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Review Article

Production and Application of Polymer Foams Employing Supercritical Carbon Dioxide

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Polymeric foams have characteristics that make them attractive for different applications. However, some foaming methods rely on chemicals that are not environmentally friendly. One of the possibilities to tackle the environmental issue is to utilize supercritical carbon dioxide ScCO_2 since it is a “green” solvent, thus facilitating a sustainable method of producing foams. ScCO_2 is nontoxic, chemically inert, and soluble in molten plastic. It can act as a plasticizer, decreasing the viscosity of polymers according to temperature and pressure. Most foam processes can benefit from ScCO_2 since the methods rely on nucleation, growth, and expansion mechanisms. Process considerations such as pretreatment, temperature, pressure, pressure drop, and diffusion time are relevant parameters for foaming. Other variables such as additives, fillers, and chain extenders also play a role in the foaming process. This review highlights the morphology, performance, and features of the foam produced with ScCO_2 , considering relevant aspects of replacing or introducing a novel foam. Recent findings related to foaming assisted by ScCO_2 and how processing parameters influence the foam product are addressed. In addition, we discuss possible applications where foams have significant benefits. This review shows the recent progress and possibilities of ScCO_2 in processing polymer foams.

1. Introduction

Polymeric foams have a wide variety of applications. Due to their versatility, nearly all industries produce or utilize some type of polymer foams. The wide-ranging uses for foams include home appliances, food industries, and spacecraft [1]. 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. Polymeric 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. The majority of the processes 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 attri-

butes of the final product. The polymer matrix has the most substantial effect on the product properties since it affects the viscoelastic behaviour of the polymer in the course of production. Process parameters such as temperature, pressure, shear, CO_2 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 above in the foaming process will modify some features concerning the foam structure and, therefore, the 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 effuse through solids like a gas and dissolve materials like a liquid [19] (Figure 1). Therefore, it is a state where gases and liquids can coexist. Among SCFs, other than N_2 ,

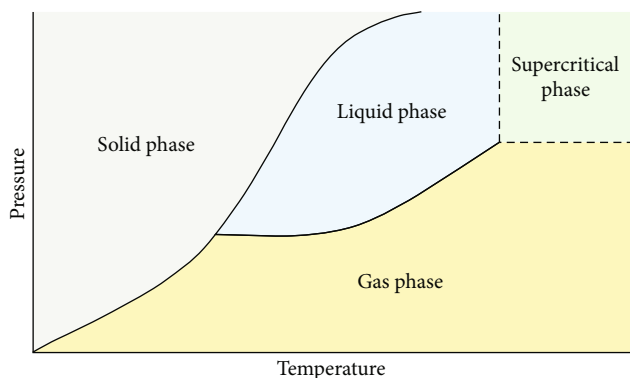


FIGURE 1: Typical phase diagram representing the possible physical states of a substance under different conditions of temperature and pressure.

supercritical carbon dioxide (scCO_2) is a promising chemical because of its relatively low critical temperature and pressure (Table 1), nontoxicity, and environmentally friendliness [20]. Within the processes utilizing scCO_2 , the combination of gas and liquid behaviour can be fine-tuned to engineer the density of the SCF with adjustments to the pressure and/or temperature of the process [21, 22].

This report summarises polymeric foams primarily produced utilizing scCO_2 as a blowing agent. Process related factors, formulation, and extrinsic influences that modify the polymeric foam properties are considered in Sections 2 and 3. In Section 4, we discuss foam cell morphology and mechanical performance. Subsequently, in Section 5, we report polymeric foam features and possible applications where polymeric foams are relevant.

1.1. Blowing Agents in Polymer Foams. To manufacture a polymeric foam, blowing agents are necessary to 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 create a gas and consequently create the cell pocket [23]. The blowing agent used is directly related to the properties of the end material, such as density, morphology, and the structure of the pocket of the foam. Therefore, in most cases, the blowing agent is an important parameter to be considered for manufacturing the 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.

1.1.1. Chemical Blowing Agent (CBA). CBAs function over thermal decomposition or chemical reactions where the

TABLE 1: Critical temperature and pressure of the most common solvents utilized in industry.

Substance	Temperature ($^{\circ}\text{C}$)	Pressure (bar)
Ethylene	9.3	50.4
Carbon dioxide	31.1	73.8
Ethane	32.2	48.8
Nitrous oxide	36.5	71.7
Propane	96.7	42.5
Isopropanol	235.2	47.6
Methanol	239.5	81.0
Benzene	289.0	48.9
Toluene	318.6	41.1
Water	374.2	220.5

agent produces gases (usually N_2 and CO_2) inside the polymer matrix for the polymer expansion [27]. Overall, 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 once they decompose, 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 make 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 take into consideration the polymer compatibility with the chosen CBA and thermal behaviour 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, the implementation of the CBAs theoretically requires a smaller investment in equipment [28]. Besides, the incorporation of CBAs in the process is simply done directly into the hopper of the equipment or mixed with the polymer matrix before 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 possible contamination, the recycling of the foam 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].

1.1.2. Physical Blowing Agents (PBA). PBAs are used in polymer foaming through volatilisation 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 CO₂ [34, 35], N₂ [36, 37], short-chain molecules, and halogenated aliphatic hydrocarbons [38]. Currently, there are three main PBAs used by industry: hydrocarbons, halogenated hydrocarbons, and inert gases.

Halogenated hydrocarbons as blowing agents provide unique features to the foam as high insulation performance and give them a certain advantage over other blowing agents [38]. The possibility of using halogenated hydrocarbons, i.e., 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 major 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 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. However, HFC does not achieve the same polymer foam morphology compared to CFC production.

Inert gases are promising in the field of foam 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 has the viscosity of a gas and almost no surface tension [40]. When a polymer is subjected to a supercritical fluid, i.e., CO₂, it becomes supersaturated, inducing diffusion over time and followed by cell nucleation when thermodynamic instability occurs [41]. Later during depressurisation, 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 CO₂, which has a critical point at mild temperature and pressure, many gases can only reach supercritical behaviour under high temperatures and high pressures to surpass the crucial point. Furthermore, scCO₂ 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 of the blowing agents can be flammable, and 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, there are some hydrocarbons (HC) applicable for industries that display a lower boiling point, potentially suitable as a blowing agent. Some of the alternatives are cyclopentane, isopentanes, and propane. These alternatives offer lower cost, relative small impact on the environment, and compatibility with polymers and are abundantly available [46]. Nonetheless, cyclopentane, for instance, is notably flammable with remarkable low energy of ignition, 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 (i.e., CO₂, N₂, and O₂) are the most used blowing agents in industry because of their price, widespread availability, and the most environmentally friendly when compared to other blowing agents previously described. Despite CO₂ 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 CO₂ emissions [47]. Carbon capture, storage and utilization, is a technology under development where CO₂ is captured from various sources and further reused or stored [48]. Therefore, CO₂ can be captured and utilized for foam production, allowing multiple life cycles of CO₂ [49].

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 a gas and the density of a liquid, therefore, performing as an excellent solvent and plasticizer and enhancing the expansion of the polymer [50]. Supercritical CO₂ (scCO₂) is a nontoxic, nonflammable, chemically inert, and reasonably low critical point. Thus, recent studies investigated the interaction of some polymers with scCO₂. For instance, experiments using scCO₂ as the foaming agent have been performed together with polyethersulfone (PES) [51], poly(butylene succinate) (PBS) [52], poly(methyl methacrylate) (PMMA) [53], polylactide (PLA) [54], polystyrene (PS) [55, 56], and poly(ϵ -caprolactone) (PCL) [57]. In addition, some authors have included different fillers, additives, cblowing agents, and other extra steps to improve the mechanical properties of the foam, optimize nucleation, improve the homogeneity of the cells, or introduce an extra feature to the final product.

The polymer foaming process assisted with scCO₂ has some advantages, such as the absence of organic solvent and the plasticization effect. Nonetheless, utilizing scCO₂ in the foaming has many variables and parameters to be tuned, independently of the process being extrusion, batch reactor foaming (Figure 2), or other possible foaming systems [58]. Batch reactor foaming proceeds with the polymer

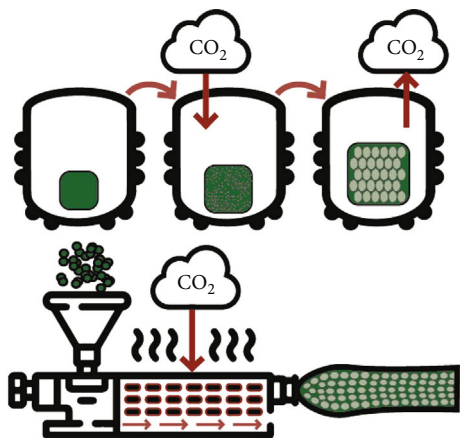


FIGURE 2: Principle of polymer foam production in (top) batch reactor and (bottom) extrusion, polymer pellets feed, and foamed product. Both processes assisted with supercritical carbon dioxide

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]. Extrusion foaming process polymer continuously where a screw blends CO_2 and polymer. The temperature of the extruder is near the melting point of the polymer, and pressure increases along the screw, which is related to the feeding of the 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, such as injection mold, require more attention due to the mold and different shear forces involved with the process. However, the method can be conventionalized as batch foaming since the foam growth occurs inside the mold in 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 lowers the melting point of crystalline regions of the polymer [61]. This chain of events results in different outcomes concerning morphology, mechanical properties, and applications. Moreover, as explained later in this article, the polymer itself will change its behavior according to the method protocol or how it is pretreated. The following subsections describe some of the process' influences and effects on the properties of the foam.

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 behaviour of the polymer itself might change due to melt strength, swelling, saturation, crystallization rate, etc. Li et al. [62] have described one of the inflexion points related to pres-

sure. 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 the temperature rising according to the pressure up to 12 MPa, and at higher pressures, the swelling was not as significant. It is also studied the T_g of the samples, estimated according to the inflexion point in the plot of volume ratio with temperature. The T_g of PMMA drops with an increase in pressure to a minimum of 311.4 K at 12 MPa and then increases again to 323.1 K at pressures higher than 12 MPa. According to Li et al. [62], this change of pattern at 12 MPa is attributed to the solubility of CO_2 in the polymer being less crucial when compared to the hydrostatic pressure effect with CO_2 pressure increase (Figure 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 in different pressure, temperatures, and time scenarios. The foaming method system includes a 25 cm long internal cavity with a gradient of temperature. The unique equipment Ngo et al. built can produce polymer foam displaying gradient cell morphology in multiple directions. Moreover, it is possible to perceive that at the same temperature, cell size is inversely proportional to the pressure. Cell density is defined by nucleation density, which is affected by pressure and pressure drop; therefore, cell density is proportional to the pressure. Cell size and temperatures are directly proportional at a given pressure but do not directly change the cell density other than possible cell collapsing. Due to the protocol adopted by Ngo et al. [66], it was possible to assess the penetration depth of the CO_2 into the sample, effectively describing an estimation of the CO_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, nearly double the CO_2 diffusion coefficient. Moreover, at constant pressure, when temperature increases from 28 to 65, the CO_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 rather recent approach to polymer foaming is the idea of foam products showing multiple morphological structures. Polymer foam with diversified morphology and bigger and small cells combined, gains a bigger window of possible properties, 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 and Huang [68] created a

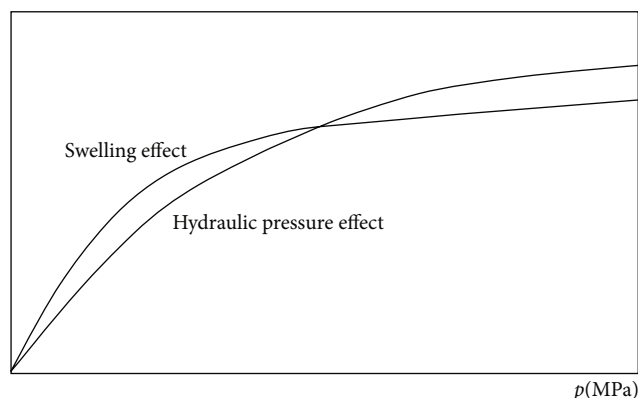


FIGURE 3: Theoretical relationship between pressure and foaming process effects. A crossing point of swelling effect and hydrostatic pressure effect of CO_2 with increasing the pressure describe the inversion of impact over the foam (adapted with permission from [62]).

bimodal cell structure in PS by simultaneously adjusting the temperature and the depressurisation rate. This method is based on the fact that cell nucleation not only occurs during depressurisation but also in the temperature variance during polymer saturation. Similar results were found by authors Xu and Huang [69] in a previous article utilizing PLA. The authors claim that raising the temperature before the depressurisation leads to higher crystallinity, especially in the outer layer of the sample. Therefore, microcells appear in the skin region of the foamed samples when compared to the sample foamed without temperature change over the process but at the same saturation temperature. Another theory for this method to achieve bimodal structure states that the temperature boost results in lower CO_2 solubility into the polymer, thus gas supersaturation and cell nucleation. Consequently, raising temperature favours nucleation and diffusion of gas that is trapped to escape forming bigger cells compared to the cells formed during the depressurisation [18].

For the foaming process, all the parameters and their relation influence the product. There are effective connections between temperature, time, and pressure. Salerno 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 depressurisation rate is directly related and proportional to the foam density, and consequently, inversely proportional to the overall porosity. Similarly, Tsvintzelis et al. [70] research the processability 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.

2.2. scCO_2 Concentration. Concentration is directly linked to pressure and time, adjusting the concentration of scCO_2 load during the 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 the need to adjust 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 is effective to control the ratio of foam and solid regions inside the polymer; consequently, graded foam structure can be manipulated. Functionally, graded porous polymers have very appealing properties because they have continuously changing in macroscopic mechanical and physical properties (Figure 4). Mechanical property tests showed that on one hand, flexural modulus is reduced from over 3000 MPa to nearly 152 MPa, due to the foam structure formed. 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 in the process. 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 wider 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 being able to produce a similar bimodal 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 resulted in increasing cell density and thinner cell walls. In addition, it is also reported that, despite the blend of polymers, the process was able to produce 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 full dissolution of one of the parts, and partial dissolution of the other, resulting in possible similar cell growth.

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_2 adjusting temperature, pressure, scCO_2 flow rate, and time in a semibatch 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_2 to flow at a low-flow rate; meanwhile, 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_2 flow. The theory of the authors states that this combination of temperature, pressure, and scCO_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

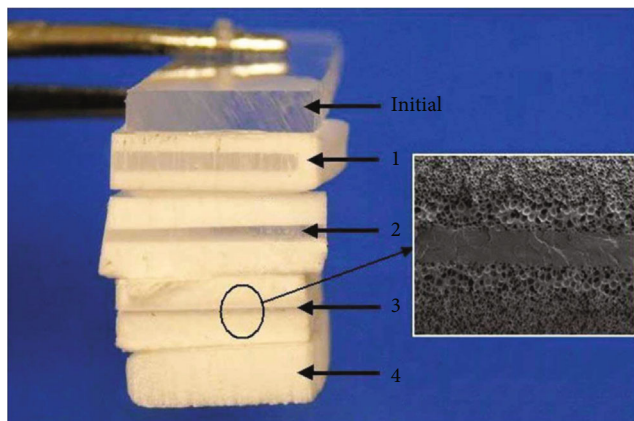


FIGURE 4: The cross-sections comparison of unfoamed (original), partially foamed (samples 1 to 3), and foamed (sample 4) PMMA samples. Foamed samples processed with different average gas concentration. The details of the graded structure are shown in the SEM image. Samples stacked up for easy visualisation (adapted with permission from [71]).

better rough cell surfaces of foam polymers, that could be implemented in buffering and energy absorption.

2.3. Coblowing Agents. Coblowing agents are usually solvents introduced to improve the foaming performance of the polymer. Within the process using scCO_2 , coblowing agents can enhance the solubility of CO_2 into the polymer, assisting in possibly expanding the foam temperature window. Attempting to evaluate the impact of a coblowing agent, Morisaki et al. [77] set fixed values for temperature, pressure, and time for the saturation of PMMA and added different concentrations of ethanol to the process. As a result, the addition of 1 to 7.5 mol% of ethanol as a coblowing agent, increase cell size, promoted cell coalescence with bimodal distribution and the outer skin thickness from 45 m to 35 m. Authors theorise that ethanol could enhance affinity between semipolar 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 $10 \pm 1 \mu\text{m}$.

Trying to optimize foam structure, Qiang et al. [55] researched the effect of butanol and decanol as coblowing agents for PS foaming assisted with scCO_2 . A computational simulation was performed previously on the physical samples and suggested that the solubility and diffusion coefficient of CO_2 for PS is directly proportional to the chain length of alcohols used as coblowing 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 to maintain a higher content of blowing agent in PS, producing higher cell density. Butanol, on account of having a larger plasticization effect on PS, improved the volume expansion ratio (VER) of the foam. Both alcohols were combined as coblowing agents causing the formation of PS foam with

smaller cells size and larger VER when compared to the foam produced with pure CO_2 .

Utilizing software for molecular modelling, as such Materials Studio [79] or Gaussian 09 software [80], is attractive when choosing from a large potential solvent as a coblowing agent, because it calculates the binding energy between the main blowing agent and possible solvents that might be applied as the coblowing agent. Hu et al. [80] studied the molecular modelling and experimental foaming behaviours of microcellular polysulfone (PSU) and polyphenylsulfone (PPSU) assisted with scCO_2 and a coblowing agent. Their study evaluated ethanol, water, acetone, and ethyl acetate as coblowing agents. Ethanol showed a stronger interaction with CO_2 according to the software and experimental analysis. The degree of interaction of ethanol with CO_2 is credited to the shorter distance between atoms. The modelling placed water as the second most suitable interaction with CO_2 , therefore, compatible as a coblowing agent in a foaming process. Nonetheless, utilizing up to 10 wt% of ethanol in the foaming process of PPSU and PSU experimentally resulted in an improvement in the expansion rate from 2.07 to 5.02 and from 3.30 to 5.25, respectively, at 15 MPa.

Just as the direct improvement in the foaming of the polymer, coblowing agents can also be used as indirect support to the foaming process. Tsimpliaraki et al. [81] confirmed that ethanol as a coblowing agent is necessary to produce polymer foaming out of the nanocomposite PCL/clay. The conclusion was that without the solvent, clusters of clay are formed in the PCL, and consequently, nonuniform cells are obtained. However, once the ethanol is introduced, the dispersion of clay is more uniform; therefore, the homogeneous distribution of cells is obtained. Following other studies [55, 82, 83], the use of cofoaming proved to be advantageous especially in polymer processing, demonstrating limited solubility of CO_2 .

3. Extrinsic Influences

As already mentioned, polymeric foams are attractive due to their lightweight, high specific strength, and good thermal and sound insulation properties. These characteristics are mostly, but not wholly, provided by the unique porous structure of the final product. Polymeric chemical modifications and the use of additives or fillers in the process of making foam also play an essential role in the final structure [84, 85]. Therefore, it is essential to study a potential combination of elements with the polymer to achieve a foam with compelling features.

3.1. Additives. Additives are used to improve the material, 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. [86] worked on a specific proposal of adopting a CO_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 silsesquioxane (POSS). Given the purpose of a polymeric foam for biomedical applications, POSSs

are biocompatible molecules with low or nontoxicity, therefore, no major drawback according to the main objective. CO₂-philic trifluoropropyl polyhedral oligomeric silsesquioxane (TFPOSS) was chosen as the nucleating agent and added to the right concentration which could increase the porosity up to 40% higher than usual with temperatures 100 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 scCO₂ in PS, Qiang et al. [35] utilized polydimethylsiloxane (PDMS) and polyvinyl acetate (PVA) as CO₂-philic additives to understand the influence of the number average molecular weight (Mn) of the additives in the foaming process of a polymer with poor affinity with CO₂ [87]. The incorporation of the lower molecular weight CO₂-philic additive PDMS had a better performance than PVA with increasing the diffusion coefficient of CO₂ and decreasing the saturation time of the process due to the strong CO₂ affinity. In comparison, the composite PS/PDMS showed smaller cell sizes, higher cell density, and finer cellular structure (Figure 5) with superior control over the CO₂ diffusion during the foaming process. The authors conclude that introducing a low Mn CO₂-philic additive helps the foaming process by producing a small cell size and large volume expansion ratio.

3.2. Fillers. Fillers are, in general, particulate materials mostly utilized to reduce costs. Contrary to additives that are also bonded to the matrix of the polymer, fillers are simply dispersed in the polymer. Once well introduced to polymers, fillers grant improved properties according to their nature. The main properties explored with fillers include increased stiffness, heat and electrical conduction, creep resistance, and nucleation agent in the case of polymer foam process. Liu et al. [88] 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 behaviour 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 6). Likewise, the fillers reinforce the nanocomposite foam structure, resulting in an enhanced compressive property (Figure 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 concentrations of fillers, the smaller the cell size, the higher the cell density, and therefore, 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.

Because carbon nanotubes (CNT) have interesting features [89] such as outstanding strength and good electrical and thermal properties, they are also studied in the field of polymeric foams [90]. Chen et al. [91] utilized multiwall 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 relative longer MWCNT exhibited lower cell density when compared to samples filled with shorter MWCNT. It is also reported that cell density has a dependency 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, increasing the cell density. Similarly, Chen et al. [92] 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 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 which is 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 nanocomposites 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 actually, lower CB content 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 5 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 it is one of the most widely used fillers for food packaging. Nanoclays are widely available, it has easy processability, good performance, and lower cost [93]. Keshtkar et al. [54] published 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 of nanoclay content is directly

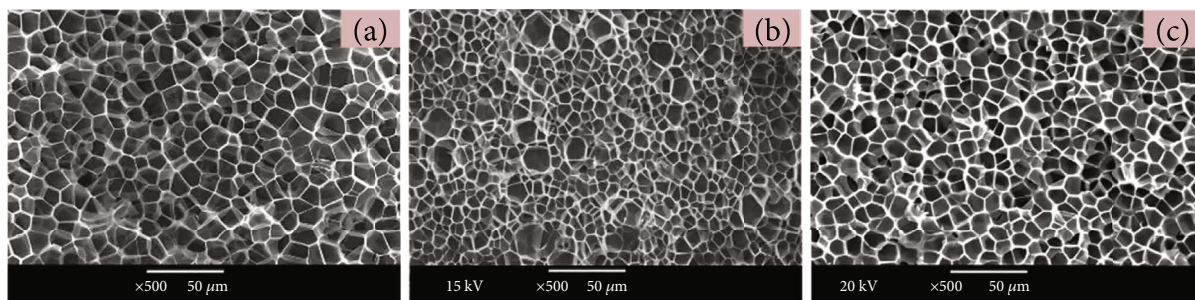


FIGURE 5: Foam morphologies of PS with the low Mn additives were (a) PS, (b) PS with polydimethylsiloxane, and (c) PS with polyvinyl acetate (adapted with permission from [35]).

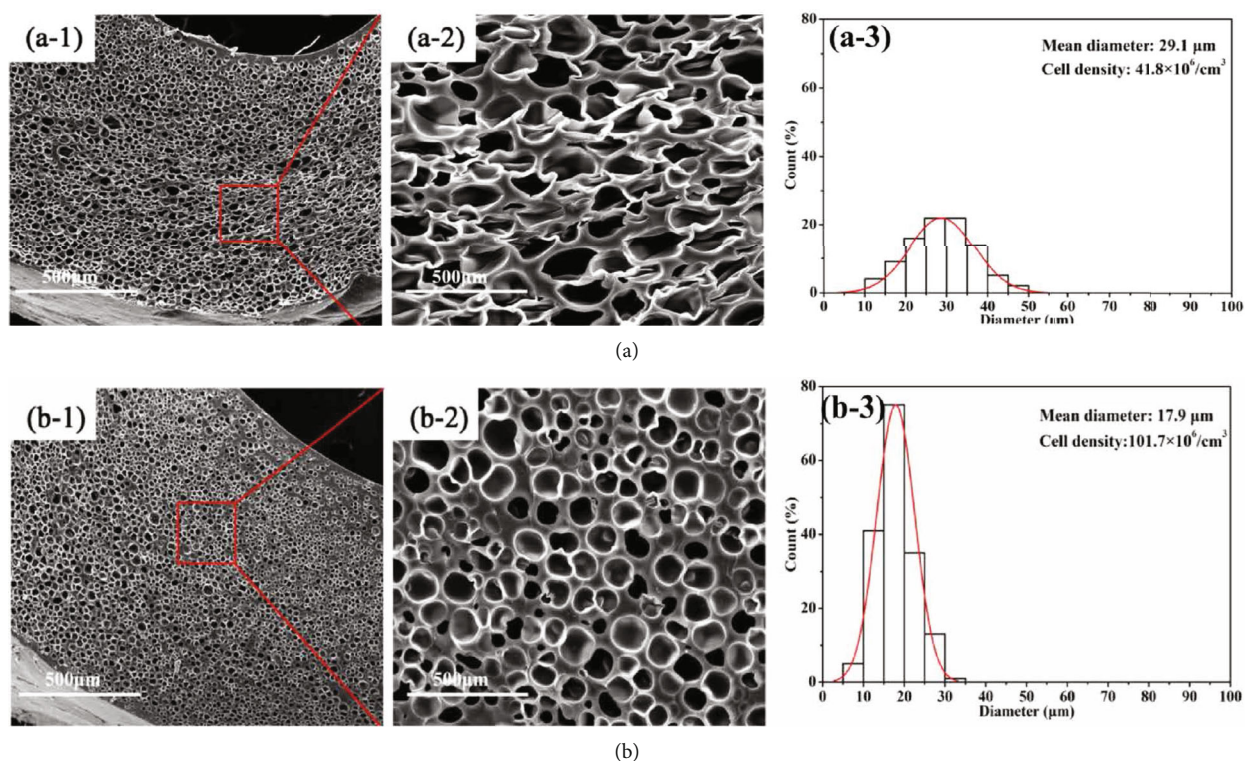


FIGURE 6: SEM images of (a) PVA and (b) PVA with 2.5 wt% of graphene composite foams obtained at same process conditions. Cell size distributions of (a-3) PVA and (b-3) PVA with 2.5 wt% graphene composite foams. Neat PVA shows many irregularly shaped bubbles after the rapid pressure drop. However, by introducing graphene sheets, the obtained foam display a more uniform and regular cellular structure with spherical bubbles (adapted with permission from [88]).

related to the increase 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 rate and cell density.

3.3. Polymer Pretreatment and Modification. Pretreatment 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, 94]. PCL samples subjected to isother-

mal scCO_2 pretreatment displayed a higher melting point and melting onset. These findings align with other researchers who link such difference in melting to the thermal history from subsequent recrystallisation after scCO_2 sorption-desorption [95]. 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 fastest cooling protocol performed in general foams with higher porosity, attributing these phenomena to the polymer's crystallization. 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 depressurisation time and

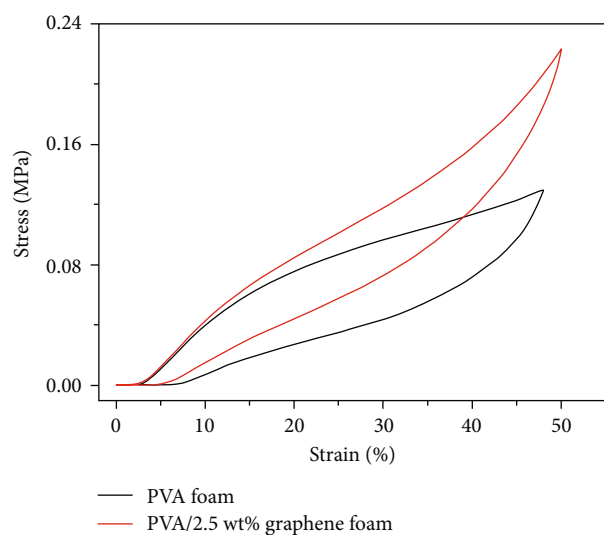


FIGURE 7: Compressive stress-strain curves of PVA and PVA/graphene composite foams. Increasing the compressive strain after a linear-elastic region, the cell walls start to bend. Therefore, the neat PVA foam exhibit a relatively low-stress value, and PVA/graphene composite foam displays a significant increase in compressive stress because of the cellular structure (adapted with permission from [88]).

crystalline structure are important in order to control foam morphology [96–98].

A key factor to produce 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 different outcomes in the same process. The thermoplastic polyester PLA is a biobased and biodegradable polymer with promising features. However, it is rather difficult to produce PLA foam materials with a high-expansion rate because of their linear molecular arrangement, low melt strength, and slow crystallization rate [99]. Consequently, to compensate for the difficulties of PLA, Najafi et al. [100] added a commercially available chain extender (CE) in order to overcome issues related to elasticity and melt viscosity of PLA (Figure 8). Long-chain branched (LCB) PLA when compared to linear 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. [101] 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 cross-linking of PLA samples with the proposed CE is directly related to the enhancement of the intrinsic viscosity. Therefore, the improvement achieved by including the CE managed to increase cell density nearly four times than neat PLA and the volume expansion ratio by three folds.

As already mentioned, PLA is a remarkable polymer, considering some of its features [102], but the foaming process still presents some challenges. To overcome the PLA foaming limitation, Li et al. [103] proposed a preisothermal

cold crystallization instead of branching agents or fillers, claiming that some of those methods can disrupt PLA biodegradability and possibly raise production costs. Among other reasons, authors claim that pretreatment 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 [104]. The article concluded that the preisothermal treatment proposed resulted in PLA with more and 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.

Aiming to produce foam for photoinduced hydrogen evolution Morisaki et al. [77] utilized $scCO_2$ to foam two different weight average molecular weight (Mw) of PMMA. Low molecular weight PMMA (LPMMA) and high molecular weight PMMA (HPMMA) produced different foams at the end of the same process. Foams produced with LPMMA displayed reasonably lower cell density and thinner walls between cells when compared with 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 [105–107].

In the same category as modification, cross-linking 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. [108] proposed using dicumyl peroxide (DCP) in HDPE to produce a micro cross-linked structure with enhanced viscoelasticity. The authors used DCP up to 0.25 parts per hundred resin into the HDPE and found that at higher concentrations, the cross-linking limited the foaming behavior restricting the 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. [109] found similar results where a high concentration of bis-tert-butylperoxy diisopropylbenzene (BIPB) into EPDM restrains the network of cell growth because of the rigid cross-link. Zheng et al. [109] report that there is increase in cross-linking degree, the cell morphology changed from polygonal to elliptic, there is more homogeneity of cells, and the wall thickness increased. Following other studies, [110–112], it is concluded that the cross-linking degree of thermoplastics indeed assists in the control and distribution of the cells of the foam.

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 employing the best properties of the

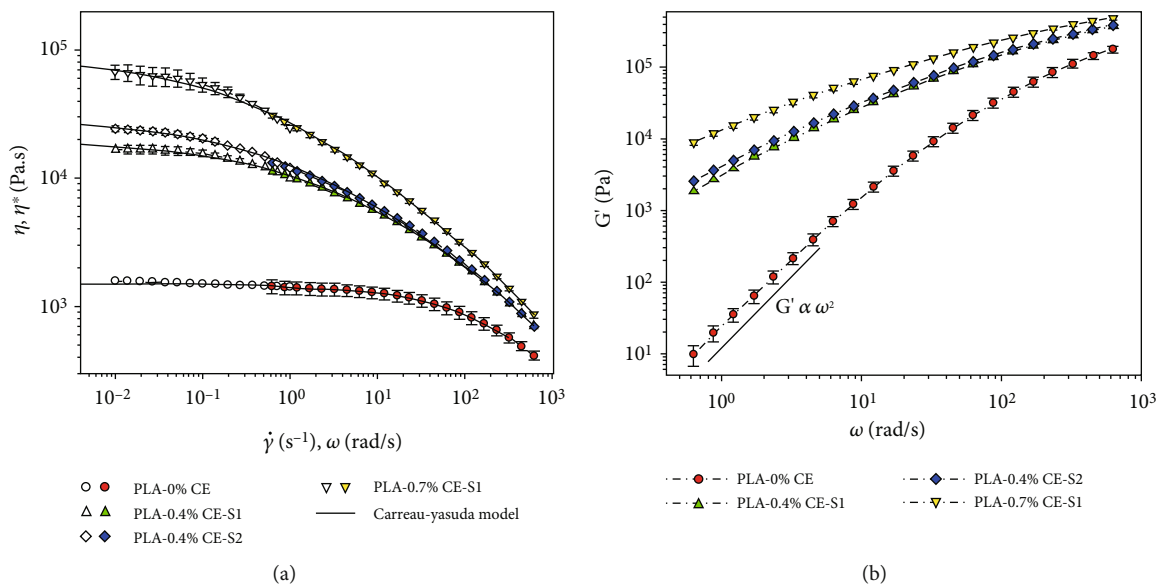


FIGURE 8: The linear viscoelastic properties of (a) shear (open symbols) and complex viscosity (filled symbols) and (b) storage modulus of the neat and CE-enriched PLAs. The addition of CE into the matrix changes the rheological response of the material according to the CE content (adapted with permission from [100]).

polymers involved, and reaching new possibilities due to the synergy of the blend. Thereupon, Wang et al. [72] studied cell nucleation in 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 PS rich phase, and small cells are formed in PP rich phase with their correspondent properties according to the morphology.

Correspondingly, biodegradable polymer foams made out of polyesters PLA, PBS, and a blend of PLA with poly(hydroxybutyrate) (PHB) have been foamed with scCO_2 , tested, and compared by Frerich [113]. The authors studied the influences of temperature and pressure on the final product. Since melting has a great influence on 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, PBS reduces to 100, and the blend PLA/PHB reduces to 111; therefore, the plasticizing effect and the effect in the melting temperature of each polymer is remarkable. The authors suggest that the smaller change observed by PBS is related to the effect of solubility and hydrostatic pressure already mentioned previously in this review. The big changes in melting temperature of PLA and the blend according to the authors 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, 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 [114, 115]. Liu et al. [116] made use of 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 [117] and comes into the mix with PCC to compensate for the brittleness of PCC. Liu et al. [116] reported that blending PPC and PBAT with a small percentage of Joncryl ADR-4368 additive (around 1%) leads 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 cells 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. [118] studied the foamability of miscible blends based on poly(ether ether ketone) (PEEK), semicrystalline engineering thermoplastics, and poly(ether imide) (PEI), an 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 increase 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 in foam density configuration. According to the authors, the described behaviour can be explained by 2 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 [119]. 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.

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 9) [120–123]. 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 article, the influence of cellular morphology (cell size and distribution, structure) on the performance of polymer foams is reviewed.

4.1. Microcellular Foams. Microcellular polymer foams have been widely used since the 1980s as they can reduce the material density and fulfil other functions (e.g., as bone scaffolds) while maintaining good mechanical properties when compared to its not-foamed form [124]. 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 [125–127].

Cellular structures have a variety of applications; henceforth, it is necessary to match their structure with engineering applications. To correlate foam porosity and cellular structure to the foam properties, Zhang et al. [53] fabricated PMMA microcellular foams by adjusting process conditions. It is reported that the relation between PMMA cell size or porosity and mechanical properties (i.e., compressive strength and modulus) exhibits quadratic growth where strength increases with the development of smaller cells or lower porosity. Cell size going from 45.7 to 15.0 μm 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 μm , usually has the shape of a polygon and thin walls which for the most part withstands the pressure. Increasing the cell size results in a decrease in wall thickness, therefore, possibly reducing mechanical strength [128, 129]. 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.

4.2. Nanocellular Foams. Studies on nanocellular foams have been revealed as the next generation of high-performance

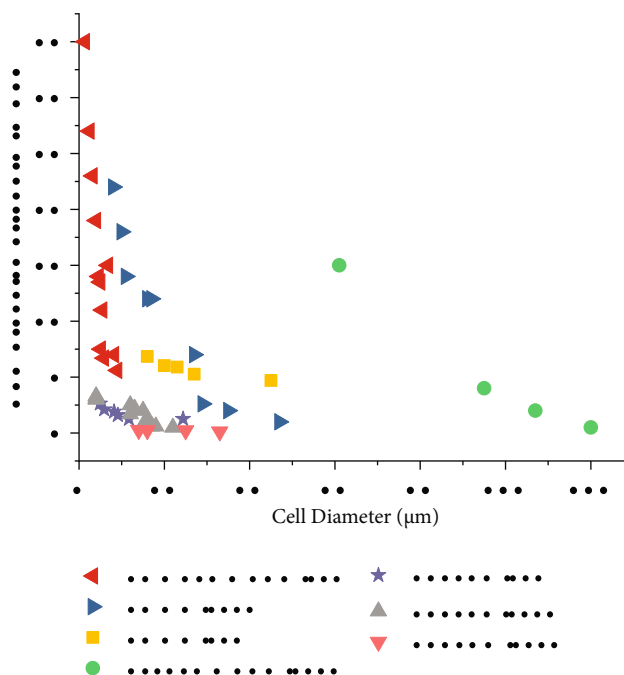


FIGURE 9: A summary of literature data showing the relationship between compressive strength and cell size.

polymeric foams [130–132]. To achieve nanocellular structures, new techniques were developed, and those are described below. For example, Sharudin and Ohshima [133] utilizing CO_2 -induced crystallisation in combination with the nanoscale dispersed-domain method [134] managed to create nanocellular foam. PP combined with styrene-ethylene-butylene-styrene (SEBS) were 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 nanocellular foam [133]. 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 nanocellular 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 [135]. The modelling of thermal transportation within the nanocellular foams suggested that increasing the refractive index or the absorption coefficient of the polymer matrix is beneficial for decreasing the thermal conductivity of foams [129, 136]. 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 nanocellular polymer foams can attain a super-insulating property [137]. 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 [136]. This mathematical model is relevant for inspiring the development of the next generation of super-insulating materials which 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 the transparency, which made the foam utterly promising for new markets. Martín-de León et al. [138] characterized 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 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. [138] comply with the theory since samples with cell sizes smaller than 50 nm display some transmittance. It is hypothesised that the future market for these materials can include super-insulating windows, nanoporous materials for filtration, energy storage, and catalyst support [139].

The issue of creating 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 [140]. Therefore, Shi et al. [141] project a method and polymeric blend that provides stable cell growth and developing high porosity nanocellular polymer foams. Utilizing CO₂ as blowing agent, the authors employed a blend of PMMA and poly(vinylidene fluoride) (PVDF). The composite choice is because PMMA can absorb a large quantity of CO₂ 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. [141] is environment friendly and simple but with high efficiency and flexibility. The authors also assert the applications of the product for filtration, energy insulator, and catalysis.

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 [142]. In general, larger cells reduce the density of the material, while smaller cells assist the mechanical and thermal insulation properties. For instance, improved acoustic performance can be produced with graded polymer foams compared to materials with uniform sizes. Although Mosanenzadeh et al. [143] did not utilize scCO₂ in their process, they managed to create a foam with cells size shifting from 600 to 200 μm along with the material. This shift in cell size enhanced the maximum sound absorption coefficient up

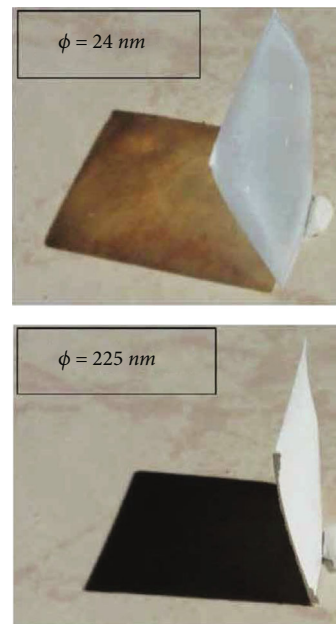


FIGURE 10: Optical images of light transmission through actual samples with the same relative density and different cell sizes. The amount of scattered light decreases with smaller cell sizes, and the amount of scattered light is higher in bigger cell sizes resulting in an opaque sample (adapted with permission from [138]).

to 20% compared to uniform cell size foams with similar porosity. As mentioned before in this report, it is possible to produce gradient foam structure utilizing scCO₂ [66].

The field of tissue engineering also takes advantage of 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. [144] developed a PCL scaffold with a bimodal pore from 100 μm to smaller than 50 μm using two-step depressurisation of scCO₂. The resultant material has potential for scaffolds since its morphology is very 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, while the small pores assist the transport of nutrients and waste [144].

5. Applications

In material science, there are broad pathways to cover special features that are attractive to obtain different functionalities. The market in general (food industry, healthy system, and aerospace engineering) demands every day more personalised foams with diverse characteristics as electrically conductive, biodegradable, and biocompatible. The foaming process using scCO₂ produces polymer foams with special features due to the versatility of the supercritical fluid (Figure 11). It has been reported that polymeric foams produced by scCO₂ with specific features could enter the market for thermal insulation [145, 146], bone tissue [147], EMI shielding [148], adsorbing materials [130, 149], and filters [150]. This section will describe some of the attributes of

polymeric foams that researchers have found and some of their applications.

5.1. Electrical Conductivity. Polymer materials have been known for decades as good insulators. However, combining polymers with additives or chemically modifying them makes it possible to create polymers that conduct electricity. Therefore, polymeric foams with electrical properties are feasible and attractive [151].

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 [152]. Gedler et al. [153] reported 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 is 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. [120] 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 $scCO_2$ for 3 hours at high temperature, dropping the temperature to foaming temperature, and followed by fast depressurisation. This process proposed by Kuang et al. [120] 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 [154–156]. 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. [157] studied low-weight polyarylene ether nitrile (PEN) polymer combined with SiO_2 as filler and nucleation agent to form polymer foams that conduct less electricity. Foaming of the polymer matrix with SiO_2 filler remarkably increased the porosity of the final material from 38%, with no filler, to more than 58% with 5 wt% SiO_2 . 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 SiO_2 added to the polymer matrix is directly related to enhancing the thermal insulation properties of PEN/ SiO_2 , and the same way, the cell density increases.

5.2. Thermal Insulation. A significant part of global energy consumption comes from heating and cooling [158]. Therefore, thermal insulation is vital for a more sustainable society. Thermal insulators improve energy efficiency in packaging, transport, construction, and industrial processes.

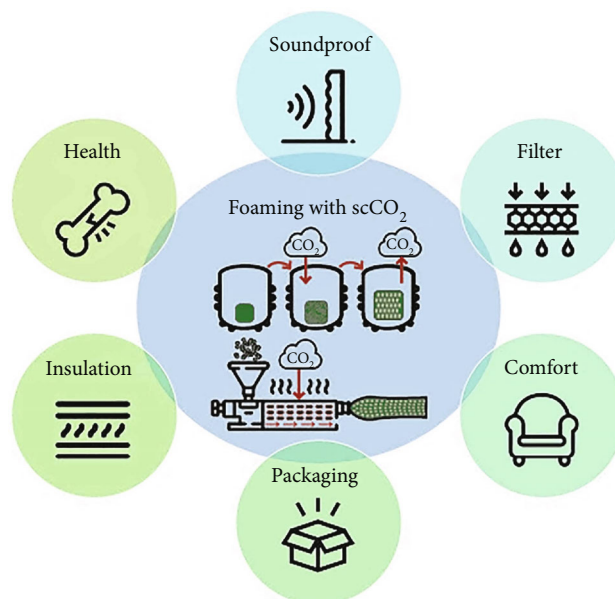


FIGURE 11: Some applications for foams are produced using $scCO_2$ as the blowing agent.

Governed by the physical structure and chemical composition, the thermal conductivity of a material describes the performance of a thermal insulator [159, 160]. 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 is a property of a material's ability to transfer heat [161]. 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 [162], making it possible for nanoporous polymers to overcome the thermal conductivity of some gases. Thus, Forest et al. [163] et al. studied the Knudsen effect by modelling foam features with micro/nano cell morphology produced with CO_2 as a blowing agent. Employing an analytical model based on a similar treatment for aerogels, Forest et al. [163] 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, which is equivalent of thermal conductivity of air. Other authors utilized the nano-cellular foam theory combined with fillers or additives to achieve the same or lower thermal conductivity of gases [164–166].

In parallel with studying heat insulation materials, other lightweight features are also very beneficial. Shi et al. [167], 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. [167] obtained a foam with open porosity up to 98.6%, the density of 0.0361 g/cm^3 , and thermal conductivity of 31.07 mW/mK. The thermal

conductivity reached by PVDF/PMMA foam blend is comparable to rock wool and PU foam [168], but with the oil-absorption feature.

Polymer foams are reliable heat insulators, but some are not environmentally friendly. Therefore, Yin et al. [169] proposed to produce a fully biodegradable foam composite of PBS and cellulose nanocrystals (CNC). In order to improve PBS foaming properties, the authors utilized a branching agent epoxy based. In addition, CNC is pretreated with hydrophobic surface modification by acetylation to raise the compatibility of CNC with PBS. The foamed PBS/CNC material produced by Yin et al. [169] 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 and VER of 37.1. Therefore, PBS/CNC is a promising material for construction and packaging, combining outstanding thermal conductivity and biodegradability.

5.3. Biodegradable. The majority of the polymers nowadays last many years in nature if wrongly discarded, and the long life of plastics causes environmental problems. Consequently, plastics biodegradable are necessary to fulfil the polymer's market demands without harming the surroundings. Thus, Ju et al. [170] 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 PBS composite was performed at cooperative temperature control variation and a two-step depressurisation. Particularly, 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 12). In addition to all the features PBS/CNC bear, it is relevant to mention that polymeric scaffolds with bimodal structures are attractive for bone regeneration due to their morphological properties [171].

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 create new healing processes. Biodegradable polymer scaffolds are one strategy to manage drug delivery. Bai et al. [172] 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. [121] use the biodegradable polymer PBS in combination with carbon fibres (CF) formulated a composite foam assisted with scCO_2 as a blowing agent. The polymer foam display not only the already mentioned benefits of using a filler but the CF specifically

granted the material to be electrically conductive. It is proven that with 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 [173]. Yet, Li et al. [149] study a fully biobased alternative for oil-absorbing material since the existing technologies to separate oil and water utilized can produce secondary pollution. Therefore, a blend of PLA with PBS foam made with scCO_2 creating open cells foam with selective oil adsorption is proposed and achieved. The PLA/PBS foam displays porosity up to 97.7% and successfully adsorb solvents and oil out of the water, reaching 21.9 g/g. 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. [149] 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.

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. [3] combining a thermoplastic polyurethane (TPU) with MWCNT processed with scCO_2 . Thus, it is recognised that in 100 cycles at a compressive strain of 30%, the composite TPU with 5% of MWCNT behaved relatively stable after the 10th 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 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, in addition to enhanced mechanical properties, make this polymer foam model for sensors that requires improved sensitivity, accuracy, recoverability, and flexible materials [174].

Polymer foam featuring shape-memory is generally an adaptive material that can undergo deformation and return to its original shape. The shape-memory feature has some limitations, and Wang et al. [175] proposed a composite with TPU and PLA foamed with the scCO_2 method to minimise 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

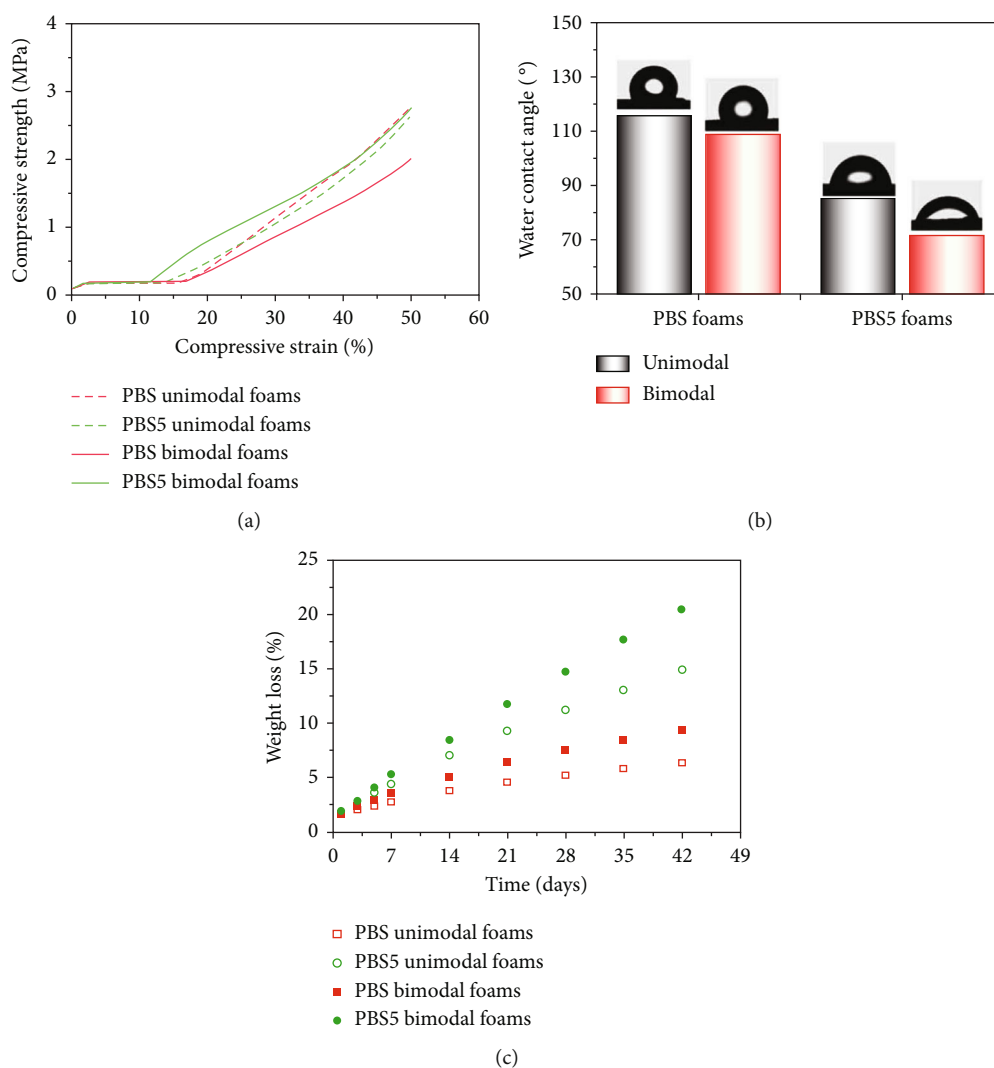


FIGURE 12: Performance of neat PBS foams and PBS5 (5 wt% CNC) foams with unimodal and bimodal structure: (a) specific compressive stress-strain curves; (b) water contact angle; (c) degradation *in vitro* on mass loss (adapted with permission from [170]).

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 mechanical properties, the proposed blend TPU/PLA has the potential to be applied in the field of sensors, packing, and intelligent medical devices [176, 177].

6. Summary

Polymeric foams are encountered in every field, from medical applications and home appliances to spacecraft. This versatility 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 very 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 itself.

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 . Pretreatments are valuable in the foaming process since they can eventually improve nucleation. Isothermal steps before the regular process can improve 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. Nonetheless, it is possible that at specific pressure and temperature, the behaviour of the polymer influences the outcome of the process other than the CO_2 density. The influence of the polymer can be estimated according to the thermal properties of the polymer (glass transition, melting, and degradation temperatures).

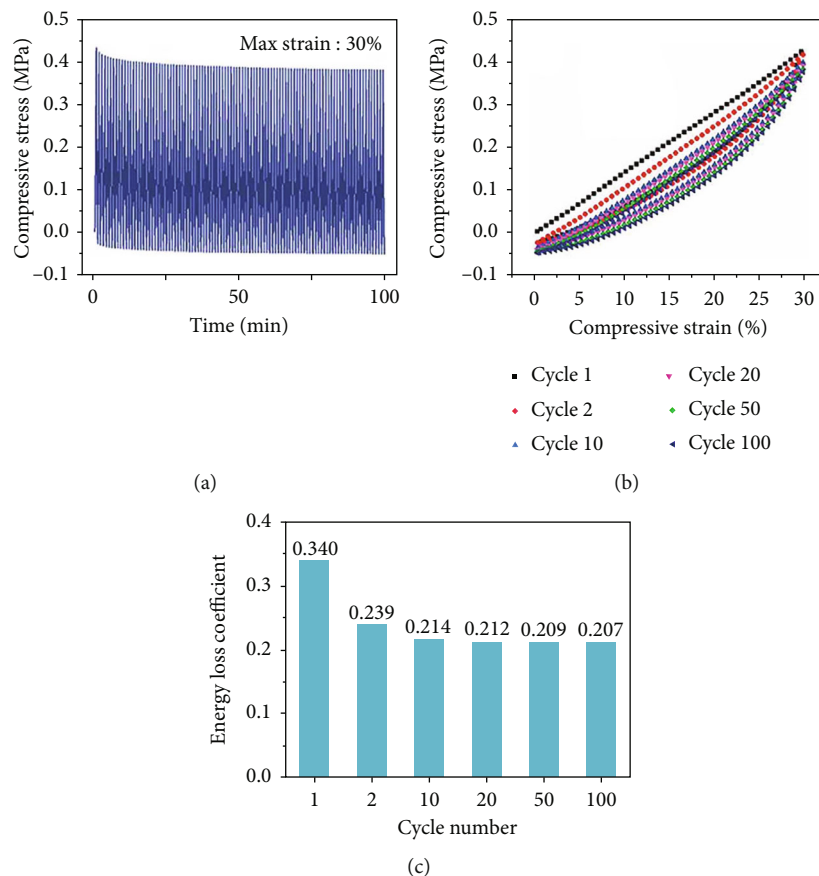


FIGURE 13: (a) 100 cycles of TPU filled with 5.0% MWCNT foam at a maximum compressive strain of 30%; (b) stress-strain curve of continuous cycles (1st, 2nd, 10th, 20th, 50th, and 100th); (c) energy loss coefficient of continuous cycles (adapted with permission from [3]).

Solvents such as coblowing agents improve solubility and diffusion of scCO_2 into the polymer. The CO_2 -polymer interaction enhancement can create foams with bigger and more homogeneous cells. In addition, utilizing coblowing agents can be essential to permit the dispersion of additives into the polymer, serving as compatibilisers. To broaden the possibilities of polymeric foams, it is necessary to use extra elements. Additives, fillers, chemical modifications, and even polymer blends have proven to reach new foam properties that can be exploited in a greater variety of 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. Fillers, when introduced to a system, may react chemically with the polymer matrix. However, due to the dispersibility of fillers and often inertness, fillers act as nucleation sites in most cases, directing CO_2 into small pockets prior to 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 modi-

fication 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. The possible downside of this approach is bringing the disadvantages of each polymer into one process, for example, having a smaller window of temperatures to process and to degrade none of the polymers 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-cell is required in the case of stiffer or energy isolating materials. Concerning cell size, a clear trend is noticed from the literature, and within the same polymer system, smaller cells tend to have higher compressive strength compared to polymeric foams with bigger cell sizes.

Combining some features is of the utmost importance in creating polymeric foams that suit different applications. From the applications assessed by this review, 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 conclusion, the future of engineering materials will be shaped by polymeric foams since they can replace most of the materials utilized in diverse applications with the main advantage of being lighter. Therefore, rethinking the process of producing polymeric foams and using scCO_2 are essential to build an environmentally friendly and sustainable production line.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declared that there is no conflict of interest.

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