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VIII. Plastic Behavior 101
IX. New Processes 106
A. Use of Organic and Inorganic Blowing Agents 106
B. Preparation of Supersoft Foams 110
Bibliography 111

I. INTRODUCTION

Of the rigid foams currently sold commercially, polystyrene foams dominate the market with urethanes second. Polystyrene foams were first made in Great Britain in 1943(1); however, this grew out of an earlier development in Sweden in the mid 1930's. Extruded polystyrene foams were made available commercially in the United States by Dow Chemical Company in 1943(1). The foam was used during World War II for the construction of life rafts on troop transports and for floating equipment to shore.

Polystyrene foams can be processed either by the direct extrusion and expansion of foamable beads and granules or by the injection of a blowing agent into the resin at high pressure, followed by expansion at atmospheric pressure. Two of the early methods of manufacture were those (2) of:

(*a*) Dow Chemical Company, in which polystyrene and an expanding agent, generally a low-boiling chlorocarbon such as methyl chloride, were blended together and subsequently extruded.

(*b*) Badische Anilin & Soda Fabrik, in which styrene monomer and a low-boiling hydrocarbon were mass-polymerized together. The resulting mixture was ground into chips and subsequently converted into low-density foam by extrusion.

The Dow process is still being used for large-scale production of extruded Styrofoam® (estimated at > 250,000 board feet in 1967). The original BASF process, however, has been displaced, mainly by the improved suspension polymerization process which produces foamable polystyrene beads. The low-boiling hydrocarbon blowing agent can be incorporated either during the polymerization reaction or later in a separate impregnation step using heat and pressure.

All current producers of foamable beads operate under a license from BASF(3–5). Since 1954 significant innovations in both process and product have been made. In spite of the major position of polyurethane foam in the cellular plastic field, the rate of growth of polystyrene foam, especially in the packaging field, is rapid enough to maintain it as the most popular expanded plastic today. The production of expandable beads (FIP beads) was estimated by *Modern*

Plastics to be 125 million lb in 1967 and is predicted to climb to 450 million lb by 1975. However, the nature of the bead and the bead-molding process is such that it is limited to rather large cross sections (> 1/8 in.). Hence mass production in the packaging area, particularly that of rigid thin-wall containers and sheet, is very limited.

Several variations of the BASF process may have far-reaching significance. Processes that produce foamable beads directly in one step have been patented; for example, pentane is injected into an extruder processing high-molecular-weight crystal grade polystyrene (6). These processes are important since they provide the proper feed stock for the extrusion of expandable sheet used in thermoformed trays and containers.

Polyurethane foams have one major advantage over polystyrene foam, that is, "put-in-place" foaming or "on-the-site placement." Because high-temperature methods are required in the manufacture of polystyrene foam, on-site foaming is not feasible. Polystyrene beads require a large quantity of heat to induce foaming; therefore, in-place foaming is out of the question. The low cost of polystyrene (6–8c/bd ft), however, is a strong inducement for its use.

Rigid thermoplastic polystyrene foams are available in densities ranging from 1 pcf to over 20 pcf. The foams can be purchased as film, sheet, and rod, made by extrusion; or as large slabs and containers, made by steam-molding techniques. Foamed film and sheet can be thermoformed into various low-cost trays and profiles used in the packaging industry.

The thermal insulation properties and low cost of polystyrene foam make it competitive with other commercial insulating materials. Because of its closed-cell structure, polystyrene foam has excellent water resistance and low water vapor transmission. These properties make it adaptable as a support for floating docks and for other flotation applications. The closed-cell structure and the inert surface render polystyrene foams resistant to rot and mold growth.

Until recently, polystyrene foams have not been noted for their solvent resistance. They are attacked by the same agents that affect the parent resin. However, new types of polystyrene copolymer foams have been produced that have excellent solvent resistance. Most aqueous systems, with the exception of strong oxidizing acids do not affect polystyrene foam.

Polystyrene foams are noted for their excellent balance of cost and performance in the insulation and packaging field. The superior shock-absorbing properties of polystyrene foam, coupled with low cost and high insulation efficiency, make it ideal for such applications

as low-temperature perimeter insulation, metal roof decks, and trays, cups, and other molded items. The mechanical properties are not affected by low temperature, and the dielectric properties are excellent.

The various methods for producing polystyrene polymer are discussed in Appendix A, Volume II. The means of producing the polystyrene and polystyrene copolymer foams, and the relationship between process and product performance, will be described in the following sections. The effect of polymer properties on foam properties is discussed in Chapter 3, Volume II. It is not our intent to review all the literature and present a multitude of unrelated facts; rather we shall cover the literature pertinent to our objective, which is to keep the reader informed of foam technology as one coherent body of science.

II. METHODS OF PREPARATION

Methods of producing polystyrene foams from *expandable beads* are as follows:

(*a*) Preparation of expandable beads and pellets.
(*b*) Pre-expansion of beads.
(*c*) Conditioning of the expanded bead.
(*d*) Molding of the expanded bead.
(*e*) Extrusion of expandable bead and pellets to form sheet and film.

Expandable polystyrene bead is not the only raw material used for extruding polystyrene foam in various profiles. Crystal polystyrene is used in the Dow process, and there is increasing evidence that foam sheet producers are turning to crystal polystyrene feed instead of FIP beads.

In this section we will describe the processes, and later we will analyze the chemical and physical phenomena taking place during these operations and discuss how the processes specifically influence the product performance, that is, the structure and properties.

A. Preparation of Expandable Polystyrene Beads

Expandable polystyrene bead is a raw material used in molding and extruding polystyrene foam in various profiles. The bead consists of high-molecular-weight crystal grade polystyrene (molecular weight is 180,000–270,000) and 5–8% low-boiling aliphatic hydrocarbon blowing agent (i.e., pentane or isopentane). Probably the most

commonly employed method for producing expandable polystyrene beads is the suspension polymerization process, which utilizes liquid styrene monomer, dispersed in an aqueous medium containing hydrocarbon foaming agent (pentane) and polymerization catalyst. The dispersion is heated for a predetermined time and temperature to produce a high-molecular-weight polystyrene bead that contains 5–7% pentane. The beads are filtered, washed, and air dried(8).

This process (or a slight modification thereof) can be used with other blowing agents, such as esters, alcohols, ethers, ketones, or aldehydes(9–11). However, the most economical one is pentane, which has the best cost/performance ratio because it fulfills the requirements of the process. It is nontoxic, gives high expansion at low cost, leaves no residue, boils at or below the softening point of the resin (second-order transition of polystyrene), and exerts very little solvent action upon the polymer.

The beads are between 0.010 and 0.100 in. in diameter if made by the BASF suspension polymerization process. The polystyrene expandable bead is available in various sizes for specific applications, as listed in Table I.

TABLE I

Bead diameter, in.	Size classification	Application
0.030–0.080	Large	Insulation and building panels (steam chest molding)
0.050–0.020	Medium	Molded items, e.g., packages, coolers, refrigerator components
0.030–0.010	Small	Thin-walled containers, e.g., coffee cups

Bead size has been observed to be directly proportional to expanded volume; that is, large beads can be expanded to lowest density (largest volume) in heavy sections, while small beads can be molded in thin sections but give products of higher density.

The bead is available in several types:

Regular.
SE: self-extinguishing (according to ASTM D-1692).
FR: self-extinguishing (according to ASTM 2125-62T).

Expandable polystyrene pellets are also used in the molding and extrusion of various foamed articles. The pellets contain polystyrene (180,000–270,000 molecular weight), special nucleating agents

(sodium bicarbonate and citric acid), and the pentane blowing agent. The patented (13) nucleating system allows one to regulate the cell size and rigidity of the extruded sheet.

The small cylindrical pellets measure 0.06–0.03 in. if prepared by the Sun Chemical process (direct injection of pentane into a pelleting extruder). The bulk density of the beads is approximately 35–40 pcf.

Expandable polystyrene beads and pellets have two disadvantages; (*a*) the bead is unstable for long periods of time because of pentane migration out of it, and (*b*) pentane is inflammable and presents a fire hazard to a manufacturer. Figure 1 shows the loss of blowing agent as a function of time when beads are stored under standard conditions. This means that one must keep rotating the stock of beads and maintain an up-to-date analysis of the pentane content of the beads, since the pentane content (% volatiles at 212°F) will determine processing characteristics, ultimate density, and economics.

Expandable beads should be stored below 90°F and in full containers (to reduce gas volume space). After the containers are opened, a time lag of 10 min is suggested to allow fumes or pentane vapor to dissipate out of the container. The flash point of Dylite beads is 120°F, and their fire point is 140°F. Care must be exercised to prevent static electricity and sparks from igniting the blowing agent vapors. This is done by using hoods to dissipate vapor and grounding all equipment to reduce sparks (18).

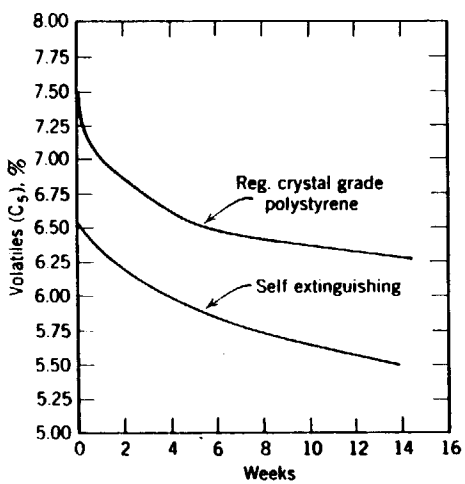

Figure 1 Expandable polystyrene beads stored in fiber drum at 70–75°F.

Freon blowing agents are nonflammable and nontoxic.* The use of Freon 12 or 11 as an expanding agent for polystyrene can be expected to produce a material less prone to ignite.

Freon 12 (CF_2Cl_2) will stay in polystyrene for as long as pentane will, if it is put in properly. The lower solubility (S) decreases permeation out of the bead ($P = DS$). Cost and high molecular weight are disadvantages of fluorocarbons.

B. Pre-expansion of Expandable Beads

Accurate control of foam density is required in all applications of polystyrene foam. Expandable polystyrene is prefoamed until the density required in the ultimate molding has been obtained. This means that the density of the final object is determined in the prefoaming stage (17). Expandable beads can be pre-expanded by means of steam, hot water, or air at 90–115°C or by use of infrared or other sources of heat (14, 16).

The problem of clumping, which may occur during pre-expansion because of partial fusion from overheating, can be minimized by proper control of steam flow and expandable bead flow. Anticlumping agents similar to those used in the baking industry (i.e., fine-sized silicas or silica gel derivatives) have been employed with some success.

Considerable effort has been directed toward the development of pre-expansion equipment involving the four heating media: steam, hot water, hot air, and radiant heaters.

1. Steam Pre-expansion

The first steam pre-expander was developed in 1956 by Koppers Company (15). Several commercial equipment manufacturers have models based on this design. The basic design is shown in Fig. 2 and the photograph (Fig. 3). It is basically a vertical, cylindrical tank with a driven agitator. The purpose of the agitator is to reduce fusion of the pellets to each other during pre-expansion. Expandable beads are fed into the bottom of the tank by a steam Venturi feeder. Inside the tank the beads are heated by the steam, expand, and displace the beads above them. This causes the lower-density expanded bead to overflow through the discharge near the top of the machine.

*It is not recommended that Freon 12 be inhaled. Several deaths have resulted from Freon sniffing by young thrill seekers who have misused the product.