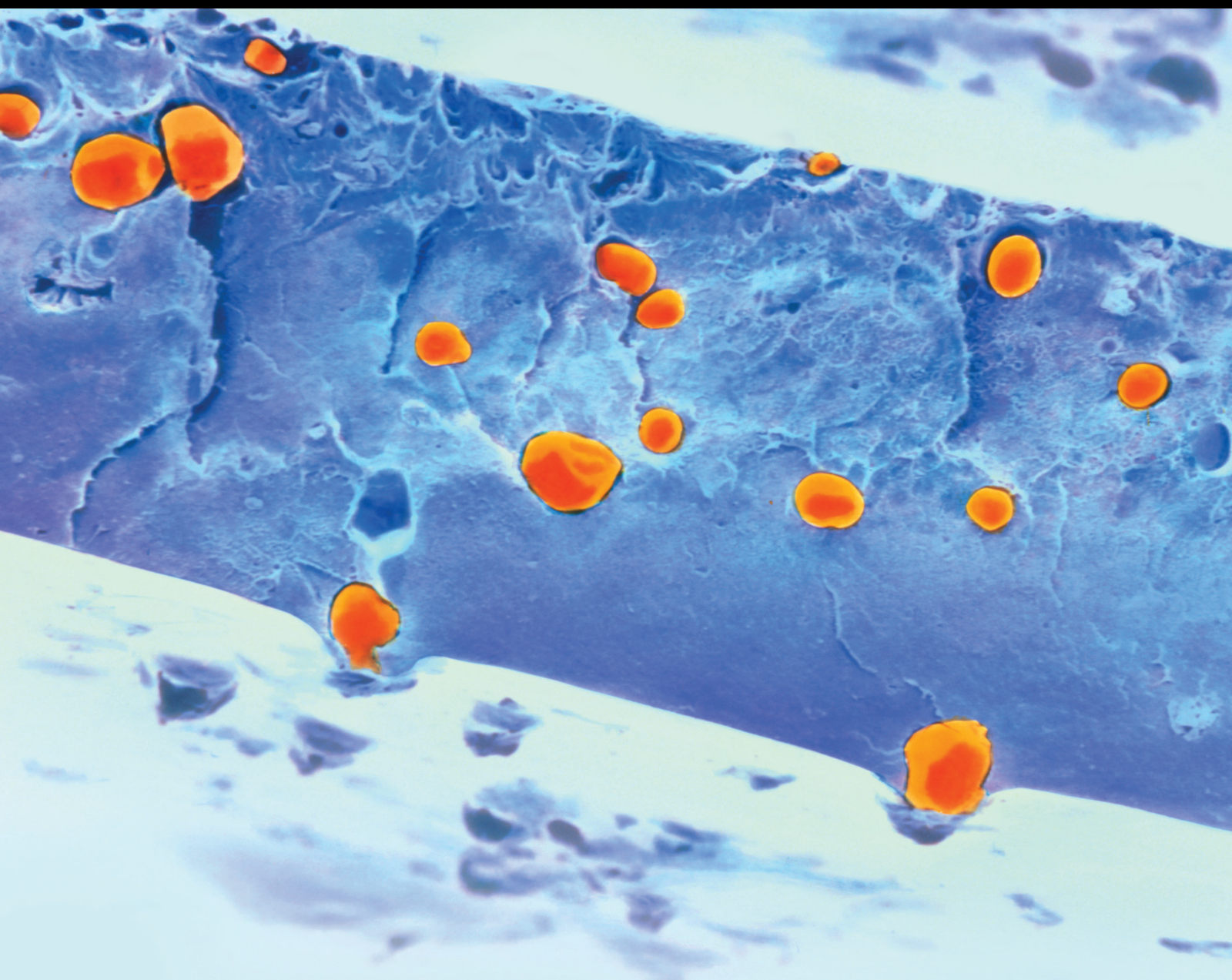


Synthesis and Applications of Biopolymer-Based Advanced Nanoporous Solids

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Review Article

Bioinspired Techniques in Freeze Casting: A Survey of Processes, Current Advances, and Future Directions

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Freeze casting, popularly known as ice templating or freeze gelation, is a mechanical method to fabricate scaffolds of desirable properties and materials. Aerospace engineering, the healthcare sector, manufacturing department, and automotive industries are the different fields where freeze casting has been used. Bioinspiration refers to the translation of biological systems into new and innovative creations. Bioinspired materials are extensively used in freeze casting methods such as ceramide, spines of porcupine fish, and collagen. Due to the tunable properties and production of complex structures with ease, biomaterials have found numerous applications in the ice templating method. This review rigorously explains the freeze casting process and the effect of thermal conductivity, stress, and electrostatic repulsion on the porous materials. Also, we have discussed the different biomaterial polymers used in freeze casting along with different methods involved.

1. Introduction

Bioinspired manufactured products are inspired by natural processes which surpass the capabilities of conventional fabricating. Freeze casting was used to produce lamellar structures with concentrated colloidal solutions using complex parameters and structures. The processing variables used were composition, freeze rating, and manipulation of freeze casting materials [1]. Due to the ability to construct biomimetic materials, the versatility of freeze casting used a physicochemical process to control the colloidal suspensions through architectural controls. Material development with driven procedures is utilized to form the permeable/porous designed material with lightweight and stiffness. Biomimetic materials were fabricated using the freeze casting process

that creates complicated scaffolds and high-performance and durable structures by controlling the slurry properties [2]. These biomaterials are the kind of materials that help repair and replace the damaged tissues and initiate the healing process with the help of chemical and physical processes. These biomaterials in the discussion are generally of two types—natural and synthetic [3]. Natural biomaterials, such as collagen derived from bones and teeth, chitosan from crustaceans, alginate, and gelatin, are available in the environment and cannot directly contribute to our needs. However, the essence of these natural biomaterials can be obtained by creating artificial materials that mimic the original functions. These are the abovementioned synthetic materials [4]. Few examples of these synthetic materials are polyesters, polyphosphazene, biomimetic nacre, etc., which

are fabricated by freeze casting ceramic-polymer scaffolds. Creating ceramic-polymer scaffolds is not done by making ceramic-polymer slurries but rather by making ceramic scaffolds and infiltrating them with molten polymer matrix. The combination of alumina as a ceramic and PMMA (poly(methyl methacrylate)) to create nacre is mostly explored as it generates properties such as high bending strength and fracture toughness which are considered ideal for many biological applications [5].

Biomaterials also play a vital role in tissue engineering as they are potential substitutes to natural materials. These artificial tissue scaffolds create an ideal porous environment to support the growth and attachment of natural tissue cells within them. Biomimetic nacre is an excellent material with its applications in many industries, especially in the biological industry, to produce support for self-healing of bones and remodeling [6]. Various researches done on biomimetic materials are studied thoroughly and analyzed, and some path-breaking research is discussed exhaustively in the upcoming sections. After going through many previous works, the biomaterials that are currently in use are identified and tabulated, explaining their nature, properties, and advantages. Some of these biomaterials are nacre, hydroxyapatite, chitosan, xyloglucan, etc. Each of these biomaterials will also be discussed one by one in detail [7].

Freeze casting (or ice templating) is a simple process used to create porous scaffolds of polymer or ceramic materials, which have gained significant attention in the past few years due to their applications in various fields such as electrical, thermal, biological, and structural, each of which will be discussed in the different sections [8]. Freeze casting can produce near-net-shape parts used in many industries like automobile, aerospace, construction, and biobased industries. Freeze casting involves many steps such as creating a ceramic or polymer-based slurry, freezing that slurry by inducing a temperature gradient in the desired direction, subliming the solidified slurry, and finally sintering to densify the walls [9]. Although water is the most used solvent in the freeze casting process, it is not the only solvent that can be used [10]. Various other solvents such as camphene, tert-butyl alcohol, or camphor-naphthalene can also be used. The solvent to be used is selected according to the type of particles involved in the process. These solvents are extensively discussed in the coming sections. A uniform slurry is necessary for any successful freeze casting process and can be achieved by adding additives and binders such as glycerol, gelatin, and polyvinyl alcohol [11]. There are various types within the freeze casting process, such as magnetic freeze casting, unidirectional freeze casting, and bidirectional freeze casting, which have their separate applications and are also widely used along with the conventional freeze casting process [12, 13]. This paper primarily focuses on some of the recent developments made on the freeze casting process by using bioinspired materials.

2. Understanding Freeze Casting

Freeze casting is a low-temperature process, popularly known as freeze gelation. Based on the solidification and

sublimation of solvent that allows obtaining a porosity of controlled size and direction (Figure 1).

In 1954, freeze casting was used to fabricate components from refractory powder, and then, it produces near-net-shape parts that are easy for sintering and machining. This casting has denser ceramic parts with more acceptable depiction of mold [15]. For solvents, various materials can be used. Still, most commonly, water is used as a solvent for multiple reasons such as ease to convenience and ice crystals with unique morphology and porosity, which is beneficial if adequately controlled and capable of different functional additives [16]. Due to its adaptability, freeze casting is applied to various materials such as polymers, metals, and ceramics. Structure formation is the main attraction of this process, which depends on physical interaction and versatility [15, 16].

The liquid in the material is frozen, solidifying and separating the solid particles. It segregates and templates the particles into a unique pattern. After the liquid phase gets fully hardened, the solvent gets removed via sublimation. Sublimation is a process that transforms the solid phase ultimately into the vapor phase without entering into the liquid phase. When the liquid gets entirely removed, a unique porous structure is formed [17].

The first step in freeze casting is to create a suitable slurry (Figure 2). Creating a slurry means dispersing the part material (ceramics, metals, polymers, etc.) particles in the solvent medium. This is a crucial step, and care needs to be taken to correctly disperse the material particles in the solvent [17]. For this to happen, plasticizers like phthalates or phosphates are used along with dispersants such as ammonium citrate and sodium citrate [18]. The next step is the essential part of this process because it determines the porosity of the final part. In this step, the whole system containing the slurry is cooled below the freezing points of the solvent, and crystals of the liquid are formed due to rapid solidification. The material particles are rejected by the solidification and cluster/concentrate around the solidified region and are entrapped between the crystals. The mold is designed so that it can accommodate the changes in volume due to solidification. In the third step, the solvent is sublimated or changed into a gaseous state by keeping the sample at low temperature and low-pressure conditions according to the properties of the solvent. For this sublimation to take place, equipment such as a freeze dryer is used. Finally, sintering is done to the resultant porous body by applying standard sintering methods like ceramic sintering, electric current-assisted sintering, and pressure-less sintering [19]. While freezing, three different phases are to be expected. The first phase is the pure ice phase and then comes the second phase, which is concentrated solute particles in water. The final phase is concentrated solute particles along with porous ice. Freezing conditions modify microstructure homogeneity and pore morphology by varying the solidification behaviors of dispersing media and the particle hindrance at the solidification fronts. Properties of freeze cast samples are solid loading and particle size [11]. Magnetic freeze casting is a process where an external rotating magnetic field is applied, and composite ceramic scaffolds with volute structures that mimic its tusk square measure are developed [5]. Under a magnetic field depending upon the given magnetic properties

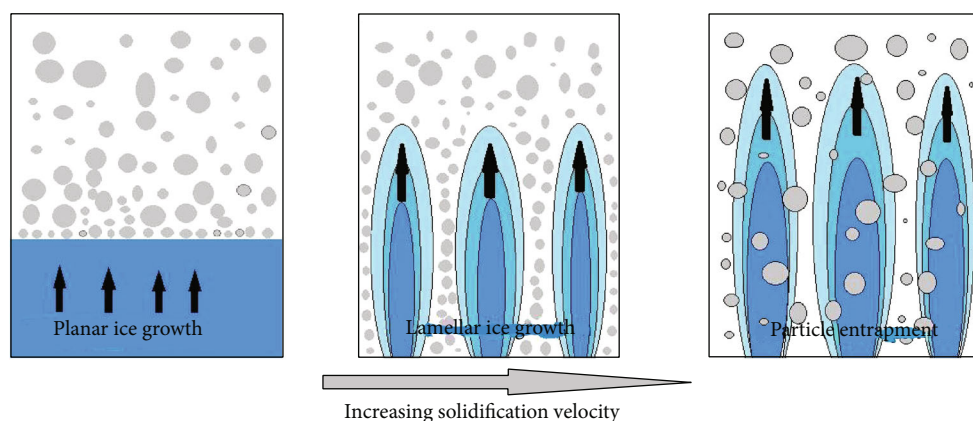


FIGURE 1: Solidification in freeze casting [14].

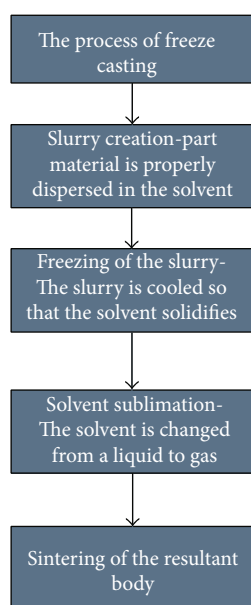


FIGURE 2: Process flowchart.

and the colloidal system, the scaffolds produced are either lamellar walls or directionally aligned bridges. Under electric fields, scaffolds with dual-aligned microstructures in the field and freezing directions are produced. Under acoustic fields, scaffolds are created with varying densities, and patterns are produced [20]. The major factors which affect microcellular ceramics are the density and size of the particles, the shape, and the distribution of sizes. This affects the intermolecular reactions between the solute particles and solution, which modifies the freezing properties and the microstructure. Cry protectants like propylene glycol, glycerol, ethanol, and dimethyl sulfoxide are used to cut back the consequences of substance dispersion and crystallization size on the action of water in ceramic-based slurries [21]. The next sections go through these substances in depth.

Oscillations in the phase-field model can be drastically reduced by using a generalized single step single solve (GSSSS) time integration method at its interface due to thermal fluctuations [22]. The organic phases should be

removed entirely before the alumina walls are sintered to produce the desired porous ceramics and dense ceramic networks void of defects. For this camphene, a well-known organic plastic crystal is used [23]. 3D aerogels such as graphene-based aerogels are exceptionally lightweight and show extraordinary mechanical properties owing to their elasticity, good porosity, and pore channels created by the interconnected sheets of graphene [24]. Ductile fabrics have reduced stiffness and strength while providing extra crack bridging and more strain to failure after initial cracking. When compared to porous ceramics, which are purely made of freeze casting, ceramic-fabric composites show greater fracture tolerance, work of fracture, mechanical properties, and strain to failure because of their crack bridging and deflecting properties. Properties observed were fabric-reinforced epoxy layers, properties of the reinforcing fibers, strength and stiffness of the porous ceramic layers, and properties of the interface [25] (Table 1).

2.1. Solvents Used in Freeze Casting. As shown in Figure 3, the solvents used are as follows:

- (a) Camphene: 2,2-Dimethyl-3-methylene norbornane or camphene, in short, is a colorless crystalline carbon compound with a molecular formula of $C_{10}H_{16}$. It is moderately flammable when heated at high temperatures and emits irritating fumes of acrid smoke [27]. It has a characteristic odor similar to camphor. Camphene is a slick organic solvent in the ice templating process which exists in the state of liquid at room temperatures. It solidifies at temperatures around 43-48°C, has a melting point around 51-52°C, and has a boiling point at around 160-162°C. Camphene provides dendritic porosity with highly branched dendritic crystals. This is because temperature gradients near the marginal region tend to decrease faster, and hence, the dendritic crystals are developed in various crystallographic directions [28]. Usage of camphene can be at its own risk. Proper precautions need to be taken while handling camphene. Its smoke irritates the nose, eyes, and throat and can lead to severe

TABLE 1: Effect of the change on the porous material.

Property changes	Effect of the change on the porous material	Ref.
Increasing thermal conductivity and residual stress	Crystal morphology transition takes place due to temperature gradient	[26]
Electrostatic repulsion steric stabilization	Increases particle dispersion	[26]
Particles of the material are large	It increases pore size and porosity	[26]
Increasing freezing temperature to freezing point	More negligible effect of directional freezing Lengthy and complex ice growth appears	[26]
Keeping freezing temperature high	The low growth rate of ice crystals Low expulsion efficiency Small pore size	[26]
Keeping supercooling low	Instead of nucleation, there was a good ice crystal growth Decrease in heat transfer Few large crystals are formed	[26]
Increasing freezing time	Columnar and lamellar microstructure occurs	[26]
Decreasing porosity	Increase in suspension solid loading Large surface area High surface curvature Increases nucleation site Many small pores	[26]
When particles of the material are small		
$V_f > V_c$ V_f : ice front velocity V_c : critical velocity	The concentration of particles decreases Ice crystal size increases	[26]
Decreasing suspension solid loading	Porosity increases Pore size increases	[26]
Increasing solid loading	Increase in particle expulsion resistance The growth of dendrites is drastically hindered from the liquid phase	[26]

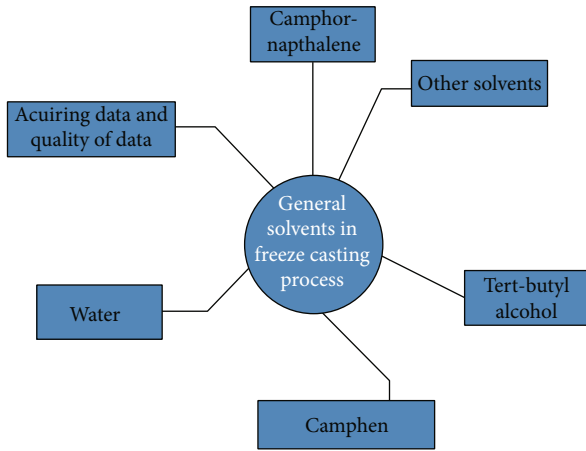


FIGURE 3: General solvents.

headaches or loss of consciousness when inhaled in large amounts. Also, camphene is hazardous to the environment. Even though it is highly insoluble in water, camphene is highly toxic to aquatic or marine life systems and has long-lasting effects

- (b) Water: Water is undoubtedly the most used solvent in the freeze casting process. As it is widely known, water exists as a liquid at room temperatures, has a freezing point of 0°C, and has a boiling point at 100°C. When converted to ice, water has the unique property of rejecting or repelling suspended particles in the

medium. This property is the main essence of the freeze casting process. When it comes to water-based slurries, the process starts with rapid freezing of the water molecules followed by the nucleation of the ice crystals [29]. Then, the rate of solidification gradually decreases, and a lamellar growth of ice crystals is observed. While this is happening, the solute particles are constantly being rejected by the advancing ice crystals. When the solidification is complete, the mold contains long, vertically aligned, and sometimes branched lamellae which alternate between solute walls and solvent (ice) crystals [15]. The usage of any other chemicals such as camphene or tert-butyl alcohol involves a certain amount of risk because of their toxicity and environmental concerns. At the same time, water is nontoxic all along the process [10]. Also, water is highly available and easy to handle, which makes it one of the most favorable solvents that can be used for the freeze casting process

- (c) Tert-butyl alcohol: Tert-butyl alcohol (TBA) is similar to camphene with respect to its physical properties. Like camphene, it is a colorless crystalline solid and has a similar odor (camphor-like). Tert-butyl alcohol has a melting point at 17°C and a boiling point of 118°C. Therefore, TBA exists as a liquid at room temperatures. TBA is relatively less toxic when compared to camphene. It has a low molecular weight and can readily sublime [30]. This particular solvent can help accelerate the freeze-drying process

because it can sublime rapidly due to its high vapor pressure. TBA also ensures that the remaining solute material after sublimation does not collapse due to its rapid sublimation. When frozen, TBA forms loosely packed, small, and pointed crystals. When these crystals sublime, it leaves behind a highly porous matrix decreasing the resistance of the partially dried solids to further drying. Primary and secondary drying are simple, efficient, and rapid when TBA is used as the solvent because it shows meager resistance towards vapor transfer and has a relatively larger surface area [31]. TBA also has a high viscosity, due to which it has lower viscous flow during the freezing process. The collapse of the resultant part material is avoided due to this property. TBA can sublime faster than water owing to its low intramolecular forces and high surface area. Even though TBA is relatively safer compared to camphene, precautions are still necessary because it is flammable. It is also irritant to the skin and eyes, and high doses can have sedative or anesthetic effects

- (d) Camphor-naphthalene: One more important solvent that is often used as a solvent is camphor-naphthalene. This is a binary compound of camphor ($C_{10}H_{16}O$) and naphthalene ($C_{10}H_8$). This solvent is used in the freeze casting process to produce denser materials and sublime faster than water. Compared to water, this solvent can be used in comfortable process conditions, and the overall process is less complex [32]. Camphor-naphthalene is successful in producing denser materials because of its low viscosity and freeze retraction mechanism. This solvent has a relatively high melting temperature and vapor pressure, which means the sublimation can freeze at milder conditions [33]. Due to these properties, this solvent is used in producing ceramic tiles in ambient environments

2.2. Additives Used in Freeze Casting. Additives incorporate the spatial redistribution in the final material and ensure continuous release in the body in antibiotics. Additives are used to control dispersion and maintain stability during the suspension, change the solvent phase morphology during the solidification process, and maintain high strength during and after sublimation [16] (Table 2). It manipulates the roughness and thickness of ice crystals which controls structure at micro- to nanolevel to fabricate biomimetic systems. There are mainly two additives: (1) binder and (2) powder dispersant. Binder provides sufficient mechanical strength to body structure and avoids collapse. Dispersion ensures the stability of the slurry. Additives can also act as structural agents. The commonly used additives are glycerol, polyethylene glycol (PEG), polyvinyl alcohol (PVA), gelatin, polyacrylamide, polystyrene, sucrose, etc. [11, 17] (Figure 4).

The additives are discussed as follows:

(1) Glycerol

Glycerol is the most commonly used additive because adding glycerol as additives increases the viscosity of the slurry.

Glycerol is also called an antifreeze agent. It is inexpensive, has a low freezing point, is highly soluble in water, and is primarily nontoxic. Liu et al. studied that, in addition, glycerol decreases the volumetric expansion of water to 7.4% from 9% with 10 wt.%. The volume of glycerol alters the freezing behavior of water. The suspension viscosity of glycerol depends on powder particles used in suspension and is also used as a lubricant between particles [11]. After adding glycerol, a flowable break is obtained, homogeneous microstructures are formed, and the uniformity of ice crystals is also improved. Glycerol is used for microstructural adjustments and also to reduce the freezing point of particles. There is a possibility of adding glycerol with other additives such as PAA and ammonium polymethacrylate. The glycerol amount should be appropriately added to get unique homogenous microstructures. Because of its low-pressure volume, glycerol should be after the casting process due to interaction between components and glycerol in slurries which improves the mechanical properties of ceramics. It is mainly used to avoid defects during the crystallization process and ensure that the ice crystal growth is always in control [34].

(2) Polyethylene glycol

Polyethylene glycol (PEG) is also widely used as an additive in the aqueous-based freeze casting process, and it affects the cast alumina microstructures and acts as a binder material. PEG is a water-soluble polymer that is added to increase the strength of ceramic. Before the sintering process, it removes the solid-liquid interference and rejects the growth of ice crystals [35]. It also directly affected the solidification process and was used to improve green strength. This process leads to a finer microstructure. These kinds of additives jeopardize the system's morphology by reducing the diffusion of water or producing more fine crystals. This additive is added in a slurry to decrease equilibrium at solidification temperature, and the interface between liquid solidification gets cooled, making finer growth of dendrites. PEG affects pore size, wall thickness, secondary dendrite spacing, and colony size [36].

(3) Gelatin

Gelatin is a natural material that comes from animal bones and skin. Gelatin is used to modify microstructures and adjust pore morphology, and it is a hydrolyzed form of collagen. The main advantage of adding gelatin is it rejects HA particles in ice crystals to form lamellae and wall porous microstructures [26, 37]. Adding 2 wt.% of gelatin in 50 wt.% HAP ceramic slurry shows structure changes from lamellar to homogenous pore. Gelatin addition affects the morphology and pore size of hydroxyapatite (HAP) particles, the viscosity of the ceramic slurry, shrinkage, and porosity of the final ceramic obtained. Gelatin scaffolds are prepared by both freezing castings and freezing dying methods [38]. It negatively affects mechanical properties, but hydrophilic structure and cell adhesion improvement cause good results. Gelatin is removed by using the sintering process. Therefore, it cannot affect the final composite. Al/SiC composite, without incorporating gelatin, shows discontinuous ceramic

TABLE 2: Effect of the additive on the porous material.

Additives	Effect of the additive on the porous material	Ref.
Glycerol molecules	It decreases the growth of ice crystals which in turn reduces the expansion of ice	[26]
Increasing glycerol concentration additive in liquid	The viscosity of liquid increases	[26]
Increasing dioxane concentration additive	A large number of delicate pores will be there in a solid sample, and a large number of dioxane crystals in suspension will be present	[26]

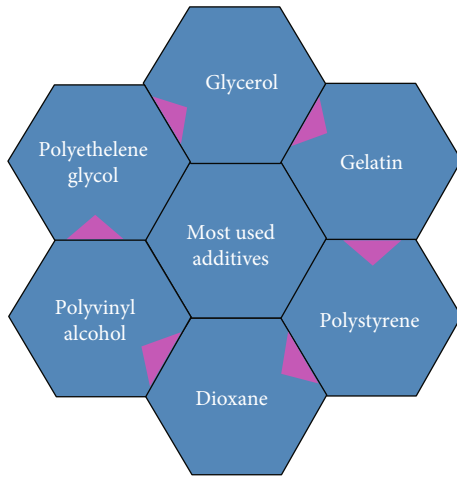


FIGURE 4: Most used additives.

lamellae, separated by the AI phase. Biomimetic titanium alloys were produced by Ti-6Al-4C powder, while gelatin is used as the binder [38, 39].

(4) Polyvinyl alcohol (PVA)

Polyvinyl alcohol (PVA) is generally used to change the pore morphology in the directional freeze casting process. PVA expels accumulated particles which block the growth of crystals. During the freezing process, PVA gets combined with particles and suppresses the growth of crystals. Adding PVA into HAP slurry changes pore morphology into lamellar pores. Pore connectivity and open porosity are improved because of adding PVA [40]. The open porosity and total porosity are the same even after adding PVA in HAP ceramic. The open porosity is enhanced after the addition of PVA, and the pore membrane gets interconnected. A soluble polymer such as PVA improves the mechanical integrity of the ceramic body. Polyvinyl alcohol is biodegradable, chemical resistant, highly water-soluble, and biocompatible, widely used for biomedical applications [41, 42].

(5) Dioxane

Dioxane is another additive for aqueous-based directional freeze casting. Dioxane can create a unique microstructure from lamellar to cellular pores. Dioxane breaks the hydrogen bond of water and forms stable dioxane-water complexes, which favors to form columnar structure. Dioxane can also affect the pore size. If dioxane concentration increases in suspension which gives an ample amount

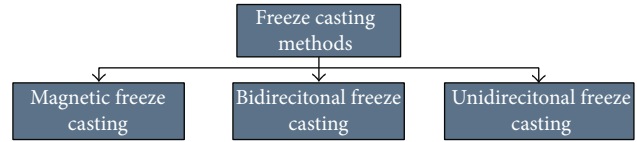


FIGURE 5: Types of freeze casting.

of dioxane crystals, dioxane evolves microstructure from more minor to cellular [26].

(6) Polystyrene

Polystyrene (PS) is an organic binder used to dilute camphene/alumina slurry. They fabricate samples with unique pore strength. Adding PS in the slurry gives exceptional viscosity for freeze casting. After incorporating PS polymer into camphene/ceramic, the power of the green sample gets increases. The PS binder and dispersant should be eradicated after the alumina walls are sintered [23].

2.3. *Types of Freeze Casting.* As shown in Figure 5, the types of freeze casting are as follows:

(i) Magnetic freeze casting

Magnetic freeze casting is a unique method to fabricate anisotropic ceramic scaffolds with high porosity and an alignment of particles in various directions. In this particular process, a rotating magnetic field with low magnitude is applied perpendicularly to the crystal growth direction for the sole reason of manipulating the magnetic particles suspended in the slurry to create many types of pore structures [12]. For this to happen, diamagnetic or paramagnetic ceramics are mixed with materials that can easily be magnetized, such as Fe_3O_4 nanoparticles, to help the alignment. It has been observed that diamagnetic materials magnetize opposite to the field direction and paramagnetic materials magnetize parallel to the field direction [43]. Magnetic freeze casting creates interconnected pore channels that can be aligned in two different directions, namely, in the crystal growth direction and in the magnetic field direction. Biomaterials created using these types of multi-directional order possess many unique and desirable properties such as light weightiness, high strength, and multifunctional. It was found in the later studies that using magnetic freeze casting results in reduced pore sizes and smaller crystals in diamagnetic solvents such as water. This is because the magnetic field weakens the hydrogen bonds in water molecules. As the magnetic field strength increases, this effect is more predominantly seen [44].

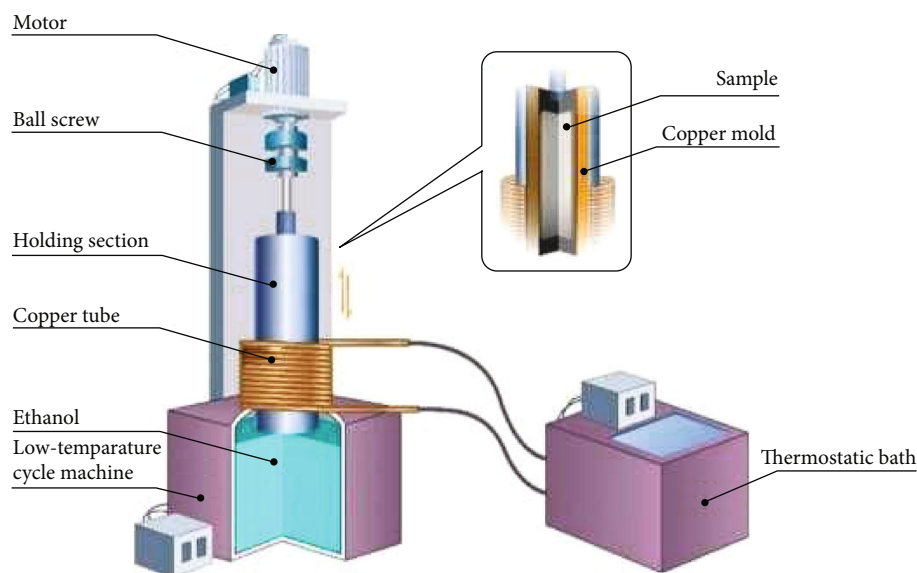


FIGURE 6: Schematic diagram of unidirectional freeze casting [50].

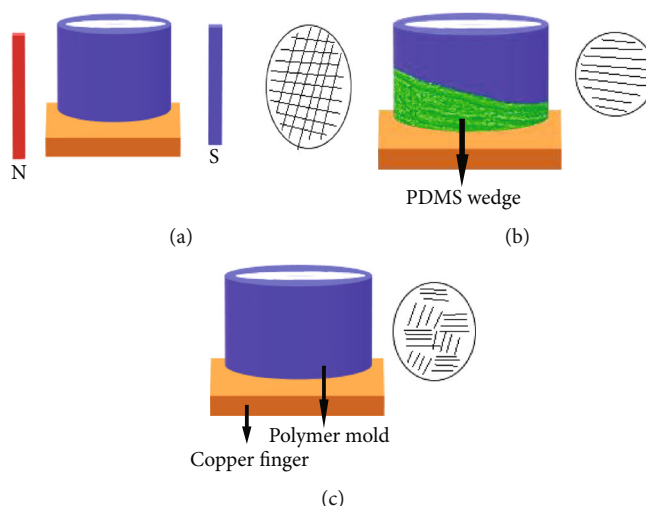


FIGURE 7: (a) Magnetic, (b) bidirectional, and (c) unidirectional microstructures of scaffolds created by various freeze casting techniques.

(ii) Unidirectional freeze casting

Unidirectional freeze casting is a process that is used mainly to fabricate lamellar porous solid structures expelling particles by a solid-liquid interface during the freezing process (as shown in Figure 6) [45]. This freeze casting method is used to fabricate bone-like anisotropy, graded porosity, and interconnected scaffold structures. This method controls the anisotropic solidification of solvent and water with the sol-gel solution, followed by sublimation. Numerous techniques such as emulsion template, electrospinning, gas forming, and freeze casting have been introduced to fabricate porous scaffold material. However, this technique is one of the few techniques which give promising results. This freeze casting technique's main advantage is that this process can be performed in a homemade colony chamber with a heat exchanger. This heat exchanger is made of aluminum in rectangular plates, and they get cooled by liquid nitrogen.

In this freeze casting, the gradient and multiphase microporous scaffolds are prepared from type 1 collagen and gelatin without adding hydroxyapatite (HAP) [46]. High porous LiFePO_4/C cathode for Li-ion batteries with precise cellular pore and lamellar structures is fabricated using the unidirectional freeze casting technique [47]. A porous titanium alloy (Ti-6Al-4V) with high strength to modulus ratio reinforced with SiC was fabricated [45]. Freeze casting of HAP under unidirectional conditions shows the temperature gradient is created in the vertical direction, and the crystals were also growing in the same direction [48]. Porous ceramics with a typical gradient structure and high increase in pore size are prepared by unidirectional freeze casting [49].

(iii) Bidirectional freeze casting

Bidirectional freeze casting is an environmentally friendly process that makes bulk mimic natural materials

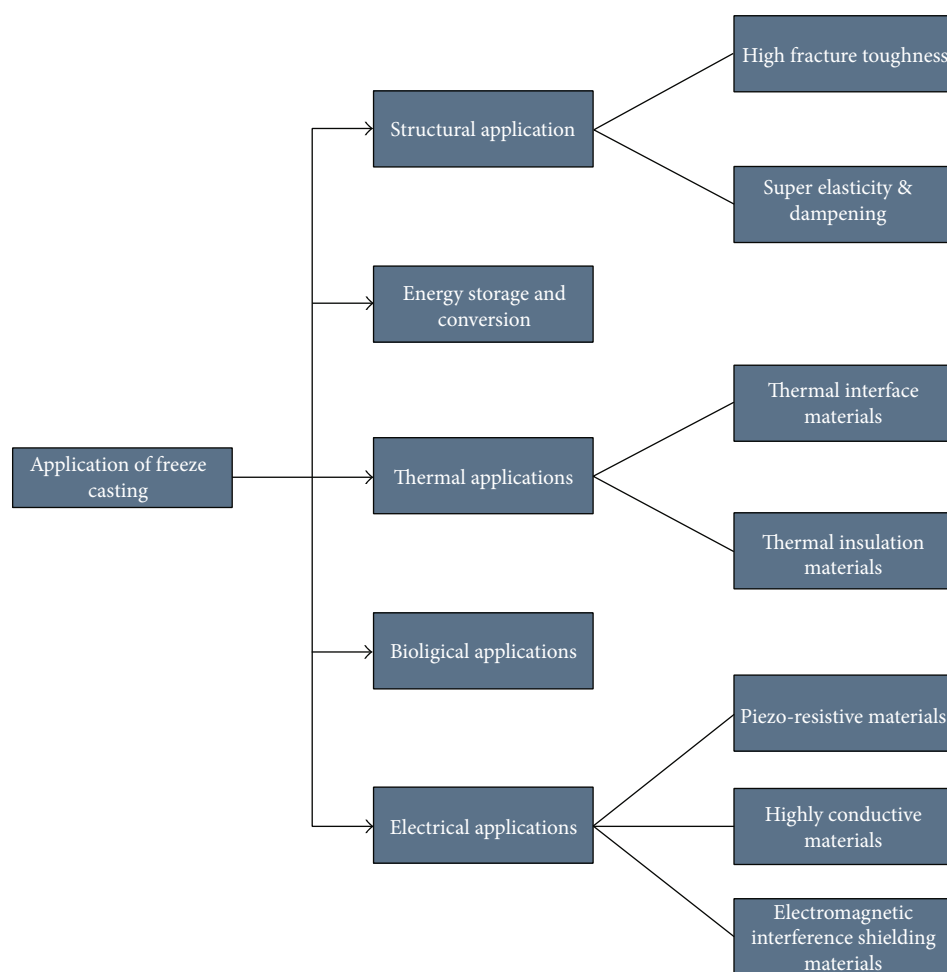


FIGURE 8: Applications of freeze casting.

in multiple scale lengths [51]. In bidirectional freeze casting, the thermal gradients are imposed in two directions, and the microstructures are directed with the crystal growth. Compared to the traditional freeze casting method, this process can synthesize metallic/ceramic walls with ordered arrays parallel in the transverse cross-sections. Bidirectional freeze casting is efficiently used in creating lamellar structures aligned in a long range. Using bidirectional phase change technique and uniaxial pressing and in place polymerization, poly(methyl methacrylate) (PMMA) composites are developed by processing massive aligned lamellar ceramic scaffolds. Though this process is used for metallic and ceramic materials, it is mainly used to create ceramic-based nacre-mimetic composites that can be used for bone reinforcements and toughening. Bidirectional freeze casting is also employed to create high sensitivity sensors with excellent antifatigue properties [13]. These sensors are usually made using aerogels created by bidirectional freeze casting and can withstand more than 6000 times their weight and fully recover their original shape after cyclic loading. This process is also used for creating inorganic fillers made of thermally conductive composites. It is used to successfully create 3D conductive systems made of nacre-mimetic materials for better thermal conductivity. The bidirectional freeze casting

technique was used to produce lamellar ceramic scaffolds. This was done under a double temperature gradient. The ice crystal grew in the aligned direction due to the binder concentration, which fabricated the porous materials. The conventional freeze casting technique was used to achieve the ceramics. The apparatus consisted of cooling rods, as shown in Figure 7. These were maintained at a constant temperature, while the lower layer varied between three cooling layers. The PDMS layer covered the copper mold to generate bidirectional temperature.

2.4. Applications of Freeze Casting. Freeze casting has come a long way since its recognition in the early 2000s. The process, which was initially used only to fabricate limited products, is now being used to create a wide range of products in various applications (Figure 8). Such major applications are discussed in the current section.

(i) Thermal applications

The aerospace and space industries are always in ardent need of highly productive thermal insulating systems. These systems can be well fabricated utilizing freeze casting techniques such as the sol-gel method or supercritical drying

[52]. While these systems were only manufactured using materials based on silica or other ceramics, it was known from recent researches that carbon or biomacromolecule-based materials could also be effectively used in the creation of thermal insulating systems using the freeze casting process. Freeze-cast porous ceramics are thermal and acoustic insulators, active substance delivery, electric components, filters, gas distributors, and catalysts. These materials also find applications in the clothing industry where it is used to create thermal stealth materials, insulating high-performance clothing for extreme environments [53].

Electronic devices generally have high on-chip power density. Thermal interface materials (TIMs) are an efficient way to reduce the resistance created due to the interaction of heat-generating devices and their cooling components. A more efficient thermal conductivity is produced when boron nitride or graphene sheets are used within composites made of polymer matrix while maintaining thermal insulation [14].

(ii) Electrical applications

In many applications, reducing the weight of electronic applications is very important and is one of the most desirable qualities. Ice templating can be used to fabricate highly conducting materials with extremely low specific densities. This is achieved by the porous structure of the scaffold created, which makes the product ultra-light. Graphene, nanowires, and other conductive nanomaterials are aligned in the freeze casting process to obtain bulk materials that are highly conductive with significantly less weight. Also, freeze casting nanowires or graphene networks create polymer matrix composites with high conducting properties [54]. Also, the conductors created by the freeze casting process are highly elastic to withstand any possible deformation in its lifetime [55]. Freeze cast scaffolds made of graphene, AgNWs, or SiO₂ nanofibers are also used as strain sensors such as piezoresistive sensors due to their super-elastic properties and strain-dependent electrical conductivity [55, 56]. Also, freeze casting is used to fabricate electromagnetic interference shielding materials which protect electronic devices from harmful electromagnetic frequencies [57]. The frequencies used by electronic devices are getting powerful day after day, and it is an absolute necessity that the functionality of other electronic devices is not disturbed due to these waves. Polymeric matrices and high conducting nanomaterials such as CNTs or graphene are incorporated [14]. Additional scattering or absorption of electromagnetic radiation is obtained by using foams or aerogels comprising of nanowires or nanotubes, which enhance the EMI shielding materials [58].

(iii) Structural applications

Vibration protection systems and acoustic systems for deformation and energy dissipation are developed using the freeze casting process. Energy is stored reversibly as cells are compressed, resulting in elastic deformations. The energy is constantly dissipated due to the friction in the cell walls, which results in dampening. Energy absorption efficiency and damping performance are significantly increased by creating highly ordered pore structures [59]. Also, high

strength and weight are achieved by using graphene, ceramic nanofibers, or other low-dimensional building blocks. Aligned pores created by the ice templating process can significantly improve the elastic response of the porous scaffolds and the energy absorption efficiency. Graphene aerogels fabricated by the freeze casting process are used to dissipate impact energy and acoustic insulation applications due to their low density, super elasticity, and other desired mechanical properties [60]. Also, materials with high fracture toughness are obtained by infiltration of the freeze casting process [61].

(iv) Energy storage applications

Electrodes created through the freeze casting process are usually porous and aligned and are relatively thick. Combined with high active material loading and improved volumetric energy density, these electrodes create ionic transport channels related to random porous structures [14]. Ionic conductivity can be significantly enhanced by using solid polymer composites, which can be produced by freeze casting scaffolds when used as fillers [62]. Graphene, CNTs, and other low-dimensional carbons offer good conductivity, and ceramic nanoparticles in polymer electrolytes enhance mechanical strength, thermal stability, electrochemical stability, and ionic conductivity. Freeze casting is used to create Li-ion electrodes which are mechanically robust [63]. Lithium-sulfur batteries, which have high theoretical capacities and relatively low costs, are essential and promising energy storage systems for electric vehicles. These electrodes are exclusive products of the freeze casting process. Lithium batteries are used for next-generation vehicles but have minimal charging or discharging rates. This problem can be moderately solved when the freeze casting process produces these by creating porous electrodes vertically aligned with a continuous binary network of silver nanowires. This process also fabricates graphene-based supercapacitors [64, 65]. These graphene films increase the energy and power density in the supercapacitors [66].

(v) Biological applications

Freeze casting is used to create biomaterial scaffolds such as biomimetic structures, which can tailor mechanical properties, chemical composition, and pore structure by mimicking natural extracellular matrices. Amidst many applications, research done in tissue engineering has shown the most favorable results to date. Many amorphous material systems and bioresorbable crystalline are under extensive research at atomic scales for their uses in tissue engineering [14]. Freeze casting helps in creating biomaterial scaffolds that help in bone regeneration and cell growth [67]. Many ceramics, bioactive polymers, bioglasses, and biomaterial systems can be fabricated using unidirectional freeze casting to align porous structures. These aligned porous structures imbibe favorable characteristics such as effective cell ingrowth, rapid bioresorption, and supreme strength to the scaffolds thus created [68]. When ice-templated, nanostructures such as multiwall carbon nanotubes give a wide scale of biomimetic porosity, higher strength, and high performance. Also, biocompatible polymers

are synthesized as 3D functional scaffolds by the freeze casting process. These polymers show excellent biodegradability and biocompatibility and can be exhaustively used in tissue engineering.

3. Bioinspired Techniques in Freeze Casting

Freeze casting is defined as a method to fabricate inexpensive, porous scaffolds of ceramic. It is also known as freeze gelation or ice templating [69]. The scaffold formed exhibits various properties such as high tunability and large porosity, allowing efficient transfer of cells and bioactive molecules with high mechanical strength due to complex microstructure.

Biomaterials are the materials that repair and replace the damaged tissues and initiate the healing process with the help of chemical and physical processes. It can be of two types, natural and synthetic. Natural materials include collagen derived from bones and teeth, chitosan from crustaceans, alginate, and gelatin [70]. Polyesters and polyphosphazene are few examples of synthetic biomaterials. Researchers are creating fully integrated biomaterials that can mimic the natural tissues in terms of their pore size, high vascularization and interconnectivity, and structural and mechanical properties.

The biomaterials used in freeze casting comprise a ceramic powder, water as the solvent, functional additives such as antibiotics and enzymes, and binders responsible for maintaining the morphology of the crystals [71] (Table 3).

Type I collagen is embedded with hydroxyapatite and is majorly found in bones. Bones can be of two types, compact or cortical bones, also called dense bones with significantly less porosity than spongy or cancellous bones, popularly known as hollow bones [5]. They are highly porous and are found in birds. With the help of the freeze casting technique, scientists could fabricate the artificial scaffold, reflecting the architecture of both compact and cancellous bones. For compact bones, concentric surfaces mimicking osteons were formed. Freeze gelation and polymer sponge technique mimicked the trabecular struts of spongy bones [69]. The emanated bone-like microstructures depicted great mechanical strength, better yield, and similar porosity.

Porcupine fish's spine is rich in collagen and hydroxyapatite. Like pufferfish, these fishes swell their bodies thrice the original volume to protect themselves from predators as they become difficult to swallow. However, they contain an additional layer with defensive spines providing extra protection. The spines of these species only inspire the freeze casting technique. The spines have depicted similar mechanical strength as that of natural collagen [72].

The ceramic material used in this method is made from alumina powder (Al_2O_3). Three types of freeze cast were prepared: conventional, radial, and radial-concentric. In conventional freeze cast, PVC mold was used where freezing started longitudinally in an upward direction, whereas, in radial freeze cast, a cylindrical mold of copper was used, and the formation of crystals began from the base and edges, for radial-concentric freeze casts were prepared in two steps. First, they used copper mold, which had a copper pin inside it. Freezing started from the base, outer surface, of the mold, and from the copper pin. In the second step, the pin was

removed, and the slurry was added to obtain a radial alignment. The resulted microstructures were subjected to scanning electron microscopy (SEM) to characterize and compare the radial and conventional freeze casts. They were then tested in axial compression for tensile strength, and it showed that radial casts had the maximum tensile strength. The porosity of all three casts was also measured, and it was evident that radial and conventional casts had more porosity than radial-concentric scaffolds [72].

3.1. Nacre. Nacre is a lightweight porous bioinspired material. Mostly, it is made up of 95 vol.% aragonite platelets (CaCO_3) and 5 vol.% of organic matter-like proteins which help them in strength, modulus, and toughness in the range of 80–135 MPa, 60–70 GPa, and 1.24 kJ m^{-2} . It helps in the production of natural nacre and nacre-like alumina ceramics. The main advantage of nacre is extensive mechanical strength and helps in bridging the cracks between tissues. The disadvantage of using nacre is that it restricts the sliding movement and leads to plastic deformation. Nacre-like natural material can be applied to freeze casting to increase the enhancement and develop the technique as additive production and a catalyst to promote the application [69].

3.2. Bamboo. The hierarchical structure of bamboo helps to achieve mechanical properties like bending and compression. Bamboo-like composites form Si_3N_4 . The main advantage of using bamboo is its excellent structural properties because of its high-density fibers and tubular shapes. It also provides high flexural rigidity. The disadvantage is difficult to optimize it according to the functional and mechanical requirements. The application of bamboo biomimicking material with freeze casting process is used in designing tubular structure example ureteral stents. This stent helps to drain the urine from the kidney to the bladder [70].

3.3. Epoxy. The traditional function of epoxy can be applied to the various fields, such as aerospace, electronics, and design, which is not successful in producing high-performance nanocomposite. With brick-and-mortar architecture, the nacre-like biomaterial is fabricated with epoxy under freeze casting process, producing 3D structures like honeycomb fibers, self-healing composites, and many more nanocomposites. This process is called an “inverse artificial nacre.” The composite is 4.2 times more toughness in fracture resistance than standard epoxy. Scaffolds of ZrO_2 ceramic epoxy composites compose with ethanol, butanol, and propanol as additives. The advantage is exhibiting high porosity with large interconnected pores and shows commendable variations in the microstructural properties. The disadvantage of using epoxy is that it provided considerable resistance and led to buckling mode failure, causing a decrease in strength [71].

3.4. PMMA (Poly(methyl methacrylate)). Mainly, the scaffolds will be formed by the hybrid composites. These hybrid scaffolds will work like “brick and mortar” architecture. The best example for hybrid composite is Al_2O_3 -PMMA (alumina-poly(methyl methacrylate)) which results in high bending strength and fracture toughness. The advantage is high flexural strength in the perpendicular direction

TABLE 3: Bioinspired material used in freeze casting.

S. no.	Biomaterial	Freeze casting product	Advantages	Disadvantages	Ref.
1	Nacre (composed of aragonite)	It helps in the production of natural nacre and nacre-like alumina ceramics.	Extensive mechanical strength. It helps in bridging the cracks between tissues.	It restricts the sliding movement and leads to plastic deformation.	[69]
2	Bamboo (composed of cellulose and lignin fibers)	Bamboo-like composites from Si_3N_4 .	Increases mechanical efficiency. It also provides excellent structural properties because of the presence of high-density fibers and tubular shape. It also provides high flexural rigidity.	It is challenging to optimize it according to the functional and mechanical requirements.	[70]
3	Epoxy	Scaffolds of ZrO_2 ceramic epoxy composites with ethanol, butanol, and propanol as additives.	Exhibits high porosity with large interconnected pores. Shows commendable variations in the microstructural properties.	Provided considerable resistance and led to the buckling mode failure, causing a decrease in the strength.	[71]
4	PMMA (poly(methyl methacrylate))	Al_2O_3 /PMMA hybrid material.	High flexural strength in the perpendicular direction compared to other biomaterials. They exhibit extensive toughness.	Presence of voids, promoting plastic flow, thereby reducing its efficiency.	[5]
5	KGM (konjac glucomannan)	KGM/ SiO_2 carbonaceous aerogel composite.	They show fantastic properties such as good compressibility, high thermal stability, and excellent elastic-responsive conductivity.	Optimization of the material is difficult.	[72]
6	Cellulose (plant cell wall)	Cellulose nanorod aerogels.	Promotes polymer-polymer interaction and forms elongated pores, thereby increasing the porosity.	Provides a little bit of resistance in the mechanical strength.	[73]
7	Xyloglucan (plant cell wall)		Provides structural integrity. Do not degrade due to chemical modification.	Leads to the formation of a disordered structure.	[73]
8	Hydroxyapatite	Three types of samples were prepared: (1) Nonporous sample of HA mixed with PVA (2) Microporous sample prepared using a conventional method where HA was mixed with PEG (3) Macro-microporous sample using a 3D printer	Macro and microporous samples have low relative densities, and this leads to low-cost production. Because of the use of a 3D printer, the shape and size of the pores can be easily regulated.	Achieving the desired size and shape of the pores is not possible in a nonporous sample. It also leads to irregular thermal conduction.	[75]
9	Chitosan	Carbon nanotubes are interconnected with chitosan.	They have excellent biocompatibility, high tensile strength with huge surface area, and defined shape with aligned pores.	Regulation of the structure with fewer expansion stresses is still a challenge.	[57, 76]
10	Graphene	Graphene oxide aerogels.	Formation of controlled pore structure. They exhibit unique mechanical strength with high electric conductivity.	A significant application in various researches is still negligible.	[24]

compared to other biomaterials. They exhibit extensive toughness. The disadvantage of using this presence of voids promotes plastic flow, thereby reducing its efficiency [5].

3.5. Cellulose and Xyloglucan. The scaffolds are prepared from cellulose nanocrystals (CNC) and xyloglucan (XG). The chemical properties and molecular structures of biomaterials must frequently be determined and analyzed for a variety of applications, synthesizing the plant stem tissue coordinates at various leveled structures. The cell structures situated along the stem cells are anisotropic and permeable at the tissue level. This bioinspired material is helping to

make the scaffolds without any chemicals. It is further engineered with freeze casting to produce the products in many fields such as thermal insulators, tissue engineering, and pharmaceutical and automotive components. The advantage of using cellulose promotes polymer-polymer interaction and forms elongated pores which results in increasing the porosity. A disadvantage provides a little bit of resistance in the mechanical strength [73].

3.6. Hydroxyapatite. Hydroxyapatite powder is used to prepare various slurries of freeze casting in sintering conditions which results in anisotropic and porous scaffolds and high

lamellar architecture. HAP has high load-bearing bioinspired applications in the synthesis of compact bone due to its porous lamellar strength. The three types of samples were prepared: (1) nonporous sample of HA mixed with PVA, (2) microporous sample prepared using a conventional method where HA was mixed with PEG, and (3) macro-microporous sample using a 3D printer [74]. The advantage is that macro and microporous samples have low relative densities, leading to low-cost production. Because of the use of a 3D printer, the shape and size of the pores can be easily regulated. The main disadvantage is that achieving the desired size and shape of the pores is not possible in a nonporous sample. It also leads to irregular thermal conduction [75].

3.7. Chitosan. Chitosan is used as a raw material to synthesize the bioinspired scaffolds with calcinated powder by freeze casting. The composite will reduce the processing time in synthesizing the material example to produce various raw fish powders like tilapia fish and wastewater treatment. Carbon nanotubes are interconnected with chitosan. They have excellent biocompatibility, high tensile strength with huge surface area, and defined shape with aligned pores. Regulation of the structure with fewer expansion stresses is still a challenge [76].

3.8. Graphene. A graphene sheet is used to produce bidirectional freeze casting. This helps to produce many nanocomposites like honeycomb structures. Graphene oxide aerogels are used in freeze casting. The advantage of using graphene in the freeze casting formation of controlled pore structures and they exhibit unique mechanical strength with high electric conductivity. A significant application in various researches is still negligible [24].

4. Characterization of Biomaterials

The selection of biomaterials is a very important step in the freeze casting process due to the reason that the biomaterial selected and the host tissues indulge in immunological interactions with each other and can cause patient distress, device failure, or even death. This is the sole reason why selecting an appropriate biomaterial according to the purpose is truly essential so that the material does not become toxic to the tissues. Investigating the chemical, physical, and biological characteristics of material before using it for a specific purpose is the first challenge [77].

4.1. Chemical Characterization. The chemical properties and molecular structures of biomaterials must frequently be determined and analyzed for a variety of applications. A method such as X-ray photoelectron spectroscopy is suitable for characterizing biomaterials based on the chemical and elemental compositions on their top surface itself [78]. For compound identification, infrared spectroscopy may be used. Various functional groups identify IR radiation at various frequencies, and hence, the presence of certain functional groups in a biomaterial can be identified using this method [79]. One of the first characterization methods, ultraviolet-visible (UV/Vis) spectroscopy, may be used to measure a material's absorption of UV to visible light as a

function of wavelength [80]. Mass spectrometry (MS) is a sensitive analytical method that is rapidly being used to analyze biomaterials using the mass-to-charge (m/z) ratio of gas-phase ions [81]. To identify the dynamics, conformations, and structures of biomolecules, nuclear magnetic resonance (NMR) spectroscopy can be used. This technique can be employed to get an understanding of a certain biomaterial at a molecular level [82].

4.2. Physical Characterization. Physical characteristics involve size of particles, internal microstructural features, shape, porosity, surface area, and density. One of the most common ways for imaging the morphology and microstructure of materials is to use a scanning electron microscope (SEM). In SEM, a low-energy electron beam is emitted to the material and scans the sample's surface. The use of X-ray diffraction to characterize the composition and structure of biomaterials is one of a promising strategy [83]. Transmission electron microscopy (TEM) is frequently used to provide precise information on the shape, crystal structure, and composition of biomaterials at a greater resolution than generally possible with SEM [84]. Almost any surface, be it hard, soft, conductor, insulator, natural, or synthetic, can be imaged using the atomic force microscopy (AFM). 3D features of any surface are revealed using an AFM image with spatial resolutions and can be effective in characterizing biomaterials [85]. The quantity of adsorbed inert gas such as argon, nitrogen, carbon dioxide, or krypton on solid surfaces can be used to investigate the porous structure, particle size, and surface area of biomaterials. Thus, measurements of gas adsorption can be used to characterize biomaterials [86].

4.3. Biological Characterization. The reverse transcription-polymerase chain reaction (RT-PCR) is a robust technique in vitro method that plays an important role in biomaterial research and medical science. The RT-PCR method is used to detect and compare the quantities of surface proteins and mRNA in biomaterials [87]. To identify the carcinogenic and genotoxic effects of biomaterials on the host body, carcinogenicity and genotoxicity testing is generally preferred [88]. Hemocompatibility testing is a technique for determining the harmful effects and interactions of blood with a material or medical equipment [89]. Cytotoxic effects of a biomaterial on a living body are tested by using cytotoxicity assay techniques. It was one of the most basic in vitro techniques to determine the biocompatibility of materials [90]. Some biomaterials that degrade can leach degradation products (such as toxins, corrosion products, and catalysts) into nearby tissues and organs. Hydrolytic pathways are used in the biodegradation of materials [91]. Biomaterials are implanted into the host tissue, muscle, or bone of a living creature in implantation studies to examine the harmful and pathological effects of biomaterials on tissue structure and function [89].

5. Discussions and Conclusions

This review solely focuses on a particular strategy that opens new avenues for creating epoxy nanocomposites that show

high performance and functional properties. Epoxy nanocomposites have many aerospace, electronics, transportation, building design, and biobased industries. Even though epoxy nanocomposites have many advantages, it still lacks in the area of toughness. On the other hand, nacre is a natural material that shows a brick-and-mortar structure and consists of 96% inorganic aragonite. Nacre exhibits a fracture toughness that is three times that of inorganic aragonite. Thus, by creating an inverse artificial nacre based on epoxy-graphene composite, Huang et al. have shown that the fracture toughness can be increased by 4.2 times compared to pure epoxy. Figure 9 shows the formation of dry scaffolds from the alginate powder. Fabricating the bioinspired materials shows the biocompatibility and bioactivity. This could be used in tissue engineering, bone tissue regeneration, stem cells, spinal cord, human fibroblast cells, etc.

In contrast with nacre, the epoxy-graphene composite was composed of 99 wt.% organic epoxy resins. Firstly, Huang et al. created a homogeneous colloidal suspension using graphene oxide (GO) and alginic acid sodium (SA). Then, the slurry undergoes a bidirectional freeze casting process until we obtain the scaffold. Three different scaffolds are produced, each with different freezing rates. The scaffolds thus obtained are annealed and then infiltrated with epoxy precursor and cured into the inverse artificial nacles. It was observed that, at lower freezing rates ($8 \mu\text{m sec}^{-1}$), the scaffold showed thick lamellae with wide spaces and a smooth surface [92]. When the freezing rate is increased from 8 to $15 \mu\text{m sec}^{-1}$ and then to $35 \mu\text{m sec}^{-1}$, it was observed that the scaffold lamellae become thinner, spaces between them become narrower, and a coarser surface is formed. Compared to pure epoxy, the fracture toughness is increased by 4.2 times and energy by 17.5 times. The crack patterns in the inverse artificial nacre were more tortuous, making it harder for a crack to propagate through the sample when compared to pure epoxy resins. This extra toughness is believed to cause crack deflection and interfacial delamination, which dissipates large amounts of energy and increases the crack path. It is then shown that the electrical conductivity parallel to the lamellae is nearly 100 times greater than the conductivity in the perpendicular direction. It is also shown by monitoring the change in electrical resistance that inverse artificial nacre is temperature-sensitive. Many signs of progress are made in the fabrication of various epoxy composites. Naleway et al. use bioinspired ZrO_2 -epoxy composite material fabricated by freeze casting technique followed by polymer infiltration. These materials were controlled intrinsically by adding additives such as n-propanol (n-PrOH), ethanol (EtOH), and n-butanol (n-BuOH). In freeze casting, there is a possibility of crack propagation, which the intrinsic and extrinsic mechanisms can considerably control.

The intrinsic mechanism acts within the slurry and extrinsic acts through outside forces. In recent studies, the innate mechanism of freeze casting can be held with monofunctional alcohol such as isopropanol (IPA) which acts as intrinsic additives. There is a presence of clathrate hydrate in the freezing process, which leads to enlarging final porosity. Monofunctional alcohol as intrinsic additives EtOH and

n-PrOH forms clathrate hydrates in the binary mixture at low temperatures. However, there is no presence of clathrate hydrate in n-BuOH. All scaffolds were observed by scanning electron microscopy (SEM) to measure pore size and shape. The phase transformation was investigated using a differential scanning calorimeter (DSC) which usually explores monofunctional alcohol and H_2O .

Sound velocity and liquid density must be determined because it influences the room temperature which affects the freeze casting process. Mechanical properties and microstructure of scaffold composites are calculated. It is observed that the peak AP value for n-PrOH in ZrO_2 -based freeze cast occurs at 5 to 7 vol.%, which is similar to IPA. Peak AP value for n-BuOH and EtOH in ZrO_2 -based freeze cast scaffolds occurs at 10 and 3 vol.%. It is observed that peak AP in n-PrOH produces the highest magnitude compared to the other two additives. Hydrophobic hydration is one of the critical results which occurs in a liquid state or at room temperature. The mechanical properties of bioinspired ZrO_2 -epoxy composites increase in n-BuOH and n-PrOH additives, but there is a slight change in EtOH [93].

Nowadays, much demand has turned to lightweight materials that are also strong and rigid in automotive, aerospace, and construction materials. Many researchers are trying to find out suitable materials that can make this happen and have succeeded enough. Bai et al. have worked on bioinspired hydroxyapatite (HA) composite, which has a nacre-mimetic architecture using the bidirectional freeze casting method. Biological composites like bone have ceramics such as hydroxyapatite glued together with a biopolymer and excellent toughness and strength. This is only possible due to the hierarchical architecture present on an atomic scale in these composites. Therefore, to replace these natural materials, mimicking the same process is a promising way. The bidirectional freeze casting process created an HA-based slurry and then converted into a scaffold (20% ceramic loading) with long-ranged lamellar structures. This scaffold had a ceramic volume fraction of 30%, which was then increased to 75-85% by uniaxial pressing. This pressing resulted in the breaking of long lamellar structures into individual bricks very similar to the brick-and-mortar architecture of the nacre-mimetic materials. Then, the scaffold was grated with 3-(trimethoxy silyl) propyl methacrylate so that the methyl methacrylate (MMA) reacts better with the monomer and polymerized. This HA/PMMA composite showed strong similarities with natural nacre. After performing strength and tensile tests, the average ultimate strength of the scaffolds was found to be $100 \pm 8.1 \text{ MPa}$ and an elastic modulus of $E = 20 \pm 3.9 \text{ GPa}$. These values are much greater than the general values of monolithic HA. The ceramic content was increased by 50-70%, bending strength nearly by 10%, and stiffness about 50% in the HA/PMMA composites [94]. While the typical work of fracture for monolithic HA composites is around $2.3\text{-}20 \text{ Jm}^2$, the work of fracture for HA/PMMA composites ranged between 265 and 2075 Jm^2 . This significant variation is due to the large magnitude of crack deflection along with many other toughening mechanisms. This HA/PMMA composite is one of the few composites that are incredibly similar to a

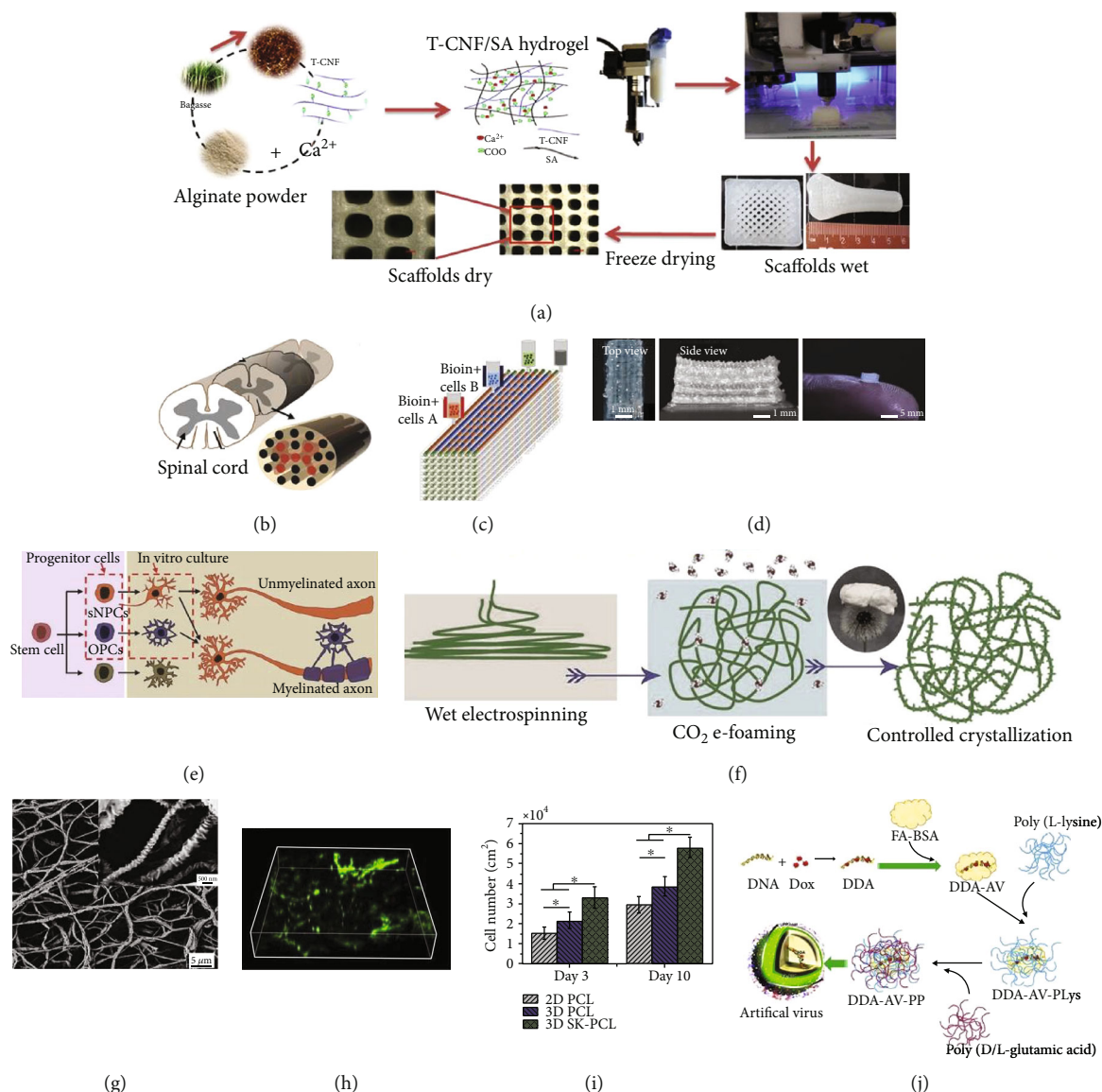


FIGURE 9: Bioinspired functional materials with bioactivity. (a) A fabrication process for 3D printing scaffolds from TEMPO-oxidized cellulose nanofibrils/sodium alginate hydrogels. (b) A schematic of the spinal cord and a design for a 3D bioprinted multichannel scaffold that models the spinal cord. (c) A schematic overview of the 3D bioprinting process. (d) The as-prepared scaffolds. (e) A schematic of the induced pluripotent stem cell reprogramming and differentiation into sNPCs or OPCs. (f) A schematic illustration of the bioinspired nanofiber scaffold preparation process. (g) The morphology of 3D SK-PCL nanofibers at different magnifications. (h) Fluorescent images of live/dead assay results for human fibroblasts cultured on an as-prepared scaffold. (i) Cell proliferation results from an MTS assay of human fibroblast cells cultured on different materials for 3 days and 10 days. (j) A schematic representation of the formation of artificial viruses [70].

natural cortical bone with similar strength and stiffness and can be used as bone substitutes and bone repair in orthopedic applications.

Membranes that can show selective super wettability and can separate oil-water are used in many applications. In nature, diatoms are materials made of hydrated silica, which shows selective super wettability. Diatoms are unicellular and photosynthetic microalgae and thrive in many water-based ecosystems producing 25% of the net oxygen on the planet. In this research done by Lo et al., diatomite membranes were fabricated using the conventional freeze casting process. Firstly, the diatomite is purchased, and a diatomite-

based slurry is created with an organic binder and dispersant. The slurry undergoes a freeze casting process, and after sintering, a highly anisotropic microstructure is obtained. This bioinspired membrane made of diatomite showed both superoleophilicity and super hydrophilicity in air. The contact angle of water with the surface of the membrane is 0° . The contact angle is also the same with oil. The oils selected for this experiment were soybean oil, sunflower oil, hexane, and hexadecane. This fabricated diatomite membrane showed excellent super wettability against the oils selected, and all contact angles were above 165° underwater [95] due to these high contact angles and insignificant adhesion

with oil. The efficiency of the diatomic membrane in various types of water is found to be nearly 99.7%. It was calculated that the membrane could withstand oil pressures until 7.2 kPa, which shows that the membrane can be used in large-scale applications. In the current scenario, where oil spills are occurring in many marine parts of the world, this membrane sure looks promising in effectively separating oil from oil spilled water.

As discussed in the previous sections, lithium-ion batteries have many applications, such as smartphones, laptops, and vehicular batteries. Although lithium-ion batteries are extensively used, one major drawback is being left unattended for a very long time. Lithium-ion batteries use graphite with a very low volumetric energy density and are not suitable for heavy-duty applications such as power grid storage and electric vehicles. Therefore, Amin et al. have worked on research to produce high-density porous graphite anodes using the conventional freeze casting process. To produce these graphite anodes, graphite powder and a 10 wt.% binder are mixed in distilled water to form a homogeneous slurry and then ice-templated to form the porous graphite scaffold. The electrochemical performance is greatly enhanced by reducing tortuosity and creating a structural alignment. Then, the fabricated anodes were cycled galvanostatically, and highly densified energy anodes were produced when they were tested in hybrid power pulse sequences. This makes them overcome all the drawbacks and become suitable materials for heavy-duty applications. The anodes were assembled to form a battery, and charging-discharging tests are done. Various charging rates ranging from C/10 to 1C were applied on the anodes. Then, the half cells were charged at a C/5 rate and underwent hybrid pulse power characterization (HPPC). Then, the cells were charged and discharged until a 90% state of charge (SOC) is obtained [96]. When tested, it was found that the area-specific capacity increased by five times compared to regular carbon electrodes under galvanostatic discharge. Although these anodes showed promising results to prove that ice-templated graphite anodes can be used in EV duty cycles, it was found that these can still not be used in practical applications due to their low mechanical strength. The authors suggest that mechanical strength enhancement be taken as a topic of research for future researchers.

Shahbazi et al. studied directional freeze casting to create new and high functional porous structures with high elegant microstructures. In recent years, this technique succeeds in providing unique morphology and shape of structure at different levels. Compared to other freeze casting techniques, directional freeze casting is a straightforward approach that processes various functional porous materials. This process starts with directional freezing of the slurry, which is in contact with a cold surface and maintains the slurry at a frozen state with controlled directions and freezing parameters. Finally, the ice growth pattern translates into the final porous structure via sublimation. Due to the versatility of technique, this process can also provide resemble structure found in natural materials to the bulk material, which assembles with bioinspired composite to gain useful physical and mechanical features. Depending on various fabrication

processes, most hierarchical porous materials are widely used in advanced technologies such as sensing, photocatalysis, separation, and biomedicine. Materials formed in this technique result in dual mesoporous structures and act as hard templates and self-assembly drivers. Directional freeze casting materials have been found in various fields such as thermal insulation, pressure sensors, structural biology, and energy storage and conversion. Directional freeze casting is used to develop multiple 3D functional structures such as 3D monoliths, films, fibers, and bead/microspheres. The most crucial application of directional freeze casting technique is thermal insulating/management, 3D biomimetic scaffolds for tissue regeneration, and pressure sensor electrodes for supercapacitors and pollutant sorption [97].

The ultrasound freeze casting (UFC) technique fabricates macroscale porous materials with specific microstructure by combining freeze casting, which manufactures porous samples with ultrasound-directed self-assembly. This process fabricates bioinspired materials, resembling concentric rings like natural materials such as Liesegang and osteon rings. UFC process creates samples with four and five concentric rings of alternating porous and dense TiO_2 material. Ogden et al. find the difference between Vickers hardness and porosity when comparing samples' denser and porous regions. Ultrasound freeze casting consists of a cylindrical piezoelectric ultrasound transducer with a frequency of 1.30 MHz, height ($h = 20$ mm), and inner diameter ($d = 22$ mm), which act as a mould and freeze colloidal slurry. This colloidal slurry is prepared by blending deionized water with 10 vol.% of TiO_2 particle, polyvinyl alcohol of 88,000–97,000 g/mol, and 1 wt.% each of polyethylene glycol 10,000 g/mol. TiO_2 is selected due to its biocompatibility which applies to biomedical applications. The characterization of the microstructure of material samples is imaged using scanning electron microscopy (SEM). The Vicker hardness of the model is measured at the central location using microindenter. ANOVA analysis is prepared to determine the UFC process. Vickers hardness and porosity of the samples are fabricated with an ultrasound DSA operating system. It observed that there are no concentric rings when ultrasound is absent. The porosity difference between denser and porous is significant, with the porosity of 37.98% and 21.73% for the porous and denser region. Vickers hardness for the denser and porous part is 24.52 Hv, and Vickers hardness of material without a concentric ring is 21.40 Hv [98].

The research in [99] focuses on fabricating bioinspired Bouligand and helical structures through magnetic freeze casting using triaxial nested Helmholtz coils. Bouligand and helical structures tend to give high-impact resistance materials. Helical structures are found in tropocollagen and DNA strands. Bouligand structures are in platelets stacked on top of others or in fiber sheets. The permanent magnets cause particle accumulation due to the high magnetic field. In freeze casting, the Helmholtz coil is used to produce a low magnetic field gradient. During the formation of ice crystals, Helmholtz coils control the magnetic field in Bouligand and helical motions, which resembles a similar pattern in biological applications. The freeze casting setup consists

of Helmholtz coils applied to the slurry's uniform low magnetic field. During directional freeze casting, it creates homogenous porous structures. Totally, 50 slurries were fabricated; the first ten were fabricated using no magnetic field. The remaining 40 slurries were divided into four different groups and fabricated using other magnetic field motions. The first two groups are under helical motion. Group 2 with θ -direction equals to 0° ($\theta = 0^\circ$) and group 3 with θ -direction equals to 45° ($\theta = 45^\circ$). Similarly, group 4 with θ -direction equals to 0° ($\theta = 0^\circ$) and group 5 with θ -direction equals to 45° ($\theta = 45^\circ$). Groups 4 and 5 are under Bouligand motion. Helical structures choose at least one complete rotation θ of 60° . Nelson et al. observe that the pore size and porosity were decreased by 42% to 20% by applying magnetic field motion. The ice growth velocity stayed constantly using the magnetic field direction. In the case of Bouligand motion with θ of 45° and helical with θ of 0° , dynamic crack follows the path of the magnetic field. Scaffolds fabricated with magnetic field produce high dynamic strains. Finally, the impact resistance of bioinspired materials was increased due to the effect of the magnetic field [76].

Porter et al. worked on a research work where they stated that biomimetic materials are engineered materials that emulate many aspects of standard biological materials' properties, functions, and designs. Nacres, made up of abalone shells, essential bones, and many similar primary biomaterials, have developed outstanding mechanical properties even though its composition is made up of material constituents that are feeble in general. The general mechanical properties are profoundly anisotropic, transforming to nature and high amounts of outer tractions. Biomimetic manufactured products are inspired by natural processes that surpass conventional fabrication capabilities like nano- and microregions. Biomimetic concepts also involve self-cleaning, self-assembly, and self-organization to nanolithography and 3D printing. Freeze casting is generally short, cheap, and versatile to fabricate mass permeable scaffolds and hybrid composites. There are many hardening components in architectural structures like nacre or bone, but its matrix is one of the most significant ones. Nacre shows an elasticity to the magnitude of nearly 4.2 MPa, but when compared with protein depleted nacres displaying a strength of just 0.33 MPa. This depletion of proteins is termed deproteinization. The natural strength of nacre can be reduced by more than 90% by just removing the natural framework by 5 vol.%. When the deproteinization mentioned above is performed, the measured stiffness is reduced from 22 GPa to 9 GPa, whereas the compressive strength is reduced to 24 MPa from 120 MPa. This has resulted in increased attention on infiltrating polymers in ceramic scaffolds to form organic-inorganic composites. Porter et al. showed that the hybrid composites of counterfeit alumina-poly(methyl methacrylate) (Al_2O_3 -PMMA) composites displayed a brick-and-mortar lamellar structure and can reach a ceramic volume phase of around 80 vol.% from a mere 35 vol.%. These newly fabricated composites display a superior fracture toughness of about 32 MPa and exceptional bending strength of nearly 210 MPa [5]. The ceramic and polymer phase networks are interconnecting and bidirectional,

which improves the fracture toughness and material strength of the ceramic-polymer composites. The possibility of delamination and subsequent interfacial shear is completely removed due to strong intermolecular bonding between the PMMA and Al_2O_3 phases achieved by the grating process.

Cheng et al. worked on research where they assembled structural materials inspired by biomaterials with the help of the freeze casting process. The improvement of more grounded and more challenging primary structures that preferably have lighter loads helps to progress in vital fields such as energy, transportation services, and many structures. The design of biomaterial creates composites with unique properties. The best example for the engineered biomaterial is nacre because of its brick-and-mortar structure which exhibits the solid physical properties and capability to mimic natural materials like chitin and protein. Nacre's high blemish resilience and break strength are because of its complex micro/nanoscale progressive design and bountiful interfaces in the natural layers and mineralized calcium carbonate. The architecture of natural materials in response to mechanical properties is unsuccessful for pragmatic material productions like layer-by-layer deposition, filtration, and hydrogel casting. Mostly, these are size limiting and time-consuming. Specific methods like freeze casting and slip casting significantly produce the best outcomes in fabricating densified materials. Freeze casting is a porous scaffold fabrication method that uses directional cementing of water-based suspensions. Kinds of microstructures can be acquired relying upon the building material, the conditional freezing, the solvent (ice in this case) utilized, or the presence of added substances bringing about clear self-gathering of particles to frame a profoundly permeable mass material. Quicker freezing rates bring about a lot better microstructure ($1\text{--}25^\circ\text{C min}^{-1}$). Finally, the freeze cast scaffold ceramics is obtained after the sublimation; then, it is subjected to sintering 10-15% of pore morphology which results in the increase of grain size with low temperature [9]. In their research, they slightly altered the conventional method to control the ice crystals' nucleation by changing the freeze casting strategy to the bidirectional freeze technique [94].

Cheng et al. stated that the nacre-like Al_2O_3 -PMMA fabricated to lamellar nanocomposites showed a momentous resistance curve (*R*-curve) like progression, pointing to their resilience to the steady development of cracks with the strength of around $30\text{ MPa m}^{1/2}$ or greater [9]. Crack resistance material was developed by *R*-curve and will never fail catastrophically. In recent times, researchers Mao et al. used ice templating to produce beta-chitin using lamellar structured chitosan and acetylation process. Then, the lamellar structure is mineralized to produce calcium carbonate up to 91 wt.%. The main drawback of the technique is less strength and toughness.

The numerous biological materials have superior primary components that constitute high mechanical properties from nano- to microlevels, such as bone, nacre, and teeth. The best example of bioengineered material is nacre which achieves a volume of above 90% of CaCO_3 platelets and also with nearly 5 vol.% of biopolymers into "brick and

mortar” structures. These high ranges of biomimetic material were further processed in freeze casting. Controlling how the ice nucleates and develops is a very crucial part. So, Zhao et al. have designed the subsequent permeable material which replicates the ice crystal morphology. The authors report successful results on the surface wettability in the freezing process. In particular, one can handle ice nucleation and its development on a predestined surface by presenting a wettability gradient. Their first endeavor was similar to ice templating methodology on copper’s surface, having hydrophobic properties that are changed homogeneously with triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octyl) silane [100]. The water contact point noted is nearly 150 degrees, and the ice nucleation rate is deferred. The ice crystals are still noted to be nucleating haphazardly over the predestined surface with no favored direction and in a short lamellar range.

Similarly, as on a hydrophilic surface, they endeavored to plan many wettability patterns with complex designs in this freeze casting process. They then altered the copper surface with Perfluorooctyltriethoxysilane by yielding a straight wettability slope, modified coating by dipping, when the contact angle of water is between 20 to 135° (wettability gradient). There is a 12 mm length change observed in the wettability (long lamellar layers). The HA-based slurry was created with 20 vol.%, and then, it was grated with PMMA polymer to mimic the nacre by mimicking the “brick and mortar” architecture. The bending strength recorded in the experiment was 109 ± 7.5 MPa, work of fracture of 2233 ± 295 J/m², and a Young’s modulus of nearly 6 ± 1.25 GPa. HA/PMMA can be used in fracture or crack resistance, while the single and cross lamellar structures are pointed towards imitating the designs of the shells of abalone and nacre under bending.

Jaafar et al. constructed the cellulose nanocrystals (CNC) and xyloglucan (XG) by synthesizing the plant stem tissue coordinates at various leveled structures. The cell structure that is situated along the stem cells is anisotropic and permeable at the tissue level. The mechanical conduct of the whole cell wall is controlled by cellulose, hemicellulose, and lignin. CNS is an evacuation of cellulose fiber with nanometric measurements utilized as support materials in hydrogels and aerogels. Xyloglucan has a high affinity to plant cellulose and absorbs it. Freeze casting is done unidirectional along with a predefined thermal gradient. The engineered materials can be applied in thermal insulators, tissue engineering, and pharmaceutical and automotive components. Chemically, cellulose nanocrystals are prepared with specific fractions of materials such as nearly 44–108 nm of length, 0.023 mmol/g of charge density, a crystalline fraction of 0.9, and lateral dimensions ranging between 2.3 and 4.5 where CNC powder is dispersed in water. After dispersion, it is sonicated for 10 min with an ultrasound probe. Xyloglucan weighed nearly 50% glucose, 33% xylose, 16% galactose, and nearly 2.3% of arabinose in *Tamarindus indica*.

The surface of the CNC is completely shielded, expanding the swarming of the polymer. The aerogels used in this experiment are named CNC2 XG0. The aerogels were kept ready in both UF and NF, where the slurry underwent a cooling process, and the crystals of ice fill arbitrarily, which

initiates the development of the nucleated crystals in the direction of the cooling direction. Highly homogeneous and solidified aerogels were effectively acquired from the CNC/xyloglucan combinations, with the density of NF being nearly 22 kg m³ and UF nearly 20 kg m³. Associatively, XG increments the yield pressure multiple times to a value of 53 kPa from a mere 7.8 kPa seen in the CNC2 XG0 [93]. This results in the protection from disfigurement before irreversible harm. This proves that XG can also create resistance in its cell walls which were only assumed as a property of cellulose to date.

6. Conclusions and Future Directions

The following conclusions and future directions are the outcome of the available research and review of the literature, designed to ultimately guide the researchers to perform an experiment that may give a possibly efficient outcome irrespective of the costs of the process. These are ultimately evidences from the available research [101–104].

- (i) Selecting the freeze rates is one of the essential steps involved in the freeze casting process. The rate at which freezing occurs determines the porosity, microstructure, freezing time, and many more characteristics of the resulting scaffold. Freeze rates are of two types—one is the homogeneous cooling rate where the cooling rate is constant throughout the process, and the other is the heterogeneous cooling rate in which the cooling rates are altered to get specific types of dendritic structures. As we have already seen in the discussion, lower freezing rates like 8 $\mu\text{m sec}^{-1}$ result in smoother surfaces with thick lamellae and broader spaces. This smooth surface of the resulting scaffold reduces the necessity for further postprocessing techniques. To achieve thinner dendritic lamellae and narrower spaces in the scaffold, faster freezing rate like 15–35 $\mu\text{m sec}^{-1}$ is used [69]. Any further increase in the freezing rates increases the brittleness of the scaffolds. Faster freezing rates also mean that the building particles are rejected much faster when compared to slow freezing rates, so particle scattering is high. The microstructure depends mainly on the freezing rates of the process. The microstructures were finer when the freezing rates were relatively fast compared to lower freezing rates [17]
- (ii) As we already know, nacre is a naturally occurring material that shows very high strength and stiffness owing to its unique brick-and-mortar architecture. Due to these appealing properties, many researchers are enthusiastic about recreating nacre-like structures using ceramic-polymer composites. Extensive research is being conducted in this area for finding an ideal material suitable for mimicking natural nacre. These fabricated materials are called nacre-mimetic structures. Many ceramic-polymer composites were tested in recent

years, and many of these materials showed none or partial success rate in mimicking nacre. However, recently, it was discovered that graphene and poly(-methyl methacrylate) (PMMA) composites were achieving promising results in producing nacre mimetic structures. Many researchers have successfully fabricated PMMA and graphene-based nacre mimetic structures in recent times. Some unusual combinations are graphene scaffolds infiltrated with polyvinyl alcohol and hydroxyapatite scaffolds infiltrated with PMMA [71]. These combinations work best while fabricating nacre mimetic structures. Also, the porosity of these scaffolds should be taken into consideration. To create strong nacre mimetic structures, the density of the scaffold should be relatively high. To achieve this, techniques such as hard pressing might be used to compress the particles of the scaffold to imitate the brick-and-mortar architecture [105]

- (iii) Sublimation is a process that transforms the solid phase ultimately into a vapor phase without entering into the liquid phase. Once the solidification process is achieved, the samples are kept under reduced pressure and low-temperature conditions. The solidification process is followed by sublimation, where the solid state is converted into vapor. As we know to perform the sublimation process, equipment called a freeze dryer had been used. For example, in camphene, the high enough sublimation is allowed at room temperature with a vapor pressure of 1.3 kPa. The time taken for the sublimation process depends on the solvent dimensions and who it has been treated. The sublimation stage should be adequately controlled to avoid of getting defect formations such as distortion and cracks. The sublimation process in the case of small pieces is more manageable than compared to large amounts. In larger pieces, it may be problematic to control the solid-vapor phase transition [17]
- (iv) Sintering is the last step of the freeze casting process, which promotes densification, wall consolidation, and impact strength. Once the sublimation is completed and the solvent is completely removed, the conventional sintering technique sinters the obtained green body. If the green body has low strength, then it prevents us from using pressure-assisted sintering. The microporosity can be removed from the ceramic walls during the sintering process, and solvent crystals retain it. The sintering process optimizes to control the density and porosity of the final piece [17]. In silicon nitride, due to the vapor-solid phase, the elongated fibrous grains have appeared after sintering. The additives such as sucrose, zirconium acetate, and polyvinyl alcohol (PVA) influenced the speed of freezing and microstructure of fabricated parts. These additives cannot be removed directly, and

they will be removed by sublimation, and always presintering technique is required. The materials with high proton conductivity require a high sintering temperature, which leads to issues during the shaping process. Usually, unique microstructures and mechanical properties are obtained after the sintering process at different temperatures by various vapor conditions such as cold plate temperature and solid cooling [106–113]

- (v) Crystal morphology is one of the most critical process parameters to get a good result in freeze casting. Crystal morphology is the study of forms of crystals. It determines the microstructure of the scaffold and the change in volume related to phase transformation. The evolution of porous microstructure by utilizing the freeze casting method depends on the particles' refusal by the proceeding solidification front, the collapsing of the solidification front to a nonplanar surface structure, and the absorption and capturing of the particles in between the solidified crystals. These attributes are governed by the factor of interactivity between the solidification front and the particles. Additives of slurry have a remarkable impact on the scaffolds' microstructures prepared by freeze casting. Changes in the pH with additives such as tricarboxylic acid, muriatic acid, caustic soda, and ethanoic acid or change in viscosity of slurry tend to change the crystal morphology by enlarging or reducing the size of the pore. The ratio of thermal conductivity of the particle to the thermal conductivity of the liquid phase also tends to change the crystal morphology of the scaffold
- (vi) The temperature gradient is another crucial process parameter to get a good result in the freeze casting process. Temperature gradient describes the rate and direction of change in temperature, which occurs most rapidly. It can control the germination and development of ice crystals, porosity, and the distribution of the size of the pore of the body of ceramic. It could also control the final microstructure obtained from the freeze cast scaffold by dominating different parameters such as cooling rate, mold slope angle, solid ceramic loading, and binder concentration. Freeze casting done under twofold temperature gradients tends to fabricate highly aligned lamellar scaffolds of ceramic, which could forge highly aligned porous materials. When we increase the freezing rate and greater the temperature gradient, the pore size tends to decrease. In the freezing suspension, the growth of ice tends to follow the direction of the temperature gradient. A strong temperature gradient at the bond between the ice framework and the suspension tends to create many tiny crystals of ice. On the contrary, a weaker temperature gradient at the center tends to create a few powerful crystals of ice

- (vii) There is a possibility for finding different solvents other than the available solvents, and there had been no progress reported in the new possible solvents for the freeze casting process

Data Availability

All data is included in the paper itself.

Conflicts of Interest

The authors declare no conflict of interest.

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