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Thermoplastic Foams: Processing, Manufacturing, and Characterization

Mihrigül Altan

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Abstract

Polymer foams have wide application area due to their light weight, resistance to impact, high thermal insulation, and damping properties. Automotive, packing industry, electronic, aerospace, building construction, bedding, and medical applications are some of the fields that polymer foams have been used. However, depending on their cell structure—open or closed cell—polymer foams have different properties and different application areas. In this work, the most used thermoplastic foams with closed cells such as polypropylene, polyethylene, and polystyrene or polylactic acid have been focused. Their melt strength, degree of crystallinity for semi-crystalline ones, and viscosity have great importance on cell morphology. Cells in small diameter with high dense in polymer matrix are preferable. However, obtaining fine cells is not easy in each case, and it is still under investigation for some polymers. There are several ways to improve cell morphology, and one of them is addition of nanoparticle to the polymer. During foaming process, nanoparticles behave like nucleating agent that cells nucleate at the boundary between polymer and the nanoparticle. Besides, foaming agents contribute the homogenous dispersion of the nanoparticles in the polymer matrix, and this improves the properties of the polymer foams and generates multifunctional material as polymer nanocomposite foams.

Keywords: thermoplastic foams, closed cell foams, foam processing, nanofiller, cell morphology, polymer foam nanocomposites

1. Introduction

Polymeric foams are widely used in different fields due to their lightness, reduced thermal conductivity, high-energy absorption, and excellent strength/weight ratio. Application area of the polymer foams has high variety such as transportation, bedding, carpet underlay, textile, toys, sport instruments, insulation appliances, and construction, biomedical, and automotive

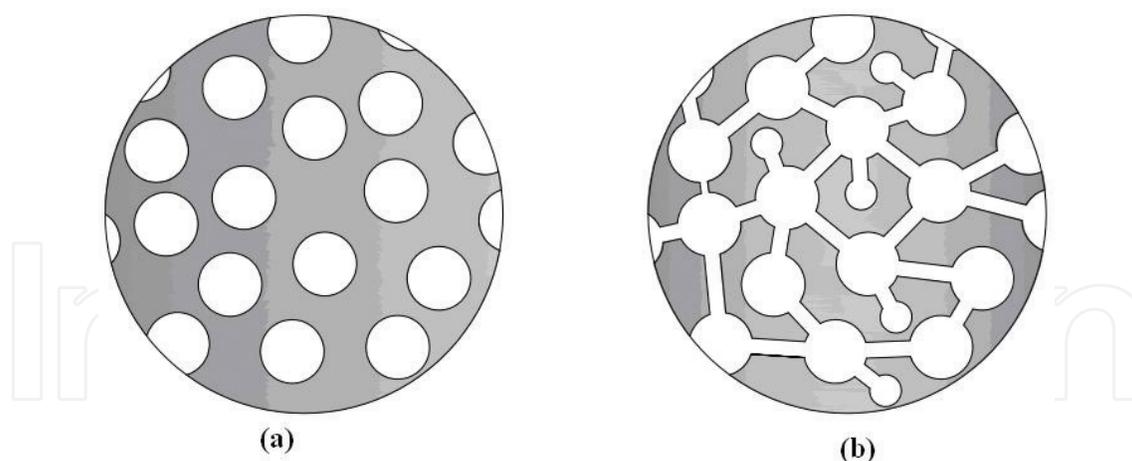


Figure 1. Illustration of polymer foam cellular structures (a) closed cell type (b) open cell type.

sectors [1–5]. A polymer foam is basically a polymer-and-gas mixture, which gives the material a microcellular structure. Polymer foams can be flexible or rigid due to their cell geometry such as open cells or closed cells (**Figure 1**). If the gas pores are roughly spherical and separated from each other by the polymer matrix, then this type is called closed cell structure. On the contrary, if the pores are interconnected to each other to some extent which provides passage of fluid through the foam, then this is called open cell structure. A close cell structure is a good candidate to be a life jacket material, while an open cell structure would be waterlogged. The open cell foams are for bedding, acoustical insulation car seating, and furniture, while the closed cell foams are suitable for thermal insulation, and they are generally rigid, which makes them a preferable lightweight material for automotive and aerospace [6–9].

The development of polymeric foams started with the macrocellular polystyrene foams having cell size above $100\ \mu\text{m}$ in the 1930s [10]. Developments continued for providing finer cells, and solid-state batch foaming method was applied and foam cells less than $100\ \mu$ in diameter were obtained in the 1980s. Since then, polymer foam processing and shaping methods have developed speedily. Besides polystyrene foams, polyurethane has become popular. However, in this work, the most used thermoplastic foams with closed cell structure are focused. The cell generation, cell size and density, mechanical properties, and shaping processes of thermoplastic foams are given in detail. The effect of nanoparticle addition is also discussed in generation of multifunctional materials, polymer nanocomposite foams.

2. Thermoplastic foam processing methods

The principle of foaming processes includes the steps of polymer saturation or impregnation with a foaming agent, providing super saturated polymer-gas mixture by either sudden increment of temperature or decrease in pressure, cell growth, and stabilization [11]. In thermoplastic foaming processes, it is important to obtain foams with closed cell structure with thin polymer cell walls covering each cell. In order to provide this structure, cell growth must be controlled through the process. Temperature limit is critical in obtaining microcellular structure.

If temperature is higher excessively, then melt strength of the polymer can be low-inducing cell rupture. On the other hand, if temperature is too low, this will result in longer foaming times and increment in viscosity of the polymer. As a consequence, cell growth will be restrained, and insufficiently foamed products will be obtained. Therefore, the process conditions have serious importance on cell morphology of the polymer foams. The most known thermoplastic foaming processes are batch foaming, extrusion foaming, and foam-injection molding.

2.1. Batch foaming

Batch foaming can be applied in two different methods as follows, pressure-induced method and temperature-induced method. In pressure-induced method (**Figure 2**), polymer is saturated with blowing agent in an autoclave, and then, cell nucleation is done by sudden depressurization of the system to atmospheric pressure. The final cell morphology is obtained by either cooling the polymer in a solvent or by cooling it within air [10].

In temperature-induced batch foaming (**Figure 3**), the beginning of the process is similar to pressure-induced foaming but at lower temperatures. After saturation is completed, the sample is taken out of the autoclave and put into hot oil bath between the temperatures of 80–150°C for a period of time in order to obtain cell generation. After this step, the sample is put into a cooling bath of water or a solvent. The important point in batch foaming is the geometry of the plastic samples. They are generally a circular disc, rectangular, or square shape with the thickness between 0.5–3 mm not to hinder gas diffusivity [10].

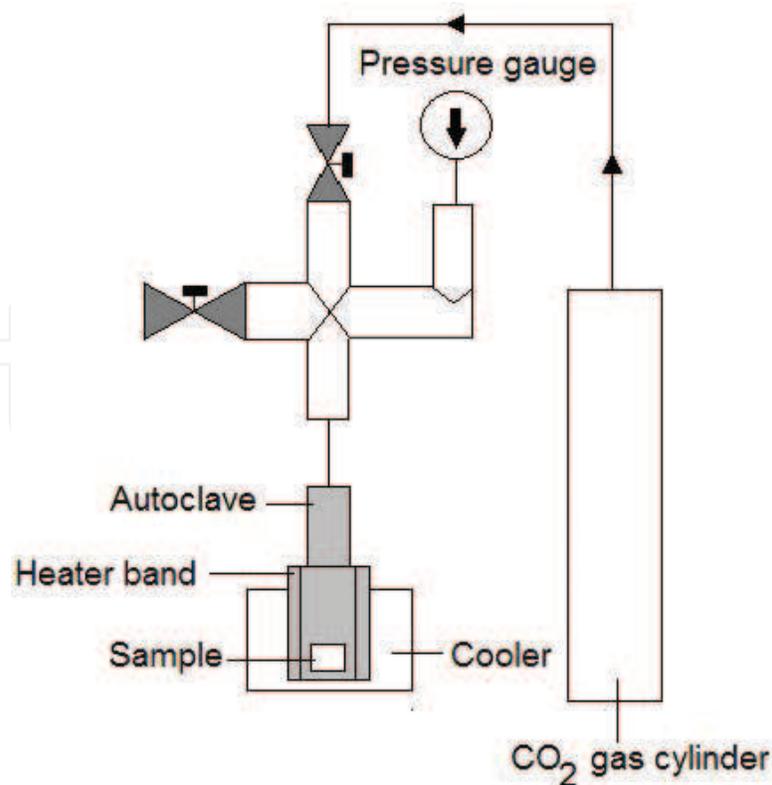


Figure 2. Pressure-induced batch foaming.

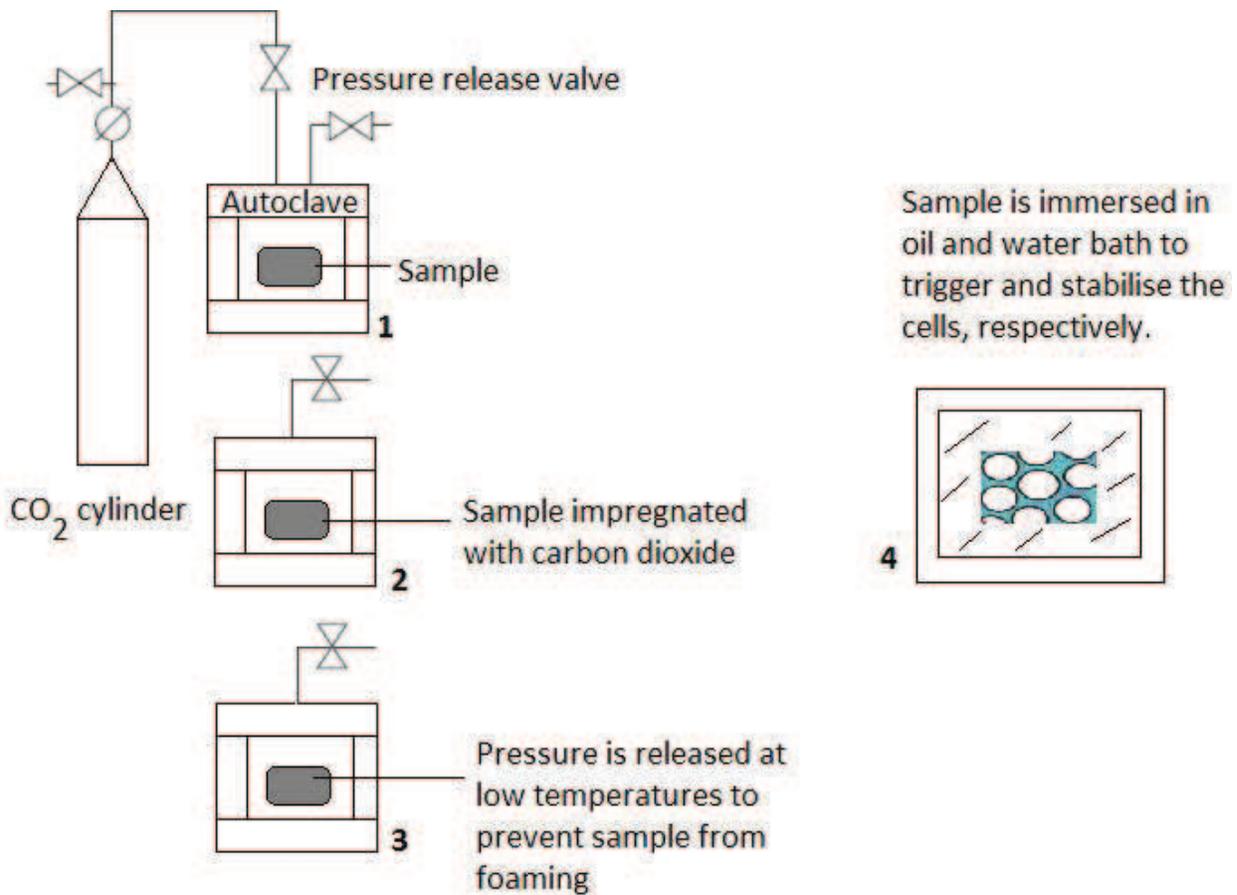


Figure 3. Steps of temperature-induced batch foaming.

2.2. Foam extrusion

In foam extrusion, a tandem line extrusion machine is equipped with a gas supply as shown in **Figure 4**. Typical product types are thermoplastic-based foamed sheets, pipes, and expanded tubes. The pellets supplied from the hopper into the barrel are melted under high pressure and blowing agent. CO_2 gas in supercritical condition is injected into the polymer. Due to the high pressure in the barrel, nucleation of the foam cells is prevented. As the polymer exits from the die, foam cells are generated by the sudden pressure drop. The final step is cooling, calibration, and cutting of the extruded foams [11, 12].

The extrusion foaming process can be either physical or chemical foaming. In **Figure 4**, physical foaming is shown that a gas supply is integrated to the extruder. In industrial applications, chemical foam extrusion is also applied due to its cheapness in tooling. In chemical foam extrusion, polymer pellets and chemical foaming agent are mixed through the barrel, and the heat in the barrel decomposes the chemical foaming agent resulting in gas which provides expansion of the polymers as it exits the die. Melt temperature is critical in decomposition of the foaming agent. The pressure must be high enough in order to keep the dissolved gas in the polymer before it exits the die. If the pressure and temperature are not set correctly, foaming agent will not be decomposed and can induce left particles or agglomerations of foaming agent, which can lead to poor cell morphology and poor surface quality [13]. The most known chemical

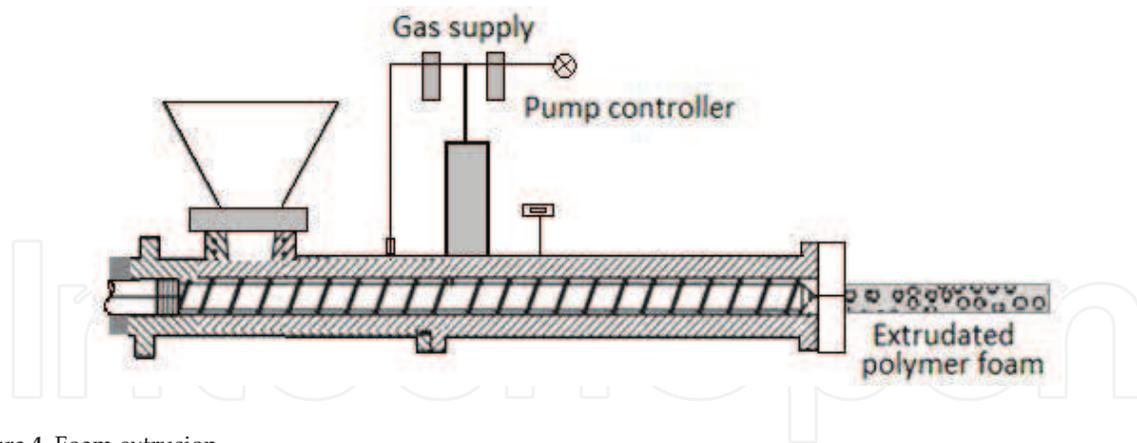


Figure 4. Foam extrusion.

foaming agent is azodicarbonamide (ADC), an exothermic chemical foaming agent. It releases high-amount of N_2 gas together with CO_2 in lower amount into the polymer. However, due to the toxic byproducts of ACD, endothermic type commercial foaming agents are being used, such as Clariant's Hydrocerol [13, 14].

2.3. Foam injection molding

Foam injection molding is similar to conventional injection molding, but an additional gas unit is integrated to the injection molding machine if physical foaming is applied (Figure 5). There are currently three widely known foam injection-molding technologies available to produce microcellular foams using CO_2 as a physical blowing agent. They are MuCell by Trexel Inc. (USA), Optifoam by Sulzer Chemtech AG (Switzerland), and ErgoCell by Demag (Germany) [15, 16].

Foam injection molding has some critical points to be considered. One of them is the presence of the back pressure. If back pressure is not applied, polymer-gas mixture would move the screw axially and instability in dosing of the polymer would be seen. Also, foaming agent would expand in the plasticization unit and leak out during injection. This would prevent cell

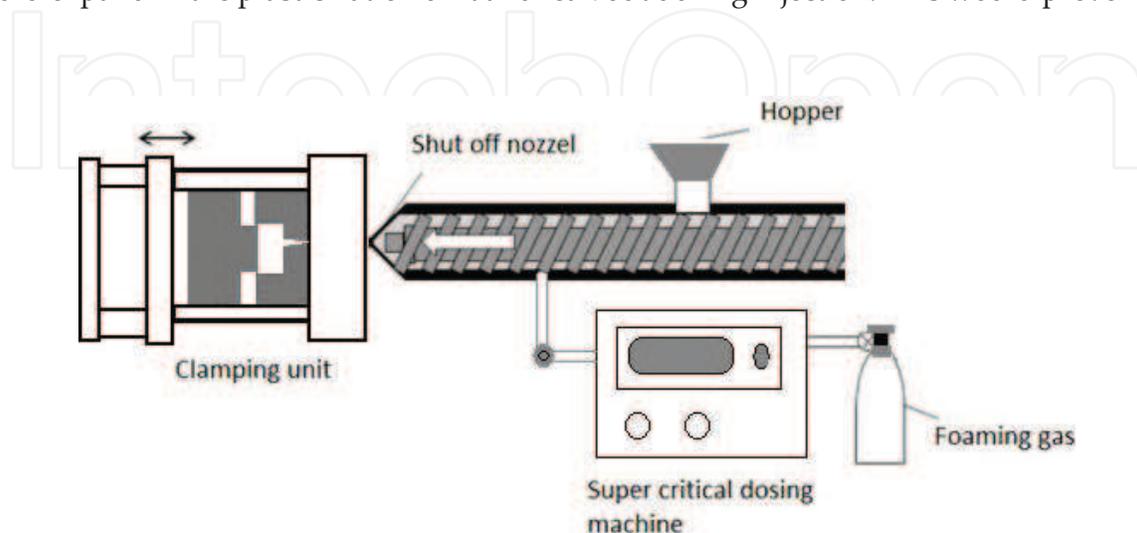


Figure 5. Foam injection molding.

generation in the polymer. The second critical point in foam injection molding is the selection of needle shut off nozzle that prevents the leak out of the nozzle and gas loss [16].

In foam injection molding, physical and chemical foaming can be applied. In chemical foaming, chemical foaming agent is added in solid form either from the hopper of the injection molding machine with the polymer pellets or during plasticization of the polymer through the barrel. Foaming agent dissolve through the process. Physical foaming agents are injected directly into the molten polymer. The difference in comparison to foam extrusion is the motion of the screw. In foam extrusion, the screw rotation pushes the melt forward and then out of the extruder die, but in foam injection molding, screw rotates and moves backward due to the collection of a pool of gas-polymer mixture at the tip of the screw. Then, polymer-gas mixture is injected into the cavity under. In physical foaming, the high pressure and high temperature in plasticization unit provide supercritical state of the foaming agent [17]. Gases like nitrogen (N_2) and carbon dioxide (CO_2) are used as physical foaming agents, and they are applied in an overcritical state in order to obtain high degree of solubility in the molten polymer [17]. In supercritical fluid state, fluid has low viscosity, low surface tension, and high diffusion properties that all these provide excellent solubility in the polymer. Depending on this, improved cell morphology is achieved. Carbon dioxide has supercritical point of 73.84 bar with $37^\circ C$, and nitrogen has 33.90 bar with $-147^\circ C$. In **Figure 6**, the supercritical phase of carbon dioxide is shown.

In order to control the dosing of gas, supercritical dosing machine is integrated to the system as shown in **Figure 5**. Furthermore, high back pressure is necessary during plasticization for dosing and homogenizing the foaming agent in the polymer melt [17]. For these reasons, a specially equipped machine similar to the conventional injection molding is necessary in foam injection molding, as shown in **Figure 5**.

The high equipped and expensive systems in physical foaming of polymer foams processing is costly. On the other hand, chemical foaming is less complicated and can liberate gases under certain processing conditions either due to chemical reaction or thermal

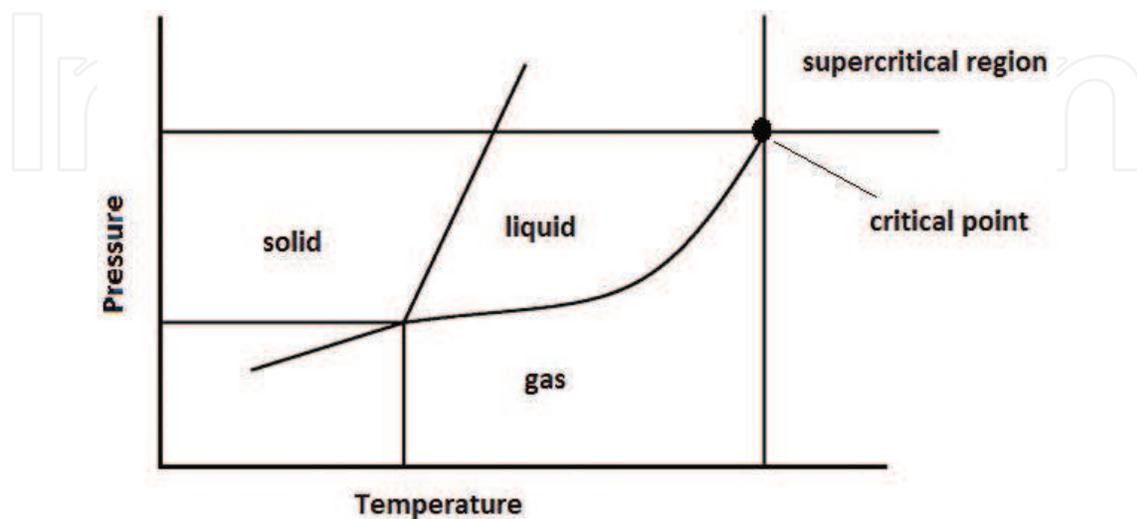


Figure 6. Supercritical fluid CO_2 .

decomposition [13]. Chemical foaming agents are added to polymer either prior to or during plasticization, similar to foam extrusion by chemical foaming agents. They can be exothermic or endothermic. Exothermic types release energy during a reaction which is dissipated through the plasticization unit. As the activation temperature is reached, no energy is needed to be added, and reaction continues until foaming agent finishes its reacting completely. In the usage of endothermic foaming agents, energy must be continuously applied in the form of heat, so that the reaction does not stop. Azodicarbonamide (AC) is the most known exothermic foaming agent with high gas yield. It has decomposition temperatures between 170 and 200°C [13]. Sodium bicarbonate and zinc bicarbonate are the most common endothermic blowing agents. In last few years, a commercial foaming agent, Hydrocerol, has been extensively employed as endothermic foaming agent. Hydrocerol has decomposition temperatures between 160 and 210°C and can be added directly into the hopper of an injection-molding machine in the form of pellets in proportions from 1% to 4 wt.% [13].

As a summary, the comparison of three foaming processes is given in **Table 1**.

2.3.1. Morphology of foams

In batch foaming, uniform cell size and homogenous distribution of the cells can be gained. The polymer parts are foamed in solid state in batch foaming; therefore, a very tiny skin layer is formed as unfoamed. In foam extrusion, uniform cell size is possible to obtain, but cells in the core of the extruded part may be larger due to the instability in cooling stage. On the other hand, morphology of the cells in foam injection molding shows locally different character through the thickness of the molded part due to the variation in temperature from mold wall to the core of the part. The mold wall has low temperature than that of polymer melt leading to a sudden freezing of the polymer close to the mold wall. In this zone, which is called skin layer, cell generation is inhibited. The foaming agent dissolved in the polymer remains in the skin layer and diffuses out of the polymer. As a result, a frontal flow in the core of the polymer melt is generated as shown in **Figure 7**. This results in a compact skin layer and a foamed core [18–20].

The morphology of the polymer foams is important and affects the mechanical strength of the material. Cells in small diameter enhance the mechanical strength when compared with the larger cells. The density of the foams can be defined by the distance between neighboring cells. It is generally defined as 0.04–0.30 g/cm³. Cell distances have shown that they have a definite influence on the mechanical properties of thermoplastic foams [16, 19]. The morphology of the foam injected part can be divided into five zones. As shown in **Figure 8**, the zones from one mold wall to the other mold in the cavity are skin layer-outer foam core-inner foam core-outer foam core-skin layer. Inner core has the cells with the largest diameter due to the slow cooling rate of the material in the core region, and cells have time to expand [16, 18–20].

Shortly, morphology of the foam injection moldings has great importance on the properties of the polymer foams such as mechanical, optical, and thermal conductivity. For this reason, setting of the injection molding parameters correctly and dosing of foaming agent precisely

Criteria	Batch foaming	Foam extrusion	Foam injection molding
Amount of material needed	Small amount (in g)	Larger amount (in kg)	Larger amount (in kg)
Pre-molding	Necessary	No needed, molding tool is in the process itself	No needed, molding tool is in the process itself
Sample state during gas loading/saturation temperature	Solid	Melt state	Melt state
Cell density range (cells/cm ³)	10 ⁶ -10 ¹⁶	10 ⁴ -10 ¹¹	10 ⁴ -10 ⁸
Cell distribution	Uniform distribution	Generally uniform but sometimes the cells in the core are different in size from those found at the edges	It is difficult to obtain foams with uniform cell
Surface quality	Good	Good and glossy	Generally poor
Skin layer thickness (μm)	Thin	Thin	Thick
Addition of nucleating agents/process flexibility	Foaming composition is fixed from the onset. Must be done in the previous processes such as injection molding or extrusion, etc.	Composition can be changed at any time. Nucleating agents can be introduced at anytime during processing	Nucleating agents can be introduced also at anytime during processing
Blowing agent supply	Sample is saturated with the blowing agent until equilibrium is reached	Blowing agent is metered but not more than the melt can take	Blowing agent is metered but not more than the melt can absorb at a certain processing condition
Tooling cost	Cheaper than the others	Expensive depending on the machine capacity	Expensive depending on machine capacity and also mold is extra cost

Table 1. Comparison on batch foaming, foam extrusion, and foam injection molding.

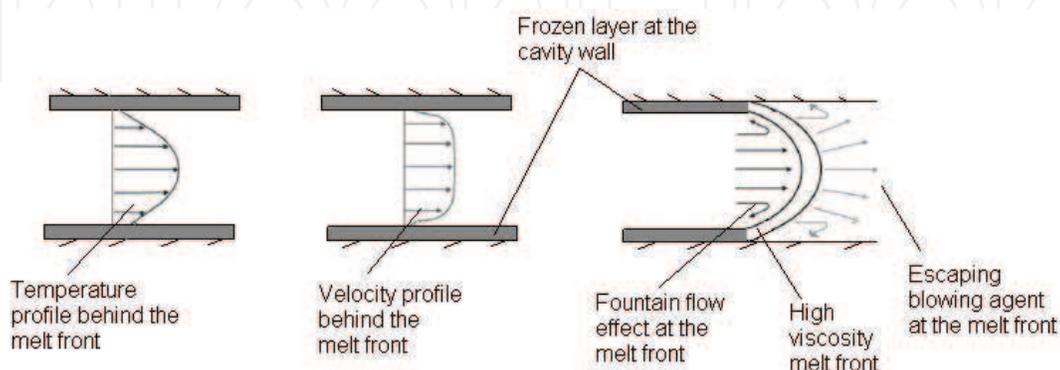


Figure 7. Illustration of the headstream in foam injection molding.

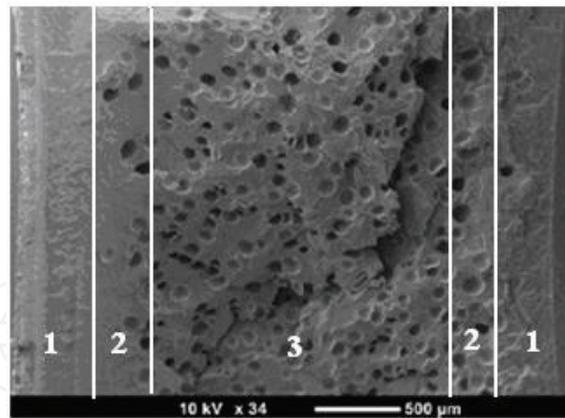


Figure 8. Zones of the injected molded foams according to the cell morphology (1) compact skin layer, (2) outer foam core, (3) inner foam core [20].

has critical effect in improving the properties of the polymer foam. Besides all, generation of the foam cells is effective in reducing the sink marks, warpage internal stresses, and shrinkage of the foam plastic, which enhance the selection of the foam injection process in the plastic industry.

3. Thermoplastic foams: processing and nanocomposites

A wide variety of thermoplastics such as polypropylene, polyethylene, polystyrene, polycarbonate, polyvinyl chloride, polylactic acid, and polycarbonate have been experienced in foam processing techniques. Depending on their viscosity, melt strength, the formation of cell morphology of the polymer foam changes. Due to the demands of improvements in foam morphology and the mechanical strength of the polymer foams, nanoparticle-reinforced polymer nanocomposites have been developed in last decade. It has known that nanoparticle usage in polymer foam processing improved cell morphology due to the nucleating agent behavior of the nanoparticles in the polymer matrix. The presence of nanoparticles is also effective in improving the mechanical, physical, and chemical properties of polymer foams. In this section, the most experienced thermoplastic foams in industrial applications and their composites are reviewed.

3.1. Polypropylene-based foams

Polypropylene, member of linear polyolefin group, has poor solubility of carbon dioxide and low melt strength. Linear olefins do not show high strain-induced hardening which is the critical requirement in withstanding the stretching force generated in the stages of cell growth. Chien et al. [21] studied on polypropylene foams obtained by conventional injection molded and traditional foaming injection molded using chemical foaming agent content under various molding conditions. They observed the effects of process parameters, part thickness and

foaming agent content on the degree foaming. Injection velocity, melt temperature, mold temperature, and back pressure on weight reduction and mechanical properties were investigated. The chemical foaming agent was azodicarbonamide used in their study. It has been reported higher injection velocity induced higher weight reduction due to the reduction in the amount of melt foaming in the screw and provided more melt foaming in the cavity. Higher melt temperature and mold temperature resulted in higher melt foaming in the cavity; consequently, weight reduction was observed. The effect of foaming agent content on weight reduction of thick parts was evaluated, and it was found that concerned the weight decreases with increasing content of foaming agent but less significantly. The mechanical test results of PP foam showed that tensile, flexural strength, stiffness, and part weight decreased with the increasing melt temperature, mold temperature, and injection velocity whereas increased with increasing back-pressure.

Sporrer and Altstadt [19] obtained PP foams by physical foaming, MuCell technique. The effect of process conditions on cell morphology was observed. Two different mold temperatures were studied as 20 and 80°C. When they worked at higher mold temperatures, the thickness of the compact skin layers was reduced by 20% as compared to the part processed using the cold mold. The SEM image is given in **Figure 9**. The mold with 80°C gave 552 μm of layer thickness, and the mold with 20°C gave 442 μm of skin layer. The thinner skin layer is the result of the lower thermal gradient between melt and mold steel and a less rapid heat transfer in hotter mold.

In **Figure 9**, morphologies of polypropylene foams are given that are foam injected molded under 20 and 40°C. The foam of 40°C gave coarser and ruptured cells, while the foam of 20°C gave thicker skin layer. The reason of thicker skin layer is the sudden frozen layer of the material as it is injected into the cold mold wall (20°C).

Xin et al. [22] applied chemical foaming by using azodicarbonamide in order to obtain microcellular polypropylene/waste rubber tire (WGRT). Their aim was to generate “a value added” product by using a waste material. They observed the effects of critical processing parameters on cell morphology and physical properties of the blend foams. They observed that under the

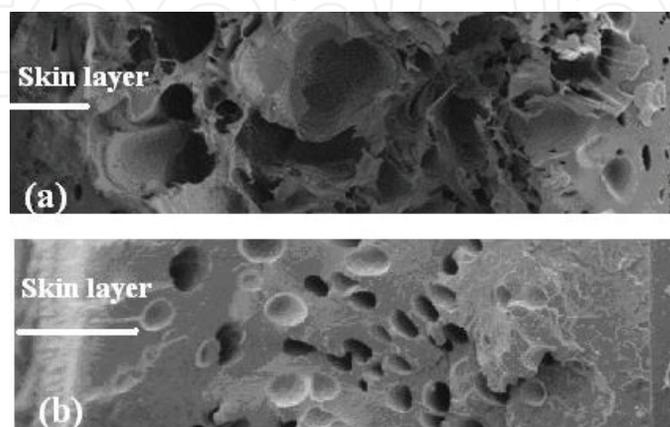


Figure 9. Morphology of the PP foams processed with different mold temperatures (a) 40°C (b) 20°C [20].

same molding conditions, the microcellular PP/WGRT blend samples had smaller cell sizes and higher cell densities than the microcellular PP samples. They reported that it was due to the behavior of the waste rubber tire powders as nucleating agent that promoted heterogeneous cell nucleation, resulting in higher cell density. On the other hand, the increase of viscosity in the PP/WGRT blend prevented the growth of the cells, leading to a smaller cell size [23].

Realinho et al. [24], developed flame-retardant polypropylene composite foams by combining a basic hydrated magnesium carbonate (hydromagnesite), an intumescent additive based on ammonium polyphosphate, an organo modified-montmorillonite (MMT), and graphene nanoplatelets with PP. Azodicarbonamide was used in chemical foaming. Addition of hydromagnesite was 60%, while the other nanoparticles were about 1%. They reported that cell size reduced to 100 μm from 900 μm with the addition of hydromagnesite. The presence of nanoparticles enhanced the cell morphology. They also mentioned that solid composites were more successful in improving the flame retardancy than foam composites.

In order to improve mechanical properties of PP foams, Hwang and Hsu [25] used nanosilica particle polypropylene. Physical foaming, MuCell technique, was applied in their study. Particle addition was between 2 and 10%. They observed that when the silica content increased, cell size decreased and the cell density increased. However, a threshold was seen in silica content that the cell size leveled off when the nanosilica loading was greater than 4%. Similarly to the previous studies, dispersion of the nanoparticles in the matrix homogeneously improved cell morphology. This is due to the nucleating agent effect of nanoparticles that cells nucleate at the boundary between the polymer matrix and the filler. Hwang and Hsu [25] also experienced the effect of microsilica particles and compare their effect on cell generation. They observed that at the same concentrations of particles, nanoparticles gave denser and smaller cells in size.

Nanoclay is another nanoparticle used in order to improve the properties of polypropylene foams. Nanoclay particles, similar to silicate, act as nucleating agent and lead homogeneity in cell size. Increment in clay content decreased the cell size due to the high viscosity of polymer [16, 26, 27]. Furthermore, authors suggested that clay particles act as secondary layer to protect the cells from being destroyed by external forces. In other words, the biaxial flow of the material during foam processing, the nanoparticles align along the flow direction which is the cell boundary (**Figure 10**). By this way, clay particles help the cells withstand the stretching force. Otherwise, the cell wall will break and weaken the mechanical strength of the polymer foam.

Doruk [28] studied on the effects of the nanocalcite and microcalcite particles on the cell morphology and mechanical strength of the PP foams. Nanoparticles were mixed with polymer in twin screw extruder, and then, foam injection molding was applied by chemical foaming agent (azodicarbonamide). When the fracture surface was observed as given in **Figure 11**, nanoparticle addition improved cell morphology. In **Figure 12**, tensile properties of the PP/calcite foams are given, and it has been seen that under the same concentration of the particle addition (1 wt.%), tensile strength of PP/microcalcite foam is slightly higher than that of PP/nanocalcite foam. This is due to the improved cell generation of the PP/nanocalcite foam as given in **Figure 11**. On the other hand, cell generation of PP/microcalcite is very poor, and the ductility of the PP/nanocalcite is apparently higher than that of PP/micro. When the weight

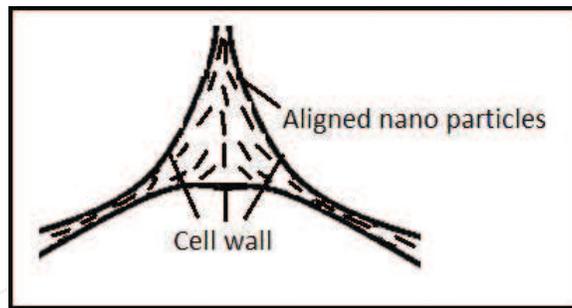


Figure 10. Illustration of the alignment of the nanoparticles during foaming process.

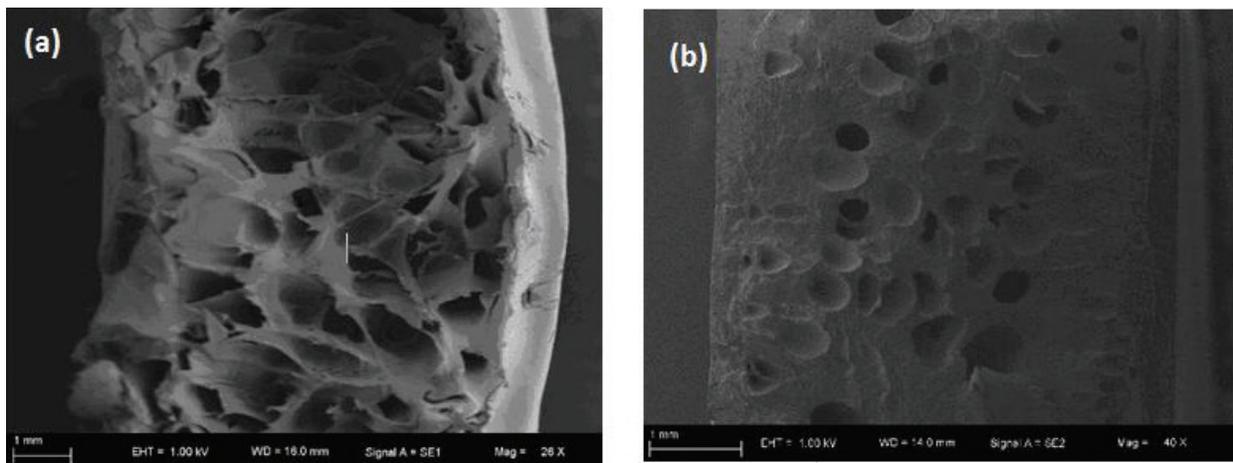


Figure 11. Cell morphology of PP/calcite foams (a) nanocalcite reinforced (b) microcalcite reinforced [28].

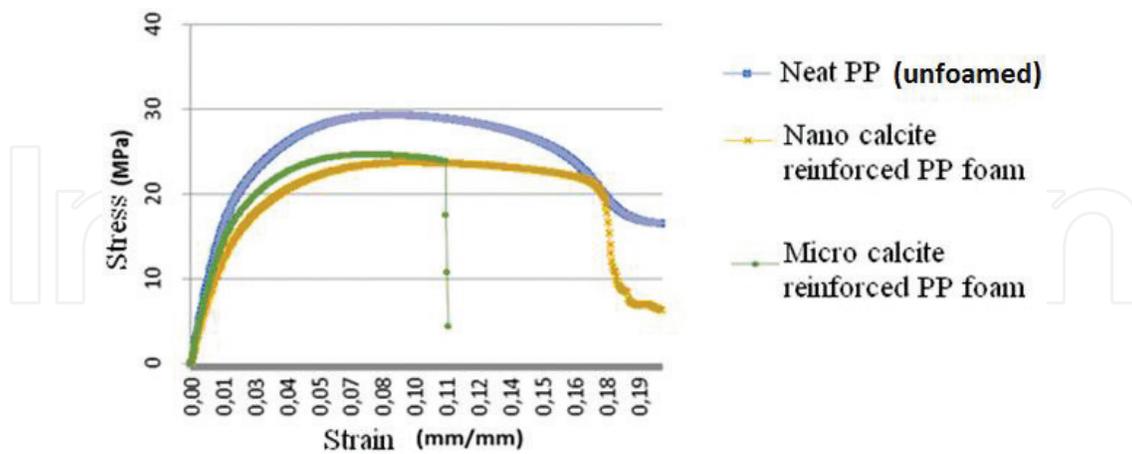


Figure 12. Comparison tensile properties of PP foams with microsized and nanosized calcite (1 wt.%) [28].

loss is considered, nanocomposite foam shows the weight loss of 20.7%, while microcomposite foams have 8.3% of weight loss.

The demand of new lightweight materials with improved transport properties for applications in electrostatic discharge, fuel system components, and electromagnetic interference shielding

such as fuel cells, gaskets for electronic devices, among others brings the generation of a multi-functional material, carbon-based nanoparticle-reinforced polymer foams. Carbon nanotubes, graphene, have been recently attractive for many applications in electronic industry. Antunes et al. used carbon nanofibers (CFN) with polypropylene in order to improve thermal and electrical properties of the polypropylene composite foams [29, 30]. In their study, they emphasized the importance of particle alignment during cell generation and the importance of this on thermal conductivity of the PP. The foaming of PP with CNF provided a kind of network of the particles through the polymer matrix which increased the thermal conductivity of the polymer. When they compared their results with foamed and unfoamed polymer composites, they observed that the unfoamed composite showed a constant thermal conductivity independently of CFN content, while PP/CNF foams showed an increment in thermal conductivity as the content of CFN increased. This shows that a kind of network of CNFs throughout the polymer was formed formation that makes the material thermally conductive. The formation of this network is similar to the clay alignment as discussed in **Figure 10**. In a different study related to PP/CNF foams [31], electrical conductivity of the polymer composite foams was investigated. When the unfoamed and foamed composite were compared, the lower concentration of CFN gave high electrical conductivity. Also, the cellular structure generated during processing with cells highly elongated along the foam thickness direction increased the through-plane electrical conductivity of the foams with regard to the in-plane one. This indicates the importance of cell morphology on the electrical properties of the polymer foams. An accurately developed cellular structure may help to develop foams for semi-conducting lightweight materials [29–31].

Altan [20] made a research on polypropylene/ nano-zinc oxide (ZnO) foams. Zinc oxide is another alternative material to improve electrical properties of the polymer foams. The concentration of ZnO was 1.5% in weight. When the cell morphologies of PP foam and PP/nano-ZnO foam were compared, it has been seen that the presence of nanoparticles decreased the cell diameter and thickness of skin layer and increased the cell dense (**Figure 13**).

Graphene is the latest nanomaterial applied in polymer foams. Similar to previous nanofillers, in literature, it has been seen that graphene loading to PP between 2.5 and 5 wt.% has great

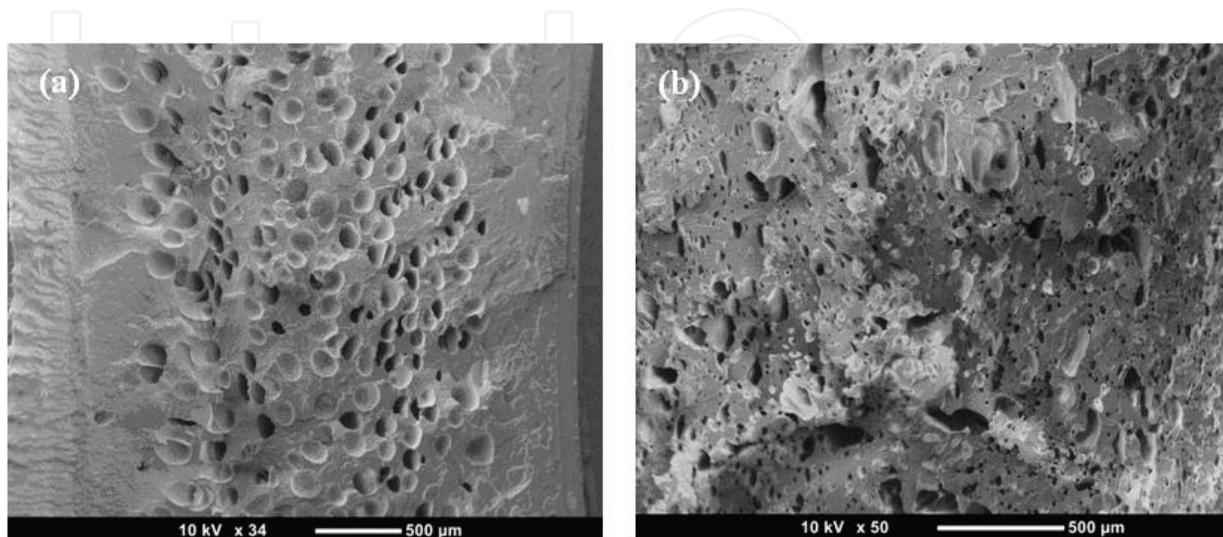


Figure 13. Fracture surfaces of polypropylene foams (a) neat PP (b) PP/ZnO [20].

effect in cell nucleation [32]. Besides, the higher expansion of polymer during foaming process induces higher exfoliation of the graphene nanoplatelets in PP matrix and brings higher mechanical strength [32].

3.2. Polyethylene-based foams

Polyethylene (PE) is a member of polyolefin-like polypropylene. High-density polyethylene (HDPE) and low-density polyethylene (LDPE) have been experienced in foam processing. LDPE foams are used as thermoplastic material for applications such as packaging and foamed sheets, sports parts due to its owing low density, high elasticity, water resistance, and low cost. One of the common problems in polymer foams is the loss of toughness and ductility of the material due to the generation of the cells. Sun et al. [33] developed a toughening mechanism for high-density polyethylene/polypropylene blends. They obtained super ductile polymeric blends using microcellular injection molding. They prepared PP/HDPE and PP/LDPE blends which were prepared at weight ratios of 75/25, 50/50, and 25/75 with melt mixing method and then by applying MuCell technique. It has been observed that during tensile test, 75/25 PP/LDPE foamed parts were highly fibrillated along the tensile load direction in the necking region. The researchers reported that the reason of this behavior—the high ductility of polymer foams—was related to two reasons. The first one was due to the microcellular foam structure cell size lower than 100 μm , and the other was an immiscible but compatible submicron-size secondary polymeric phase. During tensile test, the sub-micron phase of the blend debonds from the matrix, and the cavities collapse. Secondly, they interconnect the microscale foam cells along the load direction. This generates many fibrils that make the material highly ductile [33].

Similar to the case of PP-nanocomposites foams, various authors have reported the preparation, characterization, and properties of PE-nanocomposite foams [34–37]. Arroyo et al. [37] developed low-density polyethylene/silica nanocomposite foams by using chemical foaming agent. They applied different concentrations of silica between 1 and 9%, and foaming agent was 5% in weight. The addition of silica particles improved the cellular structure of the LDPE improved with increment of the cell densities and decrease in cell size. However, at silica concentrations over 6%, increase in cell size was reported. There are few reasons about the poor quality of foam cell morphology under higher nanoparticle concentrations. One of them is possible agglomerations of the nanoparticles at higher concentrations that they prevent the formation of the cells. Also, increase in viscosity of the polymer melt because of the higher loadings of the particles makes the cell generation difficult.

Clay is one of the most used inorganic particles in enhancing the properties of PE-based foams. Clay, such as montmorillonite (MMT), is mixed with polymers and the mechanical strength of the polymers increase [36, 38]. In the study of Hwang et al. [38], the effect of MMT on the cell morphology of the low density of polyethylene (LDPE) was observed. First of all, the researchers enhanced the nanoparticle distribution in the polymer matrix by grafting polar maleic anhydride (MA) onto nonpolar LDPE. The concentration of MMT was between 1 and 5%. Their results are similar to the previous studies that the MMT and MA act as nucleating agents that lead to a finer and more uniform cell structure. When the dispersion of the nanoparticles is homogenous, the cell size decreases and the distribution of the cells is homogeneous.

Polyethylene foams, similar to the other thermoplastic foams, can be processed either batch foaming or foam injection molding. Hayashi et al. [39] compared the organo clay PE-based ionomer composite foams obtained by batch processing and foam injection foaming. The effect of clay on foam morphology of PE is similar to the previous studies that the dispersed nanoclay particles act as nucleating sites for cell formation, and cell growth occurs on the surfaces of the clays. Different from batch processing, in foam injection molding, the moldings have two compact solid skin layers and a foamed core. In both foaming processes, the foam morphology can be improved by setting process conditions correctly depending on the viscosity of the polymer and the temperature and gas pressure limits. Hayashi et al. [39] reported that in batch process, the ionic cross linked structure provided finer cells, and the coalescence of the cells was prevented. On the other hand, by the effect of supercritical nitrogen gas as foaming agent during foam injection molding process, the viscosity of polymer was decreased, and this promoted the nucleation and also coalescence of the cells, especially at high temperatures.

3.3. Polystyrene-based foams

Polystyrene (PS) is an amorphous polymer, and it has wide application area in polymer foam processing such as thermal insulation, packing material due to its low cost, ease of processing, resistance to moisture, and recyclability. Dow Chemical Company invented PS foams as "Styrofoam" in 1941. Polystyrene foams are basically divided into two; expanded polystyrene (EPS) and extruded polystyrene (XPS). Expanded polystyrene has white color and can be used in cups for hot beverages, insulation material in whitegoods, or in packing industry. EPS consists of 96–98% air and 2–4% polystyrene. Processing method is heating the material with steam and then expanding of the material. Extruded polystyrene (XPS) has smaller air pockets inside and manufactured by extrusion process in the form of boards with different colors to identify the brand type of the product. Zhang et al. [40] produced extruded polystyrene foams (XPS) by using CO₂ and water as a co-blowing agent. Okolieocha et al. [41] carried out on a tandem foam extrusion line, similar studies on XPS. They used a slit die (0.5 mm) set at a temperature of 126°C. In order to enhance cell density, they used 1 wt.% of thermally reduced graphite oxide. However, general purpose polystyrene (GPSS) and high-impact polystyrene (HIPS) are suitable for injection molding and structural foaming, and cell generation can be provided similar to the other thermoplastics by chemical or physical foaming agents. Furthermore, PS is not characterized by low melt strength so this makes it suitable for foam injection molding. Hwang et al. [42] applied foam injection molding via MuCell for obtaining clay-reinforced PS foams. Clay was used to improve cell morphology of the polystyrene foams. They obtained PS/clay composite foams with small size cell, which makes the material highly suitable for acoustic and thermal insulation applications. On the other hand, layers of clay-like montmorillonite (MMT) are difficult to fully exfoliate in PS matrix. MMT was modified by stearylbenzyl-dimethyl-ammonium chloride prior melt mixing with polystyrene, and the concentration of MMT in the matrix was experienced in a narrow range as 0.25-0.5-1-2-3% (wt). It has been seen that organo clay presence of 1% in PS matrix gave the small cell in diameters, leading to maximum tensile strength, thermal stability, and cell density.

3.4. Polylactic acid-based foams

Poly (lactide acid) or polylactide (PLA) is a biodegradable and biocompatible polymer produced from such renewable sources as cornstarch and sugarcane [1–4]. PLA foam is a competitive material among most of other thermoplastic foams due to its biocompatibility and biodegradability, PLA has been widely used in tissue engineering applications such as skin, bones, blood vessels, due to their highly porous structure as scaffolds in last [4]. The porous surface of the PLA foams enhances the biological activities of both seeded and native cells. High porosity is important for enhancing biological properties of the scaffold such as the adhesion, proliferation, and migration of the cells. However, mechanical properties of foams decrease with the increasing of porosity. Besides, the high strength and brittle properties of PLA make it difficult to use and process it in foaming techniques. Researchers are focusing on generation of PLA with different polymers or PLA matrix composites [4].

Similar to the other thermoplastics, PLA foams with uniform cell morphology are generally obtained by physical foaming agents such as carbon dioxide and nitrogen in foam injection molding and foam extrusion. However, the poor melt strength of PLA brings difficulties in obtaining an enhanced cell morphology. There are several ways to improve PLA's foam morphology by means of improving melt strength of the polymer such as using chain extenders, using polymer blends of PLA, addition of nanoparticles, and improving crystallization kinetics. Low melt strength of PLA induces cell coalescence during cell growth. Addition of chain extenders to PLA increased the rheological properties of PLA, and depending on this, cell morphology is enhanced [43–45].

Crystallization is an important factor in improving melt strength and foaming ability of thermoplastics. The low melt strength of PLA can be promoted by improving crystallization kinetics and the poor viscoelastic behavior of the polymer. However, high crystallinity has negative effect on cell generation by suppressing the foam expansion. On the other hand, during foaming, cell nucleation starts around crystals [46, 47]. Therefore, improving crystallinity can be balanced by some nucleating agents such as additives and nanofillers behave-like nucleating agents. There are several studies on PLA nanocomposite foams that used calcite, sepiolite, and multi-walled carbon nanotube as nanofiller [46–49]. In these studies, nanomaterial addition was found to be nucleating agent for crystallinity and cell generation. There has been great interest to clay-reinforced PLA composite foams due to the enhanced viscoelastic behavior of clay particles in the polymer matrix which improves cell morphology [48, 50]. As the nano clay particles increased, the cell density of the foamed samples increased. It has been reported that even a small amount addition of carbon nanotube (CNT) promoted the cell density due to its effect on cell nucleation [47]. An interesting point about PLA/CNT composite foams that the gas used during foam injection molding behaved like a dispersant for the nanoparticles that homogenous dispersion of CNT could be obtained in the polymer matrix. This is due to the plasticization effect of the supercritical fluid phase of CO₂ [43, 47]. Therefore, in foam extrusion and foam injection molding, the foaming agents do not only provide foaming but also disperse the particles homogeneously in the matrix.

4. Conclusion

Thermoplastic foams are generally obtained by batch foaming, foam extrusion, and foam injection foaming. Batch foaming is cheaper than the others due to simple equipment, but in each method, the main aim is to promote cell morphology by providing small cell in diameter and high cell density in the polymer matrix. The thermal properties of the polymer, its viscosity, degree of crystallinity, and melt strength are the important factors in improving the cell morphology. There are several ways to improve the cell morphology of the thermoplastics such as preparation of polymer blends, using chain extenders or using nanofillers. Nanofiller addition is popular in last decade due to improvements in properties of the polymer foams. It is known that some nanoparticles are difficult to disperse in the polymer matrix because they tend to agglomerate seriously. However, in polymer foam processing, usage of foaming agent such as CO₂ or N₂ gases enhances the dispersion of the particles by reducing providing plasticization effect. The homogenous distribution of the nanoparticles contributes the cell nucleation.

Nanocalcite, nanomontmorillonite, nanosilicate, and carbon nanotube are the most used nanoparticles in polymer foams. Graphene-reinforced polymer foams are still under investigation. Both carbon nanotube and graphene-reinforced polymer foams have application area as thermal insulator or electrical conductive polymer foams. Nanocalcite or nanosilicate has been used for improving cell generation, increasing mechanical strength, and enhancing flame retardancy of the polymer foam. It has been seen that small amount of nanofiller addition improved cell morphology seriously.

Polypropylene and polystyrene foams are rigid foams that have wide application area in automotive and wind industries. On the other hand, polylactic acid is a promising biomaterial, and PLA foams are suitable materials for tissue engineering as scaffolds. The high porosity of the PLA foams, as scaffolds, provides enhanced biological activities of both seeded and native cells, and they can substitute the native tissue until the native tissue heals.

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Author details

Mihrigul Altan

Address all correspondence to: meksi@yildiz.edu.tr

Department of Mechanical Engineering, Yildiz Technical University, Istanbul, Turkey

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