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THERMALLY CONDUCTIVE SYNTACTIC FOAM

PDO 6984878, Topical Report

H. M. McIlroy, Project Leader

Project Team:
P. B. Mayfield

Published August 1976

MASTER

Prepared for the United States Energy
Research and Development Administration
Under Contract Number E(29-1)-613 USERDA

Bendix Kansas City
Division

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Technical Communications Bendix Kansas City Division

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Prepared by H. M. McIlroy, D/814, under PDO 6984878

A low density, high thermal conductivity syntactic foam has been formulated from carbon and graphite microballoons with a polyimide binder resin and graphite fibers. The flexural properties of strength and deflection were increased by using the graphite fibers and the failure mode was increased from a brittle to an elastic mode.

WPC-pls

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A prime contractor for the United
States Energy Research and
Development Administration
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SUMMARY

A syntactic foam such as Imidite, manufactured by the Whittaker Corporation, from glass microspheres, has a thermal conductivity of about 0.1 W/m•K. A current program requires a low density support part with a thermal conductivity of about 0.4 W/m•K. The required thermal conductivity and strengths have been achieved by preparing a foam from carbon and graphite microspheres with a polyimide binder resin and graphite fibers to improve handling.

The polyimide resin, Kerimid 601 (Rhodia Incorporated) offers many processing advantages over other types of polyimide resins. Since the resin is a powder that melts and flows before curing to a solid, a low density foam can be made. That is, a large volume percent of microspheres can be used with the resin. Also, since the cure is by an addition reaction, there is essentially no weight loss or shrinkage during cure. Other resins such as phenolic and silicone are being considered and evaluated as backup materials.

Carbon microspheres (Carbo-Spheres) made by Versar, Incorporated, have been used to reduce the molded density and to increase the thermal conductivity. The only other known source of carbon microspheres (CMS) is Kreha Corporation, a subsidiary of a Japanese company. Kreha carbon microspheres have not been evaluated.

The Carbo-Spheres are about 96 percent carbon with 2 to 4 percent weight loss at 700°C in nitrogen. The spheres are similar in size distribution to the glass microspheres but a large percent of the carbon spheres have small holes. The glass microspheres have a floater/sinker ratio of about 97:3 while the carbon microsphere ratio is about 65:35. If a liquid resin system were used, the carbon microspheres would fill with resin and yield a high density molding. However, with the powdered resin that softens and flows, spheres are not filled and low densities are possible.

Chopped graphite fibers with lengths of 6 mm (0.25 inch), 3 mm, and 1 mm as well as milled fiber (0.004 inch length) (0.1 mm) have been evaluated. The separation of the fiber into individual filaments and the blending of the fiber with the resin and carbon microspheres is a continuing problem. Many dry and wet methods of separating the fibers have been tried; the most promising method is a dry technique using a high speed beater or intensifier bar in a twin shell blender. With the intensifier bar, the 6 mm fibers are separated and fluffed, but the 1 mm and 3 mm are rolled into small balls. A twin shell blender is an efficient way of combining the resin, carbon microspheres, and fiber.

Test blocks were prepared with different post cure conditions. The temperature was varied from 375°F (191°C) to 525°F (274°C) for times of from 4 to 24 hours. Compressive properties were measured at 77°F (25°C) and 400°F (204°C). The test results show no increase in strength after post curing at elevated temperatures. The samples with no post cure did have slightly reduced strength when tested at 400°F (204°C).

The molded density has a significant effect on both the thermal conductivity and the compressive properties. The compressive strength at 77°F (25°C) ranges from 750 psi (5.17 MPa) at 0.28 g/cm^3 to 1800 psi (12.4 MPa) at 0.38 g/cm^3. The measured thermal conductivity is a function of both the density and the void content. With the carbon microspheres, the highest thermal conductivity was about 0.25 W/m•K. With the graphite microspheres thermal conductivities as high as 0.50 W/m•K were obtained.

Graphite fibers added to the blend of resin and microspheres do not significantly alter the thermal conductivity, compressive properties, or the tensile properties. However, the flexural properties are greatly improved by adding fibers. Not only does the strength and deflection increase with the use of fibers, but also the failure mode changes from a brittle failure to an elastic failure.

DISCUSSION

SCOPE AND PURPOSE

A structural foam part for mechanical support and thermal protection is required for a current program. This effort is to provide design data by measuring material properties and to develop manufacturing processes for a low density material with the following properties:

Thermal Conductivity	9×10^{-4} cal/cm•s•°C (0.376 W/m•K)	Minimum
Compressive Strength at 20°C	700 psi (4.86 MPa)	Minimum
Compressive Modulus at 20°C	30,000 psi (207 MPa)	Minimum
Density	0.32 g/cm^3	Maximum
Survive Impulse Test	2000 taps	Minimum

PRIOR WORK

Five materials have previously been evaluated at Los Alamos Scientific Laboratories (LASL) for the support part. These include commercially available insulation materials, carbon foam, glass microbubble filled RTV silicone, and HTF60, a polyimide foam developed by Sandia Albuquerque.[1] Parts were made by Bendix Kansas City, from the HTF60 foam, but the high shrinkage factor and weight loss made the parts expensive to manufacture.[2]

Imidite X386, a polybenzimidazole foam made by Whittaker Corporation was selected as the prime material for this support part.[3] The Imidite has superior mechanical and thermal properties, but new product requirements for higher thermal conductivity and reduced thermal resistance made the elevated temperature properties of the Imidite unnecessary and required a different formulation to improve the thermal conductivity of the Imidite. In addition, procurement and availability of the Imidite raw materials was a problem. As a result, development of the Imidite was terminated and other readily available candidate materials with greater thermal conductivity were selected for evaluation.

Aluminum honeycomb with polyimide, epoxy, phenolic, silicone, and polyurethane resins was evaluated to improve thermal conductivity. The most practical method was a foam-in-place technique using Bendix Kansas City Thermalthane 4003 (polyurethane) with the aluminum honeycomb, but problems with discontinuities relegate the honeycomb parts to a backup position.

ACTIVITY

Material Characteristics

Resins

Since the required density is low, the resins selected for this evaluation were solid, powdered materials that melt during the cure cycle and bond adjacent microspheres together. The three resins tested were a phenolic resin, a polyimide resin, and a polyaromatic resin.

The phenolic resin available was Plyophen 5655 (24-655 new designation) made by Reichhold Chemicals, Incorporated. This phenolic is a finely powdered one-step resin used primarily in the manufacture of fibrous glass insulation. The melting range is 55°C to 65°C with a set time of 2 minutes at 150°C.

Since successful molding of this part requires that the resin actually melt and flow around the carbon microspheres, the time that the resin is in a fluid state is important. A Brabender Corporation plastograph viscometer was used to provide a constant input temperature and to record the temperature change. Although some torque measurements were made, the primary interest was in the time that the polymer was fluid at a given initial temperature. Normally the cure or degree of cure is set by an arbitrary torque value. For this preliminary work, the polymer was considered cured when the material began to crumble. This phenolic resin is fluid at 65°C but cures within 5 minutes at 85°C. Only the one run was made with the phenolic resin. The fluid time is undoubtedly longer at 65°C, but the resin is still rapid cure material.

The polyaromatic resin is a H-resin made by Hercules, Incorporated. The H-resin was used to mold test blocks, but the compressive properties were significantly lower than for the phenolic or polyimide resins.

Since the phenolic resin gelled near its melting point and the H-resin did not meet the compressive strength and density requirements, the Kerimid 601 polyimide resin was selected for additional testing. Kerimid 601 polyimide resin is made by Rhodia, Incorporated, a French company. It is an addition type polyimide as opposed to a condensation type. With the addition type, the polyimide linkage is formed before the final cure. During the cure other types of chain extension and cross-linking reactions occur to form the rigid polymer. With the condensation type, the polyimide linkage is formed during the final cure of the polymer with the loss of water. Since the liberated water can be a serious processing problem, the addition type is preferred for this application. The generalized reaction for both types of polyimides is given in Figures 1 and 2.

Without going into the detailed reaction, the condensation type is formed from a dianhydride and a diamine. The initial reaction to the polyamic acid is carried out in a high boiling solvent such as dimethylformamide (DMF) or N-methylpyrrolidone (NMP). With thermal energy the amic acid is condensed to an insoluble imide. The reaction is shown in Figure 1.

The preparation of the Rhodia 601 resin is protected by U.S. Patent 3,562,223. The resin is prepared from maleic anhydride and a diamine. This product is fully imidized when received from the vendor. During the final cure, the bismaleimide reacts through the double bond with other bismaleimide molecules and also with additional diamine. The diamine reaction occurs at a faster rate and leads to chain extension without cross-linking. The rigid polymer is formed by the reaction of the bismaleimides. No by-products are evolved during the final cure.

The resin as received (a mixture of bismaleimide and diamine) has a melting range of 194°F to 230°F (90°C to 110°C) as measured by the Fisher-Johns method. As with the phenolic resin, a Brabender Corporation plastograph was used to measure the time that the resin is fluid. For these tests, the torque measurements were not as important as the temperature measurements. Several runs were made with resin only and with different initial temperatures. For all the tests the heat input to the mixing zones was constant. Any increase in temperature was due to friction or exothermic reaction. The runs for an initial melt temperature of 225°F (107°C), 250°F (121°C), and 300°F (149°C) are given in Figure 3. In all the tests, the material changed from a viscous liquid to a crumbly solid immediately after the maximum temperature was reached. While this method is by no means exact, it does show that the Rhodia 601 resin is slightly exothermic and that the time the material is fluid depends upon the initial melt temperature.

The existence of a slight exothermic reaction is also shown by the differential scanning calorimeter (DSC) trace in Figure 4. This DSC shows an exothermic reaction over the temperature range of 150°C to 260°C. Rings made in a production area with up to two inch cross section (50.8 mm) have no indications of high exothermic temperatures. Rings fitted with thermocouples have shown no unusual increase in part temperature during the melt and cure cycle. Although the pure resin does have a slight exotherm, the resin diluted with microsphere filler does not have a measurable exotherm. The Kerimid 601 resin with microsphere filler can be cured at any rate without problems due to exotherm.

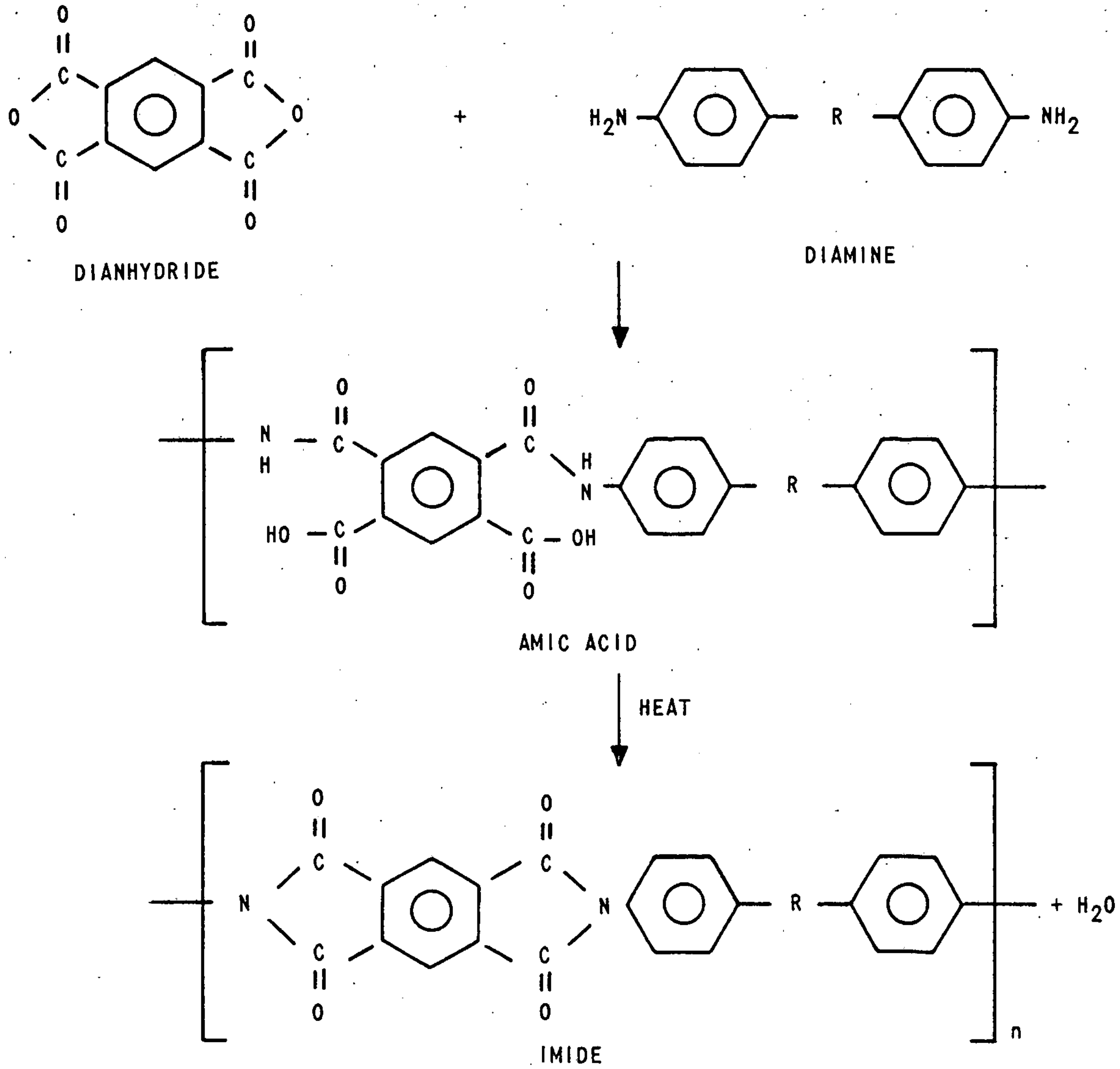


Figure 1. Reaction of Condensation Polyimide Resins

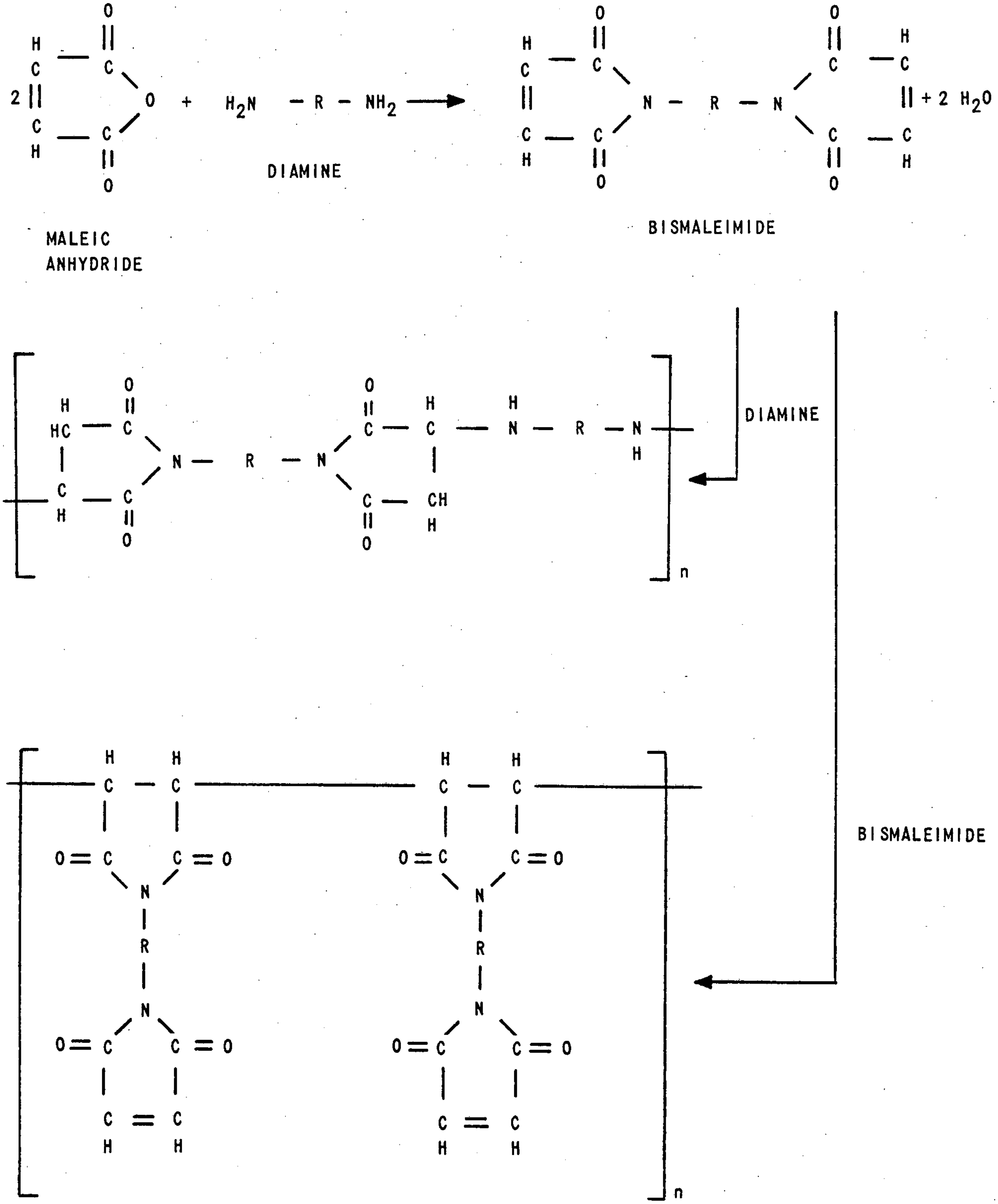


Figure 2. Reaction of Addition Type Polyimide Resins

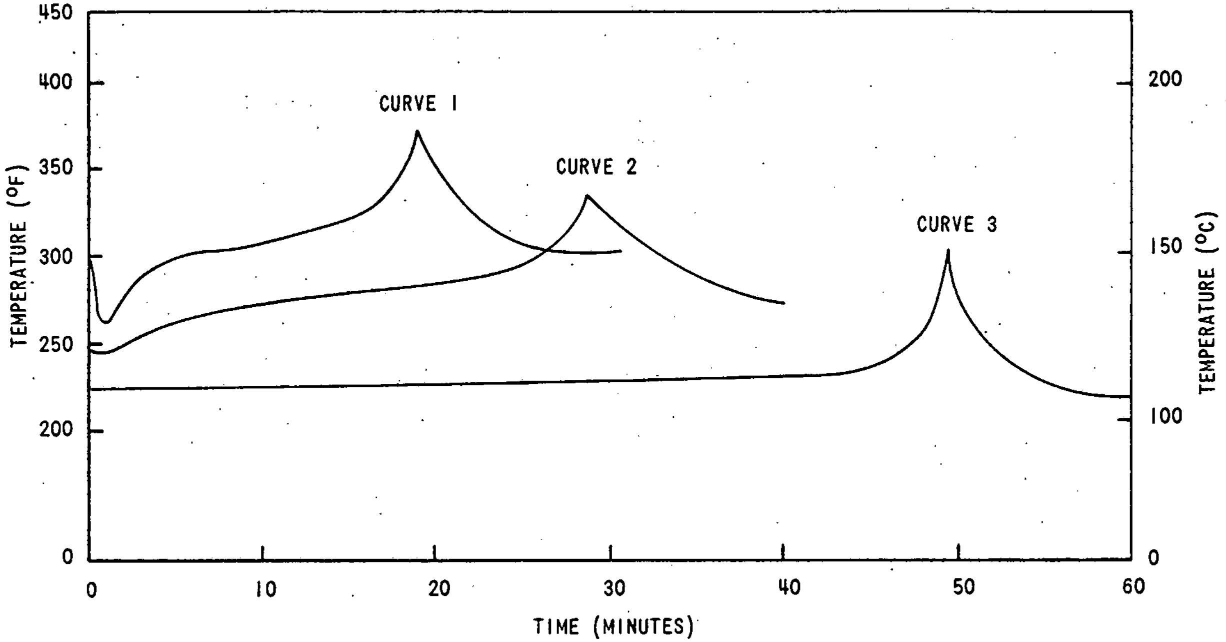


Figure 3. Effect of Melt Temperature on Fluid Time and Exotherm of Kerimid 601 Polyimide Resin

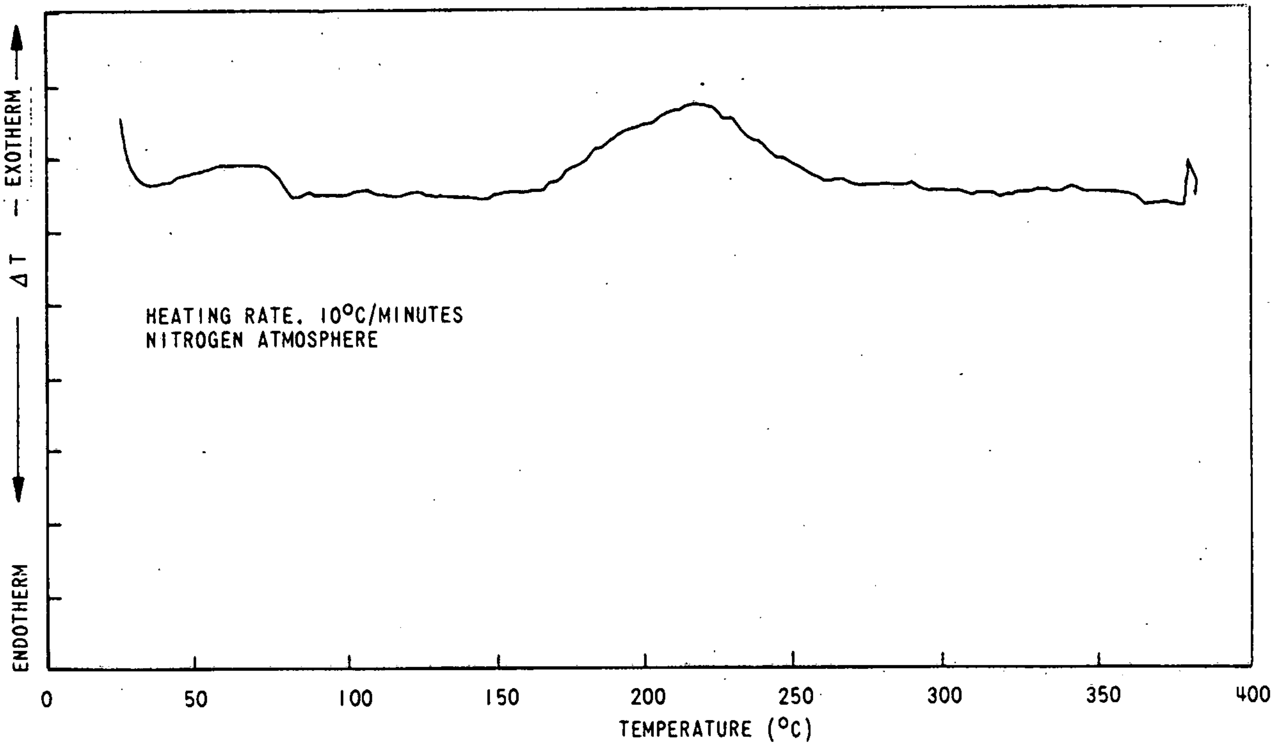


Figure 4. Differential Scanning Calorimeter Trace for Curing Kerimid 601 Polyimide Resin

By definition, the addition type polymers should not have a weight loss during cure. Weight loss measurements by TGA have been made on cured and uncured resin. These results are shown in Figure 5. There was no difference between the cured and uncured sample. This means that the reaction is of the addition type and parts made with the resin should have essentially zero weight loss during cure.

Microspheres

Microspheres made from carbon are available from two companies. Kreha Corporation of America, a U.S. subsidiary of a Japanese company, makes a carbon microsphere that they call Krecaspheres. The Krecaspheres are made from a pitch material. Approximately one year ago (March 1974), the Krecaspheres were not available in the U.S. except in 100 gram samples. The availability at this time is not known. The other source of carbon spheres is Versar, Incorporated, a company in Springfield, Virginia. All of the test billets made with carbon microspheres have been made with the Versar "Carbo-Spheres."

Seven lots of carbon microspheres have been received and tested at Bendix Kansas City. Three of the lots have been modifications of the standard product in attempts to improve the thermal conductivity of the composite. Certain chemical tests were made on Lots 2 and 3. These microspheres were analyzed by thermogravimetric analysis (TGA), mass spectrometry, elemental analysis, and emission spectroscopic analysis of the ash. The TGA in nitrogen show a weight loss of 2 to 4 percent at 700°C with an ash content of about 2 percent. The elemental analysis shows the microspheres to be about 96 percent carbon with the major constituent of the ash being sodium and silica. The outgassed products by mass spectrometry were water, air, carbon monoxide, and carbon dioxide. These tests show that the microspheres are essentially inert carbon and are thermally stable in an inert atmosphere.

As mentioned above, seven lots of the standard Carbo-Spheres have been received from Versar. These lots have been tested for apparent density, bulk density, tap density, floater/sinker ratio, ash content, weight loss, and particle size distribution. The test results are summarized in Table 1 and Figure 6.

Normally with microspheres the material properties of interest would be density, particle size distribution, and a measure of the number of broken spheres (floater/sinker ratio). The carbon microspheres have an unusual problem in that many of the spheres have one or more small holes. The spheres are not broken, but rather have small holes. A picture of a typical lot (Lot 2) is shown in Figure 7. Since the spheres do not have a continuous surface, the test results have been inconsistent. Two of the

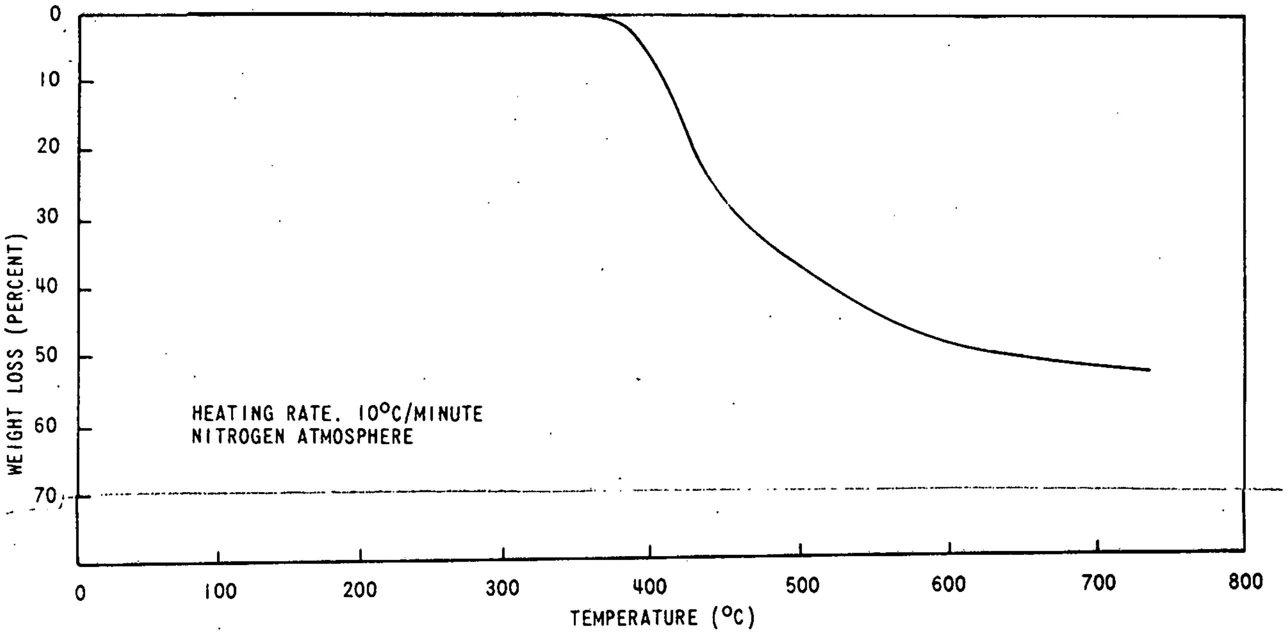


Figure 5. Weight Loss of Rhodia 601 Polyimide Resin by Thermal Gravimetric Analysis

important properties are the apparent density and float/sink ratio. Both of these properties are measured in a liquid medium. The carbon microspheres with the holes tend to be filled with the liquid (toluene or heptane) and give high densities and high sinker ratios.

The photomicrograph in Figure 7 shows that the microspheres are fused together with resin and that microspheres with holes are still present; that is, the holes do not fill with resin. Therefore, for this application, the presence of the holes does not detract from the performance. However, the holes do prevent the measurement of an apparent density. Without knowing the actual balloon (apparent) density, the amount of voids in the foam cannot be calculated. Although the sphere density cannot be measured by the conventional method, an estimate of the density was made.

The best random packing possible for equal sized spheres is about 63 percent by volume. The remaining 37 percent is air or void space between the spheres. Carbon microspheres are not monosized spheres, but do have a distribution of particle sizes. With a distribution of sizes, the smaller spheres can fit between the larger spheres and the packing factor or volume of spheres will increase. The ratio of tap density to apparent density is a measure of the packing factor. By assuming a packing factor of

Table 1. Properties of Carbon Microspheres

	Density					
Lot Number	Apparent (g/cm^3)	Bulk (g/cm^3)	Tap (g/cm^3)	Float/Sink Ratio	Ash Content (Percent)	Weight Loss 700°C-N$_2$ (Percent)
1	0.372		0.20	3.5:1		
2A		0.14	0.18	2:1	1.5	2.0
2B	0.507	0.14	0.18	3:1		
3A	0.447	0.14	0.19	3.8:1		4.0
3B	0.501	0.136	0.18	1.4:1		
Mod 3	0.580	0.145	0.21	1.5:1	7.1	15.0
4	0.497	0.126	0.18	1.3:1		
LW24W	0.604	0.137	0.19	2:1	2	9.0
LW24GRW	0.579	0.149	0.18	0.7:1	<1	0.5

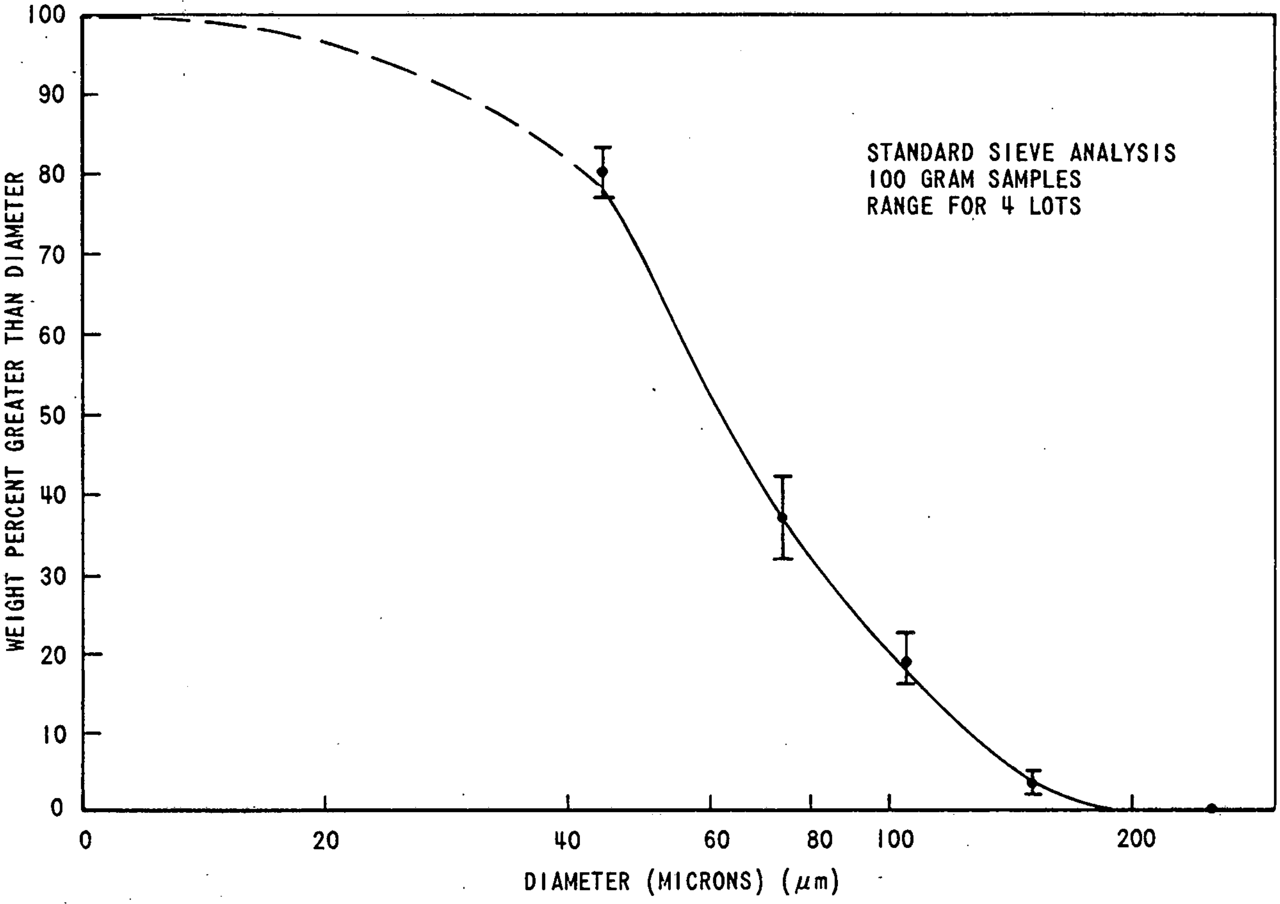


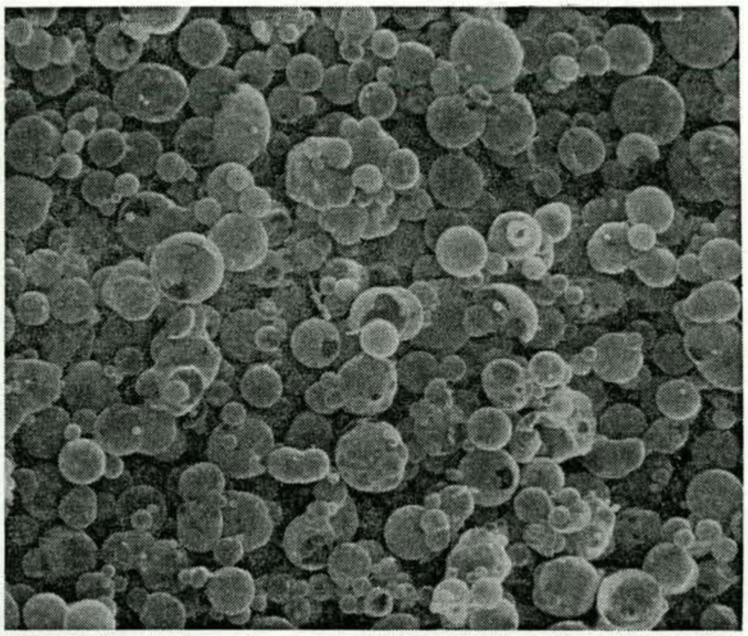
Figure 6. Average Particle Size Distribution for Carbon Microspheres

0.63, and using the tap densities from Table 1, the apparent density would range between 0.29 g/cm^3 and 0.33 g/cm^3.

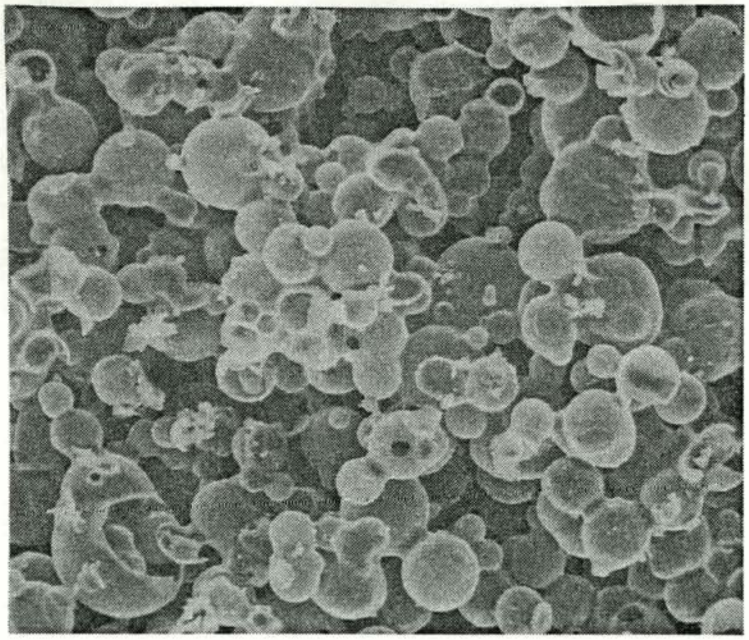
Test data are available for tap density and apparent density of several types of glass microspheres. For these glass microspheres the ratio of tap density to apparent density is 0.66 to 0.69. Since the glass and carbon microspheres are about the same size and have similar size distributions, this ratio (packing factor) is probably accurate for the carbon microspheres. By using the packing factor of 0.68 the apparent density would be between 0.26 g/cm^3 and 0.31 g/cm^3.

Graphite Fibers

Graphite fibers have been incorporated into the material formulation for two reasons. First, the graphite fibers should improve the thermal conductivity and possibly the strength of the basic



CARBO-SPHERES



CARBO-SPHERES WITH POLYIMIDE RESIN

Figure 7. Magnified Carbo-Spheres (300X)

resin-carbon microspheres material. The second reason is that the fibers improve the material resistance to the flyer plate impulse test.

Several types of graphite fiber have been purchased from Hercules, Incorporated, for testing. Fibers with lengths of 6 mm, 3 mm, and 1 mm were purchased. The 6 mm fiber had a sizing for thermoset materials, but the 1 mm, and 3 mm did not have any sizing. Milled fiber, approximately 0.004 inch long (0.1 mm), was made from the 1 mm fiber by grinding it in a mulling mill.

Processes

This section is subdivided into the headings of blending methods, molding methods, and curing cycles. The major problem has been with the blending operations. The molding methods are similar to the techniques used with the Imidite materials. However, more work is needed to optimize the cure schedules since the cure schedules recommended by the resin manufacturer do not seem to yield the best physical properties.

Blending Methods

The mixing of the powdered resin and carbon microspheres is no problem. Since the resin and microspheres have similar particle sizes and size distribution, a twin shell blender is an easy, efficient method of blending. To prevent resin rich areas caused by agglomeration, the resin and microsphere mixture is sieved before the blending operation.

The need for a three component system (resin, fiber, and microspheres) seems to greatly increase the blending problems. Blending of the resin and carbon microspheres by themselves is no problem and blending of resin and fibers alone can be accomplished, but blending the three components is a problem. Basically the approach has been to find a way of separating the fiber into individual filaments and then adding the resin and carbon microspheres. For this report the mixing methods have been divided into dry and wet methods. The wet methods have included a kitchen type blender, a Cowles dissolver, a Hobart mixer, and a high shear propeller. With these techniques the liquid is usually water, but solvents such as N-methylpyrrolidone and dichloromethane were used with the Hobart and Cowles dissolver.

The dry methods of blending have included a twin shell blender, a twin shell blender with a high speed intensifier, a ball mill, and a mulling mill. The most successful way has been with the twin shell blender with a high speed intensifier.

The high speed intensifier attachment for the Patterson-Kelly twin shell blender separates the clump of 0.25 inch (6.35 mm) fiber fairly well. Blend times of up to 30 minutes were checked. The short blend times (1 to 5 minutes) give the best separation of fiber. With mixing times longer than 5 minutes the fibers start to mat and form lumps. The intensifier on the twin shell does not really do a good job of separating the fiber, but it is the best method tried to date. Possibly modifications in the shaft speed, beater bar clearance, number of beater bars, and moisture content of the fiber could help the fiber separation.

Molding Methods

Two of the three standard methods for molding the dry powder type of syntactic foam have been used to mold the test parts. The method used most often is the compression molding technique. By this method, a certain weight of material is charged to a constant volume mold. The density of the part is determined by the charge weight and mold volume. A large percentage of air (voids) could be present in low density moldings and a significant number of broken balloons could be the result of a high density part.

The second molding method commonly used is the vacuum bag technique. By this method, a constant pressure (determined by the vacuum pump) is applied to the molding material. The part thickness and density is determined by the material formulation and temperature (melting) history. This method has the advantage of being gentle with the carbon microspheres and is used to evaluate cure schedules and to evaluate material formulations.

The vacuum bag technique does not lend itself to a production process, but the compression molding method is straightforward and has been used to prepare production type parts.

Curing Cycles

For the initial evaluation, the cure cycles recommended by the manufacturer were used.

The normal or recommended cure cycle for the polyimide resin is a melt of 200°F (93°C) for 1.5 hours, a cure of 375°F (191°C) for 1 to 2 hours, and a post cure of 480°F (249°C) for 24 hours.

With the vacuum bag molding method the pressure is applied at the beginning of the melt cycle. With the compression molding method, the pressure is applied after the melting but before the cure.

Foam Properties

Test Methods

When practical, ASTM methods were used to measure the material properties. The material properties tested are given below:

ASTM C-177, *Thermal Conductivity of Materials by Means of the Guarded Hot Plate.* Specimens: 8 inch diameter by 0.5 inch thick (203 mm by 13 mm).

ASTM D695, *Compressive Properties of Rigid Plastics.* Specimen: 1.129 inch diameter by 0.5 inch thick (28.7 mm by 13 mm). Test Conditions: 0.050 inch/min. (1.3 mm/min.) cross-head speed.

ASTM D638, *Tensile Properties of Plastics.* Specimen: 1.129 inch diameter by 0.5 inch thick (28.7 mm by 13 mm) bonded to two aluminum plugs. Test Conditions: 0.050 inch/min. (1.3 mm/min.) cross-head speed.

ASTM D790, *Flexural Properties of Plastics.* Specimen: 2 inch by 0.5 inch by 0.1 inch (508 mm by 13 mm by 2.54 mm). Test Conditions: 0.5 inch/min. (13 mm/min.) cross-head speed.

One of the design goals was low gas evolution at 550°C over a 20 millisecond time span. Two types of tests were made to measure the thermal resistance of the candidate resins. The Bendix test was made using a pyrolysis probe and gas chromatograph to detect the gases evolved. Polyimide, polyurethane, silicone, phenolic, and epoxy resins were evaluated. None of the resins tested had a measurable amount of gas given off at the 550°C for 20 millisecond level.

The other test was developed and conducted by LASL. This "mouse trap" test measures the weight loss of a foam sample after the sample is slapped against a preheated metal foil. These tests also indicate that all the foam systems considered have adequate thermal resistance.

Another design goal for the foam is a resistance to a specific impulse test. This test called a flyer plate test was conducted by Sandia Albuquerque for LASL. The test results indicate that the material formulations with graphite fibers exceed the requirements.

The formulations without fibers did have some spall and were marginal.

A series of blocks was molded and tested to determine the effect of cure time and cure temperature on the compressive properties of foams made from the Kerimid 601 resin and carbon microspheres. A formulation without graphite fibers was selected to insure a complete mix and to circumvent processing problems.

The blocks were compression molded in an 8 by 8 by 0.6 inch (203 by 203 by 1.5 mm) mold to an overall target density of 0.33 g/cm^3 with a 40/60 (Kerimid 601/carbon microsphere by weight) formulation. Tests were made with three melt temperatures, a constant cure time and temperature, and four postcure temperatures for four postcure times. After the initial melt and cure, individual test specimens (1.129 inch diameter by 0.5 inch) (28.7 mm by 12.7 mm) were machined from the molded blocks. The test disks were then postcured for the prescribed time and temperature in a nitrogen atmosphere. There was no dimensional change (as measured by vernier calipers) as a result of the postcures. The specimens for the postcure were not randomly selected from the molded block, but were rather taken in sequence. Average compressive test results for these specimens are given in Tables 2 and 3.

These test results show no significant difference between blocks made with different melt temperatures and no increase in strength resulting from postcure time or postcure temperature. Extended postcure at elevated temperature is not required to develop thermal resistance to 400°F (204°C). However, in order to develop the maximum thermal resistance, a postcure to 500°F (260°C) would be required.

Properties of a syntactic foam are dependent upon the foam density. For this work the thermal conductivity and compressive properties as a function of density were of interest. Two types of test specimens were prepared. The first type of blocks was molded at constant pressure (vacuum bag) in an 8 inch (203 mm) diameter mold and each set of blocks had a different concentration of carbon microspheres. The second type had only one material formulation, but the mold charge weight and thus the density was varied. The formulations tested are given in Table 4. All of the blocks were molded with a 250°F (121°C) for 1.5 hour melt, a 375°F (191°C) for 1.5 hour cure, and a 480°F (249°C) for 16 hour postcure. The effect of density on the compressive strength and compressive modulus is shown in Figures 8 and 9.

The strength, within an expected range of values, is a linear function of the density. Within the formulations and densities tested, the density seems to be more significant than the amount of resin in the formulation. There seems to be no difference in strength between a 0.33 g/cm^3 block molded from 40/60 (601/CMS by weight) formulation and a 0.33 g/cm^3 block molded from a 45/55 formulation. These results are contrary to the expected results of higher resin contents having higher strengths.

The compressive properties are temperature dependent. At 400°F (204°C) and 0.30 g/cm^3 the foam retains about 85 percent of its room temperature strength. The compressive modulus drops to about 70 percent of the room temperature value when tested at 400°F (204°C).

Table 2. Effect of Cure on Compressive Properties of Polyimide/Carbon Microsphere Foam at 70°F (21°C)

Test Block	Melt (°F) After 1.5 Hours	Cure (°F) After 1.5 Hours	Post Cure		Compressive Properties at 70°F		
			Temperature (°F)*	Time (Hours)	Density (g/cm^3)	Strength (psi)**	Modulus (psi)
112	200	375	475	4	0.317	1110	71300
112	200	375	475	8	0.341	1350	85100
112	200	375	475	16	0.316	1090	62500
112	200	375	475	24	0.319	1110	60800
113	250	375			0.328	1300	72300
113	250	375	475	4	0.323	1340	86300
113	250	375	475	8	0.332	1290	66700
113	250	375	475	16	0.320	1200	87500
113	250	375	475	24	0.330	1280	92000
114	250	375	375	24	0.332	1150	68700
114	250	375	425	24	0.310	930	57700
114	250	375	475	24	0.330	1280	92000
114	250	375	525	24	0.329	1270	74400
116	300	375	475	4	0.319	1110	60800
116	300	375	475	8	0.342	1420	72200
116	300	375	475	16	0.325	1240	75200
116	300	375	475	24	0.323	1190	63600

*°C = (°F-32)/1.8
**1 psi equals 6894 Pa

Table 3. Effect of Cure on Compressive Properties of Polyimide/Carbon Microsphere Foam at 400°F (204°C)

			Post Cure		Compressive Properties at 400°F		
Test Block	Melt (°F) After 1.5 Hours	Cure (°F) After 1.5 Hours	Temperature (°F)*	Time (Hours)	Density (g/cm^3)	Strength (psi)**	Modulus (psi)
112	200	375	475	4			
112	200	375	475	8			
112	200	375	475	16			
112	200	375	475	24			
113	250	375			0.311	1000	39100
113	250	375	475	4	0.330	1220	50000
113	250	375	475	8	0.331	1240	42400
113	250	375	475	16	0.329	1220	48000
113	250	375	475	24	0.330	1160	47000
114	250	375	375	24	0.318	1020	43000
114	250	375	425	24	0.331	1170	46500
114	250	375	475	24	0.330	1160	47000
114	250	375	525	24	0.327	1140	51200
116	300	375	475	4			
116	300	375	475	8			
116	300	375	475	16			
116	300	375	475	24			

*°C = (°F-32)/1.8

**1 psi equals 6894 Pa

Table 4. Formulations of Kerimid 601 and Carbo-Sphere Foams

Formulation Weight Ratio Kerimid 601/ Carbo-Sphere	Molding Method	Molded Density (g/cm^3)
35/65	Vacuum Bag	0.29
40/60	Vacuum Bag	0.31
45/55	Vacuum Bag	0.34
50/50	Vacuum Bag	0.38
40/60	Compression	0.28
40/60	Compression	0.30
40/60	Compression	0.33
40/60	Compression	0.34

Thermal conductivity has been measured by several methods. The primary method is the guarded hotplate (GHP) according to ASTM C177. This method requires two 8 inch (203 mm) diameter by 0.5 inch (12.7 mm) specimens for testing. Another method is the cut-bar method. The cut-bar apparatus requires a 1 inch (25.4 mm) diameter by 1 inch (25.4 mm) thick specimen and compares the thermal conductivity of the sample to the thermal conductivity of a known standard. The third method is a relatively new method that measures the heat flow and temperature change across a sample in a duPont differential scanning calorimeter (DSC). The results from the DSC method compare very well with results from the guarded hotplate method. The DSC method is fast and requires a very small sample. In fact, the main problem with the DSC method is the small sample size and thus the chance of measuring a heterogeneous or nonrepresentative sample.

Thermal conductivity values for both the DSC and GHP methods are shown in Figures 10 and 11, as functions of molded density and of void content. While there is spread in the data, the thermal conductivity definitely increased with increasing molded density and decreased with increasing void content. According to Figure 11, the maximum thermal conductivity possible with the carbon microspheres and Kerimid 601 resin is about 0.33 W/m•K. The blocks molded by the vacuum bag (low constant pressure) method have a void content of about 20 percent. With this void content, the expected thermal conductivity is about 0.20 to 0.25 W/m•K.

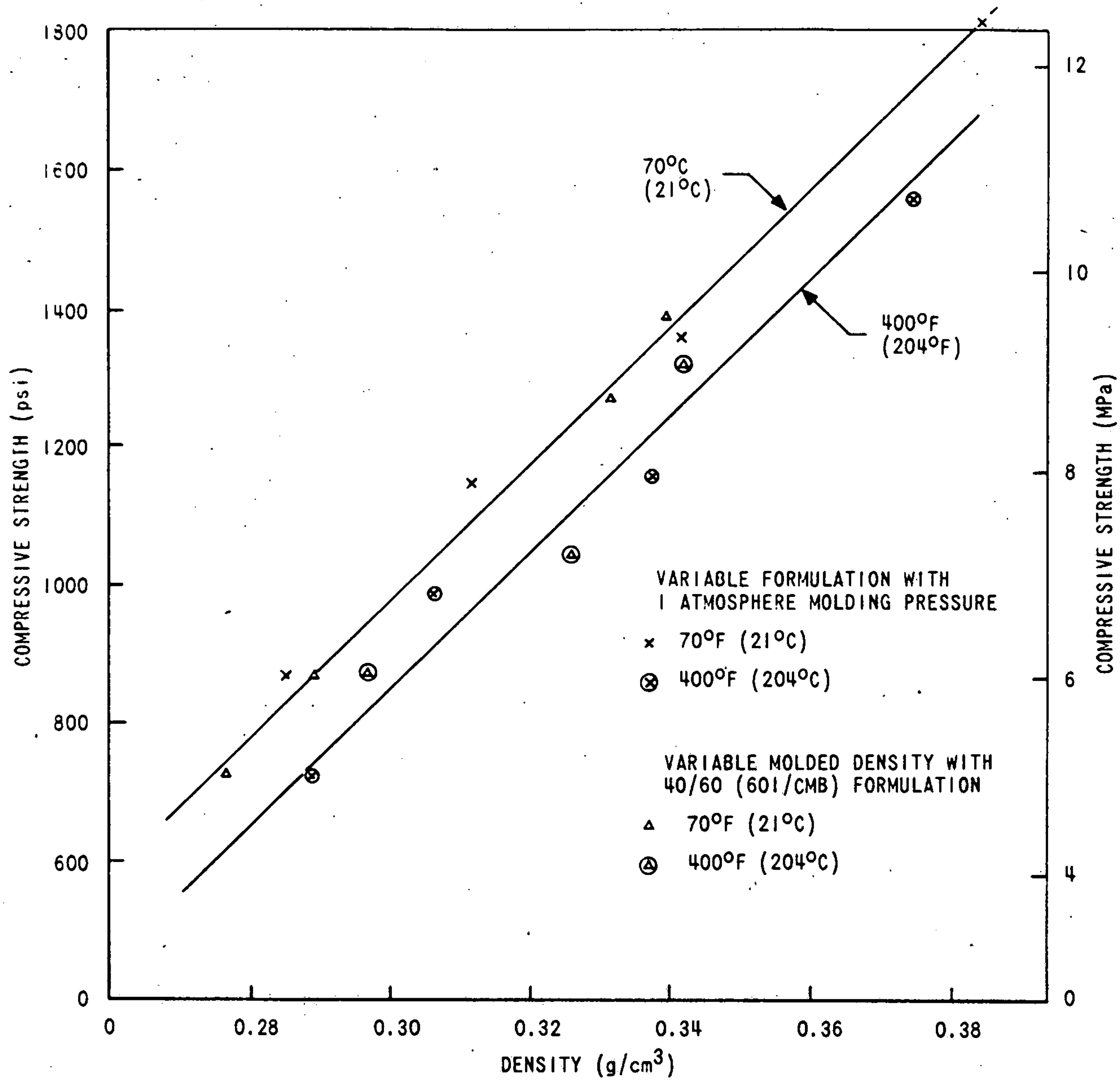


Figure 8. Density Versus Compressive Strength of Foams Made From Kerimid 601 and Carbon Microspheres

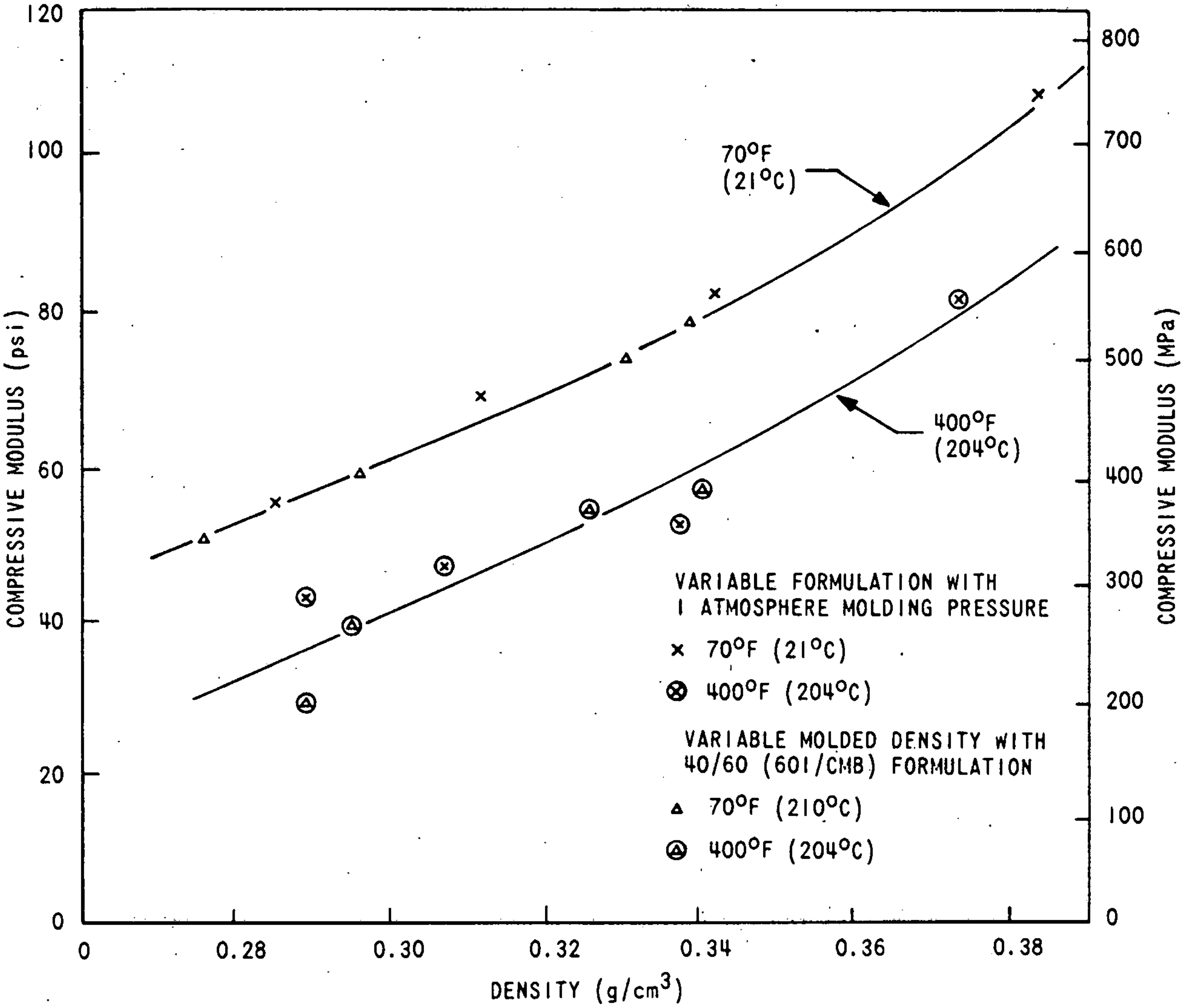


Figure 9. Density Versus Compressive Modulus of Foams Made From Kerimid 601 and Carbon Microspheres

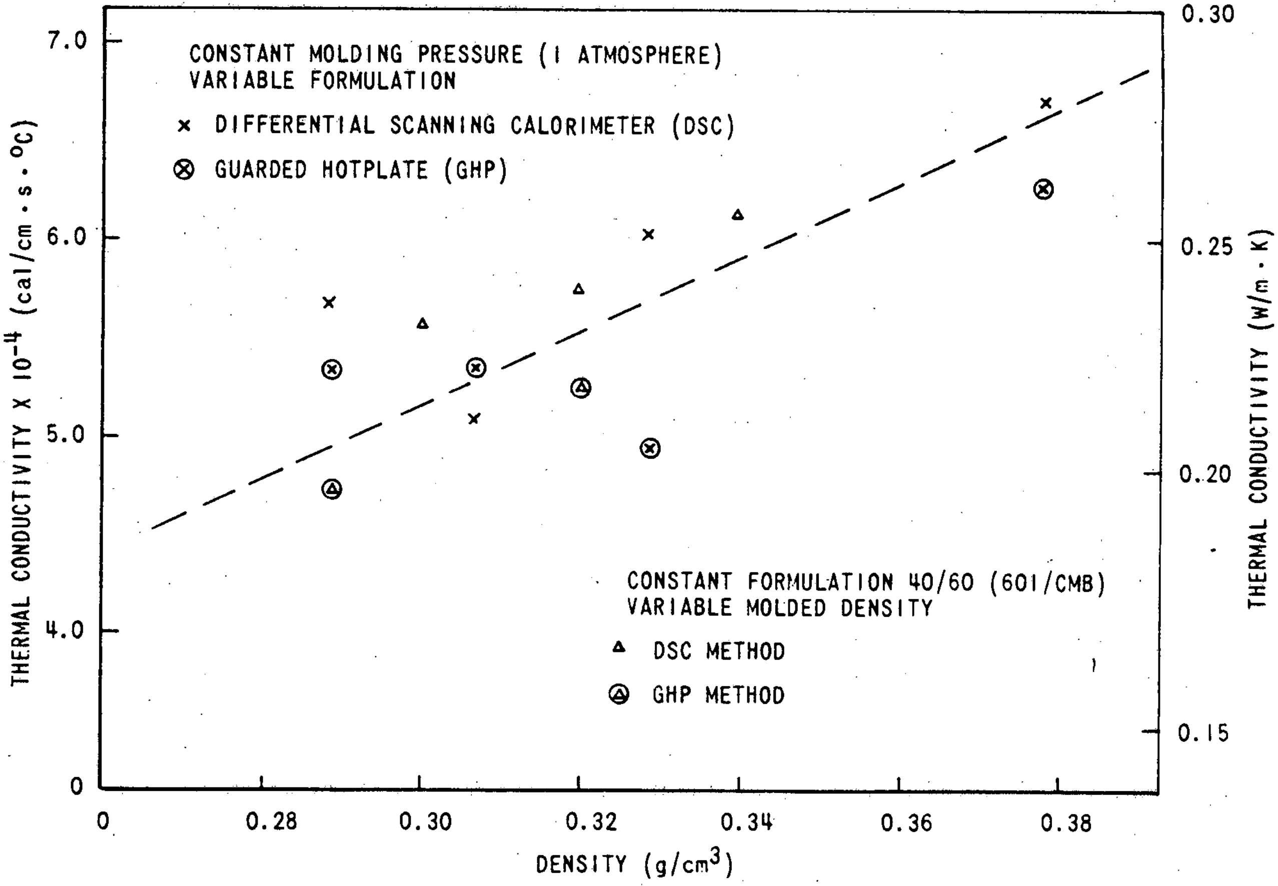


Figure 10. Effect of Molded Density on Thermal Conductivity of Kerimid 601 and Carbon Microspheres

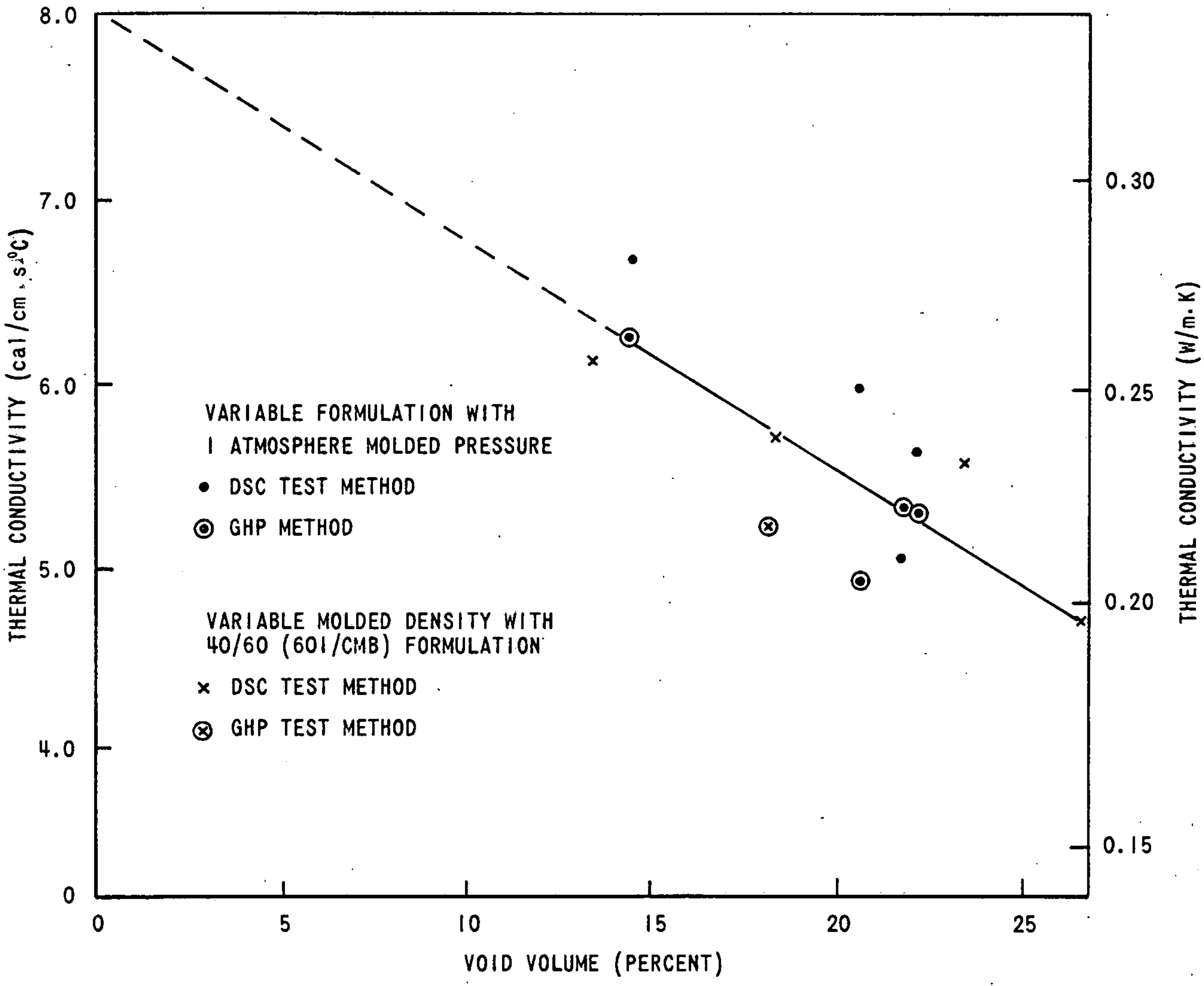


Figure 11. Thermal Conductivity as a Function of Amount of Air in a Molded Block

The foams made with the carbon microspheres could not reach the 0.37 W/m•K target value. In order to increase thermal conductivity, foam billets were made from graphite microspheres (Versar Incorporated) and from blends of graphite and carbon microspheres. The test results are summarized in Table 5. These data show that the thermal conductivity is significantly increased by using the graphite spheres. Foams made from blends of the two types of microspheres yield a material with a predictable thermal conductivity. The graphite spheres are weaker than the regular carbon microspheres. The compressive strength ranges from about 1020 psi (7.03 MPa) for all carbon to 778 psi (5.76 MPa) for all graphite microspheres. The graphite spheres (Lot LW24GRW) have lower ash content and lower volatiles than the regular carbon, and SEM photographs show a large number of broken spheres or spheres with holes.

Fiber Properties

Graphite fibers were added to blends of the 601 resin and carbon microspheres in an attempt to increase the thermal conductivity and to improve the handling properties. As discussed previously, the 6 mm fiber and the milled fiber have been blended and molded into blocks. The 1 and 3 mm fibers could not be adequately separated to blend with the resin and microsphere and no blocks were made from these fibers. A summary of the test results of foams made with the graphite fiber is given in Table 6.

All six of the formulations were molded by the low pressure, vacuum bag method. At the 1 part and 3 part fiber level, the density is lower than for the formulation without fiber even though the density of the fiber is about 1.8 g/cm^3. This is due to the bulk of the separated fiber that is not compressed by the low pressure.

The compressive strength and compressive modulus are not affected by the small volume of fiber either at room temperature or at elevated temperatures. Even the milled fiber does not increase the compressive strength.

Adding fibers did not improve the thermal conductivity. By using the milled fiber at the 25 parts level the thermal conductivity was increased, but the foam density exceeded the target value.

The tensile strength may be more of a function of the fiber concentration than the data indicate. The tensile samples were very brittle and several were broken before being tested. The small sample size and data scatter precludes an accurate prediction of the tensile strength. However, the data indicate that the modulus is higher with fiber filled foams and that the strain at failure is less with the fiber than without the fiber.

Table 5. Properties of Foams Made From Blends of Graphite and Carbon Microspheres

					Compressive Properties at 20°C	
Block	Formulation Ratio*	Density (g/cm^3)	Thermal Conductivity ($cal/cm \cdot s \cdot {}^\circ C$)	($W/m \cdot K$)	Strength (psi)**	Modulus (psi)
129	40/0/60	0.310	5.1×10^{-4}	0.213	1150	69,600
182	40/20/40	0.308	6.24×10^{-4}	0.261	914	71,400
181	40/30/30	0.297	7.96×10^{-4}	0.333	800	59,000
180	40/40/20	0.314	9.67×10^{-4}	0.405	850	66,900
158	40/60/0	0.314	12.6×10^{-4}	0.527	778	71,000

*Resin/Graphite/Carbon Microspheres

**One psi equals 6894 Pa

Table 6. Properties of Foams Made With Graphite Fibers

	Formulations					
Property	1	2	3	4	5	6
Density (g/cm^3)	0.31	0.29	0.30	0.32	0.32	0.34
Compressive Strength at 70°F* (psi)**	1150	890	1000	1050	1090	1060
Compressive Strength at 400°F (psi)	990	850	930	980	1066	1034
Compressive Modulus at 70°F (ksi)***	69.6	59.7	59.4	60.0	97.4	85.1
Compressive Modulus at 400°F (ksi)	45.5	40.5	61.0	55.8	58.4	42.1
Thermal Conductivity (W/m·K)	0.224	0.182	0.207	0.209	0.221	0.266
Flexural Strength at 70°F	470			657		670
Flexural Strain at Failure (Percent)	0.94			1.75		1.46
Flexural Modulus at 70°F (ksi)	82.9			96.7		85.2
Tensile Strength at 70°F (psi)	250	130	230	250		200
Tensile Strain at Failure (Percent)	1.5	1.2	1.4	1.3		1.2
Tensile Modulus at 70°F (ksi)	16.3	16.0	16.0	17.0		17.0

1 601/CMS (40/60)
2 601/CMS/6 mm Fiber 40/60/1
3 601/CMS/6 mm Fiber 40/60/3
4 601/CMS/6 mm Fiber 40/60/5
5 601/CMS/Milled 40/60/5
6 601/CMS/Milled 40/60/25

*°C = (°F-32)/1.8
**1 psi equals 6894 Pa
***1 ksi equals 6.894 MPa

Fibers definitely improve the flexural strength of the foam. The samples tested were 2.0 by 0.5 by 0.1 inch (50.8 by 12.7 by 2.54 mm) with a span of 1.6 inch (40.6 mm). The three formulations tested were 40/60 (601/CMS), 40/60/5 (601/CMS/fiber), and 40/60/25 601/CMS/milled fiber. The actual flexural strength increased from about 470 psi (3.24 MPa) to over 650 psi (4.48 MPa) for both the 6 mm fiber and the milled fiber.

More importantly the type of failure was different. Formulations made without fiber had a brittle type failure with the failure occurring at the proportional limit. The samples with fiber did not have a brittle failure, but rather had a yield point before an elastic type failure. Also the fiber filled samples tended to break a layer at a time. That is the failure was not catastrophic, but occurred over a finite deflection. For the span of 1.6 inches (40.6 mm) and thickness of 0.1 inch (2.54 mm), the deflection was about 0.040 inch (1 mm) for the formulation without fiber and about 0.075 inch (1.9 mm) for the formulation with 5 parts fiber. Thus a part molded from the formulation with fiber has a greater resistance to breaking and can be bent or flexed more than an equal-sized part made without fiber.

ACCOMPLISHMENTS

Methods for blending, molding and curing mixtures of resin, carbon microspheres and graphite fibers were investigated and evaluated. As a result of this work, low density syntactic foams with improved thermal conductivity and high compressive strengths were developed. While the properties of the foam formulations with only resin and carbon microspheres exceed the design requirements, the addition of small amounts of graphite fibers greatly improves the handling properties of the foam and reduces the chance of breaking or chipping.

FUTURE WORK

The evaluation of thermally conductive fillers will continue. Silver coated glass microspheres are available and are being evaluated as an alternate filler to provide increased thermal conductivity. Other types of graphite and carbon fibers will also be tested to determine the effect of fiber length and concentration on thermal conductivity and compressive strength.

The influence of relative humidity on weight and dimensional stability will be measured. In addition, the rate of moisture pickup and moisture removal in molded slabs will be determined.

REFERENCES

[1] P. B. Rand, *An Aromatic Polyimide Syntactic Foam*. Sandia Corporation Albuquerque, Report SC-DR-710131, May 1971.

[2] H. M. McIlroy, *Fabrication of Polyimide Syntactic Foam Parts* (Topical Report). UNCLASSIFIED. Bendix Kansas City: BDX-613-582, December 1972.

[3] H. M. McIlroy, *Evaluation of a High Temperature Syntactic Foam* (Topical Report). UNCLASSIFIED. Bendix Kansas City: BDX-613-1178, June 1974.

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