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SYNTACTIC FOAM FROM SILVER COATED MICROBUBBLES

Topical Report

H. M. McIlroy, Project Leader

Project Team:
R. B. Mayfield
G. L. Woodburn

Published February 1978

Prepared for the United States Department of Energy Under Contract Number EY-76-C-04-0613.

Bendix Kansas City Division

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Communications Services Bendix Kansas City Division

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Prepared by H. M. McIlroy, D/814

A low density syntactic foam made from a blend of a polyimide resin and silver coated glass microbubbles has been evaluated. Foams prepared from the silver coated glass microbubbles have more than twice the thermal conductivity of foams made from uncoated glass microbubbles, but the value is about 10 percent less than the measured thermal conductivity of carbon microbubble foams.

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SUMMARY

A syntactic foam made from a polyimide resin, carbon microbubbles, and graphite fibers is used to produce a support part. The carbon microbubbles were selected as the low density filler to achieve the high thermal conductivity required. Glass microbubbles (GMB) with a silver coating added to increase the thermal conductivity have been evaluated as an alternate filler for the syntactic foam.

Four types of GMB were coated with silver ranging from 4 to 25 percent by weight (pbw). Because of large differences in densities between the GMB and silver, the weight of the filler was significantly increased without changing the volume of the GMB. The silver coating is only 0.1 μm thick on the GMB with 25 pbw silver. Adding silver changes the density of the GMB, but does not alter other properties such as packing factor and size distribution of the GMB.

Preliminary testing of foams made from the four types of GMB with different amounts of silver indicated that B22A GMB (3M Company) with 25 pbw silver would be a good candidate filler as an alternate for the carbon microbubbles. Different formulations of resin and B22A GMB with 25 pbw silver were prepared to produce foams with densities ranging from 0.25 to 0.34 g/cm^3. At equivalent densities, the thermal conductivity and compressive properties of the foams made from silver coated GMB are lower than from foams made with carbon microbubbles. Nevertheless, the compressive strengths of the coated GMB foams are higher than the design requirement. The measured thermal conductivity is about 6 percent less than the design minimum at 0.3 g/cm^3. Modifications to the formulation could improve the thermal conductivity.

DISCUSSION

SCOPE AND PURPOSE

Carbon microbubbles are used with a polyimide binder and graphite fibers as a component of a high temperature, thermally conductive syntactic foam. Silver coated GMB have been considered as an alternate filler for the carbon microbubbles. This project is a test and evaluation program to determine if the silver coated GMB are an acceptable alternate for the carbon bubbles in this application by comparing processing methods, physical properties, and thermal properties. Since the carbon microbubbles are the primary material, this evaluation of silver coated GMB is only to show a capability and is not a complete evaluation. That is, full size production type parts were not fabricated.

PRIOR WORK

During the development of a thermally conductive foam system, several types of fillers were evaluated resulting in the selection of carbon microbubbles.[1,2] The silver coated GMB are a new product and were not available during the original evaluation.

ACTIVITY

Materials

The silver coated GMB for this evaluation were made by Potters Industries Incorporated using GMB made by the 3M Company. Potters normally markets solid glass microbubbles and has developed a process for coating their solid spheres with silver to improve the electrical conductivity. Four types of 3M Company GMB were coated by the Potters process for evaluation at Bendix. The properties of these GMB are given in Tables 1 and 2.

The coated GMB were B25B, B18A, B22A, and B40A types made by the 3M Company. All four types are a borosilicate glass. The B25B is a general purpose, low cost type of bubble while the other three types have an adhesion promoter added to the GMB and have many of the broken GMB removed during processing.

The amount of silver added to the GMB ranged from 4 to 25 pbw. As this evaluation progressed, the amount of silver was increased to improve the thermal conductivity of the foams made from the coated GMB. Even with 25 percent silver, the coating on the GMB was not complete as shown in Figure 1. These pictures also show that the coating is very thin. The theorical thickness is about 0.1 μm and Potters report about 0.03 μm as the normal thickness.

Table 1. Density Properties of Silver Coated and Standard GMB

		Particle Density			
Bubble (Type)	Silver (PBW)	Theory (g/cm^3)	True (g/cm^3)	Tap (g/cm^3)	Packing Factor
B25B	4	0.239	0.158	0.131	0.83
B25B	8	0.249	0.259	0.149	0.57
B25B			0.230	0.150	0.65
B18A	9	0.174	0.179	0.110	0.61
B18A	18	0.194	0.197	0.130	0.66
B18A			0.160	0.110	0.69
B22A	19	0.238	0.321	0.176	0.55
B22A	25	0.257	0.244	0.159	0.65
B22A			0.190	0.130	0.69
B40A	19	0.453	0.420	0.221	0.53
B40A			0.37	0.240	0.65

The true density (Table 1) is the average liquid displacement density of the individual bubbles. The tap density, measured using ASTM-D-3101, is a bulk density measurement that indicates how closely the GMB are packed and includes the volume of air between the individual bubbles. The ratio of the tap density to the true density is the packing factor (Table 1). The packing factor for equally-sized spheres in a random packing is about 0.63. Broken bubbles and small bubbles fit in the interstitial space and increase the packing factor. The theoretical density is based on an average true particle density which can vary by about ±10 percent. With this expected variation, the theoretical density compares well with the measured density.

The amount of sinkers was measured in water with a wetting agent. The silver coated GMB have a higher amount of broken GMB than the standard uncoated GMB. This difference could be due to the extra handling by Potters, but the difference is within an acceptable range.

The particle size distribution was measured using a Sharples Micromerograph. These data show that the coated and uncoated bubbles have similarly shaped distribution curves and approximately the same distribution.

Table 2. Particle Size Distribution of Silver Coated and Standard GMB

Bubble (Type)	Silver (PBW)	Particle Size Distribution in Percent by Weight Less Than 100 μm	Less Than 50 μm	Less Than 30 μm	Less Than 10 μm	Percent Sinkers
B25B	4	75	50	23	8	
B25B	8	87	64	30	2	
B25B						
B18A	9	72	24	9	0	2.6
B18A	18	82	27	12	0.5	4.1
B18A		54	10	3		3.8
B22A	19	73	26	10	1	2.0
B22A	25	94	70	34	2	3.8
B22A		88	21	6		2.0
B40A	19	92	78	58	5	2.0
B40A		93	20	6	1	0.7

Based on the data in Tables 1 and 2, coating the GMB with silver increases the weight of an individual bubble but does not alter properties such as packing factor, amount of broken bubbles, and the size of the GMB.

The resin (Kerimid 601) is an addition type polyimide made in France by Rhodia, Incorporated and protected by U.S. Patent 3,562,223. The resin has been fairly well characterized and a summary of physical and thermal properties are given in Table 3.[3,4,5] Graphite fibers made by Union Carbide Corporation, Thornel Mat, Grade VMA, were incorporated in some of the foam formulations. The individual filaments in the mat are 25 to 76 mm (1 to 3 in.) long and about 0.01 mm (0.0004 in.) in diameter.

Processes

The same processing methods were used to prepare foams from the silver coated GMB as were used with the carbon microbubbles.[2] To summarize the methods, the blending is in a twin shell blender with an intensifier bar to chop and separate the graphite fibers. A technique has been developed to disperse the fiber without damaging the microbubbles. Both vacuum bag molding and compression molding methods were used to prepare foams for this evaluation. The vacuum bag method is not well suited for high volume production but is gentle with the GMB and is used to evaluate material formulations.

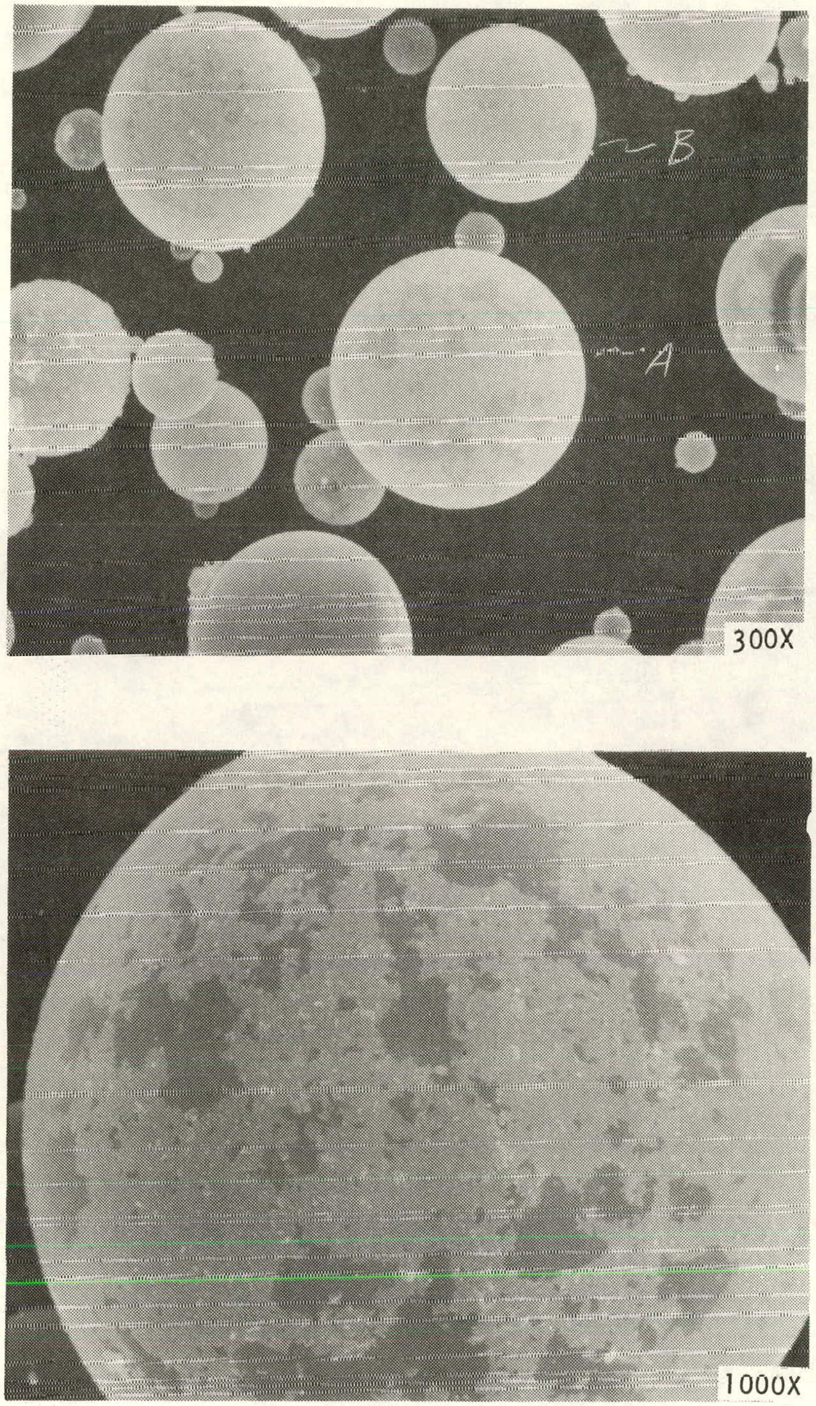

Figure 1. Silver Coated GMB

Table 3. Typical Properties of Kerimid 601 Polyimide Resin

Property	Value
Appearance	Yellow Powder
Density	1.3 g/cm^3
Melting Range	100° to 105°C
Thermal Stability	5 Percent Weight Loss at 400°C
Coefficient of Thermal Expansion	49 μm/m·°C Between 0° and 300°C
Average Particle Size	8 to 10 μm
Compressive Strength	193 MPa at 25°C (28,000 psi)
Shrinkage	Less Than 1 Percent
Thermal Conductivity	0.21 W/m·K (5 x 10^{-4} cal/cm·s·°C)

The standard cure for the Kerimid 601 resin during compression molding is a melt of 120°C for 1.5 hours, a cure of 190°C for 2 hours, and a postcure of 250°C for 16 hours in an inert atmosphere.

Screening Tests

Four types of silver coated GMB with different bubble densities and different amounts of silver were evaluated in foams. Thermal conductivity of the composite foam, compressive strength, and density were tested. The results of the screening tests are given in Table 4. All the foams for these initial tests were made without fibers and were molded in vacuum bags. The molded parts were 127 mm (5.0 in.) in diameter and 12.7 to 19 mm thick (0.5 to 0.75 in.). Since with the vacuum bag method the molding pressure is constant, the actual thickness of a molded disk depended upon the formulation.

Initial thermal conductivity tests with the coated B25B GMB were encouraging but inconsistent. The foams made from B25B GMB coated 4 pbw with silver had a higher thermal conductivity than foams made from the 8 percent silver GMB. The 4 percent silver GMB have a characteristic silver, metallic color in bulk, while the 8 percent silver GMB were a dark, almost black color. SEM photographs show the 4 percent coating to be smooth and the 8 percent coating to be rough. The rough surface diffuses the light and appears dark. The B18A bubbles with 8 percent and 18 percent silver were also a dark color and SEM photographs show a rough surface. The thermal conductivity was low for all the dark colored foams tested. It seems likely that the rough irregular surface tends to hold the GMB apart rather than locking them together.

Table 4. Properties of Foams Made From Silver Coated GMB

Bubble (Type)	Silver (PBW)	Formulation Resin/GMB (Wt Ratio)	Foam Density (g/cm^3)	Compressive Strength		Compressive Modulus		Thermal Conductivity (W/m•K)
				MPa	(PSI)	MPa	(KSI)	
B25B	4	40/60	0.228	2.34	(332)	0.217	(31.1)	0.194
B25B	4	50/50	0.324	4.94	(707)	0.636	(91.1)	0.192
B25B	8	40/60	0.291	2.79	(399)	0.246	(35.2)	0.096
B18A	8	50/50	0.219	3.10	(444)	0.296	(42.4)	0.117
B18A	8	55/45	0.247	3.88	(555)	0.432	(61.9)	0.096
B18A	18	50/50	0.245	3.75	(537)	0.416	(56.9)	0.134
B18A	18	55/45	0.270		(644)	0.367	(52.6)	0.134
B40A	19	25/75	0.324	4.50	(908)	0.418	(59.8)	0.209
B40A	19	35/65	0.362	9.19	(1316)	0.651	(93.2)	0.176
B22A	19	55/45	0.364	9.58	(1372)	0.769	(110.2)	0.201
B22A	19	65/35	0.481	16.20	(2320)	1.20	(171.7)	0.213

Both the B40A and B22A silver coated GMB had marginal but acceptable thermal conductivities. The B22A bubbles were selected for continued evaluation because the foams from the B40A were too high in density.

Candidate Foam

The B22A GMB for the screening tests were coated with 19 pbw silver. The next batch of bubbles was specified at 25 pbw silver. Formulation studies were made on blends of resin and GMB, without the graphite mat, using the vacuum bag molding method. Based upon these tests, a formulation that included the graphite mat was tested at various compression molded densities. These formulations and molded densities are given in Table 5.

Processing the silver coated GMB foams is equivalent to working with the carbon microbubbles. The same blending times and procedures are used and the molding and curing are the same for the two foams. The only difference in the processing is the weight formulation. The foams with carbon microbubbles are made using a 40/60/5 (resin/GMB/mat) ratio, while the foams made with silver coated GMB are in a 45/55/5 weight ratio. However, the resin contents of the two types of foams are similar on a volume basis. The resin content is about a 9.7 percent formulation and about 9.2 percent in the 45/55/5 formulation with silver coated GMB.

Thermal conductivity as a function of molded density is given in Figure 2 for five types of syntactic foams. Three of the foam types were vacuum bag molded with different ratios of resin and filler to obtain the different densities. The foams with Kerimid 601/carbon microbubbles were molded from 35/65, 40/60, and 45/55 weight ratios. Foams with Kerimid 601/silver coated GMB were molded from the foam formulations given in Table 5 while the foams made with Kerimid 601/GMB were molded from 50/60, 45/55, and 50/50 weight blends. Compression molded foams with the carbon microbubbles and Thornel Mat were made from a 40/60/5 weight blend of resin/microbubbles/mat molded to the desired density.

Thornel Mat in the formulation with carbon microbubbles significantly improved the thermal conductivity of the foam. However, in the silver coated GMB formulation, the addition of Thornel Mat did not improve the thermal conductivity. The reason for this difference is not known. The thermal conductivity of the 0.3 g/cm^3 foam made from silver coated GMB at 5.3 x 10^{-4} cal/cm·s·°C is slightly lower than the desired value. Based on experience gained with the carbon microbubble foams, slight modifications to the formulation and density could increase the thermal conductivity.

Compressive properties were also measured on the foams made from silver coated B22A GMB and compared to properties of foams made from both uncoated B22A GMB and carbon microbubbles. The compressive

Table 5. Formulations of Foams With 25 Percent Silver on B22A GMB

Formulation Resin/GMB/Mat (Parts by Weight)	Molding Method	Molded Density (g/cm^3)
35/65	Vacuum Bag	0.246
40/60	Vacuum Bag	0.258
45/55	Vacuum Bag	0.281
50/50	Vacuum Bag	0.308
55/45	Vacuum Bag	0.343
45/55/5	Compression	0.285
45/55/5	Compression	0.306
45/55/5	Compression	0.325
45/55/5	Compression	0.340

strengths are given in Figure 3. Based upon molded density, the foams made from uncoated GMB are stronger than either the foams made with carbon microbubbles or foams made with silver coated B22A GMB. Although there is no reason to expect the foams made from carbon and glass microbubbles to have similar strengths, the silver coated GMB were expected to have equal or even better strengths than the uncoated GMB. When the foams are compared on a resin content basis, as shown in Figure 4, the foams made from coated and uncoated microbubbles do have equivalent strengths. The silver coating adds weight and necessitates a formulation change, but it does not improve the strength properties of the foam.

The B22A GMB have a chromate adhesion promoter added to improve bonding to organic resins. Although the silver coating on the GMB reduces the effectiveness of this adhesion promoter, SEM photographs show good wetting of the silver by the resin.

The formulation for the foam system with carbon microbubbles includes the Thornel Mat graphite fiber. These fibers improve the thermal conductivity properties but do not improve the compressive properties. In the silver coated GMB formulation, the graphite fibers did not improve either the thermal conductivity or the compressive strength. Adjustments to the formulation and the molding techniques could result in improvements with the graphite fiber. Studies to optimize the properties of the silver coated GMB foams were not within the scope of this evaluation.

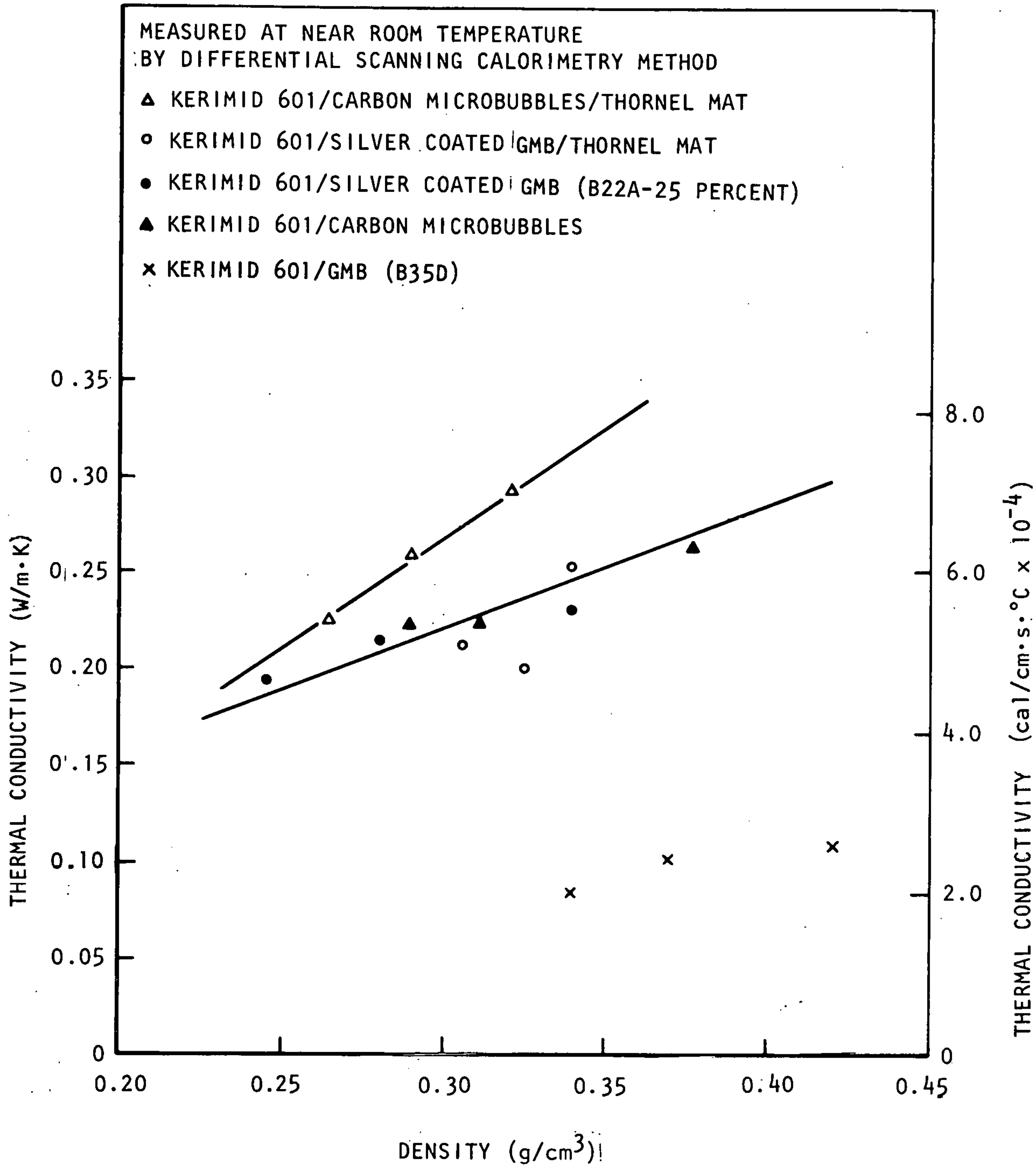

Figure 2. Thermal Conductivity of Syntactic Foams

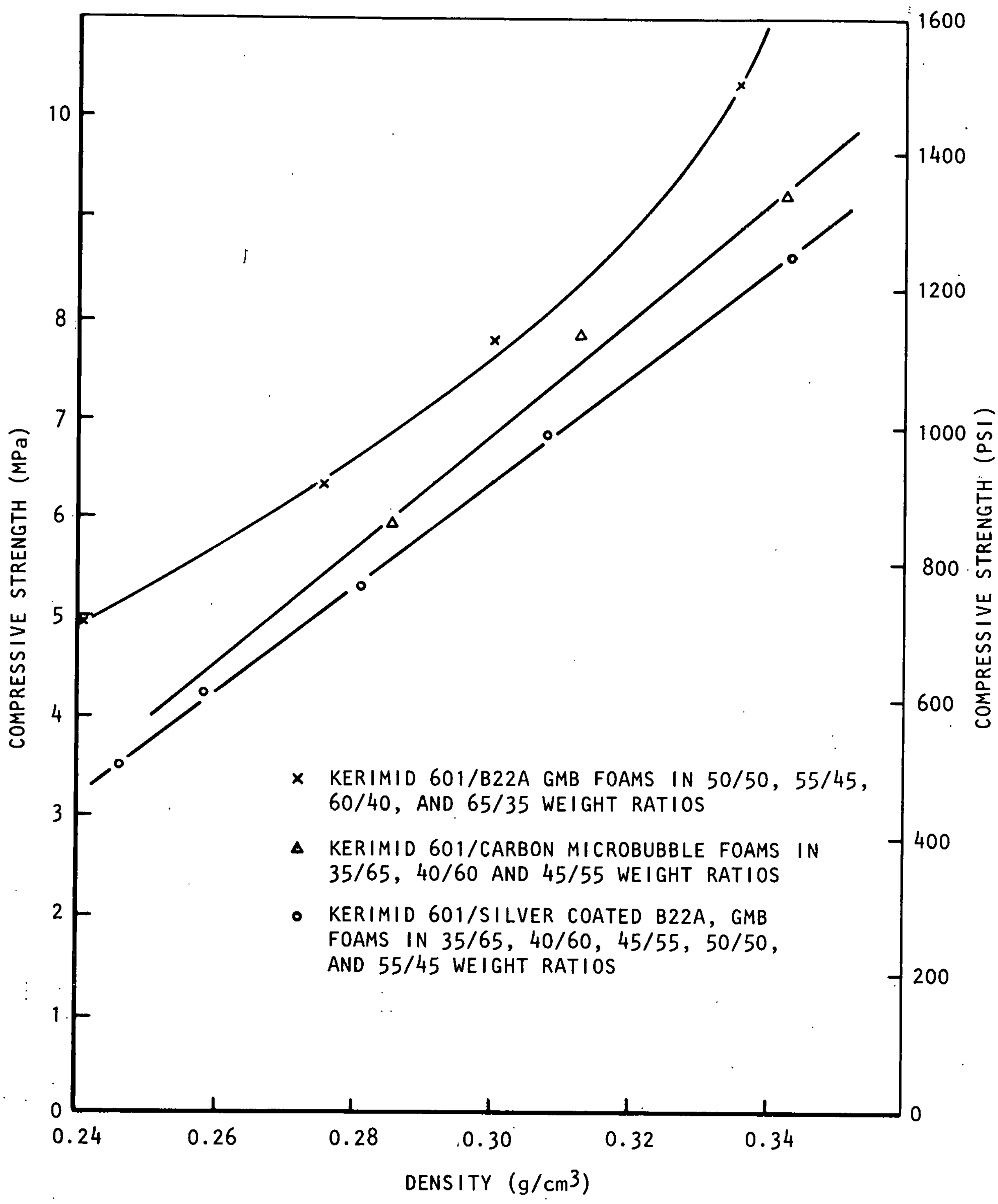

Figure 3. Compressive Strengths of Syntactic Foams as a Function of Foam Density

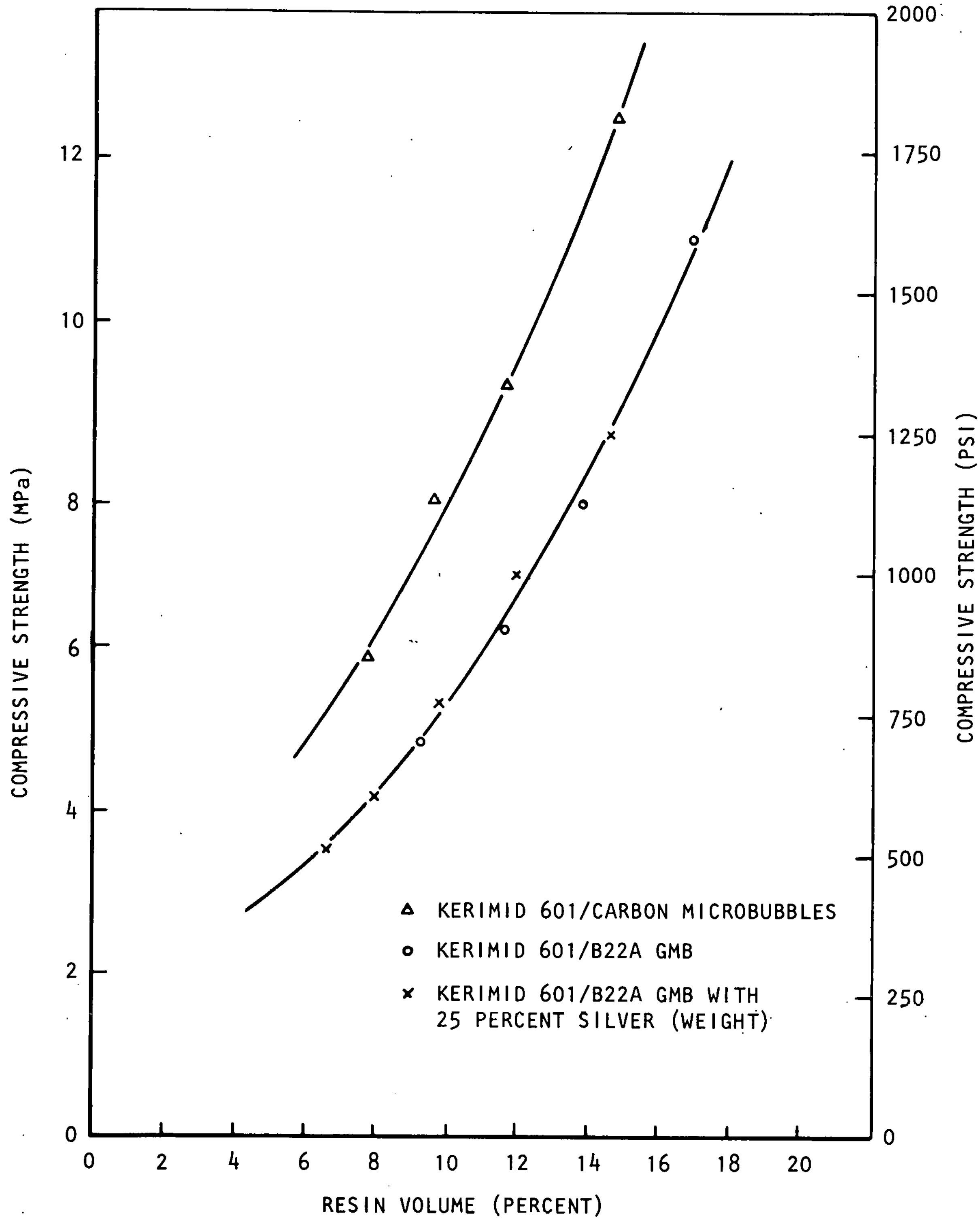

Figure 4. Compressive Strengths of Syntactic Foams as a Function of Resin Content

The measured properties of both the carbon microbubble and silver coated GMB foams are listed in Table 6. The properties are for foams with the Thornel Mat and molded to 0.30 g/cm^3. As mentioned previously, the compressive properties of the foams without Thornel Mat were stronger than foam with the Mat. Without the mat the compressive strength was about 6 MPa (900 psi) at 0.30 g/cm^3 which is stronger than the foam with carbon microbubbles and Thornel Mat. In either formulation, the strength and modulus are greater than the design requirement.

Measured thermal conductivity is slightly lower for the silver coated GMB, but the test method and specimen preparation add to the variation as well as the material properties. Additional testing is required to accurately bracket the range of values expected. The other properties are similar for the two types of foams.

ACCOMPLISHMENTS

Silver coated GMB have been shown to be an acceptable alternate for carbon microbubbles in the preparation of thermally conductive syntactic foams. The density, thermal conductivity, and compressive properties are similar for the two foam systems. Also, since the blending, molding, and curing of foams made from the two types of fillers are equivalent, the existing processing equipment can be used if the silver coated GMB are required as a second source.

Table 6. Comparison of Syntactic Foam Properties

Property	Requirement	Carbon Microbubble Foam	Silver GMB Foam
Density g/cm^3	0.30	0.30	0.30
Thermal Conductivity			
W/m•K	0.23	0.25	0.22
cal/cm•s•°C	5.5×10^{-4}	6×10^{-4}	5.2×10^{-4}
Compressive Strength at 20°C			
MPa	4.83	5.86	5.38
psi	700	850	780
Compressive Modulus at 20°C			
MPa	207	589	360
psi	30,000	85,500	52,200
Impulse Test Pa•s	200	270	280

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PLASTICS: Syntactic Foam

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