Investigation of Cell Nucleation and Growth in Foam Injection Molding through Visualization

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Mechanical and Industrial Engineering
University of Toronto

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Abstract

Foam injection molding (FIM) is one of the most promising manufacturing methods for thermoplastics, owing to its capability to produce low-density and lightweight products with high dimensional precision at fast manufacturing rates. However, achievement of a uniform fine cell structure is very challenging in this technology. The issue arises from the lack of clear understanding of cell formation mechanisms and complicated bubbles’ dynamics in FIM. Here I employed an in-situ mold visualization technique to closely and continuously monitor foaming phenomena, occurring inside the mold and during injection, in order to uncover underlying mechanisms of cell nucleation and growth in FIM. In this context, an innovative visualization mold is designed and manufactured. Using the visualization mold, I first studied cell nucleation and growth mechanisms in high-pressure FIM, and proposed the strategy of using a melt packing pressure to remove the nucleated cells during mold filling and switch nucleation mechanism from “gate-nucleation” to “shrinkage-induced” nucleation. Then, the application of a gas-counter pressure (GCP) with FIM, and cell nucleation mechanisms in this technology, was thoroughly explored. The investigation on cell nucleation and growth mechanisms was then extended to high-pressure FIM technology.
followed by precise mold-opening (or high expansion FIM). Inasmuch as composite thermoplastics foams comprise a large percentage of FIM parts, I extended this research to a comprehensive study on the mutual interaction of nucleated cells and carbon fibers dispersed in a polystyrene matrix in high-pressure FIM. The latter was successfully done using the designed visualization mold and the proposed high-pressure FIM protocol.
To My Parents
To My Lovely Wife, Sojdeh
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Figure 6.14: High-pressure FIM with mold-opening of PS-5%CO₂ at Location B: (a) packing pressure = 14 MPa; (b) packing pressure = 20 MPa; (c) packing pressure = 24 MPa (Injection speed = 80 cm³/s; packing time = 8 s; T_{melt} = 220 °C).

Figure 6.15: SEM images of the high-pressure FIM samples of PS-5%CO₂ with mold-opening at Location B: (a) packing pressure = 14 MPa; (b) packing pressure = 20 MPa; (c) packing pressure = 24 MPa (Injection speed = 80 cm³/s; packing time = 8 s; T_{melt} = 220 °C).

Figure 6.16: Cavity pressure profiles for high-pressure FIM of PS-5%CO₂ with mold-opening at Location B (Injection speed = 80 cm³/s; packing time = 8 s; T_{melt} = 220 °C; solubility pressure of 5wt% CO₂ in PS is approximated 13.2 MPs, and shown by dash line).

Figure 6.17: Cell density versus packing pressure in high-pressure FIM of PS-5%CO₂ with mold-opening (Injection speed = 80 cm³/s; packing time = 8 s; T_{melt} = 220 °C).

Figure 7.1: 2D schematic illustration of fiber alignment: a) the initial state with an initial fiber angle of α₀ and an initial fiber location of R₀; b) an instantaneous state with a fiber angle α and a fiber location R after expansion with a cell radius Rₖ. The fiber location and the fiber angle are described relative to the growing cell. The polymer envelope encompassing the fiber is shown with dashed circles.

Figure 7.2: Theoretically predicted instantaneous fiber angle and fiber location: (a) the fiber angle versus the cell radius; (b) the fiber angle versus the initial fiber angle.

Figure 7.3: Fiber displacement (rotation and translation).

Figure 7.4: Translational displacement for CF#1 and combined rotational and translational displacements for CF#2.

Figure 7.5: (a) the cell radius and the fiber angle versus time; (b) the fiber location versus the time; (c) the observed and predicted fiber angle versus the cell radius; (d) the observed and predicted fiber location versus the cell radius.

Figure 7.6: Effect of the initial fiber location on fiber orientation and fiber translation for CF#4 (R₀=0.1 mm) and CF#5 (R₀=0.37mm). (a) the fiber angle versus the cell radius; (b) the fiber location versus the cell radius.

Figure 7.7: The effect of initial fiber angle on fiber orientation and fiber translation for CF#6 (α₀=14.53°) and CF#7 (α₀=59.18°): (a) the fiber angle versus the cell radius; (b) the fiber location versus the cell radius.
Figure 7.8: The effect of fiber length on the fiber angle: (a) visualized data for CF#5 ($l = 0.28$ mm) and CF#8 ($l = 0.14$ mm); (b) theoretically predicted fiber rotation...
Chapter 1
Introduction and Overview

1.1 Introduction

Polymeric foams are advanced types of materials comprised of a thermoplastic matrix and a dispersed gaseous phase with the main interest of producing low-density and lightweight products. This class of materials offers improved properties such as enhanced mechanical properties with a microcellular structure,\textsuperscript{1-5} enhanced electrical conductivity,\textsuperscript{6} and improved heat and sound insulation.\textsuperscript{7-9} Moreover, some unique characteristics of plastic foams make them a preferred option for specific applications in water filtration industries,\textsuperscript{10} or in biomedical engineering.\textsuperscript{11} Therefore, polymer foams are technologically important engineering materials in manufacturing, automotive, construction, packaging, environment, and bioengineering industries. Microcellular foams are a category of foams characterized by cell sizes ranging from 0.1-10 μm and a cell density breadth of $10^9-10^{15}$ (cell/cm$^3$).

Foam process includes three main steps: (i) dissolution of an inert gas, i.e., a blowing agent, in the polymer melt, (ii) cell nucleation due to the induction of a rapid thermodynamic instability, and (iii) the cell growth. These foaming steps are schematically shown in Figure 1.1. Prior to cell nucleation, a homogenous, single-phase melt/gas mixture must be prepared in order to achieve a uniform high cell density structure after foaming.\textsuperscript{12} Otherwise, structural non-uniformity, formation of gas pockets, large cell size and low cell density, and surface defects are more likely. Blowing agents are classified into two groups, physical blowing agent and chemical blowing agent. Physical blowing agents such as carbon dioxide (CO$_2$) and nitrogen (N$_2$) are directly introduced and mixed with the polymer melt under certain a pressure. Chemical blowing agents such as azodicarbonamide, on the other hand, are usually added to the system together with polymer pellets; this type of the blowing agent decomposes during the processing at specific temperature and produces the required gas for foaming.\textsuperscript{13,14}
The thermodynamic instability required for nucleation is obtainable through a sudden reduction in the blowing agent’s solubility in the polymer melt, by either a fast pressure decrease or temperature rise.\textsuperscript{15,16}

![Diagram of foaming steps]

Figure 1.1: Schematic of foaming steps.

The classic nucleation theory defines a critical value \( (R_c) \) such that only nucleated cells with radii larger than the \( R_c \) survive, whereas others diminish in a foaming system.\textsuperscript{17} In other words, the critical radius determines the stability of a nucleated cell, and is estimated as:

\[
R_c = \frac{2 \gamma}{P_{\text{bubble}} - P_{\text{sys}}}
\]

(1)

Here, \( \gamma \) is the surface energy between the liquid and the gas, and \( P_{\text{bubble}} \) and \( P_{\text{sys}} \) represent the pressure inside the bubble and the system pressure respectively.

As illustrated in Figure 1.2, the free energy of the system decreases by the growth of nuclei with \( R > R_c \), and the collapse of those with an \( R < R_c \).
This nucleation critical radius is a function of the system pressure, temperature, and the concentration of the dissolved gas. Hence, it changes by the system pressure or gas concentration during the foaming process\textsuperscript{18}. During plastic foaming process, however, significant amount of stresses is imposed on the melt; this has been reported that shear/extensional stresses on the polymer/gas mixture promote the cell nucleation process\textsuperscript{19-21}. In addition, the expansion of growing cells, more tangibly about external particles, generates local flow fields and consequently local tensile (extensional) stresses which promote nucleation\textsuperscript{22}.

To account for the effect of local pressure fluctuations, the classical nucleation theory was modified as:\textsuperscript{23}

\[ R_c = \frac{2\gamma}{P_{bub} - (P_{sys} + \Delta P_{local})} \]  \hspace{1cm} (2)

at which $\Delta P_{local}$ is the difference between the system overall pressure and the local system pressure. The negative local tensile stress reduces the critical radius considerably; therefore, more nuclei get a chance to growth further as their radius becomes larger than the critical value. In addition, the super-saturation level increases locally, and as a result, satellite bubbles nucleate around primary growing bubbles\textsuperscript{23}.
Even though homogeneous nucleation is theoretically feasible, the cell nucleation practically occurs heterogeneously on more preferable nucleation sites such as mold surfaces, nucleating agents, impurities, and additives for the barrier energy to initiate heterogeneous nucleation is much less than that in homogeneous nucleation. This is attributed to the decrease in interface area between the matrix and the nucleating agent in heterogeneous nucleation. In this regard, micro- or nano-sized particles such as talc, nano-clay, nano-silica and so forth may be added to the polymer melt before injection.

The free energy barrier for homogeneous and heterogeneous nucleation is obtainable using Equation (3) and (4) respectively.

\[
\Delta G_{\text{hom}}^* = \frac{16 \pi \gamma^3}{3 (P_{\text{bub}} - P_{\text{sys}})^2}
\]  

(3)

\[
\Delta G_{\text{het}}^* = \frac{16 \pi \gamma^3 F(\theta_c)}{3 (P_{\text{bub}} - P_{\text{sys}})^2}
\]  

(4)

where \( \gamma \) is the surface energy between liquid and gas, and \( P_{\text{bub}} \) and \( P_{\text{sys}} \) represent the gas pressure inside the bubble and the system pressure respectively. The shape factor, \( F(\theta_c) \), is the ratio of the nucleated cell volume to that of a spherical bubble having the same radius as can be calculated using Equation (5).

\[
F(\theta_c) = \frac{2 + 3 \cos \theta_c - \cos^3 \theta_c}{4}
\]  

(5)

The wetting angle, \( \theta_c \), is defined as the contact angle between the nucleating agent (solid) and the bubble (gas) which should be measured in matrix phase as shown Figure 1.3. A larger contact angle indicates a better wetting ability of the nucleating phase.
The introduction of cells into the plastic matrix alters its properties significantly. Seeler and Kumar demonstrated that the fatigue life of microcellular polycarbonate, with a relative density of 0.83 and larger, is longer than that of its solid counterpart.\textsuperscript{1} They highlighted the action of cells in blunting the crack growth.\textsuperscript{1} Yuan and Turng discussed that the normalized toughness of microcellular injected polyamide-6 nanocomposites improved as microcells act as crack arrestor.\textsuperscript{2} Matuana \textit{et al.} showed that the notched izod impact strength and the elongation at break of the PVC/wood-fiber composites were improved by microcellular foaming.\textsuperscript{4} The impact strength of the blends of high-density polyethylene and polypropylene was improved by microcellular foaming.\textsuperscript{5} Motlagh \textit{et al.} showed that foaming improved the through-plane conductivity in FIM parts.\textsuperscript{25} Ameli \textit{et al.} measured a higher electrical conductivity for polypropylene/multiwalled carbon nanotube composites after foaming.\textsuperscript{6} Ameli \textit{et al.} reported on improved through-plane conductivity for foamed polypropylene/carbon fiber composites,\textsuperscript{26,27} and improved dielectric properties for foamed polypropylene/multiwalled carbon nanotube composites.\textsuperscript{28} Foams with cells in the range of nano-size, are known to be efficient thermal insulators. With cells reduced to nano-sizes the thermal conduction through the gas within cells decreases dramatically due to the Knudsen effect.\textsuperscript{29-31}

Figure 1.3: Wetting angle between gas/solid surfaces.\textsuperscript{24}
1.2 Foam Injection Molding (FIM)

Among other manufacturing methods for foams, foam injection molding (FIM) stands out because of the high dimensional accuracy and stability in manufactured parts, improved surface quality and the absence of sink marks, high stiffness-to-weight ratio, lower residual stresses, and short manufacturing cycles. In this technology, a pre-plasticated polymer melt mixed with a blowing agent (i.e., a gas-charged polymer melt) is injected into a closed mold cavity. This is essential to produce a homogeneous, one-phase melt-gas mixture prior to injection. Upon the injection, the pressure on the melt-gas mixture is removed and thereby cell nucleation occurs. In FIM technology, foam parts consist of three regions: (a) skin layer, (b) transition region, and (c) foamed core. The skin layer is usually characterized with a no foamed solid layer. The skin layer forms where the melt/gas mixture gets into contact with the (cold) mold cavity walls. Due to the high thermal conductivity of the cavity walls, the skin layer solidifies quickly. The materials in these regions experience a large shearing which may cause highly elongated chains in the skin layer. The core region, on the other hand, has the slowest cooling rate. The core is usually characterized with circular and more uniform cells. The transition layer is located between the skin layer and the core, and is characterized with sheared and elongated cells.

1.2.1 History

Structural foam is a term devoted to the foam products manufactured by conventional injection molding machines at which pre-pasticated resin is injected into the mold cavity using a plunger. The first microcellular injection molding machine was introduced by Trexel Inc. in 1997, about half a century after the invention of the structural FIM technique in 1960. A screw was used for the plasticizing and gas dosing, while a plunger (similar to the structural FIM) was designed for the injection in this technology. One year later, the first microcellular injection molding with a reciprocating screw was developed by Trexel and Engel. The most famous technology in FIM is the MuCell®, licensed by Trexal Inc. in 2000 which is better known as microcellular injection molding. This technology utilizes a reciprocating screw for blowing agent dosing which is injected through the barrel. In this
technology, the pressure inside the barrel ranges from 70 to 250 bars to produce and maintain a homogeneous gas/polymer mixture.\textsuperscript{32} In MuCell\textsuperscript{®} technology, the shearing action of mixers helps in dissolving the blowing agent very quickly and maintaining the dosing pressure at its minimum in the barrel.\textsuperscript{34} Optifoam\textsuperscript{®} is another trade name in FIM, licensed by Sulzer Chemtech. This technology uses a nozzle for dosing the super-critical blowing agent. Despite other methods which inject the blowing agent into the barrel, the gas is entered as very small droplets via special nozzles in this technology. The gas is diffused into the melt; a static blender then mixes the gas-rich melt. In this method, regular barrels and screws can be employed with no major modification\textsuperscript{34}. Ergocell\textsuperscript{®} technology, licensed by Sumitomo-Demag, is another microcellular technology developed in 2001 which needs special assemblies for different injection components such as accumulator, mixers, screws and so forth and has some limitation in the application of blowing agent.\textsuperscript{34} Shimbo \textit{et al.} reported a microcellular technology at which a plasticating screw was utilized to make a single-phase melt/gas solution, while a plunger was employed for the injection.\textsuperscript{35} Later, Park and Xu patented a technology, so called advanced structural foam molding, with a continuous melt/gas mixture formation.\textsuperscript{12,36} They argued that large pressure fluctuations in the injection barrel of the conventional low-pressure structural FIM machines, occurring due to the stop-and-flow nature of the process, cause inconsistent gas injection into the polymer melt. By addition of a (positive displacement) gear pump and an accumulator, the gas dissolution unit is separated from the injection system in advanced structural FIM machine. As a result, the screw keeps rotating between injection cycles, minimizing the barrel pressure fluctuations.\textsuperscript{12} ProFoam\textsuperscript{®} is a recent FIM technology from IKV (Aachen, Germany) at which a physical blowing agent is directly added in the hopper and mixed with the polymer during plasticizing, resulting in weight reductions up to 30\% of the part weight.\textsuperscript{12}
1.2.2 Classification of FIM

The final cellular structure, morphology, and the amount of obtained void fraction are highly dependent to the type of FIM process.

In low-pressure FIM process, a short-shot is used to partially fill out the mold cavity. Once a homogeneous, single-phase melt/gas mixture is prepared, injection occurs. Here, the cell nucleation typically occurs over the gate, and is followed by the free expansion of the nucleated cells to fill out the entire cavity. The injection pressures used in this method are relatively low, ranging from 0.5 to 10 MPa. The amount of the obtainable void fraction is relatively high in this technology, ranging between 5 to 35 %. The cavity pressure profile plays a crucial role in cell nucleation and the final cell density of the foam in low-pressure FIM. A proper gate resistance will prevent any premature nucleation prior the melt entry to the mold cavity. If the cavity pressure is remained well below the solubility pressure of the dissolved blowing agent, a high cell density structure is obtainable due to the fast pressure drop, and consequently a fast cell nucleation, at the gate. If the cavity pressure exceeds that of the gas solubility pressure, on the other hand, the cell nucleation occurs within the cavity, and not at the gate; in this case the nucleation happens over a low pressure drop rate which results in a sluggish cell nucleation and a low cell density structure. The relative cavity pressure and the gas solubility pressure profiles, and the effect of their relative distance on the location of nucleation are shown in Figure 1.4.
Therefore, strategies which help to keep the cavity pressure at low levels, below the solubility pressure of the dissolved blowing agent, enhance the cell nucleation at the gate and enhance the cell density in low-pressure FIM. By increasing the injection speed, for instance, the melt still remains at elevated temperatures when the filling is completed; this keeps the viscosity of the melt at low values, improves the melt flow-ability, and a uniform high cell density structure is expected due to a lower cavity pressure during the mold filling. At low injection speed, on the other hand, the melt cools prior to the nucleation completion which results in higher mixture viscosity and cavity pressure, detrimental to the cell nucleation at the gate. As shown in Figure 1.5, a slower injection speed resulted in cavity pressures which exceeded the solubility pressure of the dissolved blowing agent, here
N\textsubscript{2}, during the injection which cause cell nucleation within the mold cavity under a low pressure drop rate.

![Diagram](image)

Figure 1.5: The effect of injection speed on cavity pressure profiles: (a) low injection speed; (b) high injection speed.\textsuperscript{13}

The set void fraction, i.e. the shot size, also affects the cell nucleation. If a low void fraction is chosen, the pressure level within the entire mold cavity increases. This reduces the supersaturation in turn, resulting in a low cell density with less uniform cell distribution, as shown in Figure 1.6. A higher blowing agent percentage imparts more thermodynamic instability
upon the pressure drop. In addition, the gas solubility pressure increases with the blowing agent content. If the solubility pressure exceeds the cavity pressure, nucleation occurs at all cavity locations simultaneously and yields a uniform microstructure. At low blowing agent content, however, the cavity pressure may exceed the gas solubility pressure, resulting in a non-uniform cell size distribution.\textsuperscript{13} While high void fractions are easily obtainable in low-pressure FIM by using low injection pressures, the final cell structure is highly non-uniform and the cell density is low.

Figure 1.6: The effect of void fraction: (a) cavity pressure profiles; (b) the cell structure.\textsuperscript{37}
In high-pressure FIM, on the other hand, the mold cavity is entirely filled with the gas-charged melt. In this FIM scheme, the required thermodynamic instability, i.e. the cavity pressure drop, is achieved during the melt solidification and shrinkage. Hence, the amount of the obtainable void fraction is much lower compared with that from the low-pressure FIM. The foam uniformity and the absence of open cells and voids are the main advantages of this process. However, the low pressure drop rate, low void fraction, the application of high pressures, and the expensive procedure are main drawbacks of this method.

In order to improve the cell density of the foam, the amount of the expansion ratio, and the uniformity of the cell structure, both low-pressure and high-pressure FIM technologies can be performed using a gas-counter pressure (GCP), mold-opening technology, or a combination of both GCP and mold-opening with the FIM. In FIM using GCP, the mold cavity is pressurized with an inert gas such as N\textsubscript{2} before injection. The gas venting should be controlled during injection to keep a constant pressure on the increasing shot volume; hence no blowing agent loss occurs from the flow front. The high opposing pressure of the GCP prevents the cell nucleation during the injection and postpones it to the moment GCP is exhausted. Hence, the release of the GCP causes the required pressure drop for cell nucleation. Besides, the high value of the GCP, which hinders the cell nucleation/growth (expansion) at the melt flow front, significantly eliminates the surface swirl and results in a solid-like surface.\textsuperscript{34} The GCP should be selected in accordance to the blowing agent content. To be more specific, the GCP should be larger than the solubility pressure of the dissolved gas in order to suppress foaming during the mold filling (Figure 1.7). In GCP process, the shot size dictates the total void fraction. It is also possible to inject a full-shot and release the GCP completely at the end of the injection.
In mold-opening technology, usually used with high-pressure FIM, the mold cavity expands in thickness direction; therefore, foams with high expansions are obtainable in this technology. This is essential that no foaming occurs during filling. In this regard, a GCP can be used. As shown in Figure 1.8, the cavity pressure within the mold cavity is uniform in a typical high-pressure FIM using mold-opening and GCP.

![Figure 1.7: Typical cavity pressure profiles in FIM using GCP (A: near the gate; B: middle of cavity, C: end of the cavity).](image)

![Figure 1.8: Typical cavity pressure profiles in mold-opening FIM using GCP (A: near the gate; B: middle of cavity, C: end of the cavity).](image)
1.3 Problem Statement, Motivation, and Objective

Despite all its advantages, the conventional FIM process suffers from a long-range structural non-uniformity and the formation of large-size cells. Achievement of a high cell-density structure, with fine cells and high expansion, is extremely challenging in this technology. A non-uniform cell size distribution with cell sizes above 1 mm and cell densities less than $10^3$ cell/cm$^3$ is typical in structural foams. Highly sheared cells are commonplace in FIM, and severe coalescence results in the formation of large cells. In addition, the presence of silver marks and swirls reduce the surface quality and of the products.

The issue arises from the lack of a clear understanding of cell formation mechanisms and complicated bubbles’ dynamics in FIM, which limits any advancement in this technology to experimental trial-and-errors. The current FIM knowledge used in the industry and in foam simulation tools (such as Autodesk/MoldFlow and 3D Moldex) is inadequate to describe and predict the foaming phenomena. A clear understanding of the bubble nucleation/growth mechanisms, and reliable in-situ experimental data, are needed to achieve these vital insights.

The outcome of the previous researches, on much simpler systems such as static batch foaming, cannot explain the essence of cell nucleation and growth in FIM due to its dynamic nature and the large strain rates involved. In addition, most of the theoretical approaches addressing cell nucleation and growth dynamics have not been experimentally verified in this process. Hence, the governing mechanisms of structure development in FIM remain poorly understood.

Therefore, the main objective of this doctoral research is set to the identification and understanding of the cell nucleation and growth mechanisms in various FIM technologies. This objective is defined in order to learn of the underlying structure formation mechanisms in FIM, and the relationship between processing parameters, technological parameters, and the expected cellular structure. By governing the morphology and cell structure, desirable properties and applications are achievable.
1.4 Research Methodology

Former studies in FIM have relied only on structural characterization after the foamed samples were cooled and stabilized; therefore, the actual nature of cell nucleation/growth has not been fully understood in FIM. In-situ visualization techniques, on the other hand, provide an excellent opportunity to monitor and observe the entire foaming process, i.e., nucleation and growth, from the very first moment of the phenomena. The observations of phenomena can be related to the processing and technology parameters, and interpreted with the aim of the local cavity pressures. Therefore, in-situ mold visualization is adopted as the main research method in this study. In this regard, an innovative visualization mold is designed and manufactured which is detailed in Chapter 2.

1.4.1 In-situ Mold Visualization in FIM

One of the pioneer attempts for visualization of foaming phenomena in FIM return to the research of Villamizar and Han in 1978, who designed a rectangular visualization mold with transparent quartz walls as shown in Figure 1.9. Villamizar and Han observed the bubble nucleation and the growth/collapse of nucleated cells in structural FIM, using chemical blowing agents, and explained the effect of processing parameters such as mold temperature, injection pressure, melt temperature, as well as the blowing agent concentration on the final foam structure.
Yokoi et al. designed a glass-insert metal mold in which a 45° prism was mounted in the stationary plate of the mold to reflect the cavity images to a camera, as shown in Figure 1.10.38,39
Fathi and Behravesh designed a visualization mold by replacing one side of the mold cavity with a multi-layer, thermally treated glass block of a thickness of 85 mm in the moving part of the mold; a mirror was mounted in front of the glass window to reflect the cavity images to a high speed camera on the top of the setup as shown in Figures 1.11.

Figure 1.10: Visualization mold cavity using prism.\textsuperscript{38,39}

Figure 1.11: Schematic of the injection molding visualization mold, the application of a glass window and a mirror.\textsuperscript{40-41}
Ishikawa and Ohshima designed a prism-insert visualization mold, shown in Figure 1.12, to investigate the foaming phenomena in FIM experiments with high expansion, using physical blowing agent. A glass prism was mounted in the fixed plate of the mold and at the end of the mold cavity, while pressure and temperature sensors were located in the opposite side.

Figure 1.12: Prism-insert visualization mold with pressure and temperature transducers.

1.5 Research Challenges and the Reproducibility of the Results

While the in-situ mold visualization is a strong tool to investigate foaming phenomena in FIM, nevertheless, there are some limitations and challenges involved using in-situ visualization methods with FIM. First and foremost, the material under investigation should remain transparent during the visualization. Any fast crystallization on the skin layer may block the light, interfering with the image recording. Addition of additives to the matrix, i.e. visualization of composites, may also reduce the transparency of the gas-charged melt.

Rheological properties of the melt, and the gas-charged melt, change dramatically during the FIM process and result in very complicated foaming behaviors. The rheological properties
of a gas-charged melt are significantly different from those of the polymer melt alone.\textsuperscript{43,44} The plasticizing effect of the dissolved gas reduces the melt viscosity considerably. This reduced melt viscosity in turn affects cell nucleation, cell growth, and the thickness of the formed skin layers. In addition, there is a temperature gradient from the cavity walls with a lower temperature, to the cavity center at much higher temperature. The presence of this thermal gradient causes viscosity changes in thickness direction, affecting the foaming phenomena. A large amount of shear stresses and high shear rates are experienced by the melt/gas mixture during the injection. Under the high shear rates, the viscosity of the melt and the gas-charged melt will be changed through the shear-thinning mechanism. Also, it has been shown that the shear and elongation stresses enhance the foaming phenomena by stress-induced cell nucleation.\textsuperscript{45,46} The exerted shear can also change the conformation of the polymer chains, causing further chain alignment in injection direction. The latter not only changes the foaming behavior of the polymer melt by affecting the cell nucleation, also may affect the foaming by changing the solubility pressure of the dissolved blowing agent.

Rheological properties of the melt and melt-gas mixture play a crucial role in cell nucleation and growth behavior of nucleated cells in FIM.\textsuperscript{47,48} However, detailed measurement of the melt’s rheological properties in the presence of the dissolved gas, temperature gradients, and the large amount of shearing and high shear rates requires specific equipment, and is beyond the scope of this research. But the overall rheological property changes and their ultimate effects on cellular structure development is qualitatively discussed throughout the thesis.

The visualization experiments were carried out once a steady-state condition was realized at each experimental setting. Because of the very spontaneous and random nature of the cell nucleation and foaming, no standard deviation was reported for each measurement at each specific point. Rather, the overall behavior of cell nucleation and growth at different conditions are compared and the trend of multiple experiments/samples is discussed in this research.
1.6 Overview and Organization of the Research

This research is organized as follows:

Chapter 2: In this chapter, the innovative visualization mold, designed and manufactured for the interest of this research, is described in detail. Novelties of the current design over the existing visualization molds, as well as its new features are described. The capability of the designed visualization mold in analyzing different aspects of FIM is also discussed. Using the visualization technique, the prevailing nucleation mechanisms in low-pressure FIM is identified and explained. In this chapter, I explained how the inherently non-uniform cell structure is developed in low-pressure FIM with cells nucleated at the gate, and contrasted with that in high-pressure FIM with a more uniform pressure drop.

Chapter 3: This chapter includes a comprehensive investigation of cell nucleation in high-pressure FIM technology. Development of the cell structure was observed in high-pressure FIM using the visualization mold, and different active cell nucleation mechanisms were identified using a polystyrene/carbon dioxide system. According to the mold cavity pressure, the two major cell nucleation mechanisms were (i) cell nucleation over the gate, i.e. gate-nucleated cells, and (ii) cell nucleation during melt solidification and due to the melt shrinkage, i.e. shrinkage-induced cells. Depending on the nucleation mechanism, the final cell morphology and structure varied. I proposed a strategy of using a melt packing pressure to re-dissolve the cells, which nucleated during the mold filling and survived the cavity pressure, back into the melt. Hence, a higher pressure drop rate is achievable with a single-phase melt/gas mixture with lower compressibility, compared with a two-phase melt-bubble mixture. I argued that the required melt packing pressure increases by processing parameters which enhance the cell nucleation at the gate. The effect of increasing the injection speed, the percentage of the blowing agent, and the gate resistance on the required melt packing pressure and the dominant cell nucleation mechanism is discussed in this chapter. Eventually, the non-uniformity of the cellular structure in high-pressure FIM is elaborated.

Chapter 4: This chapter is about the effect of processing parameters on the overall cellular structure and cell density in a high-pressure FIM. The effects of the injection speed, the blowing agent content, the injection gate geometry, the melt flow index, and the use of talc
as a heterogeneous nucleating agent on cell nucleation are explored. The overall cell density was not affected with the injection speed or with the injection gate resistance in the high-pressure FIM process. The concentration of the blowing agent and the presence of a nucleating agent, however, affected the cell density significantly. The growth mechanism of a large number of cells in a confined space is discussed in this chapter. It was argued how the growth rate of cells decreases as the cell density increases. In addition, the formation of satellite bubbles, i.e., additional cells nucleated around the growing cells, was observed. This was due to the induced flow and pressure fluctuations in the surrounding melt, which facilitated the nucleation of new cells despite the very low gas concentration.

Chapter 5: Mechanisms of cell nucleation and growth in FIM using a gas-counter pressure (GCP) is studied in this chapter. The GCP is mainly used to improve the surface quality of the FIM parts. Also, it may increase the uniformity of the cellular structure in FIM. Using the visualization results, I identified the condition to completely suppress the cell nucleation and gas-escape by using GCP in a typical experiment. Analyzing the visualization data and the cavity local pressure, I discussed how the inherent structural heterogeneity in the regular FIM can be improved by a GCP. I recorded a much faster cavity pressure-drop using GCP, which increased the cell nucleation rate. The faster pressure-drop was due to the fact that a single-phase melt-gas mixture exhibits a lower compressibility than a two-phase melt-bubble mixture. The effect of the GCP magnitude on the cell morphology and the possibility of the formation of a bimodal structure are also investigated. With a GCP lower than the solubility pressure of the dissolved gas, bimodal foaming is likely. By increasing the GCP above the solubility pressure, the cell density increases because of the faster pressure-drop.

Chapter 6: In order to increase the cell structure uniformity, overall cell density, and the expansion of the foams, the FIM process can be followed by a precise mold-opening (MO) step. In Chapter 6, the formation of the cellular structure in a high-pressure FIM+MO is explored. I observed that a portion of cells, nucleated during the mold filling stage, sustained the cavity pressure and remained in the melt-gas mixture after the filling was completed. These cells decreased the structure uniformity and reduced the overall cell density. The latter was due to the reduced source of dissolved gas, and the high compressibility of the melt-gas mixture with bubbles which decreased the overall pressure drop rate. I employed the strategy
of using a “melt packing pressure”, proposed in Chapter 3, to clear these pre-mature cells before the mold-opening step. Therefore, the obtained pressure-drop rate during the mold-opening increased, resulting in a more uniform, high cell density cellular structure.

Chapter 7: In this chapter, the displacement of dispersed carbon fibers due to foaming in high-pressure FIM of a sample conductive polymer composite is investigated. The developed visualization mold and the established high-pressure FIM protocol were well utilized in this regard. The functionality of conductive polymer composites (CPC) is highly dependent on the orientation and alignment of dispersed fibers. These functional properties include electrical and thermal conductivity, electromagnetic interference shielding, and dielectric properties. In FIM, in particular, the alignment of fibers such as carbon fiber (CF) in the machine direction results in anisotropic properties in in-plane and through-plane directions. The formation and growth of cells modify and alter the alignment of the fibers by a local matrix deformation about dispersed fibers. In this chapter, the interactions between CFs and growing cells in a high-pressure FIM experiment of polystyrene/CF composite, blown with carbon dioxide, is studied through the in-situ visualization technique. Two types of displacement, namely translational and rotational, were identified for CFs as a result of this cell-fiber interaction. The major influential parameters on the fiber displacements were the cell size, the initial cell-fiber distance, and the initial fiber angle. I developed a geometrical model to describe the fiber orientation and location. The model predictions were in a good agreement with the experimental results. The new insight gained from this research is of great importance in thorough understanding of the mechanisms which affect the functionality and the percolation threshold in CPCs through foaming.

Chapter 8: This chapter summarizes the concluding remarks from this thesis, and suggestions for future research.
Reference


Chapter 2

2 A New Insight into Foaming Mechanisms in Injection Molding via a Novel Visualization Mold

2.1 Abstract

The complex mechanisms of bubble nucleation and dynamics in foam injection molding have not been uncovered despite many previous efforts due to the non-steady stop-and-flow nature of injection molding and the non-uniform temperature and pressure distributions in the mold. To this end, a new visualization mold was designed and manufactured for the direct observation of bubble nucleation and growth/collapse in foam injection molding. A reflective prism was incorporated into the stationary part of the injection mold with which the nucleation and growth behaviors of bubbles were successfully observed. The mechanism of bubble nucleation in low- and high-pressure foam injection molding, with and without the application of gas-counter pressure, was investigated. We identified how the inherently non-uniform cell structure is developed in low-pressure foam injection molding with gate-nucleated bubbles, and when and how cell nucleation occurs in high-pressure foam injection molding with a more uniform pressure drop.

2.2 Introduction

Foam injection molding (FIM) is an encouraging manufacturing method, owing to its capability to produce lightweight products by using less material and consuming less energy at fast production rates. In addition, recent studies have demonstrated that the formation of the cellular structure in FIM can improve mechanical and physical properties of the foamed parts.\(^1\)\(^-\)\(^3\) However, most of the underlying mechanism(s), contributing to the cellular

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structure development, are not fully understood in this technology. The absence of a comprehensive understanding of bubble nucleation mechanisms, bubble dynamics, and mutual interactions of growing bubbles and fillers not only limits any structural improvement to empirical trial and errors, also hinders new material designs for enhancement of specific properties in products.

Although extensive research has been conducted to interpret the foaming phenomena in FIM, characterization was performed on the final structure after the samples were stabilized. Therefore, the foaming phenomena were not tracked during the process. Additionally, most of hypotheses or theoretical simulations were not experimentally verified. In this context, the in-situ observation of foaming phenomena drew significant attention amongst researchers. Villamizar and Han designed a rectangular visualization mold with transparent quartz walls to investigate the bubbles’ dynamics in conventional structural FIM. Mahmoudi et al. used a visualization setup in which one side of the mold cavity was replaced with a multi-layer glass block in the moving part of the mold. They conducted full-shot FIM experiments using polystyrene (PS)/carbon dioxide (CO$_2$) system to visualize cell growth and collapse during non-isothermal mold filling. Ishikawa and Ohshima designed a visualization mold in which a glass prism targeted the far end of the mold cavity to investigate the foaming behavior of polypropylene (PP) blown with CO$_2$ during mold opening. Ishikawa et al. extended their study to compare the nucleation effectiveness of nitrogen (N$_2$) with that of CO$_2$. Yamada et al. observed a multi-layer core structure in FIM experiments of PS blown with N$_2$, and justified this phenomenon by the local cavity pressure.

Our study explains the development of a new visualization mold for online observation of bubble nucleation and growth dynamics in FIM, compatible with laboratory-scale and small size injection molding machines. Compared with previous designs, ours provides novel features such as visual accessibility to critical locations in the mold, i.e., near the gate, far from the gate, and in the area between them, while measuring the pressures at the visualized locations. Another unique component of our design is the gate pressure transducer, which can be used, along with other pressure transducers across the mold cavity, to measure the pressure difference before and after the gate. In our previous study, it was demonstrated that
the pressure distributions before the gate and along the mold cavity provide critical information about the foaming dynamics during filling. Nevertheless, most bubble nucleation and growth phenomena had to be theorized based on the pressure data because of the lack of visualization data. On the other hand, the visualized foaming results in the literature could not be properly interpreted due to the lack of pressure distributions in the cavity. The earlier researchers used a pressure transducer either at the end of the cavity, near the end, or near the gate. Although the measured pressure was used for the interpretation of their data, the local pressure and visualized data could not describe the entire foaming phenomena in the mold cavity as the pressure profile changes along the mold cavity.

Unlike most available designs, the selection of small transparent windows in our design minimizes the effective polymer/glass interface, simulating a more realistic FIM process in terms of the heat transfer and the rheological implications on the cavity surface (Figure 2.1). Also, it reduces the probability of any thermal shock, or mechanical damage under high packing pressures. The location of the viewing windows in the fixed plate, on the opposite side of the mold cavity, makes it possible to perform various experiments by simply changing the mold insert, some of which includes, but is not limited to, gas-assisted FIM studies, shear/extension induced FIM, and the study of flow in various channels. Also, the mold can be utilized to investigate other FIM technologies such as gas-counter pressure (GCP) and mold opening (core back). The designed mold can be utilized to further investigate the mechanisms of bubble nucleation/growth, interaction between bubbles and fillers, the effect of formed crystals on foaming, weld-line studies, defects, and model verifications. Since no commercial software can accurately describe the microcellular MuCell or structural FIM technologies, the use of the designed visualization mold will elucidate the details of the bubble nucleation mechanisms in FIM, and will provide reliable experimental data for model verification and software validation.

In this article, we demonstrate the dominant bubble nucleation mechanisms in low- and high-pressure FIM technologies by means of in-situ visualization. Polystyrene/CO₂ mixtures have been used as a case example.
2.3 System Development

A detailed sketch of the designed visualization mold is shown in Figure 2.1. A prism-insert was designed and manufactured at which a right-angle glass prism was mounted to reflect the cavity images to a camera. The prism was a pure non-crystalline fused silica 7980 from Meller Optics Inc., with low refractive index variations, low birefringence values, and a low thermal expansion coefficient. The view surfaces of the prism were optically polished, and its hypotenuse was silver-coated in order to provide mirror action. The physical and optical properties of the prism are summarized in Table 2.1.

The reflective prism was precisely encased in a 4-piece prism-insert (Figure 2.1a). An insert pocket was then cut into a block of P20 mold steel and the prism-insert was fixed inside the mold. Three round, fused silica windows were provided from BMV Optical and mounted in a metallic frame. To ensure that the pressure readings represented the local pressure of the visualized spot, each window was carefully located in front of each of the cavity pressure transducers on the opposite side of the cavity. To measure the pressure before the gate, a Dynisco pressure transducer (Franklin, USA) was incorporated into the mold and its sensor surface was flush-mounted. This should be noted that the pressure transducers’ surface will be in contact with the formed skin layer during injection. The measured cavity pressure would be due to the packing (if used), gas-counter pressure (if used), and the expansion of nucleated cells. This recorded pressure is different from the pressure of individual growing cells inside the foam. The complete assembly of the visualization mold with a detailed view of the assembly section is shown in Figure 2.2.

Table 2.1: Properties of fused silica.

<table>
<thead>
<tr>
<th>Part</th>
<th>Grade</th>
<th>Birefringence (nm/cm)</th>
<th>Shear Modulus* (GPa)</th>
<th>Bulk Modulus* (GPa)</th>
<th>Surface Finish (scratch/dig)</th>
<th>Surface Flatness (wave)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prism</td>
<td>7980</td>
<td>≤ 5</td>
<td>31</td>
<td>35.9</td>
<td>40-10</td>
<td>1</td>
<td>2.20</td>
</tr>
<tr>
<td>Window</td>
<td>7980KrF</td>
<td>≤ 1</td>
<td>31.4</td>
<td>35.4</td>
<td>40-10</td>
<td>1</td>
<td>2.20</td>
</tr>
</tbody>
</table>

* Properties measured at 25 °C
Figure 2.1: (a) Prism-insert; (b) top sectional view of the visualization mold stationary plate, the principle of the reflective prism, and the location of view windows; (c) detailed design of the visualization mold stationary plate; (d) top sectional view of the complete visualization mold.
Figure 2.2: (a) Visualization mold assembly and detailed location of the pressure transducers; (b) gate and cavity cross section with identified locations ($t = 0 \text{ s}$ at the entrance of the cavity).
2.4 Materials and Equipment

A grade of PS from Americas Styrenics (The Woodlands, USA), MC3650, with MFR=13.0 g/10min (200°C/5 kg), was blown using CO₂ from Linde Gas Canada (Toronto, Canada). Nitrogen from Linde Gas Canada (Toronto, Canada) was used as the GCP medium. A 50-ton Arburg ALLROUNDER 270C injection molding machine equipped with a Trexel MuCell SCF delivery system was used to perform FIM experiments. A rectangular mold cavity with nominal dimensions of 135 mm × 111 mm × 3.2 mm, fed by a fan gate, was used to mold the samples. The imaging system consisted of a CV M10 camera from JAI and a magnifying lens from Navitar connected to a computer.

To investigate the governing bubble nucleation mechanisms in FIM, three types of experiments were carried out, namely low-pressure FIM,⁴ high-pressure FIM,³ and (almost) full-shot FIM using GCP.³ The processing parameters for the FIM experiments are listed in Table 2.2. This should be noted that three critical locations were identified for the visualization of the mold cavity, such that Location A was near the gate, Location C was far from the gate and close to the end of the mold cavity, and Location B was in between Locations A and C (Locations A to C correspond to each view window illustrated in Figure 2.1c). The visual observations demonstrated in this research were carried out at Location B, and the time reference (i.e. \( t = 0 \) s) is set as the moment the melt/gas mixture enters the cavity (see Figure 2.2b).
Table 2.2: Processing parameters (in all experiments: $T_{\text{melt}} = 230^\circ\text{C}$; $T_{\text{Mold}} = 25-30^\circ\text{C}$).

<table>
<thead>
<tr>
<th>Process</th>
<th>Shot Size (cm$^3$)</th>
<th>CO$_2$ (wt%)</th>
<th>Packing Pressure (MPa)</th>
<th>Packing Duration (s)</th>
<th>Injection Speed (cm$^3$/s)</th>
<th>GCP (MPa)</th>
<th>Barrel Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-Pressure FIM (~20% void fraction)</td>
<td>48.8</td>
<td>2</td>
<td>0</td>
<td>None</td>
<td>50</td>
<td>None</td>
<td>17</td>
</tr>
<tr>
<td>Low-Pressure FIM (≤5% void fraction)</td>
<td>58</td>
<td>2</td>
<td>0</td>
<td>None</td>
<td>50</td>
<td>None</td>
<td>17</td>
</tr>
<tr>
<td>High-Pressure FIM</td>
<td>62</td>
<td>2</td>
<td>16</td>
<td>1</td>
<td>50</td>
<td>None</td>
<td>17</td>
</tr>
<tr>
<td>Full-shot+GCP</td>
<td>60</td>
<td>1</td>
<td>0</td>
<td>None</td>
<td>50</td>
<td>3.5</td>
<td>17</td>
</tr>
</tbody>
</table>

2.5 Results and Discussion

In FIM processing, a physical or chemical blowing agent (BA) is homogeneously mixed with the polymer melt, followed by a thermodynamic instability to impart bubble nucleation to the system.$^4$ The bubble nucleation mechanism and the final cellular structure are a strong function of the acquired thermodynamic instability, via the pressure drop, which in turn depends on the type of the FIM process.

In low-pressure FIM, the mold cavity was partially filled with the melt/gas mixture.$^{22}$ In this scheme, the pressure of the melt/gas mixture dropped below the solubility pressure of the dissolved BA once it entered the mold cavity; therefore myriad of cells (i.e. gate-nucleated bubbles) nucleate at the gate. Figure 2.3a schematically shows the cell nucleation and free-expansion growth in low-pressure FIM. As illustrated, gate-nucleated bubbles grow, get sheared and elongated, and coalesce during their travel along the mold cavity. Figure 2.3b shows the successive snapshots of the cavity visualization for a low-pressure FIM with 20% void fraction. Because of the large void fraction, the cavity pressure remained below the solubility pressure of the BA; hence a large number of cells were nucleated at the gate under
a fast pressure drop rate, and the (foggy) melt front was associated with fast cell nucleation and gas escape. In this case, the nucleated bubbles could not be visually detected. In order to visualize the behavior of bubbles, we increased the shot size (i.e. smaller void fraction) such that the increased cavity pressure suppressed the cell nucleation at the gate to a large extent. Therefore, a smaller number of cells were induced during feeding, and a clear image was obtained, as shown in Figure 2.4a. The bubble nucleation occurred very quickly as a result of the pressure drop obtained over the gate (where the time was set to zero). As the melt flowed along the cavity, the gate-nucleated bubbles grew as a sensitive function of the mold pressure by the diffusion of the remaining gas molecules into the nucleated bubbles, as shown for $t = 2.3$ to $8.9$ s in Figure 2.4a. Because of the pressure gradient across the mold cavity and bubble coalescence, considerable inhomogeneity in the foam morphology is typically developed at different locations of the mold.

In high-pressure FIM, on the other hand, a full shot was used to completely fill out the mold cavity. As in the case of low-pressure FIM, foaming occurred upon the entry of the melt/gas mixture into the mold cavity. However, all the gate-nucleated bubbles are to re-dissolve into the melt under the cavity pressure in this method. If the cavity pressure does not suffice for dissolution of gate-nucleated bubbles, then the melt packing pressure can be continuously applied. The pressure drop, responsible for bubble nucleation, is then attainable during melt solidification and shrinkage. As shown in Figure 2.4b, foaming started upon the entry of the melt/gas mixture into the cavity, and the melt front advancement was associated with bubble nucleation, foaming, and gas-scape. However, the gate-nucleated bubbles disappeared under the cavity pressure and new bubbles eventually nucleated, after about 9 seconds, during solidification. Therefore, the main difference between the nucleation mechanism in low-pressure and high-pressure FIM schemes was the source of the pressure drop, which induced bubble nucleation.

In order to increase the surface quality and structural homogeneity of FIM parts, the FIM process was performed using GCP.$^{12,13}$ In this method, the mold cavity was charged with GCP, higher than the solubility pressure of the dissolved BA, prior to the filling step. This high-pressure gas was then exhausted as the injection proceeded. Figure 2.4c illustrates successive snapshots from visualization results of FIM experiments using GCP. As
demonstrated, the GCP prevented foaming and gas-scape, evidenced by a smooth and transparent melt front, and postponed the bubble nucleation moment till the end of the filling stage. Once the GCP was removed, bubble nucleation occurred.

Figure 2.3: (a) schematic of low-pressure FIM (formation and growth of gate-nucleated bubbles, which get sheared and coalesced during mold filling and free expansion; the hatched area shows the formed skin layer); (b) successive snapshots for low-pressure FIM experiments of PS-2% CO₂ with 20% void fraction (Injection Speed = 50 cm³s⁻¹; T_melt = 230°C; Visualization location = B; The time was set to zero at the moment when the melt entered the mold cavity).
Figure 2.4: Mechanism of bubble nucleation in FIM: (a) Low-pressure FIM, CO\textsubscript{2} = 2%; Void fraction \textasciitilde 5%; (b) High-pressure FIM, CO\textsubscript{2} = 2%, Pack pressure = 16 MPa, Packing time = 1 s; (c) Foam injection molding using GCP, CO\textsubscript{2} = 1%, GCP removal time = 7 s (Injection Speed = 50 cm\textsuperscript{3}s\textsuperscript{-1}; T\textsubscript{melt} = 230\textdegree C; Visualization location = B; The time was set to zero at the moment when the melt entered the mold cavity).

The cavity pressure profiles, at Locations A and B, corresponding to the aforementioned experiments are shown in Figure 2.5. The cavity pressures in high-pressure FIM were higher than those in low-pressure FIM, due to the application of melt packing. Further, while discrepancy was observed in pressure-decay profiles recorded at Locations A and B in low-pressure FIM, the pressure profiles almost coincided in the cases of high-pressure FIM and FIM experiments using GCP. Compared with the high-pressure case, a greater discrepancy in the pressure-decay profiles recorded at Locations A and B of low-pressure experiments indicated on bigger bubbles at Location B and a larger structural heterogeneity. The study of pressure profiles in experiments using GCP revealed that a very rapid pressure drop, but
similar, was obtained at both Locations A and B upon the GCP release, enhancing the bubble nucleation rate and improving the structural uniformity.

Figure 2.5: Pressure profiles in FIM experiments at 50 cm$^3$s$^{-1}$: (a) Low- and high-pressure FIM; (b) FIM+GCP (The time reference is the moment of the melt entry into the mold cavity).
2.6 Conclusions

An innovative visualization mold was successfully designed and used to investigate bubble nucleation and growth in foam injection molding. Visualization results revealed that the prevailed nucleation in low-pressure foam injection molding is the one occurring as a result of the pressure drop obtained at the gate. In high-pressure foam injection molding, in contrast, the gate-nucleated bubbles disappeared under the high pressure of the mold cavity using melt packing, and the nucleation of new bubbles, happening during melt solidification and shrinkage, governed the ultimate cellular structure. The pressure profiles recorded at visualized spots indicated on a higher cavity pressure, required for the dissolution of gate-nucleated bubbles in high-pressure foam injection molding. By the application of gas-counter pressure, bubble nucleation was prevented till the end of the mold filling, and initiated upon the gas-counter pressure removal. By combining the information from in-situ visualization and cavity pressure, proper processing conditions can be effectively derived for each processing scheme.
2.7 References


Chapter 3

Study of the Bubble Nucleation and Growth Mechanisms in High-Pressure Foam Injection Molding through in-situ Visualization

3.1 Abstract

Although major efforts have been made to uncover the complex mechanisms of bubble nucleation and dynamics in foam injection molding, most theories and interpretations still require additional experimental verification. An innovative visualization mold was employed with which the mechanisms of bubble nucleation and growth in high-pressure foam injection molding were investigated. For the first time, the development of the cell structure in high-pressure foam injection molding was comprehensively explored and experimentally verified via in-situ visualization using polystyrene and supercritical carbon dioxide system. Two bubble-nucleation mechanisms were observed, namely, the nucleation due to a pressure drop at the gate during filling, and the nucleation due to melt shrinkage in the cavity after filling. It was the cavity pressure that determined which bubble-nucleation mechanism was dominated between these two in high-pressure foam injection molding. The final cellular structure and morphology of the foamed parts were, in turn, determined by the governing bubble-nucleation mechanism. It was concluded that a melt packing pressure is required to re-dissolve the bubbles nucleated at the gate back into the melt, and that a larger packing pressure was needed with a higher cell density by increasing the injection speed, the gate resistance, or the blowing-agent content. Because of the high resistance in the narrow cavity, the bubbles within the cavity were not pressurized uniformly, when the packing

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pressure was applied. A higher cell density increased the compressibility of the two-phase gas-melt mixture, aggravating the non-uniformity of the pressure in the cavity. Consequently, the bubbles far from the gate could not be pressurized immediately, and thereby could not dissolve into the polymer melt quickly. Additionally, the lower temperature of the melt far from the gate further delayed the permeation of gas into the polymer.

3.2 Introduction

The global energy crisis and environmental pollution concerns are forcing industries to find ways to manufacture lightweight products by using less materials and consuming less energy while obtaining comparable and/or superior properties to their conventional solid counterparts. In this context, the foam injection molding (FIM) technology is one of the most promising available technologies. This is because of its capability to produce low-density parts with high geometrical accuracy and a high stiffness-to-weight ratio in rapid production cycles.\textsuperscript{1} However, achieving a uniform and high-cell-density microstructure, which is critical for obtaining superior mechanical properties in foamed plastics,\textsuperscript{2} is challenging in FIM. The difficulty arises from the absence of a clear and comprehensive understanding of cell nucleation mechanism(s) and the complexities of bubble dynamics in FIM. In this regard, extensive research has been carried out devoted to investigating: (i) the effect of processing parameters on the microstructure and morphology development,\textsuperscript{3-6} (ii) the effect of micro- or nano-sized particles on cell nucleation,\textsuperscript{7-10} and (iii) the mechanical properties of foamed parts in low-pressure FIM.\textsuperscript{11-14} In addition to the experimental works, numerous theoretical and numerical studies have been done to model and predict the development of bubbles considering different processing parameters.\textsuperscript{15-21}

While a great deal of research has been conducted to improve the cellular structure,\textsuperscript{15-77} the surface quality,\textsuperscript{22-24} and the physical and mechanical properties of FIM parts,\textsuperscript{25-29} a few studies were dedicated to the investigation of governing mechanisms of bubble nucleation and growth per se, especially in high-pressure FIM experiments. Lee \textit{et al.} proposed strategies to obtain structural foams with a high void fraction and improved structure
uniformity in low-pressure FIM based on the mold cavity pressure profile, by inducing proper gate-nucleated cells.\textsuperscript{1} Wang \textit{et al.} observed that the shape of the formed bubbles in FIM experiments shifted from elongated to circular bubbles, parallel to the flow direction, by increasing the shot size.\textsuperscript{30} They argued that while elongated bubbles were formed during filling, the circular bubbles were formed during the cooling stage.\textsuperscript{30}

Although significant contributions have been made for a better understanding of complicated FIM phenomena, structure characterizations were performed mainly on the final cell morphology using empirical approaches. Thus, the details of the governing mechanism(s) remain unclear and not fully understood. Additionally, most of the theoretical simulations were not experimentally verified. Therefore, \textit{in-situ} observation of foaming phenomena drew significant attention from researchers, which was a method utilized earlier to study various aspects of injection molding,\textsuperscript{31-35} or to uncover the underlying mechanisms in simpler foaming processes such as static foaming,\textsuperscript{36,37} foaming under an extensional stress,\textsuperscript{38,39} and foaming under a shear stress.\textsuperscript{40} Online monitoring of the FIM phenomena would provide far greater insights into the governing mechanisms of each stage of the foaming process under different conditions.

A few attempts have been made to study the bubble nucleation and growth behaviors in FIM using direct visualization techniques. Villamizar and Han investigated the bubble dynamics under various processing parameters in low-pressure conventional FIM, and bubble collapse using melt packing pressure.\textsuperscript{41} Mahmoodi \textit{et al.} visualized and modeled the non-isothermal growth and collapse of carbon dioxide (CO\textsubscript{2}) bubbles in polystyrene (PS).\textsuperscript{42,43} Ishikawa and coworkers visualized the formation of CO\textsubscript{2} and nitrogen (N\textsubscript{2}) bubbles in polypropylene in high-pressure FIM followed by mold opening. They observed that the number density and the rate of formed bubbles were increased by the core-back rate and by the percentage of the dissolved gas in the melt. In addition, the number density of nucleated bubbles was much higher using N\textsubscript{2} compared to CO\textsubscript{2} in their experiments.\textsuperscript{44,45} Based upon the melt pressure inside the mold cavity in FIM, Yamada \textit{et al.} observed that the bubbles formed during filling sustained in the melt at regions with lower cavity pressures, while bubbles at high pressure and elevated temperature regions of the central core shrank completely and new bubbles
were reformed during cooling. This resulted in a multilayer cellular structure in the core region of the foam injected parts.\footnote{46}

Despite numerous efforts to study the cellular structure and morphological development in FIM, there are still ambiguities about the structural development in the high-pressure FIM. In the current research, a unique \emph{in-situ} visualization mold, equipped with 4 pressure sensors, was employed to investigate the mechanisms of bubble nucleation and growth in the high-pressure FIM process in full detail. A series of critical experiments were carried out using PS and CO\textsubscript{2} as a case example. The cell nucleation mechanisms identified from this study provide essential guidelines to optimize the processing conditions for obtaining more uniform and predictable cellular structures in high-pressure FIM.

### 3.3 Theoretical Description of Low- and High-Pressure Foam Injection Molding

In FIM process, a homogeneous melt/gas mixture is injected into a closed mold cavity and the expandable melt/gas mixture generates a foam structure. The bubble-nucleation mechanism strongly depends upon the type of FIM process, the type and amount of the blowing agent, the type and amount of the nucleating agent, and the resistance of the gate.

In low-pressure FIM such as the conventional structural foam molding technology,\textsuperscript{1,41-47} a short-shot is typically used to partially fill the mold cavity, and bubble nucleation generally occurs due to the pressure drop obtained across the gate. When the melt/gas mixture, under a pressure higher than the gas solubility pressure before the gate, enters the mold cavity and experiences a pressure lower than the gas solubility pressure, cell nucleation occurs. In this case, the relative pressure level before and after the gate is a key parameter in controlling the bubble nucleation rate.

While a high void fraction, up to 35\%, can be easily achieved in low-pressure FIM, the structure suffers from a considerable non-uniformity at different locations of the foamed part. This is attributed to the varying cell-nucleation rates from the changing pressure after...
the gate during mold filling, to the pressure gradient, to the temperature gradient, and to the coalescence of the growing cells. The pressure after the gate (defined as the “after-gate” pressure in this paper) changes as a function of the (mold filling) time. In the beginning, the mold cavity is empty; hence the after-gate pressure is equal to the ambient pressure (unless gas counter pressurized). As the melt/gas mixture enters the mold cavity, its temperature decreases (due to the contact with the cold cavity surface) and its viscosity increases, which creates more resistance and thereby increases the after-gate pressure. While the after-gate pressure is lower than the solubility pressure, cell nucleation will still occur at the gate, where the pressure goes below the solubility pressure at the gate. But since the pressure difference between the solubility pressure and the after-gate pressure (i.e., the driving force for cell nucleation) decreases, the cell nucleation rate decreases. On the other hand, if the after-gate pressure becomes larger than the solubility pressure, cell nucleation will not occur at the gate regardless of the amount of the pressure drop across the gate. Rather, cells will nucleate in the mold cavity as the pressure decreases gradually along the cavity and eventually goes below the solubility pressure. Since the pressure drops gradually along the cavity, the cell nucleation rate will be very low.

Therefore, in order to induce a high cell-nucleation rate in the low-pressure FIM, the after-gate pressure should be maintained very low during the filling time, so that the pressure difference between the solubility pressure and the after-gate pressure can be maximized during filling. Any pressure increase after the gate will negatively affect the cell nucleation rate. Especially, when foaming actively takes place at the gate, the expanding cells will further cool the melt because of the adiabatic expansion effect, and consequently, the increased viscosity will aggravate the situation. So rapid filling will be desirable to minimize the amount of foaming before complete filling. The pre-foaming in the mold cavity, before complete filling, also causes more cell coalescence. Hence, one good strategy in low-pressure FIM would be to increase the filling rate significantly such that the after-gate pressure can be maintained low while minimizing pre-foaming.

While it is challenging to maintain a constant cell-nucleation rate at the gate, growth of the nucleated bubbles is also non-uniform because of the different pressure, temperature and time history of each bubble in low-pressure FIM. The nucleated bubbles grow during their
travel towards the end of the cavity along the machine direction;\textsuperscript{25,50,51} therefore, bubbles nucleated at different times grow to different sizes. In addition, due to large shearing involved in this process, especially along with added fibers, the growing and elongated bubbles are subjected to severe coalescence through the increased cell-to-cell contact area.\textsuperscript{25,51,52} Especially, the bubbles located farthest from the gate are largely coalesced because of the long distance of travel during filling. Consequently, it is almost impossible to obtain a uniform cell structure using low-pressure FIM.

In contrast, a very uniform foam structure can be obtained in high-pressure FIM by decoupling cell nucleation from filling. Typically, a full-shot is used in high-pressure FIM to completely fill out the entire cavity first, and foaming is induced uniformly along the channel after complete filling. A schematic of high-pressure FIM is illustrated in Figure 3.1. Similar to low-pressure FIM, bubble nucleation occurs first at the gate upon entering the mold cavity. Ideally, these nucleated bubbles, so called “gate-nucleated” bubbles, must completely dissolve back into the melt under the high pressure of the mold cavity in high-pressure FIM. If the level of the cavity pressure does not suffice, then the filling step can be followed by a melt packing step in order to re-dissolve the gate-nucleated bubbles back into the melt. The driving force for bubble nucleation in this process is then provided by volume shrinkage during melt solidification after injection, or by precise mold opening (or core back) to obtain a higher void fraction.\textsuperscript{44,53,54} Then a very uniform structure can be obtained.
Figure 3.1: Ideal high-pressure FIM process: (a) mold filling and the formation of gate-nucleated bubbles due to pressure drop over the gate; (b) full-shot; (c) collapse and dissolution of gate-nucleated nucleated bubbles; (d) complete disappearance of nucleated bubbles (formation of one-phase melt/gas solution); (e) nucleation of secondary (shrinkage-induced) bubbles due to the melt shrinkage; (f) growth. (The hatched area shows the formed skin layer).

In order to promote uniform cell nucleation with shrinkage (or mold opening), we need to remove the gate-nucleated bubbles completely before the cell nucleation stage in high-pressure FIM. But removal of the gate-nucleated bubbles is challenging, especially in the presence of a large number of bubbles nucleated earlier at the gate (as discussed in detail in Sections 4.2-4.4). This difficulty arises from the increased compressibility of the polymer/gas mixture with a higher number density of the gate-nucleated bubbles (and consequently, more non-uniform packing pressures applied on the gate-nucleated bubbles). This study clearly identifies the mechanisms of forming and collapse of the gate-nucleated bubbles, and the effective processing parameters governing bubble nucleation in high-pressure FIM.
3.4 Experimental

3.4.1 Equipment and Materials

To capture the foaming phenomena occurring inside the injection mold cavity, a visualization system was setup as shown in Figure 3.2a. An innovative visualization mold was designed and manufactured at which a fused silica prism is mounted in the stationary plate of the mold. The mold cavity is located in the moving plate of the mold. Once the mold closed, the prism, which is a part of the mold wall, reflects the cavity images to a camera. A cross sectional view of the visualization plate (i.e., the mold’s stationary plate) and a schematic of a full-shot injected part are illustrated in Figure 3.2b and 3.2c. The full detail of the employed visualization mold is explained elsewhere.55

A 50-ton Arburg ALLROUNDER 270/320°C injection molding machine equipped with a Trexel MuCell SCF delivery system was used to perform the FIM experiments. A rectangular mold cavity with nominal dimensions of 135 mm × 111 mm × 3.2 mm, fed by a fan gate with a thickness of 1.70 mm (Gate #1), was used. To investigate the effect of gate resistance on the foaming mechanism, a second fan gate with a thickness of 2.78 mm (Gate #2) was also used. The imaging system, which consisted of a CV M10 camera from JAI equipped with a magnifying lens from Navitar, was connected to a computer using a frame grabber (PC Vision).

A grade of PS from Americas Styrenics, Styrene 675 with MFR 7.5 g/10 min. (200°C/5 kg; ASTM D-1238) was blown using CO₂ with 99.8% purity degree from Linde Gas Canada.
Figure 3.2: (a) Schematic view of FIM visualization setup; (b) cross sectional view of the visualization (stationary) plate; (c) full-shot injection part (A: near the gate, B: middle cavity, and C: cavity end).
3.4.2 Experimental Procedures and Processing Conditions

A series of high-pressure FIM experiments were conducted at 230 °C, and the formation of bubbles was visualized at different locations of the mold cavity. In order to remove the gate-nucleated bubbles, a melt packing pressure was implemented by injecting an excessive amount of the melt/gas mixture. The effect of injection speed (at 50 and 80 cm$^3$/s), blowing agent concentration (2 and 3 wt% CO$_2$), and the resistance of the injection gate (gate thicknesses of 1.70 and 2.78 mm) on the bubble nucleation mechanism were investigated.

3.4.3 Foam Structure Characterization

The cell density with respect to the unfoamed volume, (i.e., $N'$),$^{56}$ was measured from the visualized images by adopting the method used by Wong et al.$^{48}$ First, the cell density with respect to the foamed volume, was obtained using Equation 1:

$$N_{foamed}(t) = \left( \frac{N(t)}{A} \right)^{\frac{3}{2}}$$  \hspace{1cm} (1)

where $N(t)$ is the number of cells within the area ($A$) at each time instant ($t$). To measure the cell density with respect to the unfoamed volume ($N'$), Equation 2 was used:

$$N'(t) = N_{foamed}(t) \times VER(t)$$  \hspace{1cm} (2)
where $VER$ is the volume expansion ratio. To estimate $VER$, at least 10 (“m”) random bubbles were chosen at each time, and their radii were measured using ImageJ software. Then the $VER$ was calculated using Equation 3:

$$
VER(t) = 1 + \left[ \frac{4}{3} \pi \left( \sum_{i=1}^{m} \left( \frac{R_i^3(t)}{m} \right) \right) N_{foamed(t)} \right]
$$

To measure the growth rate of bubbles, the diameter of 10 random bubbles were measured using ImageJ software and its average was used as the bubble diameter in that time instant. For the next time instant, the diameter of the same 10 bubbles were measured and averaged.

The time reference in all experiments was set to the moment melt/gas mixture entered the mold cavity. Each experiment was repeated at least three times to ensure the consistency in results.

3.5 Results and Discussion

3.5.1 Mechanism of Bubble Nucleation and Growth in High-pressure FIM

As discussed in Section 2, different nucleation mechanisms and cellular structures are obtainable in high-pressure FIM depending on the cavity pressure. Figure 3.3 shows snapshots of high-pressure FIM of PS 675 visualized at Location B (refer to Figure 3.2c). The processing conditions are indicated in the figure caption.
Figure 3.3: Evolution of cell morphology in high-pressure FIM of PS 675-CO₂ under different melt packing pressures at Location B: (a) packing pressure = 2.5 MPa; (b) packing pressure = 8 MPa; (c) packing pressure = 15 MPa (injection speed = 50 cm³/s; packing time = 1 s; CO₂ = 2 wt%; T_{melt} = 230°C, arrows show the typical un-dissolved gate-nucleated bubbles that were nucleated at the gate).

As shown in Figure 3.3a, the amount of the packing pressure was not sufficient to dissolve back the nucleated bubbles during feeding. As a consequence, the nucleated bubbles at the gate remained in the structure and quickly grew due to the gas molecule diffusion from the polymer melt to the bubbles. As demonstrated, the morphology of the part was characterized by elongated, large bubbles and the prevailing nucleation mechanism was the pressure drop over the gate.
By increasing the packing pressure from 2.5 to 8 MPa in a separate injection trial, the local cavity pressure at Location B increased. Under this packing pressure, more (gate) nucleated bubbles were dissolved back into the melt. The flow marks along the machine direction indicate that the melt is flowing in as the bubbles are shrinking under the pressure. With this condition, the few remaining bubbles grew while new bubbles nucleated during melt solidification (Figure 3.3b). The obtained structure is thus a mixture of gate-nucleated bubbles at the gate with secondary bubbles nucleated during melt shrinkage. In the growth stage, the gate-nucleated bubbles were more elongated compared to the secondary circular bubbles. Using a packing pressure of 15 MPa, eventually all nucleated bubbles during feeding disappeared. The absence of flow marks in the snapshot at t = 3.4 s of Figure 3.3c indicates that the melt did not flow in anymore once the bubble shrinkage was completed. After a while, bubble nucleation occurred only due to the cavity pressure drop obtained during shrinkage as a result of melt solidification. These secondary nucleated bubbles, so called “shrinkage-induced” bubbles, were characterized by a completely circular shape as shown in Figure 3.3c.

The injection and melt packing pressure information (displayed from the injection-molding machine) as well as the cavity pressure profiles (obtained at Location B from an installed pressure transducer), corresponding to the experiments in Figure 3.3, were recorded and illustrated in Figure 3.4. It should be noted that the injection pressure is a state parameter, determined by the set injection speed, and does not directly contribute to the nucleation mechanisms inside the mold cavity. As shown in Figure 3.4a, the magnitude of the injection pressure was much higher than the cavity pressures built-up inside the mold, to prevent premature foaming before the melt/gas mixture reached the mold cavity. After a full-shot melt/gas mixture was injected into the mold cavity, a melt packing pressure was applied, in order to remove the gate-nucleated bubbles. By increasing the melt packing pressure, the cavity pressure increased. As shown in Figure 3.4b, the cavity pressure should be kept above the solubility pressure (corresponding to the dissolved gas content) long enough to ensure the dissolution of the gate-nucleated bubbles.
Figure 3.4: (a) The injection pressure and the packing pressure recorded by the injection-molding machine. The pressure built-up time to reach a packing pressure of 15 MPa was recorded about 0.2 s in a typical trial; (b) cavity pressures measured at Location B (high-pressure FIM of PS 675-CO$_2$ (injection speed = 50 cm$^3$/s; packing time = 1 s; CO$_2$ = 2 wt%; $T_{\text{melt}} = 230^\circ$C, the horizontal line in Figure 3.4b shows the solubility pressure for 2% dissolved CO$_2$ in PS).

Comparing the final morphology and the cellular structure acquired from different nucleation mechanisms, it was readily noticeable that the number of cells per unit area was larger at a lower packing pressure with dominant bubble nucleation at the gate. Park et al. discussed that a higher pressure drop rate results in a higher cell density, with finer cell sizes, by inducing a higher thermodynamic instability within the polymer and gas system.$^{57}$ This indicates that the pressure drop rate obtained over the gate was much higher compared with that obtained during melt shrinkage. In addition, the cellular structure obtained via each nucleation mechanism varied in final morphology. While the presence of gate-nucleated bubbles resulted in elongated, rain droplet-shaped bubbles in the final cellular structure, the morphology obtained as a result of melt solidification and shrinkage was characterized by circular bubbles. In the mechanism switch point, a mixture of both morphologies was observed.
The cavity pressure profile always decays from a maximum near the gate (or sprue) area to its minimum at the furthest cavity locations from the gate in FIM. This variation in pressure may change the active nucleation mechanisms, both in low-pressure and high-pressure FIM processes, resulting in heterogeneity of the cellular morphology of the foamed parts. To study this, FIM visualization experiments were performed in Location A (i.e., close to the gate as shown in Figure 3.2c) under a packing pressure of 8 MPa and an injection speed of 50 cm³/s, as demonstrated in Figure 3.5. Unlike the case in Figure 3.3b, the gate-nucleated bubbles were dissolved back into the melt immediately under the packing pressure of 8 MPa at Location A. In other words, while the bubbles nucleated at the gate survived at Location B, the cavity pressure removed all gate-nucleated bubbles at Location A under the same processing conditions.

Figure 3.5: Bubble nucleation at Location A; (injection speed = 50 cm³/s; packing pressure = 8 MPa; packing time = 1 s; CO₂ = 2 wt%; T<sub>melt</sub> = 230°C).

### 3.5.2 Effect of the Injection Speed on the Bubble Nucleation Mechanism in High-Pressure FIM

To investigate the impact of the injection speed on the foaming mechanism, high-pressure FIM experiments were carried out on sample PS 675-2wt% CO₂ at an injection speed of 80 cm³/s; the visualization snapshots at Location B are displayed in Figure 3.6. Up to a melt packing pressure of 15 MPa, the gate-nucleated bubbles (i.e., bubbles nucleated during feeding at the gate) survived in the melt as seen in Figure 3.6a. By further increasing the packing pressure up to 16 MPa, eventually no observable bubble was noticed for a
considerable time span, indicating that bubbles nucleated as a result of melt shrinkage, characterized with a spherical bubble shape.

Figure 3.6: Evolution of cell morphology in high-pressure FIM of PS 675-2 wt% CO₂ under different melt packing pressure at Location B: (a) packing pressure = 15 MPa; (b) packing pressure = 16 MPa (injection speed = 80 cm³/s; packing time = 1 s; T_melt = 230°C, arrows show typical un-dissolved gate-nucleated bubbles).

By increasing the injection speed from 50 to 80 cm³/s, the required packing pressure to re-dissolve all the gate-nucleated bubbles increased. As the injection speed increases, the cavity filling time decreases. In other words, the melt temperature remains higher during mold filling compared with injection at a lower speed. The higher melt temperature in turn results in a lower melt viscosity, reducing the cavity pressure. Therefore, a higher pressure drop rate can be achieved at the gate, which increases the number of gate-nucleated bubbles during feeding. In this case, a higher packing pressure is required to re-dissolve all nucleated bubbles back into the melt.
3.5.3 Effect of the Gate Resistance on the Bubble Nucleation Mechanism in High-pressure FIM

To investigate the effect of the gate resistance on the mechanism of bubble nucleation, a series of high-pressure FIM experiments were carried out using a high-resistance fan gate, with a thickness of 2.78 mm (Gate #2), under the exact processing conditions explained in Figure 3.6, and the visualization results illustrated in Figure 3.7.

Figure 3.7: Evolution of cell morphology in high-pressure FIM of PS 675-2 wt% CO₂ under different packing pressures at Location B: (a) packing pressure = 19 MPa; (b) packing pressure = 20 MPa (gate thickness = 2.78 mm; injection speed = 80 cm³/s; packing time = 1 s; T_{melt} = 230°C).

To The visualization results suggest that a higher packing pressure was required to re-dissolve all the gate-nucleated bubbles back into the melt using the gate with higher resistance. To investigate the effect of gate resistance, the cavity pressure profiles during the filling stage of the mold cavity were constructed against time as shown in Figure 3.8. Comparing pressure profiles at the gate area and Location A of the mold cavity, it is evident that the pressure drop (i.e., the pressure difference at the gate and at Location A of the mold) is larger at any time for the gate with higher resistance during the filling stage. Hence, a
larger nucleation driving force was obtained, and consequently, a larger number of bubbles were generated during feeding.\textsuperscript{57} As a result, a higher packing pressure was required for dissolution of the nucleated bubbles.

Figure 3.8: Pressure profile curves in the filling stage of injections using different gates with thickness of: Gate #1: 1.70 mm; Gate #2: 2.78 mm.

The obtained results from the direct visualization of the foaming phenomena in high-pressure FIM of PS/CO\textsubscript{2} system led us to an important mold design consideration based upon the difference in the mechanism of bubble nucleation in low- and high-pressure FIM technologies. In the low-pressure FIM, a gate with a high pressure drop rate is preferred to induce a rapid pressure drop across the gate, and thereby promoting a large cell density.\textsuperscript{1} Otherwise, a poor cellular structure would be obtained as a result of low nucleation rate and severe cell coalescence. In high-pressure FIM, on the other hand, a gate with a low pressure drop rate is favourable to minimize the number of cells nucleated at the gate, as the driving
force for nucleation is determined with the rate and extent of the melt shrinkage, or the mold opening.

3.5.4 Effect of the Gas Concentration on the Bubble Nucleation Mechanism in High-pressure FIM

The effect of the blowing agent concentration on the mechanism of bubble nucleation was explored by increasing the percentage of dissolved CO$_2$ in the melt up to 3 weight percent. The analysis of the visualization snapshots, recorded at Location B of the mold cavity in high-pressure FIM experiments, revealed that a higher packing pressure was required to make all gate-nucleated bubbles dissolve back into the melt compared with high-pressure FIM experiments using 2wt% CO$_2$ at any injection speed. At an injection speed of 50 cm$^3$/s, for instance, the nucleated bubbles disappeared entirely (and the governing nucleation mechanism became the nucleation due to melt shrinkage) under a packing pressure of 16 MPa as shown in Figure 3.9. At the injection speed of 80 cm$^3$/s, the gate-nucleated bubbles were still visible under 16.5 MPa packing pressure and eventually disappeared once packing pressure increased up to 17.5 MPa.

Based on the modified classical nucleation theory, a critical radius ($R_{cr}$) is defined for any foaming system as follows: 

$$ R_{cr} = \frac{2\gamma}{p_{bub, cr} - (p_{sys} + \Delta p_{local})} \approx \frac{2\gamma}{p_{bub, cr} - p_{sys}} $$

(4)

at which $\gamma$ is the interfacial energy between the liquid and the gaseous phase, $p_{bub, cr}$ is the pressure of the bubble, $p_{sys}$ denotes the system pressure, and $\Delta p_{local}$ represents the local pressure fluctuations. The term $\Delta p_{local}$ is generated due to the stress variations about growing bubbles, additives, or even formed crystals, and is negative under
extensional stresses; hence, its contribution increases the driving force for bubble nucleation. The thermodynamics of the system dictate that nucleated bubbles with radii larger than $R_{cr}$ grow, whereas those with radii smaller than the $R_{cr}$ collapse. For a weak solution, Henry’s law relates the bubble pressure ($P_{bub}$) to the concentration of the dissolved gas ($C$) through the Henry’s law constant ($K_H$) as:

$$C = K_H P_{bub}$$  \hspace{1cm} (5)

By substituting Equation (5) in (4), the critical radius can be re-written as follows:

$$R_{cr} = \frac{2\gamma}{\frac{C}{K_H} - P_{sys}}$$  \hspace{1cm} (6)

Equation (6) indicates that the nucleation driving force, i.e., $P_{bub,cr} - P_{sys}$, increases by the percentage of the dissolved gas. Meanwhile, the value for the critical radius reduces by increasing the percentage of dissolved gas for any foaming system. Therefore, a larger number of bubbles nucleate and more nucleated bubbles get the chance to grow and survive further in the system. Consequently, the required packing pressure, to completely re-dissolve gate-nucleated bubbles, increases in the system. Table 3.1 summarises the melt packing pressure employed to change the nucleation mechanism from “gate nucleation” to “nucleation due to melt shrinkage” with respect to the injection speed and blowing agent content.
Figure 3.9: Evolution of morphology in high-pressure FIM of PS 675-3 wt% CO₂ under different packing pressures at Location B: (a) packing pressure = 8 MPa; (b) packing pressure = 16 MPa (injection speed = 50 cm³/s; packing time = 1 s; T_{melt} = 230°C, arrows show the typical un-dissolved gate-nucleated bubbles).

Table 3.1: Applied packing pressure to re-dissolve gate-nucleated bubbles.

<table>
<thead>
<tr>
<th>Injection Speed (cm³/s)</th>
<th>CO₂ (wt%)</th>
<th>Melt temperature (°C)</th>
<th>Packing pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2%</td>
<td>230</td>
<td>15</td>
</tr>
<tr>
<td>50</td>
<td>3%</td>
<td>230</td>
<td>16</td>
</tr>
<tr>
<td>80</td>
<td>2%</td>
<td>230</td>
<td>16</td>
</tr>
<tr>
<td>80</td>
<td>3%</td>
<td>230</td>
<td>17.5</td>
</tr>
</tbody>
</table>

3.5.5 The Importance of the Melt Packing Pressure in High-pressure FIM and its Influence on Cell Structure Uniformity

If the gate-nucleated bubbles sustain under the cavity pressure, a melt packing pressure would be required to re-dissolve them back into the melt as discussed in Section 4.1. Simultaneous nucleation of new bubbles during the melt shrinkage, i.e., shrinkage-induced
bubbles, results in a uniform cellular structure in an ideal high-pressure FIM process. However, the pressure gradient in the cavity may cause non-uniformity in the structure during each injection. In Figures 3.3 and 3.5, for instance, the gate-nucleated bubbles sustained under packing pressures up to 8 MPa at Location B, whereas they disappeared immediately because of the higher cavity pressure at Location A under the same applied packing pressure. Therefore, foaming at Location A occurred only during the melt shrinkage whereas the bubbles at Location B were a mixture of gate-nucleated bubbles and shrinkage-induced. The required packing pressure, to re-dissolve all gate-nucleated bubbles in the melt, increases with the distance from the gate, from Location A to C, within the mold cavity. In any attempt to re-dissolve gate-nucleated bubbles at Location C, other locations experience much higher pressures than required. This excessive packing pressure affects the nucleation and growth behavior of bubbles which causes inevitable heterogeneity in the cellular structure.

The effect of the packing pressure and the packing time on the onset of bubble nucleation is shown in Figure 3.10. By increasing the packing pressure, the time at which the first observable bubble was detected in visualization snapshots increased. Similarly, the detection time of bubbles was increased by increasing the duration of the packing pressure.

Figure 3.10: The effect of the packing pressure and the packing time on bubble nucleation in high-pressure FIM of PS 675-1%wt CO$_2$: (a) injection speed = 80 cm$^3$/s at Location B; (b) injection speed = 50 cm$^3$/s at Location A ($T_{melt} = 230^\circ$C).
By increasing the packing pressure, the system pressure \(P_{sys}\) and consequently the critical radius value for bubble nucleation increases. Considering the fact that only bubbles with radii larger than the critical radius value grow,\(^{39}\) the statistical chance for bubble survival reduces, and only large enough bubbles will survive in the system. By increasing the packing time, on the other hand, the system temperature reduces further, resulting in sluggish nucleation. It should be noted that the melt in the sprue solidifies quickly after injection and may neutralize the melt packing pressure. In this case, only large packing pressures may influence the system. In Figure 3.10b, the solidification of the sprue after 20 seconds deactivated the packing pressure of 11 MPa, whereas higher packing pressures were influential on the system.

Figure 3.11 demonstrates the measured cell density of shrinkage-induced bubbles versus time in high-pressure FIM experiments at Location A and under different melt packing pressures. The rate at which the cell density increased was higher under a larger packing pressure as demonstrated with a steeper slope of \(N'\) vs. time graphs in Figure 3.11. The application of a higher packing pressure removed more gate-nucleated bubbles throughout the entire cavity. Hence, a higher pressure drop rate was obtained after the removal of the packing pressure compared with that of samples with more pre-existing bubbles in the system. This phenomenon was more pronounced at the injection speed of 50 cm\(^3\)/s compared to the injection speed of 80 cm\(^3\)/s. Because the larger number of gate-nucleated bubbles obtained from a faster injection rate reduced the amount of observed shrinkage, and results in a lower cell density rate.
Figure 3.11: Cell density vs. time in high-pressure FIM experiments of PS 675-2% CO₂ at Location A: (a) injection speed = 50 cm³/s; (b) injection speed = 80 cm³/s (packing time = 1 s; \( T_{\text{melt}} = 230^\circ\text{C} \)).

The effect of the packing time on the growth behavior of shrinkage-induced bubbles was studied as shown in Figure 3.12. The measured bubbles’ growth rate is summarized in Table 3.2. As demonstrated, bubble growth was supressed by increasing the packing time.

The diffusion coefficient of gas molecules is a strong function of the melt temperature (Eq. 7):

\[
D = D_0 \exp\left(\frac{-E}{RT}\right) \tag{7}
\]

By increasing the packing time, the melt was cooled further in the mold, and therefore, the gas diffusivity was decreased. Simultaneously, the melt viscosity was increased, causing more resistance to foaming. So the rate of developing bubbles was decreased.
Figure 3.12: Bubble growth rate in high-pressure FIM experiments of PS 675-1% CO₂ at Location A; (a) packing pressure = 14 MPa; (b) packing pressure = 11 MPa (injection speed = 50 cm³/s; T_{melt} = 230 °C).

Table 3.2: Growth rate of bubbles at different packing pressures and packing times.

<table>
<thead>
<tr>
<th>Packing pressure (MPa)</th>
<th>11</th>
<th>11</th>
<th>11</th>
<th>14</th>
<th>14</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packing time (s)</td>
<td>1</td>
<td>10</td>
<td>20</td>
<td>1</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Growth rate (mm/s)</td>
<td>0.137</td>
<td>0.03</td>
<td>0.032</td>
<td>0.0975</td>
<td>0.055</td>
<td>0.0185</td>
</tr>
</tbody>
</table>
3.6 Conclusion

The governing bubble nucleation mechanisms in high-pressure foam injection molding experiments of PS/CO₂ system were investigated using an in-situ mold visualization technique. It was observed that bubble nucleation is a strong function of the mold cavity pressure, and dictates the final cellular structure of the foam injection-molded parts. While the gate-nucleated bubbles govern the cell structure in low-pressure FIM technology, the cells nucleated during melt shrinkage control the final structure in high-pressure foam injection molding. In other words, the pressure drop required for bubble nucleation in high-pressure foam injection molding is obtained through shrinkage during melt solidification. In this regard, it is essential that all gate-nucleated bubbles obtained during mold filling re-dissolve back into the melt under the mold cavity pressure.

If the cavity pressure is insufficient, then a melt packing pressure should be utilized to re-dissolve all gate-nucleated bubbles. It was observed that the required packing pressure increased by increasing the injection speed, the resistance of the gate, and the content of the blowing agent. However, the application of the packing pressure may cause structural heterogeneity in the flow direction. It was observed that the onset of nucleation was postponed by increasing the packing pressure. In addition, a longer duration of the melt packing pressure reduced the growth rate of nucleated bubbles.

This research provided new insights into structural development in high-pressure foam injection molding, and the ways to reduce the inherent heterogeneity in foam injection molding technology.
3.7 References


Chapter 4

4 Effect of Processing Parameters on Bubble Nucleation and Growth Dynamics in High-Pressure Foam Injection Molding

4.1 Abstract

We used an innovative visualization mold to investigate the effect of the processing parameters on bubble nucleation and growth. This was also done to uncover the mechanisms responsible for cellular structural development in the high-pressure foam injection molding process. The effects of the injection speed, the blowing agent content, the injection gate geometry, the packing pressure, the melt flow index, and the use of talc as a heterogeneous nucleating agent on the formation and dynamics of cell bubbles were all explored. In the high-pressure foam injection molding process with a proper packing pressure, the overall cell density did not change with the injection speed nor with the injection gate resistance. However, the cell density increased significantly with the blowing agent’s concentration and with a nucleating agent. We also observed the growth mechanism of the bubbles in a confined mold cavity, and concluded that the bubble growth rate decreased as the cell density increased. In addition, the satelliting phenomenon, i.e., cell nucleation around the previously nucleated cells, was observed. This was due to the induced pressure fluctuations in the surrounding melt, which could eventually affect the final cellular structure.

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3 V. Shaayegan, G. Wang, C.B. Park, “A Study of the Effect of Processing Parameters on the Bubble Nucleation and Dynamics in High-Pressure Foam Injection Molding through Visualization” To be Submitted to Chemical Engineering and Science (June 2016)
4.2 Introduction

The popularity of plastic foams in manufacturing engineering is dramatically increasing. They offer enhanced mechanical properties,\(^1\)\(^-\)\(^4\) improved heat and sound insulation,\(^5\)\(^-\)\(^7\) enhanced electrical conductivity\(^8\) and charge storage capability.\(^9\) In particular, the functionality of foams is improved by reducing the cell size to the sub-micron levels.\(^10\)\(^-\)\(^11\) Due to the Knudsen effect, for instance, the thermal conductivity of nano-cellular foams can decrease dramatically to manufacture super-insulators.\(^12\)\(^-\)\(^14\)

Foam injection molding (FIM) is unique among foam processes because it can produce light-weight parts with high geometrical accuracy and a high stiffness-to-weight ratio in fast production cycles.\(^15\) Before molding, it is essential to prepare a homogeneous, one-phase melt/gas mixture in order to achieve a uniform cell structure in FIM products.\(^15\) The gate’s resistance should produce a sufficiently high back pressure to avoid premature bubble nucleation in the injection nozzle or in the sprue. Once the gas-charged polymer melt is injected into the confined mold cavity, bubble nucleation occurs according to the governing nucleation mechanism depending on the injection-molding method. In low-pressure FIM, where a short shot is used to partially fill the mold cavity, the required pressure drop to induce bubble nucleation is obtained over the gate. The nucleated bubbles then grow and expand even during injection until the entire cavity is filled. In high-pressure FIM, on the other hand, a full shot is used to fill the entire cavity. In an ideal high-pressure FIM, all the cells nucleated during filling dissolve back into the melt, and the pressure drop for bubble nucleation can only be achieved through melt shrinkage during the solidification process.\(^16\) It has been verified that the high-pressure FIM can produce much more uniform cell structures with a higher cell density and a higher expansion ratio.\(^16\) However, despite all its advantages, FIM suffers from an inherent heterogeneity in its cellular structure, which deteriorates the physical and mechanical properties of its foamed parts. Therefore, a wide-ranging understanding of the governing mechanism(s) of nucleation/growth in the FIM process and the relationship between its processing parameters and the final foam structure is essential to achieving a uniform and fine-cell structure with the desired properties.
Extensive research has been undertaken on structural and morphological development in the FIM process. Some studies have investigated the relationship of the processing conditions, the cellular structures, and the mechanical properties of pure and composite resins in a low-pressure FIM process. \(^{17-22}\) Ameli et al. investigated the effects of the cellular structure formation on the functional properties of the injected-molded foam through fiber orientation. \(^{9,23-25}\) Huang and Wang studied the effects of the injection speed, the nozzle temperature, and the shot size on the microcellular structure of polystyrene and the formed skin layer. \(^{26}\) Barzegari and Rodrigue investigated the effect of processing conditions on the final cellular morphology of structural foams and concluded that the injection pressure and the blowing agent’s concentration were the most influential processing parameters. \(^{27}\) Pilla et al. studied the microstructural development and evaluated the mechanical properties of microcellular injected molded PLA by adding chain extender. \(^{28}\) Ameli et al. explored the effects of talc and clay on the cellular structure of PLA foams, and showed that the foaming behavior of PLA was significantly enhanced by the presence of additives. \(^{29,30}\) The application of gas-counter pressure on both the cellular structure and the mechanical properties of FIM parts was examined by Chen and co-workers. \(^{31}\) Lee et al. analyzed how the effects of processing parameters such as the blowing agent concentration, the injection speed, and the shot size in relation to the cavity pressure profile affected the cellular structure in low-pressure FIM. \(^{32}\) Wang et al. argued that the morphology of the cellular structure in high-pressure FIM is a function of the shot size. \(^{33}\)

Besides the experimental approaches, theoretical and numerical attempts have also been made to model the development of bubbles and to predict the effect of such processing parameters as the gas concentration, the melt temperature, and the mold temperature on FIM cellular morphology. \(^{34-37}\) Han and Yoo used the DeWitt equation to model the isothermal growth of a single bubble in a large rectangular cavity of a viscoelastic fluid. \(^{38}\) Upadhyay applied the Leonov constitutive equation to model the non-isothermal growth of bubbles in FIM. \(^{39}\) Osorio and Turng adopted a numerical approach to solve the energy, mass diffusion, and continuity equations in order to predict cell growth in FIM in a non-isothermal condition. \(^{40}\) Mahmoodi et al. used the power-law model to simulate the bubble dynamics. \(^{41}\)
Each of these earlier studies contributed to a better understanding of the cellular structure development in FIM, and significant insight was gained with respect to the effect of processing conditions on the final bubbles’ nucleation and dynamics. However, the bubble nucleation mechanism and the growth phenomena in FIM are still not well understood. This can be attributed to the fact that most of the analyses were done on the finally obtained foam samples without clear understanding of the interim development of the cellular morphology, especially in the case of high-pressure FIM.

In this context, a few researchers had used in-situ visualization techniques to study the FIM process. Villamizar and Han studied the bubble growth phenomena at different processing parameters by means of visualization. However, their study focused mainly on low-pressure experiments in conventional FIM, and used chemical blowing agents with a limited gas content.\textsuperscript{42} Yamada \textit{et al.} visualized the structure development in FIM of PS/nitrogen system, and observed a multi-layer central region.\textsuperscript{43} Mahmoodi \textit{et al.} carried out high-pressure FIM experiments using polystyrene (PS) as the matrix and carbon dioxide (CO\textsubscript{2}) as the physical blowing agent to visualize cell growth and cell collapse during non-isothermal mold filling.\textsuperscript{44} Ishikawa and Ohshima investigated the foaming behavior of polypropylene blown with CO\textsubscript{2} during mold opening using visualization techniques.\textsuperscript{45} Ishikawa \textit{et al.} extended their study to compare the nucleation effectiveness of nitrogen with that of CO\textsubscript{2}.\textsuperscript{46} Recently, Shaayegan \textit{et al.} demonstrated the cell-nucleation mechanism in high-pressure FIM is different from that in low-pressure FIM\textsuperscript{16} with a newly designed a visualization mold equipped with numerous pressure transducers.\textsuperscript{47}

To uncover the FIM’s complex dynamics and bubble-nucleation processes, and to interpret each processing parameter’s effects on the final cellular structure and on the resultant foam properties, a systematic and wide-ranging research is required. Such a study would include the investigation of phenomena in real time. Further, the theoretical explanations of the FIM phenomena, proposed mechanisms, and numerical simulations need to be verified by reliable point-to-point experimental data. Thus, we used an on-line visualization method to explore the effects of the injection speed, the blowing agent content, the injection gate resistance, the melt flow index, and the nucleating agent, on bubble formation and growth in the high-pressure FIM process.
4.3 Experimental

4.3.1 Materials and Procedures

Two grades of PS, PS675 and MC3650 with MFR 7.5 g/10min. and MFR 13.0 g/10min. (200°C/5 kg) respectively, were provided from AmericasStyrenics. Carbon dioxide with 99.8% purity from Linde Gas Canada was used as the physical blowing agent. To conduct FIM experiments, a 50-ton Arburg ALLROUNDER 270/320C injection molding machine (Lossburg, Germany, 30-mm diameter screw) was used. The injection of CO₂ in a supercritical phase was done using MuCell® technology (Trexel, Inc., Woburn, Massachusetts). The FIM parts were molded in a rectangular mold cavity (nominal size: 135 mm × 111 mm × 3.2 mm), fed by a fan gate. A 40% talc-PS 675 masterbatch was diluted, using a 27 mm Leistritz twin-screw extruder, to investigate the nucleating agent’s effect on polystyrene’s foaming behavior.

We used in-situ visualization to investigate the bubble nucleation and dynamics in high-pressure FIM. The visualization setup consisted of a visualization mold and a CV M10 camera from JAI with a magnifying lens from Navitar. The details of the visualization mold are explained elsewhere. Overall, a fused silica prism was incorporated into the stationary plate of the injection mold. This then reflected phenomena occurring inside the mold cavity to a camera. Figure 3.2b and 3.2c show the different locations of the visualization windows in the mold cavity, that is, near the gate, the middle cavity, and at the end of the cavity. These are identified as A, B, and C in the figure.

Two fan gates with a thickness of 1.7 mm (Gate#1) and 2.78 mm (Gate#2) were used to study the effect of the gate geometry on bubble nucleation. High-pressure FIM experiments were carried out by injecting the gas-charged polymer melt into the visualization mold cavity. The melt packing pressure was applied by injecting an excessive amount of the melt under various packing pressures and at different packing times.
4.3.2 Characterization

To measure the cell density with respect to the unfoamed volume, (that is, $N'$), the method used by Wong et al. was employed. More details can be found in 3.4.3.

The nucleated bubbles’ growth rate was calculated by measuring the diameter of at least 10 bubbles at each visualized snapshot. The diameter values of all 10 bubbles were then averaged. These values were saved as the bubble diameter at the time instant corresponding to the analyzed snapshot. For the next time instant, the same 10 bubbles were tracked, and their diameters were measured and the averaged value was saved.
4.4 Results and Discussion

4.4.1 Effect of the Injection Speed and the Gate Resistance on Bubble Nucleation and Growth in High-pressure FIM

Figure 4.1 shows the visualization snapshots performed at Location A (see Figure 3.2) for high-pressure FIM experiments of PS 675-3wt% CO\textsubscript{2} at different injection speeds. A melt packing pressure of 80 bar was used for 1 second to ensure that all primary nucleated bubbles, that is, bubbles nucleated during the feeding stage at the gate, were dissolved back into the melt. The cell density information, in respect to the un-foamed volume, was extracted using the visualization snapshots, as Figure 4.2a shows. The bubble nucleation was entirely prevented at the visualized spot (that is, Location A) under the high-pressure FIM condition, and the overall cell density was not affected by the injection speed. Lee et al. demonstrated that cell density is increased by the injection speed in low-pressure FIM, where the nucleation mechanism is governed by the pressure drop rate at the gate. They argued that a faster pressure drop is obtainable using a high injection speed, which results in a large number of bubbles. On the other hand, as demonstrated by Shaayegan et al, the nucleation mechanism is mainly governed by the extent of the melt shrinkage during the melt solidification in high-pressure FIM, regardless of the injection speed.\textsuperscript{16} Therefore, the nucleation rate becomes independent from the pressure drop rate at the gate. As a consequence, it also becomes independent of the injection speed.
Figure 4.1: Visualization snapshots in high-pressure FIM experiments of PS 675-3wt% CO$_2$ at Location A: (a) injection speed= 25 cm$^3$/s.; (b) injection speed= 50 cm$^3$/s.; (c) injection speed= 80 cm$^3$/s. (packing pressure= 80 bar; packing time: 1 s, $T_{melt}= 230^\circ$C).

Although the overall cell density was not affected by the injection speed, the cell density graphs in Figure 4.2a indicate that the onset of nucleation, here being that moment when the first observable bubbles appeared in the snapshots, had shifted to longer durations with an increased injection speed. This is because the melt temperature is reduced more rapidly at a lower injection speed. As the nucleation mechanism in high-pressure FIM is controlled by
the rate of the melt shrinkage, faster cooling and shrinkage produces faster nucleation, as Figure 4.2a shows

Figure 4.2: Effect of injection speed in high-pressure FIM of PS 675-3% CO₂: (a) cell density vs. time; (b) cavity pressure profiles at different injection speeds; (c) bubble growth rate (visualization at Location A, packing pressure= 80 bar; packing time: 1 s, T_{melt}=230°C; Solubility pressure of 3% CO₂ in PS was estimated about 8.3 MPa at 230 °C and shown with the dash line in b).

While the injection speed had no significant effect on the final cell density of the high-pressure FIM of PS 675-3 wt% CO₂, the bubble growth rate was increased by an increased
injection speed, as Figure 4.2c shows. When a higher injection speed was used, the melt temperature remained at elevated temperatures for longer time spans. Consequently, the higher melt temperature enhanced the diffusion-induced growth of the nucleated bubbles and resulted in a faster growth rate.

The effect of injection-gate resistance on bubble nucleation was visualized, and the results are shown in Figure 4.3.

Figure 4.3: Visualization snapshots in high-pressure FIM experiments of PS 675-2% CO$_2$ at Location A: (a) Gate thickness= 2.78 mm; (b) Gate thickness= 1.7 mm (injection speed: 80 cm$^3$/s; packing pressure= 80 bar; packing time: 1 s, $T_{\text{melt}}=230^\circ$C).

Similar to the injection speed’s affect, the gate’s resistance did not significantly affect the overall cell density, as measured and shown in Figure 4.4. A high-resistance gate produces a higher thermodynamic instability and imparts a larger number of bubbles during the filling stage. However, all gate-nucleated bubbles re-dissolved back into the melt under the packing
pressure in high-pressure FIM, and the bubble nucleation occurred during the melt shrinkage. This made the overall cell density independent of the gate’s thickness.

![Graph showing cell density over time for two gates.]

Figure 4.4: Effect of injection-gate resistance on cell density in the high-pressure FIM of PS 675-2% CO₂ at Location A (Gate #1: thickness= 1.7 mm; Gate #2: thickness = 2.78 mm; injection speed: 80 cm³/s; packing pressure= 80 bar; packing time: 1 s, Tₘₐₐₖt=230°C).

While the overall cell density was not affected by the gate thickness in the high-pressure FIM experiments, bubble nucleation occurred earlier using the high-resistance gate (Figure 4.4). This could have been due to the larger amount of shearing experienced by the melt using the high-resistance gate. The higher stresses and the larger pressure fluctuation accumulated in the melt could have facilitated the bubble nucleation by reducing the value for the critical radius.
4.4.2 The Effect of Blowing Agent Concentration on Bubble Nucleation and Growth

High-pressure FIM experiments were carried out for the PS 675-CO\textsubscript{2} system using different blowing agent concentrations, and the foaming behavior was visualized at Location A. As Figure 4.5 shows, the cell density increases by the percentage of the CO\textsubscript{2}.

Figure 4.5: Visualization snapshots in high-pressure FIM experiments of PS 675-CO\textsubscript{2} at Location A: (a) 1\%wt CO\textsubscript{2}; (b) 2\%wt CO\textsubscript{2}; (c) 3\%wt CO\textsubscript{2} (injection speed: 80 cm\textsuperscript{3}/s, packing pressure: 80 bar; packing time: 1s; T\textsubscript{melt} = 230).
The corresponding cell density, with respect to the unfoamed volume, was measured and plotted against the time, as shown in Figure 4.6a. Based on classical nucleation theory, a critical radius for bubble nucleation in any foaming system is defined as follows:

\[
R_{cr} = \frac{2\gamma}{p_{bub,cr} - p_{sys}}
\]  

(1)

in which \(\gamma\) is the interfacial tension between both phases, here liquid and gas, \(p_{bub,cr}\) is the pressure of a bubble at critical size, and \(p_{sys}\) is the system pressure. The term \(p_{bub,cr} - p_{sys}\) defines the level of system supersaturation and is the driving force for bubble nucleation.

Favourable system thermodynamics calls for bubbles with radii larger than \(R_{cr}\) to grow, while bubbles with radii smaller than \(R_{cr}\) will collapse. If the polymer/gas system is a weak solution, then the pressure inside the bubble can be related to the concentration of the dissolved gas using Henry’s Law as follows:

\[
C = K_H P_{bub}
\]  

(2)

where \(C\) is the concentration of the blowing agent and \(K_H\) denotes Henry’s constant. By substituting Eq. (2) in (1) as follows:

\[
R_{cr} = \frac{2\gamma}{\frac{C}{K_H} - p_{sys}}
\]  

(3)
Therefore, the driving force for bubble nucleation, that is, \( \frac{C}{K_H} - P_{sys} \), increases by increasing the amount of the dissolved gas. Further, based on classical nucleation theory, the critical radius for nucleation decreases. Consequently, more bubbles nucleate and survive in the system, resulting in an increase in the overall cell density.

Figure 4.6: Effect of blowing agent concentration on foaming behavior in high-pressure FIM experiments of PS 675-CO\(_2\) at Location A; (a) cell density; (b) bubble growth rate (injection speed: 80 cm\(^3\)/s; packing pressure: 80 bar; packing time= 1 s; \(T_{melt}= 230^\circ\)C).

Using the visualization snapshots from Figure 4.5, the growth rate of nucleated bubbles was also extracted and shown in Figure 4.6b. As the percentage of dissolved CO\(_2\) decreased, the nucleated bubbles grew both faster and larger. In high-pressure FIM, the entire mold cavity is filled by the melt/gas mixture. Therefore, the amount of obtainable void fraction is governed by the amount of the melt shrinkage during solidification. In addition, bubble growth is a function of the total available expansion space in the confined volume. In other words, the expansion of bubbles is limited to the amount of melt shrinkage as follows:
where \( f \) and \( D \) denote the amount of melt shrinkage and the diameter of each bubble, respectively. The rate of melt shrinkage is then a function of the bubbles’ growth rate as follows:

\[
\frac{df}{dt} \approx (\text{Number of nucleated bubbles}) \times \left(\frac{\pi}{6} D^3\right)
\]

Inasmuch as the amount of the melt shrinkage, that is, the \( f \), remains the same for all experiments under the same processing conditions, the size of the nucleated bubbles becomes an inverse function of the total number of nucleated bubbles. Thus, the nucleation of a large number of bubbles, using 3wt\% CO\(_2\) for instance, results in smaller-size bubbles. By the same token, the growth rate of bubbles decreases if a larger number of nucleated bubbles grow together. This also justifies the belated observation of nucleated bubbles using higher percentages of dissolved gas, as shown in Figures 4.6a and 4.6b. In fact, bubble nucleation occurs faster by increasing the percentage of dissolved CO\(_2\) in the melt. But this cannot be observed until later due to the sluggish growth of nucleated bubbles in foaming systems with higher percentages of dissolved gas.

### 4.4.3 The Effect of the Melt Flow Index (MFR) on Bubble Nucleation

The effect of the melt flow index on bubble nucleation was investigated in high-pressure FIM experiments using PS 675 and MC3650, with a MFR of 7.5 and 13 g/10min., respectively. Figure 4.7 shows the cell density measurements at Location A.
The cell density increased faster using the PS with a lower MFR. Wong et al. argued that pressure fluctuations that were generated due to shearing and/or extension of the polymer enhanced cell nucleation and nucleation density.\footnote{52,53} The PS melt with higher viscosity, that is, with a lower MFR, experienced more deformation during injection, thus higher local stress variations. As a result, more residual stresses accumulated in the melt. These stresses may have facilitated bubble nucleation and enhanced the overall cell density.

4.4.4 The Effect of Talc on Bubble Nucleation and Growth

High-pressure FIM experiments of PS675-0.5\% talc composite were carried out using 1wt\% CO\textsubscript{2} as the blowing agent, and its foaming behavior was compared with that of pure PS 675-1wt\% CO\textsubscript{2} with the same processing parameters. Snapshots of the in-situ visualization, taken
at Location A, and the corresponding cell density and growth rate measurements are shown in Figures 4.8 and 4.9. The visualization observations and the cell density measurements indicated that the addition of only 0.5 %wt of talc significantly increased the cell density of the entire foaming.

Figure 4.8: Visualization snapshots in high-pressure FIM experiments of PS 675-1%wt CO₂ at Location A: (a) Pure PS 675; (b) PS 675+0.5%wt talc (injection speed: 80 cm³/s, packing pressure 80 bar; packing time= 1s, Tₘₑlt=230°C).
Figure 4.9: The effect of talc in high-pressure FIM experiments of PS 675-1%wt CO₂ at Location A: (a) cell density; (b) bubble growth rate (injection speed: 80 cm³/s, packing pressure 80 bar; packing time= 1s, Tₘₑₙₜ=230°C).

It is well known that a higher pressure drop rate will induce higher thermodynamic instability within the melt/gas system. A higher pressure drop rate will result in finer cell sizes as more gas is used to nucleate a greater number of cells.⁵⁴ The pressure drop rates, obtained from the slope of the pressure profile around the solubility pressure during solidification were similar for all of the experiments. Therefore, the observed difference in the nucleation rates of the various samples did not stem from the depressurization rate.

It seems that the cell density was governed by the heterogeneous nucleation scheme where cell nucleation occurred at the preferred sites.⁵⁵ The change in the free energy of the system for homogeneous and heterogeneous nucleation can be expressed, respectively, as the following:

\[
w_{hom} = \frac{16\gamma^3}{3(p_{bub,cr}-p_{sys})^2}
\]

\[
w_{het} = w_{hom} F(\theta_C, \beta)
\]
where the shape factor $F(\theta_c, \beta)$, which is equal to or less than 1, is defined as follows:

$$F(\theta_c, \beta) = \frac{1}{4} \left[ 2 - 2 \sin(\theta_c - \beta) + \frac{\cos \theta_c \cos^2(\theta_c - \beta)}{\sin \beta} \right]$$  \hspace{1cm} (8)

$\theta_c$ is the contact angle between the bubble surface and the second phase, and $\beta$ is a semiconical angle [0-90°], which shows the geometry of the nucleation site.\(^5^6\) The talc particles provide heterogeneous nucleation sites which lower the activation energy barrier for cell nucleation significantly, thereby enhancing the nucleation rates. In addition, melt wetting may be incomplete at the rough surfaces of the talc agglomerates, leaving pre-existing gas bubbles in the system. During depressurization, the $R_{cr}$ for the system decreases (see Eq. (1)). Once $R_{cr}$ becomes smaller than the radii of the entrapped CO$_2$ bubbles, the pre-existing voids get a chance to grow.

These visualization results, therefore, suggest that talc acts as an effective nucleating agent for PS.\(^5^7\) Even under a high packing pressure of 150 bar, where the bubble nucleation was highly suppressed for the PS 675-1wt%CO$_2$ system, the presence of talc had a significant influence on increasing the cell density, as Figure 4.10 shows.
Figure 4.10: Visualization snapshots in high-pressure FIM experiments of PS 675-1%wt CO$_2$ at Location A: (a) Pure PS 675; (b) PS 675+ 0.5%wt talc (Injection speed: 50 cm$^3$/s, Packing Pressure 150 bar; Packing time= 1s, $T_{melt}$=230°C).

The growth rate curves for nucleated bubbles were constructed for both pure and composite PS 675 and illustrated in Fig. 10b. Similar to the discussion in Section 3.2, the growth rate of a large number of nucleated bubbles in a confined volume was suppressed, with the bubbles growing to a smaller size in the PS675-talc system.

4.4.5 Formation of Satellite Bubbles

Careful analysis of successive visualization snapshots from different high-pressure FIM experiments revealed that new cells, so-called satellite or baby bubbles, nucleated on the surface and in close proximity to the already-nucleated, growing bubbles, as Figure 4.11 shows. Nucleation of the satellite bubbles occurred in regions that were gas-depleted due to the fast growth of former bubbles.
Figure 4.11: Formation of satellite bubbles around and on the surface of growing bubbles in high-pressure FIM at Location A; (a) and (b) PS 675-3%wt CO\textsubscript{2} (injection speed 80 cm\textsuperscript{3}/s, packing pressure 80 bar, packing time 1 s; T\textsubscript{melt}=230\textdegree C); (c) PS 675+0.5%wt talc (injection speed 50 cm\textsuperscript{3}/s, packing pressure 200 bar, packing time 1 s, 1%wt CO\textsubscript{2}).

Albalak et al. argued that the expansion of bubbles induces tensile stresses (or pressure fluctuations) in the melt around a growing bubble, which can decrease the system pressure (\(P_{sys}\)) at regions around the bubble surface.\textsuperscript{58} In other words, the biaxial stretching of the melt around a growing bubble reduces the system’s local pressure.\textsuperscript{59} Modified classical nucleation theory expresses the effect of generated stresses around a growing bubble as follows:\textsuperscript{57}

\[
R_{cr} = \frac{2\gamma}{p_{pub,cr}-(P_{sys}+\Delta P_{local})}
\]  

\[
W_{het} = \frac{16\gamma^3 F(\theta_C,\beta)}{3(p_{pub,cr}-(P_{sys}+\Delta P_{local}))^2}
\]
which $\Delta P_{\text{local}}$ is the local pressure variation which is negative under extensional (or tensile) stresses. Therefore, the growth of bubbles induces pressure fluctuations, that is, extensional stresses, to their surroundings. This reduces the local system pressure and, as a result, increases the supersaturation level of the system and facilitates the formation of new bubbles. Further, Wang et al. showed that system pressure profiles significantly change around nucleating agents. This means that the induced pressure fluctuations, due to the bubble growth, are more accented in the presence of inorganic nucleating agents such as talc (see Figure 4.11c) compared with that of pure polymer.\textsuperscript{60}

### 4.5 Conclusion

The effect of the injection speed, the resistance of the gate, the content of the blowing agent, the melt flow index, and eventually the addition of talc as a heterogeneous nucleating agent on the cell nucleation and growth was explored in high-pressure foam injection molding process. The injection speed and the resistance of the gate did not influence the overall cell density. The percentage of the dissolved gas, however, affected the cell density such that the cell density was greatly increased by the percentage of the blowing agent. The cell nucleation rate also increased with the resin with a lower melt flow index for a higher viscosity induced a larger local stress variation, facilitating the nucleation. The addition of a very low amount of talc enhanced the cell nucleation significantly, and increased the cell density dramatically, by promoting the heterogeneous nucleation. The growth behavior of a large number of cells in a confined volume was also investigated. It was concluded that the growth rate of nucleated cells decreases as their number increases. The formation of satellite or baby cells, about growing cells, was noticed. The latter was due to generated extensional stresses, and thus the stress fluctuations, around growing cells which promoted the cell nucleation in depleted-gas area near growing cells.
4.6 References


Chapter 5

5 Identification of Cell-Nucleation Mechanism in Foam Injection Molding with Gas-counter Pressure via Mold Visualization

5.1 Abstract

The mechanisms of cell nucleation and growth are investigated in foam injection molding using gas-counter pressure (GCP). An in-situ mold visualization technique is employed. The application of GCP suppresses cell nucleation, and prevents the blowing agent from escaping during mold-filling. The inherent structural heterogeneity in the regular foam injection molding improves because of the uniform cavity pressure distribution with GCP. The cavity pressure profiles show much faster pressure-drop rates using GCP, because the single-phase polymer/gas mixture has a lower compressibility than the two-phase polymer/bubble mixture. Therefore, both the cell nucleation and growth rates are significantly increased through a higher pressure-drop rate upon the removal of the GCP. The effect of GCP magnitude on the cell morphology is explored. When the GCP is lower than the solubility pressure, bimodal foaming occurs. As the GCP increases above the solubility pressure, the cell density increases because of the higher pressure-drop rate.

5.2 Introduction

The recent demand for lightweight plastic foams has significantly increased their applications. This momentum is due, in part, to the urgent need to reduce fossil fuel

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consumption and its consequent negative environmental impacts. Thus, lightweight plastic products have become part of the solution. In addition, plastic foams offer numerous enhanced properties and functions, which include the following: improved mechanical properties with a microcellular structure,\textsuperscript{1-5} improved electrical conductivity,\textsuperscript{6} improved charge storage capability,\textsuperscript{7} improved heat and sound insulation \textsuperscript{8-10} They also provide the unique and advanced characteristics that are needed in water filtration industries\textsuperscript{11} and in biomedical engineering.\textsuperscript{12} Numerous researchers have been trying to decrease the cell size to a micro- or nano-scale, so as to improve plastic foams’ functional properties.\textsuperscript{7,13,14} Nanocellular foams, for instance, have attracted a great deal of attention as highly efficient thermal insulators. In conventional low-density thermal insulation plastic foams, the major heat conduction contribution is through the gas within the cells.\textsuperscript{7} However, as the cell size is reduced to the nanoscale, and is close or even smaller than the mean free path of the air molecules, the thermal conduction through the gas is decreased dramatically due to the Knudsen effect.\textsuperscript{15-17} Therefore, the heat conductivity of plastic foams is considerably reduced by a smaller cell size, and super-thermal insulation materials can thus be obtained by nanocellular foaming.\textsuperscript{10,18,19} Ameli et al. observed that the electrical conductivity of nanocomposites is a function of the cell size and the void fraction.\textsuperscript{6} In terms of mechanical properties, reducing the cell size to a nanoscale significantly improved the nanocellular foams’ ductility, even when compared with the unfoamed materials.\textsuperscript{20} However, to reduce the cell size, it is crucial to understand the fundamental mechanisms of foaming; that is, cell nucleation and growth that occur within the polymer/gas mixtures.

Foam injection molding’s (FIM) faster cycles, better dimensional stability, and a higher stiffness-to-weight ratio make it an outstanding manufacturing technology, compared to solid injection molding.\textsuperscript{21} However, the conventional FIM process suffers from structural non-uniformity/heterogeneity, severe coalescence and large bubble size, as well as the presence of silver and swirl marks on product surfaces.\textsuperscript{21-23} To minimize these disadvantages, various FIM technologies have been developed. These include adding an extra accumulator to decouple the mixing and injection units,\textsuperscript{24,25} applying the reciprocating screw and MuCell technology,\textsuperscript{26,27} separating the plasticating and injection units,\textsuperscript{28} injecting the gas through a nozzle located between the plasticating unit and the shut-off nozzle,\textsuperscript{29} using static mixing for a better gas dispersion,\textsuperscript{30,31} modifying the screw and barrel design to
enhance the gas/melt mixing while exhausting the excessive \( N_2 \) through the ventilation hole,\(^{32} \) replacing the hopper with an autoclave,\(^ {33,34} \) and using gas-saturated pellets.\(^ {35} \) Unfortunately, the shaping (that is, mold filling) and foaming stages are coupled in most FIM technologies because foaming occurs during the mold-filling phase.\(^ {24-28} \) As a consequence, it is very difficult to control the cell morphology independently. The gas-counter pressure (GCP) technology will prevent foaming during the mold-filling phase; therefore, there is a great opportunity to control the cell morphology independently using GCP. However, both the inherently non-steady nature of injection molding and the temperature and pressure non-uniformity/heterogeneity of the foamable polymer/gas mixture inside the mold make it very challenging to identify the fundamental cell nucleation mechanism in FIM. First, a clear understanding of the cell nucleation and growth behaviors in FIM with GCP is required. To this end, we have conducted an experimental study using a unique in-situ visualization mold, equipped with cavity pressure sensors, to make a fully detailed investigation of the mechanisms of cell nucleation and growth in FIM with GCP. A series of critical experiments were conducted using PS and \( CO_2 \) as case examples.

5.3 Background

Numerous studies have been undertaken to uncover the FIM cell nucleation and growth mechanisms. Villamizar and Han visualized the formation and growth of bubbles in conventional low-pressure FIM, and evaluated the effects of processing parameters on the cellular structure.\(^ {22} \) Mahmoodi \textit{et al.} studied the growth/collapse behavior of nucleated bubbles in a non-isothermal high-pressure FIM process using mold visualization.\(^ {36} \) Lee \textit{et al.} studied structural evolution in a low-pressure FIM process using cavity pressure profiles. They correlated the effects of the processing parameters with the cavity pressure profile, and proposed strategies that resulted in a faster pressure drop over the gate.\(^ {21} \) The correlation between the gate width and the part size on the foaming behavior of polystyrene (PS) was studied by Ahmadzai and co-workers.\(^ {37} \) Ishikawa and Ohshima claimed that an increased mold-opening speed would enhance the cell density of PP foam blown with \( CO_2 \) by increasing the cavity’s depressurization rate in the core-back technology.\(^ {38} \) Recently,
Shaayegan et al. investigated the cell nucleation mechanism in high-pressure FIM without engaging any GCP. They attributed the large structural non-uniformity obtained in low-pressure FIM to the existence of gate-nucleated bubbles which grow, coalesce, and get sheared during free expansion. They proposed the application of a sufficiently high melt-packing pressure to redissolve the gate-nucleated bubbles (that is, the bubbles formed over the gate during injection) back into the melt. In that case, cell nucleation would be governed only by the pressure drop obtained from the melt’s shrinkage. The absence of gate-nucleated bubbles, and a more uniform pressure drop within the entire mold cavity resulted in a more homogeneous cellular structure.

The appearance of silver (or swirl) marks on the surfaces of FIM parts has been common; thus, deteriorating their cosmetic properties. The formation of these blemishes is attributed to gas bubbles trapped between the mold surface and the melt/gas mixture. Due to the fountain flow, the nucleated bubbles reach the surface and solidify, or else they are dragged on to the mold surface. Therefore, the roughness of the parts increases. The occurrence of these silver marks is less likely, or can be completely eliminated, by applying GCP, which prevents the nucleation of premature (or gate-nucleated) bubbles during injection. In other words, the melt/gas mixture is under high pressure during the entire filling process. When the cavity is completely filled, then the GCP is removed; this creates the pressure drop for foaming in the melt. Wang et al. showed that the silver marks disappeared, the surface roughness decreased, and the gloss was improved by increasing the GCP in their high-impact PS FIM experiments. Chen et al. demonstrated that applying GCP, simultaneously with a mold temperature control, effectively improved both the cellular structure and the surface quality. Zhao et al. reported that the surface gloss of microcellular FIM samples was improved by increased GCP. Wong et al. reported that using GCP enhanced the impact resistance of the foam injection-molded thermoplastic polyolefin samples. They found that the stress concentration on the sample’s surface with the GCP was reduced due to the reduced roughness of the surface. The absence of deformed bubbles with the applied GCP reportedly produced spherical bubbles, with reduced sizes, in the core regions of the high impact PS. It is noteworthy that the FIM+GCP process can be followed by one-step precise mold opening in the
thickness direction to increase the void fraction. Bledzki et al. achieved a uniform microcellular structure for polypropylene in FIM by using GCP followed by mold opening. Ameli et al. carried out full-shot FIM experiments using GCP with mold opening to fabricate very high void fraction (of 55%) polylactide (PLA) and PLA composite foams having a more uniform cell morphology and improved mechanical properties, in contrast to low-pressure FIM experiments. Chen et al. showed that the application of larger and longer GCP application resulted in a thicker skin layer and in smaller bubbles in the core region of the PS sample foams in FIM. They also found that using GCP improved the sample’s tensile strength.

Despite significant undertakings to improve the morphology of the cellular structures and the surface quality of FIM products by using GCP technology, the literature lacks a fully detailed investigation of the formation mechanisms and dynamics of cell bubbles in FIM with GCP. Specifically, the opinions expressed about the effects of GCP on the cells’ structural development were based mainly upon the obtained final cellular structure; that is, when the foamed part’s microstructure was fixed. Moreover, most of the interpretations made to date have been based on the acquired final properties of the foams. In our study, we used an innovative visualization mold to carefully monitor and track the entire process of cell nucleation and growth in FIM with GCP, and investigated the technology’s governing mechanisms.

5.4 Foam Injection Molding with GCP

To improve the cell morphology’s uniformity and the part’s surface quality, FIM experiments can be performed using GCP. Figure 5.1 schematically illustrates the GCP-based FIM process, and compares it with low-pressure FIM. In the GCP-based technology, the mold cavity is filled and pressurized with a gas such as nitrogen (N\textsubscript{2}) prior to mold filling. The melt/gas mixture is then injected into the pressurized mold cavity. As the melt/gas mixture is injected into the mold cavity, the pressurized gas is vented from it. If the pressurized gas’s ventilation rate is high enough, the GCP will be maintained at a constant pressure. The GCP’s role is to prevent or suppress any premature cell nucleation (especially
at the gate) during the mold-filling step.\textsuperscript{58} In other words, the high gas pressure that is exerted on the melt front keeps the dissolved gas inside the melt. Therefore, it is absolutely essential that the GCP magnitude be higher than the solubility pressure ($P_{\text{solubility}}$) of the dissolved blowing agent in the polymer melt. When the GCP is removed, foaming occurs. In an ideal GCP application, cell nucleation is initiated simultaneously in the entire melt at the same pressure drop rate. Consequently, the uniformity of the cellular structure along the part would be enhanced, and it would not have elongated bubbles in the flow direction.\textsuperscript{44,51} Other research has further indicated that the bubble cell density obtained using GCP was comparable to,\textsuperscript{49} or even better than, that obtained in low-pressure FIM.\textsuperscript{44}

![Figure 5.1: Formation of bubbles with and without the GCP application.](image)

Both low-pressure and high-pressure FIM experiments can be performed using GCP. The following three scenarios can be considered:

(i) Low-pressure (short-shot) FIM with GCP: In this case, a short-shot is used to partially fill out the mold cavity and to obtain a high void fraction. The GCP application in this case completely prevents cell nucleation at the gate. Once mold filling is completed, the GCP is released and cell nucleation occurs, due to the pressure drop obtained at the rate of the GCP release. Hence, the role of GCP in this case is to prevent cell nucleation from occurring during the mold-filling stage, and to determine the cell nucleation rate and the cell density.
(ii) Near full-shot FIM with GCP: In this case, the mold cavity is almost filled using a near full-shot. The GCP’s presence completely suppresses cell nucleation at the gate (or in the cavity). When mold filling is completed, the GCP is removed from the melt. Then, cell nucleation will occur due to the pressure drop obtained from the GCP release, which is similar to Case (i). The only difference between Case (i) and Case (ii) is the amount of foam expansion obtained. However, the cell nucleation rate is uniform along the mold cavity, because of a uniform and rapid pressure drop after the GCP removal (from the characteristic of the low compressibility of the single-phase polymer/gas mixture).

(iii) High-pressure (full-shot) FIM with GCP: In this case, a full-shot is used to completely fill out the mold cavity, and the cavity pressure after filling will not be affected by the GCP. This means that the cavity pressure will not decrease rapidly as in Case (ii) even after the release of the GCP. This is the main difference between Case (ii) and Case (iii). Cell nucleation will not occur with the removed GCP in Case (iii) because of the high cavity pressure maintained from the full shot, whereas cell nucleation will occur when GCP is removed in Case (ii). Although the GCP application entirely prevents cell nucleation at the gate (or in the cavity), cell nucleation is only governed by the pressure drop obtained during the solidification process and by the extent of the melt’s shrinkage. The role of GCP in preventing cell nucleation during mold filling in this scenario is similar to the application of the packing pressure in removing the gate-nucleated bubbles in high-pressure FIM.39

This research covers all these three cases in principle although experiments are conducted with Case (ii). We investigated in detail, not only the suppression of cell nucleation caused by GCP application, but also the mechanism of cell nucleation when the GCP was released.

5.5 Experimental

5.5.1 Equipment and Material

Figure 3.2a shows a schematic of the FIM visualization setup used for this research. The setup consists of a visualization mold, where a prism reflects the phenomena occurring
inside the closed mold cavity to a camera. A cross section of the visualization mold’s stationary part, and a full-shot of the injected part, with locations identified in relation to the cavity entrance, is shown in Figure 3.2b and 3.2c. A round window is carefully placed in front of each location identified in Figure 3.2c. There is a pressure transducer in front of each view-window on the opposite side of the cavity. A detailed design of the entire visualization assembly can be found elsewhere.\textsuperscript{59}

Polystyrene MC3650 (PS-MC3650) from Americas Styrenics with MFR 13.0 gr/10min. (200°C/5 kg) was blown using carbon dioxide (CO\textsubscript{2}) from Linde Gas Canada. To perform the GCP experiments, nitrogen (N\textsubscript{2}) from Linde Gas Canada was applied using a control module from Caropreso Associates, MA, US. The visualization mold was installed on a 50-ton Arburg Allrounder 270/320C injection molding machine equipped with MuCell technology. A CV M10 camera from JAI, equipped with a magnifying lens from Navitar, was used to record the visualization images. A Mitutoyo SJ.210 portable surface roughness tester (ISO1997) was used to measure the samples’ surface roughness.

5.5.2 Experimental Procedure and Characterization

To perform FIM experiments, a (near) full-shot melt/gas mixture was injected to completely fill the mold cavity under different processing conditions, as summarized in Table 5.1. The cavity pressure was high enough to redissolve all the gate-nucleated cells under the processing conditions.\textsuperscript{39} Therefore, the pressure drop required for cell nucleation was obtained as a result of melt shrinkage that occurred during the solidification phase. For the FIM experiments with GCP, the mold cavity was first pressurized with N\textsubscript{2}. Then, the polymer/gas mixture was injected to completely fill the pressurized cavity while the N\textsubscript{2} was being exhausted from it. The entire GCP duration was 10 s. The mold cavity had to be pressurized well before the injection. Considering the time difference between the application of the GCP and the onset of the melt/gas injection, the effective GCP duration was recorded for about 5-6 seconds. In the application of the GCP, both its value and duration were the decisive parameters.
Table 5.1: Processing conditions for FIM+GCP experiments.

<table>
<thead>
<tr>
<th>Material</th>
<th>GCP Medium</th>
<th>Injection Speed (cm$^3$·s$^{-1}$)</th>
<th>GCP (MPa)</th>
<th>GCP duration (s)</th>
<th>$T_{mel}$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>N$_2$</td>
<td>20, 35, 50</td>
<td>2.30, 3.30</td>
<td>~5-6</td>
<td>230</td>
</tr>
</tbody>
</table>

To estimate the required GCP, the solubility of the dissolved CO$_2$ in the PS is plotted in Figure 5.2 as a function of the pressure at different temperatures.$^{60}$ Figure 5.2a was used to construct the $P$ solubility for 1 wt% CO$_2$ at different temperatures, and Figure 5.2b shows the results. A solubility pressure of 2.65 MPa was estimated for 1 wt% CO$_2$ in PS at 230°C.

![Figure 5.2: (a) Solubility of CO$_2$ in PS; (b) solubility pressure for 1% CO$_2$ in PS as a function of the temperature.](image)

To measure the cell density, with respect to the unfoamed volume, (i.e., $N'$), the method of 3.4.3 was used.$^{61}$

The growth rate of the bubbles in each condition was also obtained by tracking and measuring their diameter in each snapshot.$^{39}$
5.6 Results and Discussion

5.6.1 Prevention of Premature Bubble Formation during Filling and the Improvement of Surface Quality using GCP

Figure 5.3 shows successive snapshots of the melt front recorded at Location A of the mold cavity, both with and without the GCP application. Due to the location of the view-windows, a semi-parabolic melt front was captured. As shown in Figure 5.3a, foaming occurred once the melt/gas mixture entered the mold cavity due to the pressure drop at the gate, when no GCP had been applied. The advancement of the melt front in this case, i.e., with no GCP, was recorded as a foggy front, characterized by cell nucleation and by gas escaping from it. On the other hand, with the GCP application, there was a smooth, clear and transparent melt front. This indicated that the opposing GCP, acting on the melt front, had effectively and completely suppressed cell nucleation, and had prevented the gas from escaping during the mold-filling stage.
Figure 5.3: Melt-front advancement recorded at Location A: (a) No GCP; (b) GCP = 3.30 MPa (injection speed: 35 cm$^3$s$^{-1}$; CO$_2$: 1%; $T_{melt}=230^\circ$C).

The surface roughness ($R_a$), defined in Equation 1, of the injected samples with and without the application of GCP was measured and compared in Figure 5.4.

$$R_a = \frac{1}{n} \sum_{i=1}^{n} |y_i - y_{avg}|$$  \hspace{1cm} (1)

where $y_i$ is the measured height at $i$-th location, $y_{avg}$ is the mean value, and $n$ is the number of discrete measurements. As demonstrated, the GCP application significantly decreased the samples’ surface roughness. Further, the effective GCP application decoupled the $R_a$ from
the injection speed. As discussed in the literature, the opposing pressure of the charged gas on the melt flow prevents bubbles from nucleating during the mold-filling phase. As a result, no bubble would get the chance to reach the surface of the part via the fountain flow, and no burst or dragged bubble would be observed on the surface of the injected parts.

![Graph showing the effect of GCP on surface roughness](image)

Figure 5.4; Average surface roughness ($R_a$) with and without GCP application at different injection speeds.

### 5.6.2 Effect of GCP on the Cell Nucleation Rate

Foam injection molding experiments of PS-1% CO$_2$, both with and without the application of N$_2$ GCP, were carried out at various injection speeds. Figure 5.5 shows the visualization snapshots at Location A using an injection speed of 35 cm$^3$ s$^{-1}$. Careful analysis of the visualization results indicated that the GCP application had conditioned cell nucleation to the GCP removal from the melt. In other words, cell nucleation occurred the instant that the GCP was released. The cavity filling time was measured using Equation 2:
where $d$ is the dimension of the mold cavity in the machine direction, and $y$ and $z$ are the transverse dimensions of the cavity. The calculated mold-filling times are summarized in Table 5.2.

Table 5.2: Injection speed and mold-filling time in FIM+GCP.

<table>
<thead>
<tr>
<th>Material</th>
<th>GCP Medium</th>
<th>Injection Speed (cm$^3$ s$^{-1}$)</th>
<th>GCP (MPa)</th>
<th>Filling time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>N$_2$</td>
<td>35</td>
<td>3.3</td>
<td>1.37</td>
</tr>
<tr>
<td>PS</td>
<td>N$_2$</td>
<td>50</td>
<td>3.3</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Figure 5.5: Formation of bubbles in FIM at Location A: (a) No GCP; (b) GCP = 3.30 MPa; (injection speed: 35 cm$^3$ s$^{-1}$; CO$_2$: 1%; $T_{melt}$= 230°C).
Figure 5.6: Formation of bubbles in FIM at location A: (a) No GCP; (b) GCP = 3.30 MPa; (injection speed: 50 cm$^3$ s$^{-1}$; CO$_2$: 1%; $T_{melt}$ = 230°C).

The visualization snapshots, recorded at Location A, for experiments done at an injection speed of 50 cm$^3$ s$^{-1}$ are shown in Figure 5.6. As Figure 5.5 and 5.6 illustrate, the first noticeable bubbles emerged earlier for the experiments using GCP. By assessing the time difference between the mold-filling instant and the GCP removal, one may conclude that the cell nucleation onset could be shifted to an earlier time using GCP. The cell density data of the experiments in Figures 5.5 and 5.6 were extracted using the generated snapshots, and are shown in Figure 5.7. As previously stated, the onset of cell nucleation was postponed to the GCP release instant, and could be even faster with a shorter GCP duration.
In addition, a comparison of the cell nucleation rates from both sets of experiments shows that the nucleation rate was increased significantly using the GCP. To investigate the cell nucleation mechanism, the cavity pressure profiles corresponding to Figure 5.5 (and also to Figure 5.7a) were constructed and are shown in Figure 5.8. The recorded cavity pressure profiles at the visualized points indicated that the cavity pressure drop rate was much higher upon the GCP release (~100.00 MPa/s), compared to the case of no GCP (~0.28 MPa/s). This surprise bonus from the use of GCP was earned from the much lower compressibility of the polymer/gas mixture with no nucleated bubbles compared to the polymer melt with growing bubbles. In other words, the ability to propagate the pressure (drop) in the single-phase polymer/gas mixture (with no nucleated bubbles) is much higher than that in the highly compressible two-phase polymer/bubble mixture. Because of the higher pressure drop rate experienced by the “not-yet-nucleated” single-phase polymer/gas mixture upon the removal of the GCP, the cell nucleation rates and, therefore, the final cell density, will be higher, compared with no GCP. Park et al. demonstrated that a faster pressure drop rate results in both a higher cell nucleation rate and in a higher cell density because of the greater degree of thermodynamic instability generated in the melt/gas mixture.62

Thus, the cell nucleation mechanism that was activated by the GCP differed fundamentally from the conventional low-pressure or high-pressure FIM. In low-pressure FIM, nucleation
occurs based on the pressure drop rate obtained at the gate (or inside the cavity);\textsuperscript{21} in which case cell nucleation is a strong function of the gate geometry and the cavity pressure profile during filling.\textsuperscript{59} In high-pressure FIM, the bubbles nucleated during filling are first removed by the high pressure of the mold cavity or the applied packing pressure. Then, new bubbles nucleate based on the pressure drop rate obtained during the solidification and shrinkage phases.\textsuperscript{39} With the application of GCP, however, cell nucleation occurs when the GCP is removed from the melt/gas mixture after mold filling. The pressure drop rate for nucleation is then controlled by the GCP. This means that cell nucleation in FIM with GCP is completely independent of both the gate geometry and the depressurization (rate) at the gate. The FIM with GCP is similar to the high-pressure FIM in the sense that the bubbles nucleated during filling\textsuperscript{39,59} in both processes are either prevented or removed before major cell nucleation occurs. It should be re-iterated that this pressure drop, from the GCP release, can be obtained only when the cavity is incompletely filled (Case ii in Section 3). If the cavity is fully filled with a full shot, the built-up high cavity pressure will not decrease upon the release of the GCP.

![Cavity pressure profiles with and without GCP](image)

Figure 5.8: Cavity pressure profiles with and without GCP. The rapid pressure drop for the case of applying GCP was obtained from the release of GCP with a near full-shot (injection speed: 35 cm\textsuperscript{3} s\textsuperscript{-1}; CO\textsubscript{2}: 1\%, GCP = 3.30 MPa; T\textsubscript{melt}= 230\degree C, Location A, $P_{solubility}$ for 1\% CO\textsubscript{2} is shown by horizontal dash line).
5.6.3 Effect of GCP on the Bubble Growth Rate

The growth rates of the nucleated bubbles were measured using visualization snapshots, as shown in Figure 5.9. By applying the GCP, the nucleated bubbles grew faster compared with the FIM without GCP. This growth behavior could be attributed to several parameters. The bubble growth rate is a sensitive function of the local cavity pressure. As shown in Figure 5.8, the cavity pressure with the GCP drops to zero quickly due to the sudden removal of the GCP. On the other hand, in the case without GCP, a gradual pressure decay was observed, such that there was still some pressure on the melt during the early stages of cell growth, which reduced the cell growth rate. In addition, in the case without GCP, cell nucleation occurred later according to Figure 5.9. The bubbles that appeared at a later stage grew in a melt matrix at a lower temperature. In this case, the diffusion coefficient of the gas molecules was lower, and resulted in sluggish bubble growth. Finally, the application of GCP prevented any gas loss from the melt front during mold filling, as shown in Figure 5.3b. This preserved the gas resource for further cell nucleation and growth after the pressure drop. In contrast, there was considerable gas loss in the case where no GCP was used, as Figure 5.3a shows. By increasing the injection speed, the melt temperature at the moment of the cell nucleation is higher, resulting in a faster cell growth for the injection with no GCP. However, the cell growth was lower in the case of the faster injection using GCP. The latter requires more investigations and might be due to the nucleation of more cells by experiencing higher shearing.

![Figure 5.9](image)

Figure 5.9: Bubble growth rate with and without the application of GCP: (a) injection speed: 35 cm$^3$ s$^{-1}$; (b) injection speed: 50 cm$^3$ s$^{-1}$ (1% CO$_2$; $T_{melt}$= 230°C, Location A).
5.6.4 Effect of GCP on the Uniformity of the Cellular Structure

In addition to the increased cell density and growth rate, it turned out that the GCP also enhanced the uniformity of the cell structure dramatically. Figure 5.10 shows the snapshots taken from Location A and B in the FIM experiments with a GCP. Both locations showed a very similar foaming behavior with the application of a GCP.

In order to comprehend the reasons for the enhanced uniformity of the cell structure with a GCP, the cavity pressure profiles are recorded and analyzed. Figure 5.11a shows that the cavity pressure history was a sensitive function of the location and time during filling, especially in the beginning. First of all, an initial pressure of ~1.9 MPa was detected from the pressure transducers even before the mold was completely closed (see the value at time zero in Figure 5.11a). This cavity pressure was generated as an initial GCP according to the Caropreso GCP control module. As the melt/gas mixture was being injected, the pressure measured at Location A increased to a high value up to the point of complete filling and then decreased. But the pressure measured at Location B increased more gradually during filling. As in the case of low- and high-pressure FIM, there was an inevitable pressure gradient inside the mold cavity in the beginning. With the application of GCP, however, this pressure gradient at different locations of the cavity disappeared over time, and the cavity pressures eventually became the (same) GCP level together. Consequently, different locations of the mold cavity experienced the same pressure drop rate afterwards upon the removal of the GCP. In other words, the pressures at different locations of the cavity (i.e., Location A and B in Figure 5.11a) are similar at the moment of GCP removal. Hence, cell nucleation was simultaneously initiated by a similar driving force, i.e., under the same pressure drop rate at different locations in the mold cavity upon the removal of GCP. This resulted in a similar measured cell density as shown in Figure 5.11d. In addition, it was also observed that the bubbles were not elongated at any location as in the case of full-shot high-pressure FIM because of the lack of a melt flow. It should be noted that low-pressure FIM typically has elongated bubbles because of the pressure gradient and a resultant flow present in the cavity, which can cause non-uniformity in the cell structure.
For the purpose of contrast, Figure 5.11b and 5.11c show, respectively, the cavity pressure profiles at Location A and B for a *near full-shot* FIM (without any packing pressure), and a *high-pressure* FIM (with a full shot and with an additional packing pressure), at the same processing conditions of Figure 5.11a but without GCP. The cavity pressure drop rates at the solubility pressure for all these cases were calculated using Figure 5.11a to 5.11c, and are summarized in Table 5.3. As observed, the obtained pressure drop rate was the lowest in the case of near full-shot FIM. In a typical high-pressure FIM, the pressures exerted in the cavity at the completion of mold filling were much higher, and the uniformity in the cavity pressure was greater indicating a much more uniform cellular structure. The pressure drop rate obtained in high-pressure FIM is also higher compared with that of near full-shot FIM. Nevertheless, both the pressure drop rate and the cavity pressure uniformity are greater with GCP application. Hence, more uniform cell nucleation is expected using GCP.

Table 5.3: Pressure drop rate obtained in FIM experiments with and without GCP.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Cavity location</th>
<th>dP/dt (MPa s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near full-shot FIM with GCP</td>
<td>A</td>
<td>~ -100</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>~ -100</td>
</tr>
<tr>
<td>Near full-shot FIM</td>
<td>A</td>
<td>-0.39</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>-0.24</td>
</tr>
<tr>
<td>Full-shot FIM (packing pressure = 14 MPa for 1 s)</td>
<td>A</td>
<td>-0.89</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>-0.70</td>
</tr>
</tbody>
</table>

Figure 5.10: Snapshots of the visualization results at different locations in the mold cavity: (a) Location A; (b) Location B (injection speed: 50 cm³ s⁻¹; CO₂: 1%; Tₘ₆₇ = 230°C).
Figure 5.11: (a) Cavity pressure profiles from Location A and B using GCP with a near full shot; (b) cavity pressure profiles from Location A and B without GCP with a near full shot (yet without any packing pressure); (c) cavity pressure profiles from Location A and B without GCP in high-pressure FIM, i.e., with a full shot and with an additional packing pressure; (d) cell nucleation at Location A and B observed with a near full shot using GCP; (injection speed: 50 cm$^3$ s$^{-1}$; CO$_2$: 1%; $T_{	ext{melt}}$= 230° C).
5.6.5 Effect of GCP Magnitude on the Cellular Structure

If the magnitude of the applied GCP is insufficient to prevent cell nucleation, some premature nucleation is likely. In other words, cell nucleation may partially occur during mold filling. Figure 5.12 shows a GCP trial which failed to completely suppress cell nucleation with a GCP of 2.30 MPa, which was slightly lower than the $P_{\text{solubility}}$ of 2.65 MPa (i.e., about 87% of the $P_{\text{solubility}}$) for 1% CO$_2$. Since the minimum pressure in the mold cavity was the GCP, the pressure of the polymer melt flowing in the cavity was higher than this GCP level of 2.30 MPa. In other words, the superheat, defined to be $P_{\text{solubility}} - P$ (higher than the GCP) as the initial driving force for cell nucleation, was not very high. But interestingly, foaming was readily noticeable near the melt front during mold filling (Figures 5.12a and 5.12b) despite the high melt pressure close to the $P_{\text{solubility}}$. It seems that the high shear and/or high extensional flow facilitated cell nucleation during mold filling despite the low superheat. However, the growth of the nucleated bubbles was restricted by the GCP during filling. Once the GCP was removed, new bubbles were additionally nucleated, resulting in a bimodal cellular structure, as shown in Figure 5.13. A similar bimodal foam structure, due to the application of insufficient GCP, was also reported in the FIM experiments of PLA composites.

![Figure 5.12](image)

Figure 5.12: (a) and (b) Melt front advancement in the mold-filling stage at Location B; (c) and (d) the presence of nucleated bubbles in the system (injection speed: 35 cm$^3$ s$^{-1}$; CO$_2$: 1%; GCP = 2.30 MPa; $T_{\text{melt}}$= 230°C).
Figure 5.13: Formation of a bimodal structure as a result of an insufficient GCP of 2.30 MPa (injection speed: 35 cm$^3$ s$^{-1}$; CO$_2$: 1%; T$_{melt}$= 230°C).

Careful investigation of the visualization snapshots revealed that the large number of cells nucleated during filling were shrinking and disappearing over time, and only a few bubbles survived by the time of the GCP removal. Figure 5.14a and 5.14c show that the cell density was decreased significantly from 350000 to 3000 (#/cm$^3$) in 4.7 seconds. There is a possibility that the chain orientation after filling may have affected the solubility, but it appears that the increased CO$_2$ solubility with a decreased melt temperature (see Figure 5.2a) was the main driving force to redissolve the nucleated bubbles during cooling. But not all the bubbles dissolved back to the melt completely because the GCP was below the $P_{solubility}$. Upon the GCP removal, the solubility decreased, and additional cells were nucleated in the polymer matrix while the remaining bubbles grew simultaneously.
Figure 5.14: Formation of cells during mold filling, disappearance of cells during cooling, and growth of survived cells with removed GCP: (a)-(e) visualization snapshots at various times; (f)-(j) schematics corresponding to (a)-(e), respectively (injection speed: 35 cm$^3$ s$^{-1}$; CO$_2$: 1%; GCP= 2.30 MPa; Location B; T$_{melt}$= 230$^\circ$C; the scale bar is 0.5 mm).

It is also very interesting to note that the number density of the additional cells nucleated upon the GCP removal was not as high as that obtained from the earlier case with the GCP magnitude over the $P_{solubility}$. Since majority of the cells nucleated during filling redissolved back to the polymer melt, the CO$_2$ content in the polymer matrix must have been very close to the original value of 1 wt%. But the compressibility of the PS/CO$_2$ mixture generated by the survived cells decreased the pressure drop rate significantly. As a consequence, the number density of the cells nucleated upon the GCP removal decreased dramatically, despite the similar gas content in the polymer. In other words, the remaining cells gave a large detrimental effect on the cell nucleating ability of the polymer/gas mixture through the increased compressibility.
5.7 Conclusion

The cell nucleation and growth mechanisms were explored in foam injection molding with GCP via in-situ visualization. Cell nucleation was totally suppressed during filling by using GCP, but cell nucleation occurred upon the GCP removal. This indicated that cell nucleation in the presence of GCP is fully independent of the gate geometry and the pressure drop obtained at the gate. It was also observed that a faster pressure drop was obtained when the GCP was released, which led to faster cell nucleation and growth. We demonstrated that the uniformity of the cellular structure increased with the application of a proper GCP, which was attributed to the simultaneous cell nucleation in the entire mold cavity, and to the absence of the flow and shearing during nucleation. With an insufficient GCP, a large number of bubbles were initially nucleated during filling due to the shear and extensional stresses, and most bubbles shrunk and redissolved back to the melt over time due to the increased solubility during cooling. But some bubbles survived and a bimodal cellular structure was resulted. Furthermore, a smaller cell density was obtained because of the compressibility created by the survived bubbles.
5.8 Reference


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Chapter 6

6 Mechanism of Cell Nucleation in High-Pressure Foam Injection Molding with High Expansion

6.1 Abstract

Cell nucleation mechanisms in high-pressure foam injection molding with high expansion, i.e., with using mold-opening technology, are investigated in this research. The entire formation process of the cellular structure was monitored using an in-situ mold visualization technique. We observed that a portion of cells, nucleated during the mold filling stage, sustained the cavity pressure and remained in the melt/gas mixture after the cavity filling was completed. The presence of these cells led to the formation of large cells in the structure, reduced the final cell density and the structure uniformity of the molded foams. The cavity pressure profiles were plotted and used to identify the cell nucleation mechanisms at different regions of the foamed parts. A protocol was then used to remove the pre-mature nucleated cells before the mold-opening stage, by the application of a melt packing pressure. New cells were then nucleated uniformly when the mold opened. An abrupt pressure-drop was realized during the mold-opening and cavity volume expansion when this protocol was used. This increased the cell density dramatically and enhanced the structure uniformity within the foamed samples. The effect of the melt packing pressure as well as the dwelling time of the melt/gas mixture was investigated. It was observed that the packing time, required to remove cells, increased as the packing pressure decreased. However, a too long dwelling time activated a secondary cell nucleation mechanism, so called shrinkage-induced nucleation, deteriorating to the final cell density and structure.

6.2 Introduction

The current energy crisis from one side, and the critical environmental pollution issues from the other side, drives manufacturing industries to produce light-weight materials in order to decrease the energy consumption. Under this light, it is essential to manufacture products with comparable and/or superior properties to their conventional counterparts. Foam injection molding (FIM) is a thriving technology and successful candidate for its ability to produce low-density parts at fast production cycles. In particular, numerous researches reported enhanced mechanical properties,\textsuperscript{1-5} enhanced electrical conductivity,\textsuperscript{6} as well as enhanced heat and sound insulation properties with foamed parts.\textsuperscript{7-9} These improved properties, along with advanced and specific application of FIM parts in water filtration industries\textsuperscript{10} or in biomedical engineering,\textsuperscript{11} make FIM an interesting manufacturing method. Most of the aforementioned improvements are successfully attained with a uniform micro- or nano-sized cell structure. Nevertheless, achievement of such uniform and high cell density structures, especially with a high void fraction and high expansion, is very challenging in FIM. The non-uniform cellular structure of conventional FIM is characterized with highly coalesced, large and elongated cells. In addition, the presence of silver marks reduces the surface quality of the foams. This is in part due to insufficient knowledge about the mechanisms of the cellular structure formation, that is nucleation and growth, and also lack of a proper equipment to enable an in-situ monitoring of the foaming phenomena in FIM process.

In FIM, a single-phase melt-gas mixture is prepared in the injection barrel, prior to the injection. This is crucial that the polymer melt and the gas are homogeneously mixed, otherwise large gas pockets would be formed in the product.\textsuperscript{12} The resistance of the gate provides enough pressure to prevent any pre-mature cell nucleation before the melt-gas mixture enters the mold cavity. Once a single-phase melt/gas mixture is prepared, the injection occurs. There are two major fashions to carry out FIM experiments, namely low-pressure FIM\textsuperscript{13,14} and high-pressure FIM.\textsuperscript{15}

In low-pressure FIM, the shot size is smaller than the mold cavity size (i.e. short-shot). In other words, the entire mold cavity is not fully filled, and a percentage of it is left for the
foam expansion. Once the melt-gas mixture enters the mold cavity, the high pressure is removed from the mixture and the cell nucleation occurs. Nucleated cells travel towards the end of the cavity, grow, coalesce, get sheared and get elongated. In addition, the cavity pressure increases as the filling stage proceeds, decreasing the pressure-drop rate, thereby reducing the nucleation rate. Lee et al. discussed strategies to improve the cell density and minimize the non-uniformity of the structure in low-pressure FIM, mainly by maintaining the cavity pressure at low pressure values.\textsuperscript{13} While the structure suffers from a severe non-uniformity, high void fractions (as high as 40\%) are achievable.

In high-pressure FIM, the entire mold cavity is filled by using a full-shot injection. Due to a higher cavity pressure as compared with the low-pressure FIM, the inevitable cell nucleation over the gate occurs under a low pressure-drop rate, and consequently, a very low cell density structure is obtainable. Further nucleation then occurs during the melt solidification. Therefore, the cell density is governed by the rate of the material shrinkage; for the same token, the obtainable void fraction is limited to the extent of the material shrinkage.\textsuperscript{15} The presence and expansion of these low-density nucleated cells reduces the rate of pressure-drop during shrinkage. Shaayegan et al. proposed a protocol based on using a melt packing pressure to re-dissolve cells, nucleated during mold filling, back into the melt. Hence, a faster pressure-drop is achievable with the shrinkage of the single-phase melt/gas mixture with a lower compressibility.\textsuperscript{15} In addition, the sheared or elongated cells are absent from the cellular structure for the nucleation stage is decoupled from the filling stage. Although this strategy improves the uniformity of the structure, the expansion of the foam is restricted (about 5-10\%) and the pressure-drop is very slow, especially for amorphous polymers.

The application of gas-counter pressure (GCP) with FIM is well-known to improve the surface quality of the foamed parts. Also, it is reported that the cell density and uniformity of the cellular structure improves by using GCP. Nonetheless, the application of GCP with a low-pressure FIM (i.e. free expansion) will not improve the uniformity of the structure as the cell expansion, coalescence and shearing occurs upon the GCP removal. Using a GCP with high-pressure FIM will improve the surface quality of the foamed parts, yet the pressure-drop rate remains low and therefore the cell density does not improve.
In order to increase the void fraction of the foamed parts, the FIM can be followed by one step precise mold-opening (also called breathing mold).\textsuperscript{16-19} In this technology, normally a full-shot is used to fill out the mold cavity with the gas-charged melt. Once the filling stage is completed, the cavity expands in the thickness direction for a certain distance at a set opening speed. There can be a controlled dwelling time between the mold filling and opening stages, i.e., a delay before the mold opening. This is especially important in FIM of semi-crystalline polymers.\textsuperscript{19} For mold-opening, either the entire mold cavity opens by the retraction of the clamping unit, or only part of it opens up by a core-pulling (also called core-back),\textsuperscript{20} expanding the cavity space. In the core-back technology, the part usually gets locally foamed while the remaining area remains un-foamed.\textsuperscript{20} Mold-opening speed and mold-opening distance are two major set parameters which have significant effect on cell density and the expansion ratio of the final foam respectively.\textsuperscript{21,22} In particular, the set mold-opening speed decides the amount of the pressure-drop rate,\textsuperscript{23} affecting the cell nucleation rate and overall cell density. Therefore, large expansion ratios are attainable by using mold-opening technology. Also, the homogeneity of the cellular structure significantly increases within the foamed samples in this process.

Ishikawa and Ohshima showed that the number density of nucleated cells in FIM using core-back increased by the core-back rate due to the increased depressurization rate in the cavity.\textsuperscript{16} A uniform microcellular structure for polypropylene was achieved by Bledzki et al. in FIM experiments using a GCP followed by mold-opening. The formation of the microstructure was attributed to the pressure-drop during the mold-opening.\textsuperscript{24} A relatively high void fraction cellular structure was obtained in FIM experiments of polylactide (PLA) and PLA composite foams with a GCP and with using mold-opening, which were more uniform compared with those obtained from low-pressure FIM experiments.\textsuperscript{25,26} Sporrer and Altstadt studied the foam density as well as the change in mechanical properties of the foamed parts as a function of the mold-opening distance. They also related the overall FIM structure to the mold-opening delay, i.e. the time after which the mold was opened, and discussed its effects on the cell size and mechanical properties of the final foams. Jahani et al. used the mold-opening technology to produce open-cell polypropylene foams for acoustic applications.\textsuperscript{8} They discussed that the opening distance of the mold not only affected the growth of cells, also affected their shape and morphology at different regions of
the FIM parts. Jahani et al. also discussed the formation of various cell regions, with different cell morphologies, in FIM experiments of polycarbonate using mold-opening, and analyzed the sound and thermal insulation properties of the foams at different mold-opening distances. Michaeli et al. controlled the foam morphology and density of FIM samples by adjusting the mold-opening parameters such as the opening distance and evaluated mechanical properties of foamed samples at different cell sizes, skin layer thicknesses, and densities. Stumpf et al. used the mold-opening technology to obtain foams with reduced densities, i.e. high expansions. Heim and Tromm manufactured locally foamed injection molded components using a local mold-opening technology. They observed that the thin-wall adjacent area to the locally foamed sections have a trace of foaming. Chu et al. mentioned that the foaming temperature can be controlled in the melt/gas dwelling time prior to the mold-opening stage, and mathematically estimated the temperature profiles of the melt/gas mixture inside the mold cavity as a function of the dwelling time. The final foam structure and morphology can be determined by controlling the temperature profiles within the mold cavity and during foaming, especially in FIM of semi-crystalline polymers.

Despite its wide application, no systematic research has been done to investigate active nucleation mechanisms in FIM using mold-opening. Most of the identified cellular structures were analyzed after the foam was cooled, and therefore, the full nature of the formation of different cell morphologies is not fully understood. The majority of explanation and interpretations of cellular structure development were merely based on unproven or unverified hypotheses. Here, we employed and innovative visualization mold and monitored the complete process of the FIM using mold-opening in order to uncover cell nucleation mechanisms in this technology.

6.3 Experimental

6.3.1 Materials and Equipment

To carry out FIM experiments, a 50-ton Arburg Allrounder 270/320 C injection molding machine with mold-opening technology was used. The MuCell® (Trexel, Inc., Woburn,
Massachusetts) technology was used to inject a controlled dosage of the blowing agent, in a super-critical condition, into the polymer melt. The injection was done through a fan gate into a rectangular shaped cavity with nominal dimensions of 135 mm × 111 mm × 3.2 mm. The mold cavity can expand by the opening of the mold’s moving plate to a desired distance at a set opening speed.

To monitor the cell formation and foaming phenomena, a visualization mold was used. A right-angle prism was incorporated inside the mold’s fixed plate to reflect cavity images to a camera (see Figure 3.2). This visualization mold provides visual accessibility to critical locations of the mold cavity with respect to the gate location, i.e., A, B, and C as shown in Figure 3.2c, and was featured with pressure transducers across the mold cavity.

Polystyrene (PS675) with an MFR of 7.0 g/10min (200°C/5 kg) was chosen as the resin, provided from Americas Styrenics, and was physically blown by carbon dioxide (CO₂) from Linde Gas Canada. The transparency of the PS675 after solidification was essential for our further visualization investigations. A full-shot PS675-CO₂ mixture was used to perform the FIM experiments. The melt/gas mixture was first injected into the cavity before the mold expands in thickness direction (Figure 6.1). A proper melt packing pressure was used where applicable. The processing parameters used in this research our summarized in Table 6.1.
Figure 6.1: Schematic of the mold-opening and the principle of the visualization mold.

Table 6.1: Processing parameters used in FIM+MO experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
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<tr>
<td>Melt temperature (°C)</td>
<td>220</td>
</tr>
<tr>
<td>Mold temperature (°C)</td>
<td>30</td>
</tr>
<tr>
<td>Injection flow rate (cm³/s)</td>
<td>80</td>
</tr>
<tr>
<td>CO₂ content (wt.%)</td>
<td>3, 5</td>
</tr>
<tr>
<td>Mold-opening distance (mm)</td>
<td>2</td>
</tr>
<tr>
<td>Mold-opening speed (mm/s)</td>
<td>50</td>
</tr>
<tr>
<td>Packing pressure (MPa)</td>
<td>6 to 24</td>
</tr>
<tr>
<td>Packing hold time (s)</td>
<td>2 to 18</td>
</tr>
</tbody>
</table>
6.3.2 Foam Characterization

The foam density ($\rho_{foam}$) was measured by water-displacement method (ASTM: D792-08). Using the measured foam density, the local expansion ratio of the foamed samples ($\varphi$) was obtained as follows:

$$\varphi = \frac{\rho_{solid}}{\rho_{foam}}$$

at which $\rho_{solid}$ is the density of the un-foamed (solid) sample. To characterize the cell density, the foam samples were fractured in liquid nitrogen, sputter coated with platinum, and the cellular structure was captured using a scanning electron microscopy (SEM JEOL JSM-6060). Then the cell density ($N$) was:

$$N = \left(\frac{n}{A}\right)^{3/2} \times \varphi$$

$n$ is the number of cells counted in an area of $A$ of the SEM micrographs. The visualization snapshots as well as SEM micrographs were analyzed using ImageJ software.

6.4 Results and Discussions

6.4.1 Cell Nucleation Mechanism in High-pressure FIM with Mold-opening

Figure 6.2 shows the visualization snapshots for a high-pressure FIM of PS-3%CO$_2$ at Location B. As shown in Figure 6.2a, the application of a packing pressure of 6 MPa for 8 s left most of the cells, nucleated during the filling, un-dissolved in the system. The final foam morphology is a mixture of cells nucleated during the filling stage (dominant cells
here), and those nucleated during the melt shrinkage (i.e., shrinkage-induced cells). By increasing the packing pressure up to 14 MPa for the same packing duration, more nucleated cells disappeared and the dominant cells were those nucleated during the melt solidification and shrinkage (Figure 6.2b). By further increasing the packing pressure, up to 20 MPa as shown in Figure 6.2c, eventually all nucleated cells during the filling disappeared and the dominant cell nucleation mechanism became the nucleation during the melt shrinkage.

As demonstrated, the cell nucleation mechanism switched from the major nucleation during the filling (and at the gate) to the major nucleation during the melt solidification. These different nucleation mechanisms resulted in different cell morphologies and overall cell densities. The pressure-drop required for the cell nucleation during the filling was obtained at the gate, meaning that the nucleation occurred once the melt/gas mixture entered the cavity. Then the nucleated cells travelled with the melt front during the filling stage, grew, got sheared, and coalesced.

For the shrinkage-induced nucleation, on the other hand, the pressure-drop was obtained due to the melt shrinkage. As shown in Figure 6.2, the final cell density is lesser when the shrinkage-induce nucleation is the dominant nucleation mechanism. This is due to the fact that the rate of the pressure-drop is much lower during shrinkage than that occurring at the gate. Nevertheless, the cellular structure is more uniform with circular cells, showing no trace of any elongated or coalesced cell. The latter is attributed to the decoupled filling and nucleation stages, and the fact that the cell nucleation occurred in a static melt.
The cavity pressure profiles of these experiments were recorded at Locations A and B and constructed against time in Figure 6.3. As shown in Figure 6.3a, the cavity pressure was below the required pressure for the dissolution of the blowing agent (i.e. solubility pressure of 7.8 MPa) using a 6MPa packing pressure. Therefore, the cells nucleating during the filling remained in the system as shown in Figure 6.2a, prevailing the structure. By increasing the packing pressure up to 14 MPa, the cavity pressure slightly exceeded the solubility pressure of the blowing agent (Figure 6.3b), dissolving more cells. Application of
a packing pressure about 20 MPa, as shown in Figure 6.3c, eventually removed all nucleated cells; this is the case that shrinkage-induced cell govern the structure as demonstrated in Figure 6.2c.

Figure 6.3: Cavity pressure profiles for high-pressure FIM of PS-3%CO2: (a) packing pressure = 6 MPa; (b) packing pressure = 14 MPa; (c) packing pressure = 20 MPa. (Injection speed = 80 cm³/s; packing time = 8 s; T_{melt}= 220 °C; solubility pressure of 3wt% CO₂ in PS is approximated 7.8 MPa, and shown by dash line).

In order to increase the expansion ratio of the foamed parts, the high-pressure FIM experiments were followed by one step mold-opening. Figure 6.4 shows the visualization results for the high-pressure FIM with mold-opening experiments carried out using a packing pressure of 14 MPa for 8 s. As seen, the cells nucleated at the gate and those
nucleated during filling, survived the cavity pressure until the mold-opening moment. These un-dissolved cells will grow and elongate to large sizes during the mold-opening when the mold opens. The presence of these un-dissolved cells not only results in the formation of irregular cell shapes after the mold-opening, also reduces the gas supply for the further nucleation during the mold-opening. In the snapshot at $t = 12.30$ s, large deformed cells are noticed among the newly nucleated cells during mold-opening. Eventually, the un-dissolved cells give rise to the melt/gas mixture compressibility, reducing the obtainable pressure-drop rate due to opening.

Figure 6.4: Visualization snapshots for PS-3%CO$_2$ at Location B. (Injection speed = 80 cm$^3$/s; packing pressure = 14 MPa; packing time = 8 s; $T_{\text{melt}} = 220$ °C).

The high-pressure mold-opening experiments were continued using a packing pressure of 20 MPa for 8 s, as shown in Figure 6.5. All nucleated cells from the mold filling completely disappeared before the opening stage. Hence, the pressure-drop during the mold-opening was induced on a single-phase melt/gas mixture with a negligible compressibility. No
irregular, large cell was detected in visualization snapshots after the mold-opening. A more uniform cell structure with a higher cell density is expected from this system. (The cell structure analyses is detailed in Section 4)

Figure 6.5: Visualization snapshots for PS-3%CO\textsubscript{2} at Location B. (Injection speed = 80 cm\textsuperscript{3}/s; packing pressure = 20 MPa; packing time = 8 s; T\textsubscript{melt} = 220 °C).

To investigate the cell nucleation mechanisms, the cavity pressure profiles for full-shot mold-opening experiments are constructed in Figure 6.6. The cavity pressure remained well above the solubility pressure of the blowing agent before the mold-opening step by using a 20 MPa packing pressure. As the mold opened, the cavity pressure dropped drastically, and induced myriad of cells. Compared with pressure profiles of Figure 6.3, i.e., the case of the using a full-shot alone, a sudden and much faster pressure-drop is observed due to the mold-opening and cavity expansion.
Based on the observations of Figure 6.5 and 6.6, different steps of an ideal high-pressure FIM with mold-opening is schematically explained in Figure 6.7. Before the injection, the single-phase melt/gas mixture is under the high pressure of the injection barrel. The resistance of the gate prevents any pre-mature cell nucleation. Upon the entry of the gas-charged melt into the cavity, the cell nucleation starts as the high pressure is suddenly removed from the melt/gas mixture. By further mold filling followed by a melt packing pressure, the nucleated cells will re-dissolve back into the melt, producing a single-phase melt/gas mixture again. Once the mold opens, the pressure is removed from the melt/gas mixture and the cell nucleation happens. In other words, the main pressure-drop in this technology is obtained by the sudden expansion (or volume increase) of the mold. By using this protocol, a highly expanded and uniform cellular structure is achievable as (i) the filling and nucleation stages are decoupled, omitting any coalesced or sheared cell from the
structure and (ii) no nucleated cell is in the system prior the opening stage. The overall cell density is also supposed to increase as (i) a single-phase melt/gas mixture contains more gas molecules for the further cell nucleation, increasing the nucleation driving force, (ii) a faster pressure-drop is attainable due to the reduced compressibility of the melt/gas mixture, and (iii) as the pressure-drop occurs during the mold-opening, one may increase the nucleation rate and the cell density by increasing the mold-opening speed.

Figure 6.7: High-pressure FIM with mold-opening: (a) formation of cells during mold filling; (b) application of a packing pressure to re-dissolve nucleated cells back into the melt; (c) nucleation of new cells during mold-opening.
To investigate the mutual effects of the melt packing pressure and the melt packing time on the cell nucleation, and to optimize the processing conditions, the high-pressure FIM experiments were carried out at different packing pressures and for different packing durations. Figure 6.8 shows the visualization snapshots for the high-pressure FIM of PS-3%CO₂ with mold-opening under the melt packing pressures of 22 MPa and 24 MPa for 4 and 2 s of packing duration respectively. As shown, by reducing the packing duration, a larger packing pressure was required to completely remove the cells nucleated during filling. The application of a shorter packing pressure favours the cell nucleation as the nucleation occurs at higher temperatures. Yet, an uncertainty is caused about the complete dissolution of nucleated cells. In other words, it is uncertain whether all nucleated cells are completely dissolved back into the melt, or just shrank to smaller sizes.

Figure 6.8: Visualization snapshots for PS-3%CO₂ at Location B: (a) application of a packing pressure of 22 MPa for 4 s; (b) application of a packing pressure of 24 MPa for 2 s (Injection speed = 80 cm³/s; T_melt = 220 °C).
Figure 6.9a and 6.9b show the SEM pictures taken from Location A of the PS-3%CO$_2$ samples foamed using 20 and 24 MPa packing pressures for 8 and 2 s respectively. Other processing conditions remained the same. As seen, the cellular structures differ significantly. By using a longer packing time, a more uniform cellular structure was obtained as shown in Figure 6.9a. This was attributed to the complete dissolution of cells which were nucleated during filling, before the mold-opening step. At the same time, the formed skin layer was thicker in this sample. Using a shorter packing time, on the hand, resulted in a highly non-uniform structure characterized by two types of cells: (i) large cells which are believed to be formed during the mold filling stage. In other words, these are the cells which were not fully dissolved back within a 2 s of packing, and (ii) fine, high density cells which formed during the mold opening. As the packing duration was short, the melt temperature remained higher at the moment of the mold-opening, favouring cell nucleation. As shown in Figure 6.10, the cavity pressures remained above the solubility pressure of the blowing agent before the opening, but the duration of packing pressure was short for the case of 24 MPa, resulting in a less uniform cell structure.

Figure 6.9: SEM micrographs for PS-3%CO$_2$ at Location A: (a) application of a packing pressure of 20 MPa for 8 s; (b) application of a packing pressure of 24 MPa for 2 s (Injection speed = 80 cm$^3$/s; T$_{\text{melt}}$= 220 °C).
Figure 6.10: Cavity pressure profiles for high-pressure FIM of PS-3%CO₂ with mold-opening at different holding times (Injection speed = 80 cm³/s; T<sub>melt</sub> = 220 °C; solubility pressure of 3wt% CO₂ in PS is approximated 7.8 MPa, and shown by dash line).

Figure 6.11 shows the nucleation behavior of PS-3%CO₂ at relatively long packing pressure durations (14 and 16 s). A new cell nucleation mechanism was activated before the mold-opening step in both experiments. As the melt temperature reduced, cell nucleation occurred due to the melt solidification and shrinkage. The frozen sprue must have disconnected the packing pressure from the melt/gas mixture, and thus, new cells nucleated. The circular, low density shrinkage-induced cells are observed in snapshots at t = 18.5 s and t = 11.7 s of Figures 6.11a and 6.11b respectively. The formation of these shrinkage-induced cells before the mold-opening reduced the gas supply for the further nucleation, and increased the compressibility of the melt/gas mixture. In addition, the shrinkage of the melt reduced the cavity pressure as illustrated in Figure 6.12. Therefore, these nucleated cells grew during mold-opening, and a poor nucleation was realized.
Figure 6.11: Visualization snapshots for PS-3%CO$_2$ at Location B: (a) application of a packing pressure of 16 MPa for 16 s; (b) application of a packing pressure of 18 MPa for 14 s (Injection speed = 80 cm$^3$/s; $T_{melt}$ = 220 ºC).
Figure 6.12: Cavity pressure profiles for high-pressure FIM of PS-3%CO₂ with mold-opening after long holding time (Injection speed = 80 cm³/s; T_melt = 220 °C; solubility pressure of 3wt% CO₂ in PS is approximated 7.8 MPa, and shown by dash line).

6.4.2 The Relationship Between the Nucleation Mechanism and Cellular Structure in High-pressure FIM with Mold-opening

To study the relationship between the nucleation mechanism and the cell structure, high-pressure FIM experiments of PS-5%CO₂ with mold-opening were carried out. The in-situ visualization results were then compared with the corresponding SEM micrographs. Figure 6.13a shows an SEM micrograph of a fractured FIM sample, obtained with mold-opening and using a 6 MPa packing pressure. Three cell regions were distinguished: (i) irregular and large cells near the skin, (ii) elongated and sheared cells, and (iii) fine and circular cells in the central regions of the sample. The visualization snapshots of the corresponding experiment revealed that most of cells, nucleated during the mold filling, survived the cavity pressure using a 6 MPa packing pressure (Figure 6.13b). These cells grew into irregular and large cells during the mold-opening, as evidenced in Figure 6.13c, and producing cell structures as (i) and (ii). The cells formed in Region (iii), i.e. the fine and cellular central cells, were formed during the mold-opening step, as the result of the sudden
pressure-drop obtained. This is worth noting that the temperature gradient, observed in the thickness direction of FIM samples, keeps the core regions of samples (Region (iii) in Figure 6.13a) at an elevated temperature compared with regions close to the mold cavity (Regions (i) and (ii) in Figure 6.13a). Hence, the cavity pressure in Region (iii) could dissolve nucleated cells, using 6 MPa packing pressure, prior the mold-opening.

Figure 6.13: High-pressure FIM with mold-opening of PS-5%CO₂ at Location B, using a packing pressure of 6 MPa: (a) SEM image; (b) visualization snapshot right before the mold-opening; (c) visualization snapshot right after the mold-opening (Injection speed = 80 cm³/s; Tₘₐₓ = 220 °C).
High-pressure FIM experiments of PS-5%CO$_2$ with mold-opening were further performed using higher packing pressures. Figures 6.14a to 6.14c show the visualization snapshots, before and after the mold-opening, using packing pressures of 14, 20, and 24 MPa respectively. As demonstrated, more cells, nucleated during the filling stage, were dissolved back into the melt by increasing the packing pressure from 14 MPa up to 24 MPa. By the same token, the cellular structure of the foamed sample improved. While a 14 MPa was insufficient to re-dissolve nucleated cell, as shown in Figure 6.14a, only a few cells sustained the cavity pressure under a 20 MPa packing pressure (Figure 6.14b). Using a packing pressure of 24 MPa removed all nucleated cells, improving the cellular structure significantly (Figure 6.14c).

The corresponding SEM images of the visualized samples are shown in Figure 6.15. As expected, the structural uniformity of the foamed samples was significantly enhanced by the removal of the cells, nucleated during filling, before the mold-opening stage. No irregular large cell, or sheared elongated cell was noticed in samples using packing pressure of 20 MPa or larger.
Figure 6.14: High-pressure FIM with mold-opening of PS-5%CO$_2$ at Location B: (a) packing pressure = 14 MPa; (b) packing pressure = 20 MPa; (c) packing pressure = 24 MPa (Injection speed = 80 cm$^3$/s; packing time = 8 s; $T_{melt}$ = 220 °C).
Figure 6.15: SEM images of the high-pressure FIM samples of PS-5%CO₂ with mold-opening at Location B: (a) packing pressure = 14 MPa; (b) packing pressure = 20 MPa; (c) packing pressure = 24 MPa (Injection speed = 80 cm³/s; packing time = 8 s; T_{melt} = 220 °C).

Figure 6.16 shows the recorded cavity pressure profiles for the high-pressure FIM experiments with mold-opening of PS-5%CO₂ at different packing pressures. The pressure-drop rate at each experiment was calculated using the slope of the pressure curves in the mold-opening stage, and summarized in Table 6.2. As illustrated, the application of a 20 MPa or larger packing pressure maintained the cavity pressure well above the solubility pressure of the blowing agent till the mold-opening moment. In addition, a faster pressure-drop was experienced with a single-phase gas/melt mixture during the mold-opening by increasing the packing pressure.
Figure 6.16: Cavity pressure profiles for high-pressure FIM of PS-5%CO₂ with mold-opening at Location B (Injection speed = 80 cm³/s; packing time = 8 s; Tₘₐ₇ = 220 °C; solubility pressure of 5wt% CO₂ in PS is approximated 13.2 MPa, and shown by dash line).

Table 6.2: Calculated pressure-drop rate using different packing pressures.

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<th>Packing Pressure (MPa)</th>
<th>dP/dt (MPa/s)</th>
</tr>
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<tbody>
<tr>
<td>6</td>
<td>-5.5</td>
</tr>
<tr>
<td>14</td>
<td>-11.2</td>
</tr>
<tr>
<td>20</td>
<td>-11.6</td>
</tr>
<tr>
<td>22</td>
<td>-13.6</td>
</tr>
<tr>
<td>24</td>
<td>-16.1</td>
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The local expansion ratio of the foamed parts using various packing pressure was measured and summarized in Table 6.3.

Table 6.3: Local expansion ratio at different packing pressures.

<table>
<thead>
<tr>
<th>Packing Pressure (MPa)</th>
<th>( \varphi ) (Location A)</th>
<th>( \varphi ) (Location B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.75</td>
<td>1.80</td>
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<tr>
<td>14</td>
<td>1.88</td>
<td>1.86</td>
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<tr>
<td>20</td>
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<td>22</td>
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<td>1.72</td>
</tr>
<tr>
<td>24</td>
<td>1.80</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The cell density was measured and plotted versus the packing pressure in Figure 6.17. As shown, the cell density increased by the applied packing pressure as the results of the faster pressure-drop obtained. Furthermore, the uniformity in the cellular structure was increased within the FIM samples.

Figure 6.17: Cell density versus packing pressure in high-pressure FIM of PS-5\%CO\(_2\) with mold-opening (Injection speed = 80 cm\(^3\)/s; packing time = 8 s; \( T_{\text{melt}} = 220 \) °C).
6.5 Conclusion

Mechanism of cell nucleation in high-pressure foam injection molding experiments with high expansion i.e. using mold-opening, was explored in this work by using an in-situ visualization approach. The visualization results and the cavity pressure profiles recorded at the visualized locations were used to identify the cell nucleation mechanisms within the foamed samples. It was observed that a portion of cells, nucleated during the mold filling, may sustain the cavity pressure till the mold-opening instant. The presence of these cells increased the compressibility of the melt/gas mixture, thus reducing the obtainable pressure-drop rate. Also, their presence caused considerable non-uniformity in the foamed samples after mold-opening. The strategy of using a proper melt packing pressure to remove the cells, nucleated during the filling, resulted in a faster pressure-drop, higher cell density, and a more uniform foam structure. The effect of packing duration was investigated. It was observed that a second nucleation mechanism, i.e. nucleation due to the melt shrinkage, may be activated with a very long packing pressure application. The formation of these shrinkage-induced cells resulted in a poor nucleation and cell structure after the mold opening.
6.6 Reference


Chapter 7

7 Experimental Observation and Modeling of Fiber Rotation and Translation during Foam Injection Molding of Polymer Composites

7.1 Abstract

The interactions between dispersed carbon fibers and growing cells in high-pressure foam injection molding experiments of polystyrene/carbon-fiber/carbon-dioxide system was investigated using in-situ visualization technique. It was demonstrated that fibers exhibit both translational and rotational displacements at close vicinities of growing cells. Using visualization snapshots, the rotational and translational displacements of the fibers were measured quantitatively and found to be a strong function of the cell size, the initial cell-fiber distance, and the initial fiber angle. An analytical model was developed, which describes the instantaneous fiber orientation and location as a function of the corresponding cell size and the fiber’s initial orientation and location. The theoretical predictions were in a good agreement with the experimental results, indicating the accuracy and capability of the model in predicting the fiber displacement. This research provides a deeper understanding of the mechanisms through which foaming influences the percolation threshold of conductive polymer composites.

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7.2 Introduction

Compared with metallic counterparts, conductive polymer composites (CPCs) offer numerous advantages such as chemical resistivity, barrier properties, low density, and fast and inexpensive manufacturing methods. In this regard, the application of this class of conductive materials has been increased in electromagnetic interface shielding, actuators, and fuel cell bipolar plates. To establish the (electrical) connectivity, micro-sized or nano-sized fillers can be added to polymer matrix in powder shape or fiber form. Among all the fillers, the application of carbon fiber (CF) is more popular due to its low percolation threshold, relatively high aspect ratio, and lower processing cost compared with nano-sized fillers.

The content of fibers and the level of percolation threshold critically affect the functionality, processability, and manufacturing cost of CPCs. While a higher fiber content increases the conductivity of CPCs, it limits the processing window of the composites and increases its cost. Hence, a lower fiber loading will be more favorable, provided the conductivity of the composite is maintained high.

The alignment and orientation of fibers play a crucial role in the determination of the functional properties such as the electrical conductivity, the electromagnetic interference shielding effectiveness, and the dielectric behavior in CPCs. It has been also shown that the severe alignments of the fibers increases the percolation threshold and decreases the electrical conductivity. For instance, the through-plane conductivity of injection-molded parts has been demonstrated to be several orders of magnitude lower than that in the machine direction, as a result of the machine-direction or in-plane orientation of the fibers. Further, in some applications such as bipolar plates, a high level of conductivity is required in both in-plane and through-plane directions. Therefore, any effort to reduce the anisotropy of functional properties in CPCs by controlling the fiber orientation would be of great value.

The introduction of a cellular structure with foaming to solid CPC has been reported to reduce the percolation threshold and improve the conductivity of the composite. The dissolved blowing agent contributes in lowering the electrical percolation threshold by the
enhancement of the fiber dispersion and distribution, and reducing fiber agglomeration and breakage. Ameli et al. discussed that foaming reduces the fiber breakage in polypropylene (PP)/stainless-steel fiber composites, resulting in a significant percolation threshold reduction. A lower percolation threshold was reported by Zhang et al. by foaming the polymethylmethacrylate/graphene composites. The electrical percolation threshold of PP/multiwalled-carbon-nanotube (MWCNT) foams was reduced significantly by increased volume expansion, attributed to the localization of fillers within the cell walls after foaming. Tran et al. also showed that the electrical conductivity of polymethylmethacrylate/MWCNT composite increased by foaming. Conductive networks were established at lower fiber contents in PP/carbon-nanofiber composite foams compared with solid counterparts.

Many researchers demonstrated that the rearrangement and alignment modifications of fibers, platelets, and high aspect-ratio additives, occurring during cell growth in CPC foams is one of the major responsible mechanisms for the enhancement of the CPCs functionalities. In microcellular foamed polymer/nanoclay composites, Okamoto et al., Nam et al., and Yuan and Turng observed that nanoclays were aligned along the curvature of cell walls as a result of squeezed/stretched matrix around growing cells, whereas they were randomly oriented at areas far from cells. Motlagh et al. found that foaming disrupted the flow-induced fiber orientations and enhanced the through-plane conductivity in foam injection-molded parts. Ameli et al. observed that the electrical conductivity of PP/MWCNT composites increased by foaming due to the rearrangement and reorientation of MWCNT up to the optimum void fraction, after which further cell growth deteriorated the conductivity. Thompson et al. reported that while foaming enhanced the through-plane conductivity in composites containing carbon black, or carbon black mixed with CF, it had opposite impact in samples filled only with CF. Ameli et al. demonstrated that the through-plane electrical conductivity of PP/CF composite foams was increased, and its uniformity was improved along the injection-molded sample, due to the increased fiber-to-fiber contacts. They argued that foaming altered and increased the orientation of fibers in the thickness direction by bi-axial stretching of the matrix about growing cells in the core regions of CPC foams. In the skin layer, the plasticizing effect of the dissolved blowing agent reduced the thickness of the solid layer and the degree of longitudinal fiber orientation by reducing the melt viscosity.
and the resultant applied shear. In foam injection molding (FIM) experiments of PP/MWCNT nanocomposites, Ameli et al. showed that the growth of cells caused a unique arrangement of MWCNTs, by translational and rotational displacement of MWCNT confined between adjacent cells, which imparted superior dielectric properties to CPC foams compared with their solid counterparts.

Therefore, the orientation and re-alignment of fiber fillers and the disturbance occurred through foaming exerted a significant influence on the functional properties of CPC parts. Fiber orientation has been extensively studied in injection molding. Folgar and Tucker introduced a model to predict fiber orientation distribution function, and suggested a phenomenological relationship including a fiber-fiber interaction coefficient. Advani and Tucker later introduced a second-order tensor of orientation in order to describe fiber orientation. Bay and Tucker simulated the filling and fiber orientation in injection molding of a center-gated disk and a film-gated strip, and compared them with the experimentally measured fiber orientation. Wang et al. then modified the equation of the orientation tensor from Ref. and proposed reduced-strain closure (RSC) model. The latter accounts for a slower rate of orientation of short fibers, compared with previous models based on Jeffery’s equation. Others have proposed methods to improve the computational work required for orientation predictions.

Despite the rich literature about fiber orientation prediction, less attention has been devoted to the fiber displacement (i.e., rotation and/or translation) during foam injection molding. Thus, the effect of foaming on fiber re-orientation and its effect on interconnectivity and/or distribution require additional investigations. Most analyses have been carried out on stabilized specimens, and hypotheses were suggested according to the obtained properties. In particular, no observation of the real-time behavior of dispersed fibers around the growing cells has been reported yet, although visualization has been utilized to study the mold-filling phenomena during injection molding of plastics and composites. In continuation to our previous works an in-situ visualization technique is adopted to investigate and quantitatively analyze the effect of foaming (i.e., biaxial stretching of the matrix during cell growth) on the translation and orientation of fibers. A geometrical model is also proposed to further investigate and predict the fiber displacements at close vicinities of growing cells.
Based on the experimental measurements and model analyses, the most influential factors governing the final orientation and location of fibers in foamed CPCs were identified.

7.3 Experimental

7.3.1 Materials

Polystyrene (PS) MC3650 with an MFR of 13.0 g/10min (200°C/5 kg) and a density of 1.04 g/cm$^3$ from Americas Styrenics was used as the polymer matrix. Carbon fiber with a density of 1.8 g/cm$^3$ in PP carrier was used as the fiber additive (Proprietary PP-CF composite, grade Carbo-Rite F261 with 10 vol% CF was provided by Lubrizol Corp., Wickliffe, Ohio, USA). The average CF diameter was about 8 μm, and their average length was about 90 μm. Inasmuch as the addition of CF darkens the composite and prevents the light transmission, the final CF content in the injection-molded PS was maintained less than 0.1 wt%. Carbon dioxide (CO$_2$) from Linde Gas Canada was used as the physical blowing agent.

7.3.2 Experimental Setup

High-pressure FIM experiments were carried out using a 50-ton Arburg Allrounder 270/320C injection molding machine with a 30 mm screw diameter, equipped with MuCell technology. In high-pressure FIM, the nucleated cells at the gate and during injection dissolve back into the melt under the high cavity pressure. Therefore, foaming initiates from a homogeneous melt/gas mixture as a result of melt shrinkage during solidification. This is when the PS/CF melt has settled in the mold with no more motion and, thus, the fiber displacement will be affected only by cell growth. A rectangular mold cavity with nominal dimensions of 135 mm × 111 mm × 3.2 mm, fed by a fan gate, was used to make the samples. A prism-insert visualization mold was employed to record the foaming phenomena occurring inside the mold cavity, using a camera (CVM10 camera from JAI and a magnifying lens from Navitar) connected to the computer. More details about the visualization system are given elsewhere. The amount of blowing agent, i.e., CO$_2$, in the
PS melt was adjusted to such low a content that a very low cell density was obtained assuring that the individual cells can be visually captured and tracked during cell growth without any cell-to-cell interactions. Image processing was carried out using ImageJ software, National Institutes of Health, US. To analyze the degree of fiber orientation, the fiber angle and the cell size were measured at various cell-growth instances by image processing of the in-situ visualization snapshots. Care was taken to select cell-fiber pairs such that they both are located in a plane normal to the camera view. In other words, the visual length of the fibers remained constant in all snapshots. A schematic of the visualization system is given in Figure 3.2 and the processing conditions used in this experiment are listed in Table 7.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt temperature</td>
<td>220 ºC</td>
<td>Melt packing pressure</td>
<td>8 MPa</td>
</tr>
<tr>
<td>Injection flow rate</td>
<td>80 cm³/s</td>
<td>Packing time</td>
<td>5 s</td>
</tr>
<tr>
<td>Mold temperature</td>
<td>30 ºC</td>
<td>CO₂ content</td>
<td>0.4 wt%</td>
</tr>
</tbody>
</table>

The initial distance of the fiber’s midpoint and the cell center, the initial angle of the fiber relative to the radial line from the cell center to the fiber’s midpoint, and the fiber length, used in the discussion of this research, are summarized in Table 7.2. Care was taken to decouple the effect of multiple parameters in discussions. Therefore, the fibers of similar fiber-to-cell distances, and similar initial angles, and similar fiber lengths were tracked down such that the effect of only one parameter (i.e., the fiber-to-cell distance, the fiber initial angle, or the fiber length) on the displacement of fibers could be independently investigated.
Table 7.2: Information of the analyzed fibers.

<table>
<thead>
<tr>
<th>Fiber ID#</th>
<th>Initial location (mm)</th>
<th>Initial angle (degree)</th>
<th>Fiber length (mm)</th>
<th>Initial location (mm)</th>
<th>Initial angle (degree)</th>
<th>Fiber length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF#1</td>
<td>0.22</td>
<td>~ 90</td>
<td>0.18</td>
<td>CF#5</td>
<td>0.37</td>
<td>33.91</td>
</tr>
<tr>
<td>CF#2</td>
<td>0.18</td>
<td>17.77</td>
<td>0.22</td>
<td>CF#6</td>
<td>0.30</td>
<td>14.53</td>
</tr>
<tr>
<td>CF#3</td>
<td>0.23</td>
<td>27.05</td>
<td>0.17</td>
<td>CF#7</td>
<td>0.31</td>
<td>59.18</td>
</tr>
<tr>
<td>CF#4</td>
<td>0.10</td>
<td>32.40</td>
<td>0.28</td>
<td>CF#8</td>
<td>0.40</td>
<td>36.10</td>
</tr>
</tbody>
</table>

7.4 Modeling of Fiber Location and Fiber Angle

In the modeling of the fiber translational and rotational motions about a growing cell, following assumptions were made: (1) The radial growth of a cell is symmetric; (2) Fibers are rigid and do not slip over the adjacent polymer matrix; (3) The fiber mid-point translates radially and the fiber rotates around its mid-point; (4) The fiber angle changes only with respect to the line passing through the cell center and the fiber mid-point upon growth; (5) The fiber-to-fiber interference is ignored; (6) The fiber displacement is affected by the most closely located bubble; (7) The polymer matrix is incompressible. As schematically illustrated in Figure 7.1, a set of two parameters suffices to describe the changes of the location and the orientation of a fiber as the cell size changes during cell growth. The first is the “fiber location” defined in this paper as the relative radial distance of the fiber mid-point with respect to the cell center. The second is the “fiber angle” defined in this paper as the relative angle of the fiber with respect to the line passing through the mid-point of the fiber and the cell center.
Figure 7.1: 2D schematic illustration of fiber alignment: a) the initial state with an initial fiber angle of $\alpha_0$ and an initial fiber location of $R_o$; b) an instantaneous state with a fiber angle $\alpha$ and a fiber location $R$ after expansion with a cell radius $R_c$. The fiber location and the fiber angle are described relative to the growing cell. The polymer envelope encompassing the fiber is shown with dashed circles.

The final location of the fiber’s mid-point ($R$) can be found first from the incompressibility of the melt within the sphere with $R_o$ after expansion:

$$\frac{4}{3} \pi R_o^3 = \frac{4}{3} \pi R^3 = \frac{4}{3} \pi R_c^3$$  \hspace{1cm} (1)$$

$$R = (R_o^3 + R_c^3)^{1/3}$$  \hspace{1cm} (2)$$

where $R_c$ is the cell radius.

Next, the fiber angle can be determined from the invariable volume of the spherical envelope encompassing the fiber after expansion. In the symmetric radial expansion, each surface remains spherical after the deformation (i.e., cell growth), and the volume of any chosen envelope encompassing the fiber would remain unchanged during cell growth.
\[ V_o = V \] (3)

where \( V_o \) and \( V \) are the initial and instantaneous volume of the spherical envelope, respectively (as shown with dashed circles in Figure 7.1), and can be expressed as a function of inner and outer radii of the envelope as:

\[ V_o = \frac{4}{3} \pi [(R_o + l \cos \alpha_o/2)^3 - (R_o - l \cos \alpha_o/2)^3] \] (4)

\[ V = \frac{4}{3} \pi [(R + l \cos \alpha/2)^3 - (R - l \cos \alpha/2)^3] \] (5)

where \( R_o \) and \( R \) are the initial and instantaneous distance between the cell center and the fiber mid-point, respectively. \( l \) is the fiber length, while \( \alpha_o \) and \( \alpha \) denote the angle between the fiber and the radial line (passing through the fiber mid-point and the cell center) before and after the expansion (Figure 7.1). By substituting Eq. 4 and Eq. 5 into Eq. 3, and solving for \( \alpha \) with the aid of Eq. 2 we have:

\[ \alpha = \arccos\left(\frac{2(A + B)}{l}\right) \] (6)

where \( A \) and \( B \) are:

\[ A = \left[\left(3V_o/16\pi\right) + ((3V_o/16\pi)^2 + (R_o^3 + R_c^3)^2)^{1/2}\right]^{1/3} \] (7)

\[ B = \left[\left(3V_o/16\pi\right) - ((3V_o/16\pi)^2 + (R_o^3 + R_c^3)^2)^{1/2}\right]^{1/3} \] (8)

Therefore, the instantaneous angle of any fiber is a function of its initial angle, initial location, length, and the cell size.
Figure 7.2a and 7.2b show the variations of the instantaneous fiber radial angle $\alpha$ with respect to the cell radius and the CF initial location, respectively, at various initial angles ($\alpha_o$) using the proposed model. The $\alpha_o$ randomly varied between 0-90°. At a given initial CF location and length, as seen in Figure 7.2a, the rotation degree of fibers increases with the cell size at a constant initial angle. The figure also shows that a greater degree of rotation was obtained for fibers with smaller initial angle. As the cell radius increased, the $\alpha$ spanned a narrower range with a constant upper end of 90°. At an $R_c = 5$ mm, $\alpha$ became almost 90° for the entire initial angle range, indicating that this cell size was so large that could rotate all the neighboring fibers to the extent that they all became tangent to the cell wall, independent of the initial angle. In addition, the model suggests that $\alpha$ increases and higher degree of rotation is obtained as the initial distance between the CF mid-point and the cell center decreases, as shown in Figure 7.2b.

It should be noted that the fiber displacements, i.e., the fiber translation and orientation, are an exclusive function of the initial conditions and the bubble size. So the fiber displacements can be compared for different bubbles of the same size.

Figure 7.2: Theoretically predicted instantaneous fiber angle and fiber location: (a) the fiber angle versus the cell radius; (b) the fiber angle versus the initial fiber angle.
7.5 Experimental Results and Discussion of Visualized Data around a Growing Cell

The visualized data obtained from high-pressure FIM experiments with a full-shot PS/CF mixture showed that the location and angle of the CFs were changed in the polymer matrix as the cells were growing. Upon the growth of a cell, the adjacent polymer matrix experiences biaxial stretching (and uniaxial compression) and thus deforms. Two types of motions were observed together for CFs at the close vicinities of growing cells: (i) a rotational motion and (ii) a translational motion. In the rotational motion, the radial angle of the fiber, with respect to the line connecting the center of the growing cell and the mid-point of the fiber, changed as a function of time. In translation, the distance of the cell center and the fiber mid-point changed in the radial direction. Most commonly, combined rotational and translational motions were observed, as schematically shown in Figure 7.3.

![Figure 7.3: Fiber displacement (rotation and translation).](image)

Figure 7.4 shows successive snapshots of the in-situ visualization in high-pressure FIM experiments of PS/CF around a growing bubble. As demonstrated, CF#1 is pushed back with no significant rotation about the growing cell. Such behavior was due to the fact that Fiber A was almost tangent to the cell wall, with an initial angle of about 90°. In contrast, CF#2 showed the most common fiber displacement, which was a combination of both rotational and translational displacements.
7.5.1 Effect of the Cell Growth on Fiber Displacement

To analyze the evolution of fiber angle and its translation under the influence of growing cells, the behavior of an individual fiber, CF#3, close to a growing cell was thoroughly investigated. As demonstrated in Figure 7.5a, the fiber angle changed due to the interaction between the growing cell and the fiber. An increase in the cell size resulted in a continuous increase in the fiber angle. The cell growth induced a material flow around its surrounding. In other words, the material at close vicinity of the growing cell, i.e., the spherical polymer envelope introduced in Section 3, was pushed away from the bubble, and the envelope became biaxially stretched because of the increased diameter of the polymer envelope. Consequently, the polymer envelope was squeezed in the radial (thickness) direction which then caused the orientation of the fibers located within the envelope, to be more perpendicular to the radial direction. Not only the angle of the influenced fiber changed (i.e., fiber orientation), but its distance from the cell also increased (i.e., fiber translation). As illustrated in Figure 7.5b, the distance between the fiber mid-point and the cell center increased with the cell growth time. Also, Figure 7.5b shows that the squeezing action of the material envelope reduced the distance between the fiber and the cell surface, i.e., $R - R_c$, constantly. Here, it should be emphasized that while the distance of the rotating fiber from the cell center increases, its distance from the cell wall decreases. In the same manner, the fibers under the influence of a cell become closer to each other in the radial direction as the cell grows. Since the size of a growing cell affects the orientation degree for the surrounding
fibers and the relative distance between the fibers, the foaming action in injection molding would affect the fiber percolation behaviors, resulting in a change in the conductivity of the composites. That is why it is possible to control the conductivity of CPC parts by tailoring the void fraction, the cell density, the cell uniformity, the cell shape, the skin layer thickness, and so on.

Figure 7.5: (a) the cell radius and the fiber angle versus time; (b) the fiber location versus the time; (c) the observed and predicted fiber angle versus the cell radius; (d) the observed and predicted fiber location versus the cell radius.

In order to validate and implement the proposed geometrical model (Eq. 6), these experimental results for CF#3 were compared with the simulated data for fiber orientation and translation, as shown in Figure 7.5c and 7.5d, respectively. The theoretically predicted data demonstrated a good agreement with the experimental results for both displacements of fiber orientation and fiber translation, indicating that the model is accurate in describing the interactions between fibers and growing cells.
7.5.2 Effect of the Initial Fiber Location on Fiber Displacement

As discussed in previous sections, the growth of nucleated cells caused rotational and translational displacements on the closely located fibers. However, the degree and the rate of the fiber displacement were highly affected by the initial fiber location from the cell, $R_o$. To study this, the behaviors of CF#4 and CF#5 fibers, with similar fiber lengths and initial angles but different initial locations, under the influence of growing cells were investigated and the results are shown in Figure 7.6. The fiber with closer initial location, i.e., CF#4 with $R_o = 0.10$ mm, demonstrated a greater magnitude and rate of rotation compared with the distant fiber, CF#5 with $R_o = 0.37$ mm (Figure 7.6a). Similar to the rotation, as seen in Figure 7.6b, the closely located fiber CF#4 exhibited a faster translation as a result of a stronger flow field and more effective forces on the fiber. In fact, any fiber located closer to the cell center experiences larger deformation and stretch, as reported by Ameli et al. for MWCNT fibers in PP [20]. The sensitive rotation and translation of a closer fiber is also verified from the model predictions (based on Eq. 2 and 6) as shown in Figure 7.6a and 7.6b.
Figure 7.6: Effect of the initial fiber location on fiber orientation and fiber translation for CF#4 ($R_0=0.1$ mm) and CF#5 ($R_0=0.37$ mm). (a) the fiber angle versus the cell radius; (b) the fiber location versus the cell radius.

It is worth mentioning that in all cases, any motion of fibers was slower at the beginning of cell growth. This could be attributed to the effective distance at which the cell surface became influential on the fiber orientation. As the cell size increased, the fiber location from the cell surface decreased and, consequently, a stronger interaction between the fiber and the cell was obtained. This phenomenon was more noticeable in CF#5 which was more distant from the cell surface.

7.5.3 Effect of the Initial Angle on Fiber Displacement

The rotation and translation of two fibers having similar fiber lengths, similar initial fiber locations, but different initial angles, i.e., CF#6 and #7, were investigated and the experimental results were illustrated in Figure 7.7a and 7.7b. As demonstrated, the fiber with smaller initial angle, i.e., CF#6, exhibited more and faster rotation, i.e., $45.18^\circ$ of rotation at a rate of $6.02 ^\circ$/s) compared with CF#7 with a larger initial angle ($20.3^\circ$ of rotation at a rate of $2.53 ^\circ$/s). A similar behavior was also observed in translational displacement of both fibers, as shown in Figure 7.7b. This observation was also in accordance with the simulated
results given in each figure, suggesting that a smaller initial angle results in a greater degree of fiber orientation. According to Figure 7.1 and the discussion in Section 3, a fiber with a smaller initial angle is in fact encompassed by a thicker polymer envelope, and, therefore, experiences more severe polymer thinning during cell growth. With the assumption of no-slip condition, a thicker polymer envelope undergoes a greater thickness reduction during cell growth, causing more rotation in fibers.

Figure 7.7: The effect of initial fiber angle on fiber orientation and fiber translation for CF#6 ($\alpha_o=14.53^\circ$) and CF#7 ($\alpha_o=59.18^\circ$): (a) the fiber angle versus the cell radius; (b) the fiber location versus the cell radius.

7.5.4 Effect of the Fiber Length on Fiber Displacement

The effect of the fiber length on the fiber angle during cell growth was also investigated. First of all, it was extremely challenging to identify two fibers having similar initial fiber locations, similar initial fiber angles, but different fiber length. Two fibers of CF#5 and CF#8, having moderately similar initial fiber locations and initial fiber angles but different fiber lengths, were chosen and the observed data are compared in Figure 7.8a. The length of CF#5 is almost twice of that of CF#8 (see Table 7.2). Both fibers exhibited similar displacement. Although the longer fiber, i.e., CF#5, showed slightly faster and larger
rotation than CF#8, it is believed that CF#5’s slightly closer location to the cell, and its slightly lower initial fiber angle played a role in its rotation.

The effect of the fiber length on the rotation of the fibers having the same initial fiber distance and the same initial fiber angle during cell growth was also analyzed using the proposed model, and the simulated data are shown in Figure 7.8b. Eq. 6-8 indicates that the fiber angle is a function of the fiber length, but the simulated data based on these equations clarify that the fiber length would not have a significant effect on the fiber orientation for the two CF#5 and CF#8 fibers examined here.

Figure 7.8: The effect of fiber length on the fiber angle: (a) visualized data for CF#5 ($l = 0.28$ mm) and CF#8 ($l = 0.14$ mm); (b) theoretically predicted fiber rotation.
7.6 Conclusion

The effects of a growing cell on the dispersed carbon fibers’ orientation and translation were investigated in high-pressure foam injection molding of polystyrene/carbon dioxide system by means of in-situ visualization. The processing parameters and the amount of the carbon fiber were tuned such that cell-fiber interactions could be captured. It was found that fibers exhibit both rotational and translational motions at close vicinities of a growing cell due to the biaxial stretching of the melt. The magnitude and rate of fiber orientation and translation were a strong function of the cell size, the initial distance between the fiber mid-point and the cell center, and the initial fiber orientation angle. The fiber length was found to have little or no effect on the fiber orientation and translation. A theoretical model, based on an envelope encompassing the fiber around a growing cell, was proposed and validated using the experimentally observed data. The model precisely estimated the orientation of fibers at early stages of cell/fiber interactions, and quantitatively predicted the fiber angle and fiber location over the entire experimental data points.
7.7 Reference


Chapter 8

8 Conclusive Remarks and Future Work

8.1 Conclusive Remarks and Summary of Thesis Contributions

Foam injection molding (FIM) is one of the most promising manufacturing methods because it offers outstanding advantages such as producing light-weight materials with high dimensional accuracy and stability at short cycle times. Moreover, numerous improved mechanical properties, improved electrical conductivity, and improved thermal and sound insulation properties have been reported for foams with homogeneous microcellular or nanocellular structures. Nevertheless, the conventional FIM suffers from a serious non-uniformity in the cellular structure. Large cells, sheared and elongated cells, as well as highly coalesced cells are characteristic of this technology. In order to obtain desirable and value added properties, the cell size and the cell morphology should be well controlled in FIM. In this research, various FIM processes were comprehensively studied using an in-situ mold visualization technique. The studied FIM processes were low-pressure FIM, high-pressure FIM, FIM using gas-counter pressure (GCP), and high-pressure FIM with mold-opening. The mold filling step and the mechanisms of cell nucleation and cell growth in FIM were at the center of this research.

An innovative visualization mold was designed and manufactured to monitor the foaming phenomena during FIM. A glass-prism was incorporated into the stationary plate of the injection mold to reflect the mold cavity images to a camera. One novelty in this mold design was the accessibility to critical locations of the mold cavity, from the gate area to the cavity end. The application of small view windows resembled more realistic foam injection molding conditions. Furthermore, a pressure transducer was flush-mounted in front of each visualization window by which the local cavity pressures were recorded at each visualization location. The visualization mold was successfully employed to investigate the melt front
behavior, mold filling, cell nucleation and growth, and the displacement of dispersed fibers in various FIM processes.

The main reason for the structural non-uniformity and the formation of large size cells is a simultaneous mold filling, cell nucleation and cell growth in low-pressure and conventional FIM. Once the cells nucleate at the gate, they travel with the melt front during the mold filling and grow, coalesce, and get sheared. To improve the uniformity of the structure, high-pressure FIM can be employed. In this technology, a full-shot melt/gas mixture is used. Ideally, all cells, nucleated at the gate or during the mold filling, must be re-dissolved back into the melt to re-form a single-phase melt/gas mixture again. In such case, the new cells will be nucleated during the melt solidification and shrinkage. The application of a proper melt packing pressure was proposed to re-dissolve nucleated cells back into the melt. Using this protocol, the filling and the cell nucleation stages will be decoupled, improving the uniformity of the structure. In addition, a faster pressure-drop is attainable from a single melt/gas mixture with a lower compressibility. It was also concluded that a higher melt packing pressure would be required, to re-dissolve nucleated cells, by increasing the injection speed, the blowing agent content, and the resistance of the gate for a higher compressibility of the melt/gas mixture.

In order to improve the cell structure uniformity and improve the surface quality of the foamed parts, a gas-counter pressure (GCP) can be used. In this technology, the opposing pressure of the GCP suppresses the cell nucleation during the mold filling. Hence, the filling and the cell nucleation steps will be decoupled. As the cell nucleation is prevented during the mold filling, no silver mark is formed on the foam surface, enhancing its surface quality. Upon the GCP release, a sudden pressure-drop is experienced by the melt/gas mixture and the cell nucleation occurs under a fast pressure-drop. Hence, the nucleation rate and the overall cell density increase. Moreover, the entire mold cavity experiences similar pressure level during the application of GCP, improving the structural uniformity of the FIM samples. In this technology, this is essential to apply a proper GCP, i.e., a GCP larger than the solubility pressure of the dissolved blowing agent; otherwise, the formation of a bimodal cellular structure is likely.
While high-pressure FIM technology and the strategy of using a melt packing pressure to remove cells, which nucleated during the mold filling, enhances the uniformity of the structure, the obtainable pressure-drop rate and void fraction is highly restricted. The pressure-drop during the melt shrinkage is slow, resulting in a low density cell structures. The amount of the melt shrinkage is about 3-7 % for amorphous polymers and up to 10 % for semi-crystalline polymers. Hence, the high-pressure FIM can be followed by a precise mold-opening step. Here, the mold cavity expands by opening in the thickness direction. This is essential that the cells, nucleated during filling, be removed prior the mold-opening step. Hence, either a GCP or a proper melt packing pressure should be used. Both the mold-opening speed and the rate of cavity depressurization are adjustable. Therefore, a uniform, high expanded and high cell density foam structure is obtainable using high-pressure FIM with mold-opening.

Comparing the studied FIM processes, the most promising and the most practical method to manufacture lightweight products with enhanced properties is the high-pressure FIM using mold-opening. With this FIM fashion, not only a high expansion ration, i.e. high weight reduction, is achievable, but also the uniformity of the cellular structure is significantly enhanced within the foamed parts by the removal of the cells which nucleated during the mold filling. Also, high cell-density foam structures are obtainable by controlling the mold-opening speed and mold-opening time. While the application of GCP is technologically challenging and expensive, using a GCP with the aforementioned FIM method would be the most recommended FIM method.

The interaction between dispersed carbon fibers (CF) in a polymer matrix, and the nucleated cells in a high-pressure FIM was investigated. The functionality of conductive polymer composites (CPC) is highly dependent on the orientation and alignment of the fibers. Hence; any modification and disturbance in the alignment of fibers is of high importance. It was observed that the orientation and alignment of CF were modified by the matrix deformation which occurred due to the nucleation and growth of cells. A geometrical model was proposed to describe the displacement of fibers. Both experimental and theoretical investigations revealed that the initial distance of the CFs from cells, the initial angle of CFs, and the cell size were the most influential parameters, affecting the cell/CF interaction.
8.2 Future Work

Based on the developed visualization technique, proposed procedures and the acquired knowledge, following recommendations and suggestions are made for the future work:

- The rheological and viscoelastic properties of polymer melts significantly change by the addition and dissolution of blowing agents. Inasmuch as aforementioned properties affect the foaming behavior of polymer melts, i.e. the cell nucleation and growth, comprehensive research should be conducted in order to measure the rheological properties of the gas-charged melts such as viscosity, chain relaxation time, and surface tension in order to investigate their effects on foaming behaviors of polymer melts.

- Large amounts of shearing and high shear rates are exerted on the gas-charged polymer melt during the foam injection molding process. These not only affect the viscoelastic properties of the polymer melt, but also affect the cell nucleation through the process of stress-induced nucleation. In addition, the (dynamic) solubility of the polymer melt may change during the mold filling and under the applied stresses. This can affect both the foaming phenomena as well as the formation of the skin layer during injection. Hence, a systematic study to investigate the effect of shear stresses, elongation stresses, and the shear rate on foaming behavior of polymer melts is required.

- To identify the fundamental mechanisms of cell nucleation and growth in FIM, an amorphous polymer, i.e. polystyrene, was used as the sample resin. This selection was made to eliminate any effect of structural change on foaming during the FIM. However, crystallization phenomenon plays a crucial role in foaming of semi-crystalline polymers by changing the viscoelasticity of the melt and by acting as nucleating agents. This research should be extended to the cell nucleation and growth in FIM of semi-crystalline polymers and the effects of crystallization on their foaming.
- One of the main challenges in FIM with high expansion is the molding of complex geometries. Especially, parts with very thin walls may remain un-foamed after expansion. While some remedies such as using hot mold or rapid heat-cool process are suggested, there is a great potential and interest in a comprehensive research on molding of complex geometries in FIM with high expansions.

- According to the identified cell nucleation and growth mechanisms, and identified parameters contributing to the foaming of polymers in FIM, both “nucleation” and “growth” can be modeled using proper viscoelastic models. Using the reliable, in-situ experimental data, models can be verified and used to describe foaming behavior of various polymers at different processing conditions in FIM.

- The visualization of the displacement of fibers in FIM experiments of semi-crystalline polymers is of great interest. This is recommended to employ the designed visualization mold to investigate the displacement of fibers, such as carbon fiber, during melt crystallization with and without foaming.