

Mechanical and Processing Requirements for a Shock Mitigating Phenolic Foam

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Synopsis

A high load-bearing shock-mitigating phenolic foam was developed to meet specific compression-deflection and gas permeability requirements. It was required that the foam display an almost constant compressive stress within the limits of 50–68 psi at strains ranging from 10% to 60%. Furthermore, the foam had to possess a highly open-celled structure so that its resistance to gas flow would be minimal. These properties were obtained from a chemical formulation utilizing a combination of two phenolic resins, a phosphoric-sulfuric acid catalyst system, a surfactant combination that included both a hydrophilic and a lipophilic surfactant, and a fluorocarbon blowing agent.

INTRODUCTION

A rigid phenolic foam was developed to meet the mechanical properties required for use as closure material for a missile launching system. During launch, the foam, located between the missile nose and closure shell, accelerates the closure shell while absorbing energy as it is crushed. In order that the maximum allowable axial load and pressure on the missile nose not be exceeded, the foam was developed to have certain compressive stress-strain and gas permeability characteristics.

Initial effort involved preparing many foams in quart and then gallon size paper containers and evaluating their properties. As some insights were gained, the size of the foam samples was increased to approximately 1 ft³. After further narrowing of the formulation variables, it was decided to prepare full size buns of approximately 15 ft³.

While scaling up the bun size, we considered employing a continuous process. However, this approach was precluded because of the very high expense and short time available for obtaining a foam machine that would adequately resist the corrosion from the acids and have the required capacity, perhaps as great as 150–200 lb/min.

To disperse adequately 90 lb of ingredients within the 12 sec before the onset of creaming (first visible sign of chemical reaction as evidenced by generation of small bubbles), we employed a high speed high-shear Cowles dissolver.

MECHANICAL ANALYSIS

In order that the foam accelerate the opening of the closure during launch while preventing the buildup of excessive pressure and an overburdening axial load on the missile nose, it is essential that it meet certain specified compressive stress-strain characteristics and gas permeability properties.

The required compression-deflection characteristics were designed so that the foam would absorb a sufficient quantity of energy at a stress level that would not impart excessive loads to the missile. Since a matrix of a brittle foam is broken rather than flexed during compression, its compression-deflection curve displays a considerably flatter and wider stress plateau than obtainable with a flexible foam (Fig. 1). The essentially constant stress up to the ultimate strain offers the desired property of high-energy absorption (area under the load-compression curve) while preventing the attainment of undesirably high stresses.

High permeability towards gases is required to prevent an excessive increase in stiffness of the foam that could result from air trapped inside the matrix during dynamic loading while missile launch is taking place.

The effect of the physical characteristics of the foam matrix on load bearing and energy absorption properties have been described in terms of the relationship¹⁻³

$$\sigma = E_f \epsilon \psi(\epsilon) \quad (1)$$

where E_f is the compressive modulus of the foam determined from the slope of the linear portion of the stress-strain curve (Fig. 1) prior to buckling, $\psi(\epsilon)$ is a dimensionless function of compressive strain, σ is the compressive stress, and ϵ is the compressive strain. The function $\psi(\epsilon)$ is independent of the modulus of the polymer and therefore is unaffected by temperature and strain rate. It is strongly dependent on the shape of the cells and moderately dependent on the size of the cells and density of the foam. A typical curve illustrating the nonlinear function is shown in Figure 2.

The energy E absorbed by a block of foam during compression can be determined from the equation

$$E = Ah \int_0^{\epsilon^*} \sigma d\epsilon \quad (2)$$

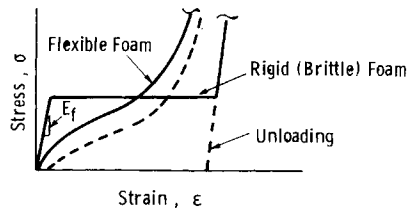


Fig. 1. Compression-deflection characteristics of rigid and flexible foams.

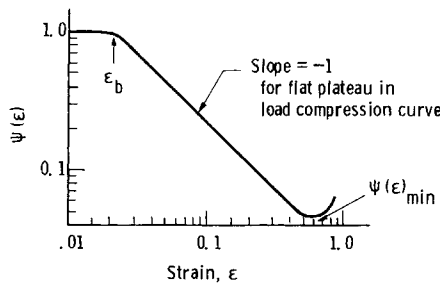


Fig. 2. Typical ψ function calculated from compressive stress-strain of rigid foam.

where A is the cross-sectional area of the foam, h is the thickness, and ϵ^* is the ultimate extent of the compressive strain. Combining eqs. (1) and (2), the energy absorption of the foam

$$E = AhE_f \int_0^{\epsilon^*} \psi(\epsilon)\epsilon d\epsilon \quad (3)$$

can be determined through graphical integration of Figure 2. Thus, eq. (3) can be used to provide some insight into the factors affecting the energy absorption characteristics of the foam.

The foam modulus E_f is primarily a function of Young's modulus of the polymer E_0 and the volume fraction ϕ of polymer. Assuming spherical cell geometry, the following empirical relationship²

$$E_f = E_0\phi(2 + 7\phi + 3\phi^2)/12 \quad (4)$$

shows that E_f is directly proportional to E_0 and very strongly dependent on ϕ . Equations (3) and (4) combine to illustrate the high increase of energy absorption with increasing foam density.

At very low strains the compression-deflection curve (Fig. 1) is linear and $\psi(\epsilon) = 1.0$. As soon as buckling of the matrix ligaments occurs, $\psi(\epsilon)$ decreases. The point at which $\psi(\epsilon)$ is equal to 0.95 has been termed the "critical buckling strain" ϵ_b .³ This is followed by progressive fracture of the brittle matrix which gives a flat plateau in the compressive stress-strain curve (Fig. 1) and a slope of -1.0 in the $\log_{10} \psi(\epsilon) - \log_{10} \epsilon$ curve (Fig. 2). A foam exhibiting the typical compression-deflection characteristics for a flexible matrix will have a slope between -1.0 and 0 ; whereas, an extremely brittle material which exhibits a maximum in the load compression curve will display a slope more negative than -1.0 . The point at which $\psi(\epsilon)$ is a minimum represents the maximum collapse of the matrix.

Even though quantitative relationships were not established, Rusch has shown for a variety of foams that $\psi(\epsilon)$ is highly sensitive towards cell geometry.¹ This finding is consistent with the observations of Mendelsohn et al.,⁴ that compression-deflection characteristics of cast cellular polyurethanes are highly sensitive towards the shape of the cells.

To minimize rate sensitivity, the ratio of dynamic- to static-load-bearing properties, the permeability of the foam matrix towards gases should be very high. The effect of entrapped air on compressive stress at low strain rates can be estimated by applying to eq. (1) a correction factor

$$\sigma = \epsilon E_f \psi(\epsilon) + Pf\epsilon/(1 - \phi - \epsilon) \quad (5)$$

where P is the ambient pressure and f is the volume fraction closed cells.² Obviously, the correction factor is negligible for an open-cell foam where f is close to zero. The importance of the last term of eq. (5) also diminishes with an increase in the modulus of the foam. As the brittleness of the polymer increases the effect of permeability of the matrix decreases since entrapped air is released during the compressive fracturing of the cell walls. Since there is no rate sensitivity function in the correction factor for entrapped air, the error in employing eq. (5) for dynamic loading conditions increases as the matrix polymer becomes more flexible.

PREPARATION OF FOAM

Materials

Bakelite BRL-2760 is a one-step heat-reactive liquid phenolic resin manufactured by Union Carbide Corporation. Its suggested use is for preparation of medium-density rigid phenolic foam. Properties listed by Union Carbide include: viscosity at 25°C, 2350–3125 cps, pH 6.0–6.8, and nonvolatile matter (78–81) %.

Bakelite BRL-2759 also is a one-step heat-reactive liquid phenolic resin manufactured by Union Carbide Corporation. Its suggested use is for low-density rigid phenolic foam. Listed properties include the following: viscosity at 25°C, 400–800 cps, pH 6.0–6.3, and specific gravity at 25°C, 1.210–1.225.

Span 80, sorbitan monooleate, is manufactured by ICI America, Inc., Atlas Chemical Division. It has the following properties: viscosity ~1000 cps at 25°C, acid number 8.0 max, saponification number 145–160, hydroxyl number 193–210, and hydrophile-lipophile-balance (HLB) number 4.3. (Higher HLB numbers indicate greater hydrophilic character. Lipophilic surfactants are assigned HLB numbers below 9.0, whereas ones that are hydrophilic are given numbers above 11.0. Those in the range of 9–11 are intermediate.)

Tween 60, polyoxyethylene sorbitan monostearate, is manufactured by ICI America, Inc., Atlas Chemical Division. Its listed properties include: viscosity 600 cps at 25°C, acid number 2.0 max, saponification number 45–55, hydroxyl number 81–96, and the HLB number 14.9.

Niax 113 or Freon 113, 1,1,2-trichloro-1,2,2-trifluoroethane, fluorocarbon blowing agent, boiling point b.p. 47.6°C, is manufactured by Union Carbide under trade name Niax or DuPont as Freon.

Process

A typical formulation consists of the following ingredients in parts by weight: BRL-2760, 180; BRL-2759, 20; Tween 60, 0.25; Span 80, 0.50; Niax or Freon 113, 12; 47.5 wt. % sulfuric acid, 25; 85 wt % phosphoric acid, 15. A description of the processing of the most frequently prepared quantities of foam is given below.

Phenolic resins BRL-2760, 29,300 ± 100 g; BRL-2759, 3250 ± 10 g; Tween 60, 41 ± 1 g; and Span 80, 81 ± 1 g are removed from storage at 0–8°C, weighed into a 20 gal galvanized steel container, and permitted to warm to 15–17°C.

Meanwhile the temperatures of the blowing agent, 1950 ± 5 g, and acid solution, 4063 ± 5 g 47–48 wt. % H₂SO₄ acid dissolved in 2438 ± 5 g 84.5–85.5 wt. % H₃PO₄, are adjusted so that these materials will be at 18 ± 1°C at the time of their addition to the resin.

The resin-surfactant mixture is warmed to 17.5–18.0°C by stirring for several minutes at 1350 rpm with the Cowles-Dissolver (Model 515-HV equipped with a 15 hp three-phase motor and a 10 in. nominal size “hi-shear” standard design

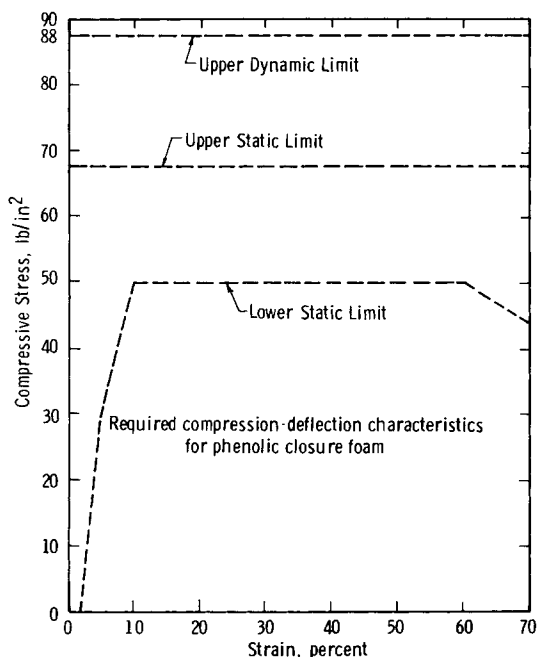


Fig. 3. Stress-strain acceptance limits.

impeller, manufactured by Morehouse-Cowles, Inc.). After reaching 18°C the mixture is stirred for an additional 60 sec at which time the blowing agent is added over a period of 5 sec. Stirring is continued for an additional 45 sec and then the rate is increased to 1750 rpm over a 10 sec time interval. As a result of excessive vibration caused by the relatively high viscosity of the chilled mixture, and to reduce evaporation losses of the blowing agent, stirring at 1350 rpm was found to be preferable to higher rates of stirring until the time for addition of the acid catalyst. Stirring at 1750 rpm during the addition of the acids provides a more uniform dispersion of the mixture over the very short period of time allowed by the very fast reaction. Addition of the $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ solution, 6500 ± 10 g, to the rapidly stirring mixture takes place over a period of 5 sec.

As soon as 17 sec have elapsed from the time of the initial introduction of the acid catalyst, the stirrer is stopped and the drive assembly raised. Within 4 sec of pressing the stop button, the mixture has been poured into a supported cardboard carton, $32 \times 26 \times 22$ in. height. The material creams almost instantly and completes its rise usually over the next 60 sec.

Within 2-4 hr of foam preparation, the skin plus about 2 in. of material is trimmed from the bun. The trimmed buns are baked in a vented forced air circulation oven for 4-8 hr at 100°C in order to remove formaldehyde and other volatile products. The above variation in post-bake time has not resulted in detectable differences in load-deflection response. After post baking, the buns are cut to the desired shape and samples are removed for testing.

To reduce corrosion of machining tools, neutralization of the foam was studied. Several trimmed buns were placed in a vacuum chamber and evacuated to 6 Torr. Ammonia gas was then passed through the chamber for 90 min. Aqueous slurries of finely powdered specimens of foam displayed pH values from 8 to 9, thereby

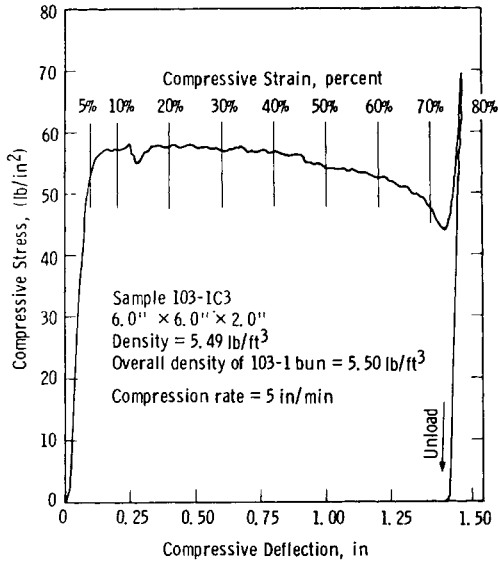


Fig. 4. Typical Instron C-D curve.

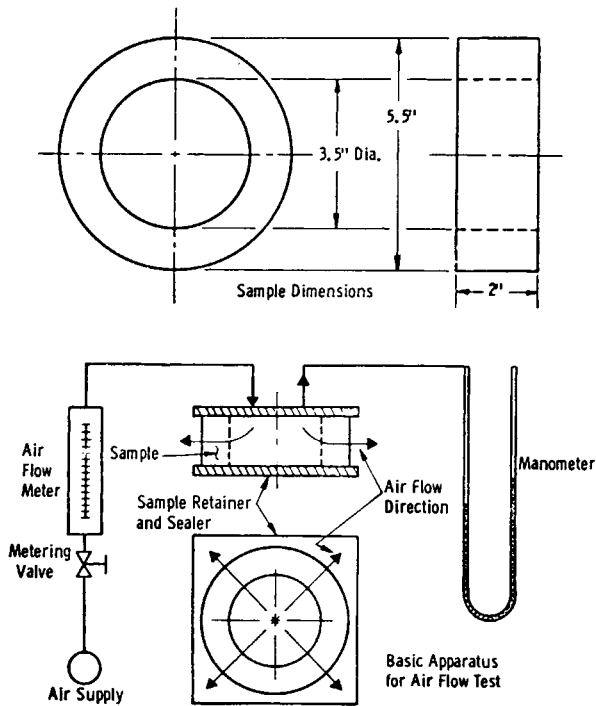


Fig. 5. Permeability test fixture and sample size.

indicating the feasibility of this type of neutralization process. The neutralization did not produce any discernible effects on the compression-deflection and permeability characteristics of the foam.

MECHANICAL TESTS AND REQUIREMENTS

Compression-Deflection Requirements

The compression-deflection properties that were specified during the initial phase of this development are shown in Figure 3. At low or essentially static rates of compression the foam exhibits stress-strain properties lying between the upper and lower static limit curves. Under a high strain rate of 1500 in./in./min the compression-deflection characteristics of the foam are delineated by the space between the upper-dynamic-limit and lower-static-limit curves.

Compression-Deflection and Density Measurements

After the foam has been post-baked the block is trimmed to $24 \times 18 \times 14$ in. Samples $6 \times 6 \times 2$ in. are then cut from various sections of the bun and crushed in an Instron Universal Test Machine at a rate of 5 in./min producing an autographic record as shown in Figure 4.

Permeability Measurements

A hollow cylindrical specimen having uniform wall thickness, 3.5 in. i.d. \times 5.5 in. o.d. \times 2.0 in. height, is cut from a 2 in. thick sample taken from near the center of the bun. The pressure differential of air flowing at a rate of 17 ft³/min from the center of the specimen in an outward radial direction is measured as shown in Figure 5. It is required that the foam have a sufficiently open cell structure so that the pressure drop will not exceed 31 Torr.

DATA OBTAINED

The effects of variations in the process variables and chemical composition of the foam are described in the following papers, Parts II and III.

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