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Phenolic Resin Syntactic Foams

By H. M. McIlroy

Published June 1980

Topical Report
R. J. McWhirter, Project Leader

Prepared for the United States Department of Energy
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Syntactic foams were prepared from blends of six phenolic resins and carbon microbubbles. The compressive strength of the phenolic resin foams is equivalent to the strength of foams made from a polyimide resin. Ammonia evolved during the cure diffuses rapidly and is not bound by the foam.

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CONTENTS

Section	Page
SUMMARY.	5
DISCUSSION	6
SCOPE AND PURPOSE.	6
PRIOR WORK	6
ACTIVITY	6
<u>Early Tests on Syntactic Foams</u>	6
<u>Preparation of Phenolic Resins</u>	8
<u>Screening Tests.</u>	8
<u>Candidate Foam Tests</u>	12
ACCOMPLISHMENTS.	15
REFERENCES	18

ILLUSTRATIONS

Figure		Page
1	Reactions of Phenolic Resins.	9
2	Weight Loss and Outgassing Products of Resin B-3	13
3	Weight Loss and Outgassing Products of Foam Cured at 175°C	14
4	Weight Loss and Outgassing Products of Foam Postcured at 230°C	15
5	Thermal Resistance of Syntactic Foams	17

TABLES

Number		Page
1	Properties of Thermally-Conductive Syntactic Foams	7
2	Properties of Phenolic Resins	10
3	Compressive Properties of Phenolic Foam at 25°C	11
4	Properties of Syntactic Foams	16

SUMMARY

Six phenolic resins were selected for evaluation as potential alternate resin binders for a thermally-conductive syntactic foam. Five of the resins were two-stage phenolics and one was a one-stage phenolic. The resins selected have relatively long melt times and have melt temperatures similar to the polyimide resin presently used as the binder resin.

High quality foams were prepared from blends of all six of the resins with carbon microbubbles. The initial compressive strengths for the screening tests ranged from 2.08 MPa at 0.264 g/cm³ to over 5.52 MPa at 0.284 g/cm³. The target strength was 4.82 MPa at 0.30 g/cm³; therefore, several of the phenolic resins were potential candidates.

With two-stage phenolic resins, hexamethylenetetramine is used to provide formaldehyde for final cure of the resin. Ammonia is another decomposition product of the hexamethylenetetramine. Mass spectrometric outgassing analysis and infrared analysis show that the ammonia is completely removed during postcure of the foam.

Based on the compressive tests and outgassing tests, two blends of phenolic resin/carbon microbubbles/graphite fiber were prepared in a 40/60/5 weight ratio in the production area. Test blocks and inner and outer billets were molded using normal processing procedures and equipment. Four of the billets were machined into inner and outer parts and were parylene coated, using the procedures developed for the polyimide foams.

Compressive properties, flexural properties, thermal expansion, and thermal conductivity were measured on foams made from the phenolic resin. The phenolic resin foams have room temperature properties equivalent to the polyimide foam. As expected, the polyimide foam is more thermally resistant than the phenolic foam. The polyimide foam maintains compressive strength to at least 260°C, while the upper limit for the phenolic foams is about 200°C.

DISCUSSION

SCOPE AND PURPOSE

A polyimide was selected as the resin binder for a carbon micro-bubble (CMB) and graphite fiber syntactic foam.¹ Phenolic resins were evaluated as alternate resin binders for this foam system. Foams made with six phenolic resin systems were prepared, tested, and evaluated. Complete characterizations of the phenolic resins and of foams prepared from the resins were not made. However, the evaluation was carried far enough to determine that existing tooling could be used to mold foams with phenolic resin binders and that these foams meet the design requirements.

PRIOR WORK

Several resin binders and fillers were evaluated earlier as materials for a syntactic foam part.¹ During the initial screening tests, foams made from polyurethane foam, polyimide resin, and a phenolic resin were molded at Bendix Kansas City and tested at LASL and Bendix.

ACTIVITY

Early Tests on Syntactic Foams

The thermal conductivity values for the phenolic and polyimide foams tested are similar. The fibers in the blend seem to improve the thermal conductivity of the syntactic foam. The urethane foams were too viscous to incorporate enough graphite fiber or aluminum powder to significantly influence the thermal conductivity. The urethane foam with aluminum honeycomb exceeded the thermal conductivity and strength requirements, but did not meet other design requirements.

Thermal resistance tests run by LASL on their test equipment yield results similar to the pyrolysis probe and gas chromatograph test used by Bendix. The tests show that even Thermalthane 4003 (polyurethane) has sufficient temperature resistance for this application. These tests also reveal that the carbon micro-bubbles foam compounded without fiber tend to be friable and have low strength. A small amount of fiber seems to improve the overall handling capabilities. Test results are summarized in Table 1.

The only part made at Bendix to give unacceptable impulse test results was the polyimide with carbon microbubbles at the 300 Pa·s impulse level. By reducing the impulse level to 200 Pa·s or by

Table 1. Properties of Thermally-Conductive Syntactic Foams

Material	Formulation By Weight	Foam Density (g/cm ³)	Thermal Conductivity (W/m·K)	Compressive Strength (MPa at 25°C)	Impulse Tests	
					Impulse (Pa·s)	Results
Polyimide/CMB	40/60	0.30	0.234	5.86	300 200	Massive Spall Slight Surface Powder
Polyimide/ CMB/Fiber	40/60/5	0.30		6.20	300	Slight Surface Powder
Phenolic/CMB	50/50	0.35	0.201	6.20	300	Slight Surface Powder
Phenolic/CMB Fiber	50/50/5	0.34	0.217	6.20	300	Very Small Spall
Urethane/Fiber	95/5	~0.30	0.134	4.40	300	Slight Surface Powder
Urethane/Al	66/33	~0.30	0.084	4.34		
Urethane/ Honeycomb	3-mil	~0.35	0.778	7.79	300	Slight Surface Powder

adding graphite fiber to the formulation, the performance of the polyimide/CMB material was improved.

Preparation of Phenolic Resins

Phenolic resins are prepared from the condensation reaction of phenol and formaldehyde (Figure 1). In a one-stage phenolic, the required amount of phenol, formaldehyde, and catalyst are partially reacted by the manufacturer. The cure is completed during the molding cycle, with a small amount of water liberated during cure. A two-stage phenolic prepared by the manufacturer does not have sufficient formaldehyde to complete the cure of the resin. The necessary formaldehyde is supplied in the form of hexamethylenetetramine which decomposes into ammonia and formaldehyde during molding.

Screening Tests

One phenolic resin of the one-stage variety and five of the two-stage type were selected for evaluation. Properties of the resins are given in Table 2. All the phenolic resins evaluated are powdered resins that melt or soften before cure. The softening ranges given in Table 2 are from vendor data; however, these compare well with softening range values measured at Bendix by Fisher Johns method and by a capillary tube method.

Particle size distribution of the powdered resins is important because the resin is blended with carbon microbubbles with a size distribution from about 10 to 250 μm . The particle size given in Table 2 is 98 to 99 weight percent less than 74 μm , which would allow the resin to blend easily with the CMB and actually fit between individual carbon microbubbles.

Foam test blocks were molded from a 40/60 weight blend (resin/CMB) using the vacuum bag molding technique. The vacuum bag method applies a constant low pressure and allows the foam to gently compress as the resin melts and flows.

The molding conditions and compressive properties are given in Table 3. The melt temperature selected was based on the reported melting range of the individual resin. Constant cure (inside mold) and postcure (out of mold in argon atmosphere) conditions were maintained on all the types of resin.

The target was a compressive strength of 4.82 MPa at 25°C and a foam density of 0.30 g/cm³. The specimen density for the vacuum bag molded foam made from the six resins varied from 0.264 to 0.284 g/cm³. The foam made from one phenolic resin (B-3) had a strength of about 5.52 MPa at 0.28 g/cm³. Compression molded foams from blends of the B-3 resin, carbon microbubbles, and

Figure 1. Reactions of Phenolic Resins

Table 2. Properties of Phenolic Resins

Property	Resin Types						
	A-1	A-2	B-1	B-2	B-3	B-4	B-5
Softening Point (°C)	97 to 108	91 to 101	55 to 65	55 to 65	64 to 74	63	100 to 112
Flow (mm at 125°C)	15 to 30	15 to 30	25 to 45	20 to 40	100 to 125	67	25 to 35
Hot Plate Cure (s at 150°C)	60 to 110	40 to 60	35 to 100	25 to 40	90 to 120	47	69 to 95
Hexamethylene-tetramine (Percent)					5.4 to 5.8	3.95	
Nitrogen Content (Percent)	3.3 to 3.8	4.6 to 5.1					
Particle Size (Weight Percent)							
On 70 Mesh				0.1	0.05	0.05	
On 100 Mesh				0.1	0.10	0.1	
On 200 Mesh	1.5 maximum	1.5 maximum		1.0 maximum	0.7 maximum	1.0 to 2.0	2.0 maximum

Table 3. Compressive Properties of Phenolic Foam at 25°C

Resin	Resin/CMB (Weight Ratio)	Time at Temperature (hr at °C)			Specimen Density (g/cm ³)	Compressive Properties (MPa)	
		Melt	Cure	Postcure		Strength	Modulus
A-1	40/60	2/110	2/150		0.280	3.79	207
			2/150	4/230	0.281	3.85	203
A-2	40/60	2/100	2/150		0.280	3.91	240
			2/150	4/230	0.271	3.01	194
B-2	40/60	2/65	2/150		0.271	3.79	261
			2/150	4/230	0.266	3.65	192
B-5	40/60		2/150		0.274	4.25	200
			2/150	4/230	0.279	4.73	225
B-4	40/60	2/80	2/150		0.264	2.26	127
			2/150	4/230	0.262	2.08	144
B-3	40/60	2/80	2/150		0.284	5.60	340
			2/150	4/230	0.279	5.21	318
B-3	40/60/5*	close 82°C	2/175		0.289	5.14	554
			2/175	4/230	0.301	6.38	767
B-3	40/60/5*	close 82°C	2/175		0.309	7.21	821
			2/175	4/230	0.313	7.89	686

*Compression molded with graphite fiber in blend; all other foams vacuum bag molded.

graphite fiber had compressive strengths of 6.29 MPa at 0.30 g/cm³ and 7.68 MPa at 0.31 g/cm³.

A major concern with phenolic resins is the potential for outgassing as the cured product ages. The outgassing would be either water from additional cure or, potentially, ammonia from the hexamethylenetetramine. The ammonia, evolved as the polymer cures, must diffuse through the polymer to escape to the atmosphere. Thick molded parts of a two-stage phenolic can outgas ammonia for a long period of time. However, the open structure of the syntactic foam allows the liberated ammonia to escape easily and quickly. Weight loss by thermogravimetric analysis (TGA) and outgassing product identification by mass spectrometric analysis were made on resin A-2, on resin B-3, and on cured and postcured foams made with resin B-3. Figures 2, 3, and 4 are for resin B-3 only, for a foam cured at 175°C, and for a foam postcured at 230°C in addition to the cure at 175°C.

The test for the resin only (Figure 2) shows that hexamethylenetetramine is evolved and can be detected. Also evolved are low molecular weight phenolic resin molecules that have not reacted. No hexamethylenetetramine or ammonia could be identified in either the cured or postcured foams (Figures 3 and 4).

Water was the major constituent of the outgassing products in both the cured and postcured foams. This water was not from additional cure but was from water absorbed by the foam. At higher temperatures, the only outgassing products were typical fragments of phenolic resins. The mass numbers of ammonia and water are similar, and trace amounts of ammonia are difficult to detect with large amounts of water present. Therefore, in addition to the mass spectrometric outgassing tests, infrared analysis (IR) measurements were made on the postcured foam. The IR spectrum showed no traces of ammonia in the foams.

Candidate Foam Tests

Based on the compressive strength and outgassing product tests, the two-stage resin B-3 was selected for additional testing. This testing was to compare the properties of the phenolic resin foams with properties of foams made with polyimide resins. One large blend (Blend 161) was made from resin B-3, carbon microbubbles and graphite fiber in a 40/60/5 weight ratio. Three types of parts were molded from this blend: two inner ring billets, two outer ring billets, and one 215.9- by 215.9- by 38.1-mm block. The cure schedule was as follows.

Preheat oven to 110°C.

Close mold when material temperature reaches 80°C.

Figure 2. Weight Loss and Outgassing Products of Resin B-3

Cure for 3 hours at 175°C.

Postcure 6 hours at 230°C in argon.

After postcure, the four billets were shipped to LASL. The molded block was machined into standard test specimens. A summary of the test results is given in Table 4.

The average compressive strength of the foam made from Blend 161 was less than expected, with an average test value of 4.41 MPa at 0.295 g/cm³ and 25°C. The strength values from the screening tests (Table 3) were 5.14 MPa at 0.289 g/cm³ and 7.4 MPa at 0.30 g/cm³. The reason for the large difference in strength between the screening test and Blend 161 was not obvious. The cure schedule for the blocks molded during the screening tests and for the block molded from Blend 161 was the same. Also, the same lot of resin B-3 was used for both the screening tests and for Blend 161. However, different lots of carbon microbubbles were used to mold the screening test blocks and for Blend 161. Normally, no more than 10 percent variation in strength is expected with different lots of carbon microbubbles.

Figure 3. Weight Loss and Outgassing Products of Foam Cured at 175°C

Blend 362 was prepared from different lots of resin B-3 and carbon microbubbles. The results of the compressive strength tests for foams made from Blend 362 also are given in Table 4. The compressive strength average value of 6.76 MPa at 0.29 g/cm³ compares well to the strength values from the screening tests. Additional testing with other lots of resin and CMB will be required to bracket the expected foam strength.

Inner and outer billets were also molded from Blend 362 in the production area using the normal production processes. Inner and outer parts were machined from the billets and parylene coated according to the normal production processes. Coated sections were sent to LASL for future use.

Thermal resistance of the polyimide foam and the phenolic foam is shown in Figure 5. The polyimide foam is stable at higher temperatures than is the phenolic resin foam. Somewhere in the neighborhood of 200°C the phenolic resin begins to drop rapidly in compressive strength. A typical lot of the polyimide will have a knee in a TGA curve at 380 to 400°C at a heating rate of 10 to 15°C/min. As shown in Figure 4, the phenolic resin has a knee at about 300°C.

Figure 4. Weight Loss and Outgassing Products of Foam Postcured at 230°C

A piece of the postcured foam from Blend 161 was analyzed by mass spectrometric outgassing. No trace of ammonia was found by this method.

ACCOMPLISHMENTS

Phenolic resins have been shown to be suitable as alternate resin binders for syntactic foam made with carbon microbubbles as filler. Foams made with phenolic resin and CMB have compressive properties and thermal conductivities equivalent to foams made with polyimide and CMB. The thermal resistance of the polyimide foam is better than the thermal resistance of the phenolic foam. The polyimide foam retains properties up to 260°C, while the phenolic foam has an upper temperature of about 200°C.

The phenolic foams can be prepared by using the same processing techniques and equipment as the polyimide foam. The machining and parylene coating of the two foams are equivalent.

Table 4. Properties of Syntactic Foams

Property	Typical Polyimide Foam*	Phenolic Foam Blend	
		161**	362†
Density (g/cm ³)	0.30	0.29	0.29
Compressive Strength (MPa)			
At 25°C	5.86	4.41	6.76
At 200°C	5.86††	4.20	5.79
At 260°C	5.79††	3.45	
Compressive Modulus (MPa)			
At 25°C	590	420	567
At 200°C	480††	370	504
At 260°C	460††	290	
Flexural Properties at 25°C			
Strength (MPa)	4.00	3.31	
Modulus (MPa)	610	630	
Strain (cm/cm)	2.8 x 10 ⁻³	5.2 x 10 ⁻³	
Linear Thermal Expansion, 25 to 200°C (cm/cm)	6 x 10 ⁻⁶	9 x 10 ⁻⁶	
Thermal Conductivity (W/m·K)	0.251	0.322	0.209

*Some properties taken from Table 18 of Reference 1.

**Blend 161 composed of 40/60/5 weight ratio of resin B-3/CMB/graphite fiber.

†Blend 362 composed of 40/60/5 weight ratio of resin B-3/CMB/graphite fiber.

††Previously unpublished data for foams made with polyimide/CMB/graphite fiber in 40/60/5 weight ratio.

Figure 5. Thermal Resistance of Syntactic Foams

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¹H. M. McIlroy, High Temperature Syntactic Foam (Final Report). Bendix Kansas City: BDX-613-1534 (Rev.), July 1977 (Available from NTIS).

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