1.4.1 Effects of Polymer Properties

1.4.1.1 Rheological Properties of Polymers

Rheological properties of polymer matrix have an important impact on the overall foaming process. During foaming, the melt around the cells undergoes tensile action, and the rheological properties of polymers directly affect cell growth. The cell would be difficult to grow within a polymer matrix with high melt strength. When the melt strength is too low, the cells tend to rupture and collapse, resulting in a low expansion rate.

The molecular structure has a huge influence on the tensile viscosity of polymers, and the viscosity of long-chain branched polymers is higher than that of linear-chain polymers. Park and Cheung [38] found that the closed cell rate of branched PP foams in extrusion foaming was much higher than that of linear PP foams, suggesting that the cells are more easily ruptured for the low melt strength linear PP. Fang et al. [39] used γ radiation to prepare a series of long-branched PLA materials and produced a bimodal foam morphology, which verified that the introduction of long-branched structures enhanced the complex viscosity, shear thinning, and storage modulus of the matrix and improved the foaming properties of the PLA materials.

The influence of the polymer matrix crystallization behavior on the rheological properties is not negligible during the foaming process. For example, PP is a crystalline polymer that barely flows below the melting temperature due to the restriction of the crystalline regions. However, as soon as the melting temperature is reached, the viscosity and melt strength decreases sharply, which induces fast gas diffusion and cell merge during foaming, making it difficult to form a well-established cellular structure. Therefore, the melt strength of polymers is often improved from the perspective of polymer modification, and the current common methods of polymer modification mainly include crosslinking modification [40], grafting modification [41], blending modification [42], and filling with nanoparticles [43].

1.4.1.2 Solubility and Diffusion of Blowing Agent

In general, the solubility of gases in molten polymers increases with increasing pressure and decreases with increasing temperature, with pressure and temperature showing opposite trends in promoting the solubility of gases in polymers (Figure 1.12). Sato et al. [44] measured the solubility of CO_2 and N_2 in molten PP and high-density polyethylene (HDPE), and the experimental data coincided with the trend of solubility change represented in Figure 1.12.

The diffusion rate of gas in a polymer matrix represents the rate of movement of gas molecules through the molten polymer, which is the mass transport capacity of gas molecules through the matrix. For large-scale production of industrial foaming products, the diffusion rate is usually a more important influencing factor. The general trend of the gas diffusion rate in the molten polymer increases with increasing temperature, quite the opposite trend of the solubility change with temperature. The decrease of surface tension is beneficial to the diffusion and mixing of substances, and the adoption of supercritical gas can reduce the surface tension of gas and polymer melts, thus, elevating the diffusion rate. Sota and Suh et al. [44, 45] studied the

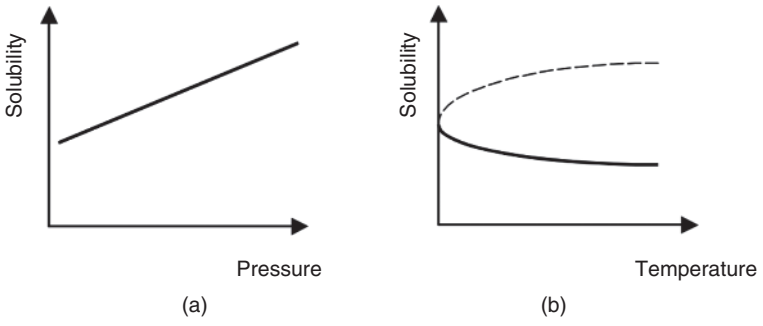

Figure 1.12 Solubility of gas in most molten polymers: (a) solubility changes with increasing pressure, and (b) solubility changes with increasing temperature.
Source: Adapted from Xu [3a] and Cha [8].

gas diffusion theory in molten polymers to provide a basis for estimating the diffusion rates of gases. Peng and Qu [46] found that introducing a vibrational force field could promote the diffusion of small molecule gases in polymers, demonstrating that changing the external force field could elevate the diffusion rate of gases.

Controlling the diffusion direction of gas in the melt also affects the cell structure of foams, since the gas diffuses into the cell voids also diffuses to the surface and external environment. Siripurupu et al. [47] found that reducing the diffusion speed of gas to the melt surface resulted in a more dense cell structure with a smaller cell size. Mi and coworkers [48] successfully produced fine cells on the surface of the thermoplastic polyurethane (TPU) and polyvinylidene fluoride (PVDF) foamed sheets by introducing various gas barrier films to reduce the diffusion speed of CO_2.

1.4.1.3 Interaction Between Foaming Agent and Polymer Matrix

As mentioned above, the addition of foaming agents may interact with the polymer matrix thus affecting the properties of the polymer as well as the foaming behavior. For example, $scCO_2$ has a plasticizing effect on the melt when saturated within the polymer matrix, which would improve the activity capacity of molecular chains, thus affecting the properties of the polymer matrix. For amorphous polymers, it decreases the glass transition temperature and viscosity of the polymer. For crystalline polymers, it usually affects the crystallinity, crystallization temperature, crystallization kinetics, and crystal structure. Garg et al. [49] proposed two mechanisms for the plasticizing effect of SCF addition. One is the alleviation of entanglement of polymer molecular chains after the addition of gas, and the other is the generation of additional free volume, which increases the mobility of molecular chains.

Chiou et al. [50] investigated the effect of CO_2 on the glass transition temperature (T_g) of polymers such as PMMA, PS, and polyvinyl chloride (PVC) using a high-pressure differential scanning calorimetry, and showed that CO_2 can significantly decrease the T_g of glassy polymers with high CO_2 solubility at moderate pressures. The effect of $scCO_2$ on the T_g of polymers can be divided into three regions, as shown in Figure 1.13. When the pressure is low (region I), the absorption of CO_2

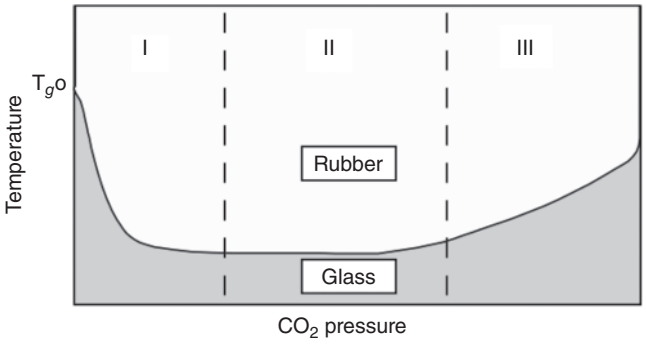

Figure 1.13 Proposed model of glass–liquid transition for a polymer–CO_2 mixture. Source: Royee [51]/with permission of NC State University Libraries.

causes swelling, and the T_g significantly decreases; With the increasing pressure (region II), the T_g tends to stabilize and is less affected by the pressure; As the pressure further increases (region III), the free volume of the system decreases, and the T_g begins to rise [51].

Zhang et al. [52] found that the presence of $scCO_2$ could significantly improve the crystallinity of PP, and the crystallinity was increased with the increase of CO_2 pressure. Liao et al. [53] found that the content of γ crystals increases continuously with the increase of CO_2 pressure in PP. Some studies found that under the influence of CO_2, the crystallization kinetics, and morphology of polymers such as PVDF [54], polyethylene terephthalate [54, 55], and polycarbonate [56] have also changed.

1.4.1.4 Nucleating Agent and Nanoparticles

The introduction of fillers into the melt is an effective method to control the cell structure mainly due to the heterogeneous nucleation effect of the nanofillers and the effect of nanofillers on the melt strength of the matrix polymer. According to the classical nucleation theory, introducing heterogeneous nucleation can greatly reduce the nucleation barrier, thus obtaining more cell nuclei during the nucleation stage and greatly increasing the cell density. Turng [57] and Park [58] studied the effect of nanoclay on the foaming of PE, and verified the heterogeneous nucleation effect of nanoclay in improving the cell density and the performance of the foams. Antunes et al. [59] studied the effects of changing foaming parameters and introducing nano montmorillonite (MMT nanoparticles) on the PP foaming system. They found that MMT nanoparticles played a dual role in heterogeneous nucleation and improving melt strength, reducing the overall cell size and increasing the cell density.

1.4.2 Effects of Foaming Process Parameters

1.4.2.1 Foaming Temperature

The processing temperature is an important parameter for polymer processing since the properties of a material are highly related to its temperature. In the foaming

process, temperature affects the viscosity of the polymer matrix, the solubility of the foaming agent in the molten polymer, the gas diffusion rate, and even the time needed for cooling. Foaming temperature affects the final cell morphology by influencing these physical properties.

In general, the higher the foaming temperature during the process, the lower the polymer viscosity, the lower the solubility of the foaming agent, and the faster the diffusion rate, which usually corresponds to lower cell nucleation rate, faster cell growth, lower density, and larger cell size. When the temperature is too low, and the polymer viscosity is too high, the cells would be difficult to grow. Therefore, a suitable foaming temperature window needs to be decided in the first place.

Yokoyama et al. [60] studied the foaming behavior of polystyrene (PS)/polystyrene perfluoro methyl acrylate copolymer (PFMA) blend system and obtained different cellular structures based on the change of viscosity of PS as a function of temperature. When the foaming temperature was set above the T_g of PS, cells in micrometer scale were obtained; When the foaming temperature was below T_g of PS, the cell size could be reduced to nano scale. Goel and Beckman [61] investigated the plasticization effect of $scCO_2$ on PMMA, and found that the solubility of CO_2 decreases with the increase in temperature, while the surface tension of the melt and the free energy barrier to nucleation rises with temperature increase, which leads to a decrease in the nucleation rate and the cell density.

1.4.2.2 Saturation Pressure or Foaming Pressure

According to the classical nucleation theory, the pressure of the saturated gas has a great influence on cell nucleation. The higher the foaming pressure is the more gas will be absorbed by the polymer, which is responsible for a greater plasticizing effect. In addition, a high foaming pressure is usually associated with a high-pressure drop rate. All these properties are favorable for enhancing the cell nucleation rate and the cell density of the foam product, while it usually causes a decrease in cell size. Goel et al. [62] found that the size of the cells decreased with increasing pressure and the density of the cells increased with increasing pressure in the foaming of PMMA using $scCO_2$ as the foaming agent. Baldwin et al. [63] investigated the foaming process of amorphous and crystalline PET depending on the foaming pressure and found that the increasing pressure had a more significant effect on the amorphous PET than the crystalline PET. This was because high pressure could activate more homogeneous nucleation points in the amorphous PET, while the crystalline region in the crystalline PET could induce heterogeneous nucleation which will cause a high cell density even without the increase in foaming pressure.

1.4.2.3 Depressurization Rate

In physical foaming with high-pressure gases, the cell nucleation and growth are generally achieved by rapid depressurization. Since cell nucleation and growth occur almost simultaneously in the system, there is clearly a competitive relationship between them. The final cell morphology is largely determined by the two processes. In the moment of pressure release, the cell nucleus started to appear in the region with a lower free energy barrier, and subsequently, more gas molecules

diffused into the cell nucleus to cause the cell growth. At a low depressurization rate, the sudden pressure drop was small, which is adverse for cell nucleation, and the time for cell growth is prolonged. Thus, more gas could diffuse into the cell nucleus forming a structure with a large cell size. On the contrary, a high depressurization rate usually refers to high cell density and relatively small cell size. Han et al. [64] studied the continuous extrusion foaming behavior of PS and adjusted the depressurization rate by changing the shape of the die. They basically found a similar tendency and prepared PS foams with different cell structures by varying the depressurization rate. Park et al. [65] designed three nozzles that can generate different depressurization rates in injection foaming to study the effect of depressurization rate on the gas competition between cell nucleation and cell growth processes. They predicted that there would be a maximum depressurization rate to enable high cell nucleation and balance the cell growth processes.

1.4.2.4 Multistage Saturation and Depressurization

In most cases, the high pressure is released in one step in the foaming process. However, the pressure could also be released step-by-step in batch foaming, which is capable of controlling the cell morphology of the final foams. Step-by-step depressurization refers to the step-by-step removal of saturated pressure after supersaturation. Similarly, the foaming temperature and supersaturation pressure could also be programed stepwise to influence the final cellular structure of the foam. Typically, a bimodal cellular morphology with distinct different cell sizes in a single foam can be obtained by these multistage foaming processes since the conventional continuous nucleation and growth process is divided into two or more stages.

The foams with a bimodal cell structure that combines large cells and small cells may have advantages in their properties. The large cells could contribute to the weight reduction and the small cells could provide particular performance. Compared with the conventional singular cell structure, the bimodal cell structure may render the foams better performance in sound absorption, heat insulation, bio-tissue engineering, and other fields. Arora et al. [66] fabricated PS foams with a bimodal cell structure using a two-step depressurization method. Bao et al. [67] studied the factors affecting the bimodal cell structure in the two-step pressure drop method. They proposed that "Holding time," the duration after the first pressure drop, is important for the control of the bimodal cell structure since it controls the time for the growth of the large cells. Mi and coworkers [68] developed a multistage soaking approach in which the saturation temperature was elevated during the soaking stage to cause the precipitation of $scCO_2$ in the PLA matrix due to the lower gas solubility at higher temperatures. The precipitated $scCO_2$ formed the large cells in the subsequent depressurization step, and the prepared bimodal foams have a dramatic difference between the large cells and the small cells.

1.5 Previlant Foaming Methods for Microcellular Foams

Foams with cell size in the micrometer level are called microcellular foams. Compared to conventional microporous foams, microcellular foams have superior

mechanical, absorption, and insulation properties. Thus, they are been heavily investigated in recent years. Microcellular foams prepared by SCF-based foaming methods are highly recognized since the SCF are environmentally friendly and will cause no chemical residual in the polymer matrix and no VOCs emission. It also has high productivity and fabrication reliability. In a typical SCF-foaming process, SCF is first injected into the polymer to form a gas-saturated system, then the system is supersaturated by means of rapid pressure drop, which induces cell nucleation and growth, and finally, the foam with microcellular structure is cooled and solidified. SCF foaming process is mainly divided into batch foaming, continuous extrusion foaming, and injection foaming.

1.5.1 Batch Foaming

Batch foaming was the earliest method used to manufacture microcellular foams. The first patent for microcellular foaming was disclosed in the United States in 1984 [69]. Two batch foaming methods are widely used in practice. The first is temperature-induced foaming, in which the cell nucleation and growth are triggered by the fast temperature rising as illustrated in Figure 1.14. In this method, solid polymer preform is put in a high-pressure vessel charged with $scCO_2$ or scN_2 at a low temperature to form a saturated homogeneous system. Then, the saturated preform is taken out from the vessel and rapidly transferred to a hot media (i.e. hot oven and hot bath) to quickly increase the temperature above the T_g of the polymer while below the melting point (T_m) of it. Thus, cell nucleation and growth will be triggered due to the increase in molecular chain

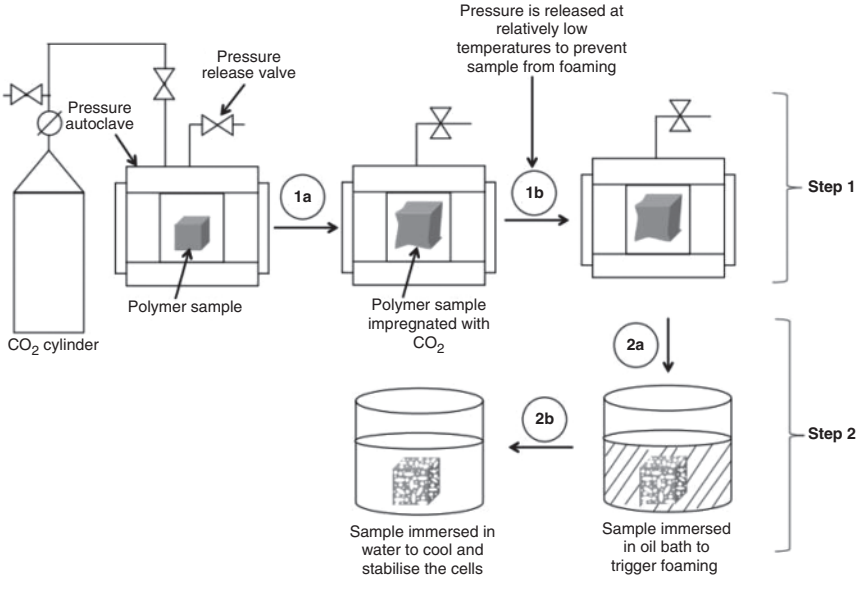

Figure 1.14 Temperature-induced batch foaming process. Source: Okolieocha et al. [70]/with permission of Elsevier.

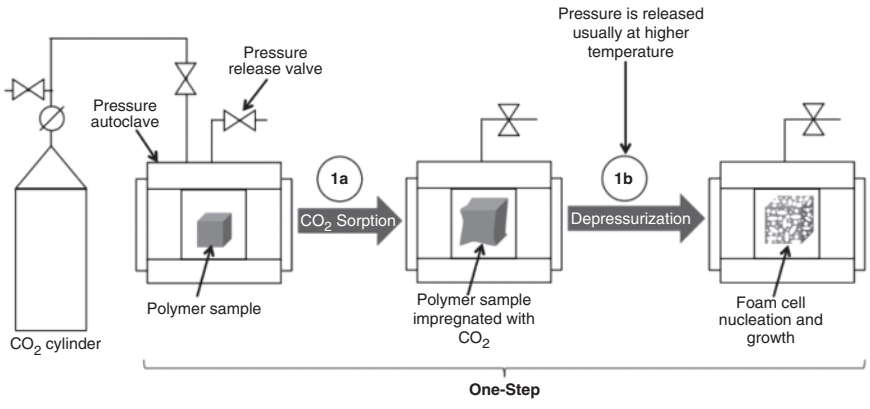

Figure 1.15 Pressure-induced batch foaming process. Source: Okolieocha et al. [70]/with permission of Elsevier.

mobility. Finally, after the expansion process, the temperature will be reduced and the foams will be solidified by quenching. Since the samples need to be transferred from a high-pressure environment to a high-temperature environment to allow the foaming process, this method is also referred to as a two-step foaming method.

The second batch foaming method, which is used more often in practice, is called one-step foaming approach. As illustrated in Figure 1.15, in the pressure-induced foaming process, the preform samples are saturated at a higher temperature that is usually the foaming temperature with the SCF. The cell nucleation and cell growth are triggered by the rapid depressurization. Then, the expanded samples would be subject to a cooling process to allow the maintaining of the foamed cellular structures [62a].

Batch foaming method has the advantages of simplicity in foaming device, easy control of the foaming process, and easy regulation of product cell structure. However, the batch foaming method is difficult to achieve continuous production in large quantities. Batch foaming has been mainly used in laboratory research on a small scale for decades, while it is now more and more used in the industrial production of foam products attributing to the invention of novel large-scale batch foaming instruments.

1.5.2 Continuous Extrusion Foaming

Continuous extrusion foaming of microcellular plastics was issued in 1990s [71], which realized the continuous foaming process and promoted the industrial application of microcellular foamed products. In industry, foam extrusion lines are usually in tandem (as shown in Figure 1.16), and simple foam extrusion single line is also used in practice. In a typical extrusion foaming process, the polymer is added through the feed hopper into the extruder, it is compressed and plasticized by the screw in the first barrel and mixed with $scCO_2$ injected into the barrel to form a homogeneous system under the action of high temperature, high pressure,

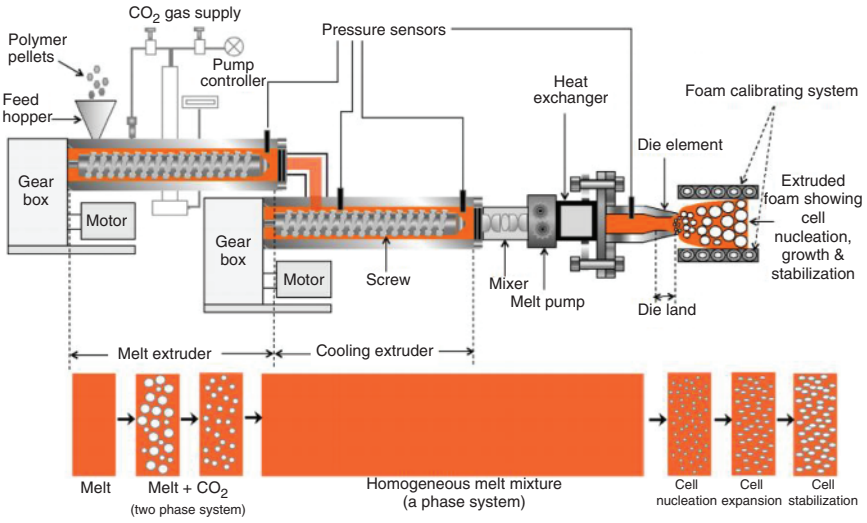

Figure 1.16 Schematic representation of foam extrusion on a tandem line. Source: Okolieocha et al. [70]/with permission of Elsevier.

and screw shear. Subsequently, the mixed system is transferred to the second barrel where preliminary cooling takes place and higher pressure continues to increase gas concentration and saturation pressures. A static mixer, a melt pump, and a heat exchanger are sometimes used between the barrel and the die to further increase the homogeneousness and the pressure of the polymer/gas system before the extruding. Finally, as the melt passes through the die, the cell nucleation and cell growth take place rapidly due to the rapid pressure drop. Continuous extrusion foaming greatly improves production efficiency and is a key step toward the commercialization of microcellular foamed products. It has been widely used in the production of foamed sheets, plates, pipes, and beads. However, due to the restriction of die geometry, continuous extrusion foaming has significant limitations in the production of foamed products with complex shapes.

1.5.3 Injection Foaming Technique

In 1995, Axiomatics (later Trexel) began to develop microcellular injection molding technology based on extrusion technology and registered MuCell® [3a], the trademark most commonly used for microcellular molding technology, which is also called injection foaming or foam injection molding. Figure 1.17 shows the basic process of the injection foaming method. Similar to extrusion foaming, the polymer was added into the barrel through the funnel, and it becomes a melt under the compression and plasticization of the screw. To the melt, a defined amount of SCF was injected via a precisely controlled valve and mixed with the polymer melt by the rotation of the screw. When the polymer/gas system is plasticized and metered in front of the screw, a high-pressure state is still maintained to prevent early foaming. Subsequently, the melt is injected into the cavity of the mold, and

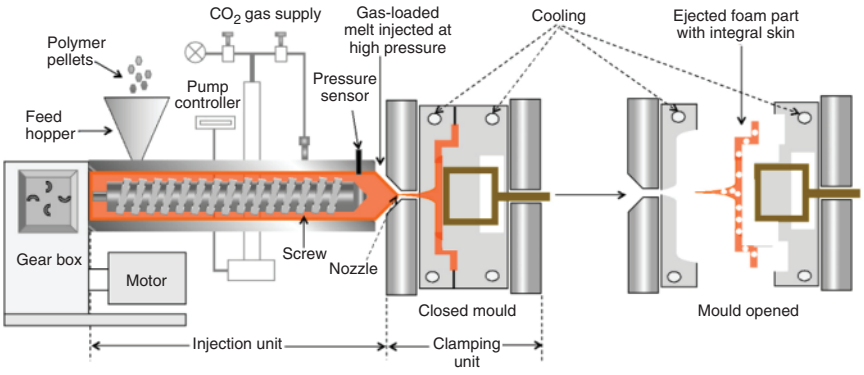

Figure 1.17 Schematic representation of foam injection molding process. Source: Okolieocha et al. [70]/with permission of Elsevier.

the melt starts to foam as the melt fills the mold cavity due to the rapid pressure drop. For injection foaming, the holding stage is removed to allow sufficient expansion of the foamed part during the cooling cycle to achieve high weight reduction. Since the injection foaming contains plasticizing, storage, injection, and cooling stages, the cell structure of injection foamed parts is affected by various parameters, including processing temperature, injection speed, injection pressure, injection volume, mold cavity geometry, back pressure, cooling temperature, cooling time, gas content, gas injection time, *L/D* ratio of the screw, etc. In general, injection foaming improves the productivity of foamed parts and allows the production of products with complex shapes. Compared with traditional injection molding, foam injection molding has the advantages of more stable dimensions, shorter foaming cycles, and material savings. However, the high cost of the SCF supply system, the flow marks left on the surface of the foamed parts, and the quality fluctuation in production are the main concerns for this technique.

1.6 Advanced Applications of Functionalized Polymer Foams

With the fast development of polymer-foaming techniques and foamed products in recent years, more and more attention has been attracted. Researchers and pioneers have been devoted to exploring the advanced applications of polymer foams and trying to develop various functionalized polymer foams in the advanced fields in the new era as cutting-edge techniques. This book will focus on the advanced polymer foams that are used in cutting-edge fields. The approach to developing such foams will be mainly focused on microcellular foaming using SCF as the physical foaming agent so as to promote the potential applicability of this green technique. The content of this book will cover novel applications of the foams, including energy absorption, acoustic absorption, superhydrophobic,

electromagnetic interference (EMI) shielding, tissue engineering scaffold, flexible sensors, triboelectric nanogenerator (TENG), and solar steam generation. A brief introduction to these advanced fields and the role or potential role of polymer foams in these fields is given below.

1.6.1 Energy Absorbing Buffer Foam

Foam materials have a long history of applications in energy absorption and cushioning. They have found use in various industries, ranging from sports equipment like exercise pads for gymnastics, high jump, and combat, to safety products like cycling helmets and bulletproof vests. Polymer foams offer several advantages over metallic or inorganic foams. They provide greater design flexibility, are easier to process and recycle, and offer a wide range of compressive strengths, from highly elastic to semi-rigid and rigid. In addition, polymer foams are lightweight, cost-effective, easy to shape, and offer numerous advantages in commercial applications. The mechanism of energy absorption, the factors influencing the energy absorption property of polymer foams, as well as the advanced fabrication approaches of energy-absorbing polymer foams will be covered in Chapter 2.

1.6.2 Thermal Insulation Polymer Foams

Heat transfer occurs through three fundamental mechanisms, namely, conduction, convection, and radiation. Insulation materials are designed to impede heat transfer by reducing its occurrence through these channels. The effectiveness of insulation is determined by the material's thermal conductivity, with lower values indicating better insulation properties. Polymer foams utilize a unique cellular structure to simultaneously obstruct thermal conduction and convection processes. Their porous structure creates multiple internal interfaces, significantly enhancing their ability to block thermal radiation. Attributing to the lightweight, high surface area, and low thermal conductivity of the polymer foams, they have become essential in various applications. In Chapter 3, the thermal insulation mechanism of polymer foams, the structural design, influential factors, and the methods of fabricating advanced thermal insulation foams will be covered.

1.6.3 Acoustic Absorption Polymer Foams

Noise pollution is a major concern in both industrial settings and daily life, with long-term exposure negatively affecting mental and physical health. Porous materials, featuring interconnected pores that allow sound waves to enter and reflect within the material, excel at absorbing sound energy. Polymer foams, with their intricate microporous structures, provide effective sound absorption due to their ability to distort and scatter incident and reflected sound waves. Consequently, various polymer foams, such as melamine foam, PS foam, polyurethane foam, and their composites, find wide application in buildings, automobiles, ships, and aircraft for

sound absorption. The sound absorption mechanism of polymer foams, the critical influencing factors, the measurement approach, and the fabrication methods of sound absorption foams will be covered in Chapter 4.

1.6.4 Superhydrophobic Polymer Foams

Superhydrophobicity, observed in nature on surfaces like lotus leaves and water striders, relies on low surface energy and multilevel surface roughness. By mimicking these features through bionanotechnology, polymer foams can be transformed into superhydrophobic materials suitable for various applications, including anti-fouling, self-cleaning, selective oil absorption, and oil–water separation. The three-dimensional porous structure of polymer foams, both internally and on the surface, enhances their roughness, robustness, and stability compared to surface-engineered materials. In Chapter 5, the surperwetting theory, the chemical and structural design for superhydrophobic surfaces and foams, the methods to fabricate superhydrophobic polymer foams, and their advanced applications will be introduced.

1.6.5 Electromagnetic Shielding Conductive Polymer Foam

Electromagnetic shielding technology is vital for countering EMI and radiation and ensuring information security in our technology-driven world. CPFs possess multiple conductive interfaces within the micro-cell structure, which increases electromagnetic wave reflection and scattering, extending their transmission path and enhancing electromagnetic wave attenuation. Thus, the CPFs have natural advantages in EMI shielding and excellent EM wave absorption properties. The EMI shielding mechanisms for CPFs, the effect of CPF material composition and porous structure, the performance characterization methods, and the advanced approaches to fabricate CPFs will be introduced in Chapter 6.

1.6.6 Medical Tissue Engineering Repair

Organ and tissue transplantation faces a significant supply–demand gap, prompting the exploration of the tissue engineering field. Tissue engineering involves creating three-dimensional structures with cells and biomaterials. Due to their adjustable highly porous structure, tunable mechanical properties and surface chemistry, and biocompatible and biodegradable properties, polymer foams have been recognized as promising candidate materials for tissue repair and artificial organs. Porous polymer scaffolds have been used in the repair of various tissues, including bone, cartilage, skin, vascular, and neural tissues. In Chapter 7, the tissue engineering process, basic requirements for tissue engineering scaffolds, the property evaluation methods, and fabrication methods of tissue engineering scaffolds will be covered.

1.6.7 Flexible Sensors Based on Porous Polymer Foams

In the era of the Fourth Industrial Revolution, there is a growing demand for lightweight, flexible, highly sensitive sensors with fast response times. Porous polymer foams, with a lightweight nature and adjustable mechanical properties, are promising candidates for flexible pressure sensors. These materials can be customized to control piezoresistance and sensitivity by regulating cell microstructure, surface microstructure, and conductive nanofiller networks. Their versatility enables applications in health monitoring, mechanical analysis, robotic tactile perception, and more. The piezoresistive sensing mechanism, the microstructure design, the criteria of pressure sensors, and the advanced fabrication approaches will be introduced in Chapter 8.

1.6.8 Triboelectric Nanogenerator Based on Polymer Foams

Micro/nano energy has gained prominence with the rise of mobile electronics and microdevices. TENGs offer a novel approach to converting mechanical energy into electrical energy by making use of the electrostatic charges generated on different triboelectric materials. Polymer foams have shown promising potential to be used as a new class of friction materials for TENGs due to their rough surface, high surface area, flexibility, abrasion resistance, and low cost. In addition, their internal porous structure enhances charge generation capacity and charge density during TENG operation, making them an attractive choice for sustainable and scalable energy generation. In Chapter 9, the classification and mechanism of TENGs, the prominent factors influencing TENG performance, the advantages of polymer foams in TENG, and advanced achievements in polymer foam-based TENGs will be covered.

1.6.9 Porous Polymers for Solar Steam Generation

Solar steam generation is a crucial technology for addressing water scarcity and seawater desalination. Porous polymers play a vital role in enhancing solar-to-steam conversion efficiency because their highly porous structure facilitates water transport, their lightweight makes them able to float on water, and their light scattering and absorption properties render them high energy conversion efficiency. The fundamental basis of solar steam generation, the effects of porous structure and the surface properties on the solar-thermal energy conversion efficiency, the methods to characterize the solar steam generation performance, and the different types of porous polymers based solar steam generators will be covered in Chapter 10.

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