GLASS MICROBUBBLE COMPOSITE FOAM

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Topical Report

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GLASS MICROBUBBLE COMPOSITE FOAM

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Prepared by H. M. McIlroy, D/814.

Syntactic foams were prepared from blends of an addition type polyimide resin and six types of glass microbubbles. Typical properties of the resin and microbubbles are given. Compressive properties were measured as a function of resin concentration and foam density.

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SUMMARY

Composite foams have been prepared from blends of Kerimid 601 polyimide resin (Rhodia Incorporated) and different types of glass microbubbles (GMB). Kerimid 601 is an addition type polyimide that offers many processing advantages over other types of polyimides. In an addition reaction, no volatiles are evolved during cure and weight loss and shrinkage during cure are small. Also, since the resin is a powder that melts and flows before curing, low density foams can be prepared.

The glass microbubbles used in this study were made by the 3M Company. Particle size distribution, bulk density, tap density, true particle density, sinker/floater ratio, and alkalinity of the six types (grades) of GMB were measured.

Processes were developed to blend, mold, and cure the foam formulations. The powdered resin and glass microbubbles were mixed together in a twin shell blender. Three methods of molding were considered: a sintering process, vacuum bag molding, and compression molding; however, all of the foams were made by the vacuum bag method. The standard cure recommended by the manufacturer of Kerimid 601 was used to cure and postcure the foam samples.

Test results show that foams with compressive strengths ranging from 500 to 26,000 psi (3.45 to 179 MPa) can be prepared depending upon 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, but the lowest foam density possible using the B40A bubbles is only about 0.35 g/cm³. Low density composites require low density glass microbubbles. Foams with densities of about 0.2 g/cm³ were made with the B18A bubbles, but the compressive strength was about 500 psi (3.45 MPa).

DISCUSSION

SCOPE AND PURPOSE

A structural foam part for energy attenuation and thermal insulation is required. This effort was to provide design data on types of glass microbubbles available and to measure the range of compressive properties of composite foams as a function of type of GMB and density of foams.

PRIOR WORK

A series of foam materials were tested by Sandia Livermore Laboratories in the spring of 1975. The crush strength at room temperature and 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

Materials

Resin

Kerimid 601 is an addition type polyimide resin made in France and marketed in the United States by Rhodia Incorporated. The preparation of Kerimid 601 is protected by U. S. Patent 3,562,223. Maleic anhydride and methylene dianiline (MDA) are used to prepare the resin which is fully imidized when received from the vendor. During cure, the bismaleimide reacts with additional MDA and through the double bond with other bismaleimide molecules. The diamine reaction occurs at a faster rate and leads to chain extension without crosslinking. The rigid polymer is formed by the reaction of the bismaleimide. Since this is an addition reaction, no by-products are evolved during the cure.

Kerimid 601 is used as a laminating resin as well as a binder for syntactic foam. The physical and thermal properties have been fairly well characterized¹⁻³ (Table 1).

The small particle size allows the resin to mix easily with the glass microbubble filler and fit between the individual GMB. The low melting temperature allows the resin to melt and flow partially around the GMB prior to cure. After cure, the resin binds adjacent GMB to form a rigid, strong foam.

Table 1. Typical Properties of Kerimid 601 Polyimide Resin

Characteristic	Amount
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 x 10 ⁻⁶ cm/cm-°C between 0 and 300°C
Average Particle Size	8 to 10 μm
Compressive Strength	28,000 psi (193 MPa) at 25°C
Shrinkage	Less than 1 percent

Glass Microbubbles

Six types of glass microbubbles (all made by the 3M Company) were used in the initial formulation study with Kerimid 601 polyimide resin. Particle size distribution, bulk density, tap density, true particle density, sinker/floater ratio, and alkalinity (pH) were measured on the different types or grades of GMB.

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. Lower 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 other properties are given in Table 2. 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 minimum 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. For equally-sized spheres, regardless of density, the maximum packing factor is about 0.63. However, with

Figure 1. Particle Size Distribution of B40A Glass Microbubbles by Micromerograph

the normal particle size distribution and some broken bubbles present, the packing factor of the glass microbubbles ranges from 0.65 to 0.75.

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 B40B 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 what the 3M Company calls "floated" microbubbles. That is, the bulk of the broken bubbles are removed by 3M during processing and prior to shipment. Also, the A and D series have a coupling agent added to improve adhesion to organic resins.

Table 2. Properties of Glass Microbubbles

Glass GMB Type	Density			Amount Floater (Percent)	Packing Factor	Alka- linity (pH)	Isostatic* Crush Strength (psi)**
	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		1000
B35D	0.179	0.214	0.318	98.6	0.673	9.5	2000
B40B	0.195	0.248	0.329	89.9	0.754	9.3	350
B40BX	0.213	0.254	0.377	93.6	0.673	9.1	2200
*Pressure to crush 10 percent by volume (vendor data)							
**Pa = psi x 6895							

Some types of glass bubbles are so highly alkaline that they react with moisture in the air. The 3M bubbles have a pH of 9.1 to 9.3, but the bubbles are insoluble in water and caking or lumping of the bulk microbubbles is not a problem.

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.

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.

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.

The vacuum bag method was used to prepare all test blocks for this work. The material formulation ranges for each type of GMB are given in Table 3. Calculated volume of GMB in the foam blocks, for all six types of GMB, is slightly lower than the expected volume based on the calculated packing factor. The foam block density is actually lower than the theoretical density based on the packing factor. This would indicate that the GMB are not packed as closely as possible and extra air is included in the foam block. No attempt was made to account for the amount

Table 3. Composite Foam Formulation Ranges

Glass GMB Type	Resin		Foam Density Range (g/cm ³)
	Weight Range (Percent)	Volume Range (Percent)	
B18A	50 to 90	9.3 to 41.7	0.197 to 0.750
B22A	50 to 90	9.2 to 58.1	0.239 to 0.844
B35D	40 to 90	10.5 to 69.1	0.342 to 0.977
B40A	40 to 90	11.3 to 69.2	0.368 to 0.980
B40B	35 to 60	10.8 to 30.0	0.400 to 0.724
B40BX	35 to 60	9.5 to 24.3	0.348 to 0.561

of broken bubbles in the bulk material, as measured by the sinker/floater ratio. Since the density is actually lower than expected and the molding pressure is very low, the number of bubbles broken in the molding operation is assumed to be very low. The effect of GMB and air cannot be accurately separated. Therefore, the resin concentration was selected as a way to compare foam formulations. The SEM photograph (Figure 2) of a section of Kerimid 601/B35D foam (45/55 by weight) shows the bonding of the resin and bubbles and the large void content.

Curing

The cure cycle for Kerimid 601 resin has been developed previously for small blocks of foam. The cure cycle used for all the test blocks is a melt of 121°C for 1.5 hours, a cure of 191°C for 2 hours, and a postcure of 249°C for 16 hours in a nitrogen atmosphere.

Foam Properties

Test Procedure

The compressive properties were measured using ASTM-D-1695, *Compressive Properties of Rigid Plastics*. The specimen size was 1.129 inch diameter by 0.5 inch thick (28.7 mm by 13 mm). All specimens were tested at room temperature with a cross-head speed of 0.05 in./min. (1.3 mm/min.). The specimens were not conditioned

Figure 2. Composite Foam Made From
Kerimid 601 and B35D Glass
Microbubbles (300X)

at a particular relative humidity prior to testing and the testing was in an unrestrained mode. Five specimens were tested from each foam formulation.

Test Results

The compressive strengths of the foams are shown (Figure 3) as a function of average specimen density. The foams made from the B40A bubbles have the highest yield strength at a given density. The B18A are the weakest. However, as expected, the B18A can be used to make lower density foams. The high density foams such as B40A, at a density of 0.98 g/cm^3 , had an average yield strength of 26,000 psi (197 MPa). Although the B35D bubbles are marketed as a "super strength" material, the foams made from the B40D high strength bubbles were consistently stronger.

The B40A, B35D, and B18A foams have similarly shaped curves, but the B40BX foam creates a differently shaped curve. Strength is not as dependent upon density with B40BX as it is with the other three types of bubbles. The data show the compressive strengths to be an exponential function of the density. Equations to fit the data are shown:

Figure 3. Compressive Strength of Kerimid 601 and Glass Microbubble Syntactic Foam

B18A Glass microbubbles, $y = 25200 x^{2.00}$

B35D Glass microbubbles, $y = 35000 x^{3.1}$

B40A Glass microbubbles, $y = 35100 x^{2.7}$

B40BX Glass microbubbles, $y = 11800 x^{2.0}$

where

y = compressive strength (psi), and

x = density (g/cm^3).

These predictions of strength are at room temperature and a strain rate of 0.0017 sec^{-1} .

The compressive modulus is shown in Figure 4. The strain value used to calculate the modulus was determined by the chart speed and cross-head speed rather than with an extensometer. This could account for part of the data variation. The modulus varies from a low of 20,000 psi (138 MPa) at 0.2 g/cm^3 for the B18A bubbles to over 400,000 psi (2.76 GPa) for B40A bubbles at 0.98 g/cm^3 . The B40BX foams have a higher modulus than the B40A foams, but the yield strengths are lower.

The specimen density is a linear function of resin concentration (Figure 5). Extrapolating the curves to zero resin concentration is a measure of the tap density or minimum density possible with a particular type of GMB. For each type of GMB, the density at zero resin content is lower than the measured tap density. This would indicate that the GMB are not as tightly packed as possible by the vacuum bag method, but would also indicate that no microbubbles are being broken during the molding operation.

The relationship between compressive strength and resin concentration is shown in Figure 6. At zero resin concentration the strength value is a measure of the crush strength of bubbles only. With 100 percent resin, the compressive strength is about 28,000 psi (193 MPa).

Preliminary data indicate that the composite strength is dependent upon the type of GMB and resin content. As mentioned previously most of the resin fits between the closely packed bubbles. Increasing the resin does not actually change the volume of GMB in the composite, but rather decreases the amount of air or void space between the GMB. According to these data, the strength increases in a predictable fashion until the space between the GMB is filled with resin (at 30 to 40 percent resin). Above the 40 percent level, the effect of resin content diminishes.

Figure 4. Compressive Modulus of Kerimid 601 and Glass Microbubble Syntactic Foam

The B40A GMB are stronger than the other types of GMB. The B35D and the B40BX have similar properties although the slopes of the curves are different. The "super strength" B35D type of bubbles were expected to be stronger than the B40A, but in this test configuration the B40A were considerably stronger.

Discussion of Results

The vacuum bag molding method does not crush the GMB during the molding operation. The volume fraction of GMB in the composite foam is actually lower than would be expected from the packing

Figure 5. Specimen Density as a Function of Resin Concentration

factor. Although the resin in the formulation should fit in the void space between bubbles, some resin would tend to separate bubbles. A higher molding pressure would force bubbles together and increase the packing factor. The data in Figure 6 shows that the bubbles themselves are stronger than expected. The B40A GMB

Figure 6. Compressive Strength as a Function of Resin Concentration

have a crush strength of over 1000 psi (6.89 MPa) and even the B18A should resist 200 psi (1.38 MPa) without crushing. Molding pressure of at least 100 psi (0.689 MPa) could be used with little chance of crushing bubbles.

Composite strength is dependent upon the type of bubbles used. The strength of an individual bubble is primarily dependent upon

density. Since the bubbles are all approximately the same size, wall thickness determines density. According to the manufacturer, the isostatic crush strength is proportional to the square of the bubble density.⁴ The process used to manufacture bubbles also influences strength. For example, the B40A and B40BX have similar particle densities and tap densities, but the composite foams have significantly different compressive strengths.

ACCOMPLISHMENTS

Blending, molding, and curing techniques were developed to make syntactic foam from Kerimid 601 and glass microbubbles. Composite foams were prepared with densities ranging from 0.20 g/cm³ to 0.98 g/cm³ with compressive strengths ranging from 500 psi to 26,000 psi (3.45 MPa to 179 MPa). Thin walled, low density microbubbles are required in order to prepare low density composites. The B40A bubbles offer the best strength to weight ratio above a composite density of 0.35 g/cm³. Foam formulations can be selected on the basis of overall strength or density depending upon design requirements.

FUTURE WORK

Lot to lot variations in the Kerimid 601 resin and glass microbubbles will be measured. When foam densities and strength requirements are defined, mechanical, thermal, environmental, and physical properties will be measured.

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