

CARBON FOAM - ITS PREPARATION AND PROPERTIES

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I. INTRODUCTION

Light weight cellular carbons are widely used in many industrial and aerospace applications as high temperature thermal insulators and as structural support materials. The Carbon Products Division of Union Carbide Corporation has for many years been engaged in the research and development of carbon foams made by means of the pyrolysis of thermo-setting organic foam precursors. This paper describes the preparation and properties of two types of carbon foams, one based on a phenolic foam and the other on a polyurethane foam precursor. By varying the conditions of preparing the precursor foams and also the rate of pyrolysis, a very broad range of product properties can be obtained.

II. PREPARATION OF CARBON FOAMS

Many factors determine the density and suitability of an organic foam as a carbon precursor; the density of the resins, the temperature and resin balance of the formulation, the molding procedures, and various post curing operations are important examples. A typical foam formulation contains four components: the resin; a surfactant to maintain cell integrity during the foaming process; a foaming aid to obtain a smooth even foaming action starting at low temperatures; and, finally, a catalyst, which is used to initiate the resin polymerization reaction.

The organic foam is converted to cellular carbon by heating in a controlled environment. The heating rate depends on both the precursor thickness and formulation. If the foam is heated improperly, the structure may melt, rupture, or even explode.

A. PYROLYSIS OF PHENOLIC FOAM

The pyrolysis of the phenolic foam is accomplished in a nonoxidizing environment which may be provided by the product gases. Heating rates from 1° to 200°C/hour have been employed in the pyrolysis of phenolic foams. The rate depends on sample size, density, and the strength requirements of the products carbon. For example, samples of low density (0.05 g/cc) phenolic foam with dimensions of 16" x 16" x 2" may be heated at a rate of 100°C/hour to 1000°C to effect the conversion to carbon.

The preferred pyrolysis schedule for any starting foam represents a compromise between product yield and properties. When 0.25 g/cc carbon foams were prepared from phenolic foam at a heating rate which gave a 90 percent yield of crack-free pieces, the compressive strength ranged from 500 to 820 psi. When the heating rate was extended over twice that period of time, the yield of crack-free pieces was increased only slightly but the compressive strength was nearly doubled, to 1000 - 1480 psi. On the other hand, when the original heating rate was doubled, the yield was less than 50 percent acceptable pieces.

The weight and volume changes which occur during pyrolysis vary with the density of the precursor foam. The high density phenolic foams lose 60 percent of their weight and 70 percent of their volume when heated to 2600°C. The shrinkage is anisotropic to the extent that the change in length is usually 3 or 4 percent greater than the change in diameter. Table I shows the changes in weight and density for high density phenolic foam (0.25 g/cc) at various temperatures from 100° to 2600°C. The cyclic behavior of the density indicates that the major weight and volume losses do not occur at the same temperatures. Most of the work was done with semi-cylindrical phenolic foam samples approximately 19" diameter and 7" long; but the trends have been verified with samples as long as 24". The results at 2000°C and higher are averages of at least 30 semi-cylindrical samples 19" diameter and 7" long. The lower temperature studies involved no fewer than four samples.

TABLE I
Heat Treatment of 0.25 g/cc Phenolic Foam

Temperature °C	Weight Loss, %	Density Change, %
100	2.7	- 1.4
200	5.6	+ .6
300	14.1	- 4.7
400	26.8	- 2.9
500	44.2	-12.8
600	50.0	- 8.2
700	54.9	- 4.2
800	54.4	- 1.2
900	56.0	- 0.9
1000	56.1	0.1
2000	60	- 3.0
2200	61	- 1
2400	61	+18
2600	61	+26

The data in Table I are characteristic of phenolic foam over the entire range of densities; however, low density foam tends to shrink slightly more at treatment temperatures above 700°C.

B. PYROLYSIS OF URETHANE FOAM

The heat treatment of the urethane foams involves a two-step oxidation prior to pyrolysis in an inert atmosphere. The specific temperature and dwell time used in the polymerization-oxidation step varies with the size and density of the urethane precursor. Typically, the foam is held at 150°C and again at 250°C for 24 hours to prevent fusion during pyrolysis. The weight and volume changes which occur during pyrolysis to 1000°C are about 55 and 60 percent respectively. There is a density increase of about 10 percent for the low density, and 20 percent for the high density carbonized urethane foam.

Union Carbide has patents (2) granted and pending which describe in detail the preparation of organic precursor carbon foam.

III. PROPERTIES OF CARBON FOAM

The physical properties of the product carbon foams are dependent on the type, quality, and treatment of the precursor. The major apparent difference among the types of organic precursor is the average cell size of the product carbon (see Table II). The cell size of the carbonized urethane foam is 8 to 32 mils for the 0.05 g/cc density and approximately 8 to 16 mils for the 0.25 g/cc density; the phenolic precursor carbon has a 2 to 6 mil cell size in the low density foam and approximately 1 to 3 mils in the high density material.

TABLE II
Cell Size of Carbon Foam

Foam Precursor	Density	Cell Diameter
Urethane	0.05 g/cc	8-32 mils
	0.25 g/cc	8-16 mils
Phenolic	0.05 g/cc	2-6 mils
	0.25 g/cc	1-3 mils

The cell structures of these carbon foams are shown in Figure 1. The cells are football shaped with the major axes parallel to the foaming directions. The pyrolyzed foams are pseudomorphs of the parent foam.

The compressive strengths, defined as the point at which a change in slope of the stress-strain curve occurs; of properly prepared 1000°C carbon foam from phenolic and urethane precursors are given in Figure 2, for foams in the density range of 0.15 to 0.35 g/cc. The strength of the phenolic precursor carbon varies from 500 to 1900 psi over the density range; the strength of urethane precursor carbon is about one-half these values.

The ultimate compressive strength of the 0.35 g/cc phenolic precursor carbon foam is usually above 3000 psi. The strength of low density foam exhibits a greater degree of anisotropy than high density foam. The strengths of 0.05 g/cc carbon perpendicular and parallel to the foaming direction are 30 and 50 psi, respectively. Subsequent heat treatment of carbon foam to 2800°C results in no change in strength for the phenolic precursor carbon but does result in as much as a 70% reduction in strength for urethane precursor.

The thermal conductivity of the foam, determined by the Fitch method, is quite low, approximately 0.1 and 0.2 BTU/ft-F°-hr for 0.05 and 0.25 g/cc carbon, respectively. The high temperature thermal conductivity was determined by the cyclic phase shift⁽¹⁾ technique for a sample of 0.27 g/cc density phenolic precursor carbon foam. The data are shown in Table III. The thermal conductivity parallel to foaming is 10 to 25 percent higher than the conductivity perpendicular to foaming. In the direction of high thermal conductivity, the range is 0.5 to 0.8 BTU/ft-F°-hr in the temperature range of 1400° to 2100°C. Other properties of material from the same sample are shown in Table III.

TABLE III

Properties of 0.27 g/cc Phenolic Precursor Carbon Foam

Property	Direction Perpendicular	Direction Parallel
Density, lb/ft ³	0.27 g/cc	0.27 g/cc
Compressive Strength, psi	1,350	2,150
Shear Strength, psi	725	570
Thermal Conductivity, BTU/ft-F°-hr		
RT →100°C	0.18	0.20
1400°C	0.47	0.53
1800°C	0.45	0.57
2100°C	0.60	0.75

Of particular interest is the high shear strength which demonstrates that when the material is used as an insulator, it can be firmly bonded to the surface to be insulated.

The permeabilities of various carbon foams are shown in Table IV along with the permeabilities of graphite and PC-45 a high density porous carbon. The best commercial grades of graphite with densities in the range of 1.6 to 1.73 g/cc have permeabilities in the range of 0.5 to 0.02 Darcy's. The permeability of phenolic carbon foam is in the range of 1.9 to 0.36 Darcy's, roughly an order of magnitude greater than that of graphite; the permeability of the urethane precursor carbon foam is in the range of 22.6 to 71.5 Darcy's, two orders of magnitude greater than that of graphite. Porous carbon, PC-45, has a porosity almost identical with that of the high density urethane precursor carbon, approximately 22 Darcy's.

TABLE IV

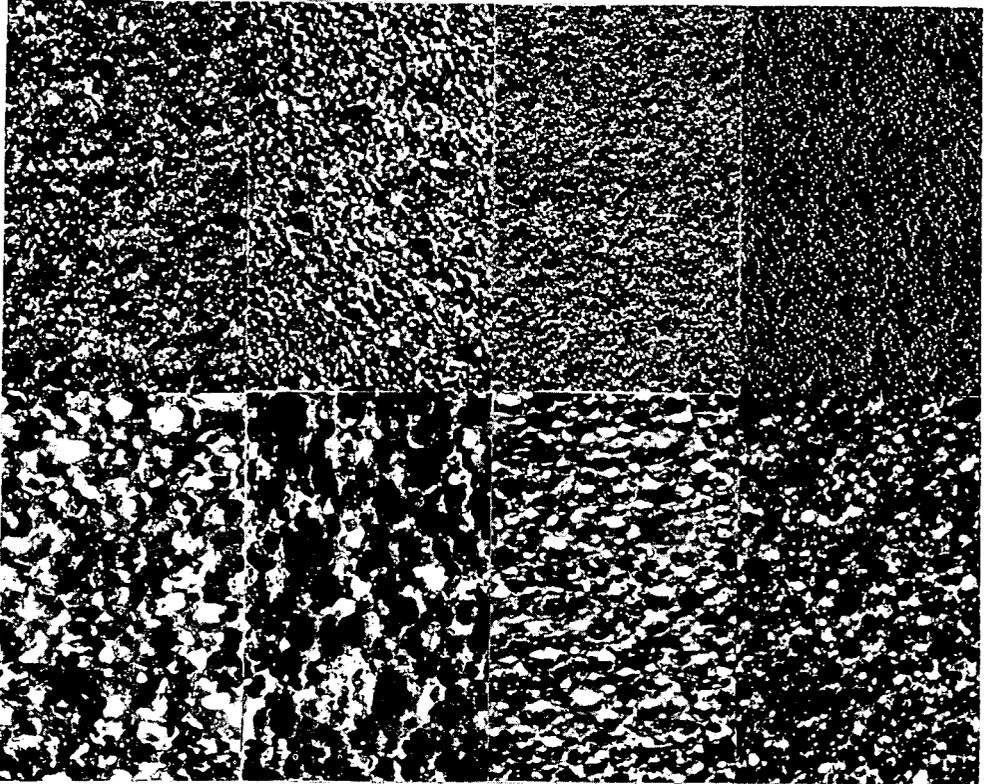
Permeability of Carbon Foam

Precursor Material 1000°C Treat	Density, g/cc	Permeability in Darcy's	
		Parallel to Foam	Perpendicular to Foam
Urethane	0.05	71.5	31.0
Urethane	0.30	24.3	22.6
Phenolic	0.08	1.9	1.1
Phenolic	0.30	0.95	0.36
PC-45	1.04	20	20
ATL Graphite	1.78	0.068	0.064

In summary, carbon foam is a light weight, high strength material which is stable above 2800°C. It may be used as an insulator, filter, or structural support material and is presently available in sizes as large as 14" diameter by 18" long.

Figure 1

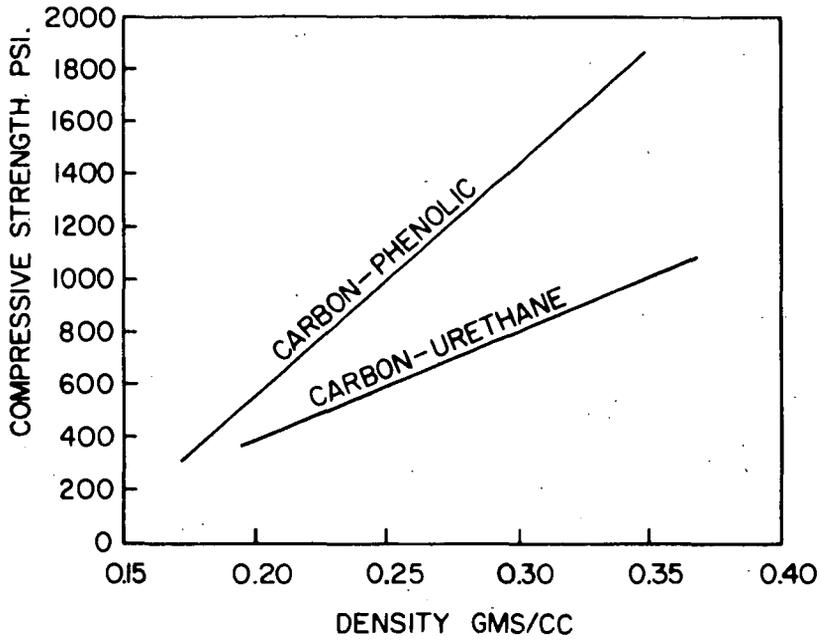
CARBON FOAM 1000°C HEAT-TREAT



The upper row is phenolic precursor carbons in both directions of 0.05 and 0.25 g/cc density. The lower row is corresponding urethane precursor carbons.

Figure 2

COMPRESSIVE STRENGTH VS. DENSITY
FOR CARBON FOAM



References

- (1) "Measurements of Thermal Diffusivity and Thermal Conductivity of Graphite with Carbon Arc Image Furnace," M. R. Null and W. W. Lozier, 5th Thermal Conductivity Conference, Denver, Colorado, October 20, 1965.
- (2) U. S. Patent 3, 121, 050; U. S. Patent 3, 302, 999; U. S. Patent 3, 387, 940.