Effects of Composition and Processing Conditions on the Properties of a Series of Shock Mitigating Phenolic Foams

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Synopsis

The effects of variations in the chemical composition and processing conditions of the series of phenolic foams described in the two previous papers were studied. Compressive stiffness and density increased with increasing concentrations of the acid catalysts, the slower reacting phenolic resin component, water, the lipophilic component of the surfactant system, and age of the phenolic resins. These properties decreased with increasing concentration of the fluorocarbon blowing agent and process temperature. The compressive stiffness and density increased to a maximum and then decreased with increasing concentrations of the hydrophilic surfactant. Permeability or "breathability" of the foam decreased with the hydrophilic surfactant at low concentrations and then became essentially independent of further increases of this component. Increasing concentrations of the lipophilic surfactant gave foam having greater breathability. In all other cases the permeability of the foam decreased as its density increased. Effects of the variations in processing and composition on the dependency of load bearing upon density, on relationships between permeability and density and permeability and compressive stiffness, and upon cell structures are also described.

EFFECT OF PROCESS AND COMPOSITION VARIABLES ON PROPERTIES

A detailed parametric study of the effect of process and composition variables was performed by varying the components and processing conditions of the phenolic foam system described in Parts I and II of this investigation.

Blowing Agent

Variation of concentration of blowing agent, 1,1,2-trichloro-1,2,2-trifluoroethane, was explored over the range of 10–16 parts (Figs. 1 and 2). Adjustment of the quantity of blowing agent provides a convenient method of controlling density and load bearing properties. A decrease in compressive stiffness of close to 60% results from an approximately 60% increase in the quantity of blowing agent. The expected decrease in permeability, as indicated by the higher pressure-drop values, follows the increased density at lower blowing agent concentrations. Over the concentration range studied, the degree of openness of the cells ($\Delta P/D$) appears essentially constant; however, a moderate increase of the permeability–load-bearing function ($\Delta P/S$) occurs with increasing quantities of blowing agent.

Journal of Applied Polymer Science, Vol. 23, 341–351 (1979)

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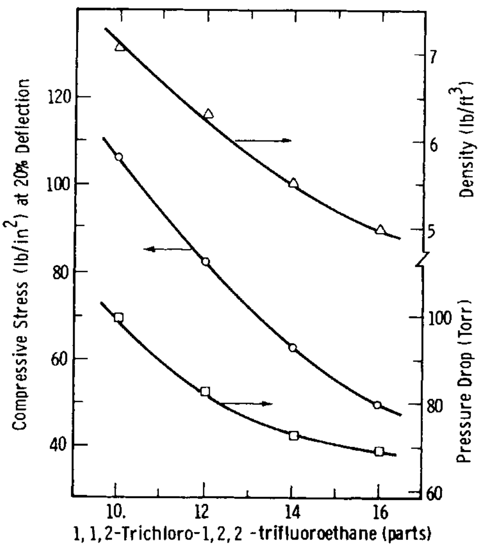

Fig. 1. Effect of blowing agent on load bearing, permeability, and density.

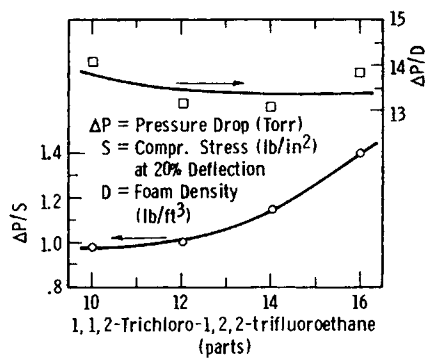

Fig. 2. Effect of blowing agent on permeability functions.

Temperature

A series of foams was studied in which the nominal processing temperature was varied between 15 and 24°C. The expected reduction in reaction rate as the temperature is reduced is shown in Figure 3. An almost 100% increase in rise time results by reducing the temperature from 24 to 15°C. As the temperature is increased, the load bearing decreases sharply and the cells become increasingly open (Figs. 4 and 5). The increase in permeability with temperature is attributed to the more vigorous formation and expansion of volatiles which cause rupturing of the cell membranes.

Sulfuric Acid

Figure 6 shows the rapid increase in rate of reaction with increasing sulfuric acid concentration. At the high concentrations of acid the resultant high rate of rigidification of the foam matrix relative to the expansile capability of the

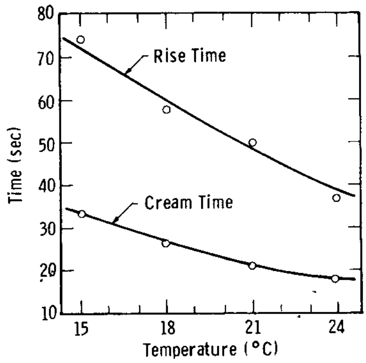

Fig. 3. Effect of process temperature on rate of reaction.

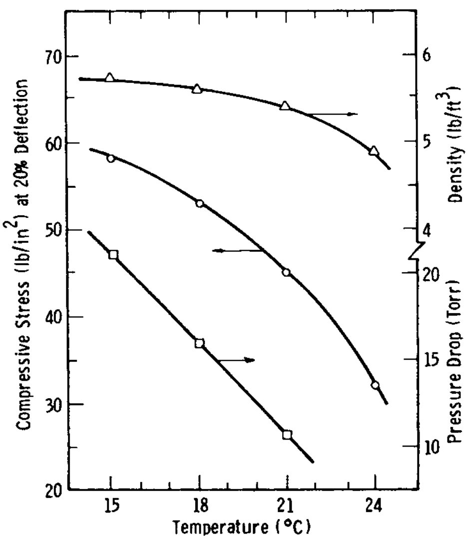

Fig. 4. Effect of process temperature on load bearing, permeability, and density.

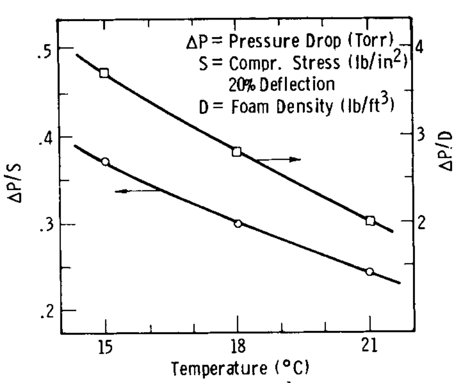

Fig. 5. Effect of temperature on permeability functions.

blowing agent results in high density and load bearing and low permeability properties (Figs. 7 and 8). The combination of rate and surface effects result in a sharp diminution of cell size with increasing acid concentration.

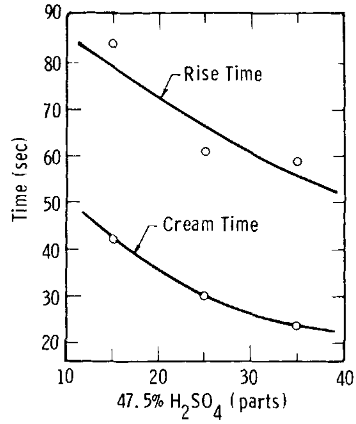

Fig. 6. Effect of sulfuric acid concentration of reaction.

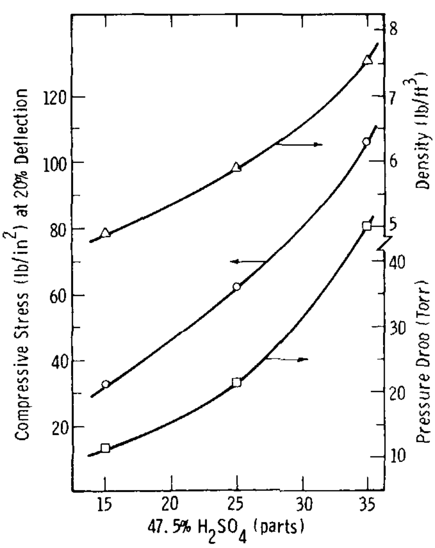

Fig. 7. Effect of sulfuric acid on load bearing, permeability, and density.

Phosphoric Acid

The effect of variation of the concentration of phosphoric acid on the rate phenomena, as expected from a consideration of the relative strengths of the acids, is less pronounced than that for sulfuric acid. In addition to moderately reducing the time required for gelation of the resin (Fig. 9), increasing concentration of phosphoric acid greatly decreases the permeability of the foam while imparting higher load bearing capability (Figs. 10 and 11). Phosphoric acid appears to have the effect of reducing the interfacial surface energy of the components of the foaming system. This phenomenon is depicted in Part II, Figure 3 in which the cell size is shown to decrease dramatically with increasing acid concentration.

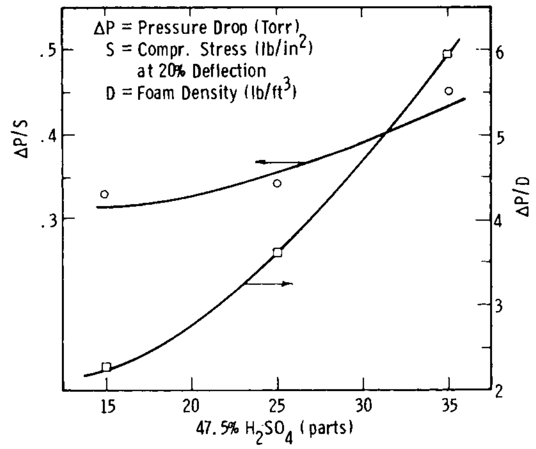

Fig. 8. Effect of sulfuric acid on permeability functions.

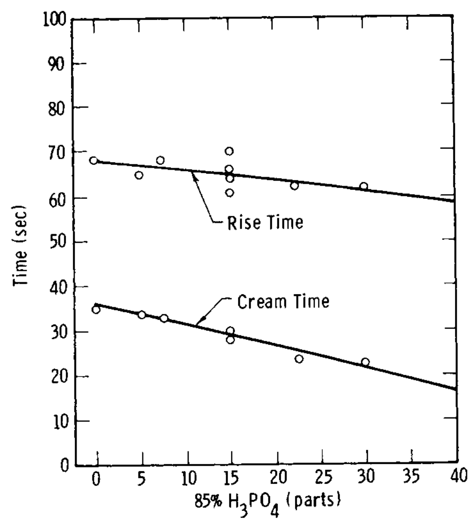

Fig. 9. Effect of concentration of phosphoric acid on rate of reaction.

Phenolic Resin Composition

Effect of composition of the phenolic resin on foam properties was studied by employing blends of resin BRL 2759 and BRL 2760. Union Carbide suggests use of BRL 2759, BRL 2760, and BRL 2761 for preparation of low-, medium-, and high-density foams, respectively.[1,2] Since foams having greater densities than necessary for meeting our requirements were obtainable with BRL 2760, work was not pursued with BRL 2761. It would have been interesting to determine whether greater permeability would result from using BRL 2761 with relatively large quantities of BRL 2759 as compared with the currently employed system of BRL 2760 with lesser concentrations of BRL 2759.

Foams prepared from blends containing from zero to 30% BRL 2759 in BRL 2760 showed that as the BRL 2759 is increased the overall rate of the foaming reaction increases, load bearing and density decrease and breathability is improved (Figs. 12–14). The large increase in cell size, 21 and 8 cells per in. for 10%

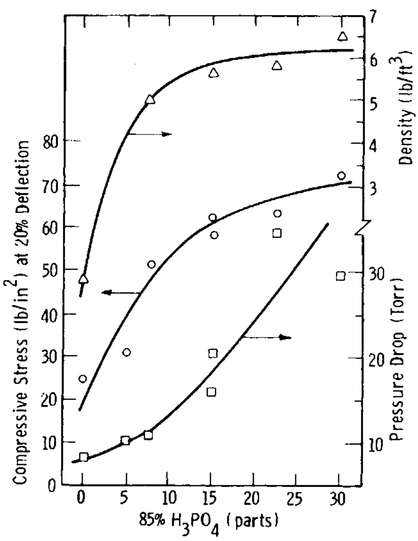

Fig. 10. Effect of phosphoric acid on load bearing, permeability, and density.

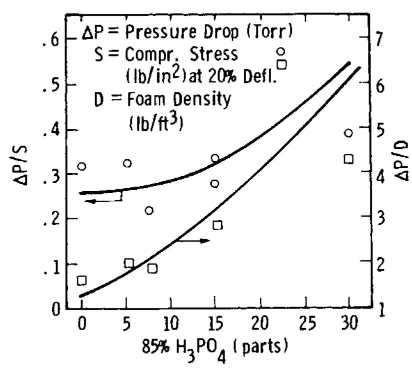

Fig. 11. Effect of phosphoric acid on permeability functions.

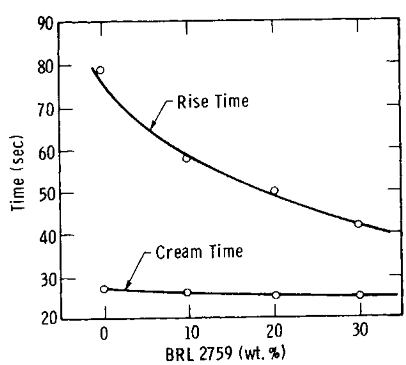

Fig. 12. Effect of phenolic resin composition on rate of reaction.

and 20% BRL 2759, respectively, accompanying the reduced density is consistent with the very large dependency of load bearing on density.

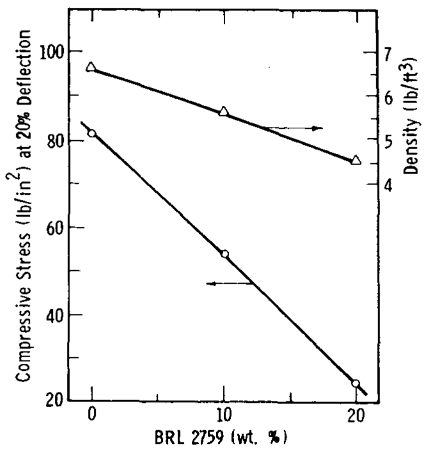

Fig. 13. Effect of phenolic resin composition on load bearing and density.

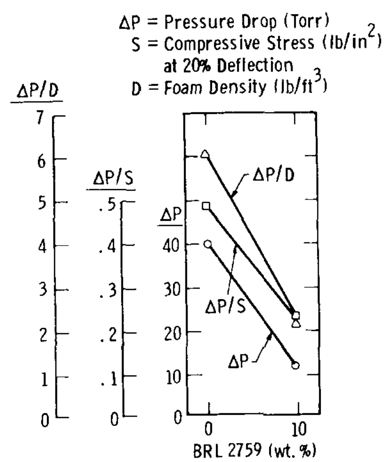

Fig. 14. Effect of phenolic acid resin composition on permeability characteristics of foam.

Aging of Phenolic Resins

The study of the effect of aging of the phenolic resins was accelerated by permitting the resin mixture, 90% BRL 2760 with 10% BRL 2759, to age at room temperature and at 37°C. As the resin polymerizes during storage, it gives more dense and concomittantly higher load bearing and less breathable foam (Figs. 15 and 16). The importance of storing the resins at close to 0°C is evident.

Surfactant System

While the surfactants do not have a discernible effect on the rate of reaction, they strongly influence the permeability and compression-deflection characteristics of the foam matrix.

Tween 60 stabilizes the foam during its formation as evidenced by the collapse of rising foam in which it was omitted while Span 80 was the only surfactant. As its concentration increases from 0.125 to 0.25 parts, while Span 80 is maintained at 0.5 parts, the cell size of the foam diminishes sharply from 17 to 42 cells per in. At higher Tween 60 levels there is no apparent trend in the size of the cells.

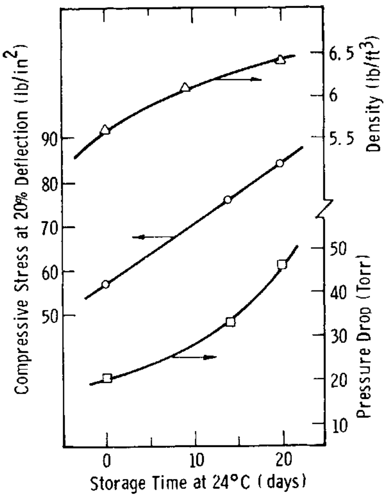

Fig. 15. Effect of aging of phenolic resins on load bearing, permeability, and density.

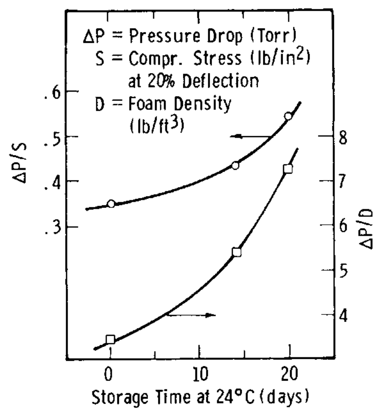

Fig. 16. Effect of aging of phenolic resins on permeability functions.

While maintaining a Span 80 concentration of 0.5 parts, the compressive stress increases with Tween 60 until 0.37 parts is reached and then diminishes with further increase in the concentration of Tween 60 (Fig. 17).

The pressure drop of air flowing through the foam matrix increases with Tween 60 reaching an apparent maximum at approximately 0.4 parts and then remains essentially constant (Fig. 17). Since the density of the foam decreases at the higher levels of Tween 60, the lack of a corresponding improvement in breathability indicates that the cells are becoming progressively more closed while the concentration of this surfactant is increasing. The plot of the effect of Tween 60 on the openness of the cells and load bearing function (Fig. 18) also indicate the increasingly closed cell structure at higher levels of this surfactant. Apparently a cell structure that provides maximum load bearing properties is obtained at an intermediate Tween 60 concentration (Fig. 17). While the cell size diminishes and the structure becomes increasingly closed, the density of the matrix increases thereby giving higher compressive stress values. After about 0.4 parts Tween 60 the apparent increasing of the closed cell content while not continuing the trend of reducing the cell size results in a reversal of the effect

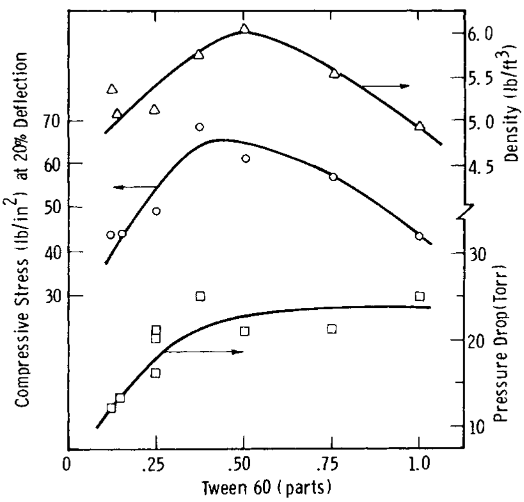

Fig. 17. Effect of Tween 60 on load bearing, permeability, and density.

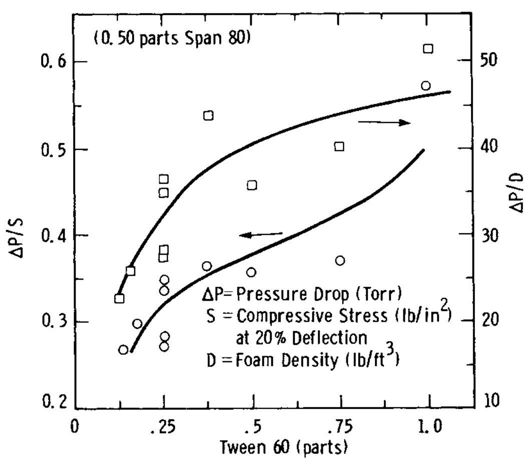

Fig. 18. Effect of Tween 60 on permeability functions.

of the Tween 60 concentration on load bearing and density. This phenomenon is attributed to the more effective trapping of the blowing agent and other volatiles within the closed cells thereby giving a net reduction in density and subsequent load bearing of the foam.

Span 80, the lipophilic component of the surfactant system, exhibits behavior that is at least partially antithetical towards that of Tween 60. Not only is its presence not required to stabilize the foam during rise but it tends to act as a destabilizer. Formulations employing 0.5 parts and perhaps even less Span 80 require the inclusion of Tween 60 to avoid collapse; whereas, a fine cell foam exhibiting good stability during the crucial rise period was prepared in which 0.25 parts Tween 60 was employed and Span 80 was omitted. Observing that stable foam has been prepared in which both surfactants are omitted, it appears that Tween 60 is necessary to counterbalance the destabilizing effects of Span 80.

Foams were studied in which the Span 80 was increased from 0 to 2.0 parts while the Tween 60 was held constant at 0.25. As the concentration of the Span

80 is increased the density and load bearing increase, the matrix becomes more permeable and the cells become progressively larger (Figs. 19 and 20, and Table II and Fig. 4 of Part II). Thus, Span 80 can be employed efficaciously to provide the unusual combination of increased breathability and load bearing. We attribute the unusual behavior of the Span 80 to its proclivity towards providing a highly open cell structure. As the foam matrix displays increasingly open cell character, it loses efficiency in trapping the expanding blowing agent thereby not rising to its full extent. The relatively low rate of increase of compressive strength with concentration of Span 80, especially above 0.5 parts, is attributed to the corresponding increase in the coarseness of the cell structure. This effect on cell geometry has been shown to give relatively low exponential dependencies of load bearing on density.

A series of runs was made in which the total surfactant concentration was varied while maintaining a constant 2:1 weight ratio of Span 80 to Tween 60. The compressive strength (Fig. 21) appears to follow almost an additive type relationship between the individual variations of each surfactant. Thus, adjustment

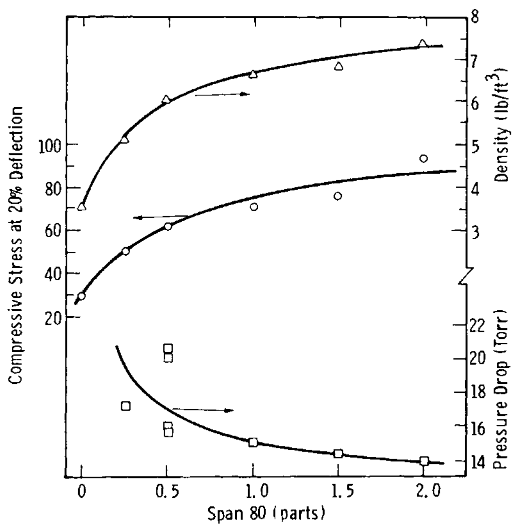

Fig. 19. Effect of Span 80 on load bearing, permeability, and density.

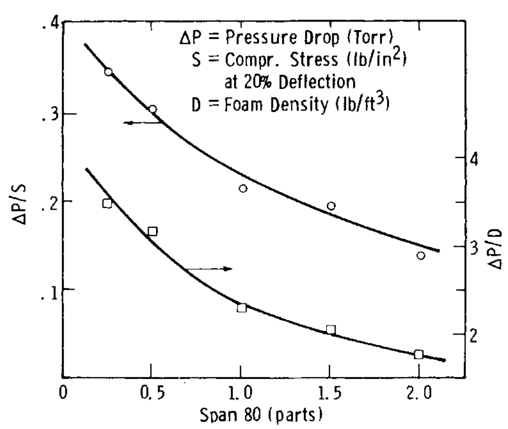

Fig. 20. Effect of Span 80 on permeability functions.

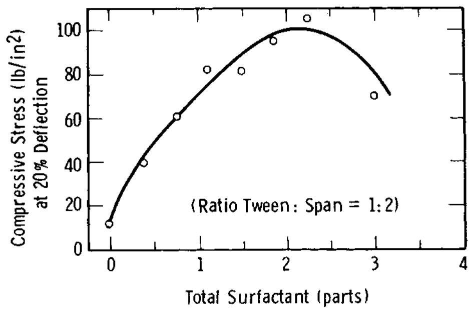

Fig. 21. Effect of total quantity of surfactant at constant composition ratio on load bearing.

of both the individual concentrations and the hydrophilic-lipophilic balance of the surfactants provides a powerful means for controlling the physical properties of the foam.

CONCLUSIONS

A phenolic foam system has been developed for use in an application requiring energy absorbtion and shock mitigation. The rigid foam is characterized by having the required combination of high breathability and load bearing capability.

Compressive stiffness and density of the foam increase with increasing concentrations of either acid, BRL 2760, water, Span 80, and with decreasing concentrations of BRL 2759 and the blowing agent. The load bearing capability increases passing through a maximum and then decreases with increasing concentration of Tween 60. Increasing process temperature gives a reduction in the density and compressive stiffness of the foam. Breathability or permeability decreases with increasing density of the foam in every case except when density increases with increasing concentrations of Span 80. Employing relatively high concentrations of Span 80 provides the unusual combination of high load bearing and breathability; however, this approach is limited by the resultant instability of the foam during its period of rise.

Data presented on the effects of variations of the processing and composition parameters provide the knowledge necessary for adjusting or "fine tuning" the permeability and compression-deflection characteristics of the foam.

References

1. *Bakelite Phenolic Resins for Rigid Foam,* Phenolic Product Data Bull., Union Carbide Corp., New York, 1976.

2. A. J. Papa and W. R. Proops, *Plastic Foams,* Part II, Marcel Dekker, New York, 1973, Chap. 11.

Received July 8, 1977
Revised November 14, 1977