Effects of Density and Structure on Load Bearing and Permeability Characteristics of a Family of Shock Mitigating Phenolic Foams

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Synopsis

The effects of reaction rate and density on the properties of the phenolic foam described in the first paper were studied. Process and formulation variables were examined through altering the basic chemical composition described below, in which all parts are by weight; phenolic resin two component intermediate, 200 parts; hydrophilic surfactant, 0.25 parts; lipophilic surfactant, 0.50 parts; fluorocarbon blowing agent, 12 parts; 47.5 wt % sulfuric acid, 25 parts; and 80 wt % phosphoric acid, 15 parts. Compressive stress values at 20% deflection were utilized for comparing the effects of the studied parameters on the load bearing cabability of the foam. Pressure drop of air flowing through the foam was employed as a measure of the permeability or breathability. Permeability load bearing functions were identified as a potential means for optimizing the relationship between breathability and compression-deflection characteristics. The overall effects of cell structure on the relationship between load bearing and density have been related in a qualitative manner.

INTRODUCTION

The first paper of this three-part series described the physical properties required for the shock absorbing phenolic foam and the chemical formulation and processing developed to obtain this material.

To learn how to adjust and optimize the properties of the foam, we undertook a detailed study of the effects of variations in the chemical formulation and process conditions (Parts II and III). Process variables consisting of temperature and aging characteristics of the resin were studied using the chemical composition described below, in which all parts are by weight (cf. Part I for description of materials and process); BRL 2760, 180 parts; BRL 2759, 20 parts; Tween 60, 0.25 parts; Span 80, 0.50 parts; fluorocarbon 113, 12 parts; 47.5 wt. % sulfuric acid, 25 parts; 80 wt. % phosphoric acid, 15 parts. The concentration units, consisting of parts, that are employed in the figures are based on the above formulation.

Variations in chemical composition were made by varying the concentration of a particular ingredient while otherwise maintaining the above described formulation and employing a nominal processing temperature of 18°C. Foams in a given series were prepared using the same batch of phenolic resin. Furthermore, since the resin continues to polymerize slowly even while under refrigeration, runs of a comparative series were made within a week of each other.

Compressive stress at 20% deflection S was arbitrarily selected to represent the load bearing capability of the foam. Pressure drop of air flowing through the foam ΔP was employed as a measure of the breathability or permeability.
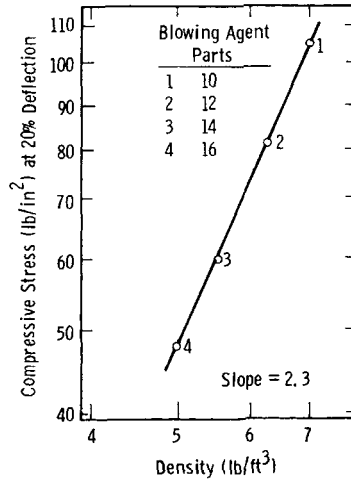
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Fig. 1. Effect of blowing agent on density and compressive stiffness of foam.
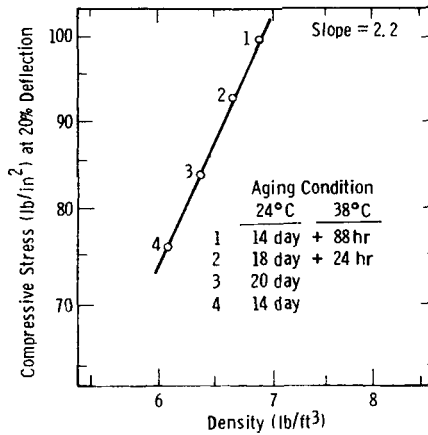

Fig. 2. Effect of aging of phenolic resin intermediates on density and load bearing of foam.

Since an increase in the density D or volume fraction polymer in the foam matrix tends to give a reduced permeability by providing less space for air to pass through, we employed a figure of merit relating to the openness of the cell membranes $\Delta P/D$, which was plotted against the investigated variable.   An analogous relationship, termed a permeability-load bearing function $\Delta P/S$ was similarly plotted.   The latter is particularly useful for design purposes, since it suggests a potential means for optimizing the relationship between breathability and compression-deflection characteristics.

EFFECT OF REACTION RATE AND DENSITY ON LOAD BEARING AND STRUCTURE

While the rate of reaction is not a design property of the completed foam, it nevertheless is important since it determines whether manufacture of a certain foam is feasible, the cost of processing equipment, and influences the properties of the finished product.

Excessively fast rates of reaction are to be avoided due to the difficulty in filling

TABLE I
Factors Affecting Dependency of Compressive Stress on Density

Variable	Range of variation	Slope of plot of log stress/log density $\left(\dfrac{\log stress}{\log density}\right)$
Blowing agent	10–16 parts	2.3
H_2SO_4 (47.5 wt. %)	15–35 parts	2.7
H_3PO_4 (85 wt. %)	0–30 parts	3.3
Tween 60	0.125–1.00 parts	2.3
Span 80	0–2.0 parts	1.6
Total surfactant (Tween 60/Span 80 = 0.5)	0–3.0 parts	2.1
BRL 2759	0–20 parts	3.2
Aging of Resins	(see Fig. 2)	2.1
H_2O (change in H_2O concentration from standard formula)	(−2.5)–(+12.5) parts	2.1
Temperature	15–24°C	3.5

TABLE II
Effect of Processing Temperature and Composition on Cell Size

Temperature (°C)	Parts H_3PO_4	Parts Span 80	Cells/in.
15	15	0.5	24
18	15	0.5	21
21	15	0.5	18
24	15	0.5	13
18	0	0.5	10
18	7.5	0.5	...
18	15	0.5	29
18	22.5	0.5	38
18	30	0.5	40
18	15	0	80
18	15	0.25	42
18	15	0.5	26
18	15	1.0	19
18	15	1.5	14

a mold without pouring foam onto already creaming and rising material. Even for a continuous conveyor process a very fast reacting material will have the disadvantage of requiring a very large capacity foam machine. A reaction rate that is too slow permits separation of the mixed ingredients prior to their reaction with the result that the foam does not possess uniform properties throughout the bun.

One cannot predict with assurance what effect the overall reaction rate will have on the foam's density, load bearing, and permeability. This is illustrated by the effect of increasing the concentration of sulfuric acid which increases the rate of the polymerization reactions and the exothermic temperature. Since in this case the higher rate of gelation is relatively more important than the more vigorous expansion of the blowing agent, the resultant foam has a greater density accompanied by higher load bearing and reduced breathability properties. However, in contrast, increasing the rate of reaction by employing a higher process temperature favors the expansion of the blowing agent relative to the rate of polymerization. Thus foams prepared at higher temperatures display reduced densities, lower load bearing capabilities and higher permeabilities.
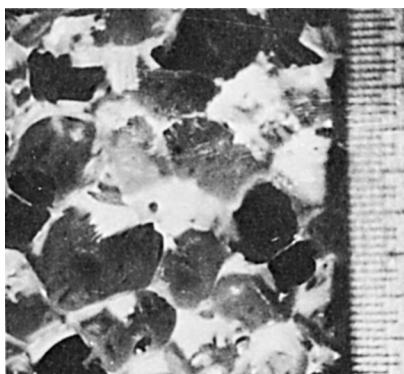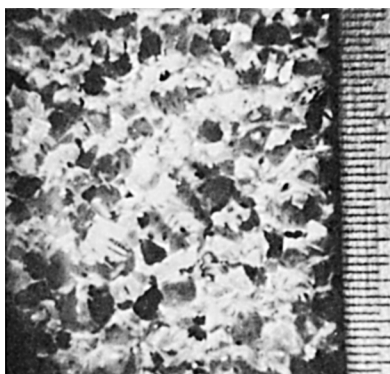
0 Parts H_3PO_4 15 Parts H_3PO_4
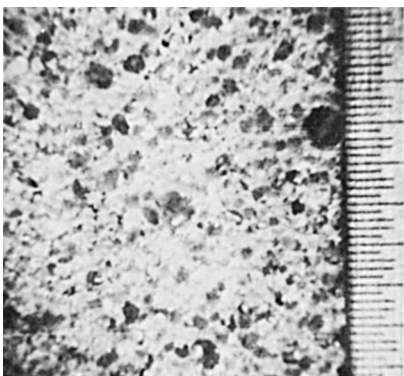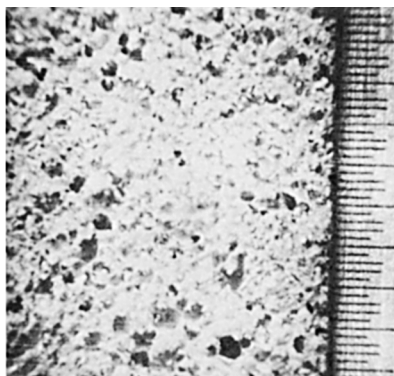
22. 5 Parts H_3PO_4 30 Parts H_3PO_4
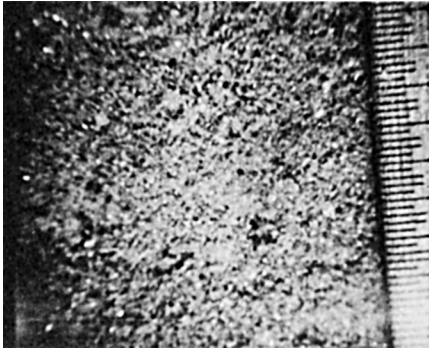
(Scale Division = 0. 01 in.)

Fig. 3. Effect of phosphoric acid concentration on cell size.

Density has a very strong influence on the load bearing properties of the foam (Figs. 1 and 2, Table I). Its dependence on compressive strength σ has been expressed by previous investigators[1–3] by the empirical relation

$$\sigma \propto D^a$$

in which D is the bulk density of the foam and a is a constant. Values of the constant a in the range of 1.4–1.6 have been reported for rigid polyurethane foams. Generally, the load bearing capability of phenolic foams herein discussed is much more dependent on density.

A single log-log plot of the compressive stress versus density for all of the foams prepared in this study displayed such a wide scatter of the data points that we felt a "best straight line" drawn through the points had little meaning. However, smooth curves resulted from stress versus density plots in which the density was affected by a single composition or process variable (see Figs. 1 and 2 for typical stress-density plots). The exponential dependency of compressive stress on density obtained from the slopes of such curves is shown in Table I.
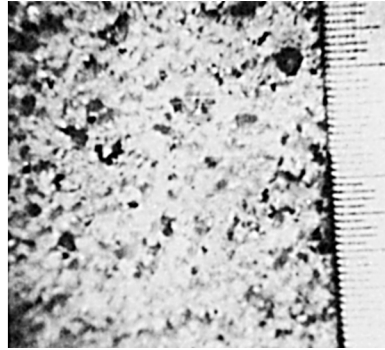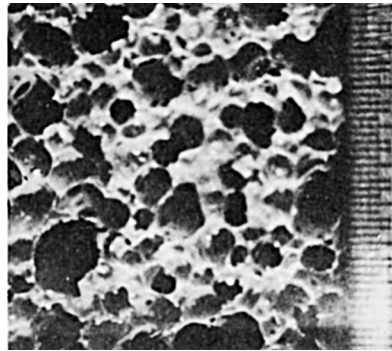
0 Parts Span 80   0. 25 Parts Span 80
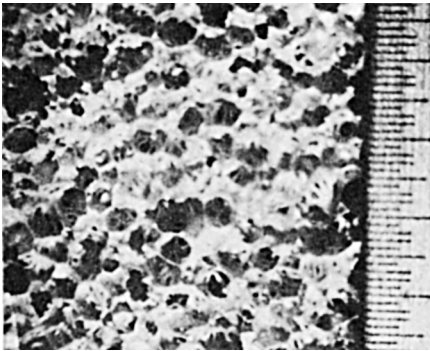
0. 5 Parts Span 80   1. 0 Parts Span 80

(Scale Division = 0. 01 in.)

Fig. 4. Effect of Span 80 concentration on cell size.

The large differences obtained in the exponential relationships suggest that variations in at least most of the process and composition variables affect, in addition to density, other intrinsic properties of the foam.   This is not surprising in view of the highly involved phenomena occurring during the formation of the foam.   For example, in addition to previously described factors such as the rate phenomena for sulfuric acid are its highly complex surface actions in which the most conspicuous effects consists of a diminution of cell size with increasing acid concentration.   The acid also affects the structure and composition of the polymer chains giving a more rigid material as its concentration increases.

Even though we cannot provide a quantitative explanation for the reported relationships between load bearing and density, we have been able to relate qualitatively the overall effects to cell structure.   Comparing the relative cell sizes of the respective members of a series, we find that when the cell size diminishes with increasing density the exponent, a, tends to be large.   The smallest exponents result when the cell size tends to increase with density.   This is evidenced by the marked increase in coarseness of the cell structure with density as the concentrations of water and Span 80 are increased.   In contrast, the rel-
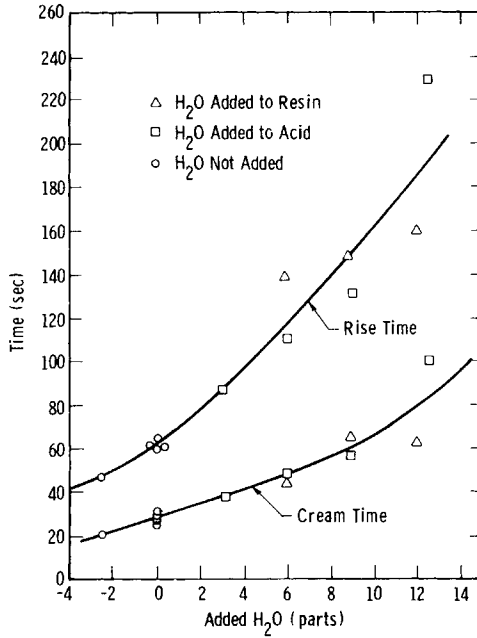
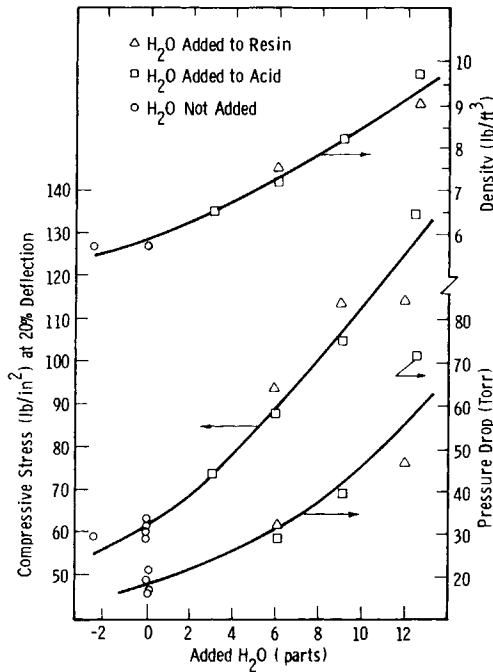Fig. 5. Effect of water on rate of reaction.

Fig. 6. Effect of water on load bearing, permeability, and density.

atively high exponential dependencies of compressive stiffness on density are obtained from the previously described series in which the increasing density, resulting from higher concentrations of phosphoric acid, sulfuric acid, phenolic resin BRL 2760, and lower processing temperature, is accompanied by a dimi-
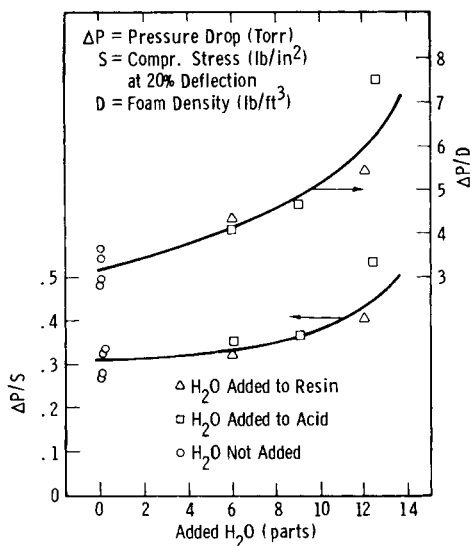
Fig. 7. Effect of water permeability functions.

nution in cell size. An example of this effect is shown in Table II which lists the cell sizes for the highly exponentially dependent temperature and phosphoric acid series and the far less dependent Span 80 series. Photomicrographs (Figs. 3 and 4) vividly depict the apparently opposing effects of increasing concentrations of phosphoric acid and Span 80 on cell size.

An example of the effect of reaction rate on properties of the finished product is provided by adjusting the concentration of water in the formulation. In a series of experiments, the concentration of water was increased by adding it to either the resin or acid components and decreased by employing acid solutions more concentrated than the standard. Since water dilutes the catalyst and reactants and absorbs heat from the exothermic reaction, the rate of reaction decreases with increasing water content (Fig. 5).

An increase in the density and compressive stress values with added water (Fig. 6) indicates that the expansion processes are more severely retarded than those involving the polymerization of the resin. Analogously to the effect of increasing the concentration of sulfuric acid, permeability decreases with increased water content (Figs. 6 and 7). However, the relatively slight effect on the permeability–load-bearing function up to about 10 parts added water indicates a means to obtain higher load bearing while experiencing only a minor diminution in breathability.

In Part III we describe the effects of the major process and composition variables on the properties of the foam.

References

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