EFFECT OF COOLING RATE AND MOLD COUNTER PRESSURE ON THE CRYSTALLINITY AND FOAMING CONTROL IN MICROCELLULAR INJECTION MOLDED POLYPROPYLENE PARTS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering

By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Jeffrey Scott Cousineau ENTITLED Effect of Cooling Rate And Mold Counter Pressure on The Crystallinity And Foaming Control In Microcellular Injection Molded Polypropylene Parts BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Engineering

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ABSTRACT

Cousineau, Jeffrey Scott. M.S.Egr. Department of Mechanical and Materials Science Engineering, Wright State University, 2012. Effect of Cooling Rate and Mold Counter Pressure on the Crystallinity and Foaming Control In Microcellular Injection Molded Polypropylene Parts

Microcellular polymer injection molding is a growing industry technique due to its ability to produce dimensionally stable stress free parts while reducing cycle time, material usage, and energy costs. The process was invented by Dr. Nam P. Suh at the Massachusetts Institute of Technology in the early 1980’s. The basic idea is to dissolve a supercritical fluid into the polymer melt which will nucleate and expand within the part core after injection during the cooling stage. Microcellular polymer injection molding is becoming increasingly popular in automotive, semiconductor, and industrial applications. While the technique has been widely successful using amorphous polymers, semi-crystalline polymers present new challenges not encountered during processing with their amorphous counterparts. The polymer chains in a semi-crystalline material develop an organized crystal structure during the cooling stage. Crystal development generates two main issues for microcellular processing. The first being that the excess heat released during the crystal formation affects the expansion of the microcellular bubble causing unpredictable non-uniform growth. The second is that the growth of the crystal structure within the polymer melt expels and displaces the supercritical fluid forcing the foaming
to occur out at the edges of the part rather than uniformly through its core. This paper
develops and explores strategies to control and overcome these problems. The first
strategy is to effectively control the cooling rate. It is well known and has been proven,
that increasing the cooling rate during the crystallization process can decrease
crystallinity effectively freezing the polymer microstructure in place before the polymer
chains can become completely organized. The second strategy is to utilize in mold
counter pressure to observe its effect of the development of the foaming and
crystallization. In mold counter pressure has been found to be an effective means of
controlling bubble size and distribution during amorphous microcellular injection
molding therefore it has merit for being an effective method to control foaming with
semi-crystalline polymers. These two strategies have been implemented on a set of
experiments and the results measured and observed by differential scanning calorimetry
and scanning electron microscopy. The results of the experiment indicate the strategies
implied are effective methods for improving part quality and also impose confidence in
further development.
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ABBREVIATIONS

ABS – Acrylonitrile Butadiene Styrene
C - Celsius
CAD – Computer aided design
CO₂ – Carbon Dioxide
CP – Counter pressure
DSC – Differential scanning calorimeter
MCP – Microcellular polymer
N₂ – Nitrogen
PA – Polyamide
PC – Polycarbonate
PE – Polyethylene
PET – Polyethylene Terephthalate
PP – Polypropylene
PS – Polystyrene
PVC – Polyvinyl Chloride
SCF – super critical fluid
SEM – Scanning electron microscope
NOMENCLATURE

A – Area of micrograph
C – Gas concentration
C_s – Solubility
D_c – Average diameter of cell size
e – Euler’s number
H – Henry’s constant
M – Magnification
n – Avrami exponent
N_j – Amount of cells per volume
n_j – Number of cells in viewpane
P_g – Gas pressure
P_m – Molten polymer Pressure
r_c – Ration of cell width over cell height
t – Temperature dependant crystallization rate
T_{poly} – Molten polymer temperature
x(t) – Crystallization fraction
x_\infty - Maximum possible degree of crystallization
X_a – Solubility within amorphous regions
$X_e$ – Crystallinity

$Z$ – Molecular weight

$\Delta H_m$ – Ethalpy

$\Delta H_m^\circ$ – Ethalpy for perfect 100% crystal polymer

$\rho_{\text{foam}}$ – density of foam

$\rho_{\text{poly}}$ – Density of polymer
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I. INTRODUCTION

Microcellular polymer (herein after referred to as MCP) injection molding is a growing industry process. Its ability to create polymeric components with up to 2% less volume makes it an attractive counterpart to conventional injection molding processes. MCP foams were first developed and studied at the Massachusetts Institute of Technology (MIT) under the direction of Professor Nam P. Suh in the early 1980’s [1]. MCP foaming was first noticed as a phenomenon appearing in structural foam molding applications. On areas of thin cross sectional areas as well as instances of high shear stress, it was noticed that the structural foam formed a more highly dense “skin” around the foam throughout the core. This phenomenon was observed and replicated with polymers by dissolving supercritical fluids (SCF) into the polymer melt before injection. The term supercritical denotes the state condition of a fluid that is above both its critical pressure and its critical temperature. The nucleation of these fluids which are dissolved into the polymer melt is the basic principle of Microcellular foaming technology. The difficult part consists of controlling this nucleation with high accuracy. The bubble size

Figure 1: Schematic of polymer-SCF mixing process
and cell density is what ultimately controls the properties of the final product. In order to induce cell nucleation the polymer SCF mixture needs to go through a rapid thermodynamic instability, this is achieved through either a quick pressure drop or a high rate temperature change. The next stage after nucleation is cell growth. During cell growth the melt is kept warm which allows for the cell structure to be formed throughout the core of the part. The ideal part structure is one where the cell nucleation is contained throughout the core and in a uniform structure, and a dense polymer “skin” is formed surrounding the core that which has no cell structure, as shown in Figure 2. The expansion of the gas within the bubbles causes an internal pressure on the walls of the skin. This pressure serves as an internal packing force resulting in a significant decrease in both sinkage and warpage. The entire microcellular foaming process was ultimately developed with a few specific concepts in mind; create a process which saves energy, material, and time. The MCP foaming process achieves this by reducing pressure and temperature requirements, creating a less dense foam core, and by eliminating the packing phase reducing overall cycle time. Fast cooling is a process in which the overall

Figure 2: Cross-section of injection molded MCP
cooling rate of the injection molded part is reduced. Fast cooling was introduced in response to a major drawback in MCP molding. This drawback is the quality of the surface of a MCP injected part. Originally it was discovered that if no specific measures are taken, the surface of the molded part exhibits low quality [2]. Semerdjev and Popov helped to explain the development of silver streaks (visible flow patterns on the part surface) by gas bubbles escaping the flow front during the filling stage, which are in turn sheared when contact is made with the cavity wall [3]. Figure 3 shows the silver streak phenomenon on a sample part of PP filled with 20 weight-% talc. It was suggested and by Chen, S. et al that increasing the mold surface temperature during filling would decrease and in many cases completely eliminate silver streaks and swirl marks [4]. This discovery has proved to be an efficient way to improve surface quality however opens up a new issue on controlling bubble size within the foam cell structure. The increase in heating creates a longer period of cell growth. This causes the cell structure to be increasingly large and far too thinly dense. In order to counter this effect, fast cooling
techniques have been developed to rapidly end the cell nucleation stage before the bubbles can grow too large and degrade the physical structure.

DESCRIPTION OF PROBLEM

Although MCP injection molding is continually being perfected for amorphous polymers, semi-crystalline polymers create issues not encountered with amorphous polymers. It had been common knowledge early on that semi-crystalline polymers were really crystallites tethered by amorphous regions, and a fully 100% crystallized material is not naturally achieved by standard injection molding procedures. However for the sake of simplicity semi-crystalline polymers and semi-crystalline structures will be referred to

Figure 4: Schematic of Problem
As crystalline ones throughout this paper. As a crystalline polymer decreases in
temperature through the cooling stage it reaches a point in which the molecules align and
form a crystal structure. During this crystallization phase an excess amount of heat is
generated, this excess heat is one way in which the foaming process is affected [5]. This
generation of excess heat is one of the two major problems that arise when dealing with
crystalline polymers during MCP injection molding. One proven method to counter this
and gain control over the foaming process within amorphous MCPs is a fast cooling
technique [6]. The newly developing technique cuts the cooling rate of the part from
about 1 °C/s to close to 10 °C/s. The purpose of the fast cool is to allow the mold to be
kept hot initially. By keeping the mold hot, the quality of the part surface is dramatically
increased. The drawback of having a hot mold and excess heat is that the cell growth
within the part is difficult to control. The cell growth occurs in a certain temperature
range and if the part is kept within this range for too long the foaming will continue to
occur. It is difficult to find an adequate balance between crystal structure and cell
structure. If the foaming occurs for too long the cell structure will become oversized and
the part will become weak [1]. By increasing the cooling rate the foaming process can be
cut short and the bubble size of the cell structure can be kept to a desirable size. The
second major problem with applying MuCell technology to crystalline polymers comes
from the tendency for the forming crystal structures to force the dissolved SCF away
from the core and out to the edges of the part [1]. In addition to fast cooling, application
of mold counter pressure has been studied for use on controlling bubble growth within
MuCell polymers. Professor Chen and his students have proved a critical pressure can be
found which greatly effects bubble size and distribution [6].
MOTIVATION

The success of the fast cooling technique as well as mold counter pressure for foaming control in amorphous MCPs gives support to the idea that the similar strategies can be used to help solve the know issues with crystalline MPC injection molding. With successful preliminary results observed, along with the amount of crystalline and semi-crystalline materials which flood the industry there are a surplus of reasons for pursuing a practical solution for solving the issues associated with MuCell injection molding with crystalline polymers. MuCell is becoming increasingly popular in applications where weight and material cost is a large issue such as automotive and aviation. With many crystalline materials having high wear and chemical resistance, obtaining a sufficient strategy to successfully apply MuCell techniques to crystalline materials is very attractive. If a method can be developed to successfully and efficiently produce injection molded parts out of foamed crystalline polymers, the industry can benefit from larger quantities of stronger, less expensive, more aesthetic molded parts.

PRIOR RESEARCH

An attempt at MuCell processing within crystalline materials can be traced back as early as 1989 where Colton studied the nucleation of microcellular foams in semi crystalline thermoplastics. He began processing the polymers above their melting points rather than at the glass transition temperature. He noted that accurate temperature control was required in order to prohibit the cells from growing too large or too quickly [7]. Doroudiani et. al. have perhaps the most relevant studies. Their work includes a study of cooling rate and diffusivity on the crystal structure and morphology which resulted in finding a strong correlation between cooling rate and degree of crystallinity [8]. Itoh et al
studied the effects of degree of crystallinity with foaming morphology. Although this work was for an extrusion process it gave valuable insight to a correlation between crystallinity and degree of foaming within the MCP [9]. Although the work was not for MCP injection molding, Sorrentino et al designed an apparatus for solidifying crystalline samples under varying cooling rates and high pressures. This work is one of the few pertaining to pressures and gives strong evidence to the theory that counter pressure control will in fact be a valid strategy to control foaming and crystallinity. Fast cooling has been applied in recent studies involving attempts to control bubble size in amorphous MCPs [10]. More support for the dependency of crystallinity on cooling rate can be found in works by Wei [11] Brucato [12] Avlar [13] Cavallo [14] Postawa [15] and Yuan [16]. Naguib Park and Reichelt studied temperature effects on foaming in an extrusion application and found data to support the observation that high temperatures result in high degrees of foaming. Chen S. C. and Tseng have successfully developed and applied fast cooling techniques to a variety of different amorphous materials [6]. In the previously mentioned experiments, counter pressure was included as a contributing factor to maintain a desirable bubble size. Filing the mold cavity with counter pressure is another method proven to control the bubble size. The counter pressure effectively keeps the bubble from growing out of control and also keeps the bubble submerged from the surface [18]. The research has also been tested in short case studies in crystalline polymers with some success. This adds more support and motivation to researching the topic more thoroughly.
II. THEORY

AMORPHOUS POLYMER

Polymers are classified into groups based on their chemical reaction to heat. The two groups are thermoplastics and thermosets. In addition to this the groups can be categorized even further by denoting amorphous, (semi-)crystalline or liquid crystalline. Amorphous can be loosely defined as polymers totally lacking molecular position and order [5]. This means that the molecules are intertwined and randomly oriented. One of the most important characteristics to amorphous polymers in regards to injection molding is that they generally do not have a specific melting point but rather a range of temperatures in which the polymer softens. Amorphous polymers are isotropic in flow meaning they shrink uniformly in the direction of flow as well as transverse to the direction of flow [5]. However, the main thing to note for the sake of this paper is that

Table 1: Commonly used amorphous polymers

<table>
<thead>
<tr>
<th>ASTM Symbol</th>
<th>Name</th>
<th>Common Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Acrylonitrile Butadiene Styrene</td>
<td>Appliance housings and interiors, automotive interior, rugged toys, machine housings</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
<td>Electronic housings and connectors, appliance housings, lighting, lenses</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
<td>Houswares, cosmetics, dust covers, toys</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
<td>Piping, chemical tanks, pumps, appliance housings, medical apparatus</td>
</tr>
</tbody>
</table>
amorphous polymers undergo no realignment phase during cooling, there is no extra energy used to restructure the molecules. Table 1 shows examples of commonly used amorphous polymers.

**CRYSTALLINE POLYMER**

While amorphous polymers are random and un-oriented, crystalline and semi-crystalline polymers are quite the opposite and have very structured and organized molecular orientations. Sophisticated electron microscopes have lead to viewing and defining various crystal structures as listed in Table 2 which is taken directly from [19].

The main quality of crystalline polymers which is most significant to this research is its behavior during the cooling process. The crystallization process is central to the physics behind the fast cooling concept. The thermodynamics of the crystallization process are

<table>
<thead>
<tr>
<th><strong>Single Crystals</strong></th>
<th>these can form in solutions and help in the study of crystal formation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spherulites</strong></td>
<td>As a polymer melt solidifies, several folded chain lamellae spherulites form which are up to 0.1 mm in diameter</td>
</tr>
<tr>
<td><strong>Deformed Crystals</strong></td>
<td>If a semi-crystalline polymer is deformed while undergoing crystallization, oriented lamellae form instead of spherulites</td>
</tr>
<tr>
<td><strong>Shish-kebab</strong></td>
<td>Shish-kebab crystals are formed by circular plates and whiskers. Shish-kebab structures are generated when the melt undergoes shear deformation during solidification</td>
</tr>
</tbody>
</table>
essential to understanding what causes the issues when trying to form microcellular bubbles. When the melt temperature decreases below the melting temperature, the crystallization process begins. The key point is that the crystal is in a lower energy state than the melt due to the decrease in entropy effects. During the crystalline structure formation this energy release is referred to as heat of crystallization or heat of fusion [19].

In order for a polymer to begin crystallization, a primary nucleation point needs to be defined. In a conventional crystalline polymer this nucleation zone usually is created by fluctuations of density and order within the melt [1]. What differs about MCP crystalline polymers is the obvious fact that the gas bubbles created from the supercritical fluids dissolving, essential create nucleation sites for crystallization. This unfortunate fact leads to two types of cell growth (crystallization and bubble nucleation) at the exact same site.

Because the melt during polymerization still has regions of amorphous material, as illustrated in Figure 5, the material becomes rubbery instead of brittle because the amorphous regions are still above the glass transition temperature. As stated previously, a material cannot by ordinary means reach a crystallization degree of 100%. However there is an equation developed to determine the crystallization fraction of a specific polymer, called the Avrami equation [20]. Where $Z$ is molecular weight, $t$ is temperature.
dependant crystallization rate and \( n \) is the Avrami exponent. Avrami also added a correction to this equation since 100% crystallization is impossible, by multiplying the equation by the maximum possible degree of crystallization. The above mentioned Avrami exponent depends on the crystal growth and can range anywhere typically between 1 and 4. It’s worth mentioning the mechanical tendencies of crystalline polymers.

Equation 1: Avrami equation

\[
x(t) = 1 - e^{-2^nt}
\]

Avrami exponent depends on the crystal growth and can range anywhere typically between 1 and 4. It's worth mentioning the mechanical tendencies of crystalline polymers. The crystallization process increases tensile strength by creating dense crystal section in which the higher number of molecular bonding resists movement creating stiffer components. However, in terms of impact strength, the ability for the molecules to resist movement doesn’t allow for the absorption and dissipation of high energy impacts. This means the more brittle crystalline polymers are not as desirable in impact situations. Also the solubility of crystalline polymers becomes much lower because of the decreased

<table>
<thead>
<tr>
<th>ASTM Symbol</th>
<th>Name</th>
<th>Common Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Polyethylene</td>
<td>Housewares, crates, toys</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
<td>Appliance housings, automotive interior</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene Terephthalate</td>
<td>Automotive structural components, handles and frames, furniture</td>
</tr>
<tr>
<td>PA</td>
<td>Polyamide</td>
<td>Light duty gears, mechanical parts, sporting goods</td>
</tr>
</tbody>
</table>
amount of space between the polymer molecules [1]. Table 3 shows a list of common crystalline polymers and their uses [1].

MICROCELLULAR POLYMER

BACKGROUND

As stated previously, the concept for foaming polymers was first developed at MIT under the direction of Dr. Nam Suh in the early 1980’s. However, it was first commercially used by Axiomatics Corp., in 1995 which shortly was renamed to Trexel Inc. [1]. Trexel first used MCPs in an extrusion processes and following its success in 1980, began applying it to injection molding processes. The most widely used and recognized term for the foaming polymer is MuCell® which was licensed by Trexel back in 2000. (Mucell® is a registered trademark of Trexel Inc., Woburn, Massachusetts). While MuCell is the most popular, Table 4 illustrates a few other injection molding companies and their respective work in foaming polymer technology [table taken directly from 1]. Advantages of using MCPs in injection molding include material reduction, reduced cycle time, reduced energy consumption, decreased part warpage, increased part
strength, and minimal if not zero residual stresses. The concept of a foaming polymer is to induce cell growth within a melted polymer, this leads directly to the previously stated advantages. By creating a sparse cell formation within the part structure, the MCP process can decrease the amount of material used during injection. Material volume reduction is beneficial in two ways, the first is the savings earned from the lower amount of required processing material. With large quantities of parts being made, every gram of material counts and can be very economical to save even the smallest percentage of plastic. The second is the savings earned from energy. With significantly less cooling
time and virtually no packing time energy costs during processing can be greatly reduced. Lastly time savings are made, for the same reasons energy is saved, less cooling and no packing, time can be reduced during a production and more components can be produced in the same amount of time.

SUPERCritical FLUIDS

Supercritical fluids are fluids which have been pressurized and heated up to a point in which they are in a liquid-like state which is just beyond both the critical temperature and critical pressure for the given fluid [1]. The goal is to dissolve the fluid into the polymer melt prior to injection while it is in the barrel. The screw within the barrel helps to shear and mix the fluid saturating the melt, as shown back up in Figure 1. The gas must be as near to supercritical state as possible therefore the fluid is injected and dissolved just before injection very near the end of the barrel. Supercritical fluids behave both like a gas and a liquid. Its’ “gas-like” property of having a low viscosity allows it to be mixed evenly throughout the melt, while its “liquid-like” property which is a high density allows it to be more easily measured for mixing the correct amount with the injection shot size [1]. The two most widely used SCFs are CO\(_2\) and N\(_2\). Both are easily extracted from the air allowing them to be inexpensive and perfectly safe for the environment. Nitrogen is capable of forming very small bubbles making it an attractive option however its solubility in melted plastic is not as good as CO\(_2\), which is why plenty of industries use it instead. In order to estimate the solubility of a gas into a molten polymer, Henry’s Law provides the following equation [1]. Where H is Henry’s constant,
\( P_m \) is molten polymer pressure, and \( T_{\text{poly}} \) is the molten polymer temperature. However for crystalline polymers, which this paper is more interested in, the solubility is dependent on the crystallinity which was discussed earlier. \( X_c \) is the crystallinity while \( X_a \) is the solubility within the amorphous regions. What makes crystalline polymers so different from amorphous ones is crystalline materials generally have a much lower solubility. According to Baldwin [21], the amount of CO\(_2\) that is dissolved into PET decreases as the amount of crystallization within part increases. Xu [1] suggests a nitrogen concentration of 0.5\% to 0.7\% to mix with crystalline materials compared to 0.3\% to 0.5\% suggested for amorphous materials.

**Equation 4: Solubility of crystalline polymers**

\[
Cs = (1 - X_c)X_a
\]

is the solubility within the amorphous regions. FOAMING PHYSICS

Cell formation within a polymer melt depends not only on the material parameters but also on the part geometry and the boundary conditions. One material property highly involved in the foaming process is the melt strength, or the polymers resistance to extensional deformation [22]. According to studies and observations made by Lee et al. when gas bubbles are formed there is biaxial stretching occurring near to the bubble within the polymer melt [23]. If a polymer melt has a low melt strength it tends to lead to poor cell formation, because of cell wall collapse and unmanageable bubble size. The full cell formation process is displayed in Figure 6. The most common way to evaluate the foaming process is by an average cell size calculation. For any given overall part density, the average cell volume is inversely proportional to the cell density [1]. Most
parts are evaluated using a scanning electron microscope (SEM). In order not to damage the cell structure it is important to break the sample rather than to cut it. In most instances the part is cooled using liquid nitrogen in order to make a clean planar break.

![Cell Formation Process Diagram](image)

**Figure 6: Cell Formation Process**

The nucleation of crystalline materials is very different than that of amorphous materials because of the addition of the crystallization process. The growth of the crystals near the crystalloid may expel the diffusing gas therefore creating a non-uniform cell structure [24]. Often times a molded sample of a crystalline material will exhibit drastically different cell sizes. The crystallization process expels gas out of the melt solution therefore at the crystallized sites there is less dissolved gas causing the bubbles grow at a slower rate and to a much smaller size. The gas expulsion is not the only factor in the crystallization process which affects cell structure; there is also a latent heat of crystallization given off during the crystal formation. It is well known that temperature has a significant impact on the cell growth. More concepts on temperature control will be discussed in a later section. There are four common failure issues to be aware of in crystalline MCP molding; non-uniform cell sizes, non-uniform cell distribution, overlapping or thin cell walls in between adjacent cells, and non-uniform wall thicknesses among cells.
Some mathematical modeling of bubble growth within molten MCPs has been developed and is worth mentioning. Ping et. al. [22] developed a numerical simulation model, Figure 7, and used a series of basic governing equations (Equation 5 - Equation 9) in order to come to some key conclusions about bubble growth. Bubble size increases rapidly accompanied by oscillation in the early stages of bubble growth [22]. Oscillation magnitude decreases and oscillation attenuation accelerates with increasing melt strength during early bubble growth stages. However, in later stages the bubble size and growth rate significantly decrease. The polymer viscoelasticity has less of an influence on bubble growth. During the early stages as it decreases, the oscillation and magnitude and growth rate decrease while the oscillation attenuation increases. However, during later stages it has little effect at all. The gas pressure $P_g$ is the driving force behind bubble growth increasing the initial $P_g$ leads to an increase in bubble oscillation and bubble
The oscillation phenomenon was noted by Ping et al. as to occur due to the melt having mass as well as elasticity which caused the bubble to shrink after a period of expansion. Osorio and Lih [25] also studied a mathematical model and a numerical simulation for bubble growth in a similar fashion but also included the equation of mass diffusion within the envelope (Equation 10) rather than assuming a polynomial profile. Also unlike Ping et. al the gas was not treated as ideal but rather as a fluid in its supercritical state which is more accurate. for this study there are a few important cell size equations including the modified cell density equation:

\[ \nabla \cdot \vec{V} = \frac{\partial r^2 V_r}{r^2 \partial r} = 0 \quad \text{simplified to} \quad V_r = \frac{R^2 \dot{R}}{r^2} \]

Equation 5: Continuity Equation

\[- \frac{\partial P}{\partial r} + \frac{1}{r^2} \frac{\partial r^2 \tau_{rr}}{\partial r} - \frac{2 \tau_{\theta \theta}}{r} = 0 \]

Equation 6: Momentum Equation

\[ \frac{d}{dt} \left( \frac{4\pi}{\beta} \rho_g R^3 \right) = 4\pi \rho D R^2 \frac{\partial C}{\partial r} \bigg|_{r=R} \]

Equation 7: Conservation of Mass

\[ \rho_g = \frac{P_g M}{R_g} \]

Equation 8: Ideal Gas Law

\[ \vec{\tau} + \lambda \frac{D \vec{\tau}}{Dt} = \eta \vec{d} \]

Equation 9: Constitutive Equation

\[ \frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} = D(T) \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) \right]; R(t) \leq r \leq S \]

Equation 10: Mass Diffusion Equation in Spherical Coordinates
from Strauss [26] as shown in Equation 11, where $n_j$ is the number of cells in the view pane of a micrograph, M is the magnification, A is the area of the micrograph view pane,

$$N_j = \left(\frac{n_j M^2}{A}\right)^{3/2} (r_c)^{1/2}$$

$r_c$ is the ratio of cell width over cell height, and $N_j$ is the amount of cells per volume (cm$^3$). However, if the density of the sample is known there is another method to calculate the cell density, if the assumption that all cells are spherical is made, shown by Equation 12.

$$N_j = \frac{6 \left(\frac{\rho_{poly}}{\rho_{foam}} - 1\right)}{\pi D_c}$$

Where $\rho_{foam}$ is the density of the foam, $\rho_{poly}$ is the density of the polymer, and $D_c$ is the average diameter of the cell size.

**COUNTER PRESSURE IN MCP INJECTION MOLDING**

One method that has been explored to control the MCP foaming process is application of counter pressure within the mold cavity. The idea of applying counter pressure is to prevent the SCF gas from emerging to the part surface during filling. To reiterate, the poor surface quality found on MCP parts is caused by the SCFs rupturing the surface during filling and being sheared along the cavity wall causing streaks along the surface. The applied counter pressure can retain these gas bubbles underneath the surface. Not only can the counter pressure keep the SCFs submerged it can also help to
control how large the cells grow. Bledzki et. al. found in their specific application and part geometry, a counter pressure of 80 bar was enough to prevent the expansion of the blowing agent as well as create a smooth part surface[27]. Figure 8 shows a schematic of a typical counter pressure set up. Professor Chen Shia Chung [6] and his students have performed extensive research on application of counter pressure in MuCell injection molding. The counter pressure coupled with mold temperature control, can keep the dissolved SCFs within a supercritical state for a longer period of time which is the main principle behind the counter pressure technique.

MOLD TEMPERATURE CONTROL

MOLD SURFACE HEATING

Another effective method for controlling the quality of plastic Microcellular parts is by controlling the surface temperature of the mold during injection. Cha and Yoon [28]
hypothesized that if the mold surface temperature can be kept greater than the glass transition temperature or the crystalline temperature then swirl marks and surface imperfections can be avoided. Cha and Yoon also discovered as gas is dissolved into the plastic its respective glass transition temperature decreases [28]. Chen et. al. found that by using rapid mold temperature heating by induction, swirl mark as well as surface roughness can be significantly decreased [4]. Chen concluded that a good surface quality can be directly related to a high mold and melt temperature as well as a faster injection speed. Also specifically that molded PC will completely lose all visible surface streaks when the mold temperature is increased to 160 C. Induction heating is not the only method for mold heating however, Yoon and Cha explained multiple methods for mold surface heating such as electrical resistive, dielectric, thermoelectric, radiation, convective, contact heating, and laser heating [29].

RAPID COOLING

An issue with mold heating application in MCP molding is that bubbles tend to continue to grow when there is sufficient heat and plastic in liquid form. When the mold surface is heated to improve surface quality the bubble size can grow to an undesirable size. This brings about one of the key features to the experiment in this paper. It has been proved that if the cooling process can be sped up, there exists a point where cell growth can be shut off completely [30]. One developing method for rapid temperature control is by changing the medium in which the heat in transferred the other is by significantly decreasing the coolant temperature. Traditionally injection molds are made of P20 tool steel which has a thermal conductivity of 29.5 W/m°C. If the thermal conductivity of the mold can be increased the amount of heat transferred into the coolant
will increase rapidly causing the part to cool much more quickly. The thermal conductivity of aluminum is roughly 250 W/m°C which means if the steel mold can be switched to an aluminum mold the part can be cooled much more rapidly shutting off cell growth. Figure 9 shows a schematic of both the steel and aluminum mold inserts and the increase of heat transfer for the aluminum one. Figure 9 also shows a mold with a steel insert but with a significantly lower coolant temperature generating a faster cooling rate. As stated earlier, the issue with foam molding crystalline polymers can be traced to two main causes, excess heat given off during the crystallization process; and the expulsion of gas at the nucleation sites preventing bubble growth. Rapid heat transfer cooling can potentially solve both of these issues by drawing out excess heat as well as hardening the plastic before gas expulsion.

Figure 9: Schematic of Steel and Aluminum Heat Transfer rates
Differential Scanning Calorimetry

Crystallinity directly affects many physical attributes to thermoplastic parts including density, permeability, and ductility, most of which can be measured in various methods of their own. However getting a value for degree of crystallinity allows for these properties to be properly predicted and designed for with specific intentions in mind. One of the most common and effective ways to calculating a materials degree of crystallinity is through differential scanning calorimetry. A differential scanning calorimeter (DSC) provides a rapid method for determining polymer crystallinity based on heat required to melt the polymer [31]. The theory behind a DSC is that as heat is added to a thermoplastic the temperature will rise, however the crystallinity affects how much heat is required to do so. A reference pan, usually empty, is used alongside a sample pan to plot heat flow as a function of temperature. When the sample begins to melt the heat required to raise the temperature increases to a peak until the polymer hits its melting temperature, causing the required heat to drop back down. This plot is called an endotherm and the area under this melting peak is the enthalpy or heat of melting (\( \Delta H_m \)).

Using previously established known \( \Delta H_m \) values for perfectly crystallized plastics, a ratio can be used to determine the percent crystallinity using Equation 13. The melting temperature and enthalpy are not the only useful pieces of information gathered from DSC; it is also an effective tool for determining glass transition temperatures and cold crystallization values [32].
III. EXPERIMENTAL DESIGN AND EQUIPMENT

EXPERIMENT OVERVIEW

In order to prove that modifying the cooling rate as well as the in mold counter pressure are effective ways to control cell growth and crystallization, an experiment must be developed which shows results from both slow and fast cooling rates as well as from increasing counter pressure values. The experiment plan is to use an injection molding machine fitted with MuCell equipment from Trexel Inc. to make parts out of a crystalline material for evaluation. The material chosen for study is Polypropylene (PP). Parts will be made first with no counter pressure and at normal processing temperatures. These parts are expected to have non-uniform bubble size and distribution as well as poor surface quality. The idea is to then add counter pressure in increasing increments along with increasing holding times. Figure 10 represents a virtual model of a sample part created using the MuCell process. The next step is to lower the temperature of the coolant which increases the cooling rate. The same samples will be made using the faster
cooling rate including samples with no counter pressure and also samples with the same
counter pressure values as before. The next phase is the evaluation phase. The parts will
be evaluated for using two separate methods, one for crystal growth and one for bubble
growth. Using a DSC to measure the melting peak of each sample, the crystallinity in
terms of percent crystal of each can be calculated by using the know heat of melting
value for 100% crystallized PP. Using the SEM a visual representation is created and
conclusions can be drawn about effects of the parameters on the bubble growth and
general part structure.

EQUIPMENT

INJECTION MACHINE

The major equipment used for the experiment includes a commercial injection
machine, MuCell injection equipment from Trexel, and a gas compressor with booster for
the counter pressure application. Figure 11 shows the Arburg Allrounder 420 C 1000-350
injection molding machine. This machine has been outfitted with Trexel MuCell
Injection Molding Equipment which is shown in Figure 12. The clamping force of the
Arburg Allrounder is 1000 N, and is equipped with a shut off nozzle intended to prevent
the Supercritical Fluid from foaming prematurely. A 45mm screw designed
specifically for MuCell applications is installed, the cross section of which is displayed in Figure 13. The mold fixed within the injection machine is shown in an actual image in Figure 14 and as a semi-transparent model in Figure 15 in order to better display the
cooling system. Although the mold was designed with several internal channels increasing its versatility to heat and cool in various methods, only a select few channels were utilized for this experiment in order to simplify the results and lower the possibility of unforeseen factors coming into involvement. The part itself was designed with the intention of being able to efficiently and effectively evaluate the counter pressure and cooling rate effects. The decided upon sample part geometry is shown in Figure 16, choosing 3mm as an ideal thickness for a MuCell study.

Figure 13: CAD model of MuCell injection screw

Figure 14: Sample mold

Figure 15: CAD model sample mold
PRESSURE AND TEMPERATURE SENSORS

In order to view the cooling rate and counter pressure effects accurately, the precise values for temperature and pressure need to be known throughout molding. In order to achieve this, sensor locations were built within the mold to capture the real time temperature and pressure data during the filling and cooling stages. The sensors are Priamus 4003A temperature sensor and 6003A pressure sensor shown in Figure 17 and Figure 18. The sensors relay real time data from the mold [33] to a Priamus monitor via the Priamus e-Daq 810 unit shown in Figure 19.
INJECTION MATERIALS

The Injection material used for evaluation was unfilled PP. The basis behind why the material was chosen includes its properties, appearance, composition and its widespread availability and usage in industry. The melting temperature of PP is not a difficult temperature to achieve during molding making it ideal for molding many samples with varying cooling rates. Also the glass transition temperature is well below room temperature allowing for a simpler, less error prone plot from the differential scanning calorimeter during the evaluation stage. Its appearance is opaque, making in somewhat feasible to view within the part to observe what is happening and get an immediate indication to how the foaming is reacting to the various parameters. The PP was left unfilled due to prior research noting that filled materials tend to create more locations for nucleation. It was decided that a filled material will undoubtedly affect the bubble size and crystallinity and furthermore may have interaction effects with the counter pressure and temperature. Therefore the filled material should be included on an

Figure 19: Priamus e-Daq and data collection notebook
extension study building on the results of this one. The other choice of materials involves the mold material. The mold material is very important due to the fact that it influences the heat transfer between the part and the coolant ultimately governing the cooling rate. It is well known that the heat transfer coefficient of QC-10 Aluminum is much higher than that of P20 steel (also proven by [6]). However the cooling rate is not controlled solely by the heat transfer coefficient of the mold material but also the temperatures involved. If a trend can be shown in the cooling rate changes simply by modifying the coolant temperatures, then it can be assumed with confidence that the trend will continue in the same manner if the heat transfer coefficient is increased with a new mold material. Therefore, for this experiment P20 steel was used. Its properties are shown in Table 5.

Table 5: Material properties for P20 steel

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity (W/m·°C)</th>
<th>Density (Kg/m³)</th>
<th>Specific Heat (KJ/Kg·°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P20</td>
<td>25</td>
<td>7850</td>
<td>0.460</td>
</tr>
</tbody>
</table>

EVALUATION EQUIPMENT

The first evaluation stage is to determine the effect of the changing variables on the crystallinity of the PP. to do this a Perkin Elmer differential scanning calorimeter 7 (DSC-7) was used shown in Figure 20. The DSC was fitted with a thermal analysis data station with Pyris thermal analysis software. Both the environment and purge gas was N₂.

The next stage for evaluation is the SEM. The SEM used is the Hitachi S-3000N Scanning Electron Microscope and is shown in Figure 21. In order for the SEM to
function, the specimen must be electrically conductive, to achieve this, a platinum coating machine is used, shown in Figure 22.

Figure 20: Perkin Elmer DSC-7

Figure 21: Hitachi S-3000N Scanning Electron Microscope
EXPERIMENTAL SETUP

EXPERIMENTAL STAGE

For the experimental stage, the first thing was to prepare the injection material. The PP was dried for 4 hours at 80°C. The machine parameters were set including a barrel temperature of 180°C at the material inlet and 220°C at the end of the barrel at the injection location. The MuCell Parameter was set at 4%wt N₂. Table 6 shows the changing parameters for each test with their corresponding assigned test numbers. Figure 23 is a layout of the entire experimental stage setup. Five samples of each test were made in order to ensure the unstable nature of the MuCell process did not create any anomalies in the test data resulting in about 175 test samples.
Table 6: Test parameters

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Slow Cool</th>
<th>Medium Cool</th>
<th>Fast Cool</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1  2  3  4  5</td>
<td>6  7  8  9  10</td>
<td>11  12  13  14  15</td>
</tr>
<tr>
<td>Coolant temperature (°C)</td>
<td>80  80  80  80  80</td>
<td>30  30  30  30  30</td>
<td>10  10  10  10  10</td>
</tr>
<tr>
<td>Counter Pressure Value (Bar)</td>
<td>0  50  50  100  100</td>
<td>0  50  50  100  100</td>
<td>0  50  50  100  100</td>
</tr>
<tr>
<td>Counter Press Hold Time (S)</td>
<td>0  0  10  0  10</td>
<td>0  0  10  0  10</td>
<td>0  0  10  0  10</td>
</tr>
</tbody>
</table>

Figure 23: Experimental stage schematic
EVALUATION STAGE

For the DSC part of the evaluation stage, small 3mg to 5mg samples were taken out of the cross section of all the test parts. These samples were crimped into aluminum pans. The first test specimen was placed into the DSC alongside the reference pan and heated at a rate of 20°C/s from 50°C up to 200°C. This process was repeated for all test specimens. A schematic of the DSC layout is shown in Figure 24. The Pyris software automatically calculates the $\Delta H_m$. Lastly the degree of crystallization was calculated by comparing the measured $\Delta H_m$ to that of 100% crystal PP. The next step in the evaluation is using the SEM to determine average bubble size and distribution. Because any method of cutting would damage the MuCell bubble, the parts need to be fractured. Since the glass transition temperature of PP is well below room temperature, the samples were notched with a saw and frozen in liquid nitrogen for two minutes in order to ensure a clean fracture through the cross-section. After each specimen was collected they were adhered to one of two observation blocks to be placed in the SEM. Because of the

![Figure 24: Perkin Elmer DSC-7 layout](image-url)
principle on which an SEM operates the surface under observation needs to me electrically conductive therefore the fracture surface is coated with a platinum film. The specimen blocks as well as the SEM schematic are shown in Figure 25 and Figure 26 respectively.

Figure 25: SEM specimen blocks
The main purpose of the experiment is to get a better understanding of cooling rate and counter pressure effects in MuCell in order to predict results in engineering applications. Because of this fact it is important to increase and enhance the methods in which to predict results. A simulation was designed in Moldex3D which nearly replicates the physical experiment. Although the technology to Model MuCell injection molding in Moldex3D exists now in newer versions, the software was only very recently released and was not available for use at the time of experimentation. Instead a traditional injection molding model was designed and simulated in order to calculate

Figure 26: SEM schematic
cooling rate predictions. These cooling rates are expected to be different from the actual measured cooling rates from the Priamus sensors however a lot of useful information can be gathered if the cooling rate data from the sensors can be matched with the cooling rate data from simulation. If a correlation is discovered from the actual data relating the crystallinity and or bubble size to the cooling rate, then the simulation data can essentially be calibrated to predict the those same results. As stated earlier, prior research has proved that the cooling rate increases when using aluminum mold inserts rather than steel. If the model is simulated with an aluminum mold insert and a value is compared to the simulated steel insert data, that trend can be used to predict actual aluminum mold cooling rates using the measured steel insert values and the calculated trend from simulation.
IV. RESULTS AND ANALYSIS

SIMULATION DATA

The simulation was performed in Moldex3D which yielded the following results. The software generated plots of temperature at virtual sensor locations over time as shown in Figure 27. The plot data was then extracted and evaluated in Excel. The data was then evaluated by setting bounds around the linear portion of the cooling history curve. By viewing the derivative of the curve, the linear portion can be extracted. These linear portions we extracted for each of the slow, medium, and fast cases as shown in Figure 28. As expected, lower coolant temperatures yield faster cooling rates. In order to better realize the effects changing mold materials, a second set of simulations were performed with aluminum QC-10 being the mold material. These results are shown in Figure 29. Table 7 outlines the simulation results. All the resulting Moldex3D plots can be found in the APPENDIX A section. One curious outcome was from the cooling rate
for the slow case of the aluminum simulation. The cooling rate shows a slower value than that of its steel counterpart. One possible explanation is that the cooling reaches steady state very early causing a shift in the overall cooling rate.

Table 7: Simulated cooling rate results

<table>
<thead>
<tr>
<th>Cooling Rate °C/sec</th>
<th>P20 Steel Mold</th>
<th>QC-10 Aluminum Mold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow (1-5)</td>
<td>0.13</td>
<td>0.09</td>
</tr>
<tr>
<td>Medium (6-10)</td>
<td>0.69</td>
<td>1.04</td>
</tr>
<tr>
<td>Fast (11-15)</td>
<td>0.92</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Figure 28: Predicted cooling rate plots for all three cooling scenarios for steel mold
Figure 29: Predicted cooling rates for QC-10 mold material
SENSOR DATA

The Sensor data contains a lot of useful information for detailing what is occurring inside the mold and also information helping to predict future outcomes. The sensor Data was gathered and imported into Excel for evaluation. Figure 30 is a plot of all the sensor data gathered on one graph which shows clear view of the distinguishable cooling rates from one another. Each cooling rate section was then looked at individually. To get a closer look at each cooling rate the data is separated into their cooling groups. Looking at each plot individually reveals no inclination to believe that the varying counter pressure values directly change the cooling rate. From plot to plot the CP lines follow no specific order or trend. It is believed that the range is simply due to the normal discrepancies found in real-life data. The cooling rates therefore are averaged together to find a specific average cooling rate value for the whole cooling rate. Those average rates are .128 for the slow .660 for the medium and .898 for the fast cooling. The following figures show the cooling rates of each of the three different groups and also their average cooling rate.
Figure 30: Sensor Data for All Runs
Figure 31: Sensor data for cases 1 through 5

Figure 32: Sensor data for cases 6 through 10
Figure 33: Sensor data for cases 11 through 15
DSC DATA

The DSC outputs a plot for each specimen showing heat flow as a function of temperature. Figure 34 shows one of these plots output by the Pyris software. In order to extract the enthalpy value, bounds need to be set around the melting peak. To determine the beginning and end of the melting plot the derivative is plotted (dashed line) on top of the heat flow curve to make it easier to see where the slope begins to increase.

As stated previously the Pyris software automatically calculates the area under the curve inside the specified bounds of the melting peak (Delta H). These values are presented in

![Figure 34: DSC Heat flow vs. Temperature plot](image)

**Table 8: DSC results**

<table>
<thead>
<tr>
<th>Counter Pressure (Bar)</th>
<th>0</th>
<th>50 - 0s</th>
<th>50 - 10s</th>
<th>100 - 0s</th>
<th>100 - 10s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow Cool</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Test Number</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>ΔH (J/g)</td>
<td>92.3753</td>
<td>90.0117</td>
<td>93.5707</td>
<td>93.5454</td>
<td>93.8351</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>44.63</td>
<td>43.48</td>
<td>45.20</td>
<td>45.19</td>
<td>45.33</td>
</tr>
<tr>
<td>Medium Cool</td>
<td>79.7104</td>
<td>75.4136</td>
<td>82.7463</td>
<td>82.4789</td>
<td>82.8746</td>
</tr>
<tr>
<td>Test Number</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>ΔH (J/g)</td>
<td>78.2900</td>
<td>74.2957</td>
<td>81.5448</td>
<td>77.1662</td>
<td>78.2379</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>37.82</td>
<td>35.89</td>
<td>39.39</td>
<td>37.28</td>
<td>37.80</td>
</tr>
</tbody>
</table>

45
Table 8 along with the calculated crystallinity. To put these values into better perspective two separate plots column graphs were constructed. The first relates the percent crystal structure to the cooling rate by grouping the tests with the same counter pressure values together. In this plot we have an expectation of what to see based on results from prior studies. This graph is shown in Figure 35. The second graph relates the Percent crystallinity to the counter pressure values by grouping together tests with the same cooling rates. It is important to view both in order to clearly see the effect of each parameter change.

![Crystallinity Due to Cooling Rate Effects](image)

*Figure 35: Crystallinity Due to Cooling Rate Effects*
Figure 36: Crystallinity Due to Counter Pressure Effects

SEM DATA

The SEM data consists of a large amount of images which are shown throughout Figure 37 to Figure 39. Table 9 gives descriptions of observations as well as measurements and calculations from images. All individual images and extra images with higher magnifications used for measurements and calculations can be found in Appendix C.
Figure 37: SEM images for tests 1-5
Figure 38: SEM images for tests 6-10
Figure 39: SEM images for tests 11-15
<table>
<thead>
<tr>
<th>#</th>
<th>Cooling Rate</th>
<th>Counter Pressure</th>
<th>Observations and initial measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Slow</td>
<td>0</td>
<td>Foaming virtually nonexistent throughout core, all bubbles pushed toward edges. Center appears to be aligned as if crystal structure is very organized. Skin thickness – 0.4887 Bubble size – small - 0.0339 large - 0.1767</td>
</tr>
<tr>
<td>2</td>
<td>Slow</td>
<td>50Bar 0 sec</td>
<td>Extremely small bubbles throughout sections of core. Large bubbles pushed out along distinct line at part skin. Few random bubbles scattered throughout Skin thickness – 0.4418 Bubble size – small - 0.0172 large - 0.1349</td>
</tr>
<tr>
<td>3</td>
<td>Slow</td>
<td>50Bar 10 sec</td>
<td>More large bubbles scattered throughout core. Still evidence of bubbles being pushed to edge, bubble size varies drastically with distance from skin. Skin thickness greatly decreased Skin thickness – 0.1548 Bubble size – small - 0.0363 large - 0.2508</td>
</tr>
<tr>
<td>4</td>
<td>Slow</td>
<td>100Bar 0 sec</td>
<td>More small bubble foaming throughout core. More uniform bubbles throughout part. Skin thickness – 0.4551 Bubble size – small - 0.0363 large - 0.2508</td>
</tr>
<tr>
<td>5</td>
<td>Slow</td>
<td>100Bar 10 sec</td>
<td>Significant foaming throughout core, very small bubbles. Random large bubbles. Layer of bubbles at skin edge still exists however is much thinner Skin thickness – 0.2432 Bubble size – small - 0.0359 large - 0.2308</td>
</tr>
<tr>
<td>6</td>
<td>Medium</td>
<td>0</td>
<td>Thick layer of small bubbles next to skin, no small bubbles throughout core appears to be randomly filled with medium sized bubbles Skin thickness – 0.4455 Bubble size – small - 0.0334 large - 0.1573</td>
</tr>
<tr>
<td>7</td>
<td>Medium</td>
<td>50Bar 0 sec</td>
<td>Core completely filled with very small bubbles. Small and medium sized bubbles at edges Skin thickness – 0.3037 Bubble size – small - 0.0152 large - 0.1621</td>
</tr>
<tr>
<td>8</td>
<td>Medium</td>
<td>50Bar 10 sec</td>
<td>Core completely filled with very small bubbles. Medium and large sized bubbles at edges Skin thickness – 0.4058 Bubble size – small - 0.0188 large - 0.2325</td>
</tr>
<tr>
<td>9</td>
<td>Medium</td>
<td>100Bar 0 sec</td>
<td>Bubble distribution more uniform throughout entire cross section. Bubble size ranges from medium, large, to very large Core completely filled with small bubbles. Medium and large sized bubbles at edges Skin thickness – 0.1090 Bubble size – small - 0.0806 large - 0.0815</td>
</tr>
<tr>
<td></td>
<td>Condition</td>
<td>Pressure</td>
<td>Duration</td>
</tr>
<tr>
<td>---</td>
<td>-----------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>10</td>
<td>Medium</td>
<td>100Bar 10 sec</td>
<td>Bubble distribution is a lot more uniform. Still have larger bubbles foaming near the skin edge however they seem to be less profound. Core completely filled with small bubbles. Medium and large sized bubbles at edges.</td>
</tr>
<tr>
<td>11</td>
<td>Fast</td>
<td>0</td>
<td>Large bubbles forming throughout core. Thin walls in between bubbles in core. Still some levels of crystallinity visible.</td>
</tr>
<tr>
<td>12</td>
<td>Fast</td>
<td>50Bar 0 sec</td>
<td>Large bubbles throughout core, highly varying bubble sizes throughout part very distinct bubble size layers.</td>
</tr>
<tr>
<td>13</td>
<td>Fast</td>
<td>50Bar 10 sec</td>
<td>More uniform, and very small foaming throughout entire part. Skin is less defined, medium and large bubbles exist in core.</td>
</tr>
<tr>
<td>14</td>
<td>Fast</td>
<td>100Bar 0 sec</td>
<td>Very defined skin line containing drastically different bubble sizes. Small foaming exists in between larger bubbles in the core.</td>
</tr>
<tr>
<td>15</td>
<td>Fast</td>
<td>100Bar 10 sec</td>
<td>Very small uniform foaming throughout core with small and medium sized bubbles lining the skin edge.</td>
</tr>
</tbody>
</table>
V. DISCUSSION

SENSOR AND SIMULATION

The first set of data to discuss is the sensor results and how it compares to the simulated data. If the simulation data can be verified by the actual data, more confidence can be placed in simulated values for the future cutting back on time and effort for more test runs. The actual sensor data shows the exact cooling trend as expected with increasing rates as the coolant temperature is lowered. By comparing all the sensor results from the same cooling rate groups (i.e. all the results from group 1-5, 6-10 etc) a conclusion is drawn about the counter pressure effect on the cooling rate. The cooling rate is nearly the same for all counter pressures in each cooling group. It is also noticed that the order of the tests are not consistent from group to group. Both of these observations lead to the assumption that changing counter pressure parameters has little to no effect on the cooling rate. It is possible that the counter pressure has a small effect however the data shows that there are other parameters that overpower the counter pressure effects and govern the cooling rate. The simulated data also exhibits very clear and expected results. Table 10 displays a comparison between the simulated results and the actual results. To get a better visual feel for these results a plot was made displaying all the cooling rates on the same chart. Figure 40 clearly displays that the simulation

<table>
<thead>
<tr>
<th>Table 10: Sensor vs. simulation comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow</td>
</tr>
<tr>
<td>Simulated Sensor</td>
</tr>
<tr>
<td>0.1278</td>
</tr>
<tr>
<td>Percent difference</td>
</tr>
</tbody>
</table>
agrees very nicely with the actual data. Table 10 shows that all three cases exhibit slight discrepancies of under 5% each and the plot displays this visually. Much more confidence can now be placed into the simulation because of the success of the simulation and sensor comparison. Even though the tests were successful in comparing cooling rates for the steel case, this does not mean that 100% confidence should be put into the simulation of the aluminum insert without some actual testing. Overall the sensor and simulation data matches up extremely well.
DSC

The DSC data proved to be very informative for showing the effects of the different parameters on the resulting crystal structure. However while some of the data is clear and yields unmistakable conclusions some of that data behaves somewhat unusually leaving room for speculation and desire for more experimentation. This is the case when observing the cooling rate effects on the crystallinity. Figure 41 puts into perspective the crystallinity as a function of cooling rate. The first three cases (no counter pressure and both of the 50 Bar cases) yield similar curves that fit perfectly into expected results. The other two tests (both 100 Bar cases) also have decreasing tendencies however follow a slightly different curve shown in Figure 42. This effect most likely is due to the fact that there is a critical pressure around that value in which changes the polymer behavior. This is more likely considering the proof from previous works which note a critical pressure value that will directly prohibit foaming. The critical pressure either directly causes a change in crystallinity or it effects the MuCell foaming which in turn creates an indirect
effect of the crystal morphology. In either case more data points are needed to find the exact behavior and transition value. Looking at the cooling rate effects, the general trend matches up exactly to what was expected; higher cooling rates translate to lower degree of crystallinity. The next phenomenon to observe is the counter pressure effects. The crystallinity as a function of counter pressure can be viewed in Figure 43 and Figure 44. The counter pressure relationship is more complex. The figures were separated to show all possible parameter effects. Figure 43 shows the crystallinity without the holding time. The plot indicates that for all three cases there is an initial decrease in crystallinity when the 50 Bar pressure is added but once the pressure is increased to 100 Bar the crystallinity goes back up higher than the original. This phenomenon can possibly be attributed to the

Figure 42: Crystallinity as a function of cooling rate for 100Bar counter pressures

Figure 43: Crystallinity as a function of cooling rate for 100Bar counter pressures without holding time.
previously mentioned critical pressure. Just as observed in the cooling rate plots, once the high pressure was used, the trend changed. One possible explanation for the increase in crystallinity is that at 100 Bar the critical pressure has been reached or nearly reached causing a large decrease in foaming, with no foaming occurring the crystalloids do not have to “fight” for space with the bubbles. Another possible reason could be that the high pressure causes an increase in density and during the cooling the crystal structures
become more tightly packed causing a higher degree of crystallization. When looking at the plot including holding time we see a somewhat different trend. The initial 50 Bar CP creates an increase in crystallinity and a slight increase from that at 100 Bar with the exception of the fast cool which shows a decrease. The reason for this could be the same as stated before for the cases without holding time. It is possible that the holding time is increasing the density during the whole cooling process. This would make for very tightly packed crystal structures leading to high crystallinity values. The reason the 100 Bar fast cool is slightly lower is most likely due to the fact that the crystalloids are frozen in place before they can continue to grow, suggesting that the cooling rate is a more important factor on crystallinity than the CP. The holding time plot in Figure 44 follows nearly the same trend as the one without holding time except the 100Bar value for the fast cooling case which shows a decrease in crystallinity rather than the increase in all the others. Overall the holding time seems to play a large role in the final degree of crystallinity. Figure 45 and Figure 46 provide visual representations for what the holding time does for each cooling rate case. In all cases the crystallinity increases however for

![Crystallinity as a Function of Holding Time (for 50 Bar)](image)

Figure 45: Crystallinity as a function of holding time for 50Bar counter pressure
the 100 Bar cases the increase is much less significant. Overall the DSC data indicates it is very possible to control degree of crystal formation within a MuCell polymer by controlling both cooling rates and counter pressures. The cooling rate data is clear and performs as expected. The Counter Pressure data is more complex and exhibits what appears to be either a non linear relationship or a limiting relationship. Either way the research gives merit for the problem to be further explored.

![Figure 46: Crystallinity as a function of holding time for 100Bar counter pressure](image)

SEM

The SEM data gives both a visual representation of what is happening to the internal part structure, and a way to give qualitative data to compare within each image. If the images support the data from the DSC more trust can be laid in into the DSC results and subsequently more trust in the overall theories on what is happening in regards to the parameter changes. The first parameter explored will be the cooling rate. In order to more easily compare the cooling rate changes the SEM images have been cropped and laid together. The DSC crystallization value has also been included in order to add more opportunities to compare data.
The first set of three images show samples 1, 6, and 11. There are noticeable differences in the three when looking at the areas labeled A, B, and C. In area A the material appears to have an organized linear pattern giving reason to believe the polymer chains are lined up in a highly crystallized fashion. For sample 6 it appears the bubbles are still being pushed outward however there are a lot more bubbles forming in the core as shown in B. In area C much larger bubbles have formed in the core with less bubbles being pushed to the edges outside. The skin thickness appears to be relatively thick in each sample.

Figure 47: SEM images comparing cooling rates for tests 1, 6, and 11
For samples 2, 7, and 12 similar results were noticed. The first area “A” shows nearly all the larger sized bubbles have been expelled out of the core. The core however is filled with many very small bubbles with noticeably large areas of no foaming which is strong indication of highly crystallized regions. In B we see larger bubbles beginning to form as well as the blank crystalline regions becoming smaller and more evenly distributed. In area C there a lot of very large grouped bubbles, it is a drastic change from the previous two images.

Figure 48: SEM images comparing cooling rates for tests 2, 7, and 12
Figure 49: SEM images comparing cooling rates for tests 3, 8, and 13

The images of samples 3, 8, and 13 display similar results to that of the other counter pressures. Area A shows more evenly distributed foaming throughout the core and a few larger bubbles are beginning to appear in the core. Area B shows an increase of larger bubbles, it is noticed that the bubbles appear to continue to be pushed to the edge but get frozen in place before they reach the edge of the skin. The images don’t show a significant change visually which is supported by the fact that the DSC results show only a 0.58% decrease in crystallinity. The line of bubbles forced to the edges creates an almost separated skin layer.
The image of samples 4, 9, and 14 show a large change foaming behavior. Area A shows there is already some foaming happening, both small distributed bubbles and some larger uniformly sized ones in the core. However Area B shows the most significant change, which appears to be a vast amount of foaming creating bubbles all many shapes and sizes. Area C shows a much more uniform bubble size and thicker more stable walls between the bubbles themselves. The DSC values also verify what is being observed from the SEM images.

Figure 50: SEM images comparing cooling rates for tests 4, 9, and 14
The Last three samples comparing cooling rate effect are samples 5, 10, and 15. The fact that there are very few large bubbles in any of the images leads to the speculation that the high counter pressure value held for a long time causes the bubble size to remain very small. As noted before the expulsion of the gas to the edges causes a sort of separation between skin and core as shown in area A. Overall the cooling rate effects as observed by the SEM agree very nicely with the measured DSC values.

Figure 51: SEM images comparing cooling rates for tests 5, 10, and 15
The next step is to explore and compare the images of the counter pressure effects. The counter pressure effects are much more difficult to analyze because of the known existence of the critical pressure, but not truly knowing if that critical pressure has been met. In samples one through five, a few characteristics can be noticed. The bubbles near the edge of the skin get smaller when the pressure is held as noticed when going from 2 to 3 and from 4 to 5. The bubbles appear to remain smaller as the pressure is increased. The skin layer seems to become more detached and thinner when the counter pressure is held. Overall the observed changes don’t seem to be extremely significant except for the previously mentioned subtle behavior changes.

Figure 52: SEM images comparing counter pressures for tests 1-5
The SEM images of tests 6 through 10 displays perhaps the clearest data to the counter pressure effects. The foaming can clearly be seen increasing in 7 and 8 as opposed to 6 and even more so it sample 9 which can be seen in area B. It appears as though the critical pressure has caused a significant decrease of foaming on sample 10 shown in area C. Again the high holding time seems to create a separation in the skin and core which is noticed at area A.

Figure 53: SEM images comparing counter pressures for tests 6-10
For tests 11 through 15 the cooling rate was at its fastest value. The general trend observed in the SEM images indicate that the addition of counter pressure tend to regulate the bubble size and shape to a more desired condition. Also the thin walls in between bubbles seen with no counter pressure and 50 Bar are not an issue as the counter pressure is increased. As seen in the previous images and area “C”, the highest counter pressure with holding time greatly decreases the number of larger bubbles.

Figure 54: SEM images comparing counter pressures for tests 11-15
Overall, the designed set of experiments, measurements, and calculations provide a strong basis to work from for understanding behavior and improving quality of Microcellular semi-crystalline injection molding applications. The main goal was to identify behavior patterns and trends for the foaming characteristics in response to certain parameter changes in order to expand on what is already known today. In a typical MuCell operation a series of changes were made to the cooling rate, counter pressure, and counter pressure holding time. This goal was achieved by noting specific changes to the degree of crystallinity, the bubble size and distribution, and to the MuCell skin after cooling. These parameter effects were observed with the use of a differential scanning calorimeter as well as a scanning electron microscope. The findings are as follows, as expected the crystallinity decreases as the cooling rate increases. It is possible to control the cooling rate simply by adjusting the coolant temperature however it is believed by the help of simulation from this experiment and studies from previous works that cooling rate can be controlled and increased even more by changing mold materials such as Aluminum rather than steel. Also the experiment proves that counter pressure also has an effect on the morphology and foaming physics. Initial data shows that adding counter pressure will result in more uniform bubble size and shapes, as well as a more even bubble distribution throughout the part. However there are two trends to notice when considering counter pressure. The first is that there appears to be a critical pressure, which is confirmed by other studies, where the foaming is inhibited and in some cases completely prevented. To obtain an exact value for desired counter pressure, many more values and trials must be tested. The second thing to note is that when the counter
pressure is held for 10 seconds there seems to be an undesired counter effect on the skin. In many samples where the counter pressure was held, the skin layer was essentially detached from the core by a foaming layer which led for the skin to easily be peeled back and separated from the rest of the part. The assumption that MuCell foaming characteristics can be controlled by implementing changes in the counter pressure and cooling rate parameters has been confirmed. Various strategies have been implemented to test this theory and found to be all valid to a certain degree. Much more room for development is left however a more confident base of data has been laid out.
VII. CASE STUDY

In order to further expand the understanding of the parameter effects on the MuCell foaming, a couple tests were run with parameters differing from those in the main experiment. The initial parts were all made MuCell however it is necessary to explore many design factors for a more complete understanding of the parameters effects, including counter pressure and cooling rate effects on traditional injection molding. The first case study is an exploration of parts made without MuCell parts which serve somewhat as control variables. These results will show if there is an interaction effect between the MuCell and the parameters or if they are independent. The second case study was developed because of the fact that all test cases were performed with the same starting mold temperature. This case study was developed where the starting mold temperature was significantly lower than that from the other tests. This study will give evidence to whether the cooling rate effect is strongly related to the initial mold temperature or rather just the rate of cooling.

NO MUCELL

The tests made without MuCell processing take the form of control runs providing less change in experiment parameters. Changes in crystallinity can be viewed without any possible unnoticed counter effects stemming from the addition of MuCell techniques. This allows for more definitive lines to be drawn connecting direct causes to resulting effects. Firstly, simulation results and actual sensor data was gathered. The results comparing the cooling rates for the different cases are shown in Table 11. These
comparisons include, MuCell simulated vs. MuCell sensor, non-MuCell simulated vs. non-MuCell sensor, and MuCell sensor vs. non-MuCell sensor. The results suggest that there is little difference between the MuCell and non-MuCell case. These are great results because they further support all of the other cooling rate results taken from simulation. The actual plot of the cooling data is shown in Figure 55 and the cooling rate comparisons are shown in Figure 56. Since there is no foaming occurring SEM analysis would be unhelpful. DSC analysis will give light to how much the foaming process

<table>
<thead>
<tr>
<th></th>
<th>MuCell</th>
<th>Non-MuCell</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulated Sensor</td>
<td>0.1313</td>
<td>0.1313</td>
<td>N/A</td>
</tr>
<tr>
<td>Percent difference</td>
<td>0.1278</td>
<td>0.1338</td>
<td>4.5142</td>
</tr>
</tbody>
</table>

Table 11: Mucell vs. non-MuCell cooling rate comparison

![Sensor Data (C1-C5)](image)

Figure 55: Sensor data for non-MuCell experiment
changes the cooling rate effectiveness on the crystallinity. Table 12 contains the DSC results for the Case of no MuCell. The results display a familiar pattern. The crystallinity follows the same trend as for all of the MuCell cases. When compared to its cooling rate counterpart (the slow case and the case study have the same cooling rate parameters) it appears that the MuCell adds a certain degree of crystallinity however the shift cannot be completely proven unless more non-MuCell samples of all of the other cooling rates are produced and recorded. Figure 57 shows a plot comparing the crystallinity of case study 1 to those of the previous test runs.

Table 12: DSC results for case study 1

<table>
<thead>
<tr>
<th>Temperatures</th>
<th>No MuCell - 80 Mold 80 Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counter Pressure</td>
<td>C1</td>
</tr>
<tr>
<td>Test Number</td>
<td>0</td>
</tr>
<tr>
<td>Delta H</td>
<td>91.8042</td>
</tr>
<tr>
<td>Percent Crystallinity</td>
<td>44.35</td>
</tr>
</tbody>
</table>
Figure 57: Crystallinity plot for case study 1
COLD MOLD

The second case study is focused on modifying an existing test parameter that was previously held constant. This parameter is the mold surface temperature and the cooling rate is dependent on the difference between the mold surface temperature and the coolant temperature. In the previous experiments the mold temperature was set at 80 degrees Celsius, in this study the starting mold temperature is lowered to 15. The cooling temperature remains the same as samples 11-15 at 10 degrees Celsius. Simulation predicts the cooling rate to be slightly under 0.3 degree Celsius per second putting it faster than the slow case (runs 1-5) but slower than the medium case (runs 6-10). The simulation plot is shown in Figure 58. This study will give more insight to the relationship between crystallinity and cooling rate. Table 13 shows the DSC results from case study 2. The results follow the trend of all the other runs. Figure 59 displays the results in comparison to all the previous runs. The resulting data fits in very nicely with

Figure 58: Case study 2 cooling simulation
the existing numbers. The line fits right above the medium test runs and below the slow test runs just as the simulation predicted. Also the trend of the line gives support to the fact that crystallinity depends highly on the rate and can essentially be a value that can be predicted with the help of more testing and simulation.

Figure 59: Crystallinity plot for case study 2

Table 13: DSC results for case study 2

<table>
<thead>
<tr>
<th>Temperatures</th>
<th>15 Mold 10 Cooling</th>
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</thead>
<tbody>
<tr>
<td>Counter Pressure</td>
<td>0</td>
</tr>
<tr>
<td>Test Number</td>
<td>16</td>
</tr>
<tr>
<td>Delta H</td>
<td>80.4678</td>
</tr>
<tr>
<td>Percent Crystallinity</td>
<td>38.87</td>
</tr>
</tbody>
</table>
REFERENCES


Figure 60: Simulated cooling rate for steel 80°C mold 80°C coolant

Figure 61: Simulated cooling rate for steel 80°C mold 30°C coolant
Figure 62: Simulated cooling rate for steel 80°C mold 10°C coolant

Figure 63: Simulated cooling rate for aluminum 80°C mold 80°C coolant
Figure 64: Simulated cooling rate for aluminum 80°C mold 30°C coolant

Figure 65: Simulated cooling rate for aluminum 80°C mold 10°C coolant
APPENDIX B

Figure 66: DSC endotherm plot for sample 1. 80°C mold 80°C coolant 0 CP

Figure 67: DSC endotherm plot for sample 2. 80°C mold 80°C coolant 50 Bar 0 sec CP
Figure 68: DSC endotherm plot for sample 3. 80°C mold 80°C coolant 50 Bar 10 sec CP

Figure 69: DSC endotherm plot for sample 4. 80°C mold 80°C coolant 100 Bar 0 sec CP
Figure 70: DSC endotherm plot for sample 5. 80°C mold 80°C coolant 100 Bar 10 sec CP

Figure 71: DSC endotherm plot for sample 6. 80°C mold 30°C coolant 0 CP
Figure 72: DSC endotherm plot for sample 7. 80°C mold 30°C coolant 50 Bar 0 sec CP

Figure 73: DSC endotherm plot for sample 8. 80°C mold 30°C coolant 50 Bar 10 sec CP
Figure 74: DSC endotherm plot for sample 9. 80°C mold 30°C coolant 100 Bar 0 sec CP

Figure 75: DSC endotherm plot for sample 10. 80°C mold 30°C coolant 100 Bar 10 sec CP
Figure 76: DSC endotherm plot for sample 11. 80°C mold 10°C coolant 0 CP

Figure 77: DSC endotherm plot for sample 12. 80°C mold 10°C coolant 50 Bar 0 sec CP
Figure 78: DSC endotherm plot for sample 13. 80°C mold 10°C coolant 50 Bar 10 sec CP

Figure 79: DSC endotherm plot for sample 14. 80°C mold 10°C coolant 100 Bar 0 sec CP
Figure 80: DSC endotherm plot for sample 15. 80°C mold 10°C coolant 100 Bar 10 sec CP

Figure 81: DSC endotherm plot for sample 16. 15°C mold 10°C coolant 0 CP
Figure 82: DSC endotherm plot for sample 17. 15°C mold 10°C coolant 50 Bar 0 sec CP

Figure 83: DSC endotherm plot for sample 18. 15°C mold 10°C coolant 50 Bar 10 sec CP
Figure 84: DSC endotherm plot for sample 19. 15°C mold 10°C coolant 100 Bar 0 sec CP

Figure 85: DSC endotherm plot for sample 20. 15°C mold 10°C coolant 100 Bar 10 sec CP
Figure 86: DSC endotherm plot for sample C1 no MuCell 80°C mold 80°C coolant 0 CP

Figure 87: DSC endotherm plot for sample C2 no MuCell 80°C mold 80°C coolant 50 Bar 0 sec CP
Figure 88: DSC endotherm plot for sample C3 no MuCell 80°C mold 80°C coolant 50 Bar 10 sec CP

Figure 89: DSC endotherm plot for sample C4 no MuCell 80°C mold 80°C coolant 100 Bar 0 sec CP
Figure 90: DSC endotherm plot for sample C5 no MuCell 80°C mold 80°C coolant 100 Bar 10 sec CP
Figure 91: SEM image test 1 30x magnification
Figure 92: SEM image test 1 30x magnification

Figure 93: SEM image test 2 30x magnification
Figure 94: SEM image test 2 70x magnification

Figure 95: SEM image test 3 30x magnification
Figure 96: SEM image test 3 150x magnification

Figure 97: SEM image test 4 30x magnification
Figure 98: SEM image test 4 400x magnification

Figure 99: SEM image test 5 30x magnification
Figure 100: SEM image test 5 150x magnification

Figure 101: SEM image test 6 30x magnification
Figure 102: SEM image test 6 150x magnification

Figure 103: SEM image test 7 30x magnification
Figure 104: SEM image test 7 150x magnification

Figure 105: SEM image test 1 80x magnification
Figure 106: SEM image test 8 150x magnification

Figure 107: SEM image test 9 30x magnification
Figure 108: SEM image test 9 100x magnification

Figure 109: SEM image test 10 30x magnification
Figure 110: SEM image test 10 150x magnification

Figure 111: SEM image test 11 30x magnification
Figure 112: SEM image test 11 150x magnification

Figure 113: SEM image test 12 30x magnification
Figure 114: SEM image test 12 150x magnification

Figure 115: SEM image test 13 30x magnification
Figure 116: SEM image test 1 150x magnification

Figure 117: SEM image test 1 30x magnification
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Figure 119: SEM image test 15 30x magnification
Figure 120: SEM image test 1 150x magnification