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Research progress of 3D printing combined with thermoplastic foaming

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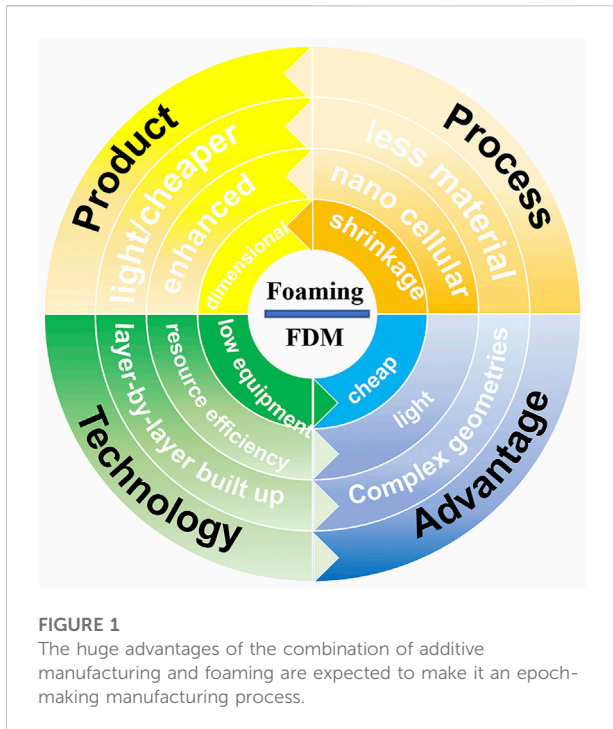
Thermoplastic foam additive manufacturing is a brand-new industry that perfectly combines the advantages of polymer foaming with AM. The 3D printing industry currently suffers from limited available materials and monolithic part manufacturing, and 3D printed foam offers a new way of thinking to address these challenges. Designing multifunctional components with additive manufacturing gives designers great flexibility, while foaming reduces the weight of materials and costs. The combination of the two allows for the creation of lightweight structural and functional items with differentiated physical properties. This one-of-a-kind and innovative approach can be achieved in the printed section. 3D printing foam, on the other hand, is still in its infancy. This review examines the respective functions and applications of additive manufacturing and foaming, and then attempts to summarize four commonly used 3D printing methods at this stage: 1) cellular scaffolds; 2) composite printing foam; 3) post-foaming of printed solid scaffolds; 4) *in-situ* foam 3D printing. Among these methods, *in-situ* foam 3D printing is the technique that properly merges the foaming and fused filament fabrication processes. Although in the early stages of research and not yet fully established, this foam 3D printing technique seems to be the trend to replace other foaming processes.

KEYWORDS

3D printing, thermoplastics, foaming, reviews, microcellular foams

1 Introduction

In today's increasingly energy-constrained world, polymer foam products are attracting widespread attention for their material-saving and low-cost qualities, as well as their good mechanical and thermal stability, low thermal conductivity and excellent dielectric properties (Di Maio and Kiran, 2018). The design concept of thermoplastic foaming perfectly fits the human pursuit of high-performance materials by improving the mechanical properties of materials while decreasing material density. Nevertheless, each high-performance thermoplastic foam has a relatively single function, and the addition of micro- and nano-nucleating agents is an effective technique to improve the foam structure and give it better mechanical properties. With the development of high-end fields such as



building materials, automotive, aerospace and military industry, thermoplastic polymer foam materials and products are also facing new challenges (Ling et al., 2013; Costeux, 2014; Forest et al., 2015). The accuracy and performance of the foam produced by traditional foam molding technology can no longer meet the increasingly stringent requirements. The foam produced by the microcellular foam molding process has smaller pore sizes than the original defects or microscopic cracks in conventional foam. These micro-pores can blunt the cracks in the original material and improve the mechanical properties of the material by increasing the strength of the plastic.

Additive manufacturing is an emerging manufacturing technology that uses digital models (Shmueli et al., 2019; Narupai and Nelson, 2020) as a basis to create solid objects from materials in a layer-by-layer build-up (Nadgorny and Ameli, 2018). Because additive manufacturing does not require the process planning of subtractive manufacturing, it largely simplifies the process of producing complex parts. This has overturned the traditional manufacturing concepts and models, and has had a profound impact on the transformation of traditional manufacturing into modern manufacturing.

The current microcellular foaming methods generally include batch foaming method, rapid temperature rise method, rapid pressure reduction method, continuous extrusion foaming method, injection molding foaming method, etc. Here, we propose that additive manufacturing technology can also be used as a novel microcellular foam molding process. Combined with seemingly unrelated concepts of thermoplastic foaming and additive

manufacturing, it enables the development of unique engineered materials with a variety of geometric shapes and specific physical properties. Figure 1 depicts the respective advantages of additive manufacturing and foaming. It is believed that 3D printing foaming technology will become an advanced technology with broad application prospects. This review will focus on these two topics (Attaran, 2017).

2 Additive manufacturing and foaming are two relatively independent technologies

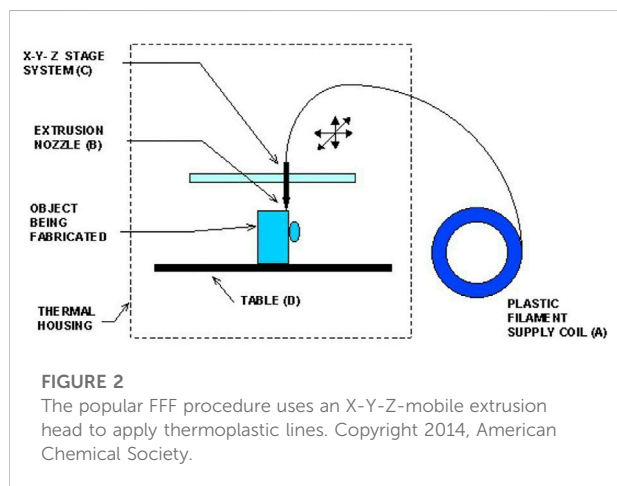
2.1 Additive manufacturing

2.1.1 3D printing methods

Often referred to as 3D printing, additive manufacturing (AM) was initially created in the 1980s to address the extremely specific demands of model creation and rapid prototyping (RP). Since then, it has evolved into a versatile technological platform for rapid prototyping and computer-assisted design (CAD) (Hofmann, 2014). A variety of techniques that quickly and easily convert virtual solid model data into physical model are what constitute additive manufacturing (Rashid, 2019). Without the requirement for molds or machining, which are typical of traditional forming and subtractive manufacturing, it allows custom components to be made from metals (Yang et al., 2022), ceramics (Felzmann et al., 2012; Franchin et al., 2022) and polymers. Polymer-based additive manufacturing can be roughly classified into four categories, each of which has its own technology. Among them, polymers are undoubtedly the most frequently used additive manufacturing material category. Table 1 summarizes the advantages and disadvantages of AM classification methods for polymers. The first additive manufacturing technique is photopolymerization, in which a liquid photopolymer in a vat is selectively cured by photoactivated polymerization (Kaiser and Chalfin, 2017). Stereolithography (SLA) (Credi et al., 2016; Palaganas et al., 2017; Voet et al., 2018), digital light processing (DLP) (Ligon-Auer et al., 2016; Zhu et al., 2017, 2018), continuous liquid interface production (CLIP) (Tumbleston et al., 2015; Januszewicz et al., 2016) and multiphoton polymerization (MPP) (Nikolić and Stevanović, 2006) etc., All fall into this category. In stereolithography, the light source may be either a laser or a projector in digital processing of the light (Borrello et al., 2018). The second technique is called powder bed fusion technology (PFT), where the polymer is delivered towards the print bed as a powder layer and then portions of the powder bed are thermally fused. Selective laser sintering (SLS) also belongs to this technology, as defined in the standard text of ASTM F2792-12 (Kaiser and Chalfin, 2017). The technique can be applied in cores or molds for manufacturing facilities made of various metal alloys as well as organic materials like sand. The powder bed used

TABLE 1 Multiple AM processes for polymers, with benefits and drawbacks.

Multiple processes	Typical and largest build volume	Typical materials	Advantages	Disadvantages
Vat photopolymerization SLA	50–100 μm	acrylates/epoxides	excellent surface quality and precision	limited mechanical properties
CLIP exposure from bottom	75 μm	acrylates	high build speed	limited mechanical properties
	25–100 μm	acrylates/epoxides	low initial vat volume	
multiphoton lithography	0.1–5 μm	acrylates	very high resolution	low build speed; limited materials
Powder Bed Fusion	50–100 μm	PA12; PEEK	greatest mechanical characteristics; least anisotropy	rough surfaces; unusable unsintered powder
Material and Binder Jetting polyjet	25 μm	acrylates	quick; allows multi-material	need for low viscosity ink
Aerosol jet printing	10 μm	conductive inks/ dielectrics	high resolution; low temp process	need for low viscosity ink
3D printing (binder jetting)	100 μm	starch, PLA, ceramics	quick; allows multi-material	low resolution; limited materials; high anisotropy
Laminated Object Manufacturing	200–300 μm	PVC, paper	compact desktop 3D printer	limited materials; low resolution; high anisotropy
Material Extrusion	100–150 μm	ABS, PLA, PC, HIPS	inexpensive machines and materials	low mechanical strength; rough surfaces
Fused Deposition Modeling				
3D dispensing	100 μm -1 cm	thermoplastics, composites	broad range of materials	rough surfaces; narrow viscosity process window



in the majority of SLS applications is made of thermoplastic polymers, especially different types of polyamide like PA11 and PA12 (Hofmann, 2014). The third technique is called material jetting, in which UV crosslinking is employed to selectively deposit viscous droplets of photopolymers (Udroiu et al., 2019). Material extrusion is the final significant additive manufacturing technique (Schirmeister et al., 2019). This technique is based on the original fused filament manufacturing (FFF) process and relies on a simple design using thermoplastic materials that appear to be essentially industry standard. (Li et al., 2020). The idea of melting a

“typical” plastic product and extruding it *via* a narrow, heated nozzle seems to be quite straightforward as shown in the schematic of Figure 2 (Hofmann, 2014). This allows the extruded melt to deposit in the X-Y control motion of the anterior layer of the manufactured element (Rashid, 2019).

Additive manufacturing technology plays an important role in meeting the needs of individual production, overcoming many of the long-standing limitations of traditional processes. However, the technology still has certain shortcomings. For example, models printed with ABS or PET have rough details and poor fineness (Fu et al., 2021). Multiple material substitution combinations are required to produce fine print details. In addition, the SLS powder sintering process requires additional curing of the printed object; otherwise, it tends to cause liquid absorption and staining of the porous surface Wang et al. (2020b). Due to the limitations of material properties, additive manufacturing is still unable to accurately replace real products and remains more at the stage of simulating products. On the other hand, additive manufacturing is not very efficient. For the 3D printers commonly used in the market, a three-dimensional plastic model the size of a puck requires 28 h (Stansbury and Idacavage, 2016) of continuous machine work. The development of lightweight thermoplastic polymer foams enables researchers to quickly print small-scale parts before expanding them. An innovative and creative manufacturing process is created by the successful combination of polymer foaming with additive manufacturing, and thermoplastic polymer foam can be produced by SLA (Wirth et al., 2020), FFF and direct ink

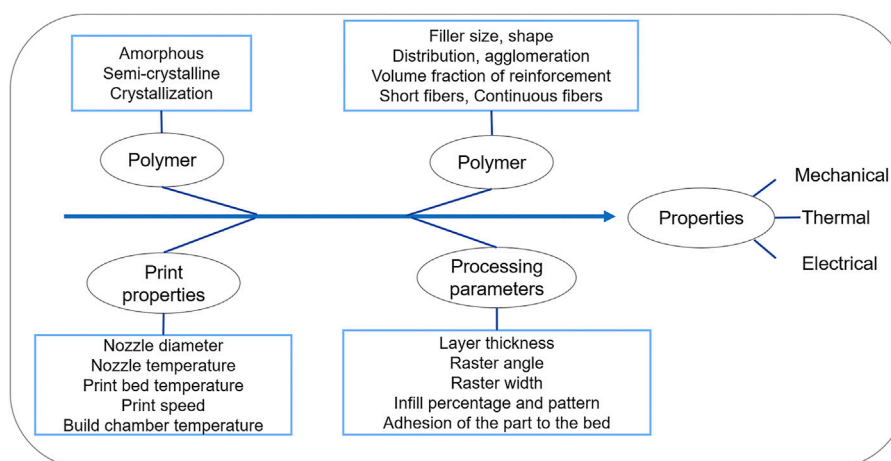


FIGURE 3
Several factors that influence the characteristics of FFF printed items.

writing (Chen et al. (2018a), 2019), etc. Of these combined foaming processes, the SLA process is available for fewer materials because it requires a higher cure rate. In addition, SLA relies on the combination of cured polymers with soluble components for post-processing to form honeycomb structures (Wirth et al., 2020). In contrast, the FFF process is well suited to thermoplastic foams due to its low system cost, wide material selection, and improved toughness. The FFF technologies will be highlighted in this review.

2.1.2 Introduction and application of fused filament manufacturing

Since Scott Crump created fused deposition modeling (FDM) and received a patent for it in 1989, the term “fused filament fabrication” (FFF) is widely used as a replacement (Schmitt et al., 2017). A fusion of thermoplastic material is extruded from the nozzle by heating and then the material is selectively printed on the platform according to the predetermined trajectory of the model slice (Zhang et al., 2020). The raw material, which is targeted at the inside of the hot-end, is bought on reels of filament with a 1.75 or 3 mm diameter (Eltorai et al., 2015). For amorphous or semi-crystalline polymers, the extruder is heated to a polymer-appropriate process temperature, which is either above the glass or melting temperature for semi-crystalline polymers (Nadiyapara and Pande, 2017). For a successful construction procedure, the CAD geometry parameters for a particular filament, build speed, processing temperature, and polymer melt rheology must all be carefully balanced (Pérez et al., 2018). The various elements that affect the performance of FFF printers are graphically represented in Figure 3. On the other hand, there are many challenges in implementing the FFF process to achieve thermoplastic foaming. Since it is printed in one piece, the structure used for support may also be

embedded inside the model during the printing process and cannot be removed. At the same time, human manipulation can lead to warping, deformation, etc. Hwang et al. effectively solves the deformation problem due to the thermal expansion of the material by embedding metal particles into the polymer (Hwang et al., 2015). In addition to the control of deformation problems, Kokkinis et al. developed a magnetically assisted 3D printing platform in terms of workpiece anisotropy (Kokkinis et al., 2015). They achieved particle orientation control by adding magnetized aluminum platelets to a polymer matrix. Owing to the arrangement of anisotropic particles, the target performance of the workpiece in a specific direction was improved (Liu et al., 2022). Another problem with the FFF process is that the printed part contains a certain amount of porosity that can adversely affect the final mechanical properties (Kakumanu and Srinivas Sundarram, 2018). Even though the technology can achieve high precision in theory, it is still very difficult to manufacture in practice.

Because it can print objects made of various material types and then alter the print substance, FFF has the obvious benefit of allowing for more users control over device manufacturing for experimental applications (Weng et al., 2016). FFF is used as a tool for bioengineering tissue, with components ranging from bones or teeth to blood vessels or organ scaffolding. FFF is being used in a multitude of ways in the building industry (Zhang et al., 2021). In contrast to complicated geometries, FFF provides design freedom that aids in the optimization of design models that enable higher functional integration and lower material waste. Biomimetic actuators, such as worm-like and flower-like actuators, are examples of intricate magnetic actuators with complex topologies. FFF has been successfully applied to these actuators (Qi et al., 2020). In conclusion, additive manufacturing is becoming increasingly prevalent outside of

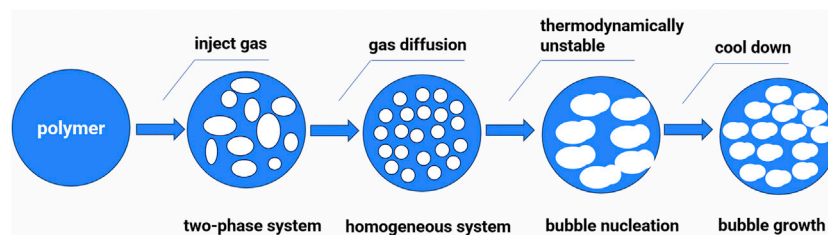


FIGURE 4
Polymer molding foaming process.

specialized industries and is currently used in a variety of fields, including lightweight engineering, energy technology, pharmaceuticals and even food production. It performs significantly more than just its conventional role in rapid prototyping, rapid tooling, and concept modeling (Gross et al., 2014).

2.2 Foaming

2.2.1 Foaming and foaming mechanism in polymers

The concept of polymer foams was originally proposed in the hope of introducing a large number of voids into the polymer matrix that were smaller than the defects already existed in the polymer. Therefore, the rigidity of the product can be improved while the quality of the product is reduced, and other properties such as strength are not significantly affected. Polymer foam materials, as compared to non-foamed materials, have certain good qualities like high impact strength, extended fatigue life, high toughness (Zhai et al., 2022), strong thermal stability (Wicklein et al., 2015; Hu et al., 2019), low thermal conductivity (Ji et al., 2013) and dielectric constant (Wu et al., 2013), etc. Polymeric foams can be generated using a variety of techniques, including physical blowing agents (PBA) (Sauceau et al., 2011; Zhai et al., 2022) and chemical blowing agents (CBA) (Sadik et al., 2018). Thermally expandable microspheres (TEMs) (Diani and Gall, 2006; Peng et al., 2013; Zhang et al., 2019) have received increasing attention as a type of PBA. The polymer foam molding process generally includes three basic stages: the formation stage of the polymer/gas homogeneous system; the nucleation stage of the bubbles; and the growth and shaping stage of the cells, as shown in Figure 4. At first, the gas diffuses and disperses into the polymer under specific conditions, and after a certain time it reaches thermodynamic equilibrium to form a homogeneous system; changing the temperature or pressure causes the gas solubility in the homogeneous system to drop quickly, resulting in a supersaturated state. Numerous microscopic bubbles are generated in the system as it tends to

revert to a low-energy steady state. The system's pressure differential between the inner and outer the bubbles increases as the system's gas solubility is further reduced, which causes the bubbles to grow and expand. Afterward, the system is cooled and shaped to take on the final cell shape and structure.

2.2.2 Polymer foam technology

In order to manufacture polymer foam materials, the foam molding process can be separated into batch autoclave foaming (Yeh et al., 2017), continuous extrusion foaming (Lee et al., 2008; Sauceau et al., 2011), and injection molding foaming (Ameli et al., 2014; Villamil Jiménez et al., 2020), depending on the degree of continuous operation. Table 2 lists the various foaming techniques in alphabetical order. Batch autoclave foaming is typically performed in a high-pressure reactor, which provides the sample being foamed with a specific high temperature and high pressure airtight environment, allowing gases like CO₂ and N₂ to gradually diffuse and dissolve into the polymer matrix. Cell nucleation develops and finally takes shape as the thermodynamic conditions change. Anson Wong (Wong et al., 2011) and colleagues examined the foaming behavior of semi-crystalline polymers and discovered that samples using the Wessling method, including HDPE, PP, and PET, showed varying degrees of crystallization. They discovered that the dissolution slope reduced as crystallinity increased. This indicates that the amorphous area of the polymer is the sole place where adsorption takes place. Due to the semi-continuous foaming process, the diffusion of the gas in the polymer matrix can take place at a much higher rate and efficiency (Yu et al., 2015). Kuma et al. (Kumar et al., 2000) proposed a method for producing solid-phase PET foamed sheets using a semi-continuous method in response to the drawbacks of discontinuous methods for producing polymeric micro-foam materials. After the gas had been saturated, the separator layer was removed with a heating device and then foamed. The last foaming technology is continuous foaming, which is currently the most popular polymer foaming technology (Rizvi et al., 2018; Li et al., 2021; Gunasekaran et al., 2022a). Supercritical CO₂ can significantly reduce the time required for polymers to reach

TABLE 2 The properties of different foaming techniques.

Techniques	Foaming technology	Phase of polymer while foaming	Melt strength of polymer	Cell morphology	Expansion	Notes
Batch process	bead foaming	high-elastic phase	high; hard segment improves melt strength	uniform and closed cell structure	high	beads made of elastomers not crosslinked
	compression molding foaming		improves melt strength		high	elastomer plates or sheets
	carbon dioxide autoclaves foaming		high			N ₂ is another option of PBA; rubbers or elastomers must be crosslinked
Semi-continuous process	injection molding foaming (Mucell process)	melt phase	low	presence of open-cells	low	extension of the chain is required to increase foamability
	injection molding foaming (core-back process)	melt state high-elastic phase	relatively high	uniform with open-cells present	high	extension of the chain is required to increase foam expansion ratio
Continuous process	extrusion foaming	melt phase	low	poor cell morphology with open-cells present	low	extension of the chain is required to increase foamability
	extrusion foaming with underwater granulator	melt phase	low	uniform with open-cells present	high	extension of the chain is required to increase foam expansion ratio

saturation, allowing for the production of microporous polymers in an industrial environment (Yeh et al., 2017; Hu et al., 2021). Therefore, it is imperative to provide a continuous preparation technology for micro-foamed materials based on established plastic processing techniques like extrusion (Nofar, 2016; Rizvi et al., 2018) and injection molding (Jahani et al., 2014, 2015; Contreras et al., 2020).

3 Approaches to generating cellular structures through additive manufacturing

When solids are converted into cellular materials, their single-valued qualities are enlarged (Ashby, 2006). Properties include stiffness, strength, thermal conductivity and diffusivity, electrical resistivity, (Wang et al. 2(2020a); Nofar et al., 2022) all of which have numerous potential applications in the areas of personal thermal management (Hu et al., 2020; Zhou and Hsieh, 2020), IR stealth (Ahn et al., 2019), superhydrophobic surfaces (Wu et al., 2020), and sensors (Hu et al., 2020). Performance is significantly influenced by density and honeycomb structure in addition to the polymer matrix. Compared to conventional production techniques, additive manufacturing offers unprecedented flexibility in achieving controlled structure, geometric characteristics, feature, and complexity (Kim and Oh, 2008). Conventional foams have a random distribution of porosity throughout, inspired by the topology of natural

honeycomb structures. Structures found in bone and wood, for example, where the solids and voids are organized in accordance with the load-bearing requirements (Jiang et al., 2020). First, it should be noted that additive manufacturing utilizes two distinct forms of porosity. When building the structure layer by layer, there are still certain voids without polymer deposition even when the filler content is set to 100% (Nofar et al., 2022). However, porosity can also be used to create certain honeycomb structures. The porosity parameter generated in this manner is controversial and even considered as a drawback in studies. Specific pore types can carry out specialized tasks like sound and thermal insulation. Regular porous scaffolds, such as cellular structures Chen et al. (2018b), truss-based lattices (Rehme, 2010), octahedron and rhombicuboctahedron structures (Liu et al., 2017), and surface based lattices like gyroid or diamond structures (Maskery et al., 2018) are the main focus of additive manufacturing research. To date, the following methods have been documented for generating cellular structures by additive manufacturing (FFF printing technology): 1) cellular scaffolds; 2) composite printing foam; 3) post-foaming of printed solid scaffolds; 4) *in-situ* foam 3D printing. Of course, there are many challenges in implementing thermoplastic foams using the FFF process. Pre-foaming must use foamed filament as the raw material for additive manufacturing, limiting the range of honeycomb mesh structures that can be obtained and also risking loss of structure during the printing process (Kuang et al., 2017). Complex post-processing stages, high pressure-reducing device requirements,

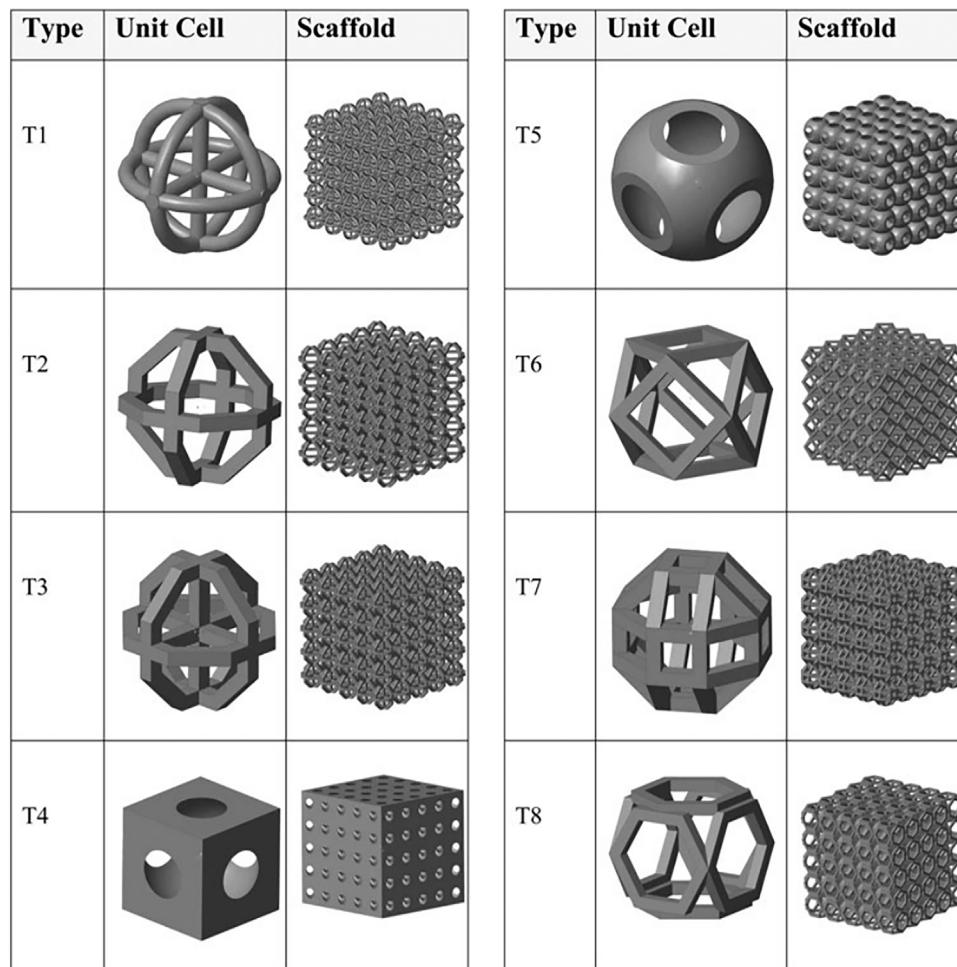


FIGURE 5

Models of all (eight) types of unit cells and scaffolds. Copyright 2016, Mary Ann Liebert, Inc.

and limited expansion may be problems for post-foaming methods, which retouch the item after printing (Zhai et al., 2022). *In-situ* foaming, on the other hand, is the most recent approach that matches the foaming and fused filament fabrication processes flawlessly. However, obtaining a uniform and stable polymer or gas solution *via* the foaming agent during the material extrusion process is difficult. The approach may result in inhomogeneous cell nucleation, poor vesicle density, uneven cell structure, and other problems. Below, we detail the particular material molding process.

3.1 Cellular scaffolds

Cellular scaffolds designed by conventional manufacturing methods (Yang et al., 2001) have a single type of pore unit, and most of them can only make coarse adjustments to individual

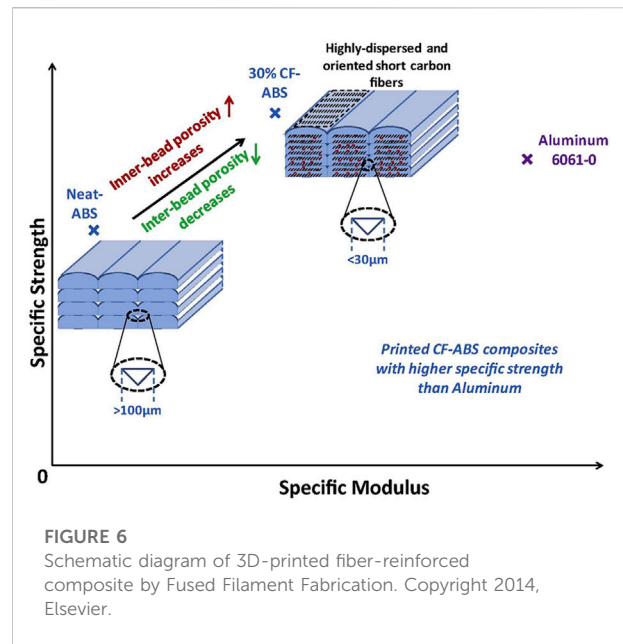
parameters such as porosity and pore size (Jia et al., 2020; Jiang et al., 2020). The internal microscopic honeycomb structure of the forming scaffold is random, and the pores are not completely connected, which cannot meet the actual needs. FFF printing technology applied to cellular scaffolds assembly can not only precisely control the spatial structure distribution of the scaffold, but also effectively control the functional gradient of the scaffold material, thus enabling the engineering of scaffold manufacturing. On the other hand, the construction of honeycomb structures by layer-by-layer printing is different from the traditional foaming process. In terms of mechanical qualities and accessible active surfaces, hierarchical cellular scaffolds perform better than their non-hierarchical counterparts. This is due to hierarchical cellular scaffolds are highly heterogeneous at mesoscale in geometry and porosity distribution, with coupling effect among cells (Wang et al., 2018; Yin et al., 2023). The FFF method may produce a variety of

random and ordered geometries. The resulting scaffold topology can then be used to modify the unit cell units, as shown in Figure 5, to alter the overall quality of the completed project (Habib et al., 2016). In this instance, the specified geometry, unit cell components, and their structures can be used to modify the mechanical characteristics of this structured cellular structure (Pajunen et al., 2019). By employing additive manufacturing, two-dimensional (2D) and three-dimensional (3D) architectures of composite have been created to investigate the impact of unit cell connection and geometry on mechanical properties. Sirui Bi et al. synthesized brittle foams with regulated morphological properties and conducted an array of tests to gauge the compressive response and strength of 3D printed foams (Bi et al., 2020).

Highly porous scaffold materials are required for tissue engineering (TE) with the aim of accommodating and directing proliferation, regeneration, and development of cells in three dimensions (Habib et al., 2016). Polymeric materials have shown strong competitiveness in cellular scaffolds, such as polyethylene glycol (PEG) (Liang et al., 2022), poly (L-lactic acid) (PLLA) (Kuang et al., 2017), polyglycolic acid (PGA) (Yang et al., 2001), polycaprolactone (PCL) and their copolymers (Cho et al., 2019). Porous scaffolds prepared from these synthetic polymers have biocompatible, high porosity and interconnected pores that allow for the accommodation of large numbers of cells in these pores (Melchels et al., 2010). FFF printing technology is used to create personalized TE scaffold materials and can even carry cells for *in situ* cell printing on tissue defect sites. Insoles for the treatment of diabetes also benefit from an optimized porous structure. The design with a variable gradient modulus enhances the contact stress between the foot and the insole to avoid ulceration. (Ma et al., 2019). However, a significant barrier to the therapeutic use of 3D printed cellular structures is the realization of tissue heterogeneity through the controlled distribution of various cell and biomaterial types at the micro- and macro-scales (Fang et al., 2022). All in all, it could be stated that the main objective of 3D printed cellular structures is novel functional integration, which can be precisely accomplished by regulating the important characteristics of unit cells (Nofar et al., 2022).

3.2 Composite printing foam

3D printing of polymer composites addresses these issues by combining the polymer matrix and nanomaterial reinforcements to generate a society with more valuable structural and functional features than either of the constituents could achieve on their own (Thomas et al., 2019). These reinforcements are usually denser and can be incorporated directly into the polymer matrix to form porous structures (Patil et al., 2019; Bharath et al., 2020; Bonthu et al., 2020). The development of polymer matrix composites, which have great mechanical performance and outstanding functionality, is made feasible by adding



reinforcements to polymers in the form of fibers, particles or nanomaterials (Wang et al., 2017). Porosity and fiber orientation of composites have a considerable impact on the properties of final composite products (Patil et al., 2019). The short fiber (0.2–0.4 mm) reinforced acrylonitrile–butadiene–styrene composite made by FFF printing composite foam is depicted in Figure 6 (Tekinalp et al., 2014). Printed composite foams had relatively higher porosity than composites made by traditional compression molding (CE), but their tensile strength and modulus were comparable. The purpose of this research is to develop a compression molding-based manufacturing technique for glass micro-balloon/high density polyethylene (GMB/HDPE) syntactic foams (Jayavardhan et al., 2017) while examining their mechanical characteristics in order to establish correlations between structures and features. They claimed that the entrapped hollow spheres were retained in the produced filaments as well as in the 3D printed samples (Jayavardhan et al., 2017; Bonthu et al., 2020). As the Figure 7 shows, particle fracture increases with increasing GMB content due to increased particle-to-particle interaction during processing and a higher breakdown of GMB is seen in the syntactic foam developed at a higher screw speed. M. Doddamani et al. generated three distinct volume fractions of GMB particles with varying wall thicknesses 20%, 40%, and 60% (particle density variations) (Doddamani, 2019). When compared to HDPE matrix resin, storage modulus, loss modulus, and damping are seen to increase with particle wall thickness and volume fraction. When these composite foams are combined, they often allow for the tailoring of properties in two dimensions (i.e., wall thickness and volume fraction modification), providing versatility in creating materials for a wide variety of purposes.

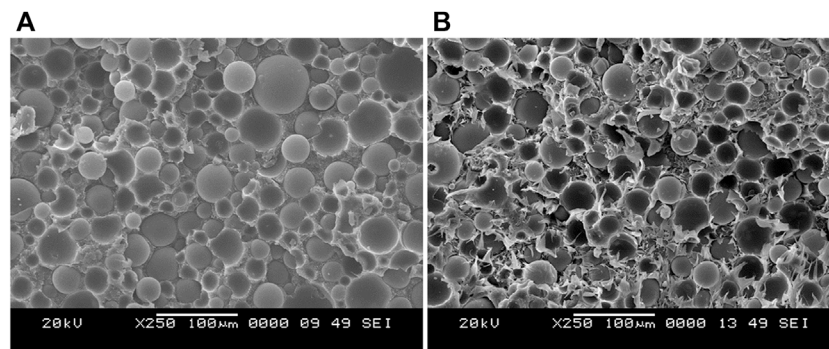


FIGURE 7

SEM image of H200-60 syntactic foam that has been formed and frozen and was taken at the same magnifications for (A) 10 and (B) 40 rpm screw rotation Copyright 2017, Elsevier.

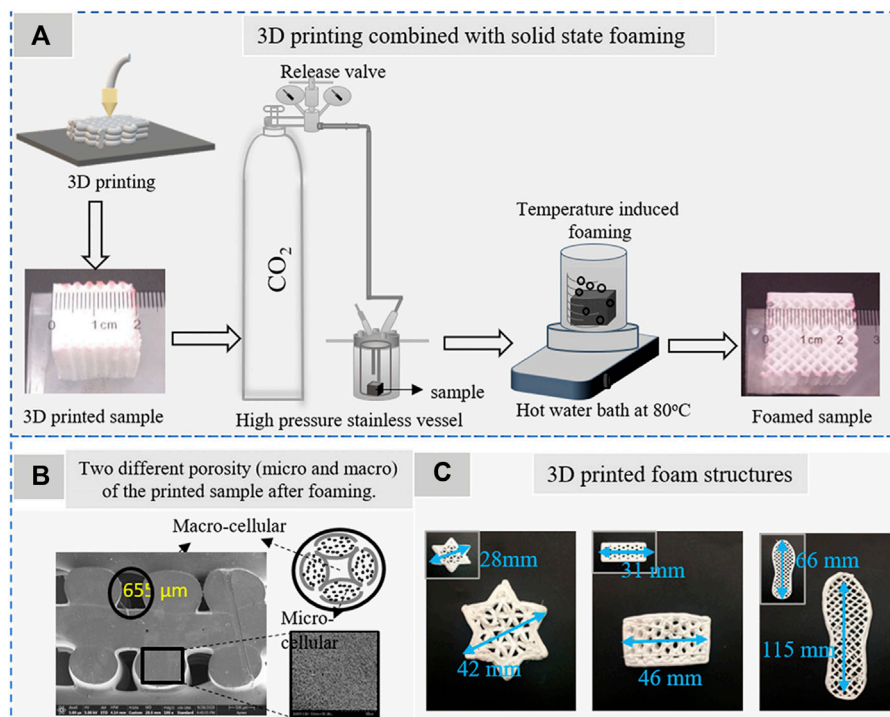


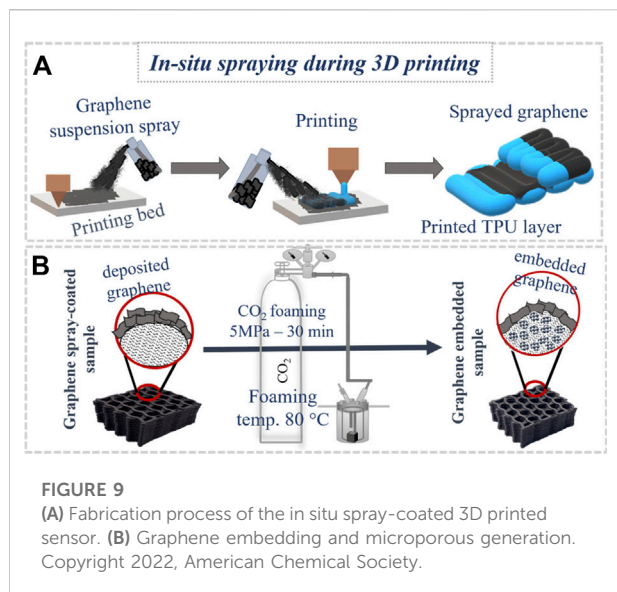
FIGURE 8

(A) Schematic presentation of the 3D printing combined CO₂ solid-state foaming process. (B) Two different porosities of the printed sample. (C) 3D printed foamed sample with different structures. Copyright 2022, American Chemical Society.

3.3 Post-foaming of printed solid scaffolds

FFF printing technology in combination with gas foaming technology was used to construct a recently created solid scaffold with a precise microstructure of about 10 µm (Zhou et al., 2016). The sample is first 3D printed using FFF in this process, and then a porous structure is created in the sample using the gas foaming

technique. By trimming and cutting stages in the post-processing of the foam, this method of printing cellular foam with post-foaming in conjunction with additive manufacturing plays an important role in decreasing the traditional supercritical gas foaming phase and minimizing material waste. Figure 8 shows the rapid CO₂ foaming process of 3D printed thermoplastic polyurethane elastomer developed by our research group



(Gunasekaran et al., 2022a). In this work, the foaming behavior of printed TPU elastomers with three different hardness values was examined. The resulting foam samples can be used for high-end applications, such as shoe bottoms, which conventional foaming cannot provide (Gunasekaran et al., 2022a). Additionally, compared to their un-foamed counterparts, microcellular TPU honeycombs showed greater elasticity and better elastic recovery (Hu et al., 2021). The foam produced through the post-foaming route also differs from prefabricated structures in terms of its properties. For example, the foaming technique produces a low mass density and high sensitivity sensor in addition to creating a conductive network on the surface and interface of the printing system. Figure 9 (Gunasekaran et al., 2022b) depicts the conductive TPU foam's assembly procedure. Our research has shown that adding graphene sensors directly to the surface of TPU has a limited impact, and that foaming creates a microporous structure that helps embed graphene and create a conductive network.

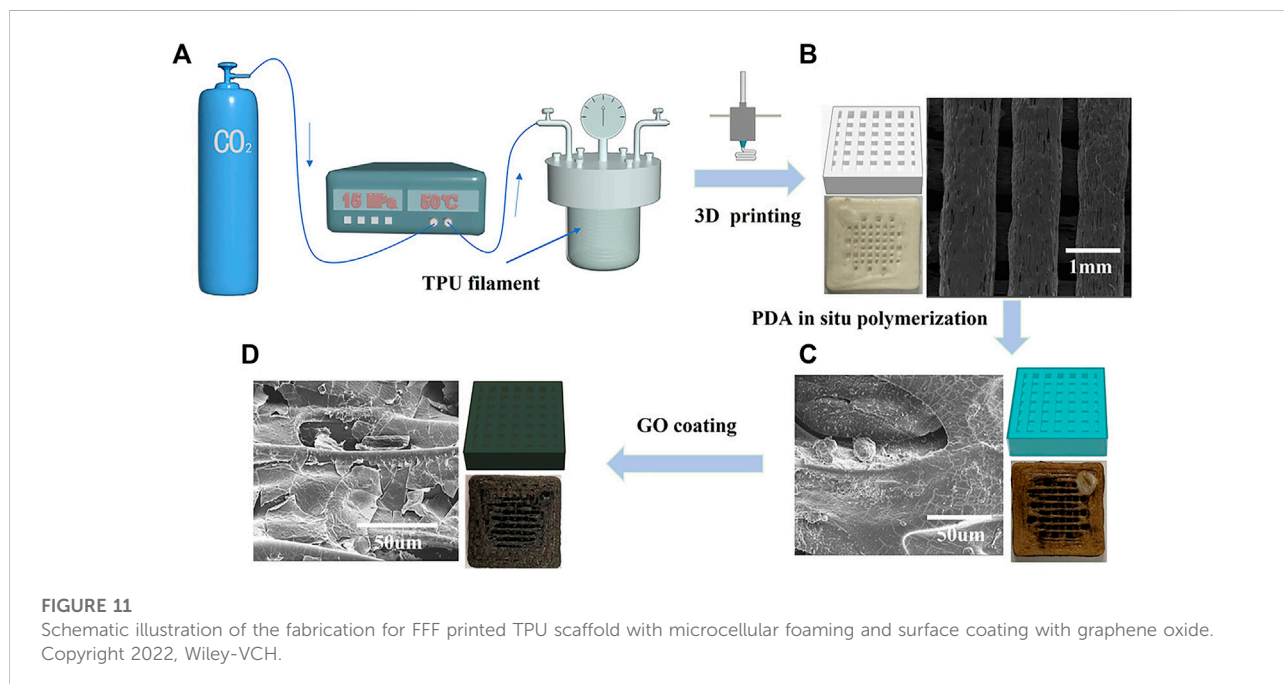
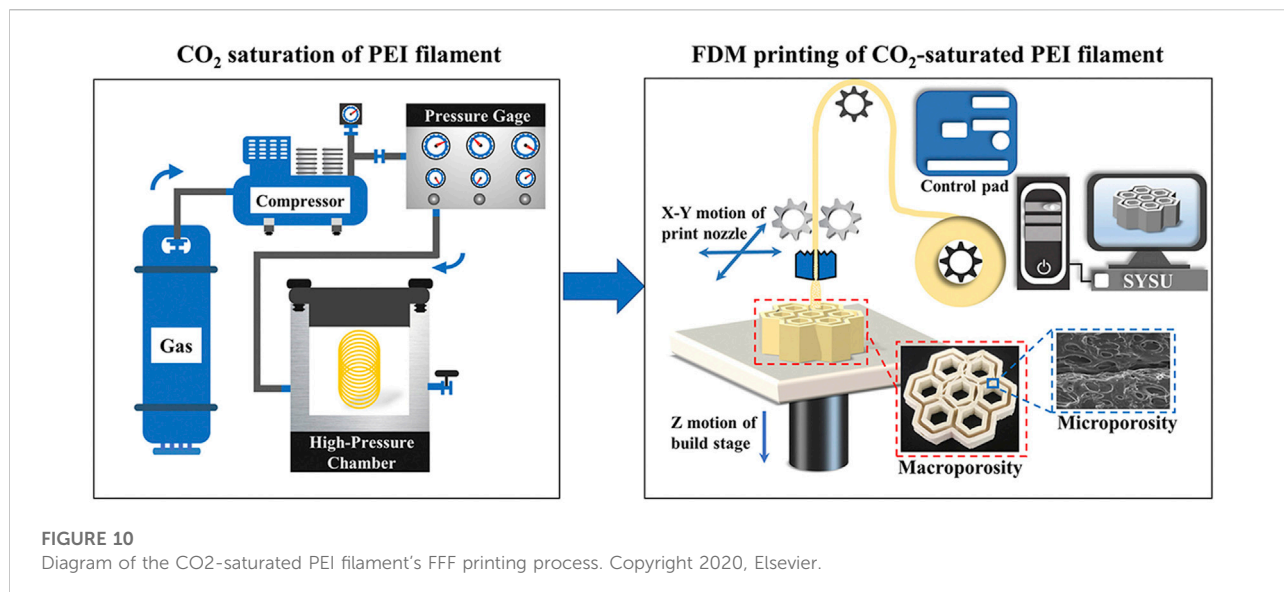
3.4 In-Situ foam 3D printing

In-situ foam 3D printing is the technique that properly merges the foaming and fused filament fabrication processes. Despite in the early stages of study and not yet fully established, this foam 3D printing technique appears to be the most successful way to produce foamed printed structures (Nofar et al., 2022). There are now two proven techniques for *in-situ* foam 3D printing, with the key distinction being whether a single-phase polymer or a gaseous solution is reached before cell nucleation and growth (Kalia et al., 2022). Unexpanded filaments containing blowing agents, either physical or chemical blowing agents, are prepared in the first technique.

Thermally expandable microspheres (TEMs) can be used to 3D print *in-situ* foam without the need for extra gas impregnation (Cai et al., 2021). TEM has also been found to provide a more homogeneous porous structure in conventional foam operations like as extrusion and injection molding when compared to alternative foaming techniques (Peng et al., 2013; Kmetty and Litauszki, 2020). This method may be able to address the aforementioned difficulties without the need for any extra preprocessing, postprocessing, or specialized 3D printing equipment (Contreras et al., 2020). In a recent study, Andersson et al. (2021) looked into the mechanical strength, micromorphology of *in situ* foam 3D printed using PLA and TEM-ethylene vinyl acetate masterbatch. However, the reported foams had substantial differences in densities, brittleness, and rough surfaces, which can be related to the formulation of the material as well as the lack of homogeneous TEM dispersion (Andersson et al., 2021). They also showed nonuniform cellular architecture.

In addition, the second *in-situ* foaming method involves foaming the extruded filament by means of an external CO₂ gas. The filament exits the nozzle during printing, and foam expands as a result of changes in the thermodynamics. As shown in Figure 10, Li et al. (2020) reported using polyetherimide and polylactic acid (PLA) filaments to manufacture hierarchical porous portions that were impregnated with CO₂ gas. Zhang et al. (2022) offered a simple solution by combining 3D FFF printing with supercritical microcellular foaming to address the primary obstacle for tissue-engineering scaffolds with hierarchical topologies. As seen Figure 11 (Zhang et al., 2022), the flexibility of additive manufacturing design results in pores are larger than microns due to layer stacking, whereas microcellular structures result in pores smaller than microns due to foaming. *In-situ* foam 3D printing requires an additional stage of gas impregnation before printing and the gas-saturated filaments commence to release gas as soon as they are removed from the high-pressure chamber, which is one of its biggest advantages. As a result, the first barrier is generating a homogeneous polymer matrix from a physical blowing agent, and the second barrier is handling and printing filaments that have been impregnated with gas.

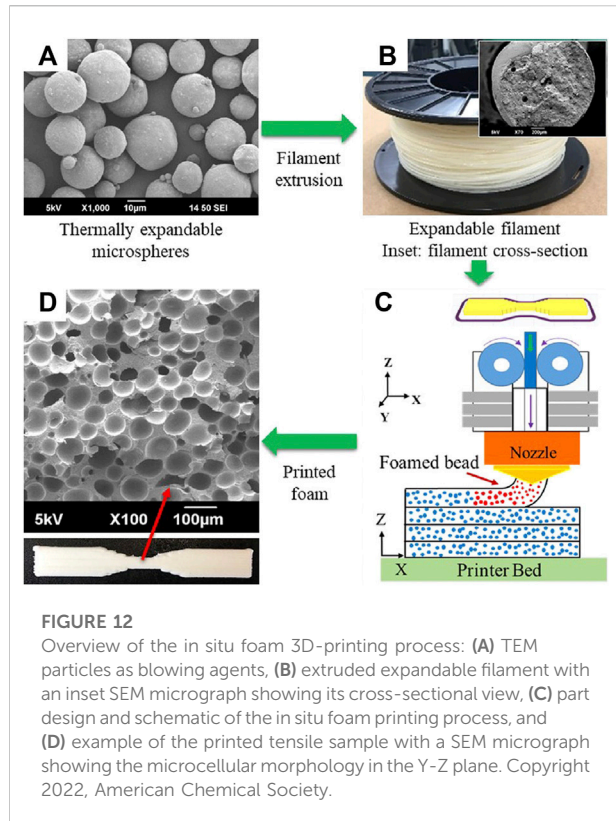
To avoid the issues of low melt strength, poor foam expansion ratio, low cell density, and uneven shape of big cells caused by the use of gaseous or chemical blowing agents, special printer systems or pretreatment processes need to be developed. (Damanpack et al., 2021). As shown in Figure 12, PLA was employed as the feedstock material along with a polyethylene carrier, two weight percent triethyl citrate (TEC) plasticizer, and zero to five weight percent acrylonitrile-based TEM (Kalia et al., 2022). An improved extrusion procedure was used to create the unexpanded filaments, and then a commercially available printer was used to 3D print foam in place (Kalia et al., 2022). The degree of foam densities and TEM content was connected with the microstructure, cellular morphology, density, thermal and mechanical properties of the printed foams.



4 Summary and trends in 3D printing foams

Overall, the combination of additive printing with polymer foam opens up new possibilities for the production of lightweight goods with complex structures and hierarchical features. Depending on the shape of the created foamed part, we can also classify the first two processes as pre-foaming, the third as post-foaming, and the final as *in-situ* foaming. Pre-foaming must use foamed filament as the raw material for additive

manufacturing, limiting the range of honeycomb mesh structures that can be obtained and also risking loss of structure during the printing process. Complex post-processing stages, high pressure-reducing device requirements, and limited expansion may be problems for post-foaming methods, which retouch the parts after printing. On the other hand, *in-situ* foaming is the latest approach that matches perfectly with foaming and FFF process. However, obtaining a homogeneous and stable polymer/gas solution *via* the foaming agent during the material extrusion process is difficult. The



approach may result in inhomogeneous cell nucleation, poor vesicle density, uneven cell structure, and other problems.

The problems that arise in the use of gas or chemical blowing agents can be avoided by developing special printer systems or pretreatment processes. However, the current 3D printing foaming still has many shortcomings and defects, and the future direction of development may focus on the development of filament-free method by free-form technology. Establishing parallel strategies for thermoplastic printing and foaming to overcome the limitations of thermoplastic material selection, uncertainties caused by inhomogeneous dissolution of foaming agents. This method eliminates the manufacturing process of filaments and injects

the foaming agent directly into the extruder barrel, thus achieving the integration of extrusion foaming and foaming injection molding.

Author contributions

LW: Funding acquisition, conceptualization, reviewing, project administration. BS: Methodology, literature search and sorting, writing.

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Conflict of interest

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