resin lots. A cure of 1 hour at 190°C in the mold followed by a 1 hour minimum postcure at 245°C (foam time and temperature) is conservative but will allow for variations in raw materials.

Preliminary Evaluation

During the preliminary evaluation, syntactic foams were prepared from the Kerimid 601 polyimide resin and six types of glass microbubbles.⁹ Basically these preliminary test results show that foams with compressive strengths ranging from 3.45 to 179 MPa can be prepared, depending on the type of GMB used and the density of the foam composite. Foam made from B40A glass microbubbles had

the best strength-to-weight ratio; however, the lowest foam density possible using the B40A bubbles is only about 0.35 g/cm^3 . Low density composites require low density glass microbubbles. Foams with densities of about 0.2 g/cm^3 were made with the B18A bubbles, but the compressive strength was about 3.45 MPa.

Information obtained since these preliminary tests were made shows the two lots of B40A GMB used were not typical, and the vendor cannot guarantee that the B40A GMB will consistently have higher strength than the B35D glass microbubbles selected as the filler for this application.

Candidate Foam Evaluation

The foam selected for additional testing was made from B35D glass microbubbles with Kerimid 601 binder. During the evolution of product design, material requirements such as part density and strength normally will change. Plans for this project were to learn about the molding and manufacturing of the foam first and to carefully characterize a final formulation at the end of the project. During the development effort certain thermal and mechanical properties were measured to answer specific questions about the foam.

Molding Studies

The overall objective was to learn how to manufacture a foam with a uniform density and predictable strength properties. To do this, information was needed on the variables associated with molding the foam. These molding studies were divided into the major areas of foam formulation, glass microbubble strength, and molding pressure.

The formulation study was to measure the relationships among resin to GMB ratios, foam density, void content, and the crush strength of the molded foam. For the tests made at Bendix, the foams were prepared from Kerimid 601 and B35D glass microbubbles by compression molding 127 by 127 by 25-mm-test blocks. Three formulations molded to 11 densities were prepared and tested. The cure was 1.5 hours at 120°C plus 2 hours at 190°C in the mold followed by a postcure of 16 hours at 250°C in a nitrogen atmosphere. Test specimens, 28.7-mm-diameter by 25.4 mm were machined from the blocks and were tested at 1.27 mm/min cross head speed in a restrained fixture to about 50 percent compression. Crush strength tests were made at 25°C and at 150°C .

The crush strength results for the 25°C tests are given in Figure 2 with a linear regression curve fit. These results indicate that the crush strength is a linear function of the foam density over a small density range. This means that, regardless of the relative amounts of resin and glass microbubbles (resin to GMB ratio), the

Figure 2. Effect of Foam Density on Crush Strength at 25°C

strength depends only on the molded density. The same data displayed as a function of resin content and GMB content are given in Figures 3 and 4. These data show that the strength of the foam is not dependent solely on either the resin concentration or the GMB concentration (volume fraction). However, for a given weight ratio or formulation of resin and GMB, the volume fraction of resin and GMB can be changed (within limits) by changing the amount of void space in the foam. The void space is changed by changing the foam density. In this case, for a specific weight formulation increasing either the volume of resin or the volume of GMB will increase the crush strength.

Because the foam crush strength is not a dependent function of either the resin content or the GMB content, several types of ratios were considered and compared to the test data. One dimensionless

Figure 3. Effect of Resin Content on Crush Strength at 25°C

parameter is a measure of the amount of resin compared to the total volume between the GMB. The crush strength values as a function of this ratio are shown in Figure 5. This representation of the data shows that the strength of the foam depends on the amount of void space between GMB that is filled with resin.

The test data for the crush tests at 150°C are given in Figures 6 and 7. These data for elevated temperature strengths show the same dependence on density.

A similar series of tests began using full size molded billets. The billets were molded at Bendix and sent to SLL for testing. Six billets were molded from Kerimid 601 and B35D glass micro-bubbles. The intent was to mold billets at 0.38, 0.34 and 0.30 g/cm³ with 65 volume percent GMB, and three billets at 0.38, 0.34, and 0.30 g/cm³ with 60 volume percent GMB. The test specimens (57 mm diameter by 38 mm thick) were machined from the billets. These samples were grouped by density and tested at 1.27, 127,

Figure 4. Effect of GMB Content on Crush Strength at 25°C

and 12700 mm/min. In addition to the specimens taken from full sized molded billets, a series of 16 individual coupons (57 mm diameter by 38 mm thick) were molded and sent to SLL for testing. These coupons were molded from Kerimid 601 and B35D glass micro-bubbles.

The crush strength data on test specimens machined from the molded billets do not agree with the data from the individually molded coupons and the specimens taken from the test block. The billet specimens indicate that, at a constant foam density, the strength will increase with an increase in GMB content. The test data for the billets and coupons are shown in Figures 8, 9, and 10. The curve for the block specimens (Figures 2, 4, and 5) are given as a reference.

The test data available are not sufficient to clarify the apparent contradiction in data. One series of tests indicate that the crush strength depends solely on the foam density and is essentially

Figure 5. Effect of Relative Resin Content on Crush Strength at 25°C

independent of the formulation. The other series indicate that the formulation (the volume fraction of GMB) is the controlling factor and at a constant density, the formulation with the highest GMB content will be the strongest.

With this syntactic foam, the type of resin, the type of GMB, and the average foam density will be specified. The density of the resin is constant, but the density of the GMB can vary between 0.30 and 0.35 g/cm³. To define a foam system, either the weight fraction or the volume fraction of the GMB must be set. The family of curves in Figure 11 is for a constant volume fraction of GMB

Figure 6. Effect of Foam Density on Crush Strength at 150°C

as a function of the true GMB density and the weight fraction of the GMB in the foam molded to 0.30 g/cm³. Changing the density of the foam will change the location of the curves. With this set of curves, foam formulations based on either volume fraction or weight fraction of GMB for any lot (density) of B35D glass microbubbles can be determined.

For example, if a foam system were based on a constant volume fraction of 0.64 GMB and the measured density of the GMB were 0.32 g/cm³, the weight ratio of GMB would be 68.5 parts of GMB to 31.5 parts of Kerimid 601 resin. If the measured density of the lot of GMB happens to be 0.35 g/cm³, the required weight formulation would be 75 parts GMB to 25 parts resin. Both formulations of 31.5/68.5 (resin/GMB) and 25/75 (resin/GMB) will have a volume fraction of 0.64 GMB when molded to an overall density of 0.30 g/cm³.

Figure 7. Effect of Relative Resin Content on Crush Strength at 150°C

As another example, suppose the volume fraction of GMB in the foam could vary from 0.66 to 0.56. In this case, if the true measured density of the GMB were 0.30 g/cm³, and the volume fraction were 0.66, the proper weight ratio would be 34 parts resin to 66 parts GMB. If the measured density of the microbubbles were 0.35 g/cm³ and the volume fraction allowed to drop from 0.66 to 0.56, the weight ratio would be the same 34/66 (resin/GMB). This would mean that a constant weight formulation of 34/66 (resin/GMB) could be used for any allowed density of GMB if the volume fraction could vary between 0.66 and 0.56.

Another consideration is the relationship between the molding pressure, the density, and the volume fraction of GMB in the molded foam. The goal is to compress or consolidate the foam in a repeatable manner without crushing microbubbles. The flow and melt

Figure 8. Effect of Billet and Coupon Foam Density on Crush Strength at 25°C

properties of the resin must be considered. A series of tests were made with two lots of Kerimid resins and two lots of glass microbubbles to measure the effect of molding pressure on the foam. The test results are shown in Figure 12.

Figure 9. Effect of Relative Resin Content of Billets and Coupons on Crush Strength at 25°C

Lot 73197 was one of the oldest lots of Kerimid 601 available and lot 76162 was one of the newest lots available. Also, lot 8907-1 was a low density lot of B35D GMB and 106 2727-3 was a high density lot of GMB. Regardless of the density of GMB or the age of resin, which is a measure of flow properties, the packing as volume fraction of GMB depends only upon the pressure applied. Earlier tests have shown that the GMB are not broken if the pressure is below 0.7 MPa. These data indicate that only low pressures are necessary to pack the GMB.

Figure 10. Effect of GMB Content on Crush Strength of Billet and Coupon Specimens at 25°C

The density of the glass microbubbles does not affect the packing or volume fraction of GMB in the foam, but the density of the GMB definitely changes the overall foam density when molded at a constant pressure.

Foam Properties

During the evolution of the product design, certain mechanical, thermal, and environmental properties were measured. The crush strength of the foam as a function of temperature, deflection, and crush rate was of paramount importance. Test data are given

Figure 11. Formulations for 0.30 g/cm³ Foam With B35D GMB

in Figures 13 and 14 for crush strength at four test temperatures and at up to 50 percent deflection. The crush strength decreases about 15 percent from -50°C to +150°C with essentially no change in strength between room temperature and 150°C. In a restraining test fixture that allows the foam to compress in only one direction, the foam can crush up to about 45 percent with only a 20 percent increase in load over an initial yield strength (Figure 14). The data in Figures 13 and 14 are for foams with a density of about 0.38 g/cm³. Test data for other densities are given in Figure 2 for 25°C tests and Figure 6 for 150°C tests.

The shear strengths for several formulations of syntactic foams are given in Table 7. The shear strength is dependent on the thickness as well as the density and lot of GMB.

Tensile strengths were measured on specimens taken from production type billets molded to 0.38 g/cm³ from a 50/50 weight blend of Kerimid 601 and B35D glass microbubbles. These tests were made as part of the cure cycle study, and the test results are listed

Figure 12. Volume Fraction of GMB as a Function of Molding Pressure

in Table 8. The density of the actual test specimen was not measured, but the range of measured densities for the compressive test specimens taken from the same billets are given in Table 8. The data are arranged so that for each postcure condition, the first value is for a specimen taken from the top of the billet and the last value is for a specimen taken from the bottom of the billet. Although the actual density values are not known, the tensile strength is extremely sensitive to variations in foam density.

Figure 13. Crush Strength as a Function of Test Temperature

Thermal conductivity was measured on machined foam specimens of six densities and three test temperatures. The test results are shown in Figures 15 and 16. The thermal conductivity of the Kerimid 601 resin is about 5×10^{-4} cal/cm·s·°C at a density of 1.3 g/cm³. The glass microbubble thermal conductivity is reported to be about 2.75×10^{-4} cal/cm·s·°C at 0.30 to 0.35 g/cm³. The low density foams made from blends of the resin and GMB have even lower thermal conductivities because of void space or air molded into the foams. The thermal conductivity not only increases with density but also increases with test temperatures, as shown in Figure 16.

The linear thermal expansion of different density foams was measured using the expansion probe of a thermal mechanical analyzer (TMA). The coefficient of expansion increases with foam density and is shown in Figure 17 over a density range of 0.34 to 0.42 g/cm³.

Figure 14. Crush Strength as a Function of Deflection

The effect of moisture on the crush strength of the foam and equilibrium moisture contents of the foam were also measured. Machined test specimens 57 mm in diameter by 25 mm thick were conditioned over sulfuric acid solutions formulated to 10, 30, or 50 percent relative humidity at 25°C. Although the test specimen weight did increase slightly between 78 and 92 days, the conditioning was terminated after 93 days. The weight gain as a function of the storage relative humidity is shown in Figure 18.

Average values for crush strength at various foam densities and moisture contents are shown in Figure 19. The drier foams are stronger. The foams at equilibrium with 10 percent relative humidity are from 8 to 9 percent stronger than the foams at 50 percent relative humidity.

Mold-To-Size

The original process to prepare these syntactic foam parts consisted of molding foam billets and later machining the billets to part configuration. For high volume production parts, machining to final dimension is expensive. One goal of this project was to develop processing and tooling to set the final part dimensions during the molding of the foam.

Table 7. Shear Strength of Kerimid 601/B35D Foams

Formulation Resin/GMB Weight Ratio	Lot Glass Microbubbles	Foam Thickness (mm)	Foam Density (g/cm ³)	Shear Strength (MPa)
45/55	8866-3	3.18	0.327	5.1
45/55	8866-3	6.35	0.327	5.5
45/55	8866-3	12.70	0.327	3.9
50/50	8866-3	3.18	0.356	6.3
50/50	8866-3	6.35	0.356	6.1
50/50	8866-3	12.7	0.356	4.7
45/55	8866-4	6.35	0.326	5.4
50/50	8866-4	6.35	0.354	6.9
45/55	2727-3	6.35	0.345	7.9
50/50	2727-3	6.35	0.383	8.0

Kerimid 601, Lot 74149, used for all test specimens.

Mold-to-size had been evaluated for foam parts made from a blend of Kerimid 601 resin, carbon microspheres and carbon fibers. The carbon fibers prevented the uniform packing of the foam blend and mold-to-size parts could not be made. However, a blend of only carbon microspheres and resin flowed easily into thin sections and molded parts had a smooth finish. No lateral flow could be obtained. As the resin softens, the blend of resin and carbon microspheres becomes like damp sand. The mixture was by no means fluid and lateral compaction could not be obtained.

However, the foam A and foam D parts could be molded by applying force in one direction. No lateral movement of the foam would be required. Although the flatness tolerance of 0.13 mm and the contour tolerance of 0.25 mm was tight, and the molding repeatability of the 0.38 gm/cm³ syntactic foam was unknown, mold-to-size efforts were initiated.

Molds were designed and fabricated to the foam A and foam D parts. Using a 45/55 parts by weight ratio of resin to glass microbubble, the charge weight on the foam A was determined to be 785 g and on the foam D was 900 g. The initial foam A parts had a warp of

Table 8. Tensile Strength Kerimid 601/B35D Foams
at 25°C

Post Cure	Density Range (g/cm ³)	Tensile Properties	
		Strength (MPa)	Modulus (MPa)
No Post Cure	0.376 to 0.412	4.48	1910
		1.90	1875
		2.86	1379
		1.93	1062
		1.62	1365
Average		2.56	1517
5 hours at 190°C	0.381 to 0.415	7.24	2027
		4.76	1641
		6.76	1603
		3.38	1400
		2.27	1551
Average		4.88	1627
5 hours at 220°C	0.380 to 0.408	8.62	1875
		8.34	1813
		6.34	1668
		6.69	1634
Average		7.49	1751
5 hours at 245°C	0.378 to 0.408	7.93	1613
		7.52	1875
		6.27	1489
		5.45	1551
		2.90	1351
Average		6.01	1579
16 hours at 245°C	0.383 to 0.412	8.96	2000
		8.69	1600
		6.90	1462
		4.34	1724
		2.72	1186
Average		6.32	1593

1.5 mm on the flat surface after post cure. With an increase of time from one to three hours at 190°C, a large number of cracks resulted. Several parts were molded using a 50/50 weight ratio,

Figure 15. Foam Thermal Conductivity as a Function of Molded Density

however cracks resulted in this case also. At this point weights were added to assist in mold closure during the initial heating. Various weights were used (50 to 150 kg) with various initial set temperatures. A flatness of 0.2 mm was obtained with 50 kg weight and 135°C set temperature.

The 50.8 mm-thick-billet mold was also used to gain information for the mold-to-size effort even though its primary purpose was to make billets which were later machined to part configuration for both the foam A and foam D. Flatness, diameter, and thickness were measured. Using the 45/55 ratio with a charge weight of 2905 g (0.38 gm/cm³ density) the flatness variation improved from about 2.0 to about 0.1 mm after precure. After postcure, flatness variation improved from 4.0 to 1.0 mm.

Figure 16. Foam Thermal Conductivity as a Function of Test Temperature

Pre-heating of the mold prior to the addition of the charge weight was done in order to decrease the heat up time. A large brown spot occurred in the center of the part and since it was a foam A mold which was used (which is quite thin in the center), it was assumed that this portion cured faster. Although flatness measurements were surprisingly good (0.20 to 0.25 mm), the appearance of the part was poor. Without an ability to accurately measure the density by DXT across this contour, one suspects that the variation in density is quite large.

With a design change to 0.30 density, the charge weight and material ratio were changed to 625 g and 37/63 respectively. A short time later all work on this project was halted by the design agency.

ACCOMPLISHMENTS

Blending, molding, and curing procedures were developed to prepare syntactic foams from Kerimid 601 and glass microbubbles. Foams from the Kerimid 601 and six types of GMB had compressive strengths ranging from 3.45 to 179 MPa for densities of 0.197 to 0.977 g/cm³. With the B35D type glass microbubbles, the crush strength decreases about 20 percent from -50°C to +150°C. In a restraining fixture

Figure 17. Coefficient of Linear Thermal Expansion as a Function of Molded Density

the foam can crush about 45 percent with only a 20 percent increase in load. Cure cycles were developed to make efficient use of molds and ovens.

Certain mechanical, thermal and environmental properties were measured to provide design data.

Figure 18. Weight Change of Foam as a Function of Relative Humidity

Mold-to-size syntactic foam parts are feasible when flow or compaction in only one direction is required. By modifying heating rates, foam formulation, and molding pressure, significant improvements were made in dimensional control of mold-to-size parts.

FUTURE WORK

The planned future work for energy attenuating syntactic foams includes:

Figure 19. Foam Crush Strength as a Function of Density and Moisture Content

Evaluation of other resins for foam binders;

Evaluation of foam formulation and packing factor effects on foam crush strength;

Development of techniques to mold-to-size specific contours; and

Development of procedures to measure density distribution in contoured foam parts.

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