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HIGH TEMPERATURE SYNTACTIC FOAM

By H. M. McIlroy
Department 814

Published July 1977

Final Report on PDO 6984878
H. M. McIlroy, Project Leader

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HIGH TEMPERATURE SYNTACTIC FOAM

BDX-613-1534 (Rev.), UNCLASSIFIED Final Report, Published July 1977

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

Resins from the polyimide, polybenzimidazole polyamide-imide, phenolic, silicone, and urethane families were formulated with glass microbubbles and carbon microspheres to produce low density, high strength syntactic foams. The polyimide and polybenzimidazole foams were the most thermally stable, but even the urethane exceeded the design goals. Foams with high and low thermal conductivity were developed and their material properties were measured. The low conductivity was achieved using glass microbubble fillers and high conductivity was achieved using carbon microsphere fillers.

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SUMMARY

Syntactic foam formulations have been developed and evaluated as materials for a low density, heat resistant support part. A group of 14 resins were evaluated along with several low density fillers and were considered for this application. Based on the results of preliminary tests, two foam systems were selected for continued testing and were well characterized for mechanical, thermal, and physical properties. These two foam systems are Imidite X386 (Whittaker Corporation), a blend of polybenzimidazole resin and glass microbubbles; and a blend of Kerimid 601 (Rhodia Incorporated), a polyimide resin, with carbon microspheres. The Imidite X386 has superior thermal resistance and mechanical properties and a low thermal conductivity. To improve the weapon storage life, the thermal conductivity was increased by using carbon microspheres instead of the glass microbubbles. Since the availability of the polybenzimidazole was a potential problem, the Kerimid 601 polyimide was the resin finally selected and evaluated with the thermally conductive filler.

The resins evaluated were powders that melted before cure, powders that softened above their glass transition temperature, solvent solutions of resins that cured by thermal energy or by a second catalyst component, and liquid resin/catalyst systems. Polymers that just softened and the solvent solution resins were difficult to process. The difference between the melting and softening was a matter of degree. Materials such as Kerimid 601 (polyimide), Imidite X386 (polybenzimidazole), H-Resin (polyphenylene), and Plyophen 24-655 (phenolic) did melt and flow around the filler particles while materials such as 2080 resin (polyimide) and R-500 (amide-imide) required high pressure to bond the resin and filler. These high pressures (1000 psi or 6.89 MPa) crushed the low density fillers and were unacceptable for this application. The "meltable" polymers became fluid enough to be fused at 15 psi (0.103 MPa).

The solvent solutions were difficult to process since the solvent had to be removed slowly to prevent cracking and warping the part.

The solutions evaluated were the 2080 resin and R-500 resin both in N-methylpyrrolidone (NMP) as well as NR-150 A and B polyimide resins. This technique coats the filler and high quality foams can be prepared, but the excessive processing times and equipment precluded serious consideration.

The liquid resin/catalyst systems evaluated included DC 2106 (silicone) DEN 438 (epoxy) and Thermalthane 4003 (urethane foam).

A solvent had to be used with both the silicone and epoxy systems to provide enough liquid volume to wet the filler and still have a low density part. That is, the low density (0.3 g/cm^3) required cannot be obtained with maximum packing of the microbubble filler with the interstitial space occupied by resin. A volatile solvent is required to create voids in the foam to reduce the density. The urethane foam was used with several fillers but the viscosity of the mix prevented the addition of a large volume of thermally conductive filler.

Imidite X386 is a blend of a polybenzimidazole resin and glass microbubbles. The resin is a condensation prepolymer of an aromatic amine and a phenylester with phenol and water evolved during the cure.

Three molding methods were developed to find different ways of forming the Imidite powder. The first technique was molding in a vacuum bag. By this method a constant pressure was applied during the softening and compacting stage and the volatiles were removed during the cure. The second technique was compression molding with sufficient pressure to close a preheated mold. The third technique was a modified compression molding procedure; the material is compacted by a low pressure (100 psi or 689 KPa) with the mold never actually closing. Test results show that the three methods yield material with equivalent properties.

Six lots of material were molded by the vacuum bag technique and mechanical, thermal, and physical properties were measured. Although the values vary from lot to lot, the measured values are above the required design values. Four cure and postcure cycles were performed to determine their effect on the properties of Imidite. A postcure of 850°F (454°C) was required to develop the high heat resistance. The slabs with no postcure and those with 700°F (371°C) postcure, had significantly lower compressive and thermal properties than the slabs with a 850°F postcure.

Since the Imidite is made with glass microbubbles, the thermal conductivity of the foam is about 0.1 W/m•K. Another foam system was developed with a thermal conductivity as high as 0.5 W/m•K. The new foam was prepared from carbon microspheres with a polyimide binder and graphite fibers to improve handling.

The polyimide resin, Kerimid 601 offers many processing advantages over other types of polyimide resins. The Kerimid 601 is a powder that melts and flows before curing to a solid. A low density foam can be made since the resin only bonds adjacent microspheres together and allows air voids in the interstitial space. Also, the cure is by an addition reaction so there is essentially no weight loss or shrinkage during cure.

The molded density has a significant affect on both the thermal conductivity and compressive properties. The compressive strength at 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 graphite microspheres thermal conductivities as high as 0.5 W/m•K were obtained. The test results show no increase in compressive strength or change in thermal conductivity after postcure at elevated temperatures.

Graphite fibers added to the blend of resin and microspheres only slightly improve the thermal conductivity, compressive properties, and tensile properties. Not only do the flexural 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 was required. Project objectives were to develop design data by measuring material properties and to develop manufacturing processes for candidate materials. High temperature resins from the polyimide, polybenzimidazole, and polyamide-imide families were evaluated with glass microbubbles as a filler. As a result of this work, the polybenzimidazole (Imidite X386 made by Whittaker Corporation) was found to meet or exceed the original set of requirements, and was selected as the prime material. A characterization study was made to measure thermal, mechanical, chemical, and environmental properties of Imidite X386. Parts for mock-ups and hydrostatic cyclinder tests were made from Imidite for Los Alamos Scientific Laboratory (LASL) on paid orders. A new project PDO 6984899 *Syntactic Foam Insulators*, was initiated to learn how to build production quantities of the support parts.

However, design changes and Imidite procurement problems required that a new foam system be developed with different performance characteristics. Testing at LASL has shown that storage life can be significantly improved by increasing the thermal conductivity of the support part and that the superior thermal resistance of the Imidite was no longer necessary. Consequently, the design agency increased the thermal conductivity requirement from 2×10^{-4} cal/cm•s•°C (0.08 W/m•K) to 9×10^{-4} cal/cm•s•°C (0.376 W/m•K) and decreased the expected temperature from 600°F to 400°F (315°C to 204°C). These changes allowed the consideration of resins from the phenolic, epoxy and silicone families, but required the identification of thermally conductive fillers.

PRIOR WORK

Five materials have previously been evaluated at LASL for the support part. These materials were two insulation materials, carbon foam, glass microbubble filled RTV Silicone, and HTF60, a polyimide foam developed by Sandia Albuquerque.[1] Since the HTF60 foam exceeded the then current requirements, LASL placed an order with Bendix Kansas City for flat slabs and cone frustums made from HTF60.[2] The parts made from HTF60 were difficult to process, expensive to manufacture, and the material had such a high shrinkage factor that parts could not be molded to size.

A polybenzimidazole syntactic foam system made by the Whittaker Corporation (Imidite SA) was used to make another part.[3,4] Imidite SA can be molded to size and has excellent high temperature properties. However, the density and mechanical properties did not meet the requirements for the support part. Orders were placed with Bendix by LASL for slabs, cylinders, and hemispheres made from two modified Imidite formulations for evaluation at LASL.

ACTIVITY

Potential Materials

Resins

Fourteen high temperature resins were evaluated and considered for this application. An original requirement was that the resin be able to withstand exposure to 600°F (316°C) for several hours with a minimum of weight loss. This requirement limited the choice of resin to the polyimide, polybenzimidazole, and possibly the amide-imide families. A reduction in the original temperature requirement allowed other resins to be considered. The resins evaluated are given in Table 1.

Fillers

Several types or grades of glass microbubbles made by the 3-M Company including B18A, B22A, B35A, and B35D types were evaluated as fillers for a low density thermal insulator. The glass microbubbles are readily available and offer low thermal conductivity; however, with the need for a foam system with high thermal conductivity, other types of fillers were required. Aluminum honeycomb filled with a blend of resin and glass microbubbles or urethane foam was considered. Problems with density discontinuities caused by the honeycomb forced a search and evaluation of other thermally conductive fillers. Other types of fillers evaluated were carbon microspheres, graphite fiber, graphite powder, metal powder, metal wool, metalized urethane foam, metal microbubbles, and metal-coated glass microbubbles.

Following sections of this report (Preliminary Material Evaluation and Candidate Material Evaluation) discuss in more detail the processing techniques and foam properties of combinations of the resins and fillers. The resins were arbitrarily selected as the major heading in the following sections. In many cases several fillers were evaluated with a particular resin and the properties of the foam systems with each filler are discussed under the resin heading.

Table 1. High Temperature Resins

Resin	Resin Type	Manufacturer
P-13N	Addition polyimide	Ciba-Geigy Corporation
P-105AC	Addition polyimide	Ciba-Geigy Corporation
Kerimid 601	Addition polyimide	Rhodia Incorporated
NR-105B	Thermoplastic polyimide	Du Pont
NR-150A	Thermoplastic polyimide	Du Pont
Polyimide 2080	Thermoplastic polyimide	Upjohn Company
Pyrolin 5081	Condensation polyimide	Du Pont
R-500	Amide-imide	Monsanto Company
H-Resin	Polyphenylene	Hercules Incorporated
DC-2106	Silicone	Dow Corning Corporation
DEN438	Epoxy	Dow Corning Corporation
Plyophen 24-655	Phenolic	Reichhold Chemicals
Imidite X386	Polybenzimidazole	Whittaker Corporation
Thermalthane 4003	Urethane foam	Bendix Kansas City

Preliminary Material Evaluation of Low Thermal Conductivity Foams

As originally designed, this material would provide both mechanical support and thermal insulation. The original desired properties are listed.

Density of about 0.35 g/cm^3

Compressive strength of about 1000 psi (6.89 MPa) at 500°F (260°C)

Compressive modulus of about 40,000 psi (276 MPa) at 500°F (260°C)

Weight loss of 2 percent maximum at 600°F (316°C)

Thermal conductivity of about 2 x 10^{-4} cal/cm·s·°C (0.08 W/m·K)

These requirements limited the resin selection to only a few types of materials and limited the filler to low density glass microbubbles. The following materials were considered or partially evaluated during screening tests.

R-500 Amide-Imide

Monsanto Company markets Resin 500 and Resin 600 as thermosetting polyamide-imide molding compounds. Both resins are free flowing powders that can be formed using conventional compression molds and molding procedures. The R-500 resin is reported to have flow characteristics similar to medium hard flow phenolics while the R-600 resin has very limited flow.

The unfilled resins were compression molded in a 1.129 inch (28.7 mm) mold to a thickness of about 0.5 inch (12.7 mm). The R-500 resin was molded at 425°F (218°C) and 4000 psi (27.6 MPa) for 20 minutes. The R-600 resin was molded at 550°F (288°C) and 6000 psi (41.4 MPa) for one hour. Both resins molded well with good flow.

Attempts to compression mold blends of R-500 resin and glass microbubbles were not successful. The pressures required to fuse the R-500 resin crush the glass microbubbles so a low density part could not be made. At pressures low enough (approximately 100 psi or 0.689 MPa) to prevent significant crushing of the glass, the R-500 resin did not flow or fuse well.

Test slabs were prepared by first dissolving the R-500 resin in N-methyl pyrrolidone (NMP) and then bending the glass microbubbles and the solution. The resin concentration was 33 percent by weight in NMP. Three formulations were prepared from the R-500/NMP solution blended with either B22A or B35A glass microbubbles. Preforms were made at room temperature and 100 psi (0.69 MPa). The 8 inch (203 mm) preforms were dried to remove the NMP for 4 hours at 250°F (121°C) and cured for 16 hours at 450°F (232°C). Test specimens were machined from the cured slabs and then part of the individual test specimens were postcured at 450°F (232°C), 550°F (288°C), or 850°F (454°C). The compressive properties are given in Table 2.

The processing problems with the solvent method of coating the microbubbles with resin were not completely worked out. The solvent removal was a problem and the cure schedule should be optimized. The measured compressive strength and modulus were lower than required, but an increase in part density would increase the compressive properties.

NR-150 Polyimide

The NR-150 polyimides were developed by Du Pont primarily for laminates and adhesives. Several papers have been presented on

Table 2. Compressive Properties of Monsanto R-500 Amide-Imide Syntactic Foams Tested at 25°C.

			Ultimate		
Formulation	Postcure (°F)*	Density (g/cm^3)	Stress (psi)**	Strain (Percent)	Modulus (psi)
1	450	0.225	333	10.6	11500
1	550	0.218	315	10.6	9800
1	850	0.210	306	13.6	7500
2	450	0.264	448	4.3	22000
2	550	0.264	440	4.5	19900
2	850	0.262	417	3.5	15600
3	450	0.258	320	2.6	15000
3	550	0.261	470	5.9	10600
3	850	0.249	268	2.5	13200

*°C = (°F-32)/1.8
**Pa = psi x 6895
Formulation 1 R-500/B22A/NMP, 50/150/100 by weight
Formulation 2 R500/B35A/NMP, 50/150/100 by weight
Formulation 3 R500/B22A/NMP, 50/50/100 by weight

the processing and properties of laminates made from NR-150.[5,6] The resin is available as an A and B precursor with 45 percent by weight resin in N-methyl pyrrolidone. During the imidization reaction, the NR-150 forms a linear amorphous polymer with little crystallinity and no crosslinking. Therefore, the polymer is thermoplastic above its glass transition temperature and can be formed with the addition of pressure. A small amount of volatiles are evolved during the gelling stage at about 300°F (149°C). The resin is fully cured by a step-cure at 50°F (28°C) increments for 20 to 30 minutes up to 600°F (316°C).

Test slabs were prepared from three formulations of NR-150A and B35A glass microbubbles. The formulations made and tested were 40/50, 50/50, and 60/50 (by weight) blends of glass microbubble-resin solution. Since the solution is 45 percent resin, the weight ratios of the cured foam are 64/36, 69/31, and 73/27 for glass microbubble resin. After blending in a Hobart mixer, preforms 5.5 inch (140 mm) in diameter were cold pressed at room temperature and 100 psi (0.689 MPa). Solvent was removed by heating the preforms at 150°F (66°C) and 6 torr (800 Pa) for 16 hours plus 24 hours at 250°F (121°C) without vacuum. The polymer was gelled by heating at 350°F (176°C) for 2 hours. Slabs were then postcured (step cure-cam controlled) to either 650°F (343°C) or 850°F (454°C). After postcure, test specimens were machined from the slabs and compressive properties were measured at 75°F (24°C) and at 500°F (260°C). Test results for the NR-150A specimens are given in Table 3.

The compressive properties of the foams made from glass microbubbles and NR-150A are acceptable. No pressure was used to mold the sample after the polymer was cured. By applying pressure above the glass transition temperature (300°C), the foam should be stronger than foams prepared without a press cure.

Although the NR-150A foams were promising, the processing problems associated with a solvent system are much greater than with a dry powder system such as the Imidite material.

P-13N Polyimide

Ciba-Geigy Corporation markets two additional type polyimides, P-13N and P-105AC. Both materials were developed as a laminating resin in the solvent, dimethyl formamide (DMF). As the solvent solution, the resin is still in the polyamic-acid stage. With heat the polyamic-acid forms the imide linkage with the evolution of water. However, both P-13N and P-105AC are also available as fully imidized powders that cure by chain extension and cross-linking to form a thermally stable polymer without the liberation of volatile by-products.

A powdered resin that melts and flows prior to cure is attractive from a processing viewpoint since the solvent mixing and solvent removal prior to resin cure is eliminated. However, according to the literature available, the P-13N softens at approximately 270°C but it also gels rapidly and cures at that temperature.[7-10] This problem with premature cure limits the size part that can be molded. The P-105AC is formulated to have a lower melt temperature and a longer flow time. Although the P-105AC system was seriously considered, the Imidite system was performing well and limited time prevented a complete evaluation of the P-105AC material.

Polyimide 2080

Polyimide 2080 made by the Upjohn Company is the reaction product of an anhydride and an isocyanate. It is a thermoplastic, fully imidized polyimide with no chemical by-products evolved during processing.[11,12] The material is available as a powder molding compound or as a 20 percent solid solution in NMP for use as a laminating resin.

Table 3. Compressive Properties of Du Pont NR-150A Polyimide Syntactic Foams Cured for 2 Hours at 350°F (177°C)

Formulation B35A/NR-150 Weight Ratio	Post-cure (°F)*	Density (g/cm^3)	70°F Tests		500°F Tests	
			Strength (psi)**	Modulus (ksi)	Strength (psi)	Modulus (psi)
64/36	850	0.339	760	33.6	850	33.8
64/36	650	0.369	1380	41.6	1060	25.5
64/31	850	0.307	750	50.0	710	47.2
64/31	650	0.327	1080	34.5	1020	33.3
73/27	850	0.301	633	28.8	669	48.9
73/27	650	0.324	923	45.5	721	31.0

*°C = (°F-32)/1.8
**Pa = psi x 6895

Several moldings were made with the 2080 powder without glass microbubble fillers. Because the resin is fully imidized, the cure consists of heating the resin above its glass transition temperature (310°C) and compressing it into a solid piece. The degree of flow is evidently low since greater than 1000 psi (6.89 MPa) are required to form an acceptable part. The unfilled 2080 powder test specimens molded at 560°F (293°C) to 670°F (354°C) with pressures of 1000 psi (6.89 MPa) to 10,000 psi (68.9 MPa) all had compressive strengths, at 2 percent offset, of about 30,000 psi (207 MPa) and moduli of 60,000 psi (4.14 GPa). The unfilled powder is a tough, high strength powder.

Although the 2080 powder by itself could be easily molded, blends of 2080 and glass microbubbles could not be successfully molded. The 2080 does not actually melt but rather softens; therefore, temperature alone was not sufficient to fuse the 2080 and encase the glass. Pressures of 1000 psi (6.89 MPa) were required to form the powder and at this pressure the glass microbubbles are crushed forming a high density part.

Since blends of the 2080 polyimide and glass microbubbles could not be molded by heat and pressure only, foams were prepared by a resin solution method. The glass microbubbles were blended with a 20 percent resin solution of 2080 in NMP. In this way the microbubbles are coated with resin and are bonded to each other. After the solvent is removed, a low density porous foam is formed.

A 20 percent solids solution of 2080 in NMP is easy to prepare at room temperature, but solutions with 25 to 30 percent are viscous and limit the amount of glass microbubbles that can be incorporated. A Hobart type mixer was used to blend the 2080 solution and glass microbubbles. The bubbles wet easily and a homogeneous mix is quickly obtained. Problems occurred in learning how to remove the solvent and to mold a shaped part. The primary molding methods evaluated were vacuum bag molding, cold preforming, and compression molding.

The vacuum bag molding investigation consisted of varying the temperature, time at temperature, and rate of temperature increase. All the moldings were made under 6 to 8 torr (800 to 1064 Pa) with a room temperature trap and a dry ice trap to collect the solvent removed. An efficient drying cycle was never really developed. The best method was the drying at a constant temperature of 250°F (121°C) for 16 to 24 hours. This evaluation was with samples 0.5 to 1.0 inch (12.7 to 25.4 mm) thick. Larger samples would require longer times.

The compression molding method was not thoroughly evaluated because the available molds and presses were not equipped to handle and remove solvents. Several moldings were made from a dry crumb type of material. The dry crumb was prepared from the liquid blend of glass microbubbles, polyimide, and NMP by sieving the material periodically during the solvent removal cycle. In this way irregularly shaped pieces of polyimide coated glass microbubbles were made. However, the moldings made from the dry crumb at 600°F (316°C) and 100 psi (0.689 MPa) did not fuse well and were friable. Small quantities of solvent (3 to 6 percent by weight) act as a plasticizer to lower the softening point and to increase the amount of flow. Although this method was not evaluated, the proper combination of solvent content, temperature, and pressure should yield a fused part.

The third molding method consisted of forming the shaped part from the glass microbubbles 2080, and solvent at room temperature with pressure only. The cohesive strength of the cold formed part is low and care is required in handling the preform. The drying or solvent removal depends upon the pressure, temperature, thickness, time, and geometry of the part. For flat slabs, cracking and curling was a problem. Expanded metal screens were used to prevent curling and still allow the volatiles to escape. For 0.5 inch (12.7 mm) thick parts, a drying time of 24 hours at 150°F (66°C) and 6 to 8 torr (800 to 1064 Pa) was required to remove 98 percent of the solvent. The remainder of the solvent is removed during the inert gas cure.

Compressive properties of two foam formulations made by the cold preforming method are given in Table 4. The cure temperature does not have a significant effect on the strength; the apparent increases in strength are due to the increase in density. The foams are remarkably strong when the amount of resin binder is considered. The volume percent resin in the 20/100 (resin/glass microbubbles by weight) formulation is only 3.2 percent with 68 percent glass microbubbles and 28.8 percent void space after solvent removal.

Another series of slabs was prepared with varying concentrations of glass microbubbles. The slabs were prepared by the cold preform method and after the solvent was removed, the slabs were postcured to 850°F (454°C). The test results are given in Table 5. Polyimide 2080 with glass microbubbles is a relatively strong, thermally stable foam. The compressive strengths were adequate for this application. The strengths could be improved by optimizing the resin concentration and by consolidating the foam at temperatures above the glass transition temperature to reduce the void content.

Although the thermoplastic polyimide and addition type polyimides are attractive from a standard compression molding viewpoint, the glass microbubbles required to make the foam complicates the

Table 4. Compressive Properties of Upjohn 2080 Polyimide Syntactic Foams With Different Cure Temperatures

Formulation* 2080/B35A Weight Ratio	Cure Temperature		Density (g/cm^3)	Compressive Properties				
				Strength		Strain at Yield (Percent)	Modulus	
	°F	°C		psi	MPa		ksi	MPa
20/100	500	260	0.278	637	4.39	4.15	26.2	180
20/100	600	315	0.277	686	4.73	5.10	26.1	180
20/100	700	371	0.278	742	5.12	4.40	29.5	203
20/100	800	426	0.291	911	6.28	3.17	37.3	257
20/120	500	260	0.267	611	4.21	3.60	23.8	164
20/120	600	315	0.261	626	4.32	3.60	23.3	161
20/120	700	371	0.270	724	4.99	3.00	27.1	187
20/120	800	426	0.272	708	4.89	4.10	33.5	231

*Foams were cold preformed from a blend of 20 percent 2080-NMP solution and B35A glass microbubbles. Preforms were dried for 24 hours at 150°F (66°C) and 6 to 8 torr (800 to 1064 Pa).

Table 5. Compressive Properties of Polyimide 2080/B35A Syntactic Foams

		Compressive Properties				
Formulation 2080/B35A Weight Ratio	Specimen Density (g/cm^3)	Strength		Strain at Yield		Modulus (MPa)
		psi	MPa	Percent	ksi	
15/85	0.266	500	3.45	1.98	33.3	229
20/80	0.272	583	4.02	1.74	43.6	300
25/75	0.289	583	4.02	1.50	49.1	338
30/70	0.311	678	4.67	1.21	59.6	411

processing. A solvent is required to coat the glass microbubbles and circumvent the need for high molding pressure. The solvent removal is a major problem even with thin slabs of 0.5 inch (12.7 mm) material. Thicker cross-section parts would require longer times to remove the solvent and special tooling to mold and hold the shaped parts during manufacture. For these reasons the powder type resins that melt and flow before curing were the only resins considered as candidate resins for this application.

Pyrolin 5081

Pyrolin 5081 is a condensation polyimide precursor made by Du Pont. The HTF60 foam developed by Sandia Albuquerque uses the 5081 resin as the binder for glass microbubbles.[1,2] The type of processing problems associated with the solvent removal are exemplified by the preparation of the HTF60 foam. The HTF60 foam has superior physical and thermal properties; but, as was mentioned in the PRIOR WORK section, the manufacturing process was difficult. Large parts were made but a cure cycle of 48 hours was required. During the cure the HTF60 parts had a weight loss of about 75 percent and a linear shrinkage of 15 percent. The planned work for this project included some effort to reduce the processing time required to prepare HTF60 parts. Preliminary tests were not successful and the foam was considered as an alternate material rather than a candidate material.

Preliminary Material Evaluation of High Thermal Conductivity Foams

As mentioned in the SCOPE AND PURPOSE section, the product or design requirements were changed during the term of this project.

Continued testing at LASL had shown that the storage life of the system could be significantly lengthened by increasing the thermal conductivity of the support part. These additional tests also indicated that the compressive strengths could be reduced and the heat resistance could be reduced.

The material specifications were changed:

Thermal conductivity to 9 x 10^{-4} cal/cm•s•°C (0.376 W/m•K),

Compressive strength to 700 psi (4.82 MPa) at 20°C,

Compressive modulus to 30,000 psi (207 MPa) at 20°C,

Density of 0.30 g/cm^3, and

Flyer Plate Test to survive 2000 taps.

These new requirements increased the types of resin that could be considered for this application. Since the glass microbubbles are excellent thermal insulators, the requirement for greater thermal conductivity forced the search for, and evaluation of, low density conductive fillers.

Although the heat resistance of the resin was not defined, a test was devised to qualitatively rank resin by measuring the gas evolved at 550°C with a time at temperature of 20 msec.[13] The measurements were made with a platinum ribbon pyrolysis probe attachment to a gas chromatograph. Samples of polyurethane, phenolic, epoxy, polyimide, and silicone were tested. No gas could be detected for any material at the 500°C, 20 msec level. Higher temperatures for longer periods of time did evolve some gas from the samples, but even the polyurethane exceeded the thermal resistance requirement.

Aluminum honeycomb with 0.25 inch (6.4 mm) hexagonal cells and 0.001-inch (0.025 mm) thick aluminum was selected as the method of increasing the thermal conductivity. By orienting the cells parallel to the axis of the part, the compressive strength of the part would not be altered. In this way the test samples could be made with the ribbon both parallel and perpendicular to the heat flow.

Six resins were selected for evaluation with the honeycomb. Three processing methods were used to fill the honeycomb and to prepare test samples. During the testing of the six resins with honeycomb, additional test data from LASL became available. These data showed that the discontinuity of the hexagonal cells was a problem and the honeycomb was not suitable for this application.

With the honeycomb unacceptable, other methods to increase the thermal conductivity were required. Some of the materials suggested were sintered metal parts, metal foam, open cell urethane foam, metal wool, metal powder, carbon fiber, carbon microspheres, and metal microspheres for fillers in an organic resin. Copper and nickel foams are commercially available from companies like Brunswick Corporation (Feltmetal Products) and Hogen Industries (Foam Metal). The reported thermal conductivities are excellent but the compressive strengths are too low at the required density of 0.35 g/cm^3. Open cell urethane foam was considered. With the open cell foam, heat would be transferred by convection from the hot to the cold side. The low compressive strength prevented continued evaluation of this material.

Metal microspheres are a logical choice for a low density, but thermally conductive filler. Bendix Kansas City has the capability for coating glass microbubbles with aluminum, but only small quantities can be made. Future work is planned to evaluate scale-up equipment and also to evaluate other metal coatings, such as copper, on glass microbubbles. Nickel microbubbles (called Solacels) have been made by Solar, Incorporated. These nickel microbubbles are expensive and were not evaluated. Silver coated glass microbubbles became available from Potters Industries toward the end of the work on this project and have been partially evaluated.

Thermalthane 4003

The rigid polyurethane foam, Thermalthane 4003, is one of the most thermally resistant urethane foams. The Thermalthane foams were developed by Bendix Kansas City about 12 years ago and have been well characterized.[13,14,15]

Aluminum honeycomb could easily be completely filled with the foam. Two 4 by 6 by 12 inch (102 by 152 by 305 mm) blocks were made at densities of 0.32 g/cm^3 and 0.38 g/cm^3. The cell direction and foam rise was through the 12 inch (305 mm) length. The measured properties are given in Table 6. The measured value of 13.5 x 10^{-4} cal/cm•s•°C (0.56 W/m•K) agrees well with the test value reported by LASL on a similar sample. At room temperature the compressive strength and modulus of the urethane filled honeycomb are adequate but at elevated temperature (200°C) the strength and modulus are drastically reduced.

There were no real problems with filling the honeycomb with the urethane foam. A production process could be developed to build the required parts. The elevated temperature properties of the foam itself would be the major problem.

Table 6. Properties of Thermalthane 4003 With Aluminum Honeycomb

	Test Direction			
Property	Perpendicular	Parallel	Perpendicular	Parallel
Density (g/cm^3)	0.32	0.32	0.38	0.38
Thermal Conductivity				
(cal/cm•s•°C)	13.5 x 10^{-4}			
(W/m•K)	(0.56)			
Compressive Strength				
20°C (psi) (MPa)	620 (4.27)	680 (4.69)	940 (6.48)	1130 (7.79)
200°C (psi) (MPa)	85 (0.58)	98 (0.68)	79 (0.54)	92 (0.63)
Compressive Modulus				
20°C (psi) (MPa)	12,500 (86.2)	11,400 (78.6)	27,800 (192)	41,800 (288)
200°C (psi) (MPa)	1400 (9.65)	2300 (15.8)	870 (6.00)	1600 (11.0)

In addition to the honeycomb as filler to increase the thermal conductivity, graphite fiber and aluminum powder were blended with the two urethane components and foamed. The graphite fiber was Thornel yarn made by Union Carbide (WYE 130.5, PVA finish, 48.9 x 10^6 psi (337 GPa) modulus, lot 04228TIE) and the aluminum powder was a 20 mesh material from Fisher Scientific Company (Number A547).

Samples of urethane/fiber were prepared at 96/2 and 95/5 weight ratios and a density of 0.30 g/cm^3. For both fiber concentrations the compressive strength was about 650 psi (4.48 MPa) at 20°C and the thermal conductivity was 3.2 x 10^{-4} cal/cm•s•°C (0.134 W/m•K). By increasing the density, the compressive strength could be increased to greater than the minimum requirement of 700 psi (4.82 MPa). However, the thermal conductivity is too low and the viscosity of the mixture limits the amount of fiber that can be added to the urethane to about 5 percent by weight.

Similar results were obtained with the blend of urethane and aluminum powder. The urethane foam is an excellent thermal insulator. Since the amount of thermally conductive filler is limited by the processing (viscosity) of the foam, only small volumes of filler can be incorporated into the foam composite. The filler particles are coated with foam and the resulting thermal conductivity is low.

Epoxy DEN 438

The epoxy resin selected was DEN 438, a high temperature novolac resin made by the Dow Chemical Company, cured with nadic methyl anhydride and DMP 30 as an accelerator. As discussed above, the urethane foam test blocks were made by a foam-in-place technique. The honeycomb parts with epoxy resin were made by another molding technique. By this second method, the glass microbubbles were packed into the honeycomb and held in place by forcing air (pulling a vacuum) through the bubbles and honeycomb. With the vacuum still applied an acetone/catalyzed resin solution was poured over the bubbles. In this way, the bubbles were closely packed and the resin filled the spaces between the bubbles and bonded the honeycomb and GMB together. The resin content and density were controlled by the amount of solvent used with the resin.

A summary of the test results and formulations used is given in Table 7. Thermal conductivity was not actually measured for the epoxy glass microbubbles/honeycomb composites. Since the aluminum honeycomb has a thermal conductivity an order of magnitude better than the epoxy/microbubbles and the polyurethane, the overall thermal conductivity should not be greatly affected by the type of resin and filler used. The compressive strengths and densities are well within the target values.

Table 7. Properties of Honeycomb/Epoxy Composites

Test Blocks*	Specific Gravity	Compressive Strength (20°C)	Compressive Strength (200°C)	Resin Content (Weight/Percent)
1**	0.39	1120		38
2	0.425	1500		48
3	0.50	2050		58
4	0.40	1050		50
5***	0.39		1360	47
6	0.40		1400	47
7	0.25		150	7
8	0.34	1050	1000	36
9	0.31	800	950	28

*B35D glass microbubbles were used in each formulation. Acetone was used as the solvent.

**Formulations 1 through 4 were 100 p/wt DEN-438, 90 p/wt nadic methyl anhydride, 1 p/wt DMP-30, and then cure 1 to 16 hours at 200° to 250°F (93° to 121°C) plus 6 hours at 350°F (176°C).

***Formulations 5 through 9 were 100 p/wt DEN-438, 90 p/wt nadic methyl anhydride, 1.5 DMP-30, and then cure for 2 hours at 250°F (121°C) plus 16 hours at 450°F (232°C).

Only the glass microbubble with honeycomb was evaluated with the epoxy resin. This technique developed for the epoxy/solvent system could be used with silver coated microbubbles, but additional solvent handling and vacuum equipment would be required.

H-Resin

The H-resin is a proprietary polyphenylene resin made by Hercules, Incorporated. The HA43, low viscosity, grade was selected for evaluation. The H-resin melts at about 90°C and cures at 150°C by an addition type reaction without volatile by-products.[16,17]

The initial tests with the honeycomb were made by first blending the H-resin powder with glass microbubbles and then adding the blend to the honeycomb. The resin/microbubbles were compacted in the honeycomb cells by vibration on a shaker table. The parts were fused and cured by either heating the blend to the resin melt temperature and then applying pressure or by first applying a low pressure and then heating through the resin melt temperature. Parts were not successfully made by either technique. Even with primers for the aluminum, the H-resin did not bond to the aluminium.

Another series of test specimens were prepared using a vacuum bag molding technique with H-resin and carbon microspheres. The resin concentration was varied from 40 percent by weight to 50 percent. The compressive strengths were lower than expected. At 0.38 g/cm^3 the yield strength at 20°C was 720 psi (4.96 MPa) and 520 psi (3.58 MPa) at 200°C. At the target density of 0.30 g/cm^3 the yield strength was only 480 psi (3.31 MPa) at 20°C and 450 psi (3.10 MPa) at 200°C. Although the thermal resistance or strength retention at elevated temperature is acceptable, the low strengths prevent the use of H-resin.

Plyophen 24-655

The phenolic resin evaluated was Plyophen 24-655 made by Reichhold Chemicals, Incorporated. This resin is a powdered one-step phenolic that melts at 150° to 190°F (66° to 88°C) and cures rapidly at near 300°F (149°C). The phenolic resin with honeycomb was molded by the same process as the H-resin. That is, the resin and microbubbles were first blended, poured into the honeycomb cells, and compacted by vibration. The adhesion of the phenolic to the honeycomb was marginal at best. To improve adhesion, several methods of cleaning the honeycomb and primers for the honeycomb were evaluated. Neither the special cleaning nor the primers improved the adhesion.

Foams were made with B18A glass microbubbles and carbon microspheres. The foams were compression molded with a melt temperature of 250°F (121°C) and a cure of 300°F (149°C). With the glass microbubbles, the room temperature compressive strength of the foam was 600 psi (4.14 MPa) at 0.25 g/cm^3 and carbon microspheres had a compressive strength of about 500 psi (3.79 MPa) at 0.32 g/cm^3. Although the compressive strength was lower than desired, the ease of processing and cost of the phenolic resin made the Plyophen 24-655 a potential candidate material. One hollow cylinder part was molded using production equipment from a 50/50/5 blend of phenolic resin/carbon microspheres/graphite fiber to show that production type parts be made.

Kerimid 601 Polyimide

The polyimide tested was Kerimid 601 made by Rhodia Incorporated. The Kerimid 601 is a fully imidized material that cures by an addition reaction without the evolution of volatiles.[18,19] Solvent solutions of Kerimid 601 are used as high temperature adhesives, but the resin would not bond to the aluminum honeycomb. A group of slabs were molded from blends of the Kerimid 601 and glass microbubbles. The strengths ranged from 650 psi (4.48 MPa) at 0.22 g/cm^3 to 1100 psi (7.58 MPa) at 0.28 g/cm^3. Based on these preliminary tests, the Kerimid 601 was selected for continued evaluation with carbon microspheres as a filler. The continued evaluation is discussed in the section of Candidate Materials.

DC2106 Silicone

Dow Corning 2106 silicone resin was used for these tests. The DC2106 resin is a solvent solution of 60 percent (weight) resin in toluene and cures by the addition of a catalyst. Three processing techniques and three cure schedules were evaluated. The silicone bonds well to the glass microbubbles, but adhesion to the aluminum honeycomb was marginal. The solvent removal was a serious problem and the resin was not considered for evaluation with other thermally conductive fillers.

Polybenzimidazole

Whittaker Corporation prepared five foam blocks from combinations of glass microbubbles, carbon microspheres, and graphite fibers with their polybenzimidazole (PBI) resin. The block compositions as well as thermal conductivity and compressive properties are given in Table 8.

The thermal conductivity was measured by the cut-bar method with a vacuum setup. The test values are about 30 percent higher than would be obtained by the more accurate guarded hot plate method. Although the reported values are high the relative relationships are valid. These data indicate that by increasing the amount of graphite fiber in the glass microbubbles the thermal conductivity will be significantly increased. However, the density is also increased. Carbon microspheres in place of glass microbubbles in the formulation increase the thermal conductivity at the expense of compressive strength.

Overall the thermal conductivity and compressive properties of the PBI foams are more than adequate. These foams would be definite candidates except that the availability is a potential problem.

Candidate Materials

Imidite X386

Imidite X386, made by the Whittaker Corporation, is a blend of glass microbubbles and a polybenzimidazole resin. The resin is a condensation prepolymer of an aromatic amine and a phenylester

Table 8. Properties of Polybenzimidazole Syntactic Foams

Formulation PBI/Fiber/Bubbles Weight Percent	Specimen Density (g/cm^3)	Compressive Properties at 200°C Strength psi	MPa	Modulus ksi	GPa	Thermal Conductivity cal/cm•s•°C	W/m•K
28/10/62*	0.313	1650	11.4	146	1.01	4.9×10^{-4}	0.205
24/37.2/38.8*	0.419	2220	15.3	204	1.41	7.7×10^{-4}	0.322
28.2/43.6/28.2**	0.335	800	5.51	111	0.76	9.5×10^{-4}	0.397
40/0/60***	0.309	790	4.45	76	0.52	7.0×10^{-4}	0.293
24.6/38.3/37.1***	0.400	1300	8.96	115	0.79	12.8×10^{-4}	0.535

*B35D Glass Microbubbles
**B22A Glass Microbubbles
***Carbon Microspheres

with phenol and water evolved during the cure. As it cures, the Imidite goes from a free flowing powder, through a soft moldable stage, to a rigid cross-linked solid.[20]

Molding Techniques

The three methods of molding that have been evaluated are a vacuum bag molding technique, a compression molding technique, and a compaction at constant pressure molding technique.

The vacuum bag technique was developed for the original Imidite work.[3,4] The same tooling and molding procedure were used for this work. Basically, the procedure consists of forming the material in a loose fitting frame and plunger mold. A flat plate is used as the mold base. The plate, frame, material, and plunger are fitted into a vacuum bag. Figure 1 shows the arrangement of the mold and material. A vacuum of 5 to 10 torr (666 to 1330 Pa) removes volatiles as they are evolved and supplies a constant pressure on the powder. As the powder heats to a softening range, the pressure of the bag on the plunger compacts the powder. The vacuum bag cycle is a step cure to 600°F (316°C) in about 7 hours. The actual cycle is 30 minutes at 250°F (121°C), 40 minutes at 300°F (149°C), 60 minutes at 350°F (177°C), 60 minutes at 400°F (204°C), 60 minutes at 450°F (232°C), 60 minutes at 500°F (260°C), 60 minutes at 550°F (288°C) and 30 minutes at 600°F (316°C).

After the initial vacuum cure, the Imidite is postcured in a nitrogen flushed retort with a cam controlled step cure to 850°F (454°C) in about 5.5 hours. The actual cycle is 120 minutes from 70° to 600°F (21° to 316°C), 60 minutes from 600° to 700°F (316° to 371°C), 20 minutes at 700°C (371°C), 60 minutes from 700° to 800°F (371° to 427°C), 20 minutes at 800°F (472°C), and 30 minutes from 800 to 850°F (427° to 454°C). The postcured material is cooled in the oven to below 300°F (149°C) before being removed from the retort.

Compression Molding Technique

The second molding technique is conventional compression molding. A sketch of the charged compression mold is shown in Figure 2. In this method, a specific amount of material is charged to the mold cavity that has been preheated to 300°F (149°C) and sufficient pressure is applied to close the mold. After a cure of 2 hours at 300°F the slabs are removed from the hot mold and postcured under nitrogen to 850°F (454°C) using the standard cam controlled cycle used for the vacuum bag technique.

Modified Compression Molding Technique

The third method uses the same type of mold as shown in Figure 2. This method uses a type of compression molding with the Imidite

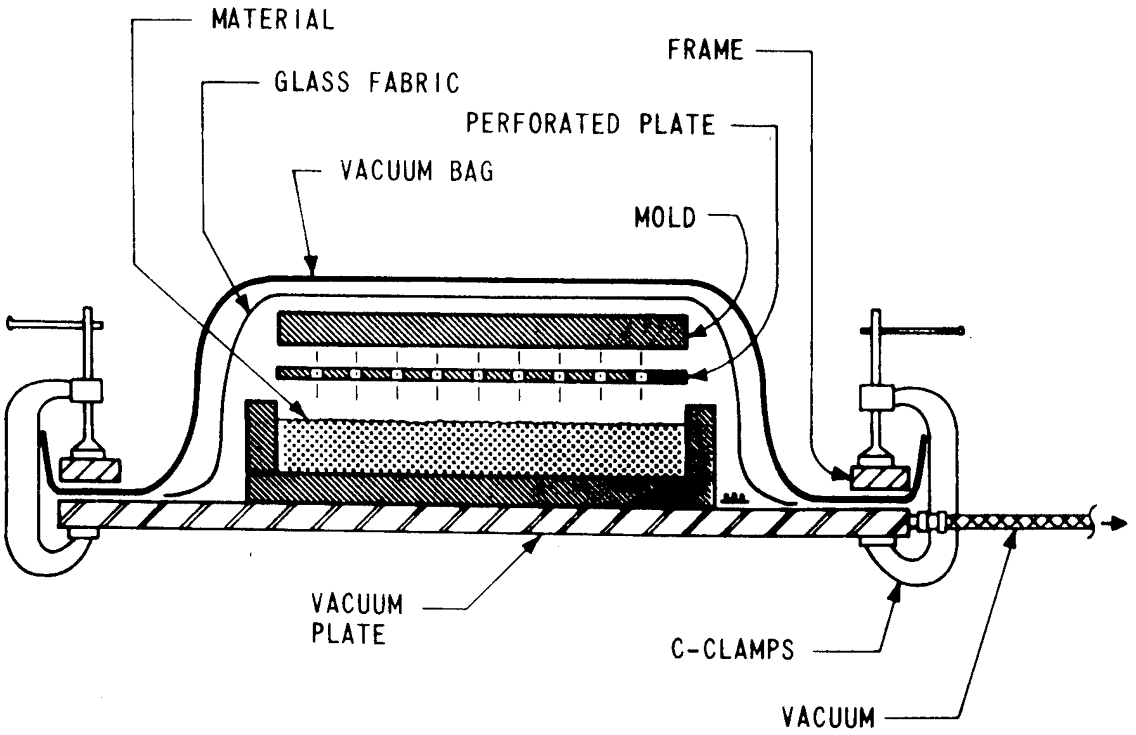


Figure 1. Vacuum Plate Assembly and Mold

carrying all the load at relatively low pressures of 50 to 100 psi (345 to 689 kPa). The mold punch does not make contact with the chase; therefore, a constant pressure is applied to the material during heat up and initial cure.

The vacuum bag method was used to mold the test specimens for the material variation study and the cure cycle study. The compression molding and compaction methods were used to mold the specimens with varying densities.

Material Properties

Six lots of Imidite X386 were available for testing. Samples of uncured powder from each lot were tested to determine possible lot acceptance tests for material specification. Samples of each lot were vacuum bag molded with the 600°F (316°C) initial cure and the 850°F (454°C) postcure, and then tested for mechanical and thermal properties.

Imidite X386 is a condensation prepolymer of an aromatic amine and a phenylester. A batch of prepolymer is prepared by stopping the condensation reaction before it goes to completion, causing

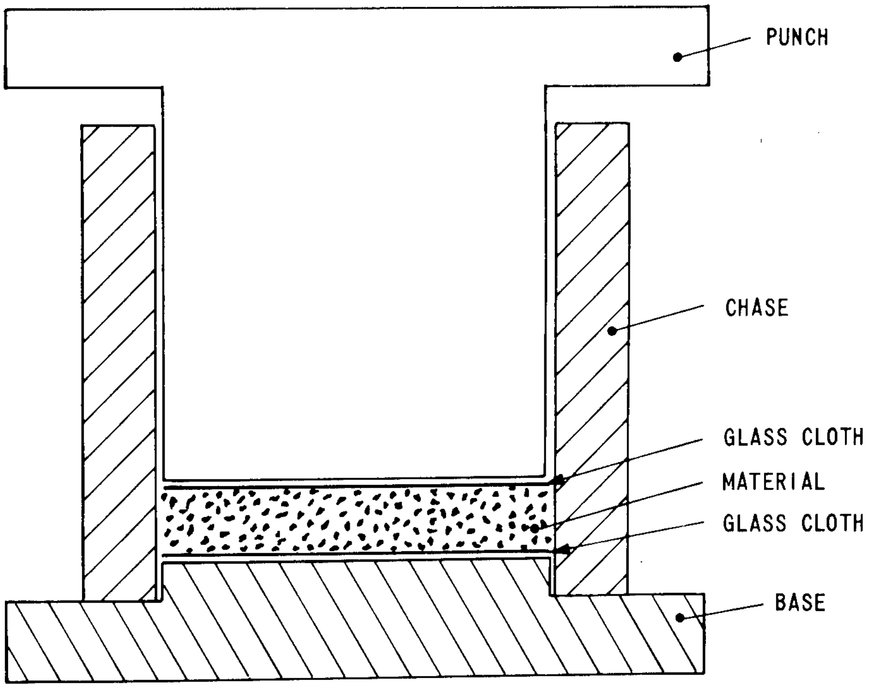


Figure 2. Compression Mold With Material

the properties of the prepolymer to vary from batch to batch. Some properties tested were color, volatiles, resin content, particle size distribution, infrared spectrum, weight loss, and melting range. These measured properties are listed in Table 9 and discussed below.

The Imidite powder changes from a yellow tan color to a dark brown after being exposed to light. A test was developed by Whittaker to measure the color.[4] Basically the procedure compares the absorbance of an acetone extract of Imidite at 435 nm to the absorbance at 343 nm. Color is not a controlling property of Imidite. Lots 311-51C and 311-51D are from the same batch of prepolymer, but the difference in color is as great between them as between the other lots. Plans are to measure the color index after 6 months and compare changes in mechanical properties to changes in color. There is no evidence that darker Imidite has different properties.

The volatile content was measured by two methods. By the first method, one gram of Imidite powder was heated for one hour at 800°F (427°C) under nitrogen in a crucible. The second method was an isothermal thermogravimetric analysis (TGA) at 800°F (427°C). The isothermal TGA was run for one hour, but the total loss occurred in the first 3 minutes. The two methods provided similar results and either could be used for lot acceptance.

Table 9. Properties of Uncured Imidite X386

	Lot Number					
Test	48	51A	51B	51C	51D	52A
Color Index	0.399	0.314	0.370	0.353	0.388	0.353
Resin Content (Percent)						
Crucible*	46.7	46.8	47.1	47.4	47.4	47.3
TGA	42.8		45.0			46.8
Volatiles (Percent)						
Crucible**	14.5	14.0	14.6	15.2	14.8	14.8
Isothermal TGA**	14.2	14.0	14.4	14.5	15.0	15.0
Sieve Analysis (Percent Retained)						
48 Mesh	0.2	0.2	0.2	0.5	0.5	0
80 Mesh	0.2	2.0	6.4	5.0	2.0	2.0
140 Mesh	6.0	6.4	11.2	10.4	11.2	5.6
200 Mesh	48.4	53.2	40.4	43.2	46.0	47.6
270 Mesh	45.2	38.2	41.8	40.9	37.1	39.2
Pan	0	0	0	0	3.2	5.6
Air Degradation Temperature (°F) (°C)	969 (521)		964 (518)			954 (512)
Initial Melting (°F) (°C)	257 (125)	257 (125)	243 (117)	243 (117)	243 (117)	243 (117)

*24 Hours at 1150°F (621°C).
**1 Hour at 800°F (427°C).

The resin content was also measured by two methods. First, the material and crucible from the volatile test were reheated to 1150°F (621°C) and held for 24 hours in air to burn off the resin. The TGA in air shows a thermal decomposition temperature of about 521°C (969°F) and a resin content of 42.8 percent. The crucible method is probably more accurate since the weights can be measured more accurately than the values can be read from the TGA trace.

A sieve analysis shows that 80 to 90 percent of the particles are between 50 and 100 μm. The microbubbles' particle size distribution was not measured but the manufacturer reports the size to be between 30 and 125 μm. The prepolymer is evidently ground and sized to about 75 μm.

With over 50 percent by weight of the Imidite X386 being glass microbubbles, the infrared spectra for all six lots are identical. Infrared analysis is not an acceptable method of distinguishing between lots of Imidite X386.

A capillary tube was used to measure the melting range. The initial melting point could be observed but the microbubble filler masked the final melting temperature. The initial melting temperature is listed in Table 9.

A test slab was molded from each lot of material using the vacuum bag technique with the stepcure to 600°F (316°C) and postcure to 850°F (454°C). Some physical properties of the slabs are listed in Table 10.

The weight losses of the six lots of Imidite were similar. Lot 311-51D does not seem to fit the other data but the prepolymer for 51D is the same as 311-51C. A possible explanation is the loss of material during loading of the mold resulting in lower cure and postcure weights. Although there is no indication of prepolymer and microbubble separation, a higher resin content sample would have a higher weight loss. The shrinkage measurements were made with calipers at the same location on the slab after each cure. The shrinkage values ranged from a low of 0.91 percent to a high of 1.14 percent with an average value of about 1.0 percent.

The remainder of the tests on the six lots used 1.129-inch-diameter (288.88 mm) specimens machined from each disk. The compressive properties were measured at room temperature, 500°F (260°C), and 600°F (316°C). Five test specimens from each lot were tested at each temperature. A summary of the results is given in Table 10.

Table 10. Properties of Six Lots of Imidite X386

Property	Lot 311 -48	Lot 311 -51A	Lot 311 -51B	Lot 311 -51C	Lot 311 -51D	Lot 311 -52A
Weight Loss (Percent)	12.7	12.9	13.7	14.1	17.6	14.1
Linear Shrinkage (Percent)	0.94	1.14	0.91	1.06	1.06	0.91
Density (g/cm^3)	0.350	0.350	0.360	0.350	0.349	0.347
Compressive Strength						
at 70°F* (psi)**	2470	2010	1800	2000	1810	2230
at 500°F (psi)			1760	1840	1750	2040
at 600°F (psi)	2200	1930	1630	1790	1740	2050
Compressive Strain at Ultimate						
at 70°F* (Percent)	8.6	11.4	8.0	10.7	9.8	8.1
at 500°F (Percent)			8.3	11.6	8.5	9.1
at 600°F (Percent)	10.0	9.8	6.6	7.7	11.4	7.7
Compressive Modulus						
at 70°F* (ksi)**	78.4	59.2	62.9	64.2	50.5	80.9
at 500°F (ksi)			81.0	69.9	61.5	83.3
at 600°F (ksi)	87.8	71.4	72.0	59.2	55.7	84.6
Isothermal Weight Loss						
4 hrs. at 500°F* (Percent)				0.27		0.12
72 hrs. at 500°F (Percent)				0.31		0.12
4 hrs. at 600°F (Percent)				0.54		0.30
72 hrs. at 600°F (Percent)				1.00		1.06
Coefficient of Thermal Expansion at 260°C (μm/m•°C)	17.4		29.4			20.7
Thermal Conductivity						
at 20°C (BTU•In./Hr•°F•Ft^2)***	0.57					
at 250°C (BTU•In./Hr•°F•Ft^2)	0.67					
Heat Capacity						
at 25°C (Cal/g•°C)†	0.203		0.199			0.178
at 100°C (Cal/g•°C)	0.253		0.241			0.227
at 200°C (Cal/g•°C)	0.221		0.209			0.193
Glass Transition Temperature (°C)	>500	>500		>500		

*°C = (°F-32)/1.8

**Pa = psi x 6895

***W/m•K = (BTU•In./Hr•°F•Ft^2) x 0.144

†J/kg•K = (Cal/g•°C) x 4187

Only a few of the specimens had a yield point. Most of the specimens had an ultimate compressive strength at 8 to 10 percent strain. The strain values varied greatly from specimen to specimen. Each set of five specimens had standard deviation for the strain of from 2 to 3 percent. Although the strain values measured at the selected ultimate strength did vary widely, the strength values at 5, 10 and 20 percent strain were similar. This means that Imidite crushes without a change in applied load. Elevated temperatures did not change this behavior. The density of each set of five specimens varied from 0.341 g/cm^3 to 0.363 g/cm^3 with a standard deviation within a set of about 0.008 g/cm^3. With the ultimate strength values normalized to a density of 0.370 g/cm^3 the ultimate strength at room temperature ranged from 2000 psi (13.8 MPa) to 2700 psi (18.6 MPa) with the average being about 2600 psi (17.9 MPa). The standard deviation for each set ranged from 80 psi (552 kPa) to 180 psi (1240 kPa) regardless of the test temperature.

The modulus values for each set of specimens had large standard deviations. For a given lot of Imidite, the modului at 500° and 600°F (260° and 316°C) were within the expected range of values for the modulus measured at room temperature. Between lots of Imidite, the modulus values are significantly different.

Isothermal weight loss was measured at 500 and 600°F (260° and 316°C) on two lots of Imidite X386. Three of the 1.129-inch-diameter (28.88 mm) specimens from each lot were tested at each temperature. The 12 specimens were weighed, dried at 250°F (121°C) for 4 hours, and weighed again. After drying, three specimens from each lot were conditioned at 500° and 600°F for either 4 hours or 72 hours in air. The test results are given in Table 10. During the drying cycle, all 12 of the specimens lost between 1.6 and 1.8 percent of their original weight. Based on the dried weight, the six specimens conditioned at 500°F (121°C) lost an additional 0.1 to 0.3 percent. The weight loss occurred during the first 4 hours. The weight loss after 72 hours at temperature was essentially the same as after 4 hours. At the 600°F (316°C) temperature the specimens lost between 0.3 and 0.5 percent after 4 hours and up to 1.1 percent after 72 hours. These data indicate that in an oxygen atmosphere the Imidite is stable at 500°F (121°C) but begins to lose weight at 600°F (310°C).

The coefficient of thermal expansion reported in Table 10 was measured at -50° and 260°C. However, at 100° to 150°C the sample displayed a linear shrinkage as the absorbed water was driven off. By drying the sample prior to testing, the shrinkage was eliminated. The heat capacity showed a similar behavior. At 100°C the heat capacity is greater than at either higher or lower temperatures due to the heat of vaporization of water.

Effects of Cure Cycle

A series of five slabs was molded from Lot 311-48 using the vacuum bag method. The cure and postcure cycles were varied as follows: cure 1, 600°F (316°C) cam controlled vacuum cure with no postcure; cure 2, 600°F (316°C) cam controlled vacuum cure with 700°F (371°C) cam controlled inert gas postcure; cure 3, 600°F (316°C) cam controlled vacuum cure with 850°F (454°C) cam controlled inert gas postcure; cure 4, 320°F (160°C) cure for 4 hours in vacuum with 850°F (454°C) cam controlled inert gas postcure; and cure 5, 320°F (160°C) cure for 4 hours, no vacuum, with 850°F (454°C) cam controlled inert gas postcure.

The vacuum bag procedure was used to make the five slabs. No vacuum, and consequently no pressure, was applied to cure 5 so the density was lower than for the other four slabs. Test data for physical, mechanical, and thermal properties are given in Table 11.

The weight loss and shrinkage values are based on a slab molded at each condition. The density values are an average of 20 of the 1.129 inch (28.68 mm) specimens while the data for the compressive and tensile properties are an average of five specimens at each condition. The thermal properties were measured on only one sample from each cure condition.

The strain and modulus values for the compressive tests were calculated from the charts and a machine correction curve, but the tensile tests were set up with an extensiometer to measure strain directly. Each property measured shows that a postcure is required to develop higher strength and thermal stability. Reference to TGA curves in both air and nitrogen indicate the Imidite is thermally stable up to 1000°F (534°C) for short periods of time. Postcure temperatures as high as 950°F (510°C) should result in higher Imidite properties; however, 850°F was the maximum postcure temperature evaluated.

Effects of Density Variation

Many properties of a foam are functions of the density of the foam; however, the density of a molded slab is not constant, but varies from location to location in the slab. Therefore, the properties will vary within a slab. As mentioned above, the overall density of the slabs vacuum bag molded from the six lots had a range of 0.341 to 0.363 g/cm^3 with a standard deviation of 0.008 g/cm^3. This means that the density variation within a slab is as great as the variation between slabs.

In order to measure the effect of density on compressive properties, a series of slabs was molded in a 5-inch-diameter (127 mm) mold. Part of the slabs were made by the compression molding

Table 11. Properties of Imidiate X386 With Five Cure Cycles

Property		Cure 1	Cure 2	Cure 3	Cure 4	Cure 5
Weight Loss (Cure)	(Percent)	8.68	8.78	12.3	12.3	12.7
Shrinkage	(Percent)	0.15	0.23	1.01	0.85	1.08
Density	(g/cm^3)	0.355	0.352	0.356	0.350	0.317
Compressive Strength						
at 70°F*	(psi)**	1380	1480	2170	2000	1420
at 500°F	(psi)	1500	1320	2100	1900	1370
at 600°F	(psi)	1760	1770	2000	1850	1440
Compressive Strain at Ultimate						
at 70°F*	(Percent)	4.8	5.3	6.4	8.0	6.9
at 500°F	(Percent)	6.4	6.2	6.5	11.0	10.0
at 600°F	(Percent)	11.8	9.1	8.8	9.4	7.4
Compressive Modulus						
at 70°F*	(ksi)**	62.3	61.6	80.3	70.0	43.3
at 500°F	(ksi)	52.5	42.1	60.3	51.7	41.3
at 600°F	(ksi)	53.1	53.4	61.5	55.4	60.4
Tensile Strength						
at 70°F*	(psi)**	392	447	1175	1144	852
Tensile Strain at Failure						
at 70°F*	(Percent)	0.182	0.182	0.518	0.578	0.544
Tensile Modulus						
at 70°F*	(ksi)**	208	246	230	198	157
Glass Transition Temperature (°C)				>500		
Weight Loss in Air						
at 250°C	(Percent)	1.2	1.6	2.5	2.6	2.8
at 350°C	(Percent)	3.6	3.1	2.5	2.6	2.8
at 500°C	(Percent)	6.4	6.9	4.4	4.4	5.4

*°C = (°F -32)/1.8
**Pa = psi x 6895

technique and part were made by the compaction method with pressures of 25, 50, and 100 psi (172, 345, and 689 kPa) applied. After an initial cure of 2 hours at 320°F (160°C) followed by a cam controlled postcure to 850°F (454°C), five compressive test specimens were machined from each slab.

The compressive strength test results are given in Figure 3 and the compressive modulus results are given in Figure 4. A best fit prediction is shown as the solid line with the average experimental data scattered about the curve. The equation of the best fit curve shows the strength to be a function of the density to the 3.5 power. However, for normalizing the compressive test data, a linear approximation was used. Although the data for Figures 3 and 4 were obtained from compression molded slabs, the data for the vacuum bag molded slabs fit the equation within an experimental error.

Imidite X386 is a thermally stable, high strength foam that can be used to prepare high quality production type parts. It was selected as the material to mold structural parts.

As mentioned previously, testing at LASL indicated that a support part with higher thermal conductivity could improve the long term storage. The Imidite X386 was also evaluated with aluminum honeycomb as a method of improving the thermal conductivity. The Imidite bonded better to the aluminum than the other powdered resins evaluated, but the distribution within the honeycomb cells was still a problem.

Providing for a consistent supply of the polybenzimidazole was a potential problem. The 3-3' diaminobenzidine used to make the polybenzimidazole was obtained from a West German subsidary of the Aldrich Chemical Company. The tetramine (3-3' diaminobenzidine) is listed as a carcinogen by Aldrich and is similar to benzidine and dichlorobenzidine both of which are listed as carcinogens by OSHA. The company in West Germany decided that they no longer wanted to make the tetramine and discontinued its manufacture.

A literature search was made to learn more about methods of preparing the 3-3'-diaminobenzidine.[21] This research revealed that while the tetramine could be made, the capital equipment and processing costs would be high. Several chemical houses with existing processing equipment were contacted, but none were interested in making the tetramine.

Kerimid 601

Kerimid 601 polyimide resin is made by Rhodia Incorporated, a French company. This polyimide resin has been evaluated with carbon microspheres as a thermally conductive syntactic foam.

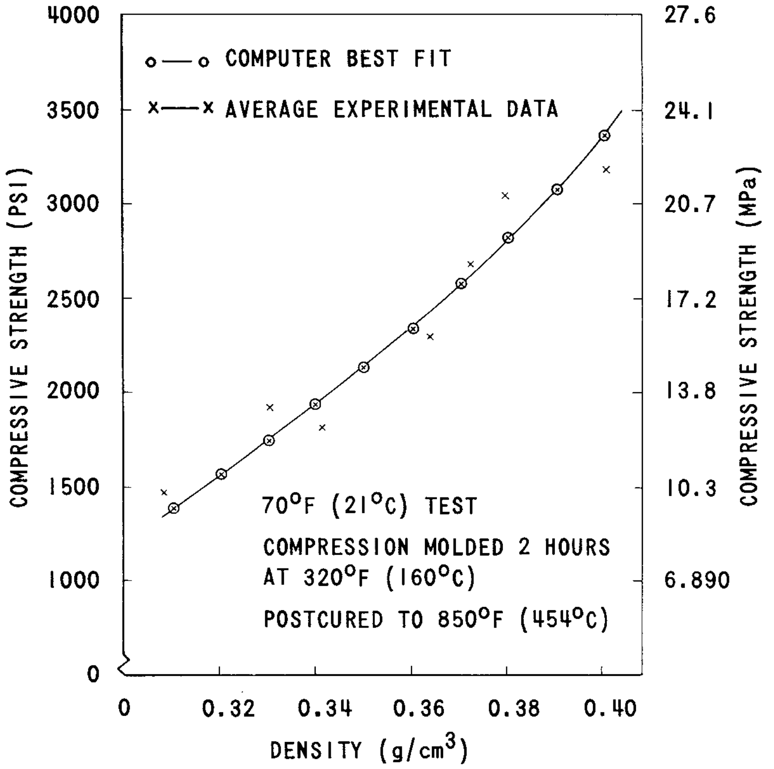


Figure 3. Effect of Density on Compressive Strength of Imidite X386

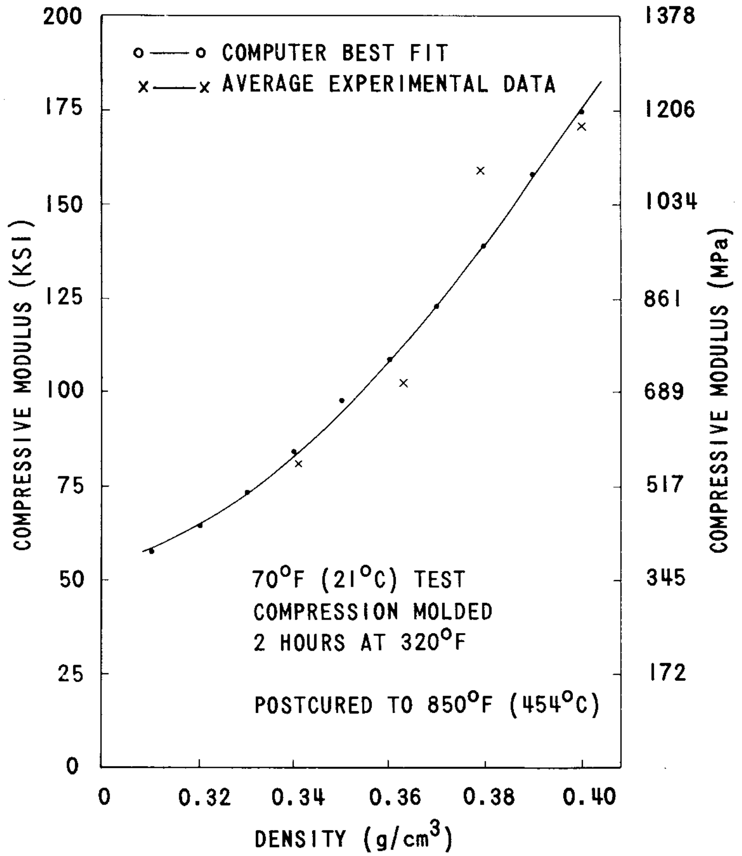


Figure 4. Effect of Density on Compressive Modulus of Imidite X386

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 as 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.

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.

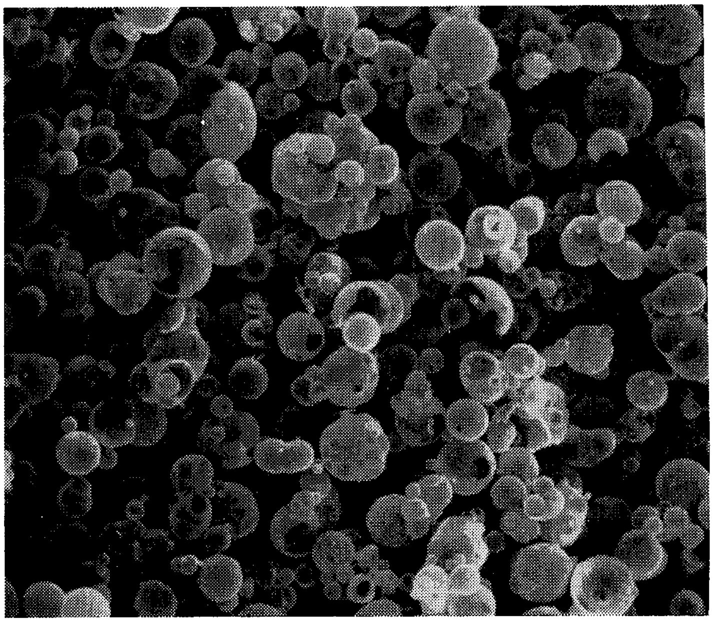
The preparation of the Rhodia 601 resin is protected by U.S. Patent 3,562,223. The resin is prepared from maleic anhydride and a diamine. This product is fully imidized when received from the vendor. During the final cure the bismaleimide reacts through the double bond with other bismaleimide molecules 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.

Microspheres

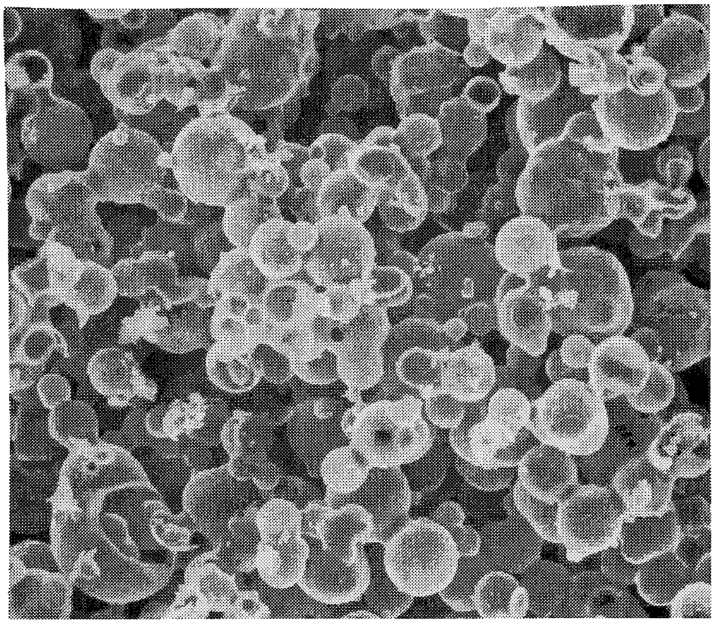
Microspheres made from carbon are available from two companies. Kreha Corporation of America, a U.S. subsidiary of a Japanese company, makes a carbon microsphere named Krecaspheres. In March 1974 the Krecaspheres were not available in the U.S. except in 100 gram samples. The availability at this time 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 the 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.

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 5. Since the spheres do not have a continuous



CARBO-SPHERES



CARBO-SPHERES WITH POLYIMIDE RESIN

Figure 5. Magnified Carbo-Spheres (300X)

surface, the test results have been inconsistent. Two of the 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 5 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 sphere 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 true density is a measure of the packing factor. By assuming a packing factor of 0.63, and using the tap densities 0.18 g/cm^3 and 0.21 g/cm^3, the true 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 microbubbles. For these glass microbubbles the ratio of tap density to true 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 true 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 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.

Thornel Mat (Grade VMA) made by Union Carbide Corporation, is composed of carbon or graphite filaments in a random-layered orientation. The individual fibers are from 1 to 3 inches (25 to 76 mm) long and are mechanically held to form a mat that is 0.4 inches (10 mm) thick and 22 inches (559 mm) wide.

Processes

This section is a description 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 recommended by the resin manufacturer does not seem to yield the best physical properties.

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.

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 spheres 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.

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 250°F (121°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

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.[14] 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 were 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 12 and 13.

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 were 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 14. 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 6 and 7.

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).

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

Table 12. Effect of Cure on Compressive Properties of Kerimid 601 Polyimide/Carbon Microsphere Syntactic Foam at 70°F (21°C)

Test Block	Melt (°F) After 1.5 Hrs.	Cure (°F) After 1.5 Hrs.	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
**Pa = psi x 6895

Table 13. Effect of Cure on Compressive Properties of Kerimid 601 Polyimide/Carbon Microsphere Syntactic Foam at 400°F (204°C)

Test Block	Melt (°F) After 1.5 Hrs.	Cure (°F) After 1.5 Hrs.	Post Cure		Compressive Properties at 400°F		
			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
**Pa = psi x 6895

Table 14. 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

that measures the heat flow and temperature change across a sample in a Du Pont 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 8 and 9, 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 9, 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.

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 15. 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

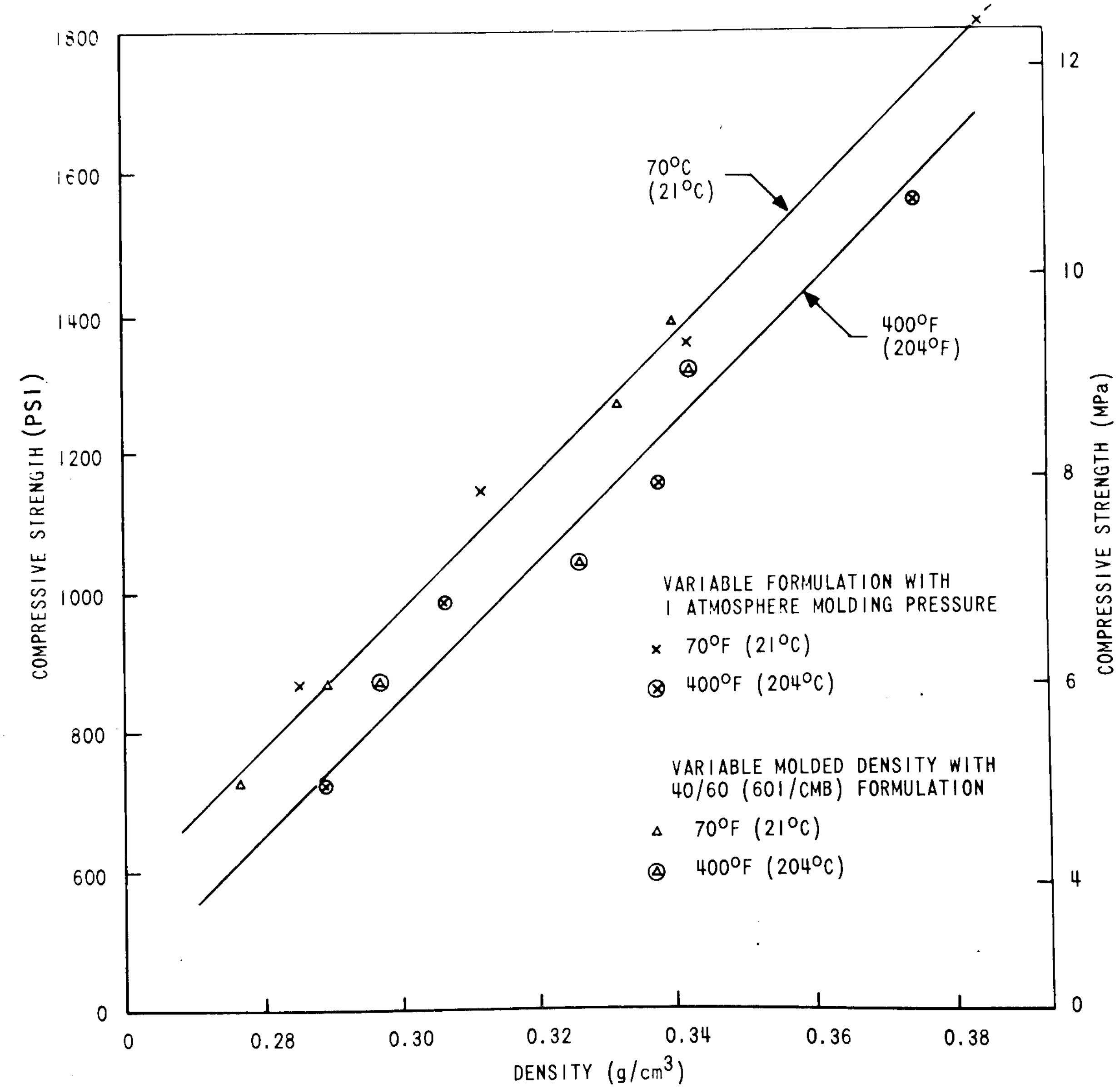


Figure 6. Effect of Density on Compressive Strength of Kerimid 601/Carbon Microsphere Foam

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.

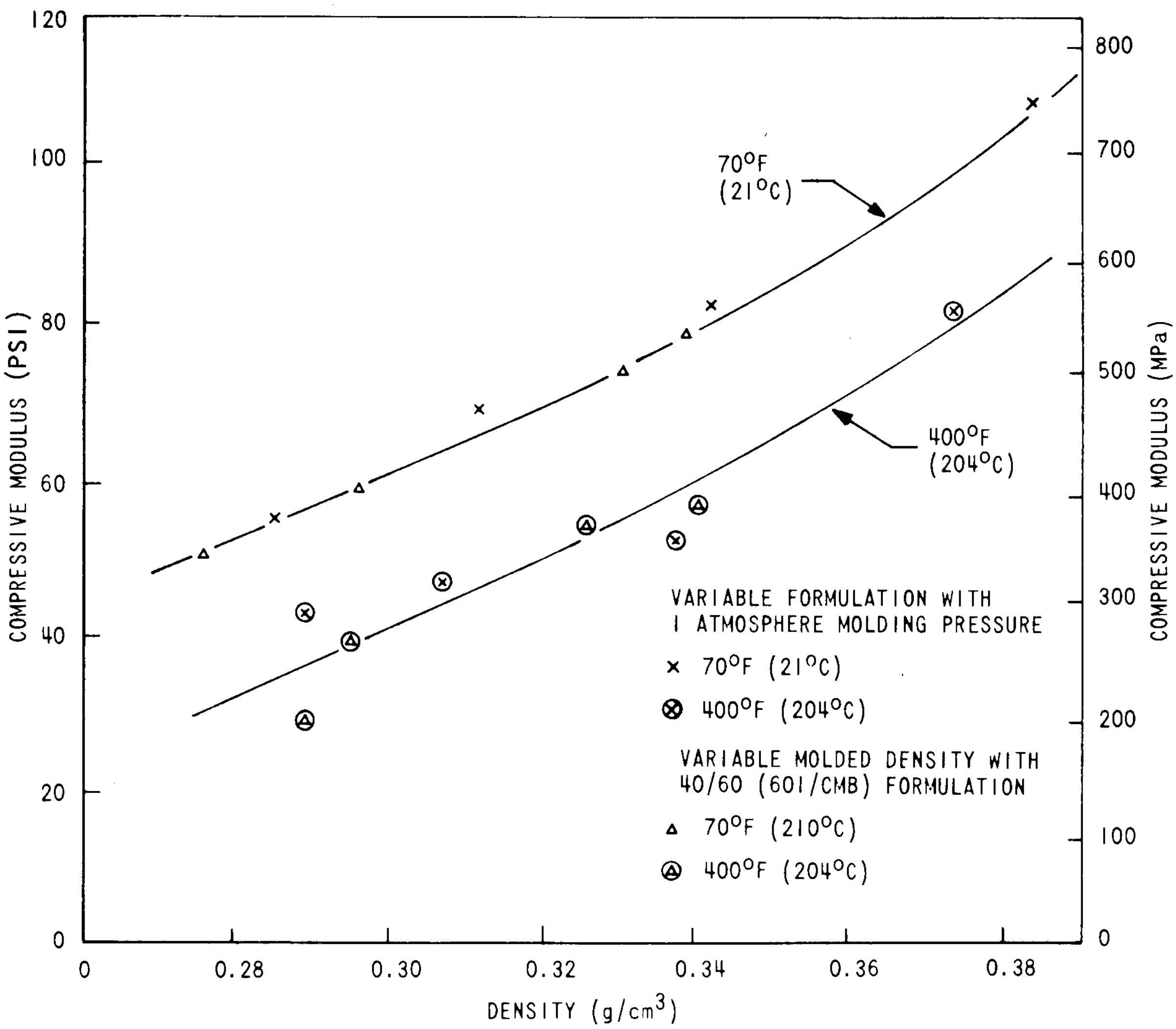


Figure 7. Effect of Density on Compressive Modulus of Kerimid 601/Carbon Microsphere Foam

Graphite fibers were added to the blend of the Kerimid 601 and carbon microspheres in an attempt to increase the thermal conductivity and to improve the handling properties. The 1 mm and 3 mm graphite fibers from Hercules, Incorporated could not be adequately separated to blend with the resin and CBS. Test blocks were molded with the 6 mm sized (Type ASMS) fiber, the 6 mm unsized (Type AS) fiber, and the chopped Thornel Mat.

Summaries of the test results of the foams made from the three types of fiber are given in Tables 16, 17, and 18.

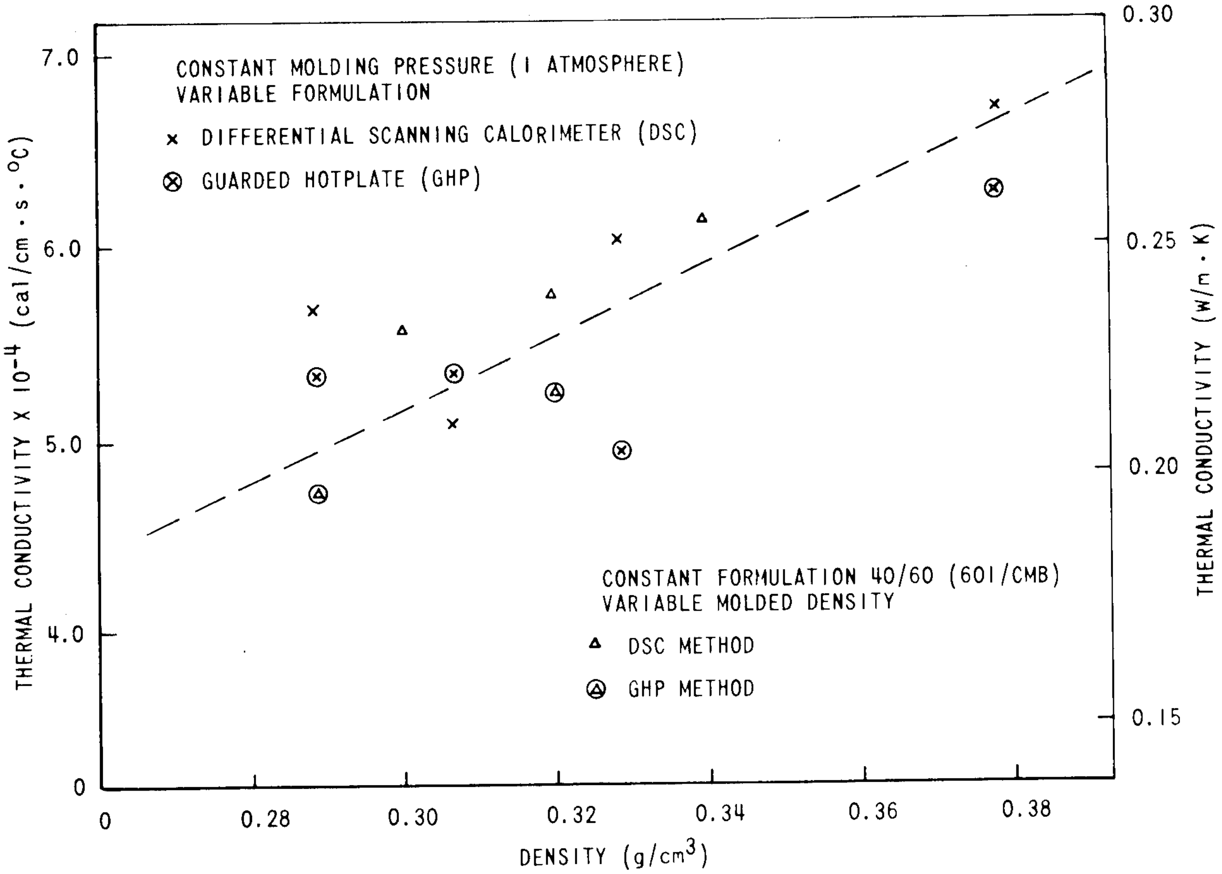


Figure 8. Effect of Density on Thermal Conductivity of Kerimid 601/Carbon Microsphere Foam

The compressive properties are not affected by the small volume of fibers either at room temperature or at elevated temperature. The density has more influence than the fiber concentration. However, of the three fibers evaluated, the sized fiber has a lower strength than the Thornel Mat or unsized fiber regardless of the density.

The fiber concentration does not affect the tensile strength, but the modulus does increase with increasing fiber concentration. The tensile strength may be more of a function of the fiber concentration and density than the data indicate. The tensile samples were very brittle and several were broken prior to testing. The small sample size and data scatter precludes an accurate prediction of tensile strength. However, the data indicate that the modulus is higher with fiber filled foams and that the strain at failure is less in foams with fiber than in foams without fiber.

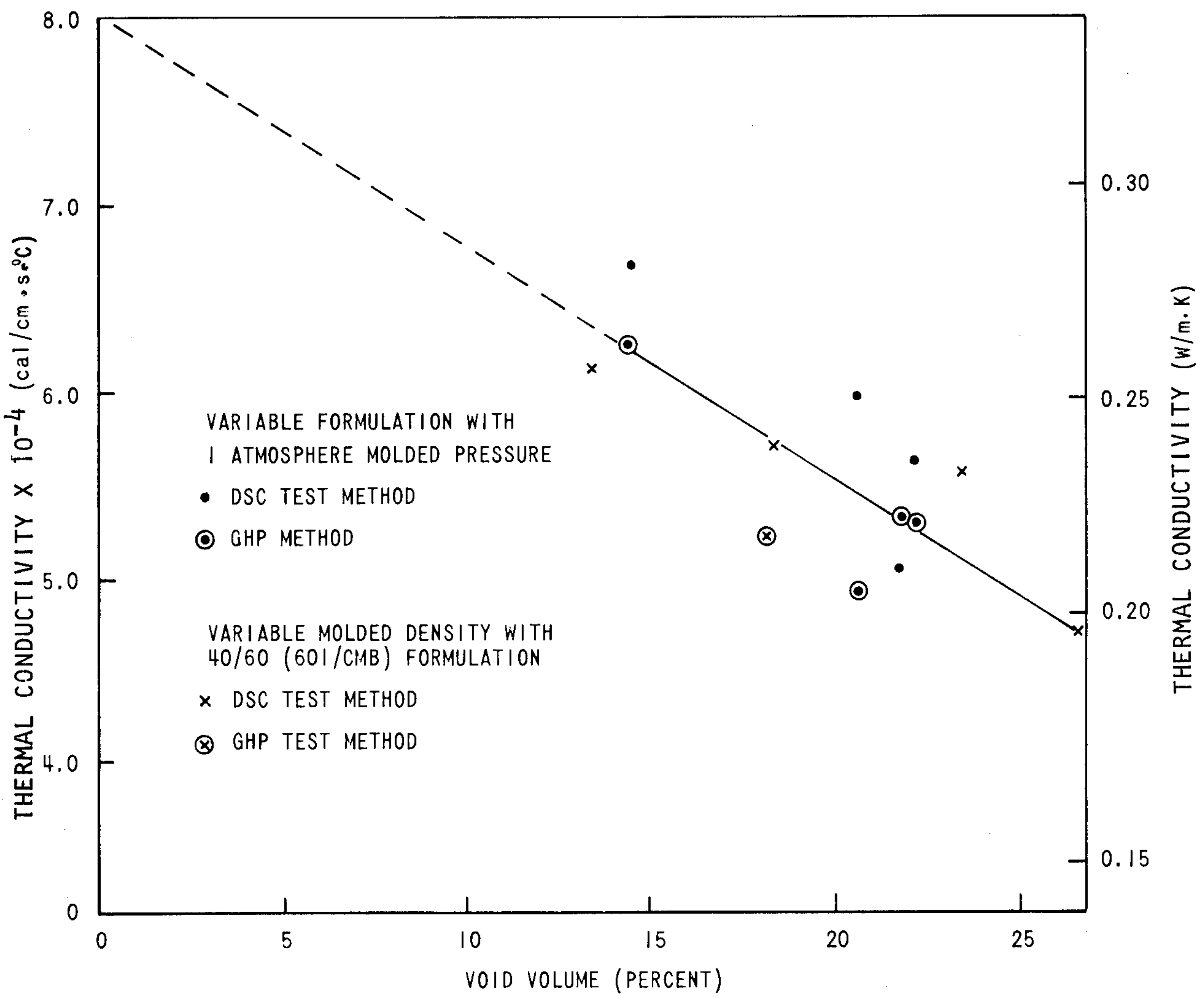


Figure 9. Thermal Conductivity as a Function of the Amount of Air in a Molded Block

The test values for flexural properties of the three types of fiber are inconsistent. The flexural strength seems to be a function of the fiber concentration, but as with the compressive and tensile properties, the increase in flexural strength may be due to density. The fibers in the foam change the type of flexural failure. Formulation made without fiber had a brittle type failure with the failure occurring at the proportional limit. The foams with fiber did not have a brittle type failure with the failure occurring at the proportional limit. The foams with fiber did not have a brittle failure, but rather had a yield 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.

Table 15. Properties of Foams Made From Blends of Graphite and Carbon Microspheres

Block	Formulation Ratio*	Density (g/cm^3)	Thermal Conductivity		Compressive Properties at 20°C	
			cal/cm•s•°C	W/m•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

**Pa = psi x 6895

Table 16. Properties of Foams Made With Type ASMS Graphite Fiber

	Formulation*					
Property	1	2	3	4	5	6
Density (g/cm^3)	0.297	0.298	0.311	0.286	0.323	0.344
Compressive Strength at 70°F** (psi)***	850	870	900	600	910	1230
Compressive Modulus at 70°F (psi)	59.6	80	76	39.9	69.8	60.5
Flexural Strength at 70°F (psi)	490	400	480	350	580	670
Flexural Strain at Failure (Percent)	2.41	2.4	2.3	3.4	2.9	3.1
Flexural Modulus at 70°F (ksi)	77.5	59.6	80	51.9	93.5	103.5
Tensile Strength at 70°F (psi)		250	190	150	190	215
Tensile Strain at Failure (Percent)		0.14	0.13	0.11	0.12	0.12
Tensile Modulus at 70°F (ksi)		93.3	77.3	83	92	118
Thermal Conductivity (W/m•K)	0.224	0.182			0.209	

*1. 601/CMS (40/60)
2. 601/CMS/Fiber (40/60/1)
3. 601/CMS/Fiber (40/60/3)
4. 601/CMS/Fiber (40/60/5)
5. 601/CMS/Fiber (40/60/5)
6. 601/CMS/Fiber (40/60/5)
**°C = (°F -32)/1.8
***Pa = psi x 6895

Table 17. Properties of Foams Made With Unsized Fiber

	Formulation*			
Property	1	2	3	4
Density (g/cm^3)	0.297	0.297	0.323	0.308
Compressive Strength at 70°F** (psi)***	850	945	1070	1020
Compressive Modulus at 70°F (psi)	59.6	37.3	46	36.9
Flexural Strength at 70°F (psi)	490	560	880	725
Flexural Strain at Failure (Percent)	2.4	0.7	1	0.9
Flexural Modulus at 70°F (ksi)	77.5	73.8	116	85.3
Tensile Strength at 70°F (psi)		300	295	220
Tensile Strain at Failure (Percent)		0.23	0.23	0.3
Tensile Modulus at 70°F (ksi)		113	108	98
Thermal Conductivity (W/m•K)	0.224			0.326

*1. 601/CMS (40/60)
2. 601/CMS/Fiber (40/60/5)
3. 601/CMS/Fiber (40/60/5)
4. 601/CMS/Fiber (40/60/5)
**°C = (°F -32)/1.8
***Pa = psi x 6895

Table 18. Properties of Foams Made With Thornel Mat Fiber

Property	Formulation*						
	1	2	3	4	5	6	7
Density (g/cm^3)	0.297	0.292	0.307	0.299	0.267	0.333	0.3
Compressive Strength at 70°F** (psi)***	850	770	1000	850	540	1200	674
Compressive Modulus at 70°F (psi)	59.6	61.1	73.2	85.5	46.6	113.6	50.3
Flexural Strength at 70°F (psi)	490	460	400	580	385	822	422
Flexural Strain at Failure (Percent)	2.4	2.7	3	2.8	3.1	2.7	0.85
Flexural Modulus at 70°F (ksi)	77.5	72.2	57.1	88.5	52.3	128.4	52.4
Tensile Strength at 70°F (psi)		300	300	290	180	320	
Tensile Strain at Failure (Percent)		0.3	0.3	0.27	0.27	0.23	
Tensile Modulus at 70°F (ksi)		93	98	104	60.5	149	
Thermal Conductivity (W/m•K)		0.224	0.226	0.251	0.259	0.226	0.293

*1. 601/CMS (40/60)
2. 601/CMS/Fiber (40/60/1)
3. 601/CMS/Fiber (40/60/3)
4. 601/CMS/Fiber (40/60/5)
5. 601/CMS/Fiber (40/60/5)
6. 601/CMS/Fiber (40/60/5)
7. 601/CMS/Fiber (40/60/5)
**°C = (°F -32)/1.8
***Pa = psi x 6895

The thermal conductivity is not significantly improved by the addition of the fibers. The thermal conductivity of the Thornel Mat samples increased slightly in a predictable manner both with density and concentration.

ACCOMPLISHMENTS

Two foam systems, one with low thermal conductivity and one with high thermal conductivity, were developed and the material properties were measured. The Imidite X386 foam (low thermal conductivity) has been shown to have superior thermal resistance and mechanical properties and can be molded to size to yield high quality parts. The support parts made from Imidite X386 met all the design requirements for low thermal conductivity material.

The need for a high thermal conductivity led to the development of the foam made from Kerimid 601/carbon microspheres/graphite fibers. Graphite microspheres, in place of carbon microspheres, are required to achieve the desired thermal conductivity of 9×10^{-4} cal/cm•sec•°C (0.376 W/m•K). Additional evaluation has shown that the thermal conductivity of foams made with only carbon microspheres is adequate and that the thermal conductivity requirement has been reduced to 5×10^{-4} cal/cm•sec•°C (0.20 W/m•K). All other properties of the thermally conductive foam exceed design goals at approximately 10 percent of the cost of Imidite X386. Other resins and fillers can be used as alternate choices for foam systems if they are needed.

FUTURE WORK

Silver coated glass microbubbles made by Potters Industries have been partially evaluated. The process developed by Potters for coating the microbubbles is still in the pilot plant stage and production quantities are not available. As the silver coated microbubbles become available, they will be evaluated with Kerimid 601 as an alternate for the carbon microsphere filler.

This syntactic foam part may be used as a desiccant to collect water vapor during long term storage. The effect of moisture on mechanical properties and dimensional stability as a function of temperature and relative humidity needs to be measured.

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Resins from the polyimide, polybenzimidazole polyamide-imide, phenolic, silicone, and urethane families were formulated with glass microbubbles and carbon microspheres to produce low density, high strength syntactic foams. The polyimide and polybenzimidazole foams were the most thermally stable, but even the urethane exceeded the design goals. Foams with high and low thermal conductivity were developed and their material properties were measured. The low conductivity was

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PLASTICS: Syntactic Foam

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