Chapter

Supercritical CO_2-Processed Polymeric Foams for Process Intensification Structure, Functionality, and Advanced Applications

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Abstract

Polymeric materials foamed using supercritical carbon dioxide ($scCO_2$) offer a sustainable and versatile basis for developing advanced porous structures with highly adjustable morphology, density, and functionality. This chapter provides a comprehensive overview of the physical principles and processing strategies involved in generating foams with hierarchical porosities, emphasizing their potential for process intensification. The correlations between structure and functionality are presented and illustrated using case studies in which porosity values of over 90%, open-cell contents of up to 96%, and functional loads of over 18% are achieved in $scCO_2$-assisted impregnation processes. The advantages of this technology for the *in-situ* formation of catalysts are analyzed, demonstrating increases in hydrogen production of up to ~60% compared to traditional packed beds. Integrating functional impregnation and foaming in a single step, together with using a clean, recyclable physical agent such as $scCO_2$, makes these foams ideal for advanced applications in compact reactors, controlled release systems and biomedical platforms. The combination of sustainability, multiscale morphological control and multifunctional properties establishes these foams as essential components in the development of more efficient, intensified, and environmentally responsible emerging technologies.

Keywords: polymeric foams, porosity, intensification, $scCO_2$ foaming, impregnation

1. Introduction

Modern chemical engineering is facing an increasing number of challenges that demand a fundamental re-evaluation of the way processes are designed and operated. The need to optimize efficiency, reduce the environmental footprint, and accelerate

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product development has led to the development of process intensification (PI). Within this framework, advanced materials—particularly polymeric foams—and innovative processing technologies, such as the use of $scCO_2$, have emerged as key drivers of industrial transformation. This chapter will explore how the combination of the unique structural properties of polymeric foams and the environmentally friendly processing capabilities of supercritical carbon dioxide contribute to PI objectives, with a particular focus on functionalizing these materials for advanced applications.

1.1 Process intensification in modern chemical engineering: Concepts and objectives

Process intensification has established itself as a revolutionary design approach in chemical engineering. Its primary purpose is to significantly reduce the size of process equipment and plants while substantially improving the overall efficiency and sustainability of operations. This paradigm goes beyond the incremental optimization of existing processes, seeking a fundamental restructuring that maximizes the effectiveness of intra- and intermolecular events. A central tenet of PI is ensuring that each molecule undergoes uniform processing by optimizing driving forces and resistances at all scales and maximizing the specific surface areas where these interactions occur. Unlike traditional engineering design, which often approaches process stages sequentially and in isolation, PI promotes an integrative approach, combining chemical and physical phenomena to achieve operational synergies. The concept was formalized by Stankiewicz and Moulijin in 2000, who described it as a 'toolbox' encompassing novel equipment and innovative methods to achieve these goals [1].

The reasons for adopting PI are multifaceted and respond to market pressures and growing demands for sustainability. In the biopharmaceutical sector, for instance, PI is vital for accelerating drug development, enhancing efficiency and productivity in line with strict Good Manufacturing Practice (GMP) standards, and improving operational flexibility to accommodate diverse therapies. Specific PI objectives include boosting productivity, reducing the cost of goods, expediting development and commercialization, and achieving greater agility in manufacturing operations. From a sustainability perspective, PI enables radical reductions in energy consumption and waste generation, resulting in technologies that are more economical, efficient, and environmentally friendly. Speed to market has become particularly important for a product's competitive position and price, highlighting the strategic importance of PI in responding to market dynamics. Sustainability is not just an ethical objective, but a necessity imposed by increasingly stringent regulations and growing corporate awareness of environmental image [2].

Process intensification is therefore a driver of industrial transformation that goes beyond mere technical optimization. By adopting PI, companies are not only seeking to improve their existing processes; they are also redefining the way they conceive and execute their chemical engineering projects. This shift is moving them toward more agile, adaptable, and responsible production. This paradigm shift is evident in the increasing popularity of continuous processes, also known as flow chemistry, as opposed to traditional batch processes. Continuous systems offer advantages in terms of scalability, safety, and efficiency. Examples of this evolution include perfusion bioreactors and single-use systems in biomanufacturing, which enable a higher throughput of individual therapies and provide unparalleled flexibility in adapting to different production methods within the same facility [3].

Another significant advance is reactive distillation, a technology that combines chemical reactions and separations in a single process, resulting in substantial energy savings and reduced CO_2 emissions. Membrane engineering and the use of immobile mixers are additional examples of PI methods and equipment that improve separation efficiency and mixing, respectively. This demonstrates how PI innovation often occurs at the intersection of design and process engineering [1]. The true power of PI lies in the co-evolution and integration of equipment and methods. Having innovative equipment is not enough if it is not accompanied by an optimized method of operation, and vice versa. This interdependence highlights the importance of a holistic approach to research and development, where equipment design and process optimization are developed together to maximize the benefits of PI.

1.2 The role of porous materials and polymeric foams in process intensification

Polymeric foams are materials composed of a mixture of polymers and gases, giving them a distinctive, porous, cellular structure. These materials are also known as cellular, blown, or expanded polymers. Their characteristic properties include low density, high strength-to-weight ratio, excellent thermal insulation, and remarkable energy absorption capacity. The most common polymers used in foam production are polystyrene, polyurethane, natural rubber, and polyvinyl chloride (PVC). Polymeric foams can be classified according to various criteria, such as hardness (elastic, flexible or rigid), density (high, medium or low foaming), and cell structure (open or closed). The distinction between open-cell and closed-cell foams is functionally critical: open-cell foams allow fluids to pass through their interconnected structure, while closed-cell foams prevent water absorption, making them ideal for buoyancy or insulation applications [4].

The porous structure of polymeric foams makes them intrinsic enablers of process intensification. The vast internal surface area they provide is crucial for enhancing mass and heat transfer in chemical processes, which aligns directly with one of the fundamental principles of PI: maximizing specific surface areas. Engineering these porous structures involves more than just creating a lightweight material; it also involves sculpting their microstructure (cell size, interconnectivity and porosity) to optimize transport phenomena. The ability to control these morphological characteristics is central to PI foam research and development, transforming morphology into a critical design variable for process efficiency.

One area of particular interest is the potential of hybrid polymeric foams for multiscale functionality. Hybrid metal foams, for example, consisting of a thin metal film on a porous polymer substrate, have been shown to improve mechanical and electrical properties while maintaining the flexibility of the polymer matrix [5]. This synergy mitigates the weaknesses of the individual materials (e.g., metals are stiff, but polymers are flexible).

Among their numerous applications, open-cell polymeric foams have shown promise as supports in catalytic systems due to their high specific surface area and excellent mass transfer properties. A detailed discussion of these catalytic applications is provided in Section 4.1.

1.3 $scCO_2$ as a green processing tool for polymers

Supercritical carbon dioxide is a unique state of matter in which the liquid and gas phases become indistinguishable due to the pressure and temperature being above their critical values (Tc = 31.1°C and Pc = 7.38 MPa). In this state, $scCO_2$ exhibits intermediate properties between a gas and a liquid, possessing a density similar to a liquid but with diffusivity and viscosity comparable to a gas. One of its most notable characteristics is its ability to 'tune' its solvent power and transport properties by making precise adjustments to the temperature and pressure. In addition to these adjustable physical properties, supercritical carbon dioxide has intrinsic advantages that make it an ideal solvent: it is inert, nontoxic, non-flammable, inexpensive, widely available, fully recyclable, and leaves no residue in the final product [6].

By replacing petroleum-derived solvents such as hexane, ethanol, and acetone, $scCO_2$ drastically reduces health and environmental risks by eliminating the production of effluents and pollutants. This feature aligns it directly with the principles of green chemistry and sustainable manufacturing practices [6]. In the polymer foaming process, $scCO_2$ is injected directly into the molten polymer, eliminating the need for chemical blowing agents, which are often toxic and harmful to the environment [7]. This improves the safety of the process and contributes to a cleaner end product.

One of the most significant advantages of $scCO_2$ is its ability to provide improved control over foam properties. It enables the precise adjustment of foaming parameters, resulting in foams with a smaller pore size, higher pore density, and superior performance in a variety of applications [7]. In addition, $scCO_2$ acts as an effective plasticizer for polymers, reducing their viscosity and glass transition temperature (Tg). This facilitates polymer processing and improves the diffusion of additives within the matrix [8]. The versatility of supercritical carbon dioxide extends to a wide range of industries, including food, pharmaceuticals, perfumery, automotive, footwear, medical devices, and composite materials.

The ability to adjust the properties of $scCO_2$ in real time by controlling pressure and temperature is a fundamental feature that enables high-precision materials engineering. In the context of foaming, for example, this 'tunability' enables the precise control of properties such as pore size and density [9]. In impregnation, it directly affects the solubility of the active ingredient and its ability to diffuse into the polymer. It can even modify the crystallinity and thermal properties of the polymer [10]. This tunability establishes $scCO_2$ as a precision engineering tool at the molecular and micrometer levels. It is essential for fabricating polymeric foams with highly customized morphologies and functionalities, which is critical for advanced applications requiring very specific properties, such as tissue engineering scaffolds with controlled porosity and connectivity [11] or drug delivery systems with precise release profiles [12].

2. Fundamentals of polymeric foam formation with $scCO_2$

2.1 Phase behavior and solubility

CO_2 acts as a physical blowing agent, and its interaction with the polymer dictates the entire cell formation and structure. At this point, it is necessary to understand and control the foaming process. Moreover, in the case of $scCO_2$, it can rapidly penetrate and diffuse into the polymer matrix, facilitating quick saturation times and providing enough gas for foam expansion. In addition, $scCO_2$ properties as density, viscosity, and thus solvent power, can be modulated by varying temperature and pressure, allowing for fine-tuning of the foaming process and resulting foam morphology.

The solubility of CO_2 in polymers generally increases with increasing pressure at a constant temperature, up to a certain point [13]. Higher pressure means more CO_2

molecules are forced into the polymer, leading to a higher concentration of dissolved gas. However, the relationship between temperature and solubility is more complex. Generally, at constant pressure, an increase in temperature can initially increase solubility due to increased polymer free volume. However, at higher temperatures, the decreased density of $scCO_2$ and reduced interaction strength can lead to a decrease in solubility [14]. The optimal foaming temperature window is often a balance between sufficient solubility for gas loading and appropriate polymer viscosity for cell growth and stability.

Another point to consider is the chemical nature of the polymer which significantly influences CO_2 solubility. Polymers with polar groups often exhibit stronger interactions with CO_2, leading to higher solubility compared to nonpolar polymers [10]. For instance, CO_2 generally has high solubility and diffusivity in polymers, especially those with polar groups, providing more gas for cell growth.

The solubility of CO_2 into the polymer is directly related with the plasticization effect. In this sense dissolved CO_2 acts as a plasticizer for the polymer, reducing its glass transition temperature and viscosity. This plasticization is essential for allowing the polymer to deform and expand during cell growth. The extent of Tg depression is directly related to the amount of dissolved CO_2 [15].

Understanding the phase equilibrium of the polymer-CO_2 system is crucial for predicting and controlling the foaming process. Phase diagrams (e.g., pressure-composition diagrams) can illustrate the conditions under which CO_2 is dissolved in the polymer, the onset of phase separation (nucleation), and the conditions for foam stability. One method to elaborate a phase equilibrium diagram is using a view cell equipment. The polymer-CO_2 mixture is directly observed in a high-pressure cell equipped with sapphire windows. Pressure and/or temperature are adjusted until turbidity (the "cloud point") is observed, indicating phase separation (either the formation of CO_2 bubbles within the polymer or the precipitation of the polymer).

2.2 Nucleation, cell growth, and stabilization

Nucleation is the birth of gas bubbles within the polymer matrix. It is the initial, crucial step that dictates the number of cells (cell density) in the final foam. The prerequisite for nucleation is supersaturation. This occurs when the dissolved CO_2 in the polymer is suddenly pushed out of its equilibrium state. In $scCO_2$ foaming, this is typically achieved by a rapid pressure drop (decompression) or, less commonly, a rapid temperature increase. The sudden reduction in solubility means the polymer now holds more CO_2 than it can at the new conditions [16].

For a new bubble to form, it must overcome an energy barrier. This barrier arises from the work required to create a new gas-polymer interface (surface tension) and the work needed to expand the polymer to accommodate the bubble. According to classical nucleation theory, a bubble becomes stable and grows when it reaches a "critical radius." Bubbles smaller than this critical size tend to collapse, while those larger will grow.

On the other hand, nucleation can be homogeneous or heterogeneous. Homogeneous nucleation occurs spontaneously within the bulk of the polymer-CO_2 solution. It requires a very high degree of supersaturation and is less common in practical foaming processes. However, heterogeneous nucleation is the dominant mechanism in most $scCO_2$ foaming processes. It occurs at pre-existing imperfections (e.g., impurities, internal voids, or intentionally added nucleating agents like nanoparticles) within the polymer. These sites lower the energy barrier for bubble formation, making it easier for nuclei to form. Rough surfaces also provide such sites.

Anyway, nucleation can be influenced by factors such as depressurization rate. A faster depressurization rate leads to a higher degree of supersaturation, resulting in a higher nucleation rate and thus more, smaller cells [17]. The initial concentration of CO_2 (generally the higher initial concentration of CO_2 the higher the nucleation) in the polymer and its plasticization level, both of which also influence the energy barrier for nucleation and this fact can be tuned by saturation pressure and temperature [18].

Moreover, polymer properties, such as viscosity, glass transition temperature, and interfacial tension with CO_2, must be taken into account [19]. For instance, lowers glass transition and viscosity, facilitating nucleation. Once nuclei are formed, they begin to grow by absorbing more CO_2 from the surrounding supersaturated polymer matrix. Cell growth is primarily driven by the diffusion of dissolved CO_2 from the polymer into the existing bubbles. The concentration gradient between the supersaturated polymer and the growing bubble drives this mass transfer.

As CO_2 continues to diffuse out of the polymer into the bubbles, the polymer matrix around the bubbles loses its plasticizing agent, leading to an increase in its viscosity. This viscosity increase eventually slows down and stops cell growth. Higher temperatures generally increase the diffusivity of CO_2 in the polymer and lower the polymer's viscosity, leading to faster and larger cell growth. However, excessively high temperatures can lead to cell coalescence.

In this step, the melt strength and viscosity of the polymer-gas mixture are critical [20]. A polymer with sufficient melt strength can resist the internal pressure of the growing bubbles without rupturing, allowing for uniform growth. In this sense, too low a viscosity can also lead to cell coalescence.

Once bubbles are formed, stabilization is needed, as the process of freezing the cellular structure to prevent cell collapse, shrinkage, or further unwanted growth and coalescence after the desired foam morphology is achieved. The most common and effective stabilization method is rapid cooling of the foamed polymer below its glass transition temperature for amorphous polymers, or below its crystallization temperature for semi-crystalline polymers. This causes the polymer to solidify, locking the cell structure in place. As the polymer cools, its viscosity rapidly increases, hindering further CO_2 diffusion, restricting cell growth, and preventing cell coalescence or collapse. As a faster cooling rate generally leads to better preservation of the fine cell structure formed during nucleation and growth, a polymer with a suitable Tg and ability to solidify quickly is ideal. Thicker cell walls provide more structural integrity and resistance to collapse.

In essence, successful $scCO_2$ foaming requires a precise control over the interplay between the thermodynamics of CO_2 solubility and the kinetics of nucleation, cell growth, and solidification to achieve a desired foam morphology with optimal properties.

2.3 Strategies for controlling cell interconnectivity and open-cell content to generate porosity

Controlling cell interconnectivity and the proportion of open cells is crucial for specific applications such as tissue engineering, filtration, and insulation, where mass transport properties are quite important [21]. Achieving precise control often requires advanced techniques beyond standard foaming parameters. Traditional single-step foaming processes offer limited control over the intricate details of cellular architecture, particularly interconnectivity. Advanced foaming techniques represent a higher level of control, enabling the creation of complex, hierarchical cellular structures.

2.3.1 Multistage depressurization

This technique allows for the creation of a wider range of pore sizes and can yield bimodal or even trimodal cellular structures. The process typically involves a slower initial depressurization step, which facilitates the formation of larger pores. This is then followed by a rapid second depressurization step, which triggers the nucleation of new, smaller pores and promotes the additional growth of existing ones [22]. For example, in poly(ε-caprolactone) (PCL) scaffolds, this method has successfully produced large pores (over 100 μm) from the slow step and smaller pores (below 40 μm) from the fast step [11]. This approach moves beyond optimizing individual parameters to designing sequences of operations, offering refined control over pore size distribution.

2.3.2 Gas counter-pressure molding (GCP)

GCP is an injection molding technique where the mold cavity is prefilled with a high-pressure inert gas before the polymer-SCF melt is injected. This pressure is maintained throughout the filling stage. The counter-pressure delays bubble nucleation during the filling stage, which not only improves the surface quality of the molded part but also helps achieve more uniform foaming throughout the material [23]. Furthermore, GCP can be leveraged to increase foam density and promote bubble coalescence between layers, which is beneficial for enhancing gas permeability in applications like filtration.

2.3.3 Temperature-induced foaming

This foaming approach begins by saturating the polymer with a supercritical fluid at lower temperatures and pressures. Foaming is then induced by quickly transferring the saturated polymer to a hot medium (e.g., hot water or oil). The sudden temperature increase significantly reduces the blowing agent's solubility (above the polymer's depressed glass transition), prompting rapid cell nucleation and growth [24].

These multistage processes represent a significant advancement in achieving hierarchical control over foam structures. They enable the creation of complex architectures that would be difficult or impossible to achieve with single-step methods. This implies that advanced manufacturing paradigms are necessary for producing highly customized foam architectures with tailored interconnectivity.

2.3.4 Post-foaming treatments

While in-process parameters establish the initial foam structure, post-foaming treatments offer a "second chance" to refine or drastically alter the cellular morphology, particularly the interconnectivity. These methods are crucial for applications demanding high levels of pore interconnectivity.

2.3.5 Ultrasonication

This technique involves applying external ultrasonic vibrations to the foamed polymer, significantly improving cell interconnection and permeability. It offers a solvent-free method for creating open-cell structures, overcoming the typically closed-cell morphology obtained with CO_2 batch foaming [25]. The mechanism involves the application of instantaneous energy through acoustic vibration, micro-jets, and ultrasonic cavitation, which generates localized high temperatures and pressures that break cell walls, thereby increasing permeability. If applied at the beginning of cell nucleation, ultrasonication can enhance nucleation and lead to higher cell density. If applied after cell nucleation and growth, it results in cell wall rupture, yielding a more open and interconnected cellular structure.

2.3.6 Polymer leaching

This method involves mixing a water-soluble sacrificial polymer (like poly(ethylene oxide) (PEO) or poly(vinyl alcohol) (PVA)) or particulate porogens (such as sodium bicarbonate ($NaHCO_3$), silica, or sodium chloride (NaCl)) with the main polymer. After foaming, the sacrificial material is washed away with water, leaving behind a highly porous and interconnected structure. For example, adding microparticulate silica has been shown to increase the interconnectivity in polylactide scaffolds [26]. In another instance, PCL/cellulose nanofiber composites, where $NaHCO_3$ acted as a porogen, achieved an impressive 82% open-cell content.

2.3.7 Annealing

In batch foaming, an isothermal thermal treatment, or annealing, is often used. This step ensures the blowing agent fully saturates the polymer and helps perfect its crystal structure. During annealing, small, imperfect crystals can mature into more stable, tightly packed, and flawless crystalline forms. This ultimately affects the foam's overall shape and stability.

2.3.8 Stretching/deformation

Applying mechanical stretching or deforming a foamed polymer can trigger strain-induced crystallization, especially in materials like polylactic acid (PLA). This process speeds up crystallization, leading to more chain orientation and crystallinity. These changes can, in turn, significantly affect the foam's mechanical properties and potentially its interconnectivity. Specifically, as cells grow, their walls experience biaxial stretching, while the struts (the thicker parts between cells) undergo uniaxial stretching.

These post-foaming treatments offer a second opportunity to modify the cellular structure, especially interconnectivity. This is particularly valuable for applications such as in biomedical scaffolds or filtration membranes. These methods enable modifications that might be difficult or impossible to achieve solely through primary foaming parameters, effectively decoupling some aspects of cell formation from cell interconnectivity.

2.3.9 Polymer blending and chemical modification for interconnectivity

Beyond process and post-foaming treatments, the inherent design of the polymer material itself, through polymer blending and chemical modification, offers proactive strategies for controlling cell interconnectivity.

2.3.10 Blending immiscible polymers

This method involves blending two or more polymers that do not easily mix, creating a heterogeneous melt structure. The boundaries between these unmixable phases act as nucleation sites for gas bubbles. As these bubbles grow and collide at these interfaces, they thin and eventually rupture the cell walls, leading to open-cell structures. For example, when creating foams from PLA and poly(butylene succinate) (PBS), researchers have achieved a very high open-cell content (up to 97.7%), with PBS effectively acting as a cell opener [27]. This is a clever technique that uses phase separation to precisely control the foam's final shape and structure.

2.3.11 Chemical modifications

Setting a polymer's molecular architecture is a direct way to control its rheological properties and, by extension, a foam's interconnectivity. Techniques like chain extension, branching, and crosslinking are used to boost the polymer's melt strength. A stronger melt is vital; it prevents cells from collapsing or rupturing, keeping the cell walls intact. These modifications typically ramp up the polymer's molecular weight and viscosity, which helps reduce the loss of blowing agent gas during expansion. Plus, these chemical changes can form crystalline regions, acting as extra spots for bubbles to form, leading to a finer foam structure.

2.3.12 Advanced plasticizers

Certain specialized plasticizers [28] can be incorporated to enhance pore interconnectivity. For example, eugenol has been shown to improve pore interconnectivity in PCL foams, while also offering bioactive properties. When it comes to designing materials for specific foam structures, a smart strategy involves both blending different materials and modifying them chemically.

One clever way to manage how cells connect within a foam is by using immiscible blends. These blends, where the materials do not mix, naturally separate into distinct phases. This phase separation can be precisely controlled to intentionally rupture cell walls, creating the desired foam structure.

Another critical aspect is directly improving the melt strength of the material. A stronger melt means the cell walls can maintain their integrity better during the foaming process, which is essential for controlling the final foam structure.

3. Functionalization *via* supercritical impregnation

Material functionalization is a key aspect of advanced materials engineering, enabling existing structures to take on new properties for specific applications. In this field, supercritical impregnation (SSI) is a cutting-edge technique for imparting specific functionalities to polymeric foams. This section will provide a detailed discussion of the principles and mechanisms governing SSI, the critical factors influencing its effectiveness and a comprehensive review of its most recent and promising applications in various technological fields.

3.1 Principles and mechanisms of impregnation with $scCO_2$ in polymers

Supercritical solvent impregnation (SSI) is a modern technique that uses the unique transport properties of supercritical fluids to fabricate materials with advanced functionalities. The most commonly employed supercritical fluid is $scCO_2$, which exhibits an ideal combination of low viscosity, high diffusion coefficients, liquid-like densities, and virtually zero surface tension. These characteristics are critical to the success of the process [29].

The SSI mechanism proceeds in several interconnected stages. First, the $scCO_2$ acts as an effective solvent for the desired active ingredient, whether a drug, dye, bioactive compound, or nanoparticle. Thanks to its high diffusivity and zero surface tension, the $scCO_2$ solution and the active ingredient penetrate deep into the polymer matrix, even into the most intricate pores and microstructures of the material [29]. This deep, homogeneous penetration capability is a distinct advantage of SSI over conventional impregnation techniques, which often only reach the surface of the material or result in non-uniform distribution of the active agent.

Once the active ingredient has been dissolved and distributed evenly throughout the polymeric material, the system proceeds to the depressurization stage. During this critical phase, the CO_2 rapidly transitions from a supercritical state to a gaseous state and leaves the system. As a result of this controlled depressurization, the active principle precipitates and is uniformly deposited in the polymeric matrix. The final product is a dry, impregnated material free of organic solvent residues, simplifying further processing and purification steps. SSI can be implemented in batch mode for preliminary and laboratory-scale studies, and in semi-continuous mode for greater efficiency and scalability [29].

The effectiveness of impregnation is intrinsically linked to the complex interactions established between $scCO_2$, the polymer, and the active compound [30]. The $scCO_2$ acts as a solvent for the active compound and interacts directly with the polymer matrix. When absorbed by the polymer, the $scCO_2$ acts as a plasticizer, increasing the polymer's fractional free volume and reducing its intermolecular interaction energy [14]. This decreases the polymer's Tg and viscosity, thus facilitating the active compound's diffusion through the matrix [8]. The high diffusivity of the $scCO_2$ allows the active compound to penetrate faster and deeper into the polymer volume, ensuring a homogeneous distribution that is difficult to achieve with conventional methods.

Depressurization is not merely the removal of the solvent; it is a critical event that induces the precipitation of the solute and the 'fixation' of the new foam morphology. This interaction involves a complex balance of solute solubility in $scCO_2$, polymer plasticization and depressurization kinetics. The success of SSI hinges on the precise manipulation of these interface dynamics. Controlling pressure and temperature affects not only solubility, but also the degree of plasticization and the rate of solute diffusion. This makes SSI a 'real-time materials engineering' technique, where the fluid-polymer interaction is controlled to produce specific properties. The impregnation technique can be applied in a single step while the polymer is being plasticized and the compound to be impregnated is introduced into the mold, causing subsequent expansion when the pressure is released. **Figure 1** shows a diagram of the single-step process, which has been researched in several scientific publications [31].

Despite its many advantages, $scCO_2$ has one fundamental limitation: its poor solubilization capacity for polar and ionic species. This restricts the range of compounds that can be efficiently impregnated. However, this limitation has driven innovation in the field. To overcome it, research has explored the use of "binding agents" or "co-solvents" such as ethanol, water, or acetone [32]. These co-solvents can enhance the solubility of CO_2 in the polymer and increase the interaction between CO_2 and polymer chains, allowing impregnation of more polar compounds and modification of the porous structure. This inherent limitation of $scCO_2$ is not a dead end, but a catalyst for innovation, significantly broadening the spectrum of materials and composites that

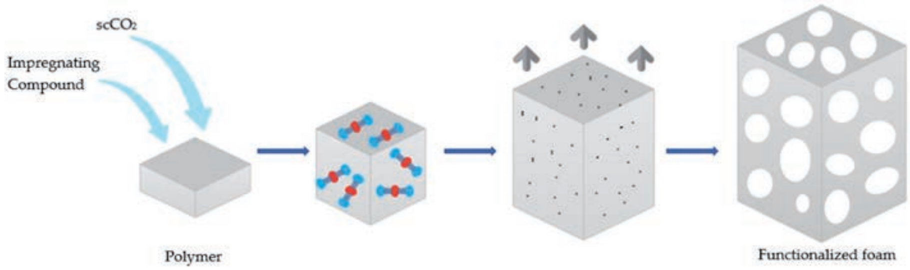

Figure 1.
Scheme of polymer foam formation and impregnation from CO_2 in a single-step.

can be functionalized, albeit at the cost of increased process complexity. Optimizing the SSI process requires a thorough understanding of the key factors that influence its development. **Table 1** summarizes these factors and their impact on the impregnation of polymeric foams with $scCO_2$.

3.2 Advanced applications and recent case studies

The ability to functionalize polymeric foams through impregnation with $scCO_2$ has opened up a wide range of advanced applications, demonstrating the versatility of this technology across various sectors. The impact of this technique is illustrated by recent case studies presented below.

3.2.1 Catalytic functionalization and nanoparticles

Polymeric foams are ideal supports for catalysts and nanoparticles thanks to their high surface area and controllable porous structure. Using $scCO_2$ enables the

Key factor	**Summary of influence**
Pressure	Controls $scCO_2$ density and solvent power; higher pressure increases CO_2 solubility and affects foam structure.
Temperature	Affects solute solubility and polymer-$scCO_2$ diffusion; also influences polymer crystallinity and thermal properties.
Impregnation time	Determines how much and how well the active compound is loaded and distributed; overly long times may reduce effectiveness.
Depressurization rate	Key for proper solute precipitation; too fast can cause uneven distribution or unwanted foaming.
Nature of the active compound	Solubility in $scCO_2$ depends on polarity and molecular structure; nonpolar or specific structures dissolve better.
Nature of the polymer	Polymer-$scCO_2$ affinity and crystallinity affect CO_2 absorption and solute diffusion; polymer plasticization is crucial.
Use of Co-solvents/binding agents	Helps dissolve polar compounds and enhance interactions, but can complicate the process.
Compound-polymer affinity	Strong interactions are essential for retaining and evenly distributing the active compound in the matrix.

Table 1.
Key factors influencing $scCO_2$ impregnation in polymers [6].

production of nanocellular foams with a diameter of less than 100 nm, which significantly improves catalytic activity by increasing the surface area. Foams stabilized with nanoparticles (e.g., nanosilica) have been developed for enhanced oil recovery (EOR), achieving stable structures containing 100–150 nm particles. Inorganic TiO_2 has also been incorporated into PCL foams using $scCO_2$-assisted foaming to obtain composite materials with density values in the $0.2–0.5\,g/cm^3$ range, pore size between 360 and 720 nm and narrow pore size distribution [33]. Furthermore, coating metal catalysts (Ag, Au, Pt, Pd, Zn and Cu) with polymers has been shown to improve activity, stability, and selectivity. For instance, biopolymers such as chitosan have been employed to coat catalytic metal-organic frameworks (MOFs) [34]. Finally, the $scCO_2$ technique has been shown to enable the tuning of pore size and density in PMMA foams, making it useful for designing customized catalytic supports.

Growing concerns about public health and food safety have led to the development of polymeric foams with antimicrobial properties. Impregnation with supercritical carbon dioxide is an ideal, nontoxic technique for biomedical applications, as it avoids the harmful residues left by conventional, solvent-based methods.

3.2.2 Antimicrobial functionalization

Recently, research has focused on impregnating polymers with natural bioactive compounds and plant extracts to impart antimicrobial activity. For instance, polypropylene nonwoven fibers impregnated with thymol have demonstrated high efficacy against common bacteria and fungi, such as *Escherichia coli*, *Staphylococcus aureus,* and *Candida albicans*, with loading reaching up to 19.6%. Similarly, 15% carvacrol was incorporated into cotton gauze, yielding comparable antibacterial results [29].

In tissue engineering, PCL and PCL-HA scaffolds impregnated with carvacrol were fabricated, reaching a loading of up to 10.57% in PCL-HA and demonstrating the potential of this approach for functionalized biomaterials [35]. Additionally, clove extract impregnated into polycarbonate (PC) achieved a loading of up to 18.5%, suggesting its potential use in antimicrobial food packaging thanks to the presence of eugenol [36]. These cases confirm that solid impregnation with $scCO_2$, also known as supercritical fluid impregnation (SFI), allows the development of safe, functional and antimicrobial materials that can be adapted for various applications.

3.2.3 Drug and bioactive compound delivery systems

The development of controlled drug release systems has been transformed by $scCO_2$ impregnation, which allows polymeric nanocarriers to be formulated with precise control of particle size, morphology, and drug loading. Furthermore, it eliminates the need for the purification steps that are common in traditional techniques [37]. For instance, impregnating aspirin in poly(lactic acid) (PLA) and linear low-density polyethylene (LLDPE) yielded higher loadings and a more prolonged release than traditional methods. PLLA released 60% of the drug within 74 days, which is ideal for long-term treatment. Similarly, the release of thymol from TPS and TPS-PCL mixtures can be modulated by varying the temperature, time, and PCL content [38]. Sustained release for up to 5 days has also been achieved under specific pressure, temperature and depressurization conditions [39]. Furthermore, micronation techniques using $scCO_2$ improve oral solubility and bioavailability, thereby reducing dosage and side effects. This also facilitates the development of pulmonary delivery systems [12].

Another example is the impregnation of PHB-HV with mango leaf extract to create materials with antioxidant and antimicrobial properties, which are modulated by operating conditions.

3.2.4 Fabric engineering scaffolds

Porous polymeric scaffolds are essential in tissue engineering, as they offer a three-dimensional structure that allows cell adhesion, proliferation and regeneration. The use of $scCO_2$ has established itself as a “green” alternative by avoiding organic solvents and high temperatures that could damage cells or sensitive molecules [32]. PCL scaffolds have been obtained by $scCO_2$-assisted foaming, achieving pores of 70–180 μm, 90% porosity and 96% interconnectivity, ideal for regenerative applications [11]. PDLLA and PLGA scaffolds, capable of releasing growth factors in a controlled manner, have also been fabricated, showing the versatility of the method.

An outstanding advance is the combination of 3D printing with supercritical foaming, which allows obtaining anisotropic structures with enhanced interconnected porosity, overcoming the limitations of conventional 3D printing. More homogeneous structures have also been achieved in crystalline polymers such as PCL, using $scCO_2$-ethanol blends [40].

3.3 Advantages and challenges of functionalization of polymeric foams with $scCO_2$

The functionalization of polymeric foams with $scCO_2$ is a highly efficient process intensification strategy, as it often allows foaming and functional loading to occur in a single step. This reduces the need for intermediate steps, as well as energy consumption and waste generation. The main advantages of this method are its sustainability and solvent-free nature, as it uses recycled CO_2 as the process medium, thereby decreasing the environmental footprint. The mild operating conditions (low temperature and inert atmosphere) enable the incorporation of thermo- or photo-sensitive compounds without causing degradation. Furthermore, the ability to adjust pressure and temperature provides precise control over pore morphology, density, and distribution, as well as the loading and release of functional agents. This unified approach clearly demonstrates intensification, as it reduces the number of steps, improves mass transport efficiency, and increases overall process efficiency. The result is purer, more active products with custom-designed structures from a single integrated operation.

However, there are challenges that hinder its industrial adoption. The high cost of pressurized equipment makes it difficult to scale up. Additionally, the low solubility of polar compounds in $scCO_2$ limits its scope without the use of co-solvents, which partly compromises the ‘green chemistry’ of the process. Morphological control scaling and achieving homogenous functional loading remain technical challenges, as does the end-of-life management of treated foams. Furthermore, the interaction of CO_2 with certain polymers can induce undesirable phenomena, such as secondary foaming or structural alterations, necessitating precise control of the operating conditions [41].

In conclusion, the functionalization of foams with $scCO_2$ embraces the spirit of process intensification, offering higher efficiency, a lower environmental impact, and multifunctional capabilities. Overcoming technical and economic barriers will be key to consolidating its large-scale industrial adoption.

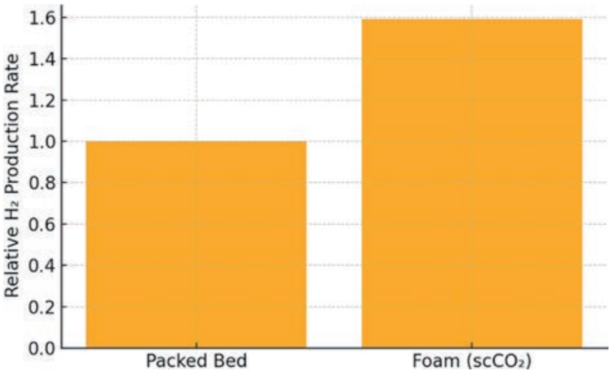

Figure 2.
Comparison of relative hydrogen production rate between packed bed and $scCO_2$-processed foam catalyst under identical conditions: dehydrogenation of H_{18} DBT at a temperature between 280 and 320°C at atmospheric pressure [46].

4. Applications in-process intensification

4.1 Polymeric foams as catalytic supports: Performance and process intensification potential

In the field of catalysis, open-cell foams are exceptional candidates for supporting structured catalysts in gas-solid catalytic processes. Their design enables them to achieve high reaction rates controlled by gas-solid diffusional mass transfer. These foams offer superior heat and mass transfer properties combined with low pressure drops, outperforming traditional packed beds in terms of high porosity volume [42]. Specific examples include palladium-alumina-coated metal foams for catalytic CO oxidation and metal supports in the form of honeycomb monoliths and open-cell foams as strong candidates for intensifying nonadiabatic catalytic processes [43]. In addition to catalysis, the controllable porosity and tunable surface functionality of porous polymers make them ideal for use in applications that require enhanced mass transfer, such as air purification and water treatment [44].

Recent studies have demonstrated that Pd/HDPE foams formed using $scCO_2$ exhibit open-cell structures (20–60 μm), significantly outperforming pellet-based supports in hydrogenation reactions [45]. Musavuli et al. (2025) discovered that Pt/Al_2O_3 catalysts supported on metal foams yielded 59% more hydrogen in LOHC hydrogenation processes than conventional packed beds (**Figure 2**) [46].

Jiang et al. demonstrated that $scCO_2$-assisted synthesis of metal nanoparticles enables precise control of morphology and loading, which is essential for upgrading biomass-derived molecules [47]. Furthermore, the oxidation of Cu nanoparticles in $scCO_2$, followed by electroreduction, generated amorphous CuO structures with over 65% Faradaic efficiency for C_2^+ products [48]. Together, these findings suggest the strong potential for integrating functionalized foams into compact reactor modules.

4.2 Advance media for mass and heat transfer

The physical properties of $scCO_2$—liquid-like density, gas-like diffusivity, and low viscosity—(**Figure 3**) enhance its role as a mass and heat transfer agent. Significant improvements in-process efficiency are the result of combining these properties with porous foams.

As illustrated in **Figure 3**, supercritical CO_2 has a density similar to that of a liquid and a diffusivity and viscosity similar to those of a gas. This combination offers unique advantages for mass and heat transfer. It is important to note that the density of typical process gases at ambient pressure and temperature is several orders of magnitude lower than that of supercritical CO_2 and liquids, often being less than 1 kg/m^3.

Versteeg et al. developed a model to analyze the correlations between the Sherwood and Reynolds numbers in $scCO_2$ flows [49]. These correlations are of fundamental importance for the design of heat exchangers and foam reactors. Furthermore, Nguyen et al. employed direct numerical simulations to unveil orientation-dependent heat transport behavior close to the critical point [50].

Experimental studies involving porous silicon carbide (SiC) tubes exposed to $scCO_2$ have confirmed superior convective heat transfer, thus indicating that foam-integrated $scCO_2$ [51]. Furthermore, Coupled-Matrix-Foam simulations enable the prediction of multiphase behavior in real-time reactor operation [52].

4.3 Lightweight and thermally insulative materials

$ScCO_2$-foamed polymers, including polylactic acid (PLA) and polycaprolactone (PCL), have been demonstrated to yield ultralight structures with low thermal conductivity, a property that is paramount for the insulation of reactors. The utilization of these materials as diffusion barriers or passive structural components is a subject that is being investigated with increasing frequency. Zhou et al. reviewed hybrid processing strategies (e.g., freeze-drying combined with supercritical carbon dioxide foaming) to generate uniform microcellular foams [53]. Furthermore, TPU-based foams processed using $scCO_2$ offer flexibility and durability, rendering them ideal for adaptive insulation in dynamic environments [54].

4.4 Integration into foam reactors and diffusion layers

Functional foams created with $scCO_2$ are increasingly incorporated into integrated reactor modules, where reaction, separation, and heat exchange co-occur. $scCO_2$ enables in-situ nanoparticle synthesis and impregnation, reducing steps and waste.

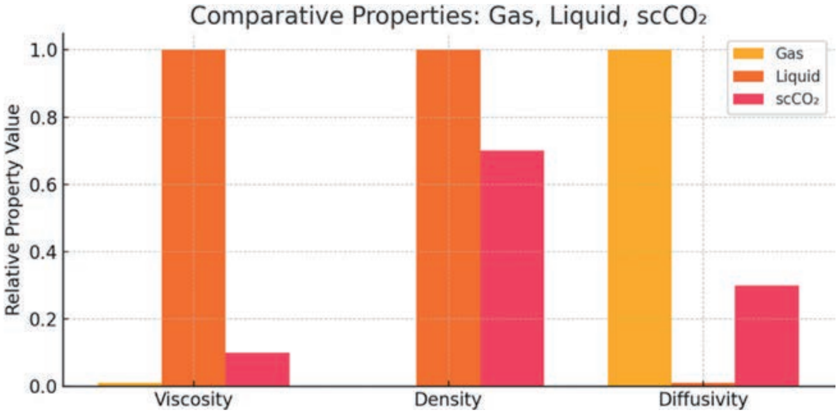

Figure 3.
Relative comparison of gas, liquid, and $scCO_2$ properties. Source: Own elaboration based on data from Ref. Brunner [35].

Sauceau et al. showed the new challenges, as a one-step $scCO_2$ extrusion method for catalytic foams, eliminating the need for post-processing [7]. Jiang et al. and Nguyen et al. both highlight how these foams are used in biomass valorization, gas reforming, and antimicrobial layer formation [47, 50]. The potential to use these foams in electrochemical systems—where $scCO_2$-processed Cu-based catalysts show enhanced C_2 product selectivity—demonstrates their versatility and alignment with green chemistry goals [48].

5. Environmental, energy and recycling benefits and scale-up challenges

5.1 Environmental sustainability and energy efficiency

The utilization of $scCO_2$ obviates the requirement for toxic chemical blowing agents. In contrast to chemical foaming agents, which release harmful by-products such as azodicarbonamide decomposing to CN compounds, $scCO_2$ is nontoxic, inert, and abundant, aligning with the principles of green chemistry [9].

The utilization of $scCO_2$ foaming as a substitute for synthetic blowing agents, in conjunction with a reduction in solvent usage, results in a substantial decrease in CO_2 and VOC emissions. Evaluations suggest that it mitigates the impact of greenhouse gases more effectively than conventional polymer foam production.

Integration of $scCO_2$ foaming with extrusion, microwave-assisted heating, or ultrasound-assisted batch foaming has been demonstrated to reduce energy demand (**Figure 4**) by up to 45% in comparison with traditional methods [52]. The application of ultrasound in conjunction with $scCO_2$ foaming has been demonstrated to enhance the porosity of the resultant material, whilst concomitantly reducing both the temperature and duration of the process.

Since $scCO_2$ does not introduce residual solvents and uses physical desorption, polymer foams can be reprocessed more easily. Initial studies demonstrate the feasibility of recovering and re-foaming PCL, PLA, and PMMA in closed-loop systems, thereby supporting circular economy models [55].

5.2 Technical and scale-up challenges

The consistent production of cellular morphology in continuous processes remains challenging, particularly for polymers such as polypropylene, which possess low melt

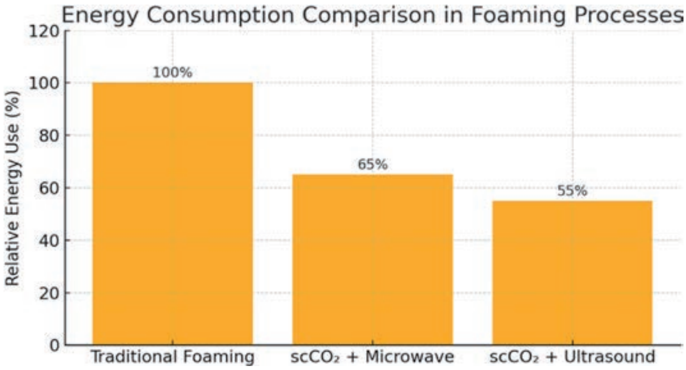

Figure 4.
Relative energy consumption in foaming processes using traditional vs. $scCO_2$-assisted methods [9, 52].

Benefit/challenge	Highlights
Environmental	Solvent-free, reduced GHG emissions, supports circular economy
Energy efficiency	Integrated heating/foaming methods reduce power demand up to ~45%
Morphological control	Requires rheological modifiers and precise process variables
Capital expense	High equipment costs limit adoption at mid-scale
Foam stability and durability	Needs robust design against mechanical and environmental degradation
Recycling infrastructure	Recycling pathways still underdeveloped
Limited agent diversity	Predominantly CO_2, few viable alternatives studied

Table 2.
Summary of key points.

strength. It is evident that techniques such as long-chain branching, chain extenders, blending, or fillers are utilized in order to enhance rheology. However, it is imperative to note that these techniques require meticulous fine-tuning [56].

The financial outlay required at the outset for $scCO_2$ foaming systems, including those of the Mucell® brand, and for custom extrusion units, is considerable. According to industry reports, capital costs are estimated to exceed those of traditional foam lines by approximately 30–40%, thereby reducing economic appeal at moderate scales [9].

The stabilization of foam under real-world conditions is contingent upon precise control of gas diffusion, polymer crystallinity, additives, and saturation/desaturation kinetics. In the absence of optimization, the integrity of the foam may be compromised, resulting in premature loss of its designated properties.

Despite the chemical superiority of $scCO_2$ foaming, the recycling of foamed polymer waste is not yet subject to a standardized set of methodologies. In the absence of effective reclamation technologies, the environmental benefits of these materials may be compromised.

The predominant agents in use at present are $scCO_2$ and, to a lesser extent, scN_2. Exploration of alternative supercritical gases remains in its infancy and is confronted with challenges pertaining to leakage, cost, and safety (**Table 2**).

6. Challenges and future perspectives

6.1 Future perspectives and hybrid composite foams

In the context of increasing demand for multifunctional, sustainable materials, there has been a notable integration of $scCO_2$ foaming with advanced processing techniques, leading to the production of hybrid foams. The combination of additive manufacturing (3D printing) and $scCO_2$ enables hierarchical architectures with tunable properties suitable for thermal management, shock absorption, and filtration.

Recent advancements in the field have focused on the utilization of nanocomposites comprising carbon nanotubes, graphene oxide, and lignin-derived particles, resulting in enhanced electrical conductivity, mechanical robustness, and thermal stability. These hybrid foams have also been demonstrated to be attractive for electromagnetic interference shielding and flexible electronics [56].

Emerging area	Key $scCO_2$ foam advantage
Hybrid nanocomposites	Enhanced conductivity, strength, and thermal stability
3D printing integration	Custom architectures, complex porous designs
EOR and CO_2 sequestration	Foam stability, shear thinning, and conformance control
Smart sensors and soft actuators	Flexible, resilient, and pressure-sensitive foams
Building insulation and packaging	Lightweight, low thermal conductivity, and green processing
Biomedical scaffolds	Porous, biocompatible, and antimicrobial surface functionalization

Table 3.
Summary of trends and applications.

The introduction of bio-based components (for example, PLA with lignin or cellulose nanofibers) into $scCO_2$ foamed structures is an area of research that is focused on reducing the environmental impact of the process, whilst maintaining or improving performance characteristics. These directions align with the overarching objective of the circular economy and are currently under active exploration.

6.2 Emerging applications in intensified systems

$scCO_2$-processed foams are being explored in various cutting-edge applications, especially in chemical engineering and energy systems:

- In enhanced oil recovery (EOR), $scCO_2$ foams exhibit shear-thinning behavior and improved reservoir conformance, enhancing sweep efficiency and reducing gas mobility. This supports CO_2 sequestration and recovery in fractured formations [57].

- In the domain of soft robotics and sensors, TPU-based $scCO_2$ foams with conductive fillers are utilized as pressure sensors and actuators, benefiting from their compressibility, resilience, and functional surface area.

- Advanced insulation panels for sustainable buildings and high-efficiency packaging leverage the low thermal conductivity and lightweight structure of $scCO_2$ foams. These panels often combine aerogels or phase-change materials within a foam matrix for energy regulation [10].

- Additionally, researchers are evaluating the use of foamed materials in biomedical applications such as drug delivery scaffolds and antimicrobial surfaces, particularly for implantable systems where porosity and sterility are crucial (**Table 3**) [58].

7. Conclusions

The use of $scCO_2$ as a foaming and impregnation agent represents an effective and sustainable strategy for the design of porous polymeric materials with advanced functionalities. Throughout this chapter, we have demonstrated how the precise tuning of parameters such as pressure and temperature allows for the control of polymer morphology—pore size, density, and degree of interconnectivity—while facilitating the incorporation of active compounds in a single processing step.

The cases analyzed include catalytic supports with improvements of up to 60% in hydrogen production, scaffolds with interconnected porosities greater than 90% and controlled release systems with profiles sustained for several days. These results confirm the potential of $scCO_2$-processed foams in applications aimed at process intensification, especially in catalysis, biomedicine, and heat and mass transfer.

While the environmental and functional advantages of using $scCO_2$ are evident—solvent-free processes, energy reduction, and recyclability—challenges remain related to scalability, compatibility with polar compounds, and end-of-life management of materials. Overall, polymer foams obtained using $scCO_2$ are a versatile tool for the development of compact, efficient, and environmentally friendly systems, in line with the principles of the circular economy and emerging technologies in chemical engineering.

Acknowledgements

We gratefully acknowledge the Spanish Ministry of Science and Innovation (Project PID2020-116229RB-I00) for financial support.

Conflict of interest

The authors declare no conflict of interest.

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