Kirk-Othmer Encyclopedia of Chemical Technology.

FOAMED PLASTICS

Foamed polymers, otherwise known as cellular polymers or polymeric foams, or expanded plastics have been important to human life since primitive people began to use wood, a cellular form of the polymer cellulose. Cellulose (qv) is the most abundant of all naturally occurring organic compounds, comprising approximately one-third of all vegetable matter in the world (1). Its name is derived from the Latin word *cellula,* meaning very small cell or room, and most of the polymer does indeed exist in cellular form as in wood, straws, seed husks, etc. The high strength-to-weight ratio of wood, good insulating properties of cork and balsa, and cushioning properties of cork and straw have contributed both to the incentive to develop and to the background knowledge necessary for development of the broad range of cellular synthetic polymers in use.

The first cellular synthetic plastic was an unwanted cellular phenol–formaldehyde resin produced by early workers in this field. The elimination of cell formation in these resins, as given by Baekeland in his 1909 heat and pressure patent (2), is generally considered the birth of the plastics industry. The first commercial cellular polymer was sponge rubber, introduced between 1910 and 1920 (3).

Many cellular plastics that have not reached significant commercial use have been introduced or their manufacture described in literature. Examples of such polymers are chlorinated or chlorosulfonated polyethylene, a copolymer of vinylidene fluoride and hexafluoropropylene, polyamides (4), polytetrafluoroethylene (5), styrene–acrylonitrile copolymers (6, 7), polyimides (8), and ethylene–propylene copolymers (9).

Cellular polymers have been commercially accepted in a wide variety of applications since the 1940s (10–19). The total usage of foamed plastics in the United States has risen from 441×10^3 t in 1967 to 1.6×10^6 t in 1982, and has been projected to rise to about 2.8×10^6 t in 1995 (20).

1. Classification

A cellular plastic has been defined as a plastic the apparent density of which is decreased substantially by the presence of numerous cells disposed throughout its mass (21). In this article the terms cellular plastic, foamed plastic, expanded plastic, and plastic foam are used interchangeably to denote all two-phase gas–solid systems in which the solid is continuous and composed of a synthetic polymer or rubber.

The gas phase in a cellular polymer is distributed in voids, pores, or pockets called cells. If these cells are interconnected in such a manner that gas can pass from one to another, the material is termed open-celled. If the cells are discrete and the gas phase of each is independent of that of the other cells, the material is termed closed-celled.

The nomenclature of cellular polymers is not standardized; classifications have been made according to the properties of the base polymer (22), the methods of manufacture, the cellular structure, or some combination of these. The most comprehensive classification of cellular plastics, proposed in 1958 (23), has not been adopted and is not consistent with some of the common names for the more important commercial products.

One ASTM test procedure has suggested (24) that foamed plastics be classified as either rigid or flexible, a flexible foam being one that does not rupture when a $20 \times 2.5 \times 2.5$ cm piece is wrapped around a 2.5 cm mandrel at a uniform rate of 1 lap/5 s at 15–25°C. Rigid foams are those that do rupture under this test. This classification is used in this article.

In the case of cellular rubber, the ASTM uses several classifications based on the method of manufacture (25, 26). These terms are used here. Cellular rubber is a general term covering all cellular materials that have an elastomer as the polymer phase. Sponge rubber and expanded rubber are cellular rubbers produced by expanding bulk rubber stocks and are open-celled and closed-celled, respectively. Latex foam rubber, also a cellular rubber, is produced by frothing a rubber latex or liquid rubber, gelling the frothed latex, and then vulcanizing it in the expanded state.

The term structural/integral foam has been defined as flexible or rigid foams having a foamed core which gradually transforms to solid skins (27), but is used here to refer to those rigid foams produced at greater than about 320 kg/m^3 density having holes in a foamed core with solid skins rather than a typical lower density structure of pentagonal dodecahedron type (28).

2. Theory of the Expansion Process

Foamed plastics can be prepared by a variety of methods. The most important process, by far, consists of expanding a fluid polymer phase to a low density cellular state and then preserving this state. This is the foaming or expanding process. Other methods of producing the cellular state include leaching out solid or liquid materials that have been dispersed in a polymer, sintering small particles, and dispersing small cellular particles in a polymer. The latter processes are relatively straightforward processing techniques but are of minor importance.

The expansion process consists of three steps: creating small discontinuities or cells in a fluid or plastic phase; causing these cells to grow to a desired volume; and stabilizing this cellular structure by physical or chemical means.

2.1. Initiation and Growth of Cells

The initiation or nucleation of cells is the formation of cells of such size that they are capable of growth under the given conditions of foam expansion. The growth of a hole or cell in a fluid medium at equilibrium is controlled by the pressure difference (ΔP) between the inside and the outside of the cell, the surface tension of the fluid phase γ, and the radius r of the cell:

$$\Delta P = 2\gamma/r \qquad (1)$$

The pressure outside the cell is the pressure imposed on the fluid surface by its surroundings. The pressure inside the cell is the pressure generated by the blowing agent dispersed or dissolved in the fluid. If blowing pressures are low, the radii of initiating cells must be large. The hole that acts as an initiating site can be filled with either a gas or a solid that breaks the fluid surface and thus enables blowing agent to surround it (29–32)

During the time of cell growth in a foam, a number of properties of the system change greatly. Cell growth can, therefore, be treated only qualitatively. The following considerations are of primary importance: (*1*) the fluid viscosity is changing considerably, influencing both the cell growth rate and the flow of polymer to intersections from cell walls leading to collapse; (*2*) the pressure of the blowing agent decreases, falling off less rapidly than an inverse volume relationship because new blowing agent diffuses into the cells as the pressure falls off according to equation 1; (*3*) the rate of growth of the cell depends on the viscoelastic nature of the polymer phase, the blowing agent pressure, the external pressure on the foam, and the permeation rate of blowing agent through the polymer phase; and (*4*) the pressure in a cell of small radius r_2 is greater than that in a cell of larger radius r_1. There is thus a tendency to equalize these pressures either by breaking the wall separating the cells or by diffusion of the blowing agent from the small to the large cells. The pressure difference ΔP between cells of radii r_1 and r_2 is shown in equation 2.

$$\Delta P = 2\gamma\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad (2)$$

2.2. Stabilization of the Cellular State

The increase in surface area corresponding to the formation of many cells in the plastic phase is accompanied by an increase in the free energy of the system; hence the foamed state is inherently unstable. Methods of stabilizing this foamed state can be classified as chemical, eg, the polymerization of a fluid resin into a three-dimensional thermoset polymer, or physical, eg, the cooling of an expanded thermoplastic polymer to a temperature below its second-order transition temperature or its crystalline melting point to prevent polymer flow.

2.2.1. Chemical Stabilization

The chemistry of the system determines both the rate at which the polymer phase is formed and the rate at which it changes from a viscous fluid to a dimensionally stable cross-linked polymer phase. It also governs the rate at which the blowing agent is activated, whether it is due to temperature rise or to insolubilization in the liquid phase.

The type and amount of blowing agent governs the amount of gas generated, the rate of generation, the pressure that can be developed to expand the polymer phase, and the amount of gas lost from the system relative to the amount retained in the cells.

Additives to the foaming system (cell growth-control agents) can greatly influence nucleation of foam cells, either through their effect on the surface tension of the system, or by acting as nucleating sites from which cells can grow. They can influence the mechanical stability of the final solid foam structure considerably by changing the physical properties of the plastic phase and by creating discontinuities in the plastic phase that allow blowing agent to diffuse from the cells to the surroundings. Environmental factors such as temperature and pressure also influence the behavior of thermoset foaming systems.

2.2.2. Physical Stabilization

In physically stabilized foaming systems the factors are essentially the same as for chemically stabilized systems but for somewhat different reasons. Chemical composition of the polymer phase determines the temperature at which foam must be produced, the type of blowing agent required, and the cooling rate of the foam necessary for dimensional stabilization. Blowing agent composition and concentration controls the rate at which gas is released, the amount of gas released, the pressure generated by the gas, escape or retention of gas from the foam cells for a given polymer, and heat absorption or release owing to blowing agent activation.

Additives have the same effect on thermoplastic foaming processes as on thermoset foaming processes. Environmental conditions are important in this case because of the necessity of removing heat from the foamed structure in order to stabilize it. The dimensions and size of the foamed structure are important for the same reason.

3. Manufacturing Processes

Cellular plastics and polymers have been prepared by a wide variety of processes involving many methods of cell initiation, growth, and stabilization. The most convenient method of classifying these methods appears to be based on the cell growth and stabilization processes. According to equation 1, the growth of the cell depends on

Table 1. Methods for Production of Cellular Polymers

Type of polymer	Extrusion	Expandable formulation	Froth foam	Compression mold	Injection mold	Sintering
cellulose acetate[a]	X					
epoxy resin[b]		X	X			
phenolic resin		X				
polyethylene[a]	X	X		X	X	X
polystyrene	X	X			X	X
silicones		X				
urea–formaldehyde resin			X			
urethane polymers[b]		X	X		X	
latex foam rubber			X			
natural rubber	X	X		X		
synthetic elastomers	X	X		X		
poly(vinyl chloride)[a]	X	X	X	X	X	
ebonite				X		
polytetrafluoroethylene						X

[a] Also by leaching.
[b] Also by spray.

the pressure difference between the inside of the cell and the surrounding medium. Such pressure differences may be generated by lowering the external pressure (decompression) or by increasing the internal pressure in the cells (pressure generation). Other methods of generating the cellular structure are by dispersing gas (or solid) in the fluid state and stabilizing this cellular state, or by sintering polymer particles in a structure that contains a gas phase.

Foamable compositions in which the pressure within the cells is increased relative to that of the surroundings have generally been called expandable formulations. Both chemical and physical processes are used to stabilize plastic foams from expandable formulations. There is no single name for the group of cellular plastics produced by the decompression processes. The various operations used to make cellular plastics by this principle are extrusion, injection molding, and compression molding. Either physical or chemical methods may be used to stabilize products of the decompression process.

A summary of the methods for commercially producing cellular polymers is presented in Table 1. This table includes only those methods thought to be commercially significant and is not inclusive of all methods known to produce cellular products from polymers.

3.1. Expandable Formulations

3.1.1. Physical Stabilization Process

Cellular polystyrene [9003-53-6], the outstanding example; poly(vinyl chloride) [9002-86-2]; copolymers of styrene and acrylonitrile (SAN copolymers [9003-54-7]); and polyethylene [9002-88-4] can be manufactured by this process.

3.1.1.1. Polystyrene. There are two types of expandable polystyrene processes: expandable polystyrene for molded articles and expandable polystyrene for loose-fill packing materials.

Expandable polystyrene for molded articles is available in a range of particle sizes from 0.2 to 3.0 mm, and in shapes varying from round beads to ground chunks of polymer. These particles are prepared either by heating polymer particles in the presence of a blowing agent and allowing the blowing agent to penetrate the particle (33) or by polymerizing the styrene monomer in the presence of blowing agent (34) so that the blowing agent is entrapped in the polymerized bead. Typical blowing agents used are the various isomeric pentanes and hexanes, halocarbons, and mixtures of these materials (35).

The fabrication of these expandable particles into a finished cellular-plastic article is generally carried out in two steps (36–39). First the particles are expanded by means of steam, hot water, or hot air into low density replicas of the original material, called prefoamed or pre-expanded beads. After proper aging enough of these prefoamed beads are placed in a mold to just fill it; the filled mold is then exposed to steam. This second expansion of the beads causes them to flow into the spaces between beads and fuse together, forming an integral molded piece. Stabilization of the cellular structure is accomplished by cooling the molded article while it is still in the mold. The density of the cellular article can be adjusted by varying the density of the prefoamed particles.

Expandable polystyrene for loose-fill packaging materials is available in various sizes and shapes varying from round disks to S-shaped strands. These particles can be prepared either by deforming the polystyrene under heat and impregnating the resin with a blowing agent in an aqueous suspension (40) or by the extrusion method with various die orifice shapes (41). The expansion of these particles into a product is usually carried out in two or three expansions by means of steam with at least one day of aging in air after each expansion (42). Stabilization is accomplished by cooling the polymer phase below its glass-transition temperature during the expansion process.

3.1.1.2. Poly(vinyl chloride). Cellular poly(vinyl chloride) can be produced from several expandable formulations as well as by decompression techniques. Rigid or flexible products can be made depending on the amount and type of plasticizer used (43).

3.1.1.3. Polyethylene. Because polyethylene has a sharp melting point and its viscosity decreases rapidly over a narrow temperature range above the melting point, it is difficult to produce a low density polyethylene foam with nitrogen or chemical blowing agents because the foam collapses before it can be stabilized. This problem can be eliminated by cross-linking the resin before it is foamed, which slows the viscosity decrease above the melting point and allows the foam to be cooled without collapse of cell structure.

Cross-linking of polyethylene can be accomplished either chemically or by high energy radiation. Radiation cross-linking is usually accomplished by x-rays (44) or electrons (45, 46). Chemical cross-linking of polyethylene is accomplished with dicumyl peroxide (47), di-*tert*-butyl peroxide (48), or other peroxides. Radiation cross-linking (49) is preferred for thin foams, and chemical cross-linking for the thicker foams.

Expandable polyethylene foam sheet can be made by a four-step process: (*1*) mixing of polyethylene, chemical blowing agent, and cross-linking agent (in the case of chemical cross-linking) at low or medium temperature (examples of decomposable blowing agents used for expandable polyethylene are azodicarbonamide, 4,4′-oxybis(benzenesulfonyl hydrazide), and dinitrosopentamethylene-tetramine (35); (*2*) shaping at low or medium temperature; (*3*) chemical cross-linking at medium temperature or radiation cross-linking; and (*4*) heating and expanding at high temperature. Expansion of the cross-linked, expandable polyethylene sheet can be accomplished either by floating the sheet on the surface of a molten salt bath at 200–250°C and heating from above with ir heaters or by circulating hot air, or by expanding in the mold with a high pressure steam.

3.1.2. Chemical Stabilization Processes

This method is more versatile and thus has been used successfully for more materials than the physical stabilization process. Chemical stabilization is more adaptable for condensation polymers than for vinyl polymers because of the fast yet controllable curing reactions and the absence of atmospheric inhibition.

3.1.2.1. Polyurethane Foams. The most important commercial example of the chemical stabilization process is the production of polyurethane foams, which began in the mid-1950s. Depending on the choice of starting materials and processing techniques, it is possible to generate a wide variety of foams for such diverse uses as wood replacement in decorative cabinetwork or all-foam mattresses; to insulate portable coolers or for ultrasoft furniture cushions; as a sprayed-on insulating foam for pipes; or molded seat cushions for cars. Excellent summaries of the chemistry and technology of these polymers have been published (13, 50, 51) (see Urethane polymers).

The urethane forming ingredients in a polyurethane foam formulation are the isocyanate **1** and the polyol **2** as shown in equation **3**.

$$\underset{(\mathbf{1})}{\mathrm{OCN{-}R{-}NCO}} + \underset{(\mathbf{2})}{\mathrm{HO{-}R'{-}OH}} \longrightarrow \underset{(\mathbf{3})}{-\!\left(\overset{\overset{\displaystyle O}{\|}}{C}\mathrm{{-}NH{-}R{-}NH{-}}\overset{\overset{\displaystyle O}{\|}}{C}\mathrm{{-}O{-}R'{-}O}\right)\!-} \qquad (3)$$

Another useful reaction is the reaction of water with isocyanate to generate CO_2 and urea groups which modify the polymeric structure. This vigorous reaction is also a prime source of exothermic heat to drive equation **3** to completion.

$$\mathrm{OCN{-}R{-}NCO} + 2\,\mathrm{HOH} \longrightarrow \mathrm{NH_2{-}R{-}NH_2} + 2\,\mathrm{CO_2} \qquad (4)$$

Further reaction of the active hydrogens on nitrogen in the urethane groups **3** can occur with additional isocyanate **1** at higher temperatures to cause formation of allophanate structures. The active hydrogens in urea groups can also react with additional isocyanate to form disubstituted ureas which can still further react with isocyanate to form biurets (13).

The urethane-forming reaction (eq. **3**) is known as the gelling reaction since it is the primary means of polymerizing the starting materials into long-chain polymer networks. The CO_2 forming reaction is known as the blowing reaction due to its contribution of CO_2 as an *in situ* blowing agent. The amount of blowing reaction is controlled by the water level of the formulation. The gelling and blowing reaction rates are determined by the catalyst choices. Typically, tertiary amines are used to foster the blowing reaction and organometallics are used to promote gellation although both contribute to both reactions. Urethane reactions often use a combination of catalysts to achieve the desired reactivity balance. Additional blowing may be obtained through the use of an auxiliary blowing agent such as methylene chloride, CFC-11, or HCFC-141b.

Silicone surfactants are used to assist in controlling cell size and uniformity through reduced surface tension and, in some cases, to assist in the solubilization of the various reactants (52, 53).

The foam process may be described as follows: the materials are metered in appropriate quantities into a mixing chamber and thoroughly mixed. Tiny air (or gas) bubbles are generated in the liquid to effect nucleation. After a short induction period the blowing agents begin to diffuse into and enlarge the tiny nucleation bubbles causing a creamy appearance. The period from mixing to this point is known as the cream time which is normally about 6–15 s for flexible foams. As more blowing agents are generated the foaming mixture continues to expand and becomes more viscous as the polymerization occurs in the liquid phase. The total number of bubbles remains constant during the foam rise. The reduction of surface tension by the surfactant stabilizes the tender foaming mixture to prevent coalescing of the bubbles.

About 100–200 s after mixing, the blowing reaction ceases but the gelling reaction continues, strengthening the struts of the foam cells. The thin cell walls of a flexible foam then burst (blow-off) and the gases are released throughout the foam which has polymerized sufficiently to prevent collapse. The period from mixing to full rise (with blow-off in flexible foams) is known as rise time. The polymerization continues until the foam has gelled, usually 20–120 s after rise time. Loss of surface tackiness is known as tack free time. Rigid foams display a gel time prior to full rise. Additional cure time is necessary to achieve full polymer physical properties. This is a time/temperature characteristic which may vary from hours to days in duration.

The physical properties of the final foam can be varied broadly by controlling the degree of cross-linking in the final polymer as well as the structure of R and R′ in **1** and **2**. The average molecular weight between cross-links is generally 400–700 for rigid polyurethane foams, 700–2500 for semirigid foams, and 2,500–20,000 for flexible foams (13). The structure of the diisocyanate is limited to some six or eight commercially available compounds (13, 54). For this reason the variation between cross-links is controlled primarily by the polyol **2**; it is common to use the equivalent weight (the ratio of molecular weight to hydroxyl units) as a criterion for the expected foam rigidity. The equivalent weights of polyhydroxy resins used for rigid foams are less than 300, for semirigids between 70 and 2000, and for flexibles from 500 to 3000.

Two general types of processes have been developed for producing polyurethanes on a commercial scale: the one-shot process and the prepolymer process. In the one-shot process, which is most widely used today, all primary streams (some of which may be premixed) are delivered to the foam mixing head at once for mixing and dispensing. In the prepolymer process the polyhydroxy component first reacts with isocyanate as shown in equation **5** to form an isocyanate terminated molecule, which can ultimately react with water to liberate CO_2 for foaming and obtain chain linkage via the urea groups. Use of excess isocyanate results in the formulation of an isocyanate/polyol adduct which contains a quantity of free isocyanate as well as a structured prepolymer. This adduct may be used as the source of isocyanate in a conventional system using additional polyol, catalysts, blowing agents, etc.

$$\mathrm{OCN{-}R{-}NCO + HO{-}R'{-}OH \longrightarrow OCN{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}O{-}R'{-}O\overset{\overset{O}{\|}}{C}{-}NH{-}R{-}NCO} \qquad (5)$$

The foam forming ingredients are carefully metered to obtain the proper ratio of reactants, thoroughly mixed by either mechanical or impingement means, then applied as a liquid, a spray, or a froth with subsequent expansion and curing.

3.1.2.2. Polyisocyanurates. The isocyanurate ring formed by the trimerization of isocyanates is known to possess high thermal and flammability resistance as well as low smoke generation during burning (55–58). Cross-linking via the high functionality of the isocyanurates produces a foam with inherent friability. Modification of the isocyanurate system with a longer chain structure such as polyether polyols or terephthalate-based polyester polyols increases the abrasion resistance of the resultant foam. Aluminum foil-faced sheets of modified isocyanurate-based foams are now widely used as an insulation material. The manufacturing process for isocyanurate foams is similar to that for rigid polyurethane foams (see Isocyanates, organic).

3.1.2.3. Polyphenols. Another increasingly important example of the chemical stabilization process is the production of phenolic foams (59–62) by cross-linking polyphenols (resoles and novolacs) (see Phenolic resins). The principal features of phenolic foams are low flammability, solvent resistance, and excellent dimensional stability over a wide temperature range (59), so that they are good thermal insulating materials.

Most phenolic foams are produced from resoles and acid catalyst; suitable water-soluble acid catalysts are mineral acids (such as hydrochloric acid or sulfuric acid) and aromatic sulfonic acids (63). Phenolic foams can be produced from novolacs but with more difficulty than from resoles (59). Novolacs are thermoplastic and require a source of methylene group to permit cure. This is usually supplied by hexamethylenetetramine (64).

A typical phenolic foam system consists of liquid phenolic resin, blowing agent, catalyst, surface-active agent, and modifiers. Various formulations and composite systems (65–67) can be used to improve one or more properties of the foam in specific applications such as insulation properties (63, 68–71), flammability (72–74), and open cell (76–78) (quality).

Several manufacturing processes can be used to produce phenolic foams (59, 79): continuous production of free-rising foam for slabs and slab stock similar to that for polyurethane foam (61, 80); foam-in-place batch process (61, 81); sandwich paneling (63, 82, 83); and spraying (70, 84).

3.1.2.4. Other Materials. Foams from epoxy resins (59, 60, 85, 86) and silicone resins (32, 60, 87, 88) can also be formed by a chemical stabilization process.

3.2. Decompression Expansion Processes

3.2.1. Physical Stabilization Process

Cellular polystyrene, cellulose acetate, polyolefins, and poly(vinyl chloride) can be manufactured by this process.

3.2.1.1. Polystyrene. The extrusion process for producing cellular polystyrene is probably the oldest method utilizing physical stabilization in a decompression expansion process (89). A solution of blowing agent in molten polymer is formed in an extruder under pressure. This solution is forced out through an orifice onto a moving belt at ambient temperature and pressure. The blowing agent then vaporizes and causes the polymer to expand. The polymer simultaneously expands and cools under such conditions that it develops enough strength to maintain dimensional stability at the time corresponding to optimum expansion. The stabilization is due to cooling of the polymer phase to a temperature below its glass-transition temperature by the vaporization of the blowing agent, gas expansion, and heat loss to the environment. Polystyrene foams produced by the decompression process are commercially offered in the density range of 23–53 kg/m^3 (1.4–3.3 lbs/ft^3) as well as at higher densities (90).

The extrusion of expandable polystyrene beads or pellets containing pentane blowing agent was originally used to produce low density foam sheet (91, 92). The current method is to extrude polystyrene foam in a single-screw tandem line or twin-screw extruder and produce foam sheet by addition of pentane or fluorocarbon blowing agents into the extruder (93, 94). For sheet thicknesses of less than 500 μm (20 mil), the blown-bubble method is normally used. This method involves blowing a tube from a round or annular die, collapsing the bubble, and then slitting the edges to obtain two flat sheets. For greater sheet thicknesses the sheet is pulled over a sizing mandrel and slit to obtain a flat sheet. Cooling of the expanded material by the external air is necessary to stabilize the foam sheet with a good skin quality.

Cellular polystyrene can also be produced by an injection-molding process. Polystyrene granules containing dissolved liquid or gaseous blowing agents are used as feed in a conventional injection-molding process (95). With close control of time and temperature in the mold and use of vented molds, high density cellular polystyrene moldings can be obtained.

3.2.1.2. Cellulose Acetate. The extrusion process has also been used to produce cellular cellulose acetate (96) in the density range of 96–112 kg/m^3 (6–7 lbs/ft^3). A hot mixture of polymer, blowing agent, and nucleating agent is forced through an orifice into the atmosphere. It expands, cools, and is carried away on a moving belt.

3.2.1.3. Polyolefins. Cellular polyethylene and polypropylene are prepared by both extrusion and molding processes. High density polyolefin foams in the density range of 320–800 kg/m^3 are prepared by mixing a decomposable blowing agent with the polymer and feeding the mixture under pressure through an extruder at a temperature such that the blowing agent is partially decomposed before it emerges from an orifice into a lower pressure zone. Simultaneous expansion and cooling take place, resulting in a stable cellular structure owing to rapid crystallization of the polymer, which increases the modulus of the polymer enough to prevent collapse of cell structure (29, 39, 97). This process is widely used in wire coating and structural foam products. These products can also be produced by direct injection of inert gases into the extruder (98, 99).

Low density polyethylene foam products (thin sheets, planks, rounds, tubes) in the range of 32–160 kg/m^3 (2–10 lbs/ft^3) have been prepared by an extrusion technique using various gaseous fluorocarbon blowing agents (100, 101). The techniques are similar to those described earlier for producing extruded polystyrene foam planks and foam sheets.

3.2.1.4. Thermoplastic Structural Foams. Structural foams having an integral skin, cellular core, and a high strength-to-weight ratio are formed by means of injection molding, extrusion, or casting, depending on product requirements (102–104). The two most widely used injection molding processes are the Union Carbide low pressure process (105) and the USM high pressure process (106).

In the low pressure process, a short shot of a resin containing a blowing agent is forced into the mold where the expandable material is allowed to expand to fill the mold under pressures of 690–4140 kPa (100–600 psi). This process produces structural foam products with a characteristic surface swirl pattern produced by the collapse of cells on the surface of molded articles.

In the high pressure process, a resin melt containing a chemical blowing agent is injected into an expandable mold under high pressure. Foaming begins as the mold cavity expands. This process produces structural foam products with very smooth surfaces since the skin is formed before expansion takes place.

Extruded structural foams are produced with conventional extruders and a specially designed die. The die has an inner, fixed torpedo located at the center of its opening, which provides a hollow extrudate. The outer layer of the extrudate cools and solidifies to form solid skin; the remaining extrudate expands toward the interior of the profile. One of the most widely used commercial extrusion processes is the Celuka process developed by Ugine-Kuhlmann (107).

Large structural foam products are produced by casting expandable plastic pellets containing a chemical blowing agent in aluminum molds on a chain conveyor. After closing and clamping the mold, it is conveyed through a heating zone where the pellets soften, expand, and fuse together to form the cellular products. The mold is then passed through a cooling zone. This process produces structural foam products with uniform, closed-celled structures but no solid skin.

3.2.1.5. Poly(vinyl chloride). Cellular poly(vinyl chloride) is prepared by many methods (108), some of which utilize decompression processes. In all reported processes the stabilization process used for thermoplastics is to cool the cellular state to a temperature below its second-order transition temperature before the resin can flow and cause collapse of the foam.

A type of physical stabilization process, unique for poly(vinyl chloride) resins, is the fusion of a dispersion of plastisol resin in a plasticizer. The viscosity of a resin–plasticizer dispersion shows a sharp increase at the fusion temperature. In such a system expansion can take place at a temperature corresponding to the low viscosity; the temperature can then be raised to increase viscosity and stabilize the expanded state.

Extrusion processes have been used to produce high and low density flexible cellular poly(vinyl chloride). A decomposable blowing agent is usually blended with the compound prior to extrusion. The compounded resin is then fed to an extruder where it is melted under pressure and forced out of an orifice into the atmosphere. After extrusion into the desired shape, the cellular material is cooled to stabilize it and is removed by a belt.

Another type of extrusion process involves the pressurization of a fluid plastisol at low temperatures with an inert gas. This mixture is subsequently extruded onto a belt or into molds, where it expands (109, 110). The expanded dispersion is then heated to fuse it into a dimensionally stable form.

Injection molding of high density cellular poly(vinyl chloride) can be accomplished in a manner similar to extrusion except that the extrudate is fed for cooling into a mold rather than being maintained at the uniform extrusion cross-section.

3.2.2. Chemical Stabilization Processes

Cellular rubber and ebonite are produced by chemical stabilization processes.

3.2.2.1. Cellular Rubber. This material is an expanded elastomer produced by expansion of a rubber stock, whereas latex foam rubber is produced from a latex. The following general procedure applies to production of cellular rubbers from a variety of types of rubber (111). A decomposable blowing agent, along with vulcanizing systems and other additives, is compounded with the uncured elastomer at a temperature below the decomposition temperature of the blowing agent. When the uncured elastomer is heated in a forming mold, it undergoes a viscosity change, as shown in Figure 1. The blowing agent and vulcanizing systems are chosen to yield open-celled or closed-celled cellular rubber. Although inert gases such as nitrogen have been pressurized into rubber and the rubber then expanded upon release of pressure, the current cellular rubbers are made almost entirely with decomposable blowing agents as exemplified by sodium bicarbonate [144-55-8], 2,2′-azobisisobutyronitrile [78-67-1], azodicarbonamide [123-77-5], 4,4′-oxybis(benzenesulfonyl hydrazide)

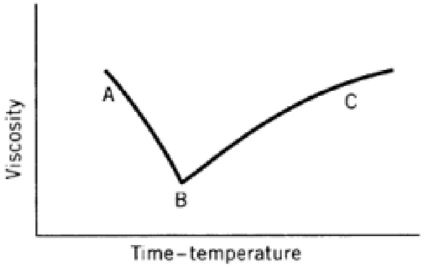

Fig. 1. Viscosity of cellular rubber stock during a production cycle (111).

[80-51-3], and dinitrosopentamethylenetetramine [101-25-7]. The compound named is the most important commercial compound in its particular class.

To produce open-celled cellular rubber the blowing agent is decomposed just prior to point A in Figure 1 so that the gas is released at the point of minimum viscosity. As the polymer expands the cell walls become thin and rupture; however, the connecting struts have developed enough strength to support the foam. This process is ordinarily carried out in one step inside a mold under pressure.

The timing for blowing-agent decomposition is more critical in making closed-celled cellular rubber; it must occur soon enough after point A to cause expansion of the elastomer but far enough past point A to allow the cell walls to become strong enough not to rupture under the blowing stress. The expansion of closed-celled rubber is often carried out in two main steps: a partial cure is carried out in a mold that is a reduced-scale replica of the final mold; removed from this mold, it expands partly toward its final form. It is then placed in an oven to complete the expansion and cure.

Most elastomers can be made into either open-celled or closed-celled materials. Natural rubber, SBR, nitrile rubber, polychloroprene, chlorosulfonated polyethylene, ethylene–propylene terpolymers, butyl rubbers, and polyacrylates have been successfully used (4, 111, 112).

A continuous extrusion process, as well as molding techniques, can be used as the thermoforming method. A more rapid rate of cure is then necessary to ensure the cure of the rubber before the cellular structure collapses. The stock is ordinarily extruded at a temperature high enough to produce some curing and expansion and then oven-heated to complete the expansion and cure.

A unique process for chemical stabilization of a cellular elastomer upon extrusion has been shown for ethylene–propylene rubber: the expanded rubber obtained by extrusion is exposed to high energy radiation to cross-link or vulcanize the rubber and give dimensional stability (9). EPDM is also made continuously through extrusion and a combination of hot air and microwaves or radio frequency waves which both activate the blow and accelerate the cure.

Polyurethane structural foam produced by reaction injection molding (RIM) is a rapidly growing product that provides industry with the design flexibility required for a wide range of applications. This process is more efficient than conventional methods in producing large area, thin wall, and load-bearing structural foam parts. In the RIM process, polyol and isocyanate liquid components are metered into a temperature controlled mold that is filled 20–60%, depending on the density of structural foam parts (113). When the reaction mixture then expands to fill the mold cavity, it forms a component part with an integral, solid skin and a microcellular core. The quality of the structural part depends on precise metering, mixing, and injection of the reaction chemicals into the mold.

3.2.2.2. Cellular Ebonite. Cellular ebonite is the oldest rigid cellular plastic. It was produced in the early 1920s by a process similar to the processes described for making cellular rubber. The formulation of rubber and vulcanizing agent is changed to produce an ebonite rather than rubber matrix (114).

3.3. Dispersion Processes

In several techniques for producing cellular polymers, the gas cells are produced by dispersion of a gas or liquid in the polymer phase followed, when necessary, by stabilization of the dispersion and subsequent treatment of the stabilized dispersion. In frothing techniques a quantity of gas is mechanically dispersed in the fluid polymer phase and stabilized. In another method, solid particles are dispersed in a fluid polymer phase, the dispersion stabilized, and then the solid phase dissolved or leached, leaving the cellular polymer. Still another method relies on dispersing an already cellular solid phase in a fluid polymer and stabilizing this dispersion. This results directly in cellular polymers called syntactic foams.

3.3.1. Frothing

The frothing process for producing cellular polymers is the same process used for making meringue topping for pies. A gas is dispersed in a fluid that has surface properties suitable for producing a foam of transient stability. The foam is then permanently stabilized by chemical reaction. The fluid may be a homogeneous material, a solution, or a heterogeneous material.

3.3.1.1. Latex Foam Rubber. Latex foam rubber was the first cellular polymer to be produced by frothing. (*1*) A gas is dispersed in a suitable latex; (*2*) the rubber latex particles are caused to coalesce and form a continuous rubber phase in the water phase; (*3*) the aqueous soap film breaks owing to deactivation of the surfactant in the water, breaking the latex film and causing retraction into the connecting struts of the bubbles; (*4*) the expanded matrix is cured and dried to stabilize it.

The earliest frothing process developed was the Dunlop process, which made use of chemical gelling agents, eg, sodium fluorosilicate, to coagulate the rubber particles and deactivate the soaps. The Talalay process, developed later, employs freeze-coagulation of the rubber followed by deactivation of the soaps with carbon dioxide. The basic processes and a multitude of improvements are discussed extensively in Reference 3. A discussion more oriented to current use of these processes is given in Reference 115.

Latex rubber foams are generally prepared in slab or molded forms in the density range 64–128 kg/m^3 (4–8 lbs/ft^3). Synthetic SBR latexes have replaced natural rubber latexes as the largest volume raw material for latex foam rubber. Other elastomers used in significant quantities are polychloroprene, nitrile rubbers, and synthetic *cis*-polyisoprene (115).

One method (116) of producing cellular polymers from a variety of latexes uses primarily latexes of carboxylated styrene–butadiene copolymers, although other elastomers such as acrylic elastomers, nitrile rubber, and vinyl polymers can be employed.

3.3.1.2. Urea–Formaldehyde Resins. Cellular urea–formaldehyde resins can be prepared in the following manner: an aqueous solution containing surfactant and catalyst is made into a low density, fine-celled foam by dispersing air into it mechanically. A second aqueous solution consisting of partially cured urea–formaldehyde resin is then mixed into the foam by mechanical agitation. The catalyst in the initial foam causes the dispersed resin to cure in the cellular state. The resultant hardened foam is dried at elevated temperatures. Densities as low as 8 kg/m^3 can be obtained by this method (117).

3.3.1.3. Polyurethanes. Polyurethane foam systems have also been frothed using both low boiling dissolved materials and whipped-in air or other gas. Rigid polyurethane foam systems using a previously mixed polyol, surfactant, and catalyst system pressurized in a container with blowing agent are used for froth discharge into pour-in-place cavity filling (118). Flexible polyurethane foam is mechanically frothed by whipping dry gas such as air into the combined polyol and isocyanate. The thick, creamy froth is then doctored onto a carpet or textile back to form a variety of coatings ranging from a very thin unitary to a 1.8-cm thick resilient foam (119).

3.3.2. Syntactic Cellular Polymers

Syntactic cellular polymer is produced by dispersing rigid, foamed, microscopic particles in a fluid polymer and then stabilizing the system. The particles are generally spheres or microballoons of phenolic resin, urea–formaldehyde resin, glass, or silica, ranging 30–120 μm dia. Commercial microballoons have densities of approximately 144 kg/m^3 (9 lbs/ft^3). The fluid polymers used are the usual coating resins, eg, epoxy resin, polyesters, and urea–formaldehyde resin.

The resin, catalyst, and microballoons are mixed to form a mortar which is then cast into the desirable shape and cured. Very specialized electrical and mechanical properties may be obtained by this method but at higher cost. This method of producing cellular polymers is quite applicable to small quantity, specialized applications because it requires very little special equipment.

In a variation on the usual methods for producing syntactic foams (120, 121), expandable polystyrene or styrene–acrylonitrile copolymer particles (in either the unexpanded or prefoamed state) are mixed with a resin (or a resin containing a blowing agent) which has a large exotherm during curing. The mixture is then placed in a mold and the exotherm from the resin cure causes the expandable particles to foam and squeeze the resin or foamed matrix to the surface of the molding. A typical example is Voraspan, expandable polystyrene in a flexible polyurethane foam matrix (122). These foams are finding acceptance in cushioning applications for bedding and furniture.

3.4. Other Processes

Some plastics cannot be obtained in a low viscosity melt or solution that can be processed into a cellular state. For these cases two methods have been used to achieve the needed dispersion of gas in solid: sintering of solid plastic particles and leaching of soluble inclusions from the solid plastic phase.

Sintering has been used to produce a porous polytetrafluoroethylene (16). Cellulose sponges are the most familiar cellular polymers produced by the leaching process (123). Sodium sulfate crystals are dispersed in the viscose syrup and subsequently leached out. Polyethylene (124) or poly(vinyl chloride) can also be produced in cellular form by the leaching process. The artificial leather-like materials used for shoe uppers are rendered porous by extraction of salts (125) or by designing the polymers in such a way that they precipitate as a gel with many holes (126).

3.4.1. Phase Separation

Microporous polymer systems consisting of essentially spherical, interconnected voids, with a narrow range of pore and cell-size distribution have been produced from a variety of thermoplastic resins by the phase-separation technique (127). If a polyolefin or polystyrene is insoluble in a solvent at low temperature but soluble at high temperatures, the solvent can be used to prepare a microporous polymer. When the solutions, containing 10–70% polymer, are cooled to ambient temperatures, the polymer separates as a second phase. The remaining nonsolvent can then be extracted from the solid material with common organic solvents. These microporous polymers may be useful in microfiltrations or as controlled-release carriers for a variety of chemicals.

4. Properties of Cellular Polymers

The mechanical properties of rigid foams vary considerably from those of flexible foams. The tests used to characterize these two classes of foams are, therefore, quite different, and the properties of interest from an application standpoint are also quite different. In this discussion the ASTM definition of rigid and flexible foams given earlier is used.

Several countries have developed their own standard test methods for cellular plastics, and the International Organization for Standards (ISO) Technical Committee on Plastics TC-61 has been developing international standards. Information concerning the test methods for any particular country or the ISO procedures can be obtained in the United States from the American National Standards Institute. The most complete set of test procedures for cellular plastics, and the most used of any in the world, is that developed by the ASTM; these procedures are published in new editions each year (128). There have been several reviews of ASTM methods and others pertinent to cellular plastics (32, 59, 129–131).

4.1. Mechanical Properties of Commercial Foamed Plastics

The properties of commercial rigid foamed plastics are presented in Table 2. The properties of commercial flexible foamed plastics are presented in Table 4. The definition of a flexible foamed plastic is that recommended by the ASTM Committee D 11. The data shown demonstrate the broad ranges of properties of commercial products rather than an accurate set of properties on a specific few materials. Specific producers of foamed plastics should be consulted for properties on a particular product (137, 138, 142).

The properties that are achieved in commercial structural foams (density >0.3 g/cm^3) are shown in Table 3. Because these values depend on several structural and process variables, they can be used only as general guidelines of mechanical properties from these products. Specific properties must be determined on the particular part to be produced. A good engineering guide has been published (103).

4.1.1. Structural Variables

The properties of a foamed plastic can be related to several variables of composition and geometry often referred to as structural variables.

4.1.1.1. Polymer Composition. The properties of foamed plastics are influenced both by the foam structure and, to a greater extent, by the properties of the parent polymer. The polymer phase description must include the additives present in that phase as well. The condition or state of the polymer phase (orientation, crystallinity, previous thermal history), as well as its chemical composition, determines the properties of that phase. The polymer state and cell geometry are intimately related because they are determined by common forces exerted during the expansion and stabilization of the foam.

4.1.1.2. Density. Density is the most important variable in determining mechanical properties of a foamed plastic of given composition. Its effect has been recognized since foamed plastics were first made and has been extensively studied.

4.1.1.3. Cell Structure. A complete knowledge of the cell structure of a cellular polymer requires a definition of its cell sizes, cell shapes, and location of each cell in the foam.

Cell size. has been characterized by measurements of the cell diameter in one or more of the three mutually perpendicular directions (143) and as a measurement of average cell volume (144, 145). Mechanical, optical, and thermal properties of a foam are all dependent upon the cell size.

Cell geometry. is governed predominantly by the final foam density and the external forces exerted on the cellular structure prior to its stabilization in the expanded state. In a foam prepared without such external forces, the cells tend to be spherical or ellipsoidal at gas volumes less than 70–80% of the total volume, and they tend toward the shape of packed regular dodecahedra at greater gas volumes. These shapes have been shown to be consistent with surface chemistry arguments (144, 146, 147). Photographs of actual foam cells (Fig. 2) show a broad range of variations in shape.

In the presence of external forces, plastic foams in which the cells are elongated or flattened in a particular direction may be formed. This cell orientation can have a marked influence on many properties. The results of a number of studies have been reviewed (59, 60).

Table 2. Physical Properties of Commercial Rigid Foamed Plastics[a]

													Polyurethane			
				Polystyrene											Isocyanurate	
Property	ASTM test	Cellulose acetate[b]	Phenolic[c]	Extruded plank[b,d]			Expanded plank[e, f]		Extruded sheet		PVC[g]		Polyether[h]		Bun[g]	Laminate[i]
density, kg/m^3[j]		96–128	32–64	35	53	16	32	80	96	160	32	64	32–48	64–128	32	32
mechanical properties																
compressive strength, kPa[k] at 10%	D1621	862	138–620	310	862	90–124	207–276	586–896	290	469	345	1035	138–344	482–1896	210	117–206
tensile strength, kPa[k]	D1623	1172	138–379	517		145–193	310–379	1020–1186	2070–3450	4137–6900	551	1207	138–482	620–2000	250	248–290
flexural strength, kPa[k]	D790	1014	172–448	1138		193–241	379–517				586	1620	413–689	1380–2400		
shear strength, kPa[k]	C273	965	103–207	241			241				241	793	138–207	413–896	180	117
compression modulus, MPa[l]	D1621	38–90		10.3			3.4–14				13.1	35	2.0–4.1	10.3–31		
flexural modulus, MPa[l]	D790	38		41			9.0–26				10.3	36	5.5–6.2	5.5–10.3		
shear modulus, MPa[l]	C273		2.8–4.8	10.3			7.6–11.0				6.2	21	1.2–1.4	3.4–10.3		1.7
thermal properties																
thermal conductivity, W/(m·I)	C177	0.045–0.046	0.029–0.032	0.030		0.037	0.035	0.035	0.035	0.035	0.023		0.016–0.025	0.022–0.030	0.054	0.019
coefficient of linear expansion, 10^{-5}/°C	D696		0.9	6.3	6.3	5.4–7.2	5.4–7.2	5.4–7.2					5.4–7.2	7.2	7.2	
max service temperature, °C		177	132	74		74–80	74–80	74–80	77–80	80			93–121	121–149	149	149
specific heat, kJ/(kg·K)[m]	C351			1.1									ca 0.9	ca 0.9	ca 0.9	
electrical properties																
dielectric constant	D1673	1.12	1.19–1.20	<1.05	<1.05	1.02	1.02	1.02	1.27	1.28			1.05	1.1	1.4	
dissipation factor		20	0.028–0.031	<0.0004	<0.0004	0.0007	0.0007	0.0007	0.00011	0.00014			13	18		
moisture resistance																
water absorption, vol %	C272	4.5	13–51	0.02	0.05	1–4	1–4	1–4								
moisture vapor transmission, g/(m·s·GPa)[n]	E96			35		<120	35–120	23–35	86	56	15		35–230	50–120		230

[a] Data on epoxy resins can be found in Ref. 132; on urea–formaldehyde resins, Ref. 133.

[b] Ref. 22.

[c] Refs. 134 and 135.

[d] Refs. 22 and 136.

[e] Refs. 135 and 137.

[f] Ref. 138.

[g] Ref. 139.

[h] Ref. 140.

[i] Ref. 141.

[j] To convert kg/m^3 to lb/ft^3, multiply by 0.0624.

[k] To convert kPa to psi, divide by 6.895.

[l] To convert MPa to psi, multiply by 145.

[m] To convert kJ/(kg·K) to Btu/(lb·F), divide by 4.184.

[n] To convert GPa to psi, multiply by 145,000.

Table 3. Typical Physical Properties of Commercial Structural Foams

Property	ASTM test	ABS		Noryl[a]	Nylon[b]	PC[c]	Polyester[d]	HDPE	Polypropylene		High impact polystyrene		Polyurethane[e]			PVC
glass-reinforced		no	yes	no	yes	no	30%	no	no	20%	no	20%	no	no	no	no
density, g/cm^3		0.80	0.85	0.80	0.97	0.80	1.10	0.60	0.60	0.73	0.70	0.84	0.40	0.50	0.60	0.50
tensile strength, kPa[f]	D1623	18,600	48,000	22,700	101,000	37,900	76,000	8,900	13,800	20,700	12,400	34,500	11,000	17,200	23,400	6,900
compression strength, kPa[f] at 10% compression	D1621	6,900		34,500		51,700	76,000	8,900					5,500	12,400	19,300	
flexural strength, kPa[f]	D790	25,500	82,700	41,400	172,000	68,900	137,900	18,800	22,000	41,400	31,000	58,600	22,000	31,700	41,400	
flexural modulus, GPa[g]	D790	0.86	5.2	1.7	5.2	2.1	6.6	0.83	0.83	2.8	1.4	5.2	0.7	0.9	1.1	
max use temperature, °C		82		96	203	132	193	110	115							

[a] Noryl is an alloy of poly(2,6-dimethyl-1,4-phenylene ether) and polystyrene.

[b] Nylon-6,6 glass-reinforced.

[c] Polycarbonate.

[d] Thermoplastic polyester.

[e] Ref. 160.

[f] To convert kPa to psi, divide by 6.895.

[g] To convert GPa to psi, multiply by 145,000.

Table 4. Physical Properties of Commercial Flexible Foamed Plastics

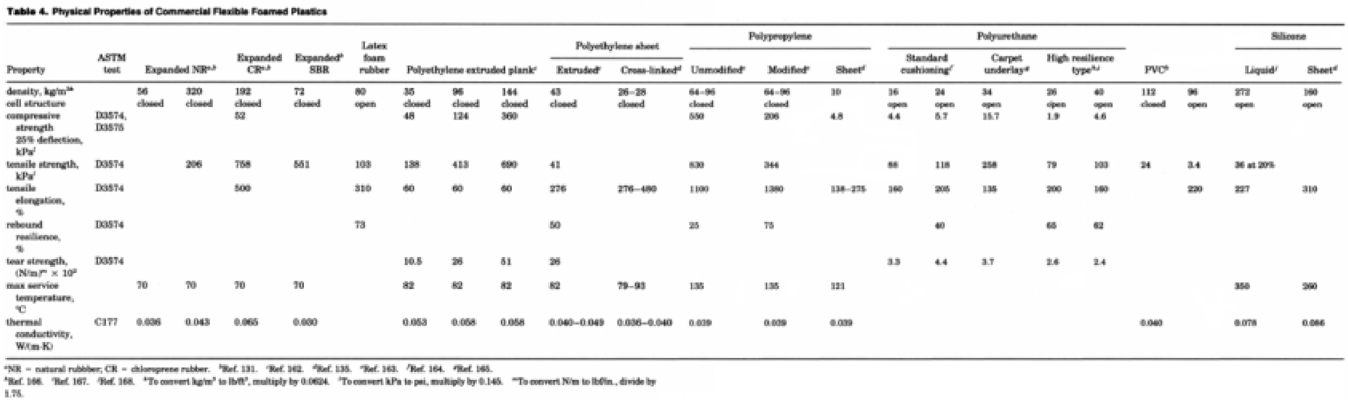

Table 4. Physical Properties of Commercial Flexible Foamed Plastics

Property	ASTM test	Expanded NR[a,b]		Expanded CR[a,b]	Expanded[b] SBR	Latex foam rubber	Polyethylene extruded plank[c]			Polyethylene sheet		Polypropylene			Polyurethane					PVC[b]		Silicone	
										Extruded[e]	Cross-linked[d]	Unmodified[e]	Modified[e]	Sheet[f]	Standard cushioning[f]		Carpet underlay[g]	High resilience type[h,i]				Liquid[j]	Sheet[g]
density, kg/m^3[k]		56	320	192	72	80	35	96	144	43	26–28	64–96	64–96	10	16	24	34	26	40	112	96	272	160
cell structure		closed	closed	closed	closed	open	closed	closed	closed	closed	closed	closed	closed		open	open	open	open	open	closed	open	open	open
compressive strength 25% deflection, kPa[l]	D3574, D3575			52			48	124	360			550	206	4.8	4.4	5.7	15.7	1.9	4.6				
tensile strength, kPa[l]	D3574		206	758	551	103	138	413	690	41		830	344		88	118	258	79	103	24	3.4	36 at 20%	
tensile elongation, %	D3574			500		310	60	60	60	276	276–480	1100	1380	138–275	160	205	135	200	160		220	227	310
rebound resilience, %	D3574					73				50		25	75			40		65	62				
tear strength, (N/m)[m] × 10^2	D3574						10.5	26	51	26					3.3	4.4	3.7	2.6	2.4				
max service temperature, °C		70	70	70	70		82	82	82	82	79–93	135	135	121								350	260
thermal conductivity, W/(m·K)	C177	0.036	0.043	0.065	0.030		0.053	0.058	0.058	0.040–0.049	0.036–0.040	0.039	0.039	0.039						0.040		0.078	0.086

[a] NR = natural rubber; CR = chloroprene rubber. [b] Ref. 131. [c] Ref. 162. [d] Ref. 135. [e] Ref. 163. [f] Ref. 164. [g] Ref. 165.
[h] Ref. 166. [i] Ref. 167. [j] Ref. 168. [k] To convert kg/m^3 to lb/ft^3, multiply by 0.0624. [l] To convert kPa to psi, multiply by 0.145. [m] To convert N/m to lbf/in., divide by 1.75.

The *fraction of open cells* expresses the extent to which the gas phase of one cell is in communication with other cells. When a large portion of cells are interconnected by gas phase, the foam has a large fraction of open cells, or is an open-celled foam. Conversely, a large proportion of noninterconnecting cells results in a large fraction of closed cells, or a closed-celled foam.

The nature of the opening between cells determines how readily different gases and liquids can pass from one cell to another. Because of variation in flow of different liquids or gases through the cell-wall openings, a single measurement of fraction open cells does not fully characterize this structural variable, especially in a dynamic situation.

4.1.1.4. Gas Composition. In closed-celled foams, the gas phase in the cells can contain some of the blowing agent (called captive blowing agent), gas components of air which have diffused in, or other gases generated during the foaming process. Such properties as thermal and electrical conductivity can be profoundly influenced by the cell gas composition. In open-celled foams the presence of air exerts only a minor influence on the static properties but does affect the dynamic properties such as cushioning.

4.1.2. Rigid Cellular Polymers

A separate class of high density, rigid cellular polymers has grown continually since the 1970s to become significant commercially. These are the structural foams with a density >300 kg/m^3. They are treated here as a separate category of rigid foams.

Compressive strength and modulus are widely used as general criteria to characterize the mechanical properties of rigid plastic foams. Rigid cellular polymers generally do not exhibit a definite yield point when compressed but instead show an increased deviation from Hooke's law as the compressive load is increased (148, 149). For precision the compressive strength is usually reported at some definite deflection (commonly 5 or 10%). The compressive modulus is reported as extrapolated to 0% deflection unless otherwise stated. Structural variables that affect the compressive strength and modulus of a rigid plastic foam are, in order of decreasing importance: plastic-phase composition, density, cell structure, and plastic state. The effect of gas composition is minor, with a slight effect of gas pressure in some cases.

Density and polymer composition have a large effect on compressive strength and modulus (Fig. 3). The dependence of compressive properties on cell size has been discussed (22). The cell shape or geometry has also been shown important in determining the compressive properties (22, 59, 60, 153, 154). In fact, the foam cell structure is controlled in some cases to optimize certain physical properties of rigid cellular polymers.

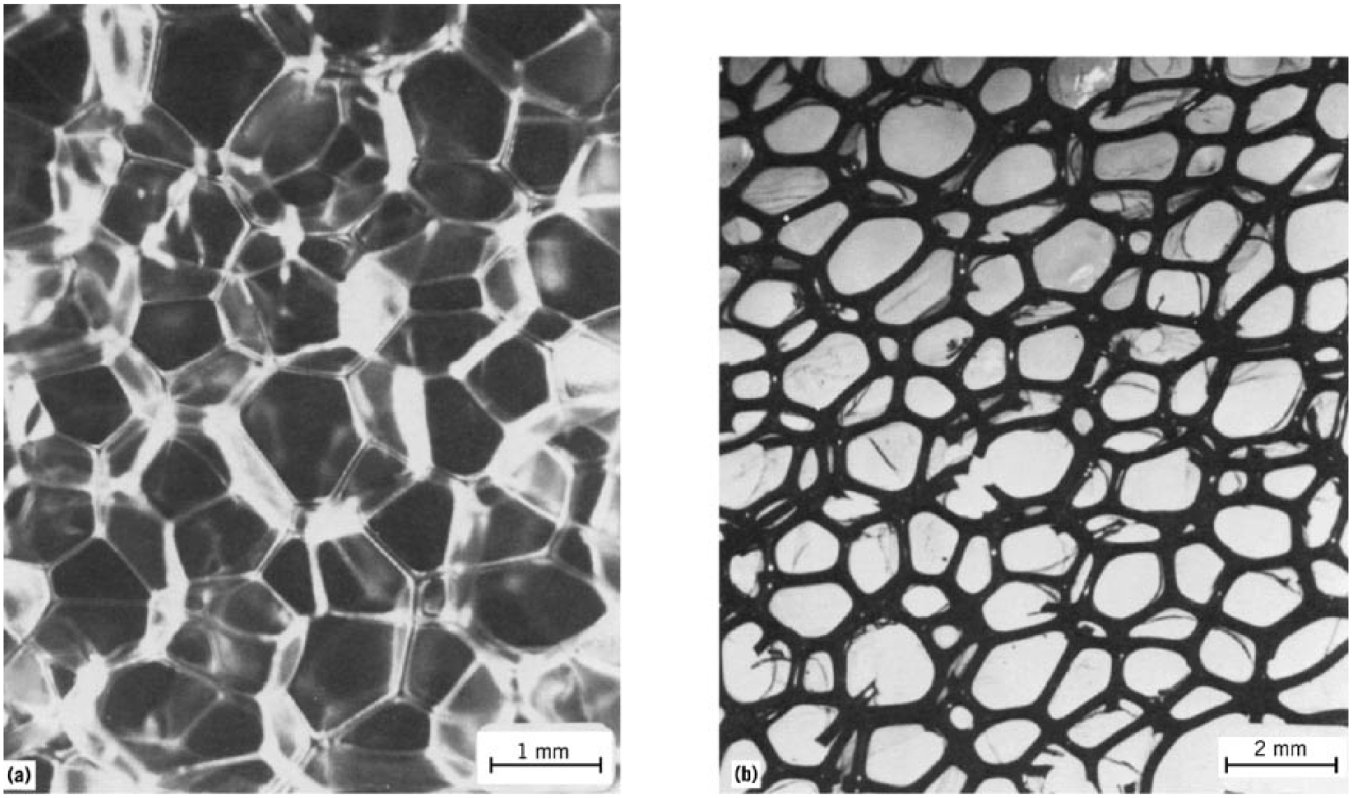

Fig. 2. Photomicrographs of foam cell structure: (**a**) extruded polystyrene foam, reflected light, 26×; (**b**) polyurethane foam, transmitted light, 26×; (**c**) polyurethane foam, reflected light, 12×; (**d**) high density plastic foam, transmitted light, 50× (22).(Courtesy of Van Nostrand Reinhold Publishing Corp.)

Strengths and moduli of most polymers increase as the temperature decreases (155). This behavior of the polymer phase carried over into the properties of polymer foams and similar dependence of the compressive modulus of polyurethane foams on temperature has been shown (151).

Tensile strength and modulus of rigid foams have been shown to vary with density in much the same manner as the compressive strength and modulus. General reviews of the tensile properties of rigid foams are available (22, 59, 60, 131, 156).

Those structural variables most important to the tensile properties are polymer composition, density, and cell shape. Variation with use temperature has also been characterized (157). Flexural strength and modulus of rigid foams both increase with increasing density in the same manner as the compressive and tensile properties. More specific data on particular foams are available from manufacturers literature and in References (22, 59, 60, 131) and 156. Shear strength and modulus of rigid foams depend on the polymer composition and state, density, and cell shape. The shear properties increase with increasing density and with decreasing temperature (157).

4.1.2.1. Creep. The creep characteristic of plastic foams must be considered when they are used in structural applications. Creep is the change in dimensions of a material when it is maintained under a constant stress. Data on the deformation of polystyrene foam under various static loads have been compiled (158). There are two types of creep in this material: short-term and long-term. Short-term creep exists in foams at all stress levels; however, a threshold stress level exists below which there is no detectable long-term creep. The

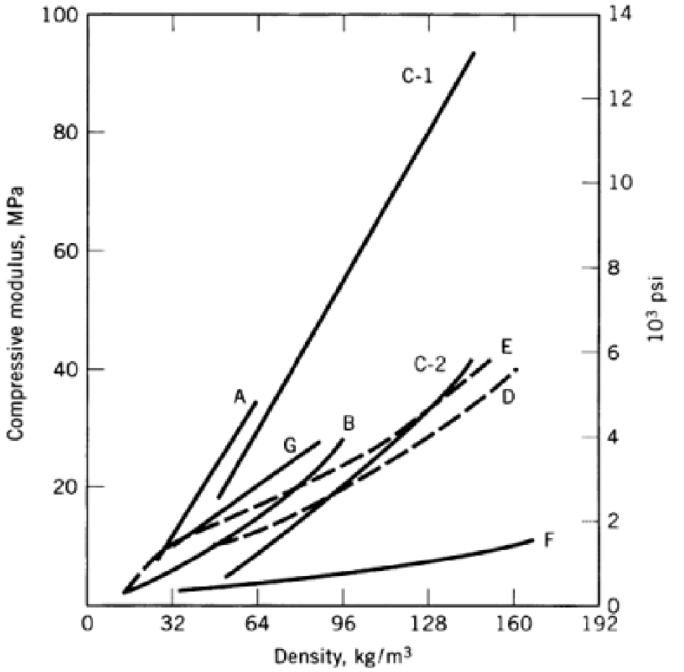

Fig. 3. Effect of density on compressive modulus of rigid cellular polymers. A, extruded polystyrene (131); B, expanded polystyrene (150); C-1, C-2, polyether polyurethane (151); D, phenol–formaldehyde (150); E, ebonite (150); F, urea–formaldehyde (150); G, poly(vinylchloride) (152). To convert kg/m^3 to lb/ft^3, multiply by 0.0624.

minimum load required to cause long-term creep in molded polystyrene foam varies with density ranging from 50 kPa (7.3 psi) for foam density 16 kg/m^3 (1 lb/ft^3) to 455 kPa (66 psi) at foam density 160 kg/m^3 (10 lb/ft^3).

The successful application of time–temperature superposition (159) for polystyrene foam is particularly significant in that it allows prediction of long-term behavior from short-term measurements. This is of interest in building and construction applications.

4.1.3. Structural Foams

Structural foams are usually produced as fabricated articles in injection molding or extrusion processes. The optimum product and process match differs for each fabricated article, so there are no standard commercial products for one to characterize. Rather there are a number of foams with varying properties. The properties of typical structural foams of different compositions are reported in Table 3.

The most important structural variables are again polymer composition, density, and cell size and shape. Structural foams have relatively high densities (typically >300 kg/m^3) and cell structures similar to those in Figure 4**d** which are primarily comprised of holes in contrast to a pentagonal dodecahedron type of cell structure in low density plastic foams. Since structural foams are generally not uniform in cell structure, they exhibit considerable variation in properties with particle geometry (103).

The mechanical properties of structural foams and their variation with polymer composition and density has been reviewed (103). The variation of structural foam mechanical properties with density as a function of polymer properties is extracted from stress–strain curves and, owing to possible anisotropy of the foam, must be considered apparent data. These relations can provide valuable guidance toward arriving at an optimum structural foam, however.

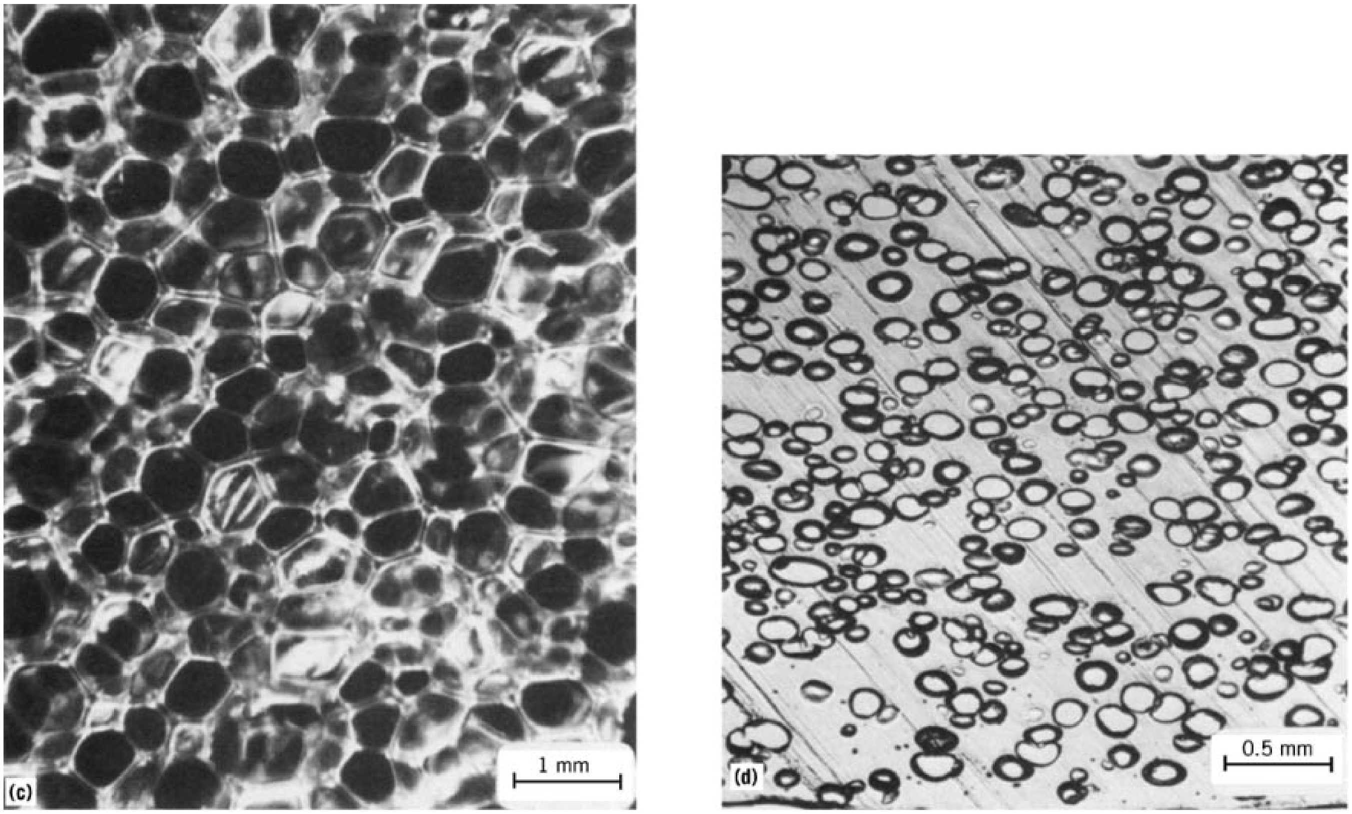

Fig. 4. Continued

4.1.4. Flexible Cellular Polymers

The application of flexible foams has been predominantly in comfort cushioning, packaging, and wearing apparel (161), resulting in emphasis on a different set of mechanical properties than for rigid foams. The compressive nature of flexible foams (both static and dynamic) is their most significant mechanical property for most uses (Table 4). Other important properties are tensile strength and elongation, tear strength, and compression set. These properties can be related to the same set of structural variables as those for rigid foams.

4.1.4.1. Compressive Behavior. The most informative data in characterizing the compressive behavior of a flexible foam are derived from the entire load-deflection curve of 0–75% deflection and its return to 0% deflection at the speed experienced in the anticipated application. Various methods have been reported (3, 161, 169–172) for relating the properties of flexible foams to desired behavior in comfort cushioning. Other methods to characterize package cushioning have been reported. The most important variables affecting compressive behavior are polymer composition, density, and cell structure and size.

Polymer composition is the most important structural variable (Fig. 5). Although the polystyrene and polyethylene foams are approximately the same density and the open-celled latex foam significantly more dense, all three show markedly different compressive strengths. The compressive behavior of latex rubber foams of various densities (3, 173) is illustrated in Figure 6. Similar relationships undoubtedly hold for vinyl and flexible polyurethane foams as well. In the case of polyurethane foams there are many variables in addition to density which heavily influence compressive behavior (32, 50, 60). For example the effects of reaction water content, polyol molecular weight, polymer polyol content, and isocyanate index on polymer tensile stiffness

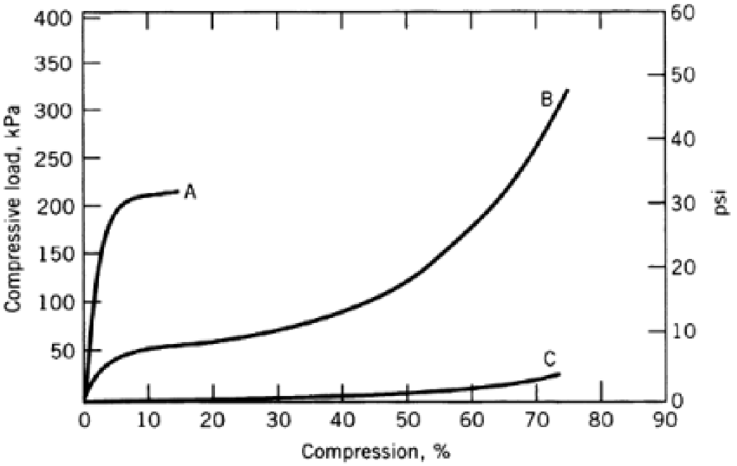

Fig. 5. Load vs compression for plastic foams (149). A, polystyrene, 32 kg/m^3 (2 lbs/ft^3); B, polyethylene, 32 kg/m^3; C, latex rubber foam. To convert kg/m^3 to lb/ft^3, multiply by 0.0624.

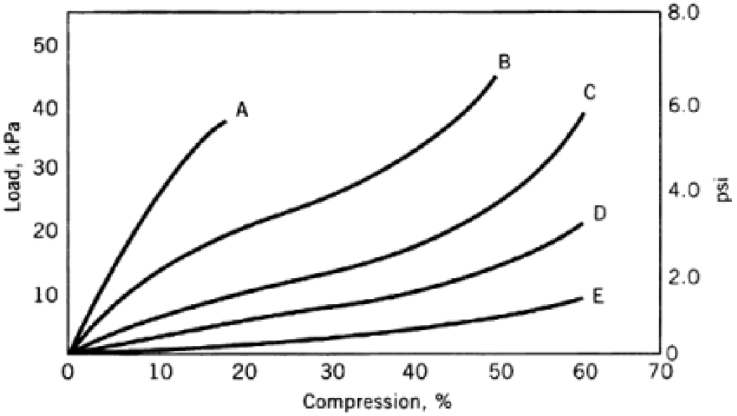

Fig. 6. Effect of load on compression for latex foams of different densities (3, 173). A, 304 kg/m^3; B, 208 kg/m^3; C, 179 kg/m^3; D, 139 kg/m^3; E, 99 kg/m^3. To convert kg/m^3 to lb/ft^3, multiply by 0.0624.

have been described (174). A further strong variation of flexible polyurethane foam compressive behavior can occur due to changes in the closed-cell content as measured by means of an airflow manometer described in ASTM method D3574.

Various geometric coring patterns in polyurethanes (171, 175) and in latex foam rubber (176) exert significant influences on their compressive behavior. A good discussion of the effect of cell size and shape on the properties of flexible foams is contained in References 60 and 156. The effect of open-cell content is demonstrated in polyethylene foam (173).

4.1.4.2. Tensile Strength and Elongation. The tensile strength of latex rubber foam has been shown to depend on the density of the foam (149, 177) and on the tensile strength of the parent rubber (177, 178). At low densities the tensile modulus approximates a linear relation with density but increases with a higher power of density at higher densities. Similar relations hold for polyurethane and other flexible foams (156, 179, 180).

The tensile elongation of solid latex rubber has been shown to correlate well with the elongation of foam from the latex (178). The elongation of flexible polyurethane has been related to cell structure (180, 181).

4.1.4.3. Tear Strength. A relation for the tearing stress of flexible foams that predicts linear increase in the tearing energy with density and increased tearing energy with cell size has been developed (177). Both relationships are verified to a limited extent by experimental data.

4.1.4.4. Flex Fatigue. Considerable information on the measurement and cause of flex fatigue in flexible foams has been published (182–184). Changing compressive strength and volume upon repeated flexing over long periods of time is a significant deterrent to the use of polyurethane foam in many cushioning applications. For polyurethane foams these changes have been correlated mainly with changes in chemical structure.

4.1.4.5. Compression Set. The compression set is an important property in cushioning applications. It has been studied for polyurethane foams (185, 186), and has been discussed in reviews (32, 60, 156). Compression set has been described as flex fatigue and creep as well.

4.2. Other Properties

The thermal, electrical, acoustical, and chemical properties of all cellular polymers are of such a similar nature that the discussions of these properties are not separated into rigid and flexible groups.

4.2.1. Thermal Properties

4.2.1.1. Thermal Conductivity. More information is available relating thermal conductivity to structural variables of cellular polymers than for any other property. Several papers have discussed the relation of the thermal conductivity of heterogeneous materials in general (187, 188) and of plastic foams in particular (132, 143, 151, 159, 189–191) with the characteristic structural variables of the systems.

The following separation of the total heat transfer into its component parts, even if not completely rigorous, proves valuable to understanding the total thermal conductivity, k, of foams:

$$k = k_s + k_g + k_r + k_c \qquad (6)$$

where k_s, k_g, k_r, and k_c are the components of thermal conductivity attributable to solid conduction, gaseous conduction, radiation, and convection, respectively.

As a good first approximation (187), the heat conduction of low density foams through the solid and gas phases can be expressed as the product of the thermal conductivity of each phase times its volume fraction. Most rigid polymers have thermal conductivities of $0.07 - 0.28$ W/(m·K) and the corresponding conduction through the solid phase of a 32 kg/m^3 (2 lbs/ft^3) foam (3 vol %) ranges $0.003 - 0.009$ W/(m·K). In most cellular polymers this value is determined primarily by the density of the foam and the polymer-phase composition. Smaller variations can result from changes in cell structure.

Although conductivity through gases is much lower than that through solids, the amount of heat transferred through the gas phase in a foam is generally the largest contribution to the total heat transfer because the gas phase is the principal part of the total value (ca 97 vol % in a 32 kg/m^3 foam). Table 5 lists values of the thermal conductivity for several gases that occur in the cells of cellular polymers. The thermal conductivities of the halocarbon gases are considerably less than those of oxygen and nitrogen. It has, therefore, proved advantageous to prepare cellular polymers using such gases that measurably lower the k of the polymer foam. Upon exposure to air the gas of low thermal conductivity in the cells can become mixed with air, and the k of the mixture of gases can be estimated by a mixing rule such as the Riblett equation 7.

$$k_m = \sum_i k_i M_i^{1/3} P_i / \sum_i M_i^{1/3} P_i \qquad (7)$$

Table 5. Thermal Conductivity at 20°C of Gases Used in Cellular Polymers[a]

Compound[b]	Thermal conductivity, W/(m·K)
trichlorofluoromethane (CFC-11)	0.0084
dichlorodifluoromethane (CFC-12)	0.0098
trichlorotrifluoroethane (CFC-113)	0.0072
dichlorotetrafluoroethane (CFC-114)	0.0104
dichlorofluoromethane (CFC-21)	0.0112
chlorodifluoromethane (HCFC-22)	0.0106
difluoromethane (HFC-32)	0.0163
2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124)	0.0106
pentafluoroethane (HFC-125)	0.0131
1,1,1,2-tetrafluoroethane (HFC-134a)	0.0127
1,1-dichloro-1-fluoroethane (HCFC-141b)	0.0083
1-chloro-1,1-difluoroethane (HCFC-142b)	0.0108
trifluoroethane (HFC-143a)	0.0137
1,1-difluoroethane (HFC-152a)	0.0136
dichloromethane	0.0063
methyl chloride	0.0105
2-methylpropane	0.0161
carbon dioxide	0.0168
air	0.0259

[a] Refs. (192, 193).

[b] CFC = chlorofluorocarbon; HCFC = hydrochlorofluorocarbon; see FLUORINE COMPOUNDS, ORGANIC–ALIPHATIC.

where k_{m} is the k of the gaseous mixture; k_{i}, M_{i}, and P_{i} are the component thermal conductivity, molecular weight, and partial pressure, respectively. Changes in total k calculated by equations 6 and 7 with change in gas composition agree well with experimental measurements (144, 191, 194, 195).

There is ordinarily no measurable convection in cells of diameter less than about 4 mm (143). Theoretical arguments have been in general agreement with this work (151, 191). Since most available cellular polymers have cell diameters smaller than 4 mm, convection heat transfer can be ignored with good justification. Studies of radiant heat transfer through cellular polymers have been made (143, 151, 191, 196, 197).

The variation in total thermal conductivity with density has the same general nature for all cellular polymers (143, 189). The increase in k at low densities is owing to an increased radiant heat transfer; the rise at high densities to an increasing contribution of k_{s}.

The thermal conductivity of most materials decreases with temperature. When the foam structure and gas composition are not influenced by temperature, the k of the cellular material decreases with decreasing temperature. When the composition of the gas phase may change (ie, condensation of a vapor), then the relationship of k to temperature is much more complex (143, 191, 198).

The thermal conductivity of a cellular polymer can change upon aging under ambient conditions if the gas composition is influenced by such aging. Such a case is evidenced when oxygen or nitrogen diffuses into polyurethane foams that initially have only a fluorocarbon blowing agent in the cells (32, 130, 143, 190, 191, 198–201).

Thermal conductivity of foamed plastics has been shown to vary with thickness (197). This has been attributed to the boundary effects of the radiant contribution to heat-transfer.

4.2.1.2. Specific Heat. The specific heat of a cellular polymer is simply the sum of the specific heats of each of its components. The contribution of the gas is small and can be neglected in many cases.

4.2.1.3. Coefficient of Linear Thermal Expansion. The coefficients of linear thermal expansion of polymers are higher than those for most rigid materials at ambient temperatures because of the supercooled-liquid nature of the polymeric state, and this applies to the cellular state as well. Variation of this property with density and temperature has been reported for polystyrene foams (202) and for foams in general (22). When cellular polymers are used as components of large structures, the coefficient of thermal expansion must be considered carefully because of its magnitude compared with those of most nonpolymeric structural materials (203).

4.2.1.4. Maximum Service Temperature. Because the cellular materials, like their parent polymers (204), gradually decrease in modulus as the temperature rises rather than undergoing a sharp change in properties, it is difficult to precisely define the maximum service temperature of cellular polymers. The upper temperature limit of use for most cellular polymers is governed predominantly by the plastic phase. Fabrication of the polymer into a cellular state normally builds some stress into the polymer phase; this may tend to relax at a temperature below the heat-distortion temperature of the unfoamed polymer. Of course, additives in the polymer phase or a plasticizing effect of the blowing agent on the polymer affect the behavior of the cellular material in the same way as the unfoamed polymer. Typical maximum service temperatures are given in Tables 2, 3, and 4.

4.2.1.5. Flammability. The results of small-scale laboratory tests of plastic foams have been recognized as not predictive of their true behavior in other fire situations (205). Work aimed at developing tests to evaluate the performance of plastic foams in actual fire situations continues. All plastic foams are combustible, some burning more readily than others when exposed to fire. Some additives (131, 135), when added in small quantities to the polymer, markedly improve the behavior of the foam in the presence of small fire sources. Plastic foams must be used properly following the manufacturers recommendations and any applicable regulations.

4.2.1.6. Moisture Resistance. Plastic foams are advantageous compared to other thermal insulations in several applications where they are exposed to moisture pickup, particularly when subjected to a combination of thermal and moisture gradients. In some cases the foams are exposed to freeze–thaw cycles as well. The behavior of plastic foams has been studied under laboratory conditions simulating these use conditions as well as under the actual use conditions.

In a study (206) of the moisture gain of foamed plastic roof insulations under controlled thermal gradients the apparent permeability values were greater than those predicted by regular wet-cup permeability measurements. The moisture gains found in polyurethane are greater than those of bead polystyrene and much greater than those of extruded polystyrene.

Moisture pickup and freeze–thaw resistance of various insulations and the effect of moisture on the thermal performance of these insulations has been reported (207). In protected membrane roofing applications the order of preference for minimizing moisture pickup is extruded polystyrene $\gg$ polyurethane $>$ molded polystyrene (207). Water pickup values for insulation in use for five years were extruded polystyrene 0.2 vol %, polyurethane without skins 5 vol %, and molded polystyrene 8–30 vol %. These correspond to increases in k of 5–265%. For below-grade applications extruded polystyrene was better than molded polystyrene or polyurethane without skins in terms of moisture absorption resistance and retention of thermal resistance. Increased water content has been related with increased thermal conductivity of the insulations (208–212).

4.2.2. Electrical Properties

Cellular polymers have two important electrical applications (22). One takes advantage of the combination of inherent toughness and moisture resistance of polymers along with the decreased dielectric constant and dissipation factor of the foamed state to use cellular polymers as electrical-wire insulation (97). The other combines the low dissipation factor and the rigidity of plastic foams in the construction of radar domes. Polyurethane foams have been used as high voltage electrical insulation (213).

4.2.3. Environmental Aging

All cellular polymers are subject to a deterioration of properties under the combined effects of light or heat and oxygen. The response of cellular materials to the action of light and oxygen is governed almost entirely by the composition and state of the polymer phase (22). Expansion of a polymer into a cellular state increases the surface area; reactions of the foam with vapors and liquids are correspondingly faster than those of solid polymer.

Foams prepared from phenol–formaldehyde and urea–formaldehyde resins are the only commercial foams that are significantly affected by water (22). Polyurethane foams exhibit a deterioration of properties when subjected to a combination of light, moisture, and heat aging; polyester-based foam shows much less hydrolytic stability than polyether-based foam (50, 199).

A great deal of work has been done to develop additives that successfully eliminate environmental degradation (214). The best source of information on specific additives for specific foams is the individual manufacturer of the foam. The resistance to rot, mildew, and fungus of cellular polymers can be related to the amount of moisture that can be taken up by the foam (150). Therefore, open-celled foams are much more likely to support growth than are closed-celled foams. Very high humidity and high temperature are necessary for the growth of microbes on any plastic foam.

4.2.4. Miscellaneous Properties

The acoustical properties of polymers are altered considerably by their fabrication into a cellular structure. Sound transmission is altered only slightly because it depends predominantly on the density of the barrier (in this case, the polymer phase). Cellular polymers by themselves are, therefore, very poor materials for reducing sound transmission. They are, however, quite effective in absorbing sound waves of certain frequencies (150); materials with open cells on the surface are particularly effective. The combination of other advantageous physical properties with fair acoustical properties has led to the use of several different types of plastic foams in sound-absorbing constructions (215, 216). The sound absorption of a number of cellular polymers has been reported (21, 150, 215, 217).

The permeability of cellular polymers to gases and vapors depends on the fraction of open cells as well as the polymer-phase composition and state. The presence of open cells in a foam allows gases and vapors to permeate the cell structure by diffusion and convection flow, yielding very large permeation rates. In closed-celled foams the permeation of gases or vapors is governed by composition of the polymer phase, gas composition, density, and cellular structure of the foam (194, 199, 215, 218, 219).

The penetration of visible light through foamed polystyrene has been shown to follow approximately the Beer-Lambert law of light absorption (22). This behavior presumably is characteristic of other cellular polymers as well.

Comfort cushioning is the largest single application of cellular polymers; flexible foams are the principal contributors to this field. Historically, cushioning in particular and flexible foams in general have been the greatest volume of cellular polymers. However, the rapid growth rate of structural, packaging, and insulation applications has brought their volume over that of flexible foams during the past few years. Table 6 shows United States consumption of foamed plastics by resin and market (20).

4.2.5. Comfort Cushioning

The properties of greatest significance in the cushioning applications of cellular polymers are compression–deflection behavior, resilience, compression set, tensile strength and elongation, and mechanical and environmental aging; compression–deflection behavior is the most important. The broad range of compressive behavior of various types of flexible foam is one of the strong points of cellular polymers, since the needs of almost any cushioning application can be met by changing either the chemical nature or the physical structure of the foam. Flexible urethanes, vinyls, latex foam rubber, and olefins are used to make foamed plastic cushioning for

Table 6. Market for Cellular Polymers,[a] 10^3 t

Item	1967	1982	1995[b]
	By market		
insulation	58	261	472
flooring	20	98	154
other construction	9	136	288
cushioning	52	195	336
other furniture	40	103	175
packaging	43	177	311
transportation	76	140	238
consumer	44	136	225
bedding	18	57	113
appliances	14	40	61
other	68	225	408
Total	*441*	*1567*	*2781*
	By resin		
flexible urethane	181	511	844
rigid urethane	68	248	449
styrene	125	410	699
vinyl	61	232	413
others	6	165	376
Total	*441*	*1567*	*2781*

[a] Ref. 20.
[b] Projected.

automobile padding and seats, furniture, flooring, mattresses, and pillows. These materials compete with felt, fibers, innerspring, and other filling materials.

Latex foam rubber was initially accepted as a desirable comfort-cushioning material because of its softness to the touch and its resilience (equal to that of a steel spring alone but with better damping qualities than the spring).

Cellular rubber has been used extensively as shoe soles, where its combination of cushioning ability and wear resistance, coupled with desirable economics, has led to very wide acceptance. In this case the cushioning properties are of minor importance compared with the abrasion resistance and cost. Other significant cushioning applications for cellular rubbers and latex foam rubbers are as carpet underlay and as cushion padding in athletic equipment.

4.2.6. Thermal Insulation

Thermal insulation is the second largest application of cellular polymers and the largest application for the rigid materials. The properties of greatest importance in determining the applicability of rigid foams as thermal insulants are thermal conductivity, ease of application, cost, moisture absorption and transmission permeance, and mechanical properties (see Insulation, thermal). Plastic foams containing a captive blowing agent have considerably lower thermal conductivities than other insulating materials, whereas other rigid cellular plastics are roughly comparable with the latter.

4.2.6.1. Domestic Refrigeration. The very low thermal conductivity of polyurethanes plus the ease of application and structural properties of foamed-in-place materials gives refrigeration engineers considerable freedom of styling. This has resulted in an increasingly broad use of rigid polyurethane foams in home freezers and refrigerators which has displaced conventional rock wool and glass wool.

4.2.6.2. Commercial Refrigeration. Again, low thermal conductivity is important, as are styling and cost. Application methods and mechanical properties are of secondary importance because of design latitude in this area. For example, large institutional chests, commercial refrigerators, freezers, and cold storage areas, including cryogenic equipment and large tanks for industrial gases, are insulated with polystyrene or polyurethane foams. Polystyrene foam is still popular where cost and moisture resistance are important; polyurethane is used where spray application is required. Polystyrene foam is also widely used in load-bearing sandwich panels in low temperature space applications.

4.2.6.3. Refrigeration in Transportation. Styling is unimportant. The volume of insulation and a low thermal conductivity are of primary concern. Volume is not large, so application methods are not of prime importance. Low moisture sensitivity and permanence are necessary. The mechanical properties of the insulant are quite important owing to the continued abuse the vehicle undergoes. Cost is of less concern here than in other applications.

4.2.6.4. Residential Construction. Owing to rising energy costs, the cost and low thermal conductivity are of prime importance in wall and ceiling insulation of residential buildings. The combination of insulation efficiency, desirable structural properties, ease of application, ability to reduce air infiltration, and moisture resistance has led to use of extruded polymeric foam in residential construction as sheathing, as perimeter and floor insulation under concrete, and as a combined plaster base and insulation for walls.

4.2.6.5. Commercial Construction. The same attributes desirable on residential construction applications hold for commercial construction as well but insulation quality, permanence, moisture insensitivity, and resistance to freeze–thaw cycling in the presence of water are of greater significance. For this reason cellular plastics have greater application here. Both polystyrene and polyurethane foams are highly desirable roof insulations in commercial as in residential construction.

Cellular polymers are also used for pipe and vessel insulation. Spray and pour-in-place techniques of application are particularly suitable, and polyurethane and epoxy foams are widely used. Ease of application, fire properties, and low thermal conductivity have been responsible for the acceptance of cellular rubber and cellular poly(vinyl chloride) as insulation for smaller pipes.

The insulating value and mechanical properties of rigid plastic foams have led to the development of several novel methods of building construction. Polyurethane foam panels may be used as unit structural components (220) and expanded polystyrene is employed as a concrete base in thin-shell construction (221).

4.2.7. Packaging

Because of the extremely broad demands on the mechanical properties of packaging materials, the entire range of cellular polymers from rigid to flexible is used in this application. The most important considerations are mechanical properties, cost, ease of application or fabrication, moisture susceptibility, thermal conductivity, and aesthetic appeal.

The proper mechanical properties, particularly compressive properties, are the primary requirements for a cushioning foam (222, 223). The reader is referred to the following sources for more specific information: package design (224); general vibration and shock isolation (225); protective package design (226); selection of cushioning material (222, 227); and characterization of cellular polymers for cushioning applications (223, 225, 226, 228).

Creep of a cushion packaging material when subjected to static stresses for long periods of storage or shipment is also an important consideration. Polystyrene foam shows considerable creep (158) at high static loadings but that creep is insignificant under loadings in the static stress region of optimum package design (22). The ability of polystyrene foam to withstand repeated impacts has also been studied (152, 229).

The low density of most cellular plastics is important because of shipping costs for the cushioning in a package. Foams with densities ranging from 4 to 32 kg/m^3 are used in this application. The inherent moisture resistance of cellular plastics is of added benefit where packages may be subjected to high humidity or water. Many military applications require low moisture susceptibility. Foamed polystyrene is used as packaging inserts and as containers such as food trays, egg cartons, and drinking cups which require moisture resistance, rigidity, and shock resistance. Foamed polyurethane is also used as specialty packaging materials for expensive and delicate equipment.

The clean, durable, nondust-forming character of polyethylene foam has led to its acceptance in packaging missile parts (230). Polyethylene foam sheet has also displaced polystyrene foam sheet for packaging glass bottles and containers because of its greater resiliency and tear resistance.

Antistatic protection is an important consideration within the electronic industry and various antistatic agents are used commercially to alleviate this problem in cushion packaging materials.

4.2.8. Structural Components

In most applications structural foam parts are used as direct replacements for wood, metals, or solid plastics and find wide acceptance in appliances, automobiles, furniture, materials-handling equipment, and in construction. Use in the building and construction industry account for more than one-half of the total volume of structural foam applications. High impact polystyrene is the most widely used structural foam, followed by polypropylene, high density polyethylene, and poly(vinyl chloride). The construction industry offers the greatest growth potential for cellular plastics.

The sandwich-type structure of polyurethanes with a smooth integral skin produced by the reaction injection molding process provides a high degree of stiffness as well as excellent thermal and acoustical properties necessary for its use in housing and load-bearing structural components for the automotive, business machine, electrical, furniture, and materials-handling industry.

4.2.9. Buoyancy

The low density, closed-celled nature of many cellular polymers coupled with their moisture resistance and low cost resulted in their immediate acceptance for buoyancy in boats and floating structures such as docks and buoys. Since each cell in the foam is a separate flotation member, these materials cannot be destroyed by a single puncture.

The combination of structural strength and flotation has stimulated the design of pleasure boats using a foamed-in-place polyurethane between thin skins of high tensile strength (231). Other cellular polymers that have been used in considerable quantities for buoyancy applications are those produced from polyethylene, poly(vinyl chloride), and certain types of rubber. The susceptibility of polystyrene foams to attack by certain petroleum products that are likely to come in contact with boats led to the development of foams from copolymers of styrene and acrylonitrile which are resistant to these materials (6, 7).

4.2.10. Electrical Insulation

The substitution of a gas for part of a solid polymer usually results in large changes in the electrical properties of the resulting material. The dielectric constant, dissipation factor, and dielectric strength are all generally lowered in amounts roughly proportional to the amount of gas in the foam.

For low frequency electrical insulation applications, the dielectric constant of the insulation is ideally as low as possible (see Insulation, electrical). The lower the density of the cellular polymer, the lower the dielectric constant and the better the electrical insulation. Dielectric strength is also reduced at lower density; the insulation is, therefore, susceptible to breakdown from voltage surges from such sources as lightning and short circuits. Because physical properties are also diminished proportionally to density, optimum density is determined by a compromise in properties. For many applications this compromise has been at an expansion of two or three volumes, mainly because the minimum physical properties required for fabrication and use are obtained at that point. Polyolefin foams have been most used as low frequency electrical insulation; poly(vinyl chloride) and polystyrene foams are used also. Producing a completely homogenous, closed-celled foam at lower densities in high speed wire-coating apparatus is difficult.

In high frequency applications, the dissipation factor is of greater importance. Coaxial cables using cellular polyolefins have been quite successfully used for frequencies in the megahertz range and above. Cellular plastics have also been used as structural materials in constructing very large radar-receiving domes (232). The very low dissipation factor of these materials makes them quite transparent to radar waves.

4.2.11. Space Filling and Seals

Cellular polymers have become common for gasketing, sealing, and space filling. Cellular rubber, poly(vinyl chloride), silicone (103), and polyethylene are used extensively for gasketing and sealing of closures in the automotive and construction trade (111). Most cellular materials must be predominantly closed-celled in order to provide the necessary barrier properties. The combination of chemical inertness, excellent conformation to irregular surfaces, and ability to be compressed to greater than 50% with relatively small pressures and still function satisfactorily contribute to the acceptance of cellular polymers in these applications.

In the construction industry, cellular polymers are used as spacers and sealant strips in windows, doors, and closures of other types, as well as for backup strips for other sealants.

4.2.12. Miscellaneous Applications

Cellular plastics have been used for display and novelty pieces from their early development. Polystyrene foam combines ease of fabrication with lightweight, attractive appearance, and low cost to make it a favorite in these uses. Phenolic foam has its principal use in floral displays. Its ability to hold large amounts of water for extended periods is used to preserve cut flowers. Cellular poly(vinyl chloride) is used in toys and athletic goods, where its toughness and ease of fabrication into intricate shapes have been valuable.

Cellular urea–formaldehyde and phenolic resin foams have been used to some extent in interior sound-absorbing panels and, in Europe, expanded polystyrene has been used in the design of sound-absorbing floors (233). In general, cost, flammability, and cleaning difficulties have prevented significant penetration of the acoustical tile market. The low percent of reflection of sound waves from plastic foam surfaces has led to their use in anechoic chambers (216).

5. Commercial Products and Processes

5.1. Flexible Polyurethane

These foams are produced from long-chain, lightly branched polyols reacting with a diisocyanate, usually toluene diisocyanate [1321-38-6] (TDI), to form an open-celled structure with free air flow during flexure. During manufacture these foams are closely controlled for proper density, ranging from 13 to 80 kg/m^3 (0.8–5 lbs/ft^3), to achieve the desired physical properties and cost.

In flexible polyurethane foams, the primary blowing agent is carbon dioxide, which is formed by the reaction of water and toluene diisocyanate. Softer foams with lower densities require an auxiliary blowing agent such as CFC-11, HCFC-141b, or methylene chloride. Since the load bearing characteristics of the foam are of great importance to the ultimate consumer this property is also closely controlled during manufacture.

5.1.1. Raw Materials

Polyether polyols are used in about 90% of polyurethane foams. The elastomeric polymer is provided additional toughness in the overall polymer matrix by the presence of hard segment urea-based polymers derived from the water/isocyanate reaction (see Isocyanates, organic; Urethane polymers). Intermolecular hydrogen bonding plays a further role in overall foam hardness. The polyols are typically trifunctional but di- and tetrafunctional polyols are also used. The polyol chain initiator determines the functionality of the final product; glycerol or trimethylolpropane are the most common triol initiators. Propylene oxide (PO) is then polymerized onto the initiator to form a long-chain triol with an equivalent weight of 1000 to 1500. PO chains are characterized by pendent methyl groups and terminal secondary hydroxyl groups which provide the lower level of reactivity used for slab foam manufacture. Ethylene oxide (EO) can be used in conjunction with PO to modify the polyether chain by reducing the pendent methyl groups. This is called a hetero polyol with the possibility of adding a mixed PO/EO feed to form a random hetero or a batch EO feed to form a block hetero polyol. Additionally, EO can be used at the end of the polyol polymerization to produce primary hydroxyl groups at chain termination. This is known as EO capping and results in polyols with considerably higher reactivities toward isocyanates which is the polyol type required for molded foam production.

Another type of polyol often used in the manufacture of flexible polyurethane foams contains a dispersed solid phase of organic chemical particles (234–236). The continuous phase is one of the polyols described above for either slab or molded foam as required. The dispersed phase reacts in the polyol using an addition reaction with styrene and acrylonitrile monomers in one type or a coupling reaction with an amine such as hydrazine and isocyanate in another. The solids content ranges from about 21% with either system to nearly 40% in the styrene–acrylonitrile system. The dispersed solids confer increased load bearing and in the case of flexible molded foams also act as a cell opener.

The isocyanates used in the manufacture of flexible foam are toluene diisocyanate (TDI) and polymeric 4,4′-methylenediphenyl diisocyanate [101-68-8] (MDI). Slab foam manufacturing is based almost entirely on TDI which is most often supplied as a blend of 80% 2,4 isomer and 20% 2,6 isomer by weight. There have been efforts to develop slab foaming technology using polymeric MDI in place of TDI (237–239). Polymeric MDI is often used in manufacturing molded foams usually blended with TDI, often at a 4 to 1 ratio of TDI to MDI by weight. The acidity and isomer distribution are key factors controlling the reactivity of these isocyanates. Foams are generally produced with a slight excess of isocyanate groups. The stoichiometric balance of a foam formulation is known as the foam index with 100 index as the balance point and 110 index indicating 110% isocyanate equivalents compared to active hydrogen equivalents.

Catalysis of the flexible polyurethane foaming operation is accomplished through the use of tertiary amine compounds, often using two different amines to balance the blowing and gelling reactions. Organometallic compounds, usually stannous salts, are also used to facilitate gelling and promote final cure.

Hydrolyzable or nonhydrolyzable siloxane compounds provide nucleating assistance for fine, uniform cells and surface tension depression for stabilization of the expanding cell walls prior to gelation of the polymer. The slab foam cells are mostly open after ultimate foam rise and blow off. Too much surfactant or too much tin gelation catalyst cause the foam to have a larger number of closed cells. This tight foam lets very little air pass through a cut block of foam. Tight foams are prone to shrink as the hot gas inside the closed cell cools thus producing less pressure and volume. Molded foams often need to be crushed after demolding to mechanically open closed cells and prevent shrinkage. Surfactants must be carefully chosen for use in flexible slab, high resilience (HR) slab, and HR or hot molded systems since most are not interchangeable.

Fillers (qv) are occasionally used in flexible slab foams; the two most commonly used are calcium carbonate (whiting) and barium sulfate (barytes). Their use level may range up to 150 parts per 100 parts of polyol. Various other ingredients may also be used to modify a flexible foam formulation. Cross-linkers, chain extenders, ignition modifiers, auxiliary blowing agents, etc, are all used to some extent depending on the final product characteristics desired.

5.1.2. Process and Equipment

The critical requirements for urethane foam dispensing equipment are accurate metering of the ingredients to the mixing chamber, adequate short-cycle mixing, and proper dispensing ability. The polyol, isocyanate, and water must all be delivered at an accurate rate to maintain the desired stoichiometry which is essential for predicting final foam performance and properties. The other ingredients must also be precisely controlled to obtain optimum processing and performance. Thorough ingredient mixing is made more critical because the components are reactive and thus may not remain in the mixing chamber for more than a few seconds. There is also a wide range of component viscosities; low viscosity isocyanates are dispersed in fairly high viscosity polyols. Additionally the mixing head must deliver the foam ingredients in a smooth flowing manner to minimize air entrainment or splashing.

There are two basic metering/mixing systems (based on pressure) in wide use. Low pressure (less than 2,000 kPa) systems use positive displacement pumps to deliver material via a heat exchanger and recycle valve to a mixing chamber with a mechanically driven impeller. High pressure (2,000–20,000 kPa) systems use precision high pressure pumps to deliver material via flow adjusting valves and/or orifices to a cylindrical impingement mixing chamber. Following each use the impingement mixing chamber is cleared by advancing a piston that eliminates the need for solvent flushing as is required for low pressure machines.

The mixing head dispenses the foam in several ways depending on the particular foam production process. Flexible foam molding requires the head to be positioned over the open mold, moved in relation to the mold for the best pour pattern and to dispense material on a required quantity shot basis. After the ingredients are placed in the mold cavity the lid is closed and the mold heated. The materials foam and expand to fill the mold, then gel and cure. The mold is then opened, the foam part removed, and a fresh layer of mold release sprayed onto the mold. The foam object is crushed to enhance cell opening and then may be post-cured. The two basic processes for molding are the earlier developed hot process where the molds are subjected to a high temperature (204–371°C) and the cold process where the mold ranges from room temperature to about 120°C. The chemistry used for the cold process is called high resilience or HR foam system.

Flexible slab operations often use a traversing arrangement to dispense the foam ingredients back and forth on a layer of polyethylene film carried on a conveying belt. Side papers are brought up to the edge of the film and the assembly enters a tunnel fitted with an exhaust system. The liquid foam ingredients begin to react and the foam rises to full height within 3–4.5 m after entering the tunnel. As the slab bun exits the tunnel the side papers are pulled off; the bun is then cut into appropriate lengths and delivered to a cure area. Generally a minimum of 24 hours is required to cure the bun prior to cutting into blocks for shipping. This simplest form of slab foam manufacture leaves the top of the bun with a rounded cross-section much like the top of a loaf of bread. This rounding introduces a waste factor during subsequent cutting of the bun into rectangular blocks for final use as furniture cushions, mattresses, etc. Starting in the late 1970s a number of patented processes were introduced to provide a square block with less wasted foam. These include side paper lifting, top smoothing, and bottom dropping, in which case the foam ingredients are fed to an overflow trough and the expanding foam is allowed to grow down instead of up.

Alternative processes are block pouring into a large, open-topped box lined with plastic film from which the cured bun is subsequently removed, or a recently introduced vertical foaming operation. In the latter case the foam ingredients are fed to the bottom of an enclosed trough. As the foam expands vertically it is pulled up by side conveyors. At the top of the square conveyor the foam is cut into length (usually about 2 m) and laid on its side for further curing. Since one of the large foam markets, carpet underlayment, uses long thin sections of foam it is also desirable to generate cylinders of foam which can then be peeled using a long sharp blade. Round buns of foam are generated by proprietary techniques using conventional conveyors and also with the vertical foaming apparatus modified accordingly. Scrap foam is utilized by shredding into small pieces, adding a prepolymer glue, tumbling to mix, compressing into a mold, then curing with steam. This so-called rebond foam is prepared in a variety of density grades then cut, sliced, or peeled to proper form for a number of applications including carpet underlayment.

5.1.3. Applications

Carpet underlayment as just described is a substantial market. Most furniture cushioning is made from blocks of slab-produced polyurethane foam in the density range of 16 to 29 kg/m^3 (1.0–1.8 lbs/ft^3). A minor portion of the market, 9–14 thousands of metric tons (20–30 million pounds) uses 40 kg/m^3 (2.5 lbs/ft^3) high resilient

(HR) foam for higher priced furniture cushions. The furniture market for polyurethane foams grew strongly until saturation occurred around 1979. Market use now tends to reflect the current economic trends.

For passenger car seating about 90% is made by the molded foam process. The transportation market has experienced a decline since 1979 due to decreased automotive production and also because U.S. cars have been downsized, resulting in the use of less polyurethane foam per car.

Consumption of polyurethane foam in bedding reached a maximum in 1978 and has since declined. The innerspring mattress has remained the standard in the United States whereas all-foam mattresses have gained a dominant market share in Europe.

Textile uses are a relatively stable area and consist of the lamination of polyester foams to textile products, usually by flame lamination or electronic heat sealing techniques. Flexible or semirigid foams are used in engineered packaging in the form of special slab material. Flexible foams are also used to make filters (reticulated foam), sponges, scrubbers, fabric softener carriers, squeegees, paint applicators, and directly applied foam carpet backing.

5.1.4. Economics

Flexible polyurethane foam is generally sold by the board foot, 1 in. × 1 ft × 1 ft ($0.083\ \text{ft}^3 = 0.0024\ \text{m}^3$), in the United States. Typical densities are 18.5–32.0 kg/m^3 (1.15 to 2.0 lbs/ft^3) for conventional foams and 40.0 kg/m^3 (2.5 lbs/ft^3) for HR foam. Foam prices are usually double the cost of the chemicals for standard grades. Thus typical foam prices in 1992 were about $2.75/kg ($1.25 per pound). This provides a range of foam costs from $0.12 per board ft at 1.15 lbs/ft^3 to $0.21 per board ft at 2.0 lbs/ft^3 ($51–$88/m^3).

5.2. Rigid Polyurethane

These foams are characterized by closed-celled structure and very high compressive strength. They are produced by using a highly branched, short-chain polyol reacted with an aromatic isocyanate of two or more functionality which is often polymeric. Pour-in-place and free rise rigid polyurethane foams usually have a density in the region of 32.0 kg/m^3 (2.0 lbs/ft^3), although molded rigid foams have densities ranging up to 640 kg/m^3 (40 lbs/ft^3) in structural foams. Insulation effectiveness is one of the outstanding characteristics of rigid polyurethane foams which display thermal conductivities as low as $0.017\ \text{W/(m·K)}$.

5.2.1. Raw Materials

The highly branched, short-chain polyols used for rigid foams can be initiated from amines such as diethylenetriamine to provide five functional sites or saccharides such as sorbitol or sucrose that have 6 or 8 functional sites, respectively. Subsequent polymerization of PO and/or EO at low levels further controls viscosity and reactivity of the resultant polyol. The level of oxide addition also contributes to the rigidity of the final foam product by controlling the molecular weight per branch point as well as influencing shrinkage resistance and moisture sensitivity. Amine-initiated polyols tend to be autocatalytic due to the tertiary amine groups residual in the molecule.

The isocyanates used with rigid foam systems are either polymeric MDI or specialty types of TDI. Both contain various levels of polymerized isocyanate groups which contribute to molecular weight per cross-link and also may affect reactivity due to steric hindrance of some isocyanate positions.

Surfactants for use with rigid foams are also silicone based but are quite different from those used for flexible foams. In this case it is more important for the surfactant to also act as a compatibilizer in assisting the intermixing of the isocyanate and polyol during the reaction period. Of course nucleation and cell stabilization during the early phase of foaming are also important functions of the surfactant. Water may also be used in rigid formulations but to a much lesser degree than in flexible foams.

Rigid polyurethane foams are normally foamed with CFC-11 or HCFC-141b as a blowing agent which has very low thermal conductivity. Because of the closed-celled structure of these foams and the low permeability of CFC-11 or HCFC-141b, the blowing agent is retained in the foam for a long period. Therefore, the superior insulating properties of these products is primarily due to the presence of CFC-11 or HCFC-141b in the foam cells.

Catalysis is usually accomplished through the use of tertiary amines such as triethylenediamine. Other catalysts such as 2,4,6-*tris*(*N,N*-dimethylaminomethyl)phenol are used in the presence of high levels of crude MDI to promote trimerization of the isocyanate and thus form isocyanurate ring structures. These groups are more thermally stable than the urethane structure and hence are desirable for improved flammability resistance (236). Some urethane content is desirable for improved physical properties such as abrasion resistance.

Miscellaneous chemicals are used to modify the final properties of rigid polyurethane foams. For example, halogenated materials are used for flammability reduction, diols may be added for toughness or flexibility, and terephthalate-based polyester polyols may be used for decreased flammability and smoke generation. Measurements of flammability and smoke characteristics are made with laboratory tests and do not necessarily reflect the effects of foams in actual fire situations.

5.2.2. Process and Equipment

Rigid polyurethane foam processes use the same high or low pressure pumping, metering, and mixing equipment as earlier described for flexible foams. Subsequent handling of the mixture is determined by the end product desired.

5.2.2.1. Lamination. Rigid foam boardstock with a variety of facer materials is commonly used for insulation in building construction. The boardstock is produced on a continuous basis by applying the polyurethane (or polyisocyanurate) forming mixture onto one facer sheet, allowing the mixture to begin foaming, applying the second facer on top, and passing the assembly into a fixed gap conveyor to provide heat for cure and control thickness. This is followed by edge trimming and cutting to board length. In this manner boardstock is produced with facer materials such as kraft paper, aluminum foil, tarpaper, etc, and a foam core thickness ranging up to 7.6 cm (3 in.).

5.2.2.2. Pour-in-Place. The polyurethane forming mixture can be poured into a cavity which will then be filled by the flowing, foaming reaction mixture. This method is used for such things as insulating refrigerator cabinets and filling hull cavities in boats and barges.

5.2.2.3. Molding. The reaction mixture can be discharged into a mold to flow out and fill the cavity. High density (about 320 kg/m^3 or 20 lbs/ft^3) moldings can be used for decorative furniture items such as drawer fronts or clock frames. The formulation can be adjusted to produce articles with a nonfoam skin layer and a cellular core which are known as structural foams.

5.2.2.4. Bun Stock. By pouring the reaction mixture on a continuous belt a long bun can be produced like the flexible slab foam previously described. After curing, the bun can be cut into slabs or blocks as required by the end use.

5.2.2.5. Box Foams. A measured quantity of the reaction mixture can be placed in an open-topped crate or box and allowed to foam in a free rise mode. The block is removed after gelling and is cut into end use pieces after curing.

5.2.2.6. Spray. In spray-on applications the reactive ingredients are impingement mixed at the spray head. Thickness of the foam is controlled by the amount applied per unit area and additional coats are used if greater than 2.5 cm (1.0 in.) thickness is required. This method is commonly used for coating industrial roofs or insulating tanks and pipes.

5.2.3. Applications

The principal use for rigid polyurethane foams is for insulation in various forms utilized by a variety of industries. Laminates for residential sheating (1.2 to 2.5 cm thick with aluminum skins) and roofing board (2.5

to 10.0 cm thick with roofing paper skins) are the leading products with about 45 metric tons of liquid spray systems also in use. Metal doors insulated by a pour-in-place process constitute another substantial use.

Household refrigerator and freezer designs have been influenced by the increased cost of energy and the need to develop competitive units with comparable energy efficiency ratings. These factors have increased the use of rigid polyurethane foam as pour-in-place insulation in place of the fiber glass insulation now used in only about 30% of the market. Since CFC blown foam has much better insulating effectiveness, the cabinet wall thickness can be reduced from the former fiber glass-centered design. The pour-in-place cabinet insulating process is carried out in large-scale integrated operations. Commercial refrigeration applications are found in cold storage room insulation, reach-in coolers, and retail display cases. These markets are also using more insulation to offset the higher cost of energy.

The principal use of rigid foam in the transportation market is for insulation of refrigerated truck trailers and bodies as well as refrigerated rail cars. The liquid urethane ingredients are usually poured into large panels held in a fixture. These are then used as integral components: walls, roofs, or floors of the trailer or rail car. Additional uses are insulated truck bodies, recreational vehicles, and cargo containers.

Tanks, pipes, and ducts have been increasingly insulated due to the high cost of energy. For example oil storage tanks must be kept warm to maintain a moderate viscosity for pumping. The energy required to maintain this temperature can be sharply reduced by insulating the tank with rigid polyurethane foam. This type of insulation is often spray applied but may also be cut from boardstock.

Packaging constitutes another significant use and is often a foam-in-place operation to protect industrial equipment such as pumps or motors. Furniture articles molded from rigid foam are used in the form of decorative drawer fronts, clock cases, and simulated wooden beams. Flotation for barge repair and sport boats as well as insulation for portable coolers are a few other uses.

5.2.4. Economics

Rigid foam systems are typically in the range of 32 kg/m^3 (2 lbs/ft^3) and, in 1992, had a foam price of about \$3.63/kg (\$1.65 per lb) with liquid foam systems at about \$2.75/kg. Unit prices for pour-in-place polyurethane packaging systems fall between the competitive expandable polystyrene bead foam at \$3.30/kg and low density polyethylene foams at \$5.80/kg.

5.3. Polystyrene

There are five basic types of polystyrene foams produced in a wide range of densities and employed in a wide variety of applications: (*1*) extruded polystyrene board; (*2*) extruded polystyrene sheet; (*3*) expanded bead molding; (*4*) injection molded structural foam; and (*5*) expanded polystyrene loose-fill packaging.

Expanded polystyrene. (EPS) beadboard insulation is produced with expandable polystyrene beads. These beads are produced by impregnating with 5 to 8% pentane and sometimes with flame retardants such as hexabromocyclododecane, pentabromomonochlorocyclohexane, or a synergistic mixture of antimony trioxide and dicumyl peroxide during suspension polymerization. The beads are pre-expanded by fabricators with steam or vacuum and then allowed to age. The pre-expanded beads are fed to the steam heated block molds where further expansion and fusion of beads take place. The molded blocks are then sliced into various sizes needed for specific applications after curing. Block densities range from 13–48 kg/m^3 (0.8–3 lbs/ft^3) with 24 kg/m^3 (1.5 lbs/ft^3) most common for cushion packaging and 16 kg/m^3 (1.0 lb/ft^3) for insulation applications. The 1993 price of EPS beads was \$1.58/kg (\$0.72/lb) to the molder.

Expanded polystyrene bead molding products account for the largest portion of the drinking cup market and are used in fabricating a variety of other products including packaging materials, insulation board, and ice chests. The insulation value, the moisture resistance, and physical properties are inferior to extruded boardstock, but the material cost is much less.

Expanded polystyrene loose-fill. packaging materials are produced normally by extrusion process followed by multiple steam expansions to give low density foam shapes that resemble “S”, “8”, and hollow shells. They are produced with either pentane or HCFC-141b or pentane/HCFC-141b mixed blowing agents. Expandable polystyrene loose-fill packaging material is also produced by suspension polymerization process with blowing agent incorporated into the polymer during the polymerization. These products are used as dunnage or space filling materials for cushion packaging. Under severe load conditions, vibrational settling may occur, resulting in a nonuniform cushioning protection throughout the package. They have good shock absorbency, excellent resiliency, and are odorless.

The light weight of these products reduces user’s shipping costs and conserves energy in transportation. These products are reusable, a key property from economic, ecological, and energy conservation standpoints. Most products are available in bulk densities of 4.0 to 4.8 kg/m^3 (0.25 to 0.30 lb/ft^3). Average price is about $1.50 per pound from the manufacturer.

Extruded polystyrene board. was first introduced in the early 1940s by Dow Chemical Co. with the tradename Styrofoam (89, 240, 241). The Styrofoam process consists of the extrusion of a mixture of polystyrene and volatile liquid blowing agent expanded through a die to form boards in various sizes. The continuous boards are then passed through the finishing equipment for further sizing.

In 1979, UC Industries, a joint venture between U.S. Gypsum and Condec Corp., began manufacture of a similar extruded polystyrene foam under the tradename FoamulaR. Its process is believed to consist of a single-screw tandem extrusion line (114.3-mm main extruder and 152.4-mm extruder as a cooler) and produce foam boardstock in a vacuum chamber connected to a barometric leg which acts as a vacuum seal (242, 243). The continuous foam board coming out of a pool of water is then passed through the finishing equipment for sizing.

In 1982, Minnesota Diversified Products, Inc. started to produce extruded polystyrene foam insulation under the trade name Certifoam. This product is believed to be produced by the process (244) developed by LMP (Lavorazione Materie Plastiche) SpA, Turin, Italy. The LMP process for producing extruded polystyrene board consists of a corotating twin-screw extruder (132 mm diameter, 21:1 L/D) with a single-screw extension as a cooling section, a combination motionless mixer/homogenizer and heat exchanger, a flat die, and finishing equipment for sizing and curing.

In residential sheathing insulation, fiberboard is still the most widely used product, although the use of extruded and molded polystyrene foam and of foil-faced isocyanurate foam is increasing depending on the cost, the amount of insulation required, and compatibility of insulation with other construction systems. In cavity-wall insulation, mineral wool, polyurethane, urea–formaldehyde, and fiber glass are widely used, although fiber glass batt is the most economical insulation for stud-wall construction. In mobile and modular homes, cellular plastics are used widely because of their light weight and more efficient insulation value.

The list price of foam plastic sheathing is about $0.26 per board foot (>$100/m^3) for a typical 25 mm (1 in.) sheathing material. The foam density ranges between 23 kg/m^3 (1.4 lbs/ft^3) and 40 kg/m^3 (2.5 lbs/ft^3) depending on the process and blowing agent used to produce a typical 25 mm (1 in.) sheathing product.

Extruded polystyrene foam sheet. is primarily produced in a single-screw tandem extrusion line consisting of a 114.3 mm (4.5 in.) primary extruder, screen changer, 152.4 mm (6.0 in.) secondary extruder as a cooler, and an annular die. Typical throughput rate for this size ranges from 340 to 450 kg/h. The sheet is normally extruded in thicknesses of about 0.4 to 6.5 mm, and at densities from about 50 to 160 kg/m^3. Polystyrene pellets and a nucleating agent such as talc or a combination of citric acid and sodium bicarbonate are fed to a primary extruder and melted. A blowing agent such as *n*-pentane, isopentane, HCFC-22, or HFC-152a is then injected into the primary extruder and mixed with the molten polymer. The mixture is passed through a secondary extruder to cool the mixture to appropriate foaming temperature. The cooled polymer gel is then passed through an annular die at which point foaming takes place. The foam bubble is pulled over a sizing mandrel and slit to obtain a flat sheet, which is then wound into a roll for storage and curing. The cured sheet is thermoformed into a finished product by either sheet manufacturers or fabricators. The raw material cost for the foam sheet is higher than that for the foam insulation boardstock because of its higher density. On the other hand, the capital cost for the foam sheet line is lower than that for the foam board because of its simpler finishing equipment. Primary application of foam sheet is as a packaging material in items such as disposable dishes and food containers, trays for meat, poultry and produce products, and egg cartons.

Injection molded structural foam. is used widely for high density items such as picture frames, furniture, appliances, housewares, utensils, toys, pipes, and fittings. Most of these products are produced by injection molding or profile extrusion methods from impact modified polystyrene. Almost all high density foam products are produced with a chemical blowing agent that releases either nitrogen or carbon dioxide, typically sodium bicarbonate or azodicarbonamides. Medium density products can be produced with either a physical or chemical blowing agent, or a combination of both.

5.4. Poly(Vinyl Chloride)

Cellular poly(vinyl chloride) (PVC) foam is available in both flexible and rigid foams. Flexible PVC foams are primarily produced by spread coating and calendering of fluid plastisols by means of a chemical blowing agent or mechanical frothing with air. Flexible PVC foams also are made by the extrusion process. Rigid PVC foams are produced by the extrusion or injection molding processes. Blowing is achieved by a chemical blowing agent or gas injection into the extruder.

5.4.1. Raw Materials

PVC is inherently a hard and brittle material and very sensitive to heat; it thus must be modified with a variety of plasticizers, stabilizers, and other processing aids to form heat-stable flexible or semiflexible products or with lesser amounts of these processing aids for the manufacture of rigid products (see Vinyl polymers, vinyl chloride polymers). Plasticizer levels used to produce the desired softness and flexibility in a finished product vary between 25 parts per hundred (pph) parts of PVC for flooring products to about 80–100 pph for apparel products (245). Numerous plasticizers (qv) are commercially available for PVC, although dioctyl phthalate (DOP) is by far the most widely used in industrial applications due to its excellent properties and low cost. For example, phosphates provide improved flame resistance, adipate esters enhance low temperature flexibility, polymeric plasticizers such as glycol adipates and azelates improve the migration resistance, and phthalate esters provide compatibility and flexibility (245).

In addition to modifying PVC with plasticizers, it is also necessary to incorporate heat stabilizers (qv) into the formulation in order to scavenge the evolved HCl at the processing temperatures, thereby reducing thermal degradation of the polymer. Typical heat stabilizers used for PVC are metallic compounds of barium, cadmium, zinc, lead, and tin; lead and zinc are the most common (245). Plasticizers containing epoxy linkages such as epoxidized soy bean oil or synergistic compounds such as dibasic lead phthalate and dibasic lead phosphite are also used to enhance heat stability. Other ingredients such as color pigments and fillers are added to the formulation for the desired coloration and cost reduction, respectively.

There are two principal PVC resins for producing vinyl foams: suspension resin and dispersion resin. The suspension resin is prepared by suspension polymerization with a relatively large particle size in the 30–250

μm range and the dispersion resin is prepared by emulsion polymerization with a fine particle size in the 0.2–2 μm range (245). The latter is used in the manufacture of vinyl plastisols which can be fused without the application of pressure. In addition, plastisol blending resins, which are fine particle size suspension resins, can be used as a partial replacement for the dispersion resin in a plastisol system to reduce the resin costs.

A most widely used decomposable chemical blowing agent is azodicarbonamide. Its decomposition temperature and rate of evolution of gaseous components are greatly influenced by the stabilizers containing zinc. Lead and cadmium are considered moderate activators for *p,p′*-oxybis benzenesulfonyl hydrazide (OBSH). OBSH can also be used as a blowing agent for PVC foams.

5.4.2. Process and Equipment

5.4.2.1. Flexible Poly(vinyl chloride) Foam.

Spread coating. is usually carried out by applying a thin coating of plastisol skin coat on a release paper which is then partially fused in a forced air convection oven in the range of 150°C to facilitate rolling and unrolling of the product. This product passes through the second coating head where a plastisol containing suitable chemical blowing agent is applied to the plastisol skin side of the laminate. The fabric is then adhered to the foam plastisol and passed through the final oven at 200–235°C for fusion and foaming. The paper is separated from the vinyl foam and both the paper and the product are taken away by separate winding rolls (245). The optimum oven temperatures depend on the residence time and the type of blowing agent used.

A *calender processing* is also used to produce substantial quantities of vinyl-fabric laminates. Raw materials are first blended in a Banbury mixer operated at either elevated or room temperatures to dissolve the plasticizer into the PVC resin. The blended materials are fluxed into a homogeneous mass of vinyl compound. The material is then discharged to a Banbury mill to cool the batch down. The material can now be fed to an extruder and passed through the various nips between the calender rolls to obtain a sheet of well-controlled gauge. Vinyl foam-fabric laminates may be produced by combining a vinyl film to be used as the skin layer and a vinyl sheet containing blowing agent with fabric and activating the blowing agent by passing through a forced air convection oven.

The *chemical expansion method* is most widely used for the manufacture of flexible PVC foam. The three general methods used to produce flexible vinyl foam (246) are (*1*) the pressure molding technique, which consists of the decomposition of the blowing agent and fusion of the plastisol in a mold under pressure at elevated temperatures, cooling the mold, removing the molded part, and post expansion at some moderate temperature; (*2*) the one-stage atmospheric foaming method in which the blowing agent is decomposed in the hot viscosity range that lies between the gelation and complete fusion of the plastisol; and (*3*) the two-stage atmospheric foaming method in which the blowing agent is decomposed below the gelation of the plastisol, followed by heating at high temperature to fuse the foamed resin (247).

The *mechanical process* is used to produce low density, open-celled foam by expanding the plastisol before gelation and fusion. The three general methods (246) include the Dennis process (248), elastomer process (249), and the Vanderbilt process (250, 251). The Dennis process utilizes a countercurrent adsorption technique by gravity feeding of the liquid plastisol through a packed absorption column under a low pressure (<690 kPa) of carbon dioxide in order to provide the largest surface area for absorption. The chilled plastisol mixture is pumped under pressure through a nozzle or tube and foams as it comes to atmospheric pressure. The wet foam is then gelled (170–182°C) in a conventional oven for thin sections or a high frequency oven for thick sections.

The elastomer process is very similar to the Dennis process. It involves a number of steps in which a gas, formerly carbon dioxide and now fluorocarbon, is mixed with a plastisol under pressure. When released to atmospheric pressure, the gas expands the vinyl compounds into a low density, open-celled foam which is then fused with heat.

The Vanderbilt process involves the mechanical frothing of air into a plastisol containing proprietary surfactants by means of an Oakes foamer or a Hobart-type batch whip. The resulting stable froth is spread or molded in its final form, then gelled and fused under controlled heat. The fused product is open-celled with fine cell size and density as low as 160 kg/m^3 (10 lbs/ft^3).

5.4.2.2. Rigid Poly(vinyl chloride) Foam. The techniques that have been used to produce rigid vinyl foams are similar to those for the manufacture of flexible PVC foams. The two processes that have reached commercial importance for the manufacture of rigid vinyl foams (246) are the Dynamit-Nobel extrusion process and the Kleber-Colombes Polyplastique process for producing cross-linked grafted PVC foams from isocyanate-modified PVC in a two-stage molding process.

The Dynamit-Nobel extrusion process (252) utilizes a volatile plasticizer such as acetone which is injected into the decompression section of a two-stage screw and is uniformly dispersed in the vinyl resin containing a stabilizer. The resulting PVC foam has low density and closed cells.

The Kleber-Colombes rigid PVC foam (253, 254) is produced by compression molding vinyl plastisol to react and gel the compound, followed by steam expansion. The process involves mixing, molding, and expansion. The formulation consists of PVC, isocyanate, vinyl monomers such as styrene, anhydrides such as maleic anhydride, polymerization initiators, FC-11, and nucleators. The ingredients are mixed in a Werner-Pfleiderer or a Baker Perkins type of mixer and the resulting plastisol is molded under pressure. The initial temperature of the molds is 100–110°C which increases to 180–200°C due to exothermic polymerization of the vinyl monomers and anhydride. The mold is cooled and the partially expanded PVC is removed and then further expanded by steam. After the water treatment the foam is thermoset with a closed-celled structure and a relatively low thermal conductivity.

5.4.3. Applications

Flexible cellular poly(vinyl chloride) was developed as a comfort cushioning material with compression–deflection behavior similar to latex rubber foam, and with the added feature of flame retardancy (43). It has a larger compression set than either latex rubber or polyurethane foams. The fact that the plasticizer in flexible vinyl foams can migrate to the surface restricts flexible vinyl foams in some applications. Furniture and motor vehicle upholstery is the largest market for flexible vinyl foams. Because of better aesthetics (leather-like plastics), comfort, and favorable pricing, they are expected to show good growth in upholstery, carpet backing, resilient floor coverings, outerwear, footwear, luggage, and handbags. The only application for flexible vinyl foams in protective packaging applications is for stretch pallet wraps. These wraps are produced by extrusion.

Rigid vinyl foams in construction markets have grown substantially due to improved techniques to manufacture articles with controlled densities and smooth outer surfaces. Wood molding substitute for door frames and other wood products is an area that has grown. Rigid vinyl foams are also used in the manufacture of pipes and wires as resin extenders and in sidings and windows as the replacement of wood or wood substitutes.

5.4.4. Economics

The price of rubber modified flexible PVC foam ranges between about \$2.00 to \$3.00 per board foot (\$800–1200/m^3) and that of unmodified, plasticized PVC foam is about \$0.70 to \$2.50 per board foot (\$300–\$1000/m^3) depending on the volume, thickness, and density of the product.

5.5. Polyethylene

There are three basic types of polyethylene foams of importance: (*1*) extruded foams from low density polyethylene (LPDE); (*2*) foam products from high density polyethylene (HDPE); and (*3*) cross-linked polyethylene foams. Other polyolefin foams have an insignificant volume as compared to polyethylene foams and most of their uses are as resin extenders.

Extruded low density foam produced from LDPE is a tough, flexible, and resilient closed-celled foam used in a wide variety of applications such as cushion packaging and safety components. The resiliency of this product gives excellent energy absorption so important in cushion packaging, athletic pads, flotation devices, and occupant safety applications. Unlike other resilient products, uniform energy absorption can be achieved with low density polyethylene foam over an extremely wide temperature range from -54 to 71°C. The closed-celled nature of this product leads to negligible water pickup. This is important in military packaging where outdoor tropical storage or shipments in high humidity ship holds is common or where freeze–thaw arctic storage conditions are encountered. These products are produced with HCFC-142b, butane, or HFC-152a, or a mixture of these blowing agents depending on the foam thickness. Therefore, these blowing agents play a unique role in achieving the dimensional stability of the flexible low density polyethylene foam over the wide range of temperatures due to their close matching of permeability through LDPE with that of air.

HDPE foam is primarily used as a high density rigid product. Shipping pallets are a rapidly growing market at a projected growth rate of about 26% per year for the mid–1990s. Most of these products are produced by thermoforming sheet and injection molding.

Cross-linked polyethylene foams are produced by either radiation or chemical cross-linking of an extruded expandable sheet containing a chemical blowing agent. The cross-linked expandable sheet is subsequently passed over a molten salt bath or passed through hot air ovens. This process is somewhat complicated, expensive, and limited to the thin products in the continuous process but thicker foams can be produced in a more complicated batch process. A batch molding process utilizing expandable beads is also used to produce thicker foams. These products can be produced in a wide range of densities and thicknesses with fine cell size, having more flexibility, higher resiliency, and better thermoforming capability than the extruded foam products from LDPE. These products also have finer texture and a softer, more resilient feel than extruded low density polyethylene foams and are used in comfort cushioning and cushion packaging applications.

Kanegafuchi Chemical of Japan has introduced a chemical cross-linking process for producing PE foams by the bead technique similar to EPS. Their Eperan beads have been used to produce molded articles as cushioning materials, sound insulating panels, etc. Asahi-Dow and BASF have also been reported to have developed similar products.

The list price of 35 kg/m^3 polyethylene foam boards is about \$0.58/BF (\$6.90/kg) and that of cross-linked polyethylene foam is about \$0.33 to \$0.88/kg more expensive than uncross-linked polyethylene foam depending on the density and thickness of the foam.

6. Health and Safety

6.1. Flammability

Plastic foams are organic in nature and, therefore, are combustible. They vary in their response to small sources of ignition because of composition and/or additives (255). All plastic foams should be handled, transported, and used according to manufacturers' recommendations as well as applicable local and national codes and regulations.

Virtually all plastic foams are blown with inert gases (CO_2, N_2, H_2O), chemical blowing agents that release inert gases, hydrocarbons containing 3–5 carbon atoms, chlorinated hydrocarbons, chlorofluorocarbons such as CFC-11, CFC-12, CFC-113, and CFC-114, and hydrochlorofluorocarbons or hydrofluorocarbons such as HCFC-22, HCFC-141b, HCFC-142b, HFC-152a, and HFC-134a. Among these blowing agents, hydrocarbons and some of the HCFs and HFCs are flammable and pose a fire hazard in handling at the manufacturing plants (see Fluorine compounds, organic–fluorinated aliphatic compounds).

6.2. Atmospheric Emissions

Certain organic compounds are found to be smog generating substances because of their high photochemical reactivity at ambient conditions. Since fully or partially halogenated hydrocarbons are considered to have low reactivity in the lower atmosphere (troposphere), substitution of photochemically reactive compounds for the current blowing agents may reduce ozone depletion in the stratosphere, but has adverse impact on the indoor ambient air quality. Therefore, ozone/oxidant interaction with the total environment needs to be considered in developing environmentally acceptable alternative blowing agents (256).

6.3. Toxicity

The products of combustion have been studied for a number of plastic foams (257). As with other organics the primary products of combustion are most often carbon monoxide and carbon dioxide with smaller amounts of many other species depending on product composition and test conditions.

The presence of additives or unreacted monomers in certain plastic foams can limit their use where food or human contact is anticipated. Heavy metals can also be found in various additives. The manufacturers' recommendations or existing regulations again should be followed for such applications.

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