Cell Nucleation in High-pressure Foam Injection Molding of Semicrystalline Polymers

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Abstract

We investigated the solidification behavior and foaming behavior of a grade polypropylene in high-pressure foam injection molding process by means of an in-situ mold visualization technique. We observed that the solidification behavior of polypropylene had a clear influence on the cell nucleation and on the final cellular morphology of the foam injection molded parts. By adjusting the processing condition, we could control the sequence of the cell nucleation and melt solidification such that either would occur earlier, influencing the final cell morphology and structure.

Introduction

The capability to produce light-weight products with geometrical accuracy at relatively fast production rate places foam injection molding (FIM) amongst best manufacturing technologies in plastic industries [1-4]. In this technology, an inert gas such as carbon dioxide (CO₂) or nitrogen (N₂), so called blowing agent, is mixed with the polymer melt to make a single-phase melt/gas mixture. The blowing agent can be introduced to the melt physically in super critical condition, or chemically through the decomposition of a chemical blowing agent such as azodicarbonamide. Once the gas/charged melt is injected into the mold cavity, cell nucleation occurs due to the sudden pressure drop experienced by the melt. The cell nucleation is then followed by further cell growth. The final properties of the foamed parts are highly dependent to the final cell size and cell density [5-9]. Therefore, it is crucial to control the cell nucleation and growth rate in order to achieve desirable properties and functions.

The cell nucleation mechanism in FIM technology is strongly dependent on the type of injection. In low-pressure FIM, where a short shot is used, the majority of cell nucleation occurs due to the pressure-drop obtained at the gate [10]. Lee et al. suggested strategies which enhanced cell nucleation at the gate by maintaining a low cavity pressure [10]. In high-pressure FIM, where a full shot is used, the governing cell nucleation mechanism is the nucleation occurring during the melt solidification and shrinkage [11]. Shaayegan et al. suggested the application of a proper packing pressure to remove all cells which were nucleated during the mold-filling. They argued that a faster pressure drop would be obtained from a single-phase melt/gas mixture [11]. The mechanism of cell nucleation in the presence of a gas-counter pressure (GCP) depends on the GCP magnitude, the instant and the rate of the GCP removal; the cell nucleation can occur at the time of GCP removal with a fast pressure drop-rate [12]. If a mold-opening technology is used with FIM, the cell nucleation should occur over the pressure drop obtained due to mold opening [13].

In addition to the cell nucleation mechanism, that is, the induced pressure drop which causes the nucleation of cells, nucleating agents play a substantial role in determination of final cell density and cell morphology in FIM [14-16]. The nucleating agents can be added in micron and/or nano sizes to enhance cell nucleation via heterogeneous nucleation mechanism. According to the classical nucleation theory, a critical radius is defined as [17]:

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

(1)

where \(\gamma\) is the melt/gas interfacial tension, \(P_{bub}\) is the bubble pressure at the critical size, and \(P_{sys}\) represents the system pressure. Basically, nucleated cells with radii greater than \(R_{cr}\) grow while others disappear from the system. In homogeneous nucleation, the nucleation barrier energy is defined as [18]:

\[
w_{hom} = \frac{16\gamma^3}{9(P_{bub}-P_{sys})^2}
\]

(2)

In heterogeneous nucleation, on the other hand, the nucleation barrier energy is expressed as [18, 19]:

\[
w_{het} = w_{hom} F(\theta_C, \beta)
\]

(3)

Here \(\theta_c\) represents the contact angle between the bubble surface and the second phase, and \(\beta\) is an angle (0-90°), indicating on the geometry of the nucleation site. The nucleating agents provides preferred nucleating sites, and
since $F(\theta_c, \beta) \leq 1$, the heterogeneous nucleation occurs faster and easier with much lower nucleation activation energy.

Formation of crystals in semicrystalline polymers can enhance the cell nucleation during foaming [20-22]. In fact, the formed crystals may act as heterogeneous cell nucleation sites. Keshktar et al. discussed that the cell density of PLA and PLA/nanoclay nanocomposites extrudates was enhanced by the formation of crystallites during extrusion foaming [21]. In addition, the local stress variations produced about the formed crystals promote the cell nucleation [23-26]. Taki et al. showed that the cell nucleation rate increased by the number of spherulites in a polylactide/CO$_2$ foaming system [20]. The dissolved gas can be expelled from the formed and growing crystals, supersaturate the crystals’ boundaries, and facilitate the formation of cells [20].

In this study, the foaming behavior and solidification phenomena in polypropylene (PP)/carbon dioxide was investigated. An in-situ visualization method was used in this regard.

**Materials and Equipment**

A homopolymer polypropylene, DM55Pharm, from Borealis with MFR of 2.8 g/10 min (230°C, 2.16 kg), was blown with CO$_2$ from Linde Canada. A 50-ton Arburg Allrounder injection molding machine was used to perform injection molding experiment. Supercritical CO$_2$ was injected into the melt using MuCell® technology. The mold cavity, a rectangular cuboid with dimensions of 135x111x3.2 mm, was fed by a fan gate. A visualization mold was used to monitor foaming phenomena occurring inside the mold cavity. The principle of the operation of the visualization mold is schematically shown in Figure 1. In brief, a right-angle prism is incorporated in the stationary half of the injection mold which reflects the cavity images to a camera. The details of this equipment can be found elsewhere [27].

![Figure 1](image1.png)

Figure 1. (a) Schematic of the stationary half of the visualization mold [27]; (b) schematic of a full-shot injected part with defined locations (A, B, C) with respect to the injection gate.

To perform experiments, the high-pressure FIM method was employed [11]. Once the gas/charged melt entered the mold cavity, the pressure was dropped. A packing pressure was used which increased the cavity pressure above the solubility pressure of the dissolved CO$_2$, and redissolved cells which were nucleated during the injection back into the melt. This packing pressure was applied once the mold filling was completed; according to the injection flow rate and the mold geometry, the mold filling time was about 0.6 s. The visualization snapshots suggest that this applied packing pressure was sufficient to remove cells during packing. Eventually, foaming occurred due to the cavity pressure decay obtained during melt shrinkage. These steps and the corresponding pressure changes are schematically shown in Figure 2. Other processing parameters are summarized in Table 1.

![Figure 2](image2.png)

Figure 2. Pressure changes during high-pressure FIM (A: single-phase melt/gas solution under a pressure above the solubility pressure of the dissolved gas; B: cell nucleation, as the pressure drops (the cavity pressure is below the solubility pressure of the dissolved gas); C: increase in the cavity by packing, and dissolution of nucleated cells; D: drop in the cavity pressure and nucleation of new cells (shrinkage-induced cells)).

<table>
<thead>
<tr>
<th>Table 1: Processing set parameters in high-pressure FIM.</th>
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<tr>
<td>Parameter</td>
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<tr>
<td>Melt temperature (°C)</td>
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<td>Mold temperature (°C)</td>
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<td>Injection flow rate (cm$^3$/s)</td>
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<td>CO$_2$ content (wt.%)</td>
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<td>Packing pressure (MPa)</td>
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<td>Packing hold time (s)</td>
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**Results and Discussion**

Figure 3 shows a snapshot from the in-situ mold visualization of high-pressure FIM experiments of PP/CO$_2$ at 240°C. Two types of cells were realized as denoted (i) and (ii) in Figure 3. The solidified (or crystallized) melt is identified by the white area. Cell Type (i) nucleated in the melt due to the pressure drop.
obtained during the melt shrinkage. Cells Type (ii), on the other hand, nucleated on the boundaries of the solidified polymer. We suspect the nucleation of these cells, i.e., type (ii), was facilitated through the heterogeneous cell nucleation mechanism on the surface of the formed solid parts. In addition, the gas which was expelled from the solidified area supersaturated the melt near the solid-melt boundaries, promoting the cell nucleation. It is worth noting that the number of cells nucleated on the boundary of the solidified part is larger, and their size is smaller as compared with Cells Type (i).

Figure 3. Formation of cells in melt (i), and on the solidified part (ii).

Figure 4 shows visualization results for high-pressure FIM experiments of PP/CO\textsubscript{2} using an 8 MPa packing pressure for 1 s. As demonstrated, cells were first formed in the melt and due to the pressure drop achieved over the melt shrinkage. In snapshots t = 12.6 s and longer, the melt solidification was noticed and new cells were nucleated on the surface of solidified parts.

Figure 4. (a) 9.7 s; (b) 12.6 s; (c) 16.0 s; (d) 24.0 s (injection speed: 80 cm\textsuperscript{3}/s; CO\textsubscript{2}: 3%; T\textsubscript{melt}: 240 °C; visualization Location A; the time reference is the moment melt entered the cavity).

In Figure 5, visualization snapshots for high-pressure FIM experiments of PP/CO\textsubscript{2} are shown when an 8 MPa packing pressure was used for 5 s. The nucleation of cells in the melt was concurrent with the melt solidification, and therefore the cells nucleating on the boundaries of the solidified area. The application of a 5 s packing pressure delayed the nucleation of cells; hence they appeared at almost the same time melt solidification started.

High-pressure FIM experiments of PP/CO\textsubscript{2} were carried out under a packing pressure of 8 MPa, applied for 10 s. The results for this case are shown in Figure 6. A longer application of packing pressure postponed the nucleation of cells. Therefore, majority of cells were nucleated on the surface of solidified area. Some cells were then nucleated at close vicinities of the solidified area in the gas-rich regions.

Figure 5. (a) 13.5 s; (b) 16.5 s; (c) 21.0 s; (d) 25.0 s (injection speed: 80 cm\textsuperscript{3}/s; CO\textsubscript{2}: 3%; T\textsubscript{melt}: 240 °C; visualization Location A; the time reference is the moment melt entered the cavity).

Figure 6. (a) 14.2 s; (b) 16.0 s; (c) 17.0 s; (d) 20.0 s (injection speed: 80 cm\textsuperscript{3}/s; CO\textsubscript{2}: 3%; T\textsubscript{melt}: 240 °C; visualization Location A; the time reference is the moment melt entered the cavity).
Conclusion

The foaming and solidification behavior of polypropylene/carbon dioxide was investigated in high-pressure foam injection molding process. While portion of cells nucleated in the melt and due to the pressure drop obtained during melt shrinkage, some cells nucleated on the surface of the solidified area. It was observed that the application of a packing pressure can postpone the formation of cells. Based upon the applied packing time, cells could nucleate in the melt or on the surface of solidified area. In either nucleation, the size and the morphology of formed cells differ such that the nucleated cells on the solidified area were smaller in size and larger in number. This knowledge can be further utilized to control the cell structure of the semicrystalline polymer foams.

References