Supercritical CO_2 Foaming Technologies

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Poly(lactic acid) (PLA) foaming is divided into physical foaming and chemical foaming; in contrast with the latter, the use of a physical foaming agent for PLA foaming has the characteristic of being green and non-polluting in line with the current carbon-neutral development plan. At the same time, the foam obtained by physical foaming has the properties of lightweight, low density, and more stable. Common physical blowing agents are CO_2 and N_2. Due to the plasticizing effect of CO_2, and its high solubility in PLA, which can promote the crystallization of PLA, the current research on the supercritical foaming of PLA, especially intermittent foaming, mainly uses CO_2 as the preferred foaming agent. However, due to the fast diffusion rate of N_2, smaller bubbles can be obtained in microcellular injection foaming using N_2. Therefore, N_2 is commonly used as a blowing agent in the microcellular injection foaming process. In the supercritical foaming process, foaming parameters, such as saturation temperature, saturation pressure, and saturation time have a great influence on the structure and properties of the bubble pores. The cell diameter, cell density, and foam volume expansion ratio are three fundamental parameters for characterizing the cell structure. The variation in the three parameters has a great influence on the cell structure and the performance of the foam. Cell diameter generally refers to the average diameter of at least 100 cell units in the foaming image obtained from electron microscopy. Cell density refers to the number of cells per cubic centimeter of the foamed sample. Volume expansion ratio refers to the density ratio of the unfoamed sample to the foamed sample.

foaming poly(lactic acid) carbon dioxide modification

1. Batch Foaming Technology

Batch foaming involves saturating the polymer with a supercritical fluid in an autoclave for a while and then inducing polymer cell nucleation with rapid pressure reduction or rapid temperature increase, resulting in cell growth by gas diffusion. A sudden drop in pressure or a sudden temperature rise causes the system to change from a homogeneous system to a thermodynamically unstable state, thus inducing cell nucleation. Before saturation is generally low-pressure purging of the reactor, after foaming to ensure the stability of the bubble pore structure requires the operation of cooling the foam. Batch foaming is mainly divided into the pressure-induced foaming method and temperature-induced foaming method.

Pressure-induced foaming refers to the foaming method in which the polymer is saturated in a reaction kettle at a certain temperature and pressure for a certain time and then the pressure is quickly released to form microporous directly.

Wang et al. [1] prepared polycaprolactone (PCL)/PLA composites using pressure-induced foaming at different foaming temperatures (foaming temperatures: 45 °C, 50 °C, 55 °C, and 60 °C). As the foaming temperature increased, the pore diameter increased, the pore density decreased, and the pore wall became thinner or even ruptured. The increase in temperature decreased the PLA melt strength and gas solubility, which were insufficient to support the growth of cells. Then the pores merged or even collapsed, increasing the cell opening rate. Similar conclusions were obtained by Li et al. [2]. They used a pressure-induced method to prepare PLA/poly(butylene succinate) (PBS) composite foam. The cell opening rate decreased, and the cell diameter decreased with the decrease in foaming temperature.

It is noteworthy that the pressure-induced foaming method is the primary foaming means of PLA foams studied so far in the last three years. Some researchers have optimized the one-step method mentioned above and implemented a two-step foaming method. Li et al. [3] prepared PLA foams by combining pre-melting and pressure-induced foaming. They investigated the effects of different foaming temperatures and pressures on the pore morphology and material properties. The pre-melt treatment can ensure the CO_2 adsorption equilibrium. The results show that closed or open cell foam can be obtained under different foaming processes by optimizing the intermittent foaming process, which provides a theoretical basis for applying functional PLA foams. The effect of foaming temperature on the morphology of the foam pores was similar to the results of the above article [1][2]. As the saturation pressure increases, the cell size gradually decreases, and the cell density increases. This result is thought to be caused by the increased solubility of CO_2 in PLA. In this article, the authors also pointed out that the saturation pressure of the foaming process has a more significant effect on the morphology of the pores than the foaming temperature.

Interestingly, for unmodified PLA, spherical crystals appear at low-temperature foaming and disappear as the foaming temperature increases, foaming in an amorphous state. Another paper from the same research group [3] reported the preparation of unmodified PLA foams by pre-crystallization combined with pressure-induced foaming. In the pre-crystallization process, PLA can form lamellar structures at low temperatures and transform into non-lamellar structures at higher temperatures. Therefore, different foam morphology can be obtained at different foaming temperatures. As the saturation pressure increases, the migration rate of amorphous molecular chains increases and crystallization decreases, leading to interfacial surface tension and melt strength being insufficient to support the growth of cells, and cell walls become thinner. Cells merge to form high open-cell rate foams.

As shown, temperature-induced foaming means that the polymer is first saturated in the reactor at low temperature and low pressure and then removed from the reactor and quickly put into a certain temperature medium (usually hot water, oil and so on) for heat bath-induced foaming. When choosing water bath-induced foaming, the ease of hydrolysis of PLA should be taken into account, which may impact the performance of the foamed material, although temperature-induced foaming is a relatively short process. Sun et al. [4] prepared PLLA/PBS/PDLA composite foam by temperature-induced intermittent foaming. The effects of the introduction of poly(butylene succinate) (PBS) and PDLA on the crystallization behavior and cellular structure of PLLA were investigated. It was found that the introduction of both polymers resulted in the formation of stereo-complex crystals in the PLLA matrix. This stereo-complex structure, while limiting the movement of molecular chains, reduced the nucleation rate of

PBS. However, it improves the compatibility of PLLA/PBS composites, plays a positive role in foaming, refines the micropore size, and provides the idea of using PLA stereo-crystals to improve the foaming behavior of PLA. Zhang et al. [5] prepared CA/PLA composite foams using a temperature-induced intermittent foaming method to investigate cellulose acetate foam's properties (CA). The results illustrated that the addition of PLA reduced the system's storage modulus and complex viscosity, increased the loss factor, and improved the rheological properties of CA. The cell size increased, and the impact strength of the foam slightly decreased with the increase of PLA content.

2. Extrusion Foaming Technology

The principle of polymer extrusion foaming was shown. Extrusion foaming enters polymer particles through the feed port and melting plasticization through the screw. When passing through the homogenizing section of the screw with a physical blowing agent (supercritical CO_2 on the figure), molten PLA and supercritical fluid form a homogeneous system, and the extrusion process has a sudden pressure drop, which puts the homogeneous system in a thermodynamically unstable state and induces bubbles to generate. After extrusion, the cells grow. Finally, a cooling device is provided to stabilize the cell structure. For the better dissolution of the gas in the polymer, an oil bath can be used for a static mixing process prior to extrusion. Since extrusion foaming is a continuous process, it is currently one of the primary methods for the industrial production of PLA foams, the other being microporous injection molding.

In the extrusion foaming process, extrusion process parameters such as processing temperature, extrusion outlet die pressure and screw speed are essential factors affecting the structure and properties of the bubbles. Chauvet et al. [6] obtained PLA/thermoplastic starch (TPS) composite foams using the extrusion foaming process and investigated the effect of die temperature on the bubble morphology of the composite foams. The results showed that the composite foams with 20 wt% TPS content showed a decrease in nucleation rate, a decrease in cell size, and an uneven distribution of bubbles as the die temperature increased. The increase in die temperature decreases the melt strength of the system and generates gas escape, which can cause the cells to merge and collapse in severe cases. In addition, due to the amorphous nature of thermoplastic starch, the lower glass transition temperature is also conducive to gas escape. The uneven distribution of the TPS structure at high temperatures can cause uneven distribution of the final vesicles. The authors also confirmed the poor compatibility between pure thermoplastic starch and PLA/TPS composites containing 50 wt% TPS by studying the bubble morphology.

Sadeghi et al. [7] added hydrophilic cellulose nanofibers (CNF) to PLA and prepared microporous foams by twin-screw extrusion foaming and found that the addition of CNF promoted cell nucleation and increased cell density. The molecular weight of pure PLA was reduced by about 25% after extrusion, probably due to the hydrolysis of ester groups that occurred during the melting process. The higher the extrusion outlet die pressure, the more significant the pressure difference in the extrusion process and the higher the pressure plunge, which favors the nucleation rate. It has been shown that higher levels of CO_2 promote foaming during the extrusion process [8].

3. Microporous Injection Molding Foaming Technology

Microporous injection molding (MIM) foam technology was first patented by Trexel Corporation in 1997 and applied to industrial production. The molding principle is similar to the polymer injection molding process. The difference is that a supercritical fluid module is added to the MIM injection process that is mixed by a screw to form a molten polymer/supercritical fluid homogeneous system that is then injected into the mold. Depending on the mold, it can be divided into low-pressure and high-pressure injection molding. When the gas/polymer melt enters the mold, it immediately undergoes a pressure drop. Foaming occurs instantaneously and expands in the mold cavity, called low-pressure injection molding (a short shot). The mold is filled with the gas/polymer melt at high pressure, and during the mold opening process, the rapid pressure relief induces bubble formation, followed by the growth of the gas-filled cell, which is called high-pressure injection molding (full shot). The foam obtained by injection foaming has sandwich structure characteristics, as shown; its microscopic bubble structure consists of a harmful foaming effect epidermal layer and a foaming core layer composed of different bubbles [9]. In the process of injection molding, the pressure, holding time [10][11], opening speed and mold opening distance (for high pressure injection foam) have great influence on the foam structure after molding.

Li et al. [12] used chemical injection foaming technique to prepare PLA/random terpolymer (ethylene, acrylate, and glycidyl methacrylate) composite foams with improved foam morphology. Wang et al. [13] explored a new in situ fiber reinforcement combined with high-pressure microporous injection molding (HPMIM) technique for the preparation of PLA composite foams. Herein, in situ nanofibrillation plays the role of chain expansion/cross-linking, and nanofiber poly(ethylene terephthalate) (PET) with 10 wt% content acts as reinforcement and CO_2 as blowing agent to prepare a composite foam with high impact strength and tensile strength and good thermal insulation. The differences between the morphology and properties of foams obtained by HPMIM and regular microporous injection molding (RMIM) methods were compared under the same injection foaming parameters (melt temperature, mold temperature, injection speed, gas dosage), and the results showed that the improved cell morphology made by HPMIM was attributed to the decoupling of the melt filling process and the enhanced melt strength under high pressure conditions. The high-pressure holding time affects the cell morphology and the PLA/PET composite foam cell morphology prepared by HPMIM is significantly improved compared to that of pure PLA, which is shown to be the result of the action of nanofiber PET. It is of interest that the PLA/PET foam made by this newly developed process has an expansion multiplicity (26.2) that is the maximum obtained by foam injection molding at that time.

In a similar study, Zhao et al. [14] prepared PLA/ethylene-propylene terpolymer (EPDM) composites using in situ nanofibrillation combined with ultraviolet (UV) crosslinking. The experimental procedure was to construct a PLA/EPDM fibrillar structure by melt blow molding and curing the EPDM fibrillar structure using UV crosslinking. The PLA/PEPDM composite foam was obtained using a high-pressure injection molding technique. UV crosslinking acted as a curing agent to further enhance PLA crystallization and melt strength. The authors also investigated the effect of mold opening distance on the bubble morphology, and the mold opening distance had a small effect on the expansion multiplicity of pure PLA foam. As the opening distance increased (at 5 mm to 35 mm), the cell stretching along the opening direction increased, affecting the cell growth orientation. Like the results of the previous study,

microcellular injection foaming combined with in-situ fibrillation resulted in high expansion multiplicity PLA/EPDM composite foams (maximum expansion multiplicity up to 28 times). Meanwhile, in situ fibrillation can obtain microporous materials with high toughness and high impact strength, which has great potential for commercial application.

4. Other Foaming Technologies

3D printing foaming has been introduced as a foaming technology for the future [15]. 3D printing's high degree of freedom in design enables the design of complex and diverse porous structures to meet the characteristics of lightweight porous materials [16]. PLA 3D printing foaming technology [17][18][19], which generally uses fused deposition printing (FDM) foaming, is based on the principle of introducing supercritical fluid at the nozzle of FDM to induce foaming during printing. However, this process is still in its embryonic stage. In the FDM printing process, a systematic solution has not yet been established for how to introduce gas into the nozzle in a stable manner or how to saturate the gas in a small diameter wire and not to escape as well as for the bonding between layers during the printing process. The current application of 3D printing technology for foaming generally means that the sample is printed and processed first and then foamed using intermittent foaming methods, which is only applicable to scientific research and challenging to produce [20][21].

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