History of Science and Technology of Polymeric Foams

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ABSTRACT

The history of the science and technology of polymeric foams is traced from its early beginnings starting in the late 1920s with latex foam. Two major methods evolved for producing the latter, the Dunlop and Talalay processes, both reaching industrial stages in the 1930s. Both natural and synthetic latices, notably SBR, as well as blends were extensively used. With the development of many other synthetic elastomers during the last three decades, many flexible and semiflexible foams were produced from them including polyvinyl chloride, polyolefin, and urethane foams among the major flexible foam categories but which also included specialty foams such as silicone and fluorocarbon-based foams. Among rigid foams, low density foams were first produced from special phenolic resins, and various foaming procedures evolved subsequently for the production of phenolic foams. Urea-formaldehyde foams were developed as early as 1933. The most widely used types of rigid foams today, polystyrene and polyurethane foams, underwent many technological changes. Rigid urethane foams became available as early as the late 1930s. Other rigid foams, including epoxy foams, and more specialized high-temperature-resistant foams were developed in more recent years with urethane-modified isocyanurate foams reaching significant industrial use.

SPONGE RUBBER AND LATEX FOAM

The first cellular polymer which reached the marketplace was sponge rubber, which was developed as early as 1914 [1]. It was produced by the addition of acid to natural rubber latex containing gas-generating agents such as ammonium carbonate, sodium carbonate, or sodium polysulfide. The product, introduced as Quala sponge, ceased production at the outbreak of World War I.

Latex foam had its beginning in the late 1920s when Untiedt [2] developed a dense spongy cushioning material by stabilizing natural latex of about 40% total solids content with soap, beating air into it, and refining the resulting foam until a fine-celled froth was formed which was dried in an oven.

The Dunlop latex foam process [3, 4] originated at the end of 1928 and was based on a series of steps as follows: 1) beating air into compounded latex, 2) adding the gelling agent to the foam latex, 3) pouring the foam into a mold, 4) gelling and vulcanizing the foam rubber, 5) stripping the foam rubber from the mold, and 6) washing and drying the foam rubber.

The early latex foam was produced using a batch process employing large bakery type mixers and beating air into the compounded latex. A method for foaming latex was developed using the Oakes mixer in which air is injected into a stream of latex to produce a coarse foam which is forced between toothed rotor and stator plates which results in a fine-celled foam [5].

The earliest conveyor plant for the production of latex foam was started in 1932 [6], the same year when latex foam cushions were first installed in London buses. Continuous production of latex foam was described 5 years later [7].

A number of other processes were subsequently developed for the production of latex foam rubber but the only major competitive process to achieve commercial importance was the Talalay process which had its beginning in the mid-1930s [8] and was commercialized after World War II. Foaming of the compounded latex was accomplished in the mold by the catalytic decomposition of hydrogen peroxide. This method was subsequently replaced by a vacuum foaming method in the late 1950s.

Latices used after World War II in foam rubber were primarily synthetic latices in blends with natural latex. Today the major portion of latex foam is based on synthetic latices, especially SBR. Newer developments in SBR latex foam includes co-agglomeration of two or more latices, e.g., SBR and polystyrene latices [9]. Special carboxylated SBR latices for foam backing of tufted carpets were developed more recently [10]. Foams possessing oil and solvent resistance were prepared from nitrile latices [11] while foam rubber having both solvent and flame resistance was made from neoprene latex [12]. Other expanded synthetic rubbers include EPDM, which can be extruded in various densities depending upon the concentration of the blowing agent [13].

The oldest rigid cellular plastic was cellular ebonite. It was produced in the early 1920s by a process similar to the processes described for making foam rubber, but changing the foam formulation and vulcanizing agent to yield an ebonite rather than a rubber matrix [14]. Cooper [15, 16] has described some of the new developments in cellular ebonite, especially for low temperature applications.

PHENOLIC FOAMS

The history of phenolic foams is tightly interwoven with the early development of phenolic resins. Baekeland [17, 18] observed the formation of "spongy" and "porous" products as the result of the evolution of gaseous products during the processing of phenol formaldehyde resins which he characterized as "unfit for commercial use." Before 1942, phenolic foams had little commercial value. During World War II, phenolic foams were used under the tradename of Troporit P as a structural replacement for balsa wood in the aircraft industry [19-21]. At about the same time, the Expanded Rubber Company introduced Thermozote phenolic foams in Great Britain [22]. These foams had a density of 6-8 pcf and were used primarily for buoyancy applications [23]. However, due to their relatively high costs, they were later replaced by polystyrene and polyurethane foams.

In the United States, the Union Carbide Corp. initiated development work on low density phenolic foams as early as 1945.

Continuous production of phenolic foams for sandwich construction panels was achieved in France [24, 25] and in Germany [26].

Despite some very desirable properties, such as high thermal resistance, low combustibility and good chemical resistance, their relatively high brittleness (friability), and high proportion of open cells, phenolic foams have found uses only in more specialized applications including certain structural applications (building panels), floral displays, fissile material containers, and various void-filling applications [27].

Very recently closed cell phenolic foams have been reported by Moss et al. [28, 29] using combinations of phenol and cresol- or other substituted phenol-formaldehyde resins, thereby reducing the crosslink density of the resulting phenolic foams, resulting in relatively low friability.

Hybrid phenolic-urethane foams prepared from phenol-formaldehyde resins and polyisocyanates have recently been reported possessing a combination of low combustibility and good mechanical properties [30, 31].

URETHANE FOAMS

While the chemistry of isocyanates dates back to 1849 when Wurtz [32] synthesized aliphatic isocyanates for the first time, the chemistry

and technology of polyurethanes are of more recent origin. In 1937 Professor Otto Bayer and his co-workers [33, 34] discovered the diisocyanate addition polymerization that resulted in the preparation of many different types of polyurethanes and polyureas. About the same time as polyurethane developments started in Germany, work on isocyanates began in the United States, especially by DuPont, although this early work was primarily directed toward coatings, adhesives, and fibers [35-37].

During World War II, work in the laboratories of the Farben-fabriken Bayer, a branch of the former I.G. Farbenindustrie, led to the development of rigid and flexible urethane foams [38]. In particular, rigid urethane foams were developed by German scientists for use in lightweight, high-strength sandwich materials for aircraft construction. These foams were also used as insulation in submarines and tanks. While applications of urethane foams reached moderate commercial acceptance in Germany, they were not recognized in the United States until after the war. During 1945-1947, scientific teams studying German developments issued a number of PB Reports describing the polyurethane systems and their applications. The rigid foam applications in the German aircraft industry led the U.S. Air Force to place research contracts with Goodyear and Lockheed Aircraft Corps. as well as other organizations. While DuPont and Monsanto supplied tolylene diisocyanate in pilot quantities, Goodyear Aircraft Corp. [39] and Lockheed Aircraft Corp. [40] developed techniques during 1946-1948 for rigid urethane foam production that were similar to the Bayer systems. These early foams were based on polyesters having a relatively high acid number and some residual water of esterification. The foaming of these systems was the result of the reaction of the isocyanate group with the free carboxyl groups and water to yield carbon dioxide.

The carboxyl reaction with isocyanate to generate carbon dioxide was gradually replaced by the water-isocyanate reaction which in turn was replaced (for low density closed cell foams) by trichloro-fluoromethane (F-11). The use of this inert blowing agent resulted in greatly improved insulating properties as well as lower costs [41-43].

Polyether-based rigid foams were developed in the late 1950s [44-47] and they slowly replaced most of the rigid polyester ure-thane foams.

Farbenfabriken Bayer developed suitable foam machines for the continuous production of rigid as well as flexible foams as early as 1951, based on the so-called nozzle injection principle (U machines) [48, 49].

The announcement of flexible urethane foams was made by Höchtlen [50] in 1952. During 1952-1954, Bayer chemists and en-gineers developed a flexible polyester-based urethane foam system to a degree suitable for commercial production including the neces-sary continuous machinery. A similar system was introduced into the United States by Bayer in 1953, and accelerated with the formation

of the Mobay Chemical Co., jointly owned by Monsanto and Bayer, in 1954. While flexible polyester urethane foams were suitable for many applications because of their high mechanical strength and resistance to oxidative aging, oils, and solvents, they lacked the resilience and cushioning qualities of foam rubber.

The commercial entry in 1957 of low cost urethane grade polyether polyols derived from propylene oxide brought about a major change in urethane foam technology and markets [51-53]. Earlier polyether urethane foam research was disclosed by Heiss et al. [54] in 1954 and in various patents by Monsanto [55, 56], Bayer [57], and DuPont [58]. A patent issued to Price [59] also proved to be of great importance to urethane foam manufacturers since it covered a broad range of urethane compositions based on polyether polyols. In addition, DuPont had previously introduced the first semicommercial polyether foam system in the United States employing poly(1,4-oxybutylene) glycols [60]. This foam had excellent properties including high resilience and excellent hydrolysis resistance. However, due to the successful production of lower coast foams based on poly(oxypropylene) glycols, its production was discontinued.

The early flexible polyether foam systems were made from isocyanate-terminated prepolymers and water, employing tertiary amine catalysts and surfactant to control the cell geometry. The development of "one shot" flexible foams in 1958 using higher functionality polyether polyols, e.g., poly(oxypropylene) adducts of glycerol and trimethylolpropane in combination with triethylene diamine ("Dabco") [61] and organotin catalysts [62, 63], as well as the use of silicone copolymer surfactants [53], permitted the foam manufacturers greater economy as well as a broad spectrum of foam systems which could be "tailor-fashioned" to specific end use applications. These developments led to the broad acceptance of flexible polyether urethane foams in the bedding, furniture, and automotive markets.

More recently, the development of high resilience (HR) flexible urethane foams has greatly contributed to the continued rapid rise of flexible urethane foams. These foams are based on polyether polyols which are based on glycerol containing both poly(oxypropylene) and poly(oxyethylene) groups, terminated with a plurality of ethylene oxide units of 4500-6500 MW, using either a blend of TDI (80%) and polymeric MDI (20%) or TDI alone [64-68]. In addition, graft copolymers of polyether polyols (acrylonitrile or combinations of acrylonitrile-styrene grafts) [69-71], usually in combination with the above polyether polyols, are widely used in HR foams.

In recent years a new technology for the production of urethane foams and elastomers was introduced into the United States. Reaction injection molding (RIM) is also referred to in many cases as high pressure impingement mixing (HPIM), liquid reaction molding (LRM), or liquid injection molding (LIM). Liquid injection molding of urethane elastomers was first developed by USM (United Shoe Machinery) in 1965 for shoe sole applications. Bayer AG in Germany developed RIM (HPIM) between 1966-1969 for the molding of high

density, integral skin, rigid urethane foam (Duromer) for furniture applications. In 1969 General Motors Corp. started work on RIM-produced elastomers and microcellular elastomers for the automotive industry. At first RIM was employed in the United States automotive industry for the production of fascias (soft body panels used in conjunction with an energy management system designed to absorb some energy when the automobile is involved in a collision) [72]. Starting with the 1975 models, RIM-produced fascias were used in a number of GM cars and since then other car manufacturers have followed their lead. Today fascias, bumpers (consisting of microcellular elastomers), and other automotive parts are produced by RIM processes.

The RIM process can be defined as the precise metering of two highly reactive liquid components; the resin component (consisting of a blend of polyether-based macropolyol and one or more short diols together with suitable catalysts and blowing agent (if a foam is desired)] and the polyisocyanate component (generally using direct impingement with intimate mixing of the two components at relatively high pressure to a mixing head followed by injection into a closed mold and completion of the reaction within the mold). An essential feature of this process is the rapid demolding which can be accomplished within 1 min.

Very recently, reinforced RIM (RRIM) has been introduced for the molding of high modulus parts including automotive body components and other nonautomotive applications. Fillers used for RRIM include glass fibers, Wollastonite, mica, and carbon fibers [72-74].

ISOCYANURATE FOAMS

Conventional methods for reducing the combustibility of urethane foams have included the addition of phosphorus and/or halogen-containing compounds either in the form of an additive, a reactive component, or, to a lesser extent, in the form of a protective coating. Although these methods have been satisfactory for many industrial applications, they have some obvious shortcomings such as relatively high smoke evolution, limited heat resistance, and, in many cases, reduced hydrolytic stability. Hence numerous efforts have been made to modify urethane foams by the incorporation of heat-stable groups. Among these, the isocyanurates, or more exactly, urethane-modified isocyanurate foams, have reached broad acceptance in the building and construction industry.

Monomeric isocyanurates have been known for over a century. Special credit should be given to both Professor Wurtz [75], who first prepared isocyanurates, and to Professor Hofmann [76, 77], who contributed greatly to the chemistry of isocyanurates, cyanurates, and s-triazines. However, the preparation of rigid isocyanurate-urethane foams was first described only in 1961 by Burkus [78] who trimerized an isocyanate-terminated prepolymer. By far the best and most

convenient method for the preparation of isocyanurates is the trimeri-
zation of isocyanates. Many trimerization catalysts have been de-
scribed in literature. In particular, tertiary amines, metal carboxyl-
ates, combination catalysts, and, more recently, certain zwitterion
catalysts [79-85] have been found to be very effective in the cyclo-
trimerization of isocyanates.

Nicholas and Gmitter [86] described the formation of heat-resist-
ant, rigid isocyanurate foams by trimerization and simultaneous
blowing of isocyanate-terminated polyester prepolymers.

One-shot isocyanurate foams of low combustibility were reported
by Bernard et al. [87]. These were prepared from polymeric MDI,
a trimerization catalyst (e.g., DMP-30), a silicone surfactant, and a
fluorocarbon blowing agent (F-11). However, despite their low com-
bustibility and low smoke density rating, these foams displayed very
high friability. In order to reduce the friability of these foams and
to make them more acceptable for commercial applications, a num-
ber of investigators, notably Ashida and Yagi [88], Bernard et al.
[92], and Moss and Skinner [93], have introduced modifications into
isocyanurate foams, such as polyols and epoxies.

Isocyanurate foams are characterized by higher thermal resistance
than conventional rigid urethane foams, low smoke density rating, and
low thermal conductivity, but exhibiting generally higher friability
than urethane foams at equal density.

Isocyanurate foams have also been modified with epoxy resins
alone or in combination with polyols [86, 88, 94, 95]. The epoxide
can be utilized either as a minor component of an isocyanurate foam
or to produce a broad spectrum of foams ranging from mainly iso-
cyanurate to mainly oxazolidinone structures.

Another modification of isocyanurate foams is by means of cyclic
imide groups [88, 96]. The polyimide formation takes place by the
reaction of isocyanate with anhydride groups generating carbon di-
oxide. Although these foams have a high thermal conductivity factor,
they have excellent thermal stability and relatively low friability.

Isocyanurate foams have also been modified with carbodiimide
groups with either open or closed cells having excellent thermal
stability [97, 98]. Today isocyanurate foams, unfilled or containing
various fillers, notably fiber glass and alumina trihydrate, are being
widely used in building panels and other applications.

POLYSTYRENE FOAMS

According to R. N. Kennedy [99], the concept of cellular polysty-
rene may be credited to the Swedish inventors Munters and Tandberg,
who referred to a patent filing date of August 20, 1931, in U.S. Patent
2,023,204 (1935) on the product "Foamed Polystyrene." Since poly-
styrene was then in the early stages of development as a molding and
extrusion materials, it was not until the early 1940s that cellular
polystyrene became commercially available. In 1942, the Dow

Chemical Co. started research on the development of an extrusion process for the production of cellular polystyrene. This process consisted of blending polystyrene and a low boiling chlorocarbon such as methyl chloride with subsequent extrusion into large foam logs which were then cut into the desired boards, planks, or other shapes. This material, trademarked Styrofoam, in the form of large logs was introduced in July 1943 [99]. The Styrofoam process consists of the extrusion of a mixture of polystyrene and nucleating agents together with a volatile liquid blowing agent. The foam may be cut into board stock or it can be furnished with continuous integral polystyrene skins to a desired thickness. Its uses include comfort and low temperature insulation in commercial and residential construction, packaging, buoyancy, as well as decorative and novelty applications. This foam was used by the U.S. Coast Guard and Navy as a buoyancy medium in life-saving equipment and by the Quartermaster Corps as insulation.

Other methods for producing polystyrene foams were developed in Great Britain by the Expanded Rubber Co. and in Germany by BASF. Polystyrene foams were made in Great Britain as early as 1943 [100, 101].

The original BASF process was displaced mainly by the improved suspension polymerization process which produces foamable polystyrene beads.

The most significant property responsible for the remarkable commercial growth of expandable polystyrene is its ability to be steam-molded into lightweight, closed-cell, low cost foams suitable for beverage cups, packages, ice buckets, picnic chests, insulation board, etc.

The low boiling hydrocarbon blowing agent, e.g., pentane, can be incorporated during the polymerization of styrene or it can be introduced later in a separate impregnating step employing heat and pressure. Many other blowing agents were shown to be useful for expandable polystyrene, including neopentane (tetramethylmethane), isopentane, and sym-dichlorotetrafluoroethane [106-108] as well as solid gas-releasing blowing agents such as residual azobisisobutyronitrile (from its use as a polymerization initiator), azodicarbonamide, and various carbonates that release carbon dioxide [109-111].

All current producers of foamable polystyrene beads took out a license from BASF [102-105]. Expandable polystyrene in bead form was introduced in the United States by the Koppers Co. [105] in 1954. However, significant growth of this market did not start until 1958 when 10 million pounds of expandable polystyrene were sold.

In the late 1960s polystyrene foam sheet emerged as a major commercial product with a remarkable growth rate [112]. The products which were most responsible for this growth were trays for meat, vegetables, and fruit. Although the technical development of foam egg cartons did not proceed as rapidly as that of meat trays, the subsequent market penetration for polystyrene sheet for this application justified the earlier optimistic forecasts [113]. The early

development of extruded polystyrene sheet was carried out by extruding mixtures of cell-nucleating agents and expandable polystyrene in the form of beads or pellets. At that time pellets were preferred because extruders were not designed to handle beads conveniently [114]. In order to produce sheet at the lowest possible cost, extruders were later developed for introduction of the blowing agent into the barrel, thereby eliminating the more expensive expandable pellets as a raw material.

POLYOLEFIN FOAMS

A process for the preparation of expanded polyethylene was disclosed by Johnston of DuPont in 1942 [115] employing nitrogen as blowing agent. However, no commercial use was made of this process. Among the earliest patents to be issued for the preparation of expanded polyethylene was that of Hamilton [116] assigned to Callender's Cable and Construction Co. in 1945 using carbon dioxide as blowing agent. In general, blowing agents for polyolefins are either normally gaseous materials or decomposable solids although other methods of forming a dispersed gas phase in polyolefins have been described. These include the liberation of hydrogen by irradiation with high energy electrons [117] or leaching of soluble salts [118], but these methods have not attained any significant commercial success. Many other patents have been issued dealing with the expansion of polyolefins, notably polyethylene by incorporating or dissolving a gas in the molten resin under high pressure and expanding under atmospheric or reduced pressure with simultaneous cooling [115, 116, 119-123]. While these processes were not commercially successful, similar methods employing low boiling solvents or chemical blowing agents found broad market acceptance. Commercial production of expanded polyethylene as an electric cable insulation started in the early 1950s. The process used consisted of direct extrusion of polyethylene using a chemical blowing agent resulting in a polyethylene foam with a specific gravity of 0.5 [124].

In 1958 another process was introduced utilizing 1,2-dichlorotetrafluoroethane [125, 126] which could be injected into polyethylene during extrusion resulting in a gel which expands spontaneously as it is extruded under pressure. An example of a foam produced by these techniques is Dow Chemical's Ethafoam. In order to produce stable polyethylene foams, special techniques such as coating [125] and cross-linking by means of radiation [127, 128] have been employed.

Prior to 1958, all of the foamed polyethylene insulation was based on high pressure or low density polyethylenes. The introduction of high density polyethylene provided a tougher and more rigid material than the low density resins. This resulted in new areas of applications, such as miniature coaxial cables, and various contour and structural designs. This was accomplished by proper choice of resins, blowing agent, foamed density, design, and proper tooling for fabrication of the end products [129].

In almost 50 years, over 1000 different compounds have been pro-
posed as chemical blowing agents and among these only about a dozen
have proven to be commercially significant [130]. Even fewer have
shown to be useful in the foaming of polyolefins. These include
chemical blowing agents such as azodicarbonamide, N,N'-dinitroso-
pentamethylenetetramine, and 4,4'-oxybis(benzene sulfonyl hydrazide).
The decomposition temperature of the blowing agent determines the
usefulness of a chemical foaming agent for a particular polyolefin
and also governs the processing conditions. Hence, some of the above
foaming agents are unsuitable for the foaming of isotactic polypropyl-
ene. Suitable blowing agents for polypropylene were developed which
have the necessary additional stability required for the expansion of
polypropylene [129].

Among the physical blowing agents, fluorocarbons such as mono-
chlorodifluoromethane, dichlorodifluoroethane, and dichlorotetra-
fluoroethane [128] have been preferred, with the latter one the most
widely used for low density polyethylene foam.

A number of new processes which are termed "structural foam"
molding have been developed in more recent years. Since rigidity
and toughness are usually the most desirable properties, high density
polyethylene and polypropylene rather than low density polyethylene
are the materials of choice for the structural polyolefin foam prod-
ucts. Angell of Union Carbide [131] disclosed an extrusion-injection
process for the production of molded parts. This method consists of
extruding a mixture of the polymer and blowing agent to an expanding
accumulator zone where the melt is held at the foaming temperature
under pressure to prevent foaming. The hot polymer-blowing mixture
is then poured rapidly into a mole where expansion and cooling takes
place. Union Carbide's structural foam molding process has been
licensed to many companies [132].

Other structural foam processes include the Engelit process,
licensed by Phillips Petroleum Co. [133, 134], and the Celka process,
developed by Ugine Kuhlmann [135]. The latter consists of direct
extrusion of structural foam products and is adaptable to most extru-
sion profiles such as planks, rounds, tubes, and moldings.

UREA-FORMALDEHYDE FOAMS

Urea-formaldehyde (U-F) foams were developed as early as 1933
by investigators of the German I.G. Farbenindustrie [136]. They were
first introduced commercially for use in insulation under the trade
names Iporka (I.G. Farbenindustrie) and Isoschaum (BASF) [137].
Later on BASF utilized modified U-F foams as agricultural mulch
under the trademark of Hydromull, and other uses for U-F foams in
the horticultural field were commercialized in the United States by
a number of companies [138-140].

In England, Thermalon, Ltd. reached a commercial stage in the
development of U-F resins for foamed-in-place insultation.

Applications of these foams in over 27,000 sites in Europe, including Scandinavia, were so successful that in 1959 a pilot plan scheme was started in England in conjunction with building contractors [140]. Imperial Chemical Industries contributed greatly toward the introduction of U-F foams (Ufoam) in the construction industry in England, and in more recent years Ciba (foamed Aerolite resins) was actively engaged in the marketing of U-F foams in the United Kingdom [141]. In the United States a number of companies including Filfast Corp., U. F. Chemical Corp., Brand Industrial Services, and A. L. Randall Co. introduced U-F foams for a variety of applications [142].

Numerous methods have been used to produce U-F foams. Generally, they are prepared from an aqueous solution of urea-formaldehyde resin and foaming agent (surfactant) and employing acid catalysts for the curing of these foams. The liquid U-F resin can be foamed by the dispersion of air or another gas employing high speed agitation, followed by the addition of an acid catalyst to cure the foam.

In another procedure, gas is dissolved under pressure in the liquid resin followed by foaming of the froth by the sudden release of pressure [143].

In addition to foam processes utilizing mechanized expansion of the U-F resins, foams can also be produced by chemical expansion of gases such as carbon dioxide produced by the reaction of inorganic carbonates or bicarbonates with the acidic curing agents [141].

Another technique consists of the expansion of the U-F resin by the evaporation of low boiling solvents such as fluorocarbons or pentane caused by the heat of the exothermic reaction of the U-F condensation cross-linking in the presence of an acidic catalyst, e.g., phosphoric acid [144, 145]. Foams prepared by this technique exhibit a predominantly closed-cell structure, whereas foams prepared by other methods are usually open-celled.

A series of processes has been developed for the continuous manufacture of U-F foams [143, 146-148]. The property of U-F foams to absorb water, which is a disadvantage in insulation applications has been utilized in a large number of applications, especially in the agricultural and horticultural fields [149, 150]. Other applications which make use of the good absorption of liquids by U-F foams include surgical sponges and dressings after sterilization of the plasticized foam [149].

EPOXY FOAMS

Epoxy foams were first developed in the late 1940s as lightweight encapsulation materials for electronic components [151]. The early epoxy foams consisted of standard bisphenol A-epichlorohydrin resins in combination with a hardener, a surfactant, and an organic or inorganic chemical blowing agent [152]. These foams, developed by investigators at the Shell Development Co. [151-153], were cured with an aliphatic polyamine, with heat applied in order to facilitate

the decomposition of the blowing agent. The heated foam resin mixture was cast into heated closed molds, resulting in expansion of the resin by the carbon dioxide or nitrogen generated from the decomposition of the blowing agent.

In some cases an auxiliary blowing agent such as toluene was added in order to reduce the exothermic heat within the foam core and to reduce the viscosity of the undiluted resin [153].

Due to their excellent electrical properties, high temperature resistance, and toughness, epoxy foams found applications in the electrical and aircraft industries, usually in densities greater than 5pcf [151, 154].

Further study led in 1953 to the development of epoxy foams with a density of 2 pcf for the Bureau of Ships and for the aircraft industry [155]. This was about the same time that so-called "syntactic" foams were developed utilizing phenolic "microballoons" (hollow microspheres made of phenolic resins and filled with an inert gas, e.g., nitrogen) dispersed in epoxy resins.

Delmonte [156] has described some of the later developments such as the use of epoxy foams as reinforcements for laminated glass fiber structures in the mid-1950s.

In the late 1950s and early 1960s, investigators at Shell Development developed other processes. These included novel epoxy-boroxine foams which exhibited high heat resistance (rigid at 300°C) [157]. These systems consisted of liquid epoxy resins, (e.g., diglycidyl ether of bisphenol A), an aromatic diamine, (e.g., 4,4'-diaminodiphenyl sulfone), and trimethoxyboroxine. The resulting cross-linked polymer liberates 3 moles of methanol per mole of boroxine. Other contributions by Shell scientists consisted of the development of a fluorocarbon-blown epoxy foam system that could be employed in foamed-in-place one-shot systems [151, 158]. The main applications of these are in foamed-in-place insulation for construction, pipe, storage vessels, and fishing vessels [159].

DeBell and Richardson developed specialized applications for epoxy foam composites for aircraft components [160] and for making complicated patterns for foundry casting [161].

In addition to the above-mentioned early syntactic foams utilizing phenolic microballoons dispersed in epoxy resins, other syntactic foams were developed using glass microballoons [162, 163]. For deep submergence applications, glass microspheres are preferred to the phenolic microspheres.

POLYVINYL CHLORIDE FOAMS

The first published reports on cellular polyvinyl chloride (PVC), also termed "vinyl foams," appeared in Germany prior to World War II. These foams, made by expansion of vinyl resins with chemical blowing agents, originally utilized materials which gave off toxic products on decomposition which caused a considerable delay in

their commercial development [164]. However, the subsequent use of nontoxic blowing agents resulted in market acceptance of these foams. A process employing mechanical blowing consisting of the incorporation of an inert gas, such as carbon dioxide, followed by expansion of the resin dispersion or solution was originally developed in the United States prior to 1950. The development of vinyl foams was greatly aided by the availability of vinyl plastisols which can be fused without the application of pressure. Vinyl plastisols are prepared from dispersion grade PVC manufactured by an emulsion polymerization process which yields a powder in the 0.2-2 μm range. The resulting PVC particles are coated with a layer of surfactant (about 0.5-3.5% of the resin weight) which enables the surface-treated, fine particle size resin to be mixed with plasticizers to form a stable and uniform dispersion of PVC particles in a continuous phase of plasticizer. The plasticizers used in vinyl plastisols usually consist of a blend of monomeric plasticizers, e.g., dioctyl phthalate, with polymeric plasticizers, e.g., glycol adipates, azelates, and sebacates. In addition, the other ingredients used in vinyl plastisol formulations, such as stabilizers (e.g., Ba, Ca, Zn, Sn stabilizers and epoxy stabilizers), pigments, and fillers, are added to the liquid systems [165].

In addition to dispersion resins produced by emulsion polymerization, plastisol blending resins, which are fine particle size suspension resins, can be used as partial replacement (up to 50%) for the dispersion resin in a plastisol system. The reason for utilizing the plastisol blending resins is to reduce the costs of the plastisol system [165].

The classical mechanical processes of foaming liquid plastisol include the Elastomer and Dennis processes [166, 167] while the Vanderbilt process employing air is of more recent vintage [168, 170]. The Dennis process employs a countercurrent absorption technique by gravity feeding of the liquid plastisol through a packed absorption column under a low pressure (< 100 psi) of carbon dioxide, the CO_2 flows countercurrently thus providing 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 or a high frequency oven (for thick sections) [171].

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 fluorocarbons, is mixed with a plastisol under pressure. After release to atmospheric pressure, the gas expands the vinyl resin into a low density, open cell foam which is then fused with heat [166].

The Vanderbilt process [168-170] is based on the mechanical frothing with air of a specially compounded plastisol. The air is added by the mixing action of an Oakes foamer or a Hobart type batch whip. The resulting foam may be spread or poured onto a suitable substrate or into a mold, then gelled and fused. The key to this

process lies in the use of proprietary surfactants which enable the plastisol to mechanically entrain air as a result of the mixing action in the mixing head of the foam machine and retain it in tiny discrete bubbles with sufficient stability as it is pumped, poured, spread, and finally gelled and fused. This foam is open-celled with fine cell structure with densities as low as 10 pcf. Although this type of foam has found some recognition in the United States, it has achieved its major success in Europe.

The chemical expansion techniques for the manufacture of flexible PVC foam have become the dominant processes with over 80% of the total flexible PVC foam production [171]. The three general methods which evolved for the production of flexible PVC foams are: 1) the two-stage atmospheric foaming method in which the blowing agent is decomposed below the gelation point of the plastisol followed by heating at elevated temperature to fuse the foamed resin [172]; 2) the one-stage, also termed "hot viscosity," foaming method in which the blowing agent is decomposed in the "hot viscosity" range which lies between the gelation and complete fusion of the plastisol; and 3) 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 followed by cooling of the mold, removing the molded part, and postexpansion at some moderate temperature.

Many different plasticizers, stabilizers, and blowing agents for PVC foams have been developed in the past four decades. The studies of Lasman [173], Nass [174], and Harris [175] have greatly contributed to the understanding of the rate processes involved in the gelation, fusion, and expansion of PVC foams. The investigations of Harris [175] have thrown considerable light on the importance of rheology and the catalytic effects of stabilizers on the manufacture of PVC foam.

Early in 1959 investigators at the B. F. Goodrich Chemical Co. published data on the extrusion of PVC foam [176, 177]. These foams were made by extrusion followed by a postexpansion and had densities of 7-40 pcf. The cell structure of these foams consisted of a mixture of open and closed cells.

Another method which was successfully commercialized was the production of high density (40 pcf or higher) closed cell PVC foams by direct extrusion on expansion. This system employs a prefluxed compound in pellet form containing a low temperature blowing agent which is fed into the extruder. The extrusion conditions are regulated in such a way that the blowing agent decomposes in the extruder. The foam is formed when the material comes out of the die and is immediately cooled [177, 178].

A very important development in PVC foams was their use in the formation of foam-fabric laminates for synthetic leather. These consist of sheets of vinyl foam on a cloth backing on an embossed, unexpanded vinyl skin [179, 180]. The relatively high density cellular structure can be produced either by calenderizing or plastisol casting and is generally characterized by a solid surface of 10 mils, a cellular section of 40 mils, and a backing fabric.

Cellular vinyl products have also been produced by injection molding employing a reciprocating screw injection molding machine. Today, the greatest volume of cellular vinyl molding compounds are used for shoe soles [165].

A number of processes used for the manufacture of flexible PVC foams have also been employed for the production of rigid PVC foams. For instance, extrusion foaming [176-178] can also be applied to the manufacture of rigid PVC foams. There are two processes in particular which have reached commercial importance for the production of rigid foams. These are: 1) the Dynamit-Nobel extrusion process, and 2) the Kleber-Colombes Polyplastique process for the manufacture of cross-linked grafted PVC foams from isocyanate-modified PVC in a two-stage molding process.

In the Dynamit-Nobel extrusion process [181], a volatile solvent, acetone, is injected into the decompression section of a two-stage screw and is uniformly dispersed in the vinyl resin containing a stabilizer. The pressure is kept above 30 atm, the partial pressure of acetone, in order to prevent pre-expansion of the vinyl resin. The resulting PVC foam is thermoplastic and of high molecular weight.

Early in 1963 rigid PVC foams possessing high compressive strength and shear modulus as well as relatively high thermal and dimensional stability were introduced in Europe. B. F. Goodrich, Johns Manville, and other companies were licensed under the Kleber-Colombes patents [182, 183] to produce these foams. A typical formulation would consist of PVC, a diisocyanate (e.g., TDI), vinyl monomers (e.g., styrene, acrylonitrile), anhydrides (e.g., maleic anhydride), polymerization initiators, fluorocarbon blowing agent (F-11), and a nucleating agent. The Kleber-Colombes process involves mixing, molding, and expansion. The resulting low density foams possess a closed cell structure and exhibit a relatively low thermal conductivity factor (K factor).

SILICONE FOAMS

Silicone foams were first developed during the early 1950s for use in lightweight thermal insulation which could withstand long-term exposure to temperatures of 200-300°C [184]. The first foamable silicone resin was a silicone resin in the form of a crumbled solid. The resin was melted, and an amine catalyst together with a chemical blowing agent added. After blending the components, the mixture was poured into place and foamed by additional heating [185]. This foam system was gradually replaced by foams prepared from heat-activated silicone foaming powders consisting of the resin, blowing agent, catalyst, and filler [186]. On melting these materials, they expanded to foams and cured at temperatures above 150°C. Due to the disadvantages in the preparation of these foams such as high density (10-16 pcf), high activation temperature, and slow cure, new types of two-component foams systems were developed based on liquid room-temperature-foaming silicone resins [187]. These resins consist

of combinations of silicone prepolymers containing both silanol and
silicon-hydride groups. Basic catalysts such as quaternary ammonium
hydroxides are used to activate the foaming and cross-linking reaction.
The splitting of the SiH bond by means of water or alcohol proceeds
very rapidly under basic conditions, resulting in silanol, siloxane, or
alkoxysilane and hydrogen formation. These silicone resin foams,
which exhibit excellent thermal stability and electrical properties,
are used mainly as thermal insulation and electronic encapsulation
[188]. Although the silicone resin foams could be modified in order
to obtain semirigid plastic properties, they still had a high cross-link
density and hence were not suitable for cushioning or for applications
requiring elastic deformation. New types of silicone rubber foams
were developed, primarily by the Dow Corning Corp. and the General
Electric Co., which had lower cross-link densities and exhibited
greatly improved elasticity. These are the silicone rubber sponges
and the room-temperature-expanding liquid silicone rubber foams.
The silicone sponge rubbers are prepared by blending a high molecu-
lar weight linear polysiloxane with catalysts, filler, and blowing
agents. Curing is achieved by means of small amounts of organic
peroxides which results in hydrogen abstraction from the methyl
groups on the silicone chain, followed by combination of two methylene
radicals to form ethylene links between the siloxane chains [189].
Small amounts of vinyl groups may also be included by means of co-
polymerization and these can act as cross-linking sites to regulate
the degree of cross-linking.

Of special interest was the development of the room-temperature-
vulcanizing silicone (RTV) rubber foams. These systems consist of
liquid silicone prepolymers containing terminal silanol groups which
cure by means of condensation of the silanol groups to form siloxane
cross-links [189-191]. Foaming and curing takes place at room
temperature by employing organotin catalysts. Like other silicone
rubbers, RTV foams maintain their resilience over a temperature
range of -75 to 200°C. RTV silicone foams are used in thermal and
electrical insulation, mechanical shock, and vibration damping. In
addition, a number of medical applications for RTV foams, such as
in prosthetics and diagnostic enemas, have been developed [192-194].

Syntactic silicone foams which contain mixtures of small, hollow
glass, ceramic, or plastic spheres have been developed in the form of
liquid two-component systems which cure at room temperature or
slightly elevated temperatures [188]. These products have found
extensive use as ablators and were used in the heat shield of the
Gemini spacecraft [195]. Similar materials were also used as ther-
mal insulation on the Titan III and Saturn launch vehicles as well as
for abradable seals on jet engines [188].

In addition to the foams described, many other types of flexible
and rigid foams have been developed, based on both natural and syn-
thetic products. These include foams based on cellulose acetate,
ionomers, copolymers of poly(phenylene oxide) and styrene (Noryl),

ABS, polycarbonates, polyfluorocarbons, acrylics, polyesters, and polyamides, just to mention a few. It can be safely assumed that foams can be made from almost any polymer by employing one or more processing techniques. This is borne out by the growing number of types of foams appearing in technical journals and in the patent literature.

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