

Chapter 2

Introduction on Foam Manufacture



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1 Introduction

1.1 Mechanism of Foaming

Foaming is generally defined as putting of bubbles into a matrix. Depending on the nature of the bubble, matrix, and the type of putting the bubble into the matrix, a wide range of foams can be prepared. The traditional method of preparing foams is based on using a mechanical stirrer or whipping of the surfactant solution. However, this method is not suitable for industrial production or quantitative laboratory studies because it is difficult to precisely control the amount of bubbles that must enter the liquid. The industrial production involves passing a stream of gas through an orifice (sparging) and then growing bubbles in solution. Several factors including interfacial tension, surface cleanliness, and gas flow rate affect the nucleation, growth, and separation of bubbles from the orifice. The size of the bubble determines the speed of the rise. According to Dickinson [1], the size of the bubble produced by an orifice can be estimated via balancing the buoyancy force and the surface tension acting on the bubble. As the bubble rises and reaches the interface, a thin layer forms on the surface of the column. The lifespan of this thin layer and the possibility of forming a foam layer depend on several factors including surfactant concentration, drainage rate, surface tension gradient, diffusion, and external disturbance factors. The nucleating of gas bubbles is an alternative method of foam production. The supersaturating of a liquid with gas or in situ production of gas, for example, by a chemical reaction is the basis of this method. In this process, by reducing the pressure, the gas is released

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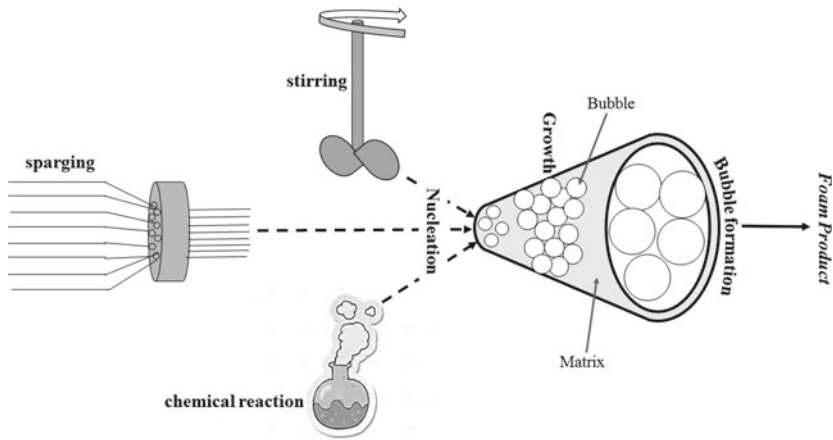


Fig. 1 Illustration of foaming mechanisms

from the solution and size of the bubble is affected by the dynamic surface properties. Cavity model and Fick's law can be used to describe bubble nucleation and growth, respectively [1–8]. The described mechanisms of foaming are illustrated in Fig. 1.

1.1.1 Water Foam

The most common method of water foaming is the severe shaking of a closed vessel containing a little amount of surfactant solution. The aerosol method is also usual in the production of shaving cream, hair styling mousse, and whipped cream. Another popular method is to bubble the gas directly into the surfactant solution. Pure liquids cannot generate foam because when the bubble enters below the surface of the pure liquid, the gas bubble bursts immediately after draining. On the other hand, in the presence of a surfactant solution, the liquid–air interface increases, and a restoring force restores the equilibrium. Two governing mechanisms of this phenomenon are Gibbs and Marangoni effect. These are inline with each other and usually both of them are considered. Polymers, particles, cations, and special anions that are adsorbed on mineral salts are surfactants that make foaming in the aqueous medium. These materials are often able to form a foam at very low concentrations of about 10^{-9} M. The cleanliness of the system has an important effect on the foam formation. The purity of the water must also be assured. A simple way is to shake the water vigorously and check how long the bubble stays in it. The durability of even one second indicates the presence of active surface impurities [2, 9, 10].

1.1.2 Glass Foam

In these foams, the solid phase is glass, which is filled with a gas phase. Powder method is usually used for conversion of glass to foam, which involves sintering a mixture of glass powder and special additives that facilitate the formation of a gas phase during heating. These additives are pore-forming or gas-forming agents that are used in small amounts. As the temperature of the mixture increases and the softening temperature passes, the glass particles begin to sinter and surround pore-forming agents. After a certain temperature, the gas is released and thus cavities appear in all parts of the sintered body. Recently, cold technology has been developed to produce foam glass. In this method, the heat treatment step is deleted and the whole process is done at room temperature. The method is based on the chemical reactions of water glass and fine powder of aluminum. One of the products of this reaction is gaseous hydrogen, which causes a gas bubble to form. The advantage of this method is the possibility of applying to the established unit. The problem with this method is the presence of explosive hydrogen and the difficulty of preparing a homogeneous foam. The reaction in the interfaces of water glass and aluminum does not allow uniform distribution. The proposed solution to this problem is to delay the foaming reaction using additives [11].

1.2 Role of Mixing in Foaming

Mixing is a challenging process in the foaming of materials. The more stirring, the better the mixing, but the more foam is created and the more bubble is introduced. This will create many problems including non-controlled structural features and reduced product quality. To solve this problem, chemical defoamers are used to prevent foaming. These materials are expensive and in some cases cause contamination in the final product. Thus, some modifications which are proposed to control mixing include (1) placing the mixer blade from the center to reduce the vortex, which reduces the amount of air and foaming; (2) using a vacuum during mixing and then entering the air in a controlled way after mixing; and (3) replacing a top-entering agitator with an inline mixer that has been piped for recirculation. The return line should be extended below the liquid level to prevent foaming. For cases where the amount of solid is high, an inline rotor/stator mixer is proposed to disperse the powder at high speed. Also in the bubbling method for preparing liquid foams, due to the slow process and initial non-uniformity, the liquid solution drains significantly during the production process and the produced foams possess a wet surface and dry bottom. A system is developed based on firefighting technology for this problem, in which a jet of a high-speed solution is mixed with the gas flow. This strategy allows us to prepare a large amount of uniform foam at high speed and a variable amount of liquid. In brief, uniform massive foam is made by an apparatus providing turbulent mixing of gas with a narrow jet of surfactant solution [9, 12].

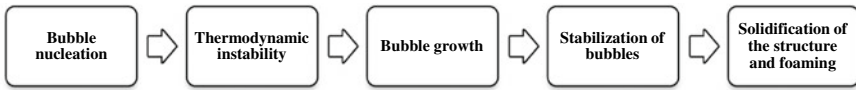
2 Foaming of Polymers

In general, polymer foaming consists of three steps: (1) the formation of a polymer/gas solution: the complete dissolution of a large amount (solubility threshold) of the blowing agent into the polymer under high pressure through temperature-dependent diffusion (stretching of a gas bubble in the shear field during the foaming process helps to improve diffusion); (2) cell nucleation and growth induced by a sudden thermodynamic instability via changing the temperature, pressure, and amount of gas in the prepared homogeneous supersaturated solution; and (3) cell stabilization by controlling the growth of bubbles and preventing coagulation and collapse. Then, the foam structure is obtained by removing the blowing agent from the mixture and the foam product is attained by stabilizing the cell via returning temperature and pressure to ambient conditions. Cells are frozen bubbles of various shapes and sizes after solidification of the plastic [5–7, 13, 14].

The first polymer foams were developed during 1930 decade. Polymeric foams are prepared by mixing a gas phase in the form of air bubbles or air tunnels into the solid phase. This mixing is very fast until the system reaches a uniform state like coffee foam. The solid phase is a polymer matrix and the gas is a blowing agent. In conventional foam processing, the most common blowing agents are fluorocarbons, chlorofluorocarbons, n-pentane, and n-butane. These materials are highly soluble in the polymer matrix. The blowing agent can be chemical or physical. Chemical agents are chemicals that take part in a chemical reaction and produce gases such as nitrogen or carbon dioxide. Physical agents are inert gases or liquids with a low boiling point that do not interact during the foaming process and are inert to the polymer matrix. Compared to chemical blowing agents, the physical type can be processed below critical temperatures with no limitation of degradation temperature. They also have a lower price and create a better foam morphology than chemical ones. However, special equipment and high skill are required to handle these blowing agents. Physical agents can be a supercritical phase. For example, supercritical carbon dioxide is used in the batch foaming method. In this way, carbon dioxide dissolves in the polymer matrix, increasing the free volume between the molecular chains and the mobility of the chains. After saturation, carbon dioxide is rapidly depressurized to induce foam in the polymer matrix. During this process, micro-foams are usually prepared. Using this method and applying nano-clay in a PLA matrix, nano-foam production has also been reported in another attempt [5–7, 15–17].

2.1 Nucleation, Growth, Stabilization, and Solidification

To initiate bubble nuclei, it is necessary to create sites with low potential energy. The most common method is to use nucleating agents, which cause supersaturated gases to escape from these sites and form bubble nuclei. The bubble nuclei are also formed by the physical mixing of foaming agents with a polymer liquid. The



Scheme 1 The mechanism of foaming

blowing gases are also obtained directly from foaming agents and there is no need to dissolve the foaming agent in the melt. These three mentioned nucleation methods are related to a certain category. The first one is widely used for polymers with high free volume, the second is appropriate for melt due to low potential energy, and the third is mainly used for thermoset plastics and reactive molded ones [8]. The use of shear field or any agent that causes the orientation of molecular chains and treatment by low-energy infrared radiation are the other methods. The bubble growth is affected by several factors including the amount and nature of foam constituents, molding process, equipment, melt viscosity, gas permeability, foaming agents, temperature, and pressure. As the bubble grows, its surface area increases and becomes unstable. One method of stabilization is using of surfactants to reduce surface tension and form fine bubbles with reducing gas penetration. Another way is to increase the melt viscosity to prevent the bubble wall from thinning. In practice, cooling or crosslinking helps to this. The next step is solidification. In thermoplastics, solidification is a completely physical process and is influenced by three factors: (1) cooling the melt with water, air, or any other media: this is related to the fact that the bubble does not conduct heat properly, the bubble wall solidifies, and inside remains at a high temperature. Almost long time is needed for cooling the bubble core, and the cooling rate should not be too high, as it will break the bubble due to wall shrinkage. (2) Gas release in the melt: dissolving the gas in the melt increases the plasticity of the melt. Then, this gas enters the bubble and increases the viscosity of the wall, which results in accelerated solidification. (3) Degradation and degassing of foaming agents: the rate of solidification is affected by heat absorption during degassing of physical foaming agents, heat absorption or degradation of chemical foaming agents, and heat release during crystallization of crystalline plastics. In thermosets, polymerization and molding occur simultaneously. Increasing the temperature and addition of a catalyst increase the solidification rate [18]. The overall concept of foaming process is illustrated in Scheme 1.

3 Classification of Polymer Foam Processing Techniques

All techniques of foam manufacturing include the three stages of cell initiation, nucleation, and stabilization. The classification of techniques is usually based on growth and stabilization. Accordingly, the most common methods of producing plastic foams include physical, chemical, and mechanical foam formation.

3.1 Physical Foaming

A liquid or gas foaming agent is added to the plastic and is released during the melting process. In some cases, such as fluoropolymers, a solid nucleating agent, which is stable at the process temperature, is used. In physical foaming, inert gases are dissolved in molten polymers or paste materials under pressure, and then, as the temperature increases or the pressure decreases, the dissolved gases are removed and foam is formed. In the process of foam beads, a liquid with a low boiling point is mixed with a polymer or filtered on polymer particles under pressure and then heated to turn the liquid into a foam. Aliphatic hydrocarbons, arenes, alcohols, ethers, ketones, aldehydes, low boiling point liquids, and hollow spheres are examples of these agents [19].

3.2 Chemical Foaming

Chemical reactions control the foaming process, i.e., the rate of polymerization. In addition, the rate of activation of the blowing agent is controlled through a decrease of solubility in monomer solution as the reaction progresses or thermal degradation occurs. This method cannot be used for non-crosslinkable polymers or those like fluoropolymers. In chemical method, foaming agents are added to the resin, then heated, and pressed to release gas—usually nitrogen—into the foam.

3.3 Mechanical Foaming

This method has limited applications. It is similar to whipping cream in which air is mixed with a melt. Mixing simply enter air into the melt, thus acting as a blowing gas. In other words, the air is drawn into the resin by mechanical agitation. The resin must be in a liquid state or have a low viscosity.

Another classification of foaming processes is based on creating a pressure difference between inside and outside the cell. If the external pressure is reduced, the process is decompression, and if the internal pressure is increased, it is expansion. Both decompression and expansion methods can be stabilized using both chemical and physical methods. Other methods are sintering resin particles in the presence of a gas or dispersion of a gas or solid in a melt polymer [18, 20, 21].

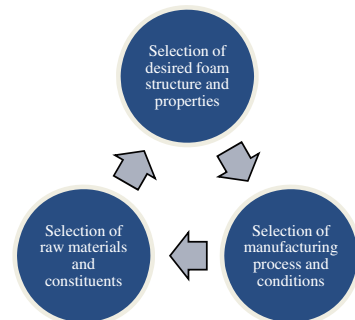
4 Polymer Foam Processing Techniques

Compared to ceramics and porous metals, the processing of plastic foams is relatively simple. It involves two main stages of mixing including the introduction and dispersion of gas and molding including cooling or curing. Cavities in these materials are formed during the molding process. In addition to the matrix, which is a high molecular weight polymer in liquid or bead form with foaming agents, fillers, additives, catalysts, and surfactants, are also used. Additives include lubricants, stabilizers, fire retardants, crosslinking agents, colorants, and nucleating agents. Fillers are usually glass, calcium carbonate, carbon black, barium sulfate, silicate, wood powder, and metal powder.

Foam products, especially polymeric type cover a wide range of applications. Hence, special properties are required in a specific application. Controlling the foam structure means that the size of the cells and the composition of the foam should be adjusted for gaining the desired properties. The determining factor of foam structure is the manufacturing process and the condition. Therefore, designing the foam structure and using the appropriate processing make it possible to provide products with the desired properties and high quality [3, 4, 6, 7, 18, 20–22]. Depending on the type of polymer, the size and shape of the foam cells, and the final application of the foam product, diverse manufacturing methods can be applied to prepare the foam (Scheme 2). The suitable selection of equipment and process conditions also results in low cost and reliability.

The manufacturing of plastic foams is comparable to that of common processing plastics. The common methods and equipment of plastic production such as extrusion are also usable to prepare foams. From film and sheet to molded products can be prepared in this way. Extrusion, injection molding, and bead foaming are the most preferred processes due to higher productivity than other methods. Continuous foam production processes such as extrusion and injection molding are limited to melt-processable polymers. Discontinuous processes are developed for non-melting and thermally degradable polymers. Laboratory-scale methods have also been developed. However, there is a need to develop new methods such as three-dimensional printing in the manufacturing of foams. This method has been specifically reported

Scheme 2 The relation of structure, properties, and manufacturing of foams



for the production of polyurethane foam. Improved properties, providing products in desired dimensions, shapes, or complex objects, and the possibility of using various materials such as polymers, composites, metals, and ceramics are the advantages of this technique [3, 4, 6, 7, 13, 15, 23, 24].

In the following sections, the manufacturing methods of polymer foams are reviewed.

4.1 Slab-Stock/Slab-Stock by Pouring

In this method, a mixture of materials is continuously poured on a moving conveyor. The conveyor has a wall and foam is formed on the wall using a mixer. The final product is a shapeless large slab, which is cut into slabs with suitable dimensions [14, 24].

4.2 Molding

The process consists of two steps: mixing and molding. Mixing is done by a paddle-type high-speed mixer. Molding includes a hydro-press, a digester, and an aluminum mold with a suitable design for gas outlet. Virgin or pre-expanded beads are poured into the mold and subjected to heating and pressing. Liquids cannot be used in this case. The molded product is then demolded after setting or curing. This method can be applied as a single step including direct placement of plastics with foaming agents in a mold and then pressing and molding or two steps including pre-forming of plastics with foaming agents and then mold pressing. Productivity, high quality, and simplicity are the advantages of this method. The molding method for obtaining products with complex shapes saves about 15% compared to slab-stock, which requires secondary operations. Molding of rigid foams is also possible but it has a limited application [18].

4.2.1 Low-Pressure Molding

In this method, the pre-heated liquid mixture is poured into the mold. The mold is preheated and covered with a release agent. Demolding is done after curing and cooling. Depending on the mold design, the amount of waste in this method is varied from zero to 5% by weight. The best results are obtained when the release agent is sprayed on a clean and hot mold just before each pouring. The release agent solvent must be completely removed before pouring the foam materials into the mold. Compared to slab-stock, which requires minor curing and infrared heaters located on top of the conveyor, the molding process needs excess heating by an

external heater. Using of microwave reduces curing time from 20 to 4 min. Additionally, improved properties are gained by microwave curing compared to conventional heating. Dielectric heating is also accepted for curing [25].

4.3 Batch Foaming

This method is used on a laboratory scale to investigate the effect of blowing materials and foam constituents on foaming behavior. In this method, the polymer sample is placed in a high-pressure chamber that saturated with an inert gas such as carbon dioxide or nitrogen. Then, the solubility of the gas in the polymer is decreased by heating the sample and removing the pressure. A major drawback of this method is a very long time required to saturate the polymer with gas, which is due to the low gas permeability of the polymer at room temperature [13, 26].

4.4 Extrusion

This method allows the production of low-density foams with simple two-dimensional geometry. The main steps of the process are mixing, extrusion, and cold molding. Expandable beads containing blowing agents are usable, but the most widely used system is the direct gas extrusion. In this process, the plastic and foaming agent are subjected to the processes of softening, mixing, and degradation (chemical foaming)/degassing (physical foaming)/injection of pressure with inert gas (mechanical) of the foaming agents. In this way, the polymer is fed to the extrusion first, and then the blowing agent is injected into the extruder barrel to dissolve the gas in the melt polymer under high pressure. The dissolved gas softens the melt polymer and a uniform mixture of polymer and gas flows along the extruder. The mixture then exits from the die and foaming occurs due to pressure drop. The extruder head provides enough pressure to prevent foaming near the outlet. After being extruded into the mold, the materials are foamed and the final product is obtained after the cold molding process. In the next step, the foam is stabilized according to the viscoelastic behavior and strain hardening. The effective parameters in this process include extrusion pressure, temperature, and residence time. Single-screw and double-screw extruders can be used. The advantages of the double-screw extruder are less energy consumption and higher efficiency of melting process compared to the single-screw type. The limiting factor is the internal high pressure, which requires special designs. The problem with both types is that the three processes of melting, mixing, and cooling must be performed at a short L/D of approximately 30 to 1. The tandem system is proposed to overcome this problem. In this way, melting and mixing of blowing agents is done in a basic extruder and then a gradual cooling profile is applied along the second extruder (tandem line), which improves the quality of the foam. Although this system is more expensive than conventional types, it is more common due to the

overall cost-effectiveness and versatility. Extrusion foaming is continuous (despite the batch method), cheap, and easy but it is still difficult to smooth the foam and create large amounts of closed cells in cases such as starch biodegradable foams. The use of thermoplastic polymers as an additive is suggested but it decreases biodegradability [13, 14, 18, 25].

4.5 Extrusion Molding

In this method, a mixture of reagents is injected into the mold, and demolding is done after curing. This method produces high-density foams with complex two- and three-dimensional geometries despite extrusion. The low cost of materials, high-dimensional stability, low energy consumption, short cycle time, and improved mechanical properties are the advantages of this method. Supercritical nitrogen is usually used as a blowing agent of this process to produce high-density foams with high cell density. Moreover, the softening effect of nitrogen in the polymer/nitrogen mixture decreases the process temperature resulting in reduction of energy and cost [13, 24].

4.6 Injection Molding

This process bears high productivity and quality. It is an applicable economical method for the production of large plastic foams with complex three-dimensional shapes and special dimensions. The method is more complex and expensive than the slab-stock method; however, it is known as the main method of producing structural foams. Depending on the mold temperature, this method is classified into the cold and hot molding. An injection molding machine that includes a plasticizing injector, mold clamping, and a driving system is the main equipment of this process. The process includes feeding of raw materials, heating, plasticizing, mold closing, injection, foaming, cooling, demolding, and post-treatment. In this way, the polymer and additives are mixed and injected into the feed cylinder to heat and soften. The physical foaming agents are injected directly at the end of the plasticization, mixed evenly, and injected into the mold at high pressure and speed. The chemical blowing agents can be injected directly from the barrel of a modified injection machine or through an accumulator. As the pressure drops sharply, the melt plastic produces a large amount of saturated gas that forms bubbles. The mixture fills a part of the mold (shot) and the gas bubbles at high pressures immediately expand and fill the cavity, completely. As the cells are collapsed against the mold surface, a thin layer of melt forms on the rigid core of the foam. The thickness of the shell can be controlled by the amount of injected melt, mold temperature, type and amount of blowing agent, temperature, pressure of the melt, and the parameters of the injection machine, especially the injection speed. Finally, after bubble expansion, cooling, molding, and

demolding, a foam product is obtained. Injection pressure, temperature, and speed are the determining factors in this method [14, 18, 25].

4.6.1 Gas Pressure Injection Molding

There are various methods of gas injection systems. In this process, when the plastic enters the mold (after injection shot), the gas pressure is removed and the remaining melt is foamed. A seal mold under pressure with inert gas is used. This pressure is to prevent the plastic mixture from foaming when entering the mold.

4.6.2 High-Pressure Molding

A mixture of heated melt with blowing agent is injected into a mold. A pressure much higher than the gas pressure of the blowing agent is created in the mold. After solidification of the shell with the desired thickness, the second step is performed by opening the mold. Thus, the pressure is reduced which causes the remaining melt to foam. Foam density, wall thickness, and surface finishing depend on the constituents and the amount of foam mixture.

4.6.3 Low-Pressure Method with Co-Injection

This process includes separate injection of two compatible plastic components. In this way, solid plastic is injected from a plasticator to form a solid and smooth shell. At the same time, another plastic containing blowing agent is injected, separately to form a foamed core.

4.6.4 Low-Pressure Method with Surface Finishing in Low-Pressure Molding

This method includes no co-injection or injection-compression molding. The volume of the mold cavity is always larger than the volume of the plastic in the unfoamed state. Low pressure allows bubbles to nucleate and grow. Foam expansion occurs during filling. Defects may occur due to bubble growth on the surface of the mold. These defects and surface roughness are visible. Therefore, secondary operations including sanding, filling, and painting are needed. Moreover, controlling of process variables including the temperature of melt and mold, injection speed, blowing agent, cyclical heating/cooling of the mold surface, and direct injection of blowing agent into the melt may improve surface properties during the manufacturing [25].

4.6.5 Reaction Injection Molding

This method is a combination of chemical processes and injection. In this process, highly reactive liquid plastics are mixed under high pressure, then injected into a mold to react, polymerize, and foam. Heating the foam mixture, mechanical mixing (high pressure), pre-injection molding, solidification and heating, extrusion, post-treatment, and heating are the steps of the process. In this method, the reaction between the raw materials causes the release of an inert gas such as nitrogen or carbon dioxide into the plastic to form foam. This method is relatively new and is used to prepare structural foams. The short production cycle of 0.5–6.0 min, low price, easy insertion, and low energy consumption are the advantages of this method. Moreover, shorter cycles with no solvent washing, improved surface finishing, and fast injection into the mold are the advantages of this method over low-pressure mechanical mixing systems. Liquid injection molding, which is a type of reaction injection molding, involves continuous mixing and injection. In this method, the whole shot is mixed in a chamber before being injected into the mold [18, 25].

4.7 Heat/Microwave Sintering

Heat sintering involves mixing the powder of foam mixture, placing the mixture in a metal mold, and finally sintering for several hours. This method is time-consuming, expensive, and requires a large number of molds. Using microwave as a heat source instead of the usual methods, the sintering time can be reduced to a few minutes. In this way, the uniformity of the sintered body is also improved. Some materials and polymers, such as polyethylene, do not absorb microwaves. Thus, a modifying coating layer such as carbon black is required. In this case, a transparent mold such as glass should be used. Thus, the mold must be selected such that it has a low microwave reflection and provides observation of the foaming process. Some holes in the mold wall are also considered as the outlet of solvent gases. The microwave foaming method has been widely used for phenolic foams. It takes a long time to produce large-sized phenolic foams by conventional systems and there are environmental restrictions on the use of blowing agents like CFC_3 . Therefore, a resole foaming method has been developed using microwave and air. The process consists of three steps: (1) mixing the resole and hardener with air bubbles (resole can be cured at 250 °C without hardener, but it takes a long time to completely cure, so the viscosity decreases before solidification, and air bubbles can escape), (2) injection of the mixture into the mold, and (3) microwave foaming. The temperature inside the resole should increase to 150–250 °C, rapidly to make the air bubbles 5–10 times large. Additionally, in the production of phenolic foams, it is necessary to remove the produced water during the curing reaction. In conventional foaming methods, the temperature is usually less than 100 °C, which reduces the possibility of water evaporation. The microwave generates heat by vibrating polar molecules such as

water or resole despite hot plate, which induces slow and non-uniform conduction heat into the material [18, 27–29].

4.8 *Bead Foaming*

This method is used to produce low-density foam products with complex three-dimensional geometries. These foams are prepared using the sintering process of the beads. These beads are unfoamed when sold, and a pre-expansion step must be performed by a pre-expander system. Then pre-expand beads must be stabilized. After stabilization, the beads are ready to enter the mold. Polystyrene bead foams are one of the most common types.

Expandable plastic foams are plastic concentrates containing blowing agents. These materials are formed into precise solid spheres. The two main stages of this process include pre-expansion of virgin beads by heat (hot steam is the most common due to economical aspect). This step brings the density of beads to the desired value within the molded product. In the next step, these beads are transferred into a two-cavity mold by air through a tube. If the beads do not fill the mold properly, the vibration of the mold is exerted to properly arrange the beads. The final expansion is done in the mold by steam or live steam, which enters through the pores of the mold. During expansion, beads melt, adhere to each other, form a relatively smooth shell, and fill the mold. Multi-cavity molds with small sections can also be used. After the heating cycle, the cooling cycle is performed. Due to the insulation of the beads, it takes a long time to cool before demolding. If the heat is not completely removed, the product will be distorted. Water is sprayed on the mold to cool it. The release agent is also used to facilitate cooling, especially for molds with complex shapes. In these processes, the molds have two walls. The inner wall is the actual shape of the product and has some pores for penetration of steam into the foam. Moreover, the produced hot gases leave the product through these pores. The outer wall is a steam cover. Before demolding, stabilization is done by vacuum and water spraying on the inner wall of the mold. The production pressure in this type of molding is low. Thus, cheap molds such as aluminum are usable. Long manufacturing cycles are required if large amounts of blowing agents (such as the production of expanded styrene-acrylonitrile) are used. Post-mold curing is not required in this process [13, 25].

4.9 *Spraying*

This method is used for filling molds where large surfaces such as panels are desired. This method can be used without a mold. The equipment has suitable price and is portable. In this method, the mixing of components and materials is done by atomization of materials when leaving the nozzle of the spray. Heat can also be used to reduce the viscosity of the polymer. In airless spraying, the spray gun moves

approximately 30 inches from the surface and the final properties are obtained 24 h after spraying. The spraying rate of 1.8–3.6 kg/min is usually applied. The surface must be completely clean. Adhesion of the foam to the spray surface is another problem. In cases where the spray surface and the foam material are not compatible, modifications should be made to the surface [24, 25].

4.10 Pour Foaming

In this method, the polymerization and molding of the foam occur simultaneously. The materials are completely mixed before pouring and converting to a fluid. The materials and molds are under little pressure or with no pressure. Therefore, there is no need for high-strength equipment and molds. Due to the low pressure of the process, this method can be used to produce large-scale products and pouring operations can be done in the established unit. The process is unable to apply for structural foams. It is mainly used for preparing thermosets with high foam-ability. High-strength products with low-dimensional accuracy are obtained in this method [18].

4.11 Rotation Foaming

The equipment in this method requires little capital but a lot of production time. The raw materials are pre-formed, then they are placed in a mold and the mold is tightly closed. The mold is then rotated in a furnace to melt the plastic and make it flow through the mold. Heating is continued until the foaming agents are degraded. The final shape is created after expansion, and finally the product is demolded, cooled, and solidified. In this method, (1) the materials are in the form of powder, small particles, or liquid that are easily melted and form a smooth surface; (2) raw materials must be melted, poured into molds, and then flowed to fill cavities instead of melting and then injecting into molds; and (3) the mold should rotate in one or two directions with low pressure. The mold is usually made of aluminum and is heated by steam from a jacket or hot air circulation system. The rotation speed of 1–5 rpm is usually applied.

4.12 Hollow Blowing

This process is performed using a two-headed mold. The method is similar to the processing of conventional plastics and includes (1) preforming of material by extrusion or injection, (2) heating the preform in the mold and foaming, (3) introducing compressed air for blowing and molding, and (4) cooling and demolding [18].

4.13 Thermal Degradation/Treatment

This method can be done in two ways: (1) thermal degradation of block or graft copolymer that has thermally stable and thermally labile blocks, (2) heat treatment of polymers with high T_g which are blended with organic materials or thermally labile polymers. The additives in this method must be completely degraded, otherwise it will contaminate the polymer matrix. In this way, we have reported the preparation of nano-foams with designed structures. Nanofoams are made through thermolysis or heat treatment of thermally labile blocks as a disperse phase in the thermally stable continuous phase. In brief, the foam is obtained via introducing thermally labile blocks into the polymer building, casting the polymer solution, then removing labile blocks and the produced gas [15, 30–34].

4.14 Frothing

This urethane process is introduced by DuPont. This method is a two-stage system based on the introduction of an excess volatile liquid into the formulation. In this method, a pre-expanded foam stream is poured into the mold, where the expansion continues until the desired density is reached. In the foaming stage, the stream is completely liquid and flows easily. This method is suitable for filling cavities and producing panels. The advantages of this method include low mold pressure during foaming, the possibility of achieving low and uniform density, and laying down of expanding foam without causing collapse or density change.

4.15 Casting

This method is a simple non-mechanical pouring method, reaction injection molding, or liquid injection molding. Plastic components and additives are dissolved in a suitable solvent and poured into molds. Polymerization and foaming take place inside the mold. Molds are usually heated or cured in the oven, or both of them. This method applies to materials with suitable solubility [25].

4.16 Phase Separation

This method involves mixing two or more polymers with additives in suitable solvents. The matrix material is then separated from the solvent by a chemically controlled method or thermal cooling so that the solvent accumulated in the polymer matrix forms two completely separated phases. The removal of the solvent gives the

final foam structure. This method is specific to non-cross-linkable polymers because the polymer must be soluble in a solvent. Today, one of the main methods of preparing porous materials is phase separation.

4.17 Leaching

This method involves dissolving the polymer matrix in a highly volatile solvent, casting the solution onto a mold, and selective leaching of water-soluble mineral salts or organic compounds, which were previously mixed with the polymer matrix. The problem with this method is the presence of unwanted contaminants such as solvents or salts in the porous polymer structure. To overcome this problem, the melt molding/particulate leaching method has been proposed instead of the solution molding/particulate leaching. In this way, the polymer matrix is pre-mixed with solid leachable additives and then pressed together. Similar to the solvent cast method, this product enters the same solid leaching stage.

4.18 Etching

This method includes using high-energy radiation to create chain scission in the polymer and remove degraded molecules. The polymer film is then etched with an acidic solution or base to remove the loose polymer. Polycarbonate and polyester films made in this way are commercially available.

4.19 Stretching

The process involves controlled stretching of semi-crystalline polymers in dry, molten, or solution state. In this method, after several times of stretching, the amorphous areas between the crystalline are degraded and the cavities are prepared in the range of a few nanometers.

4.20 Sintering

The sintering process includes mechanical compression of polymer particles at high temperatures. This method can be used for both thermoplastic and thermoset polymers [18].

4.21 Foam Preparation Methods Based on Foam Structure

In this section, some foam structures comprised of the manufacturing process and condition are described.

Foamed film and sheet: These foams are prepared by feeding plastics and additives containing specially treated expandable pellets or injection into the barrel using a tubular film extruder. In both methods, the extruded material passes from the inside to the annular tubing die and expands on an internal sizing mandrel by blowing air into the tube or drawing a tube. The die design is very important because in foam extrusion, the viscosity of the melt is very high and thus the defects are easily transferred to the product. To solve this problem, the die is designed in such a way that the flow is restricted and a uniform flow enters the die [25].

Structural foamed body: Injection molding processes with low or high pressure are used for this purpose. The conventional extruders can be used. The blowing agent can be mixed with the plastic as it enters the hopper, or entered into the melt of screw plasticator, or mixed with the melt by a stirrer. If the surface and inner materials are not the same, the surface materials do not contain foaming agents and softening is done separately. Then, the surface and core are combined during the molding. If the same material is used for the surface and the inside, different molding processes are used to form the unfoamed and foamed surfaces. Two processes of creating an unfoamed surface include: (1) increasing the temperature of the melt and the viscosity to prevent the surface from foaming, and (2) increasing the surface pressure and preventing the separation of gases from the melt. In comparison with these foams, freely foamed body structures are the foams in which foaming occurs throughout the volume of the material [18, 25].

Crosslinking foamed body: The temperature range of bubble expansion is very narrow and difficult to control. By using crosslinking agents, the viscoelasticity of the melt is increased and the temperature range of the bubble expansion is widened.

Combined foamed body: If the foaming occurs in matrix resin mostly combined plastic foam is obtained [18].

Structural web molding: This low-pressure process is the gap between structural foam molding and injection molding. It does not have the usual surface properties of structural foam or defects like the swirl pattern. It is applicable to prepare large light smooth surfaces.

Foam reservoir molding or elastic reservoir molding: This process is used to make plastic sandwiches. In this way, the plastic composite is placed in the heated mold and compressed [25].

5 Conclusion

In general, in all methods of foam production, matrix material, blowing agent, filler, composition, conditions and type of process determine the properties and characteristics of the foam product. Also, the process type and conditions determine the selection of raw materials and composition, and vice versa. Therefore, despite focusing on extrusion and injection molding as the most common methods, the appropriate manufacturing process is selected according to the desired properties of the foam product. Thus, a set of factors including the type of raw materials, structure, final properties of the foam, cost, and applicability of the process must be considered. Due to the extensive properties of foam structures, it is important to address the methods of production and develop improved new methods.

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