This thesis investigates the use of supercritical carbon dioxide (scCO$_2$) processing for environmentally sustainable and biodegradable foam production. ScCO$_2$ is a non-toxic, chemically inert substance that can dissolve in molten plastic and act as a plasticizer, making it ideal for foam fabrication. The study focuses on investigating biodegradable polymers and study the incorporation of scCO$_2$ into these polymers to produce foam materials and enhance sustainability. Reprocessing and recycling strategies for biodegradable polymers are investigated, aiming to minimize plastic waste and support closed-loop systems. Additionally, blending biodegradable polymers offers opportunities to customize foam properties, such as mechanical strength and degradation rate. This chapter comprehensively reviews advancements in scCO$_2$ foam processing and elucidates the importance of biodegradable polymers in foam manufacturing. It assesses how the integration of biodegradable polymers can contribute to reducing environmental impact, promoting circular economy principles. Additionally, this chapter addresses advancements in utilizing scCO$_2$ as a foaming agent, taking into account parameters such as pre-treatment, temperature, pressure, pressure drop, and diffusion time. The role of additives, fillers, and chain extenders in the foaming process is also studied. Recent findings on foaming assisted by scCO$_2$ and how processing parameters influence foam products are discussed, along with potential applications. Through this investigation, the study aims to provide insights into sustainable and environmentally responsible foam production practices, highlighting the possibilities of scCO$_2$ processing and biodegradable polymers.

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1.1. Introduction

Polymeric foams find widespread applications across various industries due to their versatility. From home appliances to food packaging and spacecraft, polymer foams play a pivotal role [1]. However, alongside their utility comes a significant environmental concern. Improper disposal of polymer foams aggravates environmental pollution and to address this issue, one promising approach involves using biodegradable polymers. Unlike non-biodegradable polymers, biodegradable polymers have the unique property of degrading when exposed to natural environments. Biodegradable polymers or biopolymers, depend on microorganisms like bacteria and fungi to break them down into natural resources. This process depends on the chemical composition of the biopolymer. While many studies have synthesized new biodegradable polymers with diverse properties, comprehensive research on their processing and understanding it thoroughly remains limited. Therefore, this thesis aims to characterize, reprocess, blend, and foam biodegradable polymers using supercritical carbon dioxide (scCO₂). By leveraging scCO₂ technology, the study seeks to demonstrate the advantages and potential applications of biodegradable polymers, thereby mitigating the environmental impact of conventional polymers and traditional foam processing.

Despite polymeric foams being introduced to the market in the early 1930s, there are still many improvements that researchers are trying to achieve, especially concerning the material used and the production system implemented. Foams have already shown attractive tunable features, for instance, compressibility [2]–[4], thermal insulation [5], [6], mechanical properties in general [7], [8], and lower density [9], [10]. There are different methods for producing polymeric foams. Most of the processes mostly rely on the fundamentals of nucleation, growth, and expansion of gas bubbles in a near melt, melt, or reacting liquid polymer matrix [11], [12]. Within this method, multiple variables influence the attributes of the final product. The polymer matrix has the most substantial effect on the product properties since it affects the viscoelastic behavior of the polymer in the course of production. Process parameters such as temperature, pressure, shear, CO₂ concentration, cooling protocol, pressure drop, and soaking time will, for example, impact the morphology of the cells [11]. Other domains can also influence the outcome of the material differently, such as blowing agents [13], [14], polymer modifications [15], additives [16], and fillers [17]. Indeed, minor adjustments in one of the variables described before in the foaming process will modify some features concerning the foam structure and, therefore, mechanical properties [18].

One of the promising techniques for producing foams is the use of supercritical fluids (SCFs). An SCF is a material that, at a specific temperature and pressure above its
critical point, can diffuse through solids like a gas and dissolve materials like a liquid [19] (Figure 1.1). Among SCFs, other than \( \text{N}_2 \), \( \text{scCO}_2 \) is a promising chemical because of its relatively low critical temperature and pressure (Table 1.1), non-toxicity and environmentally friendliness [20]. Within the processes utilizing \( \text{scCO}_2 \), the combination of gas and liquid behavior can be fine-tuned to engineer the density of the SCF with adjustments to the pressure and temperature of the process [21], [22].

![Figure 1.1: Typical phase diagram representing the possible physical states of a substance under different conditions of temperature and pressure.](image)

This chapter summarises polymeric foams primarily produced utilizing \( \text{scCO}_2 \) as a blowing agent. Process related factors, formulation, and extrinsic influences that modify the polymeric foam properties are early considered. Afterwards, we discuss foam cell morphology and mechanical performance. Subsequently, we report polymeric foam features and possible applications where polymeric foams are relevant.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>9.3</td>
<td>50.4</td>
</tr>
<tr>
<td><strong>Carbon dioxide</strong></td>
<td><strong>31.1</strong></td>
<td><strong>73.8</strong></td>
</tr>
<tr>
<td>Ethane</td>
<td>32.2</td>
<td>48.8</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>36.5</td>
<td>71.7</td>
</tr>
<tr>
<td>Propane</td>
<td>96.7</td>
<td>42.5</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>235.2</td>
<td>47.6</td>
</tr>
<tr>
<td>Methanol</td>
<td>239.5</td>
<td>81.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>289.0</td>
<td>48.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>318.6</td>
<td>41.1</td>
</tr>
<tr>
<td>Water</td>
<td>374.2</td>
<td>220.5</td>
</tr>
</tbody>
</table>

Table 1.1: Critical Temperature and pressure of the most common solvents utilized in the industry [19].
1. Biodegradable Polymer Foams Employing Supercritical CO₂

1.1.1. Blowing agents in polymer foams

Blowing agents are necessary to manufacture a polymeric foam and produce a cellular structure in the polymer matrix. Essentially, blowing agents used to produce polymeric foams are (i) gases that expand when pressure is released, (ii) liquids that undergo a phase transition to gases, forming pockets inside the matrix, or (iii) chemical agents that react or decompose under the influence of a catalyst or heat to form a gas and consequently form the cell pocket [23]. The blowing agents used are directly related to the properties of the end material, such as density, morphology, and the structure of the foam pocket. Therefore, in most cases, the blowing agent is an important parameter to consider when manufacturing polymer foam. Usually, blowing agents are classified as chemical or physical, with some exceptions as expandable beads [24], [25]. Most chemical blowing agents are solids at standard conditions for temperature and pressure (STP) that undergo a chemical reaction, releasing gas in the material matrix to be foamed [26]. Physical blowing agents are, in general, liquid or gas under STP that are subjected to a change of state and expansion to form pockets within the polymer matrix [12]. Details of the blowing mechanisms will be further explained in the following sections.

Chemical blowing agents (CBA)

CBAs function over thermal decomposition or chemical reactions where the agent produces gases (usually N₂ and CO₂) inside the polymer matrix for the subsequent polymer expansion [27]. CBAs are classified as exothermic [28] and endothermic [29]. Moreover, the temperature of the gas release must be compatible with the polymer. Otherwise, it might result in complications during the foaming and, therefore, the structure of the cells [30]. As the name suggests, exothermic CBAs generate heat upon decomposition, rapidly occurring within a small temperature range [31]. On the other hand, endothermic CBAs take in energy from the process, resulting in a broader spectrum of temperature range and processing times [27]. In addition to working at contrasting process temperature ranges, exothermic and endothermic CBAs can produce different foam structures. At a similar temperature, exothermic CBAs generally result in a coarser structure with a larger cell size compared to endothermic CBAs [32].

The selection criteria for CBAs in the process of the polymeric foam also consider the polymer compatibility with the chosen CBA and thermal behavior during the process [30]. Most of the advantages of utilizing CBAs are for industrial applications. Considering the product, CBAs work with self-nucleation and can produce finer cell sizes if necessary. Furthermore, in industry, implementing the CBAs theoretically requires a smaller investment in equipment [28]. Besides, incorporating CBAs in the process is done directly into the hopper of the equipment or mixed with the polymer matrix before
1.1. Introduction

handling the machinery. Most of the CBAs are solids and do not require special storage.

Nonetheless, utilizing CBAs might be inconvenient due to possible contamination in the final product because of unreacted chemicals or solid remains from the CBAs in the polymeric foam. Due to this potential contamination, foam recycling becomes more complex or impractical. Other significant disadvantages of using CBAs are related to the toxicity of the chemicals or how harmful the process can be to the environment [33].

Physical blowing agents (PBA)

PBAs are used in polymer foaming through the volatilization of a liquid or discharge of an incorporated compressed gas into the polymer. Utilizing PBAs requires time since saturation is needed and based on a diffusion process. The process of foaming with PBAs develops nearly together with the curing of the thermoset polymer, and when thermoplastic, the process occurs over temperatures near or above the polymer glass transition but mostly near polymer melting temperatures. Common liquids used as PBAs are usually low boiling fluids, short-chain molecules, and halogenated aliphatic hydrocarbons. Gases utilized frequently as PBAs are CO$_2$ [34], [35], N$_2$ [36], [37], short-chain molecules and halogenated aliphatic hydrocarbons [38]. Currently, the industry uses three main PBAs: hydrocarbons, halogenated hydrocarbons, and inert gases (in this context, carbon dioxide and nitrogen).

Halogenated hydrocarbons as blowing agents provide unique features to the foam as high insulation performance and give them a specific advantage over other blowing agents such as high blowing efficiency and thermal stability [38]. The possibility of using halogenated hydrocarbons, e.g., chlorofluorocarbons (CFC), as a blowing agent was first observed in the 1940s and widely implemented in factories around the 1950s [12] growing polymer foam production and use. A significant drawback of utilizing CFC is related to the damage to the ozone layer of the earth. If released incorrectly, the gases of CFC diffuse into the stratosphere and undergo a chemical reaction triggered by radiation, breaking the bonds of the molecule and harming the ozone layer [39]. To overcome the harmful effects of CFC, hydrochlorofluorocarbon (HCFC) was developed. HCFC is less stable but still decomposes in the lower layers of the atmosphere. Hydrofluorocarbons (HFC) [38] were also proposed as an alternative to CFC since they do not contain chlorine.

Inert gases are promising in the field of foamed polymers. One of the forms of utilizing inert gases for foaming requires the process to surpass the critical point, achieving the state of the supercritical fluid. Above the critical point, the substance has the density of a liquid but yet the viscosity of gas and almost no surface tension [40]. When a polymer is subjected to a supercritical fluid, e.g., CO$_2$, it becomes supersaturated, in-
ductiong diffusion over time and followed by cell nucleation when thermodynamic instability occurs [41]. Later, during depressurization, there is cell growth, and it continues expanding until the polymer cures or cools to the point where its melt strength prevents further expansion [42]. Contrary to CO$_2$, which has a critical point at mild temperature and pressure, many gases can only reach supercritical behavior under high temperatures and high pressures to surpass the crucial point. Furthermore, scCO$_2$ is considered a super-solvent for many polymers [40], becoming one of the most promising blowing agents used today to manufacture polymeric foams.

The selection criteria for PBAs consider compatibility with the polymers, environment, and safety since some blowing agents can be flammable, toxic, or release pollutants. The degree of importance of each factor might vary mainly according to the polymer type and the desired final product.

Halogenated hydrocarbons, in general, show some advantages concerning the production and disadvantages related to the environment. CFCs, for instance, are suitable for the process of polymer extrusion, with the possibility of producing open or closed cell foams with outstanding mechanical properties and attractive thermal insulation [43]–[45]. But at the same time, CFCs are chemically unstable and environmentally harmful, as already mentioned. Alternatively, some hydrocarbons (HC) are applicable for industries with lower boiling points and are potentially suitable as a blowing agent. Some of the alternatives are cyclopentane, isopentanes, and propane. These alternatives offer lower cost, relatively small environmental impact, compatibility with polymers, and are abundantly available [46]. Nonetheless, cyclopentane, for instance, is notably flammable with remarkably low ignition energy, making this HC an issue for transport, storage, and usage. Therefore, utilizing HC in the industry requires careful consideration of equipment from shipping to the final product during its use.

Inert gases (e.g., CO$_2$, N$_2$, O$_2$) are the most used blowing agents in the industry because of their price, widespread availability, and the most environmentally friendly compared to previously described ones. Despite CO$_2$ being a greenhouse gas, its production might be provided from a specific source, such as energy production industries, since burning fossil fuels for energy production is single-handedly the most significant source of CO$_2$ emissions [47]. Carbon capture, storage, and utilization is a technology under development where CO$_2$ is captured from various sources and further reused or stored [48]. Therefore, CO$_2$ can be captured and utilized for foam production, allowing multiple life cycles of CO$_2$ [49].
1.2. Process related factors influencing polymer foams

Utilizing supercritical fluids in the process of polymer foaming offers many benefits. Fluids in supercritical conditions combine the viscosity of gas and the density of a liquid, therefore performing as an excellent solvent and plasticizer and enhancing the expansion of the polymer [50]. Supercritical CO$_2$ (scCO$_2$) is a non-toxic, non-flammable, chemically inert, and reasonably low critical point solvent. Thus, recent studies investigated the interaction of some polymers with scCO$_2$. For instance, experiments using scCO$_2$ as the foaming agent have been performed with polyethersulfone (PES) [51], Polybutylene succinate (PBS) [52], poly(Methyl methacrylate) (PMMA) [53], polylactide (PLA) [54], polystyrene (PS) [55], [56] and poly(e-caprolactone)(PCL) [57]. In addition, some researchers have included different fillers, additives, co-blowing agents, and other extra steps to improve the mechanical properties of the foam, optimize nucleation, improve the homogeneity of the cells, or introduce an additional feature to the final product.

The polymer foaming process assisted with scCO$_2$ has some advantages, such as the absence of organic solvent and the plasticization effect. Nonetheless, utilizing scCO$_2$ in the foaming has many variables and parameters to be tuned, independently of the process being extrusion, batch reactor foaming (Figure 1.2) or other possible foaming systems [58]. Batch reactor foaming proceeds with the polymer inside the reactor, followed by an increase in temperature over or near the melting point of the polymer and injection of CO$_2$, consequently increasing the pressure. After a period in stable conditions, the gas is released, dropping the pressure and promoting the foam cell growth [59]. The extrusion foaming process involves continuously feeding polymer and CO$_2$ into an extruder. Within the extruder, a screw blends the polymer and CO$_2$ as they are heated and mixed. The temperature of the extruder sections is near or above the melting point of the polymer, and pressure increases along the screw, which is related to the feeding of polymer and injection of CO$_2$. After the die, there is a sudden decrease in pressure, promoting the foam cell growth [60]. Other foaming methods, like injection molding, need careful attention because of the complexity of the mold and the different forces involved. However, the injection molding technique can be compared to batch foaming since the foam expands inside the mold in separate batches.

Besides residence time and depressurization rate, foam production with CO$_2$ essentially relies on temperature and pressure. Operational temperature and pressure directly influence the density of the scCO$_2$, thus making the supercritical fluid behave more or less like a gas or liquid [22]. Fundamentally, temperature and pressure change the density of the scCO$_2$. The CO$_2$ density directly impacts scCO$_2$ diffusion into the polymer over
time, also influencing the plasticization effect that consequently influences the glass transition and melting temperature of the polymer [61]; this chain of events results in different outcomes concerning morphology, mechanical properties, and applications. Moreover, as explained later in this chapter, the polymer itself will change its behavior according to the processing method, formulation, and how it is pre-treated. The following subsections describe some of the process influences and effects on the properties of the foam.

1.2.1. Temperature and pressure

Temperature and pressure are often parameters adjusted in a foaming process due to their direct impact on the results. For example, if temperature and pressure are increased to high values, the behavior of the polymer itself might change due to melt strength, swelling, saturation, crystallization rate, etc. Li et al. [62] have described one of the inflection points related to pressure. The research evaluates the swelling ratio and glass transition temperature ($T_g$) relation of PMMA within a CO$_2$ pressure ranging from 2 to 22 MPa at different temperatures. This study helps to understand and improve cell nucleation and, therefore, cell morphology [63], [64]. The authors observed that the swelling
ratio increases significantly with temperature according to the pressure up to 12 MPa; at higher pressures, the swelling was not as significant. They also investigated the glass transition temperature ($T_g$) of the samples, determined by analyzing the inflection point in the plot of volume ratio versus temperature. The $T_g$ of PMMA decreases with increasing pressure, reaching a minimum of 311.4 K at 12 MPa, before rising again to 323.1 K at pressures higher than 12 MPa. According to Li et al. [62], this change in pattern at 12 MPa is attributed to the reduced significance of CO$_2$ solubility in the polymer compared to the hydrostatic pressure effect resulting from an increase in CO$_2$ pressure (see Figure 1.3). A previous theory proposed that because of plasticization, $T_g$ of amorphous polymers under scCO$_2$ decreases with pressure until loss of free volume by compression becomes more relevant, increasing $T_g$ exponentially [65].

A singular PMMA foaming system was developed by Ngo et al. [66] to evaluate the product outcome at different pressures, temperatures, and time scenarios. The foaming method system includes a 25 cm long internal cavity with a temperature gradient. The unique equipment Ngo and colleagues built can produce polymer foam displaying gradient cell morphology in multiple directions. Moreover, it is possible to perceive that cell size is inversely proportional to the pressure at the same temperature. Cell density is defined by nucleation density, which is affected by pressure and pressure drop, therefore, cell density is directly proportional to the processing pressure. Cell size and temperatures are directly proportional at a given pressure but do not directly change the cell
density other than possibly collapsing. Due to the protocol adopted by Ngo et al. [66], it was possible to assess the penetration depth of the CO\textsubscript{2} into the sample, effectively describing an estimation of the CO\textsubscript{2} diffusion coefficient dependent on temperature or pressure. Therefore, it is proven that increasing the pressure from 9 to 25 MPa in the process with PMMA at 38 °C, nearly doubles the CO\textsubscript{2} diffusion coefficient. Moreover, at constant pressure, when temperature increases from 28 to 65 °C, the CO\textsubscript{2} diffusion coefficient in PMMA increases by a factor of 1.5. Therefore, the equipment and protocol adopted by Ngo et al. [66] demonstrate the influence of process temperature and pressure on the morphology of polymer foams.

A relatively recent approach to polymer foaming is the idea of foam products showing multiple morphological structures. Polymer foam with diversified morphology, bigger and smaller cells combined, gains a bigger window of possible properties and, therefore, an opportunity for new potential applications. Inspired by nature, Huang et al. [67] have demonstrated the possibility of fabricating a biomimetic PP foam with a modifiable hierarchical tubular structure. More specifically, the inner diameter of the solid can be adjusted from 0.4 mm to approximately 20 mm by adjusting the radial temperature distribution and, consequently, the melt viscoelasticity. In comparison, Xu et al. [68] produced a bi-modal cell structure in PS by adjusting the temperature and depressurization rate simultaneously. This method is based on the fact that cell nucleation occurs during depressurization and also predominantly due to the temperature variance during polymer saturation. Similar results were found by Xu et al. [69] in a previous article utilizing PLA. The authors claim that raising the temperature before the depressurization leads to higher crystallinity, especially in the outer layer of the sample. Therefore, microcells appear in the skin region of the foamed samples compared to the sample without temperature change over the process but at the same saturation temperature. Another theory for this method to achieve bi-modal structure states that the temperature boost results in lower CO\textsubscript{2} solubility into the polymer, thus gas supersaturation and cell nucleation. Consequently, raising temperature favors nucleation and diffusion of trapped gas to escape, forming bigger cells than the cells formed during depressurization [18].

For the foaming process, all the parameters and their relation influence the product. There are effective connections between temperature, time, and pressure. Salermo et al. [57] explain that in the process of PCL saturation, the pressure is more relevant for the foam uniformity than the polymer residence time. Foaming time or depressurization rate is directly related and proportional to the foam density and, consequently, inversely proportional to the overall porosity. Similarly, Tsivintzelis et al. [70] research the process-ability of PLA. In comparison to other publications [57], [66], [71], PLA follows a similar
trend where large cells can be achieved with lower pressures or higher temperatures according to the limitations of the process and material.

1.2.2. Carbon dioxide concentration

Concentration is directly linked to pressure and time; adjusting the concentration of scCO$_2$ during the foaming process can be challenging since it might influence the plasticizing effect of the polymer. In other words, the higher the concentration of scCO$_2$, the less energy will be necessary to reach the point where the rigidity of the polymer drops. Therefore, in some cases, increasing the concentration of scCO$_2$ might result in adjusting other parameters, such as temperature, to counterbalance the polymer plasticization.

Zhou et al. [71] evaluated the partial gas saturation technique with PMMA under scCO$_2$, gauging morphology and mechanical properties. The gas concentration profile effectively controls the ratio of pores and solid regions inside the polymer, consequently, graded foam structure can be manipulated. Functionally graded porous polymers have appealing properties because they have continuously changing macroscopic mechanical and physical properties (Figure 1.4). Mechanical properties tests showed that, on the one hand, the flexural modulus is reduced from over 3000 MPa to nearly 152 MPa due to the formation of the foam structure. On the other hand, the new partially foamed structure improves the flexural toughness of the material, having its maximum at 65% of foam in total. The outcome of the mechanical properties can be extensively exploited according to the ratio of open cells and solid regions that can be fine-tuned. One of the advantages of this material is that despite the laminated foam structure, the graded foam presents a more homogenous pore variation, a solid core, and a more comprehensive range of tunable mechanical properties.

The morphology of polymer blends is generally more difficult to predict, thus this subject will be better exemplified in the following section. Furthermore, Wang et al. [72] reported cell nucleation in PP/PS foam blend in an extrusion process. The authors reported producing a similar bi-modal cell structure when increasing the concentration of scCO$_2$ and dropping the temperature due to the plasticizing effect of the scCO$_2$. With the same temperature profile, it is reported that increasing CO$_2$ concentration increased cell density and thinner cell walls. In addition, it is also reported that, despite the blend of polymers, the process produced uniform cell structure at low concentrations of CO$_2$. The authors propose that this phenomenon is because of nuclei density formed in the different phases since the solubility of scCO$_2$ in PS is lower than in PP at their process conditions [73], [74]. Low scCO$_2$ concentration results in complete dissolution of one of the parts and partial dissolution of the other, resulting in possible similar cell growth.
Figure 1.4: The cross-sections comparison of unfoamed (Original), partially foamed (samples 1 to 3), and foamed (sample 4) PMMA samples. The details of the graded structure are shown in the SEM image. Samples stacked up for easy visualization (Adapted with permission from [71]).

Other than the cell morphology, foam porosity, or mechanical properties, temperature, and pressure also may influence the surface of the cells. Wang et al. [75] studied the control of the cell structure and surface in a foam produced with scCO\textsubscript{2} adjusting temperature, pressure, scCO\textsubscript{2} flow rate, and time in a semi-batch process. The authors proposed to initiate the process as usual batch foaming (increase temperature and pressure), but after some time, open a bleed valve that would allow scCO\textsubscript{2} to flow at a low flow rate while a pump maintained the pressure inside the chamber. With this system, it is reported that denser wrinkles were achieved with high pressure, low temperatures, long time, and high scCO\textsubscript{2} flow. The theory of the authors states that this combination of temperature, pressure, and scCO\textsubscript{2} flow induces macromolecules to orient and formation of intramolecular stress, which is necessary to produce a rough cell surface [76]. The report suggests that these findings could help future work to produce and understand better rough cell surfaces of foam polymers that could be implemented in buffering and energy absorption.

1.2.3. Co-blowing agents
Co-blowing agents are usually solvents introduced to improve the foaming performance of the polymer. Within the process using scCO\textsubscript{2}, co-blowing agents can enhance the solubility of CO\textsubscript{2} into the polymer, assisting in possibly expanding the foam temperature window. Attempting to evaluate the impact of a co-blowing agent, Morisaki et al. [77] set fixed values for temperature, pressure, and time for the saturation of PMMA and
added different ethanol concentrations to the process. As a result, adding 1 to 7.5 mol% of ethanol as a co-blowing agent increased cell size and promoted cell coalescence with bimodal distribution and the outer skin thickness from 45 $\mu m$ to 35 $\mu m$. Authors theorize that ethanol could enhance affinity between semi-polar PMMA and scCO$_2$ similarly as it does between cellulose derivatives and CO$_2$ fluid [66], [78]. Further, by utilizing an extra step after the extrusion technique involving hot water, the authors could produce a nearly skinless final product with 10 ± 1 $\mu m$.

Trying to optimize foam structure, Qiang et al. [55] researched the effect of butanol and decanol as co-blowing agents for PS foaming assisted with scCO$_2$. A previous computational simulation on the physical samples suggested that the solubility and diffusion coefficient of CO$_2$ for PS is directly proportional to the chain length of alcohols used as co-blowing agents. Indeed, the simulation proposed is confirmed, where not only butanol and decanol proved to improve the interaction of scCO$_2$ and the polymer, but also the solubility is enhanced according to the chain length of the alcohols. Decanol assisted in maintaining a higher content of the blowing agent in PS, producing higher cell density. Butanol, on account of having a more significant plasticization effect on PS, improved the volume expansion ratio (VER) of the foam. Both alcohols were combined as co-blowing agents, causing the formation of PS foam with smaller cell size and larger VER when compared to the foam produced with pure CO$_2$.

Utilizing software for molecular modeling, such as Materials Studio [79] or Gaussian 09 software [80], is attractive when choosing from a large potential solvent as a co-blowing agent because it calculates the binding energy between the primary blowing agent and possible solvents that might be applied as the co-blowing agent. Hu et al. [80] studied the molecular modeling and experimental foaming behaviors of microcellular polysulfone (PSU) and poly-phenylsulfone (PPSU) assisted with scCO$_2$ and a co-blowing agent. Their study evaluated ethanol, water, acetone, and ethyl acetate as co-blowing agents. According to the software and experimental analysis, ethanol showed a more vital interaction with CO$_2$. The degree of interaction of ethanol with CO$_2$ is credited to the shorter distance between atoms. The modeling placed water as the second most suitable interaction with CO$_2$; therefore, it is compatible as a co-blowing agent in a foaming process. Nonetheless, utilizing up to 10 wt% of ethanol in the foaming process of PPSU and PSU experimentally improved the expansion rate from 2.07 to 5.02 and 3.30 to 5.25, respectively, at 15MPa.

Just as the direct improvement in the foaming of the polymer, co-blowing agents can also be used as indirect support to the foaming process. Tsimpilaraki et al. [81] confirmed that ethanol as a co-blowing agent is necessary to produce polymer foaming from
the nanocomposite PCL/clay. The conclusion was that clay clusters are formed in the PCL without the solvent, and consequently, non-uniform cells are obtained. However, once the ethanol is introduced, the clay dispersion is more uniform, therefore, the homogeneous distribution of cells is obtained. Following other studies \cite{82}–\cite{84}, the use of co-foaming proved to be advantageous, especially in polymer processing, demonstrating limited solubility of CO\textsubscript{2}.

### 1.3. Optimizing Polymeric Foam Attributes

Polymeric foams are attractive due to their lightweight, high specific strength, and good thermal properties. These characteristics are mostly, but not wholly, provided by the unique porous structure of the product. Polymeric chemical modifications, intrinsic properties, and the use of additives or fillers in making foam also play an essential role in the final structure \cite{85}, \cite{86}. Therefore, studying a potential combination of elements with the polymer is necessary for a foam with compelling features.

#### 1.3.1. Additives

Additives are used to improve the material and the processability of the polymer, implement new features to the foam, and, in some cases, aim to decrease the process energy consumption. Novendra et al. \cite{87} worked on a specific proposal of adopting a CO\textsubscript{2}-philic additive to cause nucleation formation at lower temperatures than the melting point of PLA. Their idea was based on utilizing types of polyhedral oligomeric silsesquioxanes (POSS); given the purpose of a polymeric foam for biomedical applications, POSS are biocompatible molecules with low or non-toxicity, therefore, no major drawback according to the main objective. CO\textsubscript{2}-philic trifluoropropyl polyhedral oligomeric silsesquioxane (TFPOSS) was chosen as the nucleating agent and added to the proper concentration could increase the porosity up to 40% higher than usual with temperatures 100 °C below the melting point. Moreover, it is reported that increasing TFPOSS concentration increased the average size of the cells from 624 nm to 857 nm.

Proposing to improve solubility and desorption rate of scCO\textsubscript{2} in PS, Qiang et al. \cite{35} utilized polydimethylsiloxane (PDMS) and polyvinyl acetate (PVA) as CO\textsubscript{2}-philic additives to understand the influence of the number average molecular weight (\(M_n\)) of the additives in the foaming process of a polymer with poor affinity with CO\textsubscript{2} \cite{88}. Incorporating the lower molecular weight CO\textsubscript{2}-philic additive PDMS had a better performance than PVA, increasing the diffusion coefficient of CO\textsubscript{2} and decreasing the saturation time of the process due to the strong CO\textsubscript{2} affinity. In comparison, the composite PS/PDMS showed smaller cell sizes, higher cell density, and finer cellular structure (Figure 1.5).
1.3. Optimizing Polymeric Foam Attributes

with superior control over the CO$_2$ diffusion during the foaming process. The authors conclude that introducing a low $M_n$ CO$_2$-philic additive helps the foaming process by producing a small cell size and large volume expansion ratio.

Figure 1.5: Foam morphologies of PS with the low $M_n$ additives where; (a) PS, (b) PS with polydimethylsiloxane and (c) PS with polyvinyl acetate. (Adapted with permission from [35]).

1.3.2. Fillers

Fillers are, in general, particulate materials mostly utilized to reduce costs. Contrary to additives that are also bonded to the polymer matrix, fillers are dispersed in the polymer. Once well introduced to polymers, fillers grant improved properties according to their nature. The main properties studied with fillers include increased stiffness, heat and electrical conduction, creep resistance, and nucleation agent in the case of the polymer foam process. Liu et al. [89] prepared PVA/graphene nanocomposite foam with a different weight content of fillers. Firstly, it is valuable to point out that graphene sheets are well incorporated into the polymer matrix, supporting the idea of effective exfoliation. Furthermore, the addition of the fillers not only has proved to increase the tensile strength and thermal behavior of the final material but also plays an influential role in reinforcing the bubbles inside the foam, supporting the structure during the cell growth (Figure 1.6). Likewise, the fillers reinforce the nanocomposite foam structure, enhancing compressive properties (Figure 1.7). Comparatively, Moghadas et al. [51] also use graphene oxide nanoparticles as filler and nucleation agents for PES. Thus, it has been found that the weight percentage of the nanoparticles plays a more significant role in the nucleation of the polymer when compared to foaming temperature, saturation pressure, or foaming time. Moreover, the higher the concentrations of fillers, the smaller the cell size, the higher the cell density, and, therefore, the higher Young’s modulus and % elongation of the material when compared among foamed samples. Because of the porous structure, samples foamed with bigger cells have a smaller tensile strength and elongation when compared to samples with higher cell density and smaller cells. In the same line of thought, even the most homogeneous and smaller cell morphology achieved by
the authors has a reasonably inferior tensile strength and elongation compared to raw samples that are not foamed.

![SEM images of (a) PVA and (b) PVA with 2.5 wt% of graphene composite foams obtained at same process conditions. Cell size distributions of (a-3) PVA and (b-3) PVA with 2.5 wt% graphene composite foams. Neat PVA shows many irregularly shaped bubbles after the rapid pressure drop. However, by introducing graphene sheets, the obtained foam displays a more uniform and regular cellular structure with spherical bubbles. (Adapted with permission from [89]).](image)

Because carbon nanotubes (CNT) have interesting features [90] such as outstanding strength and good electrical and thermal properties, they are also studied in the field of polymeric foams [91]. Chen et al. [92] utilized multi-wall carbon nanotubes (MWCNT) with different ratios between length and width blended into PMMA to evaluate the cell density. Under similar temperature and pressure conditions, with the same concentration of MWCNT, samples with relatively longer MWCNT exhibited lower cell density compared to samples filled with shorter MWCNT. It is also reported that cell density depends on the saturation pressure due to the assumption that at lower pressure, the nucleation happens most likely at the end of the nanotubes, so shorter fillers, in this case, showed higher cell density. On the contrary, at high saturation pressure, the nucleation is based at the sidewalls of the MWCNT, resulting in multiple nucleation sites and increasing cell density. Similarly, Chen et al. [93] observed that 1%wt of MWCNT into the PMMA matrix resulted in an 82% increase of Young’s modulus and more than double the collapse strength of the polymer foam. Also, MWCNT improves the compressive properties of the solid matrix, possibly due to the reduced size and higher density of the cells. Concerning the size of fillers, it is concluded that longer MWCNT resulted in
1.3. Optimizing Polymeric Foam Attributes

Figure 1.7: Compressive stress-strain curves of PVA and PVA/graphene composite foams. The cell walls start to bend by increasing the compressive strain after a linear-elastic region. Therefore, the neat PVA foam exhibits a relatively low stress value, and PVA/graphene composite foam displays a significant increase in comprehensive stress because of the cellular structure. (Adapted with permission from [89]).

overall polymer foam with greater Young’s modulus and collapse strength compared to any other samples. Shorter MWCNT PMMA nanocomposites displayed higher relative modulus and relative strength when compared to the not foamed nanocomposite also produced with shorter MWCNT.

Aiming to evaluate the morphology and properties of the material and the effects of carbon black (CB) filler loading into the polymer matrix, Chen et al. [52] fabricated nanocomposite foams made of PBS and CB. Coupled with the fact that CB has good dispersion in the PBS matrix, the increase in filler content increases crystallization temperature, crystallinity, thermal stability, storage modulus, and complex viscosity. It has been reported that lower CB content is displayed to have higher thermal stability and toughness when compared to higher CB content due to some agglomeration of the nanoparticles in the polymer matrix. The use of CB improved the electrical conductivity features of the foam by approximately five orders of magnitude with 5 wt% CB content when compared to the neat foam nanocomposite as well as the one with 5 wt% CB content. Furthermore, higher CB concentration resulted in polymer foams with high cell density and smaller cell sizes.

There are many other filler possibilities to be applied in polymer foam science. For instance, layered silicates are also interesting for the foaming industry since they are one of the most widely used fillers for food packaging. Nanoclays are widely available and have easy processability, good performance, and lower cost. Keshtkar et al. [54] pub-
lished a study on the foamability of PLA with nanoclay filler in a continuous extrusion using scCO₂ as a blowing agent. The authors could conclude that the increase in nanoclay content is directly related to the rise in the cell density, expansion rate of the foam, and melting strength. Moreover, Keshtkar et al. [54] reported a comparison of similar fillers, Cloisite 30B (according to authors’ lower dispersibility) and Cloisite 20A, confirming that the properties of the filler, such as dispersibility and compatibility with the polymer, notably influence the foam production process such as expansion ratio and cell density. The alteration in foam morphology and the incorporation of fillers are closely linked to the nucleation process that initiates foam formation. Fillers play a crucial role in nucleation by providing heterogeneous surfaces at the interface between the continuous polymer-gas phase and the filler material. These surfaces act as nucleation sites, facilitating the formation of nuclei [94], [95]. Consequently, fillers increase nucleation density by reducing the energy barrier required for nucleation, resulting in cell density and diameter changes, ultimately influencing the resulting foam morphology.

1.3.3. Polymer pre-treatment and modification

Pre-treatment of polymers yields some attractive results. Salerno et al. [57] studying PCL, tested different cooling procedures, foaming temperature, saturation pressure, and foaming time, similar to other studies [56], [66], [96]. PCL samples subjected to isothermal scCO₂ pre-treatment displayed a higher melting point and melting onset. These findings align with other researchers who link such differences in melting to the thermal history from subsequent re-crystallisation after scCO₂ sorption-desorption [97]. Moreover, Salerno et al. [57] utilized three cooling protocols in the samples before foaming, subjecting samples to fast, moderate, and slow cooling after shaping them. The authors concluded that samples produced with the most rapid cooling protocol performed in general foams with higher porosity, attributing these phenomena to the crystallization of the polymer. It is reported that the evidence of the melting point shifting to higher temperatures indicates higher crystalline fractions, indicating larger crystallites. Other authors have also studied similar outcomes, suggesting that depressurization time and crystalline structure are essential in order to control foam morphology [98]–[100].

A key factor in producing foams is related to the molecular structure and molecular weight of the polymers. Therefore, modifying polymers with branching agents or using polymers with different molecular weights tend to produce distinct outcomes in the same process. The thermoplastic polyester PLA is a biobased and biodegradable polymer with promising features. However, producing PLA foam materials with a high expansion rate is difficult because of their linear molecular arrangement, low melt strength,
and slow crystallization rate [101]. Consequently, Najafi et al. [102], to compensate for the difficulties of PLA, added a commercially available chain extender (CE) in order to overcome issues related to elasticity and melt viscosity of PLA (Figure 1.8). Compared to linear PLA, Long-chain branched (LCB) PLA performs with enhanced viscosity, shear sensitivity, and longer relaxation time. Therefore, LCB PLA produces foams with more homogeneous cell distribution and increased cell density. In another article, Li et al. [103] also tried to overcome PLA problems previously mentioned in the foaming process, modifying it with a random copolymer of ethylene and glycidyl methacrylate as an efficient CE. The branching and crosslinking of PLA samples with the proposed CE are directly related to enhancing the intrinsic viscosity. Therefore, the improvement achieved by including the CE increased cell density by nearly four times more than neat PLA and the volume expansion ratio threefold.

As mentioned, PLA is a remarkable polymer, considering some of its features such as biodegradability, mechanical properties, and versatility [104], but the foaming process still presents some challenges. To overcome the PLA foaming limitation, Li et al. [105] proposed a pre-isothermal cold crystallization instead of branching agents or fillers, claiming that some methods can disrupt PLA biodegradability and possibly raise production costs. Among other reasons, authors argue that pre-treatment will promote crystallization and improve melt viscosity and strength, confining the movement of the polymer, therefore contributing to a larger number of heterogeneous nucleation interfaces [106]. The article concluded that the pre-isothermal treatment proposed resulted in PLA with a more improved crystalline structure. Thus, the authors claim that the process enhanced the maximum expansion ratio from 6.4-fold to 17.7-fold. Further, the isothermal treatment enhanced the uniformity of the dispersion and size of the foam cells.

![Figure 1.8: The linear viscoelastic properties (a) shear (open symbols) and complex viscosity (filled symbols), (b) storage modulus of the neat and CE-enriched PLAs. Adding CE into the matrix changes the rheological response of the material according to the CE content. (Adapted with permission from [102]).](image)
Aiming to produce foam for photoinduced hydrogen evolution, Morisaki et al. [77] utilized scCO$_2$ to foam two different weight average molecular weight ($M_w$) of PMMA. Low molecular weight PMMA (LPMMA) and high molecular weight PMMA (HPMMA) produced different foams at the end of the same process. Foams made with LPMMA displayed lower cell density and thinner cell walls between cells than HPMMA. Essentially, the difference between LPMMA and HPMMA samples at the same CO$_2$ sorption is their viscosity, where the LPMMA polymer can be up to one-sixtieth lower than HPMMA. Lower viscosity essentially results in larger expansion and likely coalescence of cells. Other publications have reported that lower molecular weight polymers display fewer nucleation sites if taking into consideration the classical nucleation theory [107]–[109].

In the same category as modification, crosslinking of thermoplastics is an exciting alternative to compensate polymers with low molecular weight, low melt strength, or adverse crystallization nature with issues to be foamed. Therefore, to foam PE with scCO$_2$, Zhou et al. [110] proposed using dicumyl peroxide (DCP) in HDPE to produce a microcrosslinked structure with enhanced viscoelasticity. The authors used DCP up to 0.25 parts per hundred resin in the HDPE and found that crosslinking at higher concentrations limited the foaming behavior, restricting cell growth. However, with low concentrations of DCP, the authors could obtain foam structure with an improved expansion volume ratio from 3.1 for pristine HDPE to 7.7 with a gel content of 5%. In a similar study, Zheng et al. [111] found similar results where a high concentration of bis-tert-butylperoxy diisopropylbenzene (BIPB) into EPDM restrains network the cell growth because of the rigid crosslink. Zheng et al. [111] report that with an increase in crosslinking degree, the cell morphology changed from polygonal to elliptic, there was more homogeneity of cells, and the wall thickness increased. Following other studies, [112]–[114], it is concluded that the crosslinking degree of thermoplastics indeed assists in the control and distribution of the foam cells.

1.3.4. Polymer blends
Polymer blends are mainly advantageous because they make it possible to dilute the cost of some materials and also broaden the property range of products. Mixing polymers is one of the approaches to designing novel materials that employ the best properties of the polymers involved and reach new possibilities due to the synergy of the blend. Thereupon, Wang et al. [72] studied cell nucleation in a foam blend of polypropylene (PP) and PS since it is generally more difficult to predict the morphology of blends than single polymers. Firstly, the authors have established that neat PP generates smaller cells
and consequently shows higher cell density when compared to neat PS foam. Following the previous statement, the blend of PP/PS also shows a similar pattern where large cells were formed in the PS-rich phase, and small cells were formed in the PP-rich phase with their corresponding properties according to the morphology.

Correspondingly, biodegradable polymer foams made out of polyesters PLA, PBS, and a blend of PLA with polyhydroxybutyrate (PHB) have been foamed with scCO$_2$, tested and compared by Frerich et al. [115]. The authors studied the influences of temperature and pressure on the final product. Since melting greatly influences the foaming process, the authors managed to measure the melting temperature under CO$_2$ pressure up to 45 MPa. At the pressure of 45 MPa, PLA melting temperature reduces to 96 °C, PBS reduces to 100 °C and the blend PLA/PHB reduces to 111 °C, therefore the plasticizing effect and the effect in the melting temperature of each polymer are remarkable. The authors suggest that the minor change observed by PBS is related to the effect of solubility and hydrostatic pressure mentioned previously in this chapter. According to the authors, the significant changes in the melting temperature of PLA and the blend are mostly related to molecular weight, polydispersity, and high solubility of CO$_2$ in PLA compared to PBS. Related to the foamability, under their optimal conditions, it is reported that PLA and PBS have shown similar porosity of 0.81 and 0.82, respectively, and the blend PLA/PHB shows a lower porosity of 0.76. Regarding the mechanical properties, the PLA/PHB blend has the highest values of compressive modulus. However, it was found to be more brittle when compared to the other polymers. While those PBS and PLA samples were tested in the compression up to 60%, the blend PLA/PHB broke before compression of 10%. Both PLA and PBS generate different compression test graphs, however, PLA displays higher rigidity regarding compressive strength necessary to reach 60%.

Fully biodegradable polymer blends are complex to produce due to compatibility and often require petrol-based additives [116], [117]. Liu et al. [118] made use of a Joncryl chain extender to consolidate Poly(propylene carbonate) (PPC) and polybutyrate adipate terephthalate (PBAT). PPC is an amorphous aliphatic polycarbonate with a good oxygen barrier and high solubility in CO$_2$. PBAT is a random copolymer that is ductile [119] and comes into the mix with PCC to compensate for the brittleness of PCC. Liu et al. [118] reported that blending PPC and PBAT with a small percentage of Joncryl ADR-4368 additive (around 1%) led to an increase in complex viscosity fourfold. Therefore, the product foamed with scCO$_2$, out of the blend PCC/PBAT with additive showed a density of 0.083 g·cm$^{-3}$ and uniform cells with the size of 15 µm. For comparison, the same scCO$_2$ foaming method produced PBAT foam with a density of 0.4 g·cm$^{-3}$ and cell size of 75 µm.
To comply with the high demand for lighter-weight materials in high performance applications such as aeronautic and automotive, Cafiero et al. [120] studied the foamsability of miscible blends based on poly(ether ether ketone) (PEEK), semicrystalline engineering thermoplastics, and poly(ether imide) (PEI), amorphous thermoplastic polymer, using scCO$_2$ as blowing agent. It is found that foam density is inversely proportional to PEEK content up to 50%, where with higher loads, the foam density increases again. The blend of PEEK/PEI with a ratio of 50:50 displayed a limited crystallinity during foaming according to the thermal analysis, in addition to the minimum foam density configuration. According to the authors, the described behavior can be explained by two reasons: first, a slower crystallization rate occurs during the foaming process, and second, the presence of portions of amorphous PEEK remain rigid also above the glass transition temperature [121]. The presence of such a rigid amorphous fraction could slow down the crystallization rate. In conclusion, the 50:50 ratio of PEEK/PEI produced the lowest foam density, microcell structure, and high nucleated cells.

1.4. Cell morphology and performance

Cellular morphology is a critical factor that directly affects the actual performance of polymer foams, such as mechanical properties (Figure 1.9) [122]–[125]. Foams for thermal insulation and packaging possibly benefit more from closed-cell structures, while acoustic insulation foams usually require an open-cell structure. In this part of the chapter, the influence of cellular morphology (cell size and distribution, structure) on the performance of polymer foams is reviewed.
1.4.1. Microcellular foams

Microcellular polymer foams have been widely used since the 1980s as they can reduce the material density and fulfill other functions (e.g., as bone scaffolds) while maintaining good mechanical properties when compared to its not foamed form [126]. For microcellular foams, results have shown that reducing the cell size and lowering the size distribution can enhance the foam properties like tensile and impact strength [127]–[129].

Cellular structures have a variety of applications, subsequently it is necessary to match their structure with engineering applications. Zhang et al. [53] fabricated PMMA microcellular foams by adjusting process conditions to correlate foam porosity and cellular structure to the foam properties. It is reported that the relation between PMMA cell size or porosity and mechanical properties (e.g., compressive strength and modulus) exhibits quadratic growth where strength increases with the development of smaller cells or lower porosity. Cell size going from 45 to 15 $\mu m$ increased modulus from 70.48 to 98.59 MPa and strength from 4.70 to 6.84 MPa. The porosity and the mechanical properties of PMMA microcellular foam behave similarly. Varying the porosity from 82 to 40% increased modulus from 73.60 to 230.32 MPa and strength from 5.17 to 40.63 MPa. Essentially, in the case of PMMA, the authors [53] reported that a cell diameter greater than 30 $\mu m$ usually has the shape of a polygon and thin walls, which mostly withstand the pressure. Increasing the cell size results in a decrease in wall thickness, therefore possibly reducing mechanical strength [130], [131]. Moreover, decreasing the porosity or reducing the cell size in a microcellular foam structure produces materials with increased compressive strength and modulus. High cell density and small cell sizes contribute to stress transfer, thus reaching higher compressive strength due to loss of stress concentration.

1.4.2. Nanocellular foams

Studies on nanocellular foams have been revealed as the next generation of high performance polymeric foams [132]–[134]. New techniques were developed to achieve nanocellular structures, and those are described below. For example, Sharudin et al. [135] utilizing CO$_2$-induced crystallization in combination with the nanoscale dispersed-domain method [136] managed to produce nanocellular foam. PP combined with styrene ethylene butylene styrene (SEBS) was annealed in scCO$_2$ to promote the change in the crystalline morphology of the matrix blend. SEBS act as dispersed nucleation sites for CO$_2$ during rapid pressure quenching for the production of nano cellular foam [135]. The obtained foams have higher yield and ultimate tensile stresses than those of corresponding solids. Their results also suggested that elongation at break could deteriorate, possibly
due to the presence of superficial collapsed bubbles, which played the role of a notch for the tensile test. Thus, according to the authors, controlling the outer skin layer may play a more critical role in improving the elongation at the break of foams.

Besides the mechanical properties, the nano cellular foams are also anticipated to have better thermal insulation performance than conventional foams because their pore sizes fall in the range of the mean free path of gas molecules [137]. The modeling of thermal transportation within the nano cellular foams suggested that increasing the refractive index or the absorption coefficient of the polymer matrix is beneficial for decreasing the thermal conductivity of foams [131], [138]. In the case of nanocellular foams, a polymer matrix with high infrared absorption could significantly block the thermal radiation through the foam. Along with a reasonable porosity, the nano cellular polymer foams can attain a super-insulating property [139]. According to the reported model, the target cell size should be less than 200 nm, and the optimum porosity should be in the range between 0.9 and 0.95 to achieve a super-insulating property [138]. This mathematical model is relevant for inspiring the development of the next generation of super-insulating materials that can be conveniently fabricated out of polymer foam.

Nanocellular polymers show similar advantages associated with polymeric foams and extra features due to their reduced cell size. One of the recent improvements found within nanocellular polymers is transparency, which made the foam utterly promising for new markets. Martín-de León et al. [140] characterised the optical transmittance of transparent PMMA according to their cell size and material thickness. PMMA foam with a cell of 14 nm, a relative density of around 0.47, and a thickness of 0.05 mm reached an impressive transmittance of 0.94. These values are remarkable since similar materials with the exact dimensions but displaying a cell size of 225 nm result in a near-zero transmittance (Figure 1.10). The authors reported that scattering theories state that for the light to pass through, the maximum particle size should be in the order of one-tenth of the light wavelength. Visible light has wavelengths in the range of 400–700 nm. Therefore, Martín-de León et al. [140] comply with the theory since samples with smaller than 50 nm cell sizes display some transmittance. The future market for these materials is hypothesized to include super-insulating windows, nanoporous materials for filtration, energy storage, and catalyst support [141].

The issue of forming nanocells in a polymer foam is directly related to the thermodynamic instability of the nanoscale since the cells are inclined to burst during the foaming process and merge [142]. Therefore, Shi et al. [143] project a method and polymeric blend that provides stable cell growth, developing high porosity nanocellular polymer foams. Utilizing CO$_2$ as a blowing agent, the authors employed a blend of PMMA and
polyvinylidene fluoride (PVDF). The composite choice is because PMMA can absorb a large quantity of CO\textsubscript{2} while PVDF arranges consistently along the polymer, making nucleation points for microcrystals. Therefore, PMMA containing 20% PVDF at 13.8 MPa prepared by a two-step temperature foaming process produced a material with over 70% porosity and a cell size averaging 287 nm. The method proposed by Shi et al. [143] is environment friendly and straightforward but with high efficiency and flexibility. The authors also assert the applications of the product for filtration, energy insulators, and catalysis.

1.4.3. Complex cell size distribution

To achieve some functional requirements, it is necessary to engineer the design structure of porous materials. Polymeric foams with complex cell size distribution conveniently gather different magnitudes of cells [144]. In general, larger cells reduce the density of the material, while smaller cells assist the mechanical and thermal insulation properties. For instance, graded polymer foams can produce improved acoustic performance compared to materials with uniform sizes. Although Mosanenzadeh et al. [145] did not utilize scCO\textsubscript{2} in their process, they managed to make a foam with cell size shifting from 600 to 200 μm along with the material. This shift in cell size enhanced the maximum
sound absorption coefficient by up to 20% compared to uniform cell size foams with similar porosity. As mentioned in this report, it is possible to produce a gradient foam structure utilizing scCO2 [66].

The field of tissue engineering also uses foams with complex cell size distribution to develop new materials that better mimic biological structures. For example, a scaffold plays a vital role in cell adhesion and induces cell growth for bone regeneration. Chen et al. [146] developed a PCL scaffold with a bi-modal pore from 100 \( \mu m \) to smaller than 50 \( \mu m \) using two-step depressurization of scCO2. The resultant material has the potential for scaffolds since its morphology is similar to the extracellular matrix of natural bone tissue. Essentially, in this case of scaffold for bone tissue, the large pores are necessary for adhesion, proliferation, and migration of stem cells. In contrast, the small pores assist the transport of nutrients and waste [146].

1.5. Intrinsic foam material properties
In materials science, there are various avenues to develop specialized features for different purposes. These features, crucial for industries like food, healthcare, and aerospace, often originate from the polymer itself or its formulation, rather than the foam structure. These inherent properties can add numerous qualities to the final product, like being electrically conductive, biodegradable, capable of self-healing, or biocompatible. When combined with foam, these properties widen the range of potential applications (Figure 1.11). Recent studies have shown that polymeric foams created using supercritical carbon dioxide (scCO2) can have specific properties suitable for various markets. These include thermal insulation [147], [148], bone tissue engineering [149], shielding against electromagnetic interference (EMI) [150], absorption materials [134], [151], and filtration applications [152]. This section outlines the importance of biodegradable foams and other attributes of polymeric foams identified by researchers, along with examples of their applications.

1.5.1. Biodegradability
Biodegradable polymers provide a sustainable solution to environmental issues caused by traditional plastics, naturally degrading to mitigate environmental impact [153]. With increasing concerns over pollution from conventional plastics, there is a growing emphasis on the development of biodegradable alternatives [154]. Among biodegradable possibilities, aliphatic–aromatic co-polyesters have gained significant attention due to their ability to combine the excellent biodegradability of aliphatic polyesters with the desirable properties of aromatic polyesters. Notably, polybutylene adipate terephtha-
late (PBAT) stands out as particularly important in this regard [155]. Another area of focus is the development of compostable materials as alternatives to fossil-based plastics. Thus, polybutylene succinate (PBS), a type of biodegradable aliphatic polyester derived from succinic acid and 1,4 butanediol, has garnered considerable interest due to its compostability standards. PBS is valued for its mechanical endurance, ductility, toughness, and impact resistance, making it a promising candidate for various applications such as food and cosmetics packaging [156]. In the realm of medical applications, biodegradable polymeric biomaterials offer significant advantages, particularly in disposable or rapidly consumed products. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), a type of polyhydroxyalkanoate (PHA), has emerged as a promising biomaterial [157]. PHA polymers, derived as byproducts of microorganism reactions in carbon-rich environments, hold promise for everyday materials and biomedical applications. With a variety of monomers within the PHA group, PHAs allow for modifications, facilitating the production of copolymers with diverse compositions and proportions of individual monomers. Polylactic acid (PLA) represents another versatile biopolymer synthesized from renewable resources and known for its biodegradability [158]. PLA has shown promise across a wide range of healthcare applications, including tissue engineering, regenerative medicine, cardiovascular implants, dental applications, drug delivery systems, orthopedic interventions, cancer therapy, and wound healing [159]. Moreover,
PLA’s utility extends to 3D printing applications, highlighting its instrumental importance as a printable biopolymer.

In pursuit of combining the biodegradability of polymers with the versatility of foams, Ju et al. [160] developed and described the fabrication of unimodal and bimodal biodegradable PBS with cellulose nanocrystals (CNC). This composite scaffold foam displays remarkable mechanical properties, improved hydrophilicity and degradability, and promising results for tissue engineering applications. The foaming process of the PBS composite was performed at cooperative temperature control variation and a two-step depressurization. Remarkably, the incorporation of up to 5% of CNC into the composite proved to increase the compressive strength, decrease the water contact angle of the material, and nicely enhance the degradation rate according to the early experiments (Figure 1.12). In addition to all the features of PBS/CNC bear, it is relevant to mention that polymeric scaffolds with bimodal structures are attractive for bone regeneration due to their morphological properties [161].

Pharmaceutical companies also try to get the most out of biodegradable foam, and one good example is the application of scaffolding polymers as a drug delivery method. Moreover, releasing multiple medicines or stimulants at different ratios is an attractive technique that could facilitate treatments and develop new healing processes. Biodegradable polymer scaffolds are one strategy to manage drug delivery. Bai et al. [162] produced composite foam out of polylactic-co-glycolic acid (PLGA) and PLA with different biodegradation rates, making it possible to achieve sequential release of selected factors. Due to the different biodegradation rates of the polymer foam, the system can replicate the natural biological timing of the physiological process factor by fine-tuning the ratio of PLA and PLGA in the polymer foam.

Occasionally, the combination of unique features is also needed, therefore, Kuang et al. [124] use the biodegradable polymer PBS in combination with carbon fibers (CF) and formulated a composite foam assisted with scCO$_2$ as a blowing agent. The polymer foam displays not only the benefits of using a filler, but the CF specifically granted the material to be electrically conductive. It is proven that with a similar weight percentage content of CF, the foam material exhibits higher conductivity when compared to the solid polymer. Altogether, PBS/CF foams still display biodegradability as expected from PBS and improved electrical conductivity suitable for substituting metals in applications that are necessary only for a limited amount of time.

Fully biobased and biodegradable polymers are challenging due to biodegradability tuning, mechanical properties matching, price, and eventually processability [163]. Yet, Li et al. [151] study a fully biobased alternative for oil-absorbing material since the
1.5. Intrinsic foam material properties

Figure 1.12: Performance of neat PBS foams and PBS5 (5 wt% CNC) foams with unimodal and bimodal structure: (a) specific compressive stress-strain curves; (b) water contact angle; (c) degradation in vitro on mass loss. (Adapted with permission from [160]).

existing technologies to separate oil and water utilized can produce secondary pollution. Therefore, a blend of PLA with PBS foam made with scCO$_2$ producing open cells foam with selective oil adsorption is proposed and achieved. The PLA/PBS foam displays porosity up to 97.7% and successfully adsorbs solvents and oil out of the water, reaching 21.9 g·g$^{-1}$. The interconnected open-cell structure displaying microscopic channels for the diffusion of oil and solvents through the foam also enables storage. Moreover, Li et al. [151] reported that the PLA/PBS foam could withstand up to 20 cycles of adsorption and desorption of CCl$_4$, making it a remarkable high performance oil absorbing material.

1.5.2. Electrical conductivity

Polymer materials have been known for decades as good insulators. However, combining polymers with additives or chemically modifying them makes polymers that conduct electricity possible. Therefore, polymeric foams with electrical properties are feasible and attractive [164].

Since we are in the information age, developing lightweight materials with high specific strength and good thermal and sound insulation properties capable of conducting electricity or even insulating from electricity is interesting [165]. Gedler et al. [166] re-
ported a study on a foam nanocomposite made out of polycarbonate (PC) and graphene, aiming to assess how the dielectric and electromagnetic interference (EMI) shielding properties and the foam morphology are related. Maintaining graphene at the same weight content but adjusting process parameters already displayed disparate results since it changed the foam structure. Therefore, in conclusion, besides the filler content, the morphology of the polymer foam significantly impacts the EMI results. In fact, with some tailoring of the process, it is possible to reach a material with EMI shielding effectiveness roughly 35 times better than the not foamed version of the nanocomposite. Sharing comparable objectives of conductive materials and EMI shielding application, in 2016, Kuang et al. [123] reported a green method to produce foam with PLA/MWCNT nanocomposite, which resulted in a low-cost and environmentally friendly process. Their approach consists of soaking the sample of PLLA/MWCNT in scCO₂ for 3 hours at high temperature, dropping the temperature to foaming temperature, followed by fast depressurization. This process proposed by Kuang et al. [123] uniquely produced lightweight, high strength, and highly conductive biodegradable polymer composite foams. Similar studies have also proved the feasibility of producing lightweight frequency selective EMI shielding with other polymers [167]–[169]. Some of the mentioned studies suggest that this new technology for EMI polymer products is suitable for the electronics, automobiles, and packaging markets.

In contrast to the previous electric conductive studies, Qi et al. [170] studied low-weight polyarylene ether nitrile (PEN) polymer combined with SiO₂ as filler and nucleation agent to form polymer foams that conduct less electricity. Foaming of the polymer matrix with SiO₂ filler remarkably increased the porosity of the final material from 38%, with no filler, to more than 58% with 5 wt% SiO₂. In addition, there is a considerable reduction in the dielectric constant and loss tangent, meaning that the new material becomes a better insulator. Moreover, the weight content of SiO₂ added to the polymer matrix is directly related to enhancing the thermal insulation properties of PEN/SiO₂, and in the same way, the cell density increases.

1.5.3. Thermal insulation

A significant part of global energy consumption comes from heating and cooling [171]. Therefore, thermal insulation is vital for a more sustainable society. Thermal insulators improve energy efficiency in packaging, transport, construction, and industrial processes. Governed by the physical structure and chemical composition, the thermal conductivity of a material describes the performance of a thermal insulator [172], [173]. Therefore, polymer foams have the advantage of the physical structure with the void
density and low thermal conductivity of the matrix.

Essentially, thermal conductivity directly relates to molecular motion and the ability of the material to transfer heat [174]. Gases generally have a lower thermal conductivity than most polymer foams. However, the Knudsen effect states that heat conductivity is affected by the confined gaseous phase [175], making it possible for nanoporous polymers to overcome the thermal conductivity of some gases. Thus, Forest et al. [176] et al. studied the Knudsen effect by modeling foam features with micro/nano cell morphology produced with CO$_2$ as a blowing agent. Employing an analytical model based on a similar aerogel treatment, Forest et al. [176] model the effect of foam morphology on thermal conductivity. In conclusion, polymer foams with a density of 0.1 to 0.2 g·cm$^{-3}$ and cell size smaller than 100 nm would feature an effective thermal conductivity equal to or lower than 0.02 W·mK$^{-1}$, equivalent to air thermal conductivity. Other authors utilized the nano-cellular foam theory combined with fillers or additives to achieve the same or lower thermal conductivity of gases [177]–[179].

In parallel with studying heat insulation materials, other lightweight features are also very beneficial. Shi et al. [180], using scCO$_2$ as a blowing agent, produced a lightweight PVDF/PMMA open-cell foam with remarkable thermal insulation. In addition, because of the material morphology, the foam displays oil-absorption properties, making it a suitable candidate for ecological disasters. Employing a sustainable method, Shi et al. [180] obtained a foam with open porosity up to 98.6%, a density of 0.0361 g·cm$^{-3}$ and thermal conductivity of 31.07 mW·mK$^{-1}$. The thermal conductivity reached by the PVDF and PMMA foam blend is comparable to rock wool and PU foam [181], but with the oil-absorption feature.

Polymer foams are reliable heat insulators, but some are not environmentally friendly. Therefore, Yin et al. [182] proposed to produce a fully biodegradable foam composite of PBS and cellulose nanocrystals (CNC). In order to improve PBS foaming properties, the authors utilized an epoxy-based branching agent. In addition, CNC is pre-treated with hydrophobic surface modification by acetylation to raise the compatibility of CNC with PBS. The foamed PBS/CNC material produced by Yin et al. [182] presented improved cellular structure, increased volume expansion rate (VER), and consequently lower thermal conductivity. The authors claim that their composite displays thermal conductivity of 0.021 W·mK$^{-1}$ and VER of 37.1. Therefore, PBS/CNC is a promising material for construction and packaging, combining outstanding thermal conductivity and biodegradability.
1.5.4. Shape-memory

In order to achieve a polymer foam with shape memory, it is necessary to combine the shape memory features of polymer or polymer composites with the foam morphology. In polymer foams, the shaping capability is usually limited when set to repetitive or large compressive stress. Thus, a highly flexible, durable shape-memory polymer foam is proposed by Fei et al. [183] combining a thermoplastic polyurethane (TPU) with MWCNT processed with scCO$_2$. Thus, it is recognized that in 100 cycles at a compressive strain of 30%, the composite TPU with 5% of MWCNT behaved relatively stable after the $10^{th}$ cycle. In the first ten cycles, the foam showed a higher decrease in compressive strength and energy loss due to the viscoelastic properties of the polymer material, meaning that the strain change of the material lags behind the stress change (Figure 1.13). Despite the loss during the early cycles, the material is truly capable of shape-memory. Moreover, TPU embedded with MWCNT displays not only shape-memory features but also remarkable electrical conductive properties that can vary given the external force that the foam is subjected to. Both features combined and enhanced mechanical properties make this polymer foam model for sensors that require improved sensitivity, accuracy, recoverability, and flexible materials [184].

![Figure 1.13: (a) 100 cycles of TPU filled with 5% MWCNT foam at a maximum compressive strain of 30%; (b) stress-strain curve of continuous cycles (1st, 2nd, 10th, 20th, 50th, and 100th); (c) energy loss coefficient of continuous cycles. (Adapted with permission from [183]).](image-url)

Polymer foam featuring shape-memory is a generally adaptive material that can undergo deformation and return to its original shape. The shape-memory feature has some limitations, and Wang et al. [185] proposed a composite with TPU and PLA foamed with the scCO$_2$ method to minimize possible constraints of each material and combine individual advantages. A lightweight shape memory blend foam TPU/PLA is displayed with improved shape recovery from 72.7 to 91.7% compared to the not foamed blend. In addition, it is also established that the introduction of PLA into TPU assisted in the apparent shrinkage of the final material, and the content of PLA in the composite TPU/PLA is directly proportional to the expansion ratio of the foam. Together with remarkable me-
chanical properties, the blend TPU/PLA proposed has the potential to be applied in the field of sensors, packing, and intelligent medical devices [186], [187].

1.6. Summary

Polymeric foams are encountered in every field, from medical applications and home appliances to spacecraft and it is due to the tunable properties of the material. However, the process of making the foams can be rather complex. As discussed here, implementing scCO$_2$ into the foaming process can be advantageous. scCO$_2$ is a green solvent that acts as a plasticizer for polymers, facilitating the foaming process. Due to its inertness, scCO$_2$ can be processed with polymers and chemicals without reacting while still assisting the reaction between additives and the polymer.

It is valuable to understand that the density of scCO$_2$ changes under different conditions, therefore, pressure and temperature play a vital role in foaming assisted with CO$_2$. Pre-treatments are valuable in the foaming process since they can eventually improve nucleation. Isothermal steps before the regular process can improve the cell size and homogeneity of the polymeric foam. Independent of the polymer matrix, there is a trend among studies confirming that cell size is directly proportional to temperature and inversely proportional to pressure. Solvents such as co-blowing agents improve solubility and diffusion of scCO$_2$ into the polymer. The CO$_2$-polymer interaction enhancement can produce foams with bigger and more homogeneous cells. In addition, utilizing co-blowing agents can be essential to permit the dispersion of additives into the polymer, serving as compatibilizers. It is necessary to use extra elements to broaden the possibilities of polymeric foams. Additives, fillers, chemical modifications, and even polymer blends have been proven to reach new foam properties that can be exploited in various applications.

Some of the benefits of using additives are more effortless adjustment of cell structure and decreased time or temperature of the process. Fillers have a more generic role in improving the mechanical properties of the final product. Due to the dispersibility of fillers and often inertness, fillers act as nucleation sites in most cases, directing CO$_2$ into small pockets before the expansion. Since the molecular structure of the polymer is crucial for foaming, chemical modifications can be very beneficial from the perspective of melt strength and intrinsic viscosity. Adjusting the molecular branching or chain length can lead to different outcomes, so each polymer and chemical modification must be evaluated carefully. One last strategy to engineer polymeric foam properties is to blend other polymers. Foam properties can be tuned with ease depending on the fraction of each polymer in the blend.
From the product point of view, the cell size is one of the most critical parameters dictating not only the mechanical properties of the foam but also how it will perform in each application. For example, open-cell polymeric foam is proposed for applications where softer or permeable materials are needed. Closed cells are required in the case of stiffer or energy-isolating materials. Combining some features is of the utmost importance in making polymeric foams that suit different applications. From the applications assessed by this chapter, polymeric foams have the potential to be used in operations that require thermal radiation isolation, electromagnetic interference, electrical conductivity, biodegradability, shape-memory, filtering, sound isolation, packaging, biological tissues, intelligent medical devices, release control medicines, energy storage, super insulator windows, and catalyst support.

In addition, the development of new biodegradable polymers addresses pressing concerns related to fossil resource depletion and environmental pollution. Biopolymers offer practical solutions by combining biodegradability with desirable properties. Advancements discussed in this chapter highlight the importance of biodegradable polymers in addressing environmental challenges while meeting industry needs. Through ongoing research, these materials are expected to play a crucial role in sustainable materials development and environmental conservation.

In conclusion, the future of engineering materials will be shaped by biodegradable polymeric foams since they can replace most of the materials utilized in diverse applications with the main advantage of being lighter and environmentally friendly. Therefore, rethinking the process of producing polymeric foams and using scCO\textsubscript{2} is essential to building a circular economy and sustainable production line.


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