THE ROLE OF POLYMER/GAS SOLUTIONS IN
CONTINUOUS PROCESSING OF MICROCELLULAR POLYMERS

by

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Submitted to the Department of Mechanical
Engineering in Partial Fulfillment
of the Requirements for the
Degree of

DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May 1993

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Submitted to the Department of Mechanical Engineering on May 5, 1993 in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering

ABSTRACT

The goal of this research is to develop a prototype of a continuous manufacturing process for microcellular plastics. A microcellular plastic is characterized by cell densities greater than $10^9$ cells/cm$^3$ and fully grown cells smaller than 10 μm. Microcellular structures have been produced in batch processes by using a thermodynamic instability to promote a large bubble density in polymer/gas systems. In order to utilize such a thermodynamic instability in a continuous process, two major process steps must be performed: a) continuous formation of a polymer/gas solution, and b) microcell nucleation by a thermodynamic instability in the polymer/gas solution. The basic strategy for the process design is to integrate these two steps into a process such that the functions of the overall process are independently satisfied.

The aims of the research are threefold. The first is to develop a means for continuous formation of the polymer/gas solution at an industrial processing rate by creating the super gas concentration in the polymer. The second is to promote a high bubble nucleation rate in the gas-saturated polymer by making use of the thermodynamic behavior of polymer/gas systems. The third is to develop a process model for controlling the cell morphology by identifying the central parameters of polymer/gas solution formation and cell nucleation. An extrusion process for manufacturing filamentary microcellular plastics is presented as a case study. This research includes not only the basic science of the polymer/gas systems, but also the development of an industrially viable technology that exploits the full potential of the unique properties of microcellular plastics.

Thesis Supervisor: Nam P. Suh
Title: Ralph E. and Eloise F. Cross Professor of Manufacturing
ACKNOWLEDGMENTS

During the last 5 years, there has been a big change in my life. I became a manufacturing research engineer/designer. Maybe God wants me to work as a manufacturing engineer/designer. The most influential person was my advisor Professor Nam P. Suh. His enthusiasm, insight, and inspiration have been an invaluable contribution to my professional development and to this research. The most valuable thing I learned from him is the ability to define the problem as an engineer/designer. It has been a true privilege to learn from such a competent and congenial professor, wholeheartedly devoted to research and education. He will be in my heart as a paragon of the best professor.

I am also indebted to the other members of my thesis committee. I am grateful to Professor Peter Griffith for giving valuable suggestions for producing a two-phase mixture of polymer and gas. Professor Mary Boyce has been very courteous to me and has asked me sharp questions that kept me awake and thinking. I also appreciate her quickly contacting Professor McCammond with her recommendation. Professor Robert Armstrong's suggestions and criticism about the temperature rise and the pressure change of the gas/polymer solution were very helpful.

This work has been supported by the MIT-Industry Microcellular Plastics Consortium and the National Science Foundation, Grant #CTS-9114738. The member companies of the Consortium have included Kraft Inc., Amoco Foam Products Co., Amoco Chemicals Co., Neste Co., Asahi Chemicals Co., and Furukawa Electric Co. I am grateful for the support and
assistance received from many individuals in these companies. I express my
deep thanks to Dr. Hiro Tamura at Furukawa Electric Inc. for his support and
couragement. I would like to thank Frank Waldman at Axiomatic
Corporation. He helped me with the mold temperature controller during an
early stage of the project.

Many thanks to Professor Elias Gytopoulos, I would like to express. He
taught me how to teach and how to care. The debt of gratitude I owe him is
immeasurable. I am also grateful to Dr. Nannaji Saka. I frequently knocked
his door at midnights with all sorts of problems. He has always been around
to listen to my wild ideas, and in most cases, I left his office with a clearer
understanding than when I went in. He also read my papers and my thesis,
and gave me many constructive comments. I am also grateful to Dr. Sang
Gook Kim for his help during the course of this work. I could not count how
many times he helped me. With his timely comment, insight, and criticism,
I reached a turning point in this project. Thank you very much. Special
thanks are due Professor Jung-Hoon Chun for his friendship and help. Many
times, he encouraged me to get a good job. I would also like to thank
Professor Bora Mikic, Professor Shahryar Motakef, and Professor Ain Sonin
for their help with heat transfer and fluid mechanics aspects of this project.

The technical staff at the Laboratory were most helpful. Fred Cote
deserves a special thank-you. I became a skilled machinist with his help, and
I could not have finished this project without his help. Many stories behind
the parts, the machines, and the tools will remain a fond memory of my stay
at MIT. I am indebted to Kevin Baron for his time and effort building the
parts during the early stages of the project and his advice on the machining
problems. I would also like to thank Bob Kane and Kevin Spratt for their
friendship and help. I would also like to thank those who have helped me with administrative matters. Doris Elsemiller, Kathy Larson, Sally Stiffler, John Keene, Karuna Mohindra, and Dorothy Cavignano all deserve many thanks for their help and friendship.

I would like to thank my colleagues in the Microcellular Plastics Research Group for their comments, criticisms, and friendships. They include Sung Cha, Dan Baldwin, Toshi Ota, Dr. Minoru Shimbo, Julie Yang, and Derrick Tate. I had so much fun with these people, especially with Sung. I learned many things regarding management from Dan. I really enjoyed working with Dan especially during the last year. I am so glad that I met a very nice gentleman, Toshi Ota. He provided such a good manners and friendship. I would like to maintain a friendship with him for the rest of my life and help him with my technical expertise. Thank you, Julie, Derrick, and Nancy for proofreading my thesis. Derrick has also helped me immeasurably with my job application, papers, letters, and so on. I cannot tell him how much I appreciate his help. Please keep in touch. The undergraduate students in our group have included Tom Cole, Maria Yang, Seymour Liao, Scott Davie, Nancy Ho, Jeanie Cherg, etc. I owe them gratitude in many ways.

I would also like to thank my friends around the Laboratory, both past and present, for their friendship and help. They include Pyongwon Yim, Dr. Woo Chun Choi, Dr. Dae Eun Kim, Dr. Jaebok Song, Dr. Sungdo Ha, Sukyoung Chay, Tae Kang, Tim Berg, Dr. Hamid Salehizadeh, Kashun Wong, Mohsen Mosleh, Dr. Greg Dillon, Ein-Teck Neoh, Tom Nowak, Honor Passow, Dan Walczyk, Eric Kim, and Jim Bredt. My office mates deserve my thanks too. All my other Korean friends deserve thanks for their friendships.
They include Dr. Ho-Myung Chang, Dr. Eunsoo Jung, Dr. Janghyon Park, Hyunyil Lee, Dr. Byungin Choi, Dr. Sangkwon Jung, Dr. Hyun Seok Yang, Dr. Hyunjune Yim, Dr. Jangbom Chai, Jin Suk Oh, James Shin, Dr. Yun-Jae Kim, Sang-Joo Kim, Hyun-Woo Lee, and many others. Especially, I would like to thank Daeyup Lee for his help in solving a set of nonlinear equations with his good calculator. Chong Seung Yoon also deserves my thanks for his help in the preparation of samples. I would also like to thank Kyungdoug and Sukyoung for cooking dinners and waiting for me many times. Thank you!

My brothers and sisters at the Korean Presbyterian Church in Boston, especially the members of Young Adult Group One, deserve many thanks for their prayers, support and friendships. They include Pastor Dukyoung Chun, Pastor Sam Folta, Elder Shin Hoo Kang, Elder Nam Soo Song, Elder Chul Woo Hyun, Elder Euin Lee, Brother Kyu Sam Han, Brother Brian Lee, Deacon Youngsoo Bae, Deacon Man Sung Yim, Dr. Jinsang Jung, Heewan Moon, Charlie Hong, Mike Oh, Steve Kim, Jay Duk Yoo, and many others. I would like to express my gratitude to Kwang Ki Baek and his wife for their concern and prayers. Kwang Ki also helped me with the preparation of samples and many rides to and from the Logan Airport. I would also like to thank Tom and Carolyne Eynon for their prayers and love for me over the years. They tried to keep me awake to not waste my pain. I would also like to thank Brother Young Wook Kim, Brother Chigeun Noh, Brother Jin Tae Lee, Brother Dong Gap Kim, and Brother Jae Young Kim. I know how much sorrow you felt when I left the Navigators. Thank you for bearing with me.

My family, Mom, my brothers and sisters, my brother-in-laws and sister-in-laws, my nephew and nieces, my aunts and uncles, and my cousins
always have provided an endless source of love, comfort, and encouragement to me. I love you all very much. I would like to thank my father-in-law and mother-in-law for their prayers, concerns, and support. I would also like to thank my wife's aunts, uncles, brothers, sister-in-laws, and cousins for their concerns and prayers.

I owe many thanks to my lovely wife, Dong Yun, for her love, support, encouragement, and prayers. Thank you for your patience, too. No matter how things go, you are always with me. I cannot count the number of nights you stayed with me to encourage, to help, and to be with me. I would like to let you know that I could not have done it without your support.

Finally and foremost, I thank God for His grace and mercy that He has shown me every moment. Every time I fell down, He came down to deliver me. He always lived with me (especially in the times of trouble). He answered all my prayers in His due time. Without His love, care and encouragement, I could not have completed the degree. Now I give thanks to Him with this praise:

How lovely is your dwelling place, O Lord All Mighty! Even the sparrow has found a home, and the swallow a nest for herself, where she may have her young - a place near your altar, O Lord All Mighty, my King, my God. Blessed are those who dwell in your house; they are ever praising you. O Lord All Mighty, blessed is the man who trusts in you. (Psalm 84:1,3,4,12)
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NOMENCLATURE

A \hspace{1cm} \text{interfacial area of gas bubbles and polymer melt matrix, m}^2 \\
A_{ij} \hspace{1cm} \text{element of the design matrix} \\
a \hspace{1cm} \text{characteristic constant of polymer (}=\frac{1}{n}\text{)} \\
b \hspace{1cm} \text{channel depth of the screw, m} \\
C_w \hspace{1cm} \text{concentration of gas molecules in a nucleus, g/g} \\
C_i \hspace{1cm} \text{concentration of the source, g/g} \\
C_S \hspace{1cm} \text{solubility of a gas in a polymer, cm}^3\text{(STP)} / \text{g of polymer or g/g of polymer (weight %)} \\
C_0 \hspace{1cm} \text{concentration of gas molecules in solution, }#/\text{m}^3 \\
C_\infty \hspace{1cm} \text{concentration of the free-stream or initial concentration of gas molecules in solution, g/g of polymer} \\
c_p \hspace{1cm} \text{specific heat at constant pressure, kJ/kg\text{-}^\circ\text{C}} \\
D \hspace{1cm} \text{diffusivity of gas in polymer, cm}^2/\text{s} \\
D_0 \hspace{1cm} \text{diffusion coefficient constant, cm}^2/\text{s} \\
DP(s) \hspace{1cm} \text{design parameter(s)} \\
d \hspace{1cm} \text{diameter of a nozzle, m} \\
d_b \hspace{1cm} \text{unstretched diameter of disintegrated bubbles, m} \\
d_{\text{max}} \hspace{1cm} \text{maximum length of the elongated bubble in the shear field, m} \\
dC_S/\text{dt} \hspace{1cm} \text{solubility drop rate across the nozzle, 1/s} \\
-dp/\text{dt} \hspace{1cm} \text{pressure drop rate across the nozzle, Pa/s} \\
(-dp/\text{dt})_i \hspace{1cm} \text{pressure drop rate across nozzle i, Pa/s} \\
FR(s) \hspace{1cm} \text{functional requirement(s)}
$f_0$  frequency factor for homogeneous nucleation, $1/s$

$H$  Henry's Law constant for the polymer/gas system, cm$^3$(STP)/g·Pa

$H_0$  solubility gas constant, cm$^3$(STP)/g·Pa

$h$  heat transfer coefficient, W/m$^2$·°C

$k$  thermal conductivity, W/m·°C

$k$  Boltzmann's constant, J/K

$L$  length of the nozzle or the nozzle, m

$l$  edge length of a square, m

$l_d$  diffusion distance, cm

$m$  characteristic constant of a non-Newtonian fluid over a temperature range, N·s$^n$/m$^2$

$Nu$  Nusselt number ($= hd/k$)

$N_{hom}$  homogeneous microcell nucleation rate, cells/m$^3$s

$n$  dimensionless characteristic constant of a non-Newtonian fluid over a temperature range

$n_{bo}$  number of bubbles in a square of edge length 10 μm

$n_b$  number of bubbles in a square of edge length $l$

$p$  pressure, Pa

$p_b$  barrel pressure, Pa

$p_i$  gas injection pressure, Pa

$p_{in}$  inlet pressure of the flowing polymer melt, Pa

$p_{out}$  outlet pressure of the flowing polymer melt, Pa

$p_s$  gas saturation pressure, Pa

$Q_g$  gas flow rate, g/min

$Q_p$  polymer flow rate, g/min
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q$</td>
<td>volumetric flow rate of the polymer/gas solution, $\text{m}^3/\text{s}$</td>
</tr>
<tr>
<td>$R$</td>
<td>resistance of the porous material, $\text{Pa-min/g}$</td>
</tr>
<tr>
<td>$\mathcal{R}$</td>
<td>universal gas constant = $8.314 \text{ J/mol-K}$</td>
</tr>
<tr>
<td>$r$</td>
<td>radius, $\text{m}$</td>
</tr>
<tr>
<td>$r_s$</td>
<td>radius of the screw, $\text{m}$</td>
</tr>
<tr>
<td>$r_o$</td>
<td>radius of the nozzle, $\text{m}$</td>
</tr>
<tr>
<td>$s$</td>
<td>striation thickness of the mixture, $\text{cm}$</td>
</tr>
<tr>
<td>$s_0$</td>
<td>initial striation thickness of the mixture, $\text{cm or m}$</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, $\text{K or } ^\circ\text{C}$</td>
</tr>
<tr>
<td>$T_b$</td>
<td>bulk temperature of the flowing polymer melt, $^\circ\text{C}$</td>
</tr>
<tr>
<td>$T_{in}$</td>
<td>inlet bulk temperature of the flowing polymer melt, $^\circ\text{C}$</td>
</tr>
<tr>
<td>$T_{out}$</td>
<td>outlet bulk temperature of the flowing polymer melt, $^\circ\text{C}$</td>
</tr>
<tr>
<td>$T_w$</td>
<td>wall temperature of the heating tubes, $^\circ\text{C}$</td>
</tr>
<tr>
<td>$t$</td>
<td>time, $\text{s}$</td>
</tr>
<tr>
<td>$t_D$</td>
<td>diffusion time, $\text{s}$</td>
</tr>
<tr>
<td>$t_o$</td>
<td>reference time in a nozzle, $\text{s}$</td>
</tr>
<tr>
<td>$t_1$, $t_2$, $t_3$</td>
<td>arbitrarily small time period during nucleation, $\text{s}$</td>
</tr>
<tr>
<td>$u$</td>
<td>linear speed of the tip of the screw flight, $\text{m/s}$</td>
</tr>
<tr>
<td>$U_\infty$</td>
<td>velocity of the free-stream, $\text{m/s}$</td>
</tr>
<tr>
<td>$V$</td>
<td>total volume of polymer melt and gas bubbles, $\text{m}^3$</td>
</tr>
<tr>
<td>$V_i$</td>
<td>initial volume of unfoamed material, $\text{m}^3$</td>
</tr>
<tr>
<td>$V_f$</td>
<td>final volume of foamed material, $\text{m}^3$</td>
</tr>
<tr>
<td>$\dot{V}_g$</td>
<td>volume flow rate of gas ($=Q_g v_g$), $\text{cm}^3/\text{min}$</td>
</tr>
<tr>
<td>$\dot{V}_p$</td>
<td>volume flow rate of polymer melt ($=Q_p v_p$), $\text{cm}^3/\text{min}$</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity vector, $\text{m/s}$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$v_{avg}$</td>
<td>average velocity of the polymer/gas solution in the nozzle, m/s</td>
</tr>
<tr>
<td>$v_g$</td>
<td>specific volume of gas, cm$^3$/g</td>
</tr>
<tr>
<td>$v_p$</td>
<td>specific volume of polymer melt, cm$^3$/g</td>
</tr>
<tr>
<td>$v_z$</td>
<td>velocity component in z-direction, m/s</td>
</tr>
<tr>
<td>$W_e$</td>
<td>Weber number</td>
</tr>
<tr>
<td>$z$</td>
<td>axial coordinate in the flow direction, m</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>thermal diffusivity, m$^2$/s</td>
</tr>
<tr>
<td>$\Phi_v$</td>
<td>volume fraction of gas in the mixture</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>mean stretching ratio of the minor component</td>
</tr>
<tr>
<td>$\gamma_g$</td>
<td>mean stretching ratio of the gas bubbles</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>rate-of-strain tensor, s$^{-1}$</td>
</tr>
<tr>
<td>$\Delta C_s$</td>
<td>change of the gas solubility in polymer, g / g of polymer</td>
</tr>
<tr>
<td>$\Delta E_D$</td>
<td>activation energy for diffusion of a gas in a polymer, J/mol</td>
</tr>
<tr>
<td>$\Delta E_S$</td>
<td>heat of solution of polymer/gas system, J/mol</td>
</tr>
<tr>
<td>$\Delta G_{hom}$</td>
<td>change in Gibbs free energy for homogeneous nucleation, J</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>difference between initial solution pressure and nucleation solution pressure, Pa</td>
</tr>
<tr>
<td>$\Delta P_{i,j}$</td>
<td>pressure drop at time $t_i$ in the j-th nozzle, Pa</td>
</tr>
<tr>
<td>$-\Delta p$</td>
<td>difference between the inlet and outlet pressures, Pa</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>average residence time period of the polymer/gas solution in the nozzle, s</td>
</tr>
<tr>
<td>$\Delta t_i$</td>
<td>residence time period of the polymer/gas solution in the i-th nozzle, s</td>
</tr>
</tbody>
</table>
\( \Delta t_{\text{nuc}i} \) nucleation time period for the \( i \)-th nozzle, s

\( \Delta T_b \) bulk temperature rise of the flowing polymer melt

\( = T_{\text{out}} - T_{\text{in}} \), °C

\( \delta_C \) concentration boundary layer, m

\( \eta \) shear-rate dependent viscosity, Pa-s

\( \eta_p \) dynamic viscosity of polymer matrix, Pa-s

\( \eta_g \) dynamic viscosity of gas, Pa-s

\( \lambda \) the viscosity ratio \( = \eta_g / \eta_p \)

\( \rho \) density, kg/m³

\( \sigma \) surface tension or interfacial energy, N/m

\( \sigma_{bp} \) interfacial energy between gas bubble and polymer, N/m

\( \tau \) shear stress, Pa

\( \Omega \) RPM of the screw, min⁻¹
Chapter I

INTRODUCTION

I.1 Background on Foamed Plastics

There is a great demand for reducing the amount of material used in mass-produced plastics parts, for the material cost constitutes a large percentage of the total cost of a product, up to 75% (Martini, 1981). It may be noted that the price of plastics is directly related to the price of petroleum. Material reduction therefore decreases the amount of oil needed for the manufacture of plastics and thus help conserve this natural resource. Additionally, a reduction of the material reduces the weight which lowers transportation costs and eases handling.

One method of reducing the consumption of plastic materials is to use foamed plastics (Moiseyev, 1960; Hansen 1962; Benning, 1969; Saunders and Hansen, 1973; and Throne, 1979). A foamed plastic is a "composite" of a polymer matrix and gas bubbles. A foamed structure has the advantage of reduced weight and reduced material cost without a change in volume although it may increase the processing cost.
Conventional foams use physical or chemical blowing agents to nucleate gas bubbles. The quality of the foam produced depends on the amount and the distribution of the blowing agents. A nonuniform distribution of the blowing agents results in a foam that has a high concentration of gas bubbles or cells in agent-rich areas and a low concentration in agent-poor areas. The density of cells is determined by the concentration of the foaming agent. The large bubbles have a lower internal pressure and there is a steeper gas concentration gradient in the vicinity. Larger bubbles will then be energetically favored to grow at a faster rate than smaller bubbles because gas will preferentially diffuse toward the low-pressure area. As a result, larger bubbles grow at the expense of smaller bubbles and the bubble size distribution becomes highly nonuniform in the foam structure.

Because the number and the size of the bubbles are determined by the concentration of the foaming agent, the uniformity of the cell structure and the cell density (see Appendix A) are limited by the method used to mix the agent and the polymer. In fact, it is rather hard to obtain a uniform cell structure with a high cell density in chemically or physically blown foams. For conventional foams, typical cell densities are $10^3$-$10^6$ cells/cm$^3$, cell sizes are of the order of 100 μm or larger, and the cell size distribution is very nonuniform.

Furthermore, a number of issues need to be resolved in the conventional foam industry. Poor surface finish is one example. Bubbles are ruptured or flattened against the wall of the mold/die resulting in a poor finish such as surface swirl. Conventional foamed plastics also have lower strength and toughness compared with solid plastic parts. However, these
problems can be overcome by producing foams that have larger cell densities and smaller cell sizes.

Another problem with conventional foams is the hazard posed by the blowing agents. The most common blowing agents used in the foam industry are chlorofluorocarbons (CFCs) and aliphatic hydrocarbons. Because CFCs are known to destroy the ozone layer, there are strong social pressures and the government regulation to phase out the use of CFCs in order to protect the environment. Aliphatic hydrocarbons, such as pentane, used in polystyrene foams pose a severe fire hazard, which restricts the operational flexibility in foam manufacture. Because of these problems, there is a great need to replace the blowing agents in the foam industry.

I.2 Introduction to Microcellular Foamed Plastics

Microcellular plastics are foamed plastics characterized by cell densities greater than $10^9$ cells per cubic centimeter of unfoamed material and fully grown cell smaller than 10 μm. A typical fractograph of a microcellular plastic part is shown in Figure I.1. Microcellular plastics are based on the proposition that the creation of a large number of bubbles, smaller than the pre-existing natural flaws in a polymer, can reduce the material cost without major compromises to mechanical properties. Microcellular plastics have been shown to possess superior Charpy impact strength (Martini et al., 1982; Waldman, 1982) and toughness (Waldman, 1982; Baldwin and Suh, 1992) compared with solid polymers. Because of these unique properties, one can imagine a large number of innovative applications of microcellular plastics. These include light-weight and high-toughness parts, such as food containers,
Figure I.1: Typical Scanning Electron Micrograph of a Microcellular Foamed Plastic
safety helmets, sporting equipment, and structural parts in aircraft, and automotive components. Additionally, microcellular plastics would replace CFCs and aliphatic hydrocarbons in the foam industry since the processing of microcellular plastics does not use these hazardous blowing agents.

Microcellular plastics technology was originally developed by Martini and Suh (1984). Martini performed the first experiments and analyzed theoretically the formation and growth of microcellular foams (Martini, 1981; Martini et al., 1982). Waldman then investigated the mechanical properties and processing behavior of microcellular foams (Waldman, 1982). Process parameters were determined experimentally and the strategy for process design was presented. A method of producing light-weight polyester composites (LPCs) was developed by Youn (Youn, 1984; Youn and Suh, 1984). The microcellular structure of the LPCs led to weight reductions on the order of 30% compared with short fiber composites and no reduction in specific strength. In fact, the specific modulus and strength increased with microcellular foaming. Investigations into modeling microcellular thermoplastic nucleation were made by Colton (Colton, 1985; Colton and Suh, 1986; Colton and Suh, 1987abc; Colton and Suh, 1990). His model explained the effect of various additives and processing conditions on the number of bubbles nucleated. Kumar developed a semicontinuous manufacturing process using a modified thermoforming process (Kumar, 1988; Kumar and Suh, 1989, 1990). His basic approach for producing microcellular foamed parts with a geometry was to decouple the shaping process from the foaming process. The microcellular plastics technology was further improved by Cha et al. (1991). However, the majority of published research in microcellular
plastics have centered around products and batch processing of microcellular plastics. Continuous processes have not yet been developed extensively.

I.3 Objective of the Thesis

There has been a strong desire to develop a cost-effective continuous process for manufacturing microcellular plastics. When a cost-effective method of processing microcellular plastics is developed, the applications will be unlimited. The objective of this research thus is to develop a prototype of a continuous manufacturing process for microcellular plastics that makes the parts commercially viable and fully utilizes the unique properties of microcellular plastics.

I.4 Overview of the Thesis

Since the objective of the research is to develop a prototype of a continuous manufacturing process, some background on the processing of microcellular plastics is presented in Chapter II. Because gas and polymer systems are used to develop a microcellular structure, the thermodynamic and kinetic aspects of the gas and polymer systems are systematically analyzed using a batch process. In order to make use of the thermodynamic behavior of the gas and polymer system in a continuous process, in a manner similar to the batch process, two major process steps are considered: continuous formation of a polymer/gas solution and microcell nucleation by thermodynamic instability in the polymer/gas solution.

These problems are set in an axiomatic design framework in Chapter III which guides the process synthesis. First, the basic key concepts of axiomatic
design (Suh, 1990) are reviewed. Then the axiomatic approach is used in the
design of the overall manufacturing process. The main strategy for the
synthesis of the process is to integrate the central steps into an extrusion
process such that the overall process has independently controllable
functions. Then the polymer/gas solution formation process is decomposed
into the sub-levels of the hierarchical structure in the axiomatic framework.
The highest level functional requirements for the solution formation are
defined as: a) continuous formation of a two-phase polymer/gas mixture, and
b) completion of the dissolution process. A detailed design of the solution
formation process is carried out by choosing the appropriate design
parameters in the axiomatic framework.

Two central steps for the solution formation process are described in
detail in Chapters IV and V. Chapter IV focuses on the two-phase mixture
formation while Chapter V on the completion of the dissolution process.
First in Chapter IV, the solubilities of various gases in polymers at working
temperatures and pressures are estimated because only a soluble amount of
gas should be injected into the polymer melt stream. Next, the necessary flow
rate control of the gas and polymer streams for maintaining a constant weight
ratio of gas and polymer is presented. As a way of metering a minute flow of
a high pressure gas, a porous plug is used and the gas flow rate through the
porous material is calibrated for CO2 and N2. A high pressure pump for CO2
is also designed since commercial CO2 is available only up to 1,000 psi.

In order to produce a uniform and homogeneous single-phase solution
from a two-phase mixture at a rate appropriate for industrial processing, a
diffusion enhancing device is needed because the solution formation is
governed by gas diffusion. In Chapter V, a convective diffusion device for
enhancing the effectiveness of mixing and diffusion is designed for fast solution formation. The required processing time for solution formation is estimated from experimental data and the dispersive mixing theory based on an order of magnitude analysis. The diffusion coefficients of CO₂ and N₂ at high temperatures and pressures are estimated from the published data.

The next critical step is to promote a high rate of bubble nucleation in the polymer/gas solution. Chapter VI presents a rapid decompression element as a nucleation device for continuous processing of microcellular plastics. In order to make use of a thermodynamic instability of polymer/gas systems for promoting a high nucleation rate, a rapid drop in the solubility of the gas in the polymer is needed. Since the gas solubility in a polymer changes with pressure, a high nucleation rate can be induced by rapidly dropping the pressure. A theoretical analysis of the pressure drop rate for flowing non-Newtonian fluids is carried out in order to design a rapid decompression device.

The kinetics of polymer/gas solution formation and microcell nucleation by a thermodynamic instability is examined experimentally. In Chapter VII, based on the proposed design, the construction of an experimental extrusion set-up is detailed. Experiments are carried out to verify the design and to identify the critical parameters of the process. Various plastics including amorphous polymers and semicrystalline polymers are processed with high pressure carbon dioxide and nitrogen. Then discussions are presented. The experimental results are quantitatively compared and analyzed. Qualitative reasoning and arguments about the critical parameters are discussed to model the developed prototype.
Chapter VIII presents a summary and the conclusions of the thesis. Suggestions for future work are offered in Chapter IX.
Chapter II

BACKGROUND AND FOCUS OF RESEARCH

II.1 Background on Processing of Microcellular Plastics

In order to develop a prototype of a continuous manufacturing process for microcellular plastics, the physical phenomena underlying the batch process should be analyzed and the process variables of microcellular plastics should be characterized.

The key to producing a microcellular structure with a uniform bubble distribution is to nucleate all the bubbles at the same time and allow them to grow at the same rate. The blowing agent, gas, must be uniformly distributed, and simultaneous nucleation must be induced. A uniform concentration of gas can be produced by diffusing an inert gas under high pressure into a polymer; instantaneous nucleation can be induced through a thermodynamic instability which reduces the gas solubility very rapidly and precipitates the gas from the solution.
Figure II.1 shows a typical example of a batch process for producing microcellular plastics. A polymer is saturated with an inert gas, such as carbon dioxide or nitrogen, under a high pressure. This can be accomplished by placing the plastic in a pressure chamber for a desired period of time at room temperature (see Figure II.1 (a)). Then the gas-saturated polymer is subjected to a rapid pressure drop and a rapid temperature increase resulting in the nucleation and growth of billions of gas nuclei. This can be accomplished by opening the pressure chamber and heating the plastic above its glass transition temperature (see Figure II.1 (b)). The rapid decompression and rapid heating induce a sudden solubility drop of a gas in the polymer (Newitt and Weale, 1948; Durril and Griskey, 1966 and 1969). This is illustrated in Figure II.2. The sudden drop of gas solubility creates a thermodynamic instability in the polymer/gas solution, which is the main driving force for nucleation of microvoids. Martini (1981) and Waldman (1982) under the direction of Professor N. P. Suh at MIT conceived and developed this idea to promote a microcellular structure in polymers (Martini, Suh, and Waldman, 1984).

II.2 Problem Statement and Focus of Research

Figure II.3 shows the morphological change of gas and polymer systems in the batch process described in the previous section. Initially, the gas and polymer were separate systems that later become a single-phase solution. Then, a thermodynamic instability is induced in the polymer/gas solution to promote microcell nucleation. The formation of the polymer/gas solution and microcell nucleation are critical steps of microcellular manufacturing
Figure II.1: Typical Batch Process for Microcellular Foamed Plastics (Martini et al., 1984)
Figure II.2: Solubility Change of Polymer and Gas Systems in the Batch Process of Figure II.1
Figure II.3: Schematic of the Morphology Change of Polymer/Gas Systems in Overall Microcellular Foaming Process
processes.

In order to use a thermodynamic instability due to a sudden drop of gas solubility in the continuous process, in a manner similar to the batch process, these two central steps should be integrated into a single process. As a case study, this research considers a continuous extrusion process. The basic strategy for designing a continuous process is to decouple each step in the process by choosing appropriate design parameters (DPs) so as to satisfy the independence of functional requirements (FRs).

This thesis focuses on the design of the polymer/gas solution formation and microcell nucleation devices, the integration of the solution formation and nucleation steps into the conventional extrusion process, and the modeling of the process. The designed process is examined and analyzed through experimental work.
Chapter III

Axiomatic Design of an Extrusion Process

III.1 Review of the Key Concepts of Axiomatic Design (Suh, 1990)

The axiomatic approach is a systematic method for guiding the design of processes and analyzing the results. The axiomatic design approach comprises the following steps: 1) establishing design goals that fulfill a given set of observed needs, 2) conceptualizing design solutions, 3) analyzing the proposed solutions, 4) choosing the most suitable design from those proposed, and 5) implementing the chosen design. These activities occur between and within the four different design domains as illustrated in Figure III.1. The synthesis phase of the design process is called "mapping", which describes traversing from one domain to another. In general, synthesis involves taking what we want from one domain and mapping how we choose to achieve what we want onto the next domain. The first domain contains the customer needs for the design. These customer needs in the
Figure III.1: Concept of Domain, Mapping and Spaces in Design
consumer domain are mapped onto the functional domain where they are translated into a set of functional requirements (FRs). These functional requirements constitute a characteristic vector. These FRs are then mapped onto the physical domain by suitable design parameters (DPs). The DPs in the physical domain are mapped onto the process domain in terms of the process variables (PVs).

Another important aspect of axiomatic design is that the elements in each domain are decomposed into a hierarchy. However, the decomposition in each domain depends on the hierarchies in other domains. For example, in order to decompose a given level of the FR hierarchy, we must first proceed to the physical domain and construct a set of design parameters which satisfy the FRs. Then, we can return to the functional domain and decompose the FR. This is illustrated in Figure III.2.

Finally, the most important tenet of axiomatic design is the existence of two design axioms which must be satisfied during the mapping process. The first axiom provides the criterion for acceptable design; the second deals with the complexity of design. They are stated as follows:

Axiom 1: The Independence Axiom
Maintain the independence of functional requirements

Axiom 2: The Information Axiom
Minimize the information content.
Figure III.2: Hierarchical Tree Structures of Functional Requirements and Design Parameters
Once the functional requirements are defined and the design parameters are identified, the mapping process between the functional domain and the physical domain can be represented by a design equation as

\[ \{\text{FRs}\} = [A] \{\text{DPs}\} \]  \hspace{1cm} (III-1)

where \(\{\text{FRs}\}\) and \(\{\text{DPs}\}\) are vectors representing the functional requirements and the process variables, respectively, and \([A]\) is the design matrix. The elements of the matrix represent the degree of coupling between FR\(_i\) and DP\(_j\). The element, \(A_{ij}\), given by

\[ A_{ij} = \frac{\partial \text{FR}_i}{\partial \text{DP}_j} \]  \hspace{1cm} (III-2)

represents the magnitude effect of DP\(_j\) on FR\(_i\). For example, if the coefficient \(A_{ij}\) is zero, FR\(_i\) has a weak or independent relationship with DP\(_j\). If there is a strong relationship between FR\(_i\) and DP\(_j\), \(A_{ij}\) has some physical value and is denoted by "X". The main advantage of using this form is that it allows quick evaluation of the degree to which a proposed process satisfies the independence requirement of the first axiom.

In order to satisfy the Independence Axiom, \([A]\) must be either a diagonal or a triangular matrix. A design which has a diagonal matrix is called an uncoupled design. A design which has a triangular matrix is a decoupled design. Decoupled designs satisfy the Independence Axiom, provided that DPs are set in a specific sequence. When the design matrix is neither diagonal nor triangular, the design is termed coupled. Coupled
designs are unsatisfactory in the axiomatic approach and redesign is suggested.

III.2 Design of an Overall Process

The issues involved in developing a continuous process for making microcellular plastics are threefold. The first is to plasticate the polymer. The second is to create a polymer/gas solution at a rate appropriate for industrial production. The third is to promote a high rate of bubble nucleation in the polymer/gas solution. Therefore, the functional requirements (FRs) for developing a microcellular structure continuously can be stated as follows:

\[
\begin{align*}
FR_1 &= \text{plastication} \\
FR_2 &= \text{polymer/gas solution formation} \\
FR_3 &= \text{microcell nucleation.}
\end{align*}
\]

A plasticating screw in extrusion can be used for the plastication of the polymer. Then, a diffusion enhancing device can be employed for fast synthesis of a polymer/gas solution. Finally, a thermodynamic instability, in a similar manner to the batch process, can be utilized for microcell nucleation. Therefore, the design parameters (DPs) for satisfying the FRs can be chosen as follows:

\[
\begin{align*}
DP_1 &= \text{a plasticating screw} \\
DP_2 &= \text{a diffusion enhancing device} \\
DP_3 &= \text{a nucleation device which creates a thermodynamic}
\end{align*}
\]
instability.

Let us consider an extrusion process based on the chosen DPs as shown in Figure III.3. First, the plastication of the polymer will be accomplished in the extrusion barrel using a plasticating screw. Thereafter, a metered amount of gas will be delivered to the polymer melt stream. The polymer/gas mixture will become a single-phase solution in the solution formation device. Finally, a microcellular structure with a large cell density will be produced when the polymer/gas solution experiences a thermodynamic instability in the nucleation device. In this study, a simple filament die was chosen to simplify the shaping and cell growth stages.

The design equation for the extrusion process may be written as

\[
\begin{bmatrix}
\text{Plastication} \\
\text{Gas dissolution} \\
\text{Microcell nucleation}
\end{bmatrix}
= \begin{bmatrix}
A_{11} & A_{12} & A_{13} \\
A_{21} & A_{22} & A_{23} \\
A_{31} & A_{32} & A_{33}
\end{bmatrix}
\begin{bmatrix}
a \text{plasticating screw} \\
\text{a diffusion enhancing device} \\
\text{a nucleation device}
\end{bmatrix}
\]

(III-3).

The elements $A_{ij}$, representing the degree of coupling between FR$_i$ and DP$_j$, are next examined. The diagonal elements $A_{ii}$ are all non-zero because each DP$_i$ was chosen to directly correspond to FR$_i$. Let us examine the off-diagonal elements of the design matrix. The diffusion enhancing device and the nucleation device cannot affect the plastication. Therefore, the elements $A_{12}$ and $A_{13}$ are both zero. The plasticating screw affects the solution formation since the screw motion generates a shear field (see Chapter 5). However, the solution formation is not affected by the nucleation device.
Figure III.3: Designed Overall Extrusion Process
Therefore, $A_{21}$ is non-zero while $A_{23}$ are zero. The plasticating screw does not affect the microcell nucleation. The diffusion enhancing device does not affect the microcell nucleation when the polymer/gas solution is properly made with no potential nucleation sites left in the form of voids. Therefore, $A_{31}$ and $A_{32}$ are zero. According to these observations, Equation (III-3) now becomes

\[
\begin{bmatrix}
\text{Plastication} \\
\text{Gas dissolution} \\
\text{Microcell nucleation}
\end{bmatrix} =
\begin{bmatrix}
X & 0 & 0 \\
X & X & 0 \\
0 & 0 & X
\end{bmatrix}
\begin{bmatrix}
\text{a plasticating screw} \\
\text{a diffusion enhancing device} \\
\text{a nucleation device}
\end{bmatrix}
\] (III-4)

where "X" means that there is a strong relationship between the relevant FR and DP. Equation (III-4) is the design equation of the first level in the FR-DP hierarchy of Figure III.2. Since the design matrix is triangular, the considered extrusion process is decoupled. Therefore, this is an acceptable design.

### III.3 Design of a Solution Formation Process

One objective of this study is to produce a uniform and homogeneous polymer/gas solution at industrial processing rates from separate streams of gas and polymer. The physical phenomena behind the solution formation process should be analyzed and the critical process variables of the solution formation should be identified.

Figure III.4 shows the morphology change of polymer and gas systems in the solution formation process. Initially, a soluble amount of gas is injected into a polymer melt stream, forming a two-phase polymer/gas
Figure III.4: Schematic of the Morphology Change of Polymer/Gas Systems in the Solution Formation Process
mixture. Then, the injected gas bubbles are broken into smaller bubbles and stretched through shear mixing. Eventually, the gas diffuses into the polymer matrix, forming a single-phase solution.

Therefore, in order to continuously produce a single-phase polymer/gas solution out of two separate streams, two critical steps must be accomplished: a two-phase polymer/gas mixture with a constant weight ratio must be formed, and gas dissolution must be completed. Thus, the functional requirements (FRs) for the continuous solution formation can be stated as follows:

\[ \text{FR}_{21} = \text{continuous formation of a two-phase mixture with a constant weight ratio} \]
\[ \text{FR}_{22} = \text{completion of the dissolution process.} \]

The two-phase mixture formation with a constant weight ratio can be accomplished by metering each flow, and the completion of the dissolution process can be controlled by a mixing device. Mixing of the injected gas and polymer melt enhances gas diffusion because the mixing brings the polymer melt with a low gas concentration into contact with high gas concentration bubbles and increases the polymer/gas interfacial area per unit volume of polymer melt. Therefore, the design parameters (DPs) for satisfying the FRs can be chosen as follows:

\[ \text{DP}_{21} = \text{metering of the gas and the polymer melt flow} \]
\[ \text{DP}_{22} = \text{mixing.} \]
A solution formation process based on the chosen DPs is shown in Figure III.5. The design equation for this process can be written as

\[
\begin{bmatrix}
\text{Continuous formation of 2-phase mixture} \\
\text{Completion of dissolution process}
\end{bmatrix} =
\begin{bmatrix}
A_{11} & A_{12} \\
A_{21} & A_{22}
\end{bmatrix}
\begin{bmatrix}
\text{metering of each flow} \\
\text{mixing}
\end{bmatrix}
\]

(III-5).

The diagonal elements \(A_{ii}\) are all non-zero because each DP\(_i\) was chosen to satisfy the corresponding FR\(_i\). The formation of the two-phase mixture has no relationship with the mixing device; \(A_{12}\) is zero. However, the completion of the single-phase solution formation is affected by the metering of each flow because excessive gas would result in void formation in the polymer/gas solution. So, \(A_{21}\) is non-zero. Therefore, according to these observations, Equation (III-5) becomes

\[
\begin{bmatrix}
\text{Continuous formation of 2-phase mixture} \\
\text{Completion of dissolution process}
\end{bmatrix} =
\begin{bmatrix}
X & 0 \\
X & X
\end{bmatrix}
\begin{bmatrix}
\text{metering of each flow} \\
\text{mixing}
\end{bmatrix}
\]

(III-6).

Equation (III-6) is the design equation of the second level in the FR-DP hierarchy of Figure III.2. Since the design matrix is triangular, the design for the solution formation process is decoupled.

The two-phase mixture formation and the convective diffusion for completion of dissolution processes are described in detail in Chapter IV and
Figure III.5: Polymer/Gas Solution Formation in an Extrusion Barrel
Chapter V, respectively. The nucleation device mentioned in Section III.2 is described further in Chapter VI.
Chapter IV

FORMATION OF A TWO-PHASE POLYMER/GAS MIXTURE

IV.1 Estimation of Gas Solubility in Polymers at Elevated Temperatures

Only a soluble amount of gas should be injected into the polymer melt stream. Excessive gas would result in the formation of undesirable voids in the melt. Voids could be detrimental to the cell structure unless hollow cores are intended in the final product (Berins, 1991). The existence of voids prevents homogeneous nucleation because the gas molecules prefer to diffuse to larger cells (Martini, 1981), which results in the formation of hollow cavities in the final product.

The first task is to estimate the solubility of a gas in the polymer melt at the processing pressure and temperature. The control scheme for each flow will be discussed in a subsequent section.

In general, the solubility of a gas in a polymer changes with the
temperature and pressure (Newitt and Weale, 1948; Lundberg et al., 1966; Veith et al., 1966; Durril and Griskey, 1966 and 1969; van Krevelen, 1976; Koros and Paul, 1980; Weinkauf and Paul, 1990). As the pressure changes, the solubility can be expressed approximately as

\[ C_S = H p_S \]  

(IV-1)

where

\[ C_S = \text{solubility of a gas in a polymer, cm}^3(\text{STP}) / \text{g of polymer} \]

or \[ g \] / \[ g \text{ of polymer (weight %)} \]

\[ H = \text{Henry's Law constant for the polymer/gas system, cm}^3(\text{STP}) / \text{g-Pa} \]

\[ p_S = \text{gas saturation pressure, Pa}. \]

Equation (IV-1) is known as the Henry's Law. The Henry's Law constant is a function of temperature which can be expressed as

\[ H = H_0 \exp \left( - \frac{\Delta E_S}{RT} \right) \]  

(IV-2)

where

\[ H_0 = \text{solubility gas constant, cm}^3(\text{STP}) / \text{g-Pa} \]

\[ \Delta E_S = \text{heat of solution of polymer/gas system, J/mol} \]

\[ R = \text{universal gas constant} = 8.314 \text{ J/mol-K}. \]

Combining Equations (IV-1) and (IV-2), the solubility can be expressed as

\[ C_S = H_0 p_S \exp \left( - \frac{\Delta E_S}{RT} \right) \]  

(IV-3).
Only a limited amount of data is available for polymer/gas solubilities at high temperatures and pressures (Newitt and Weale, 1948; Lundberg et al., 1966; Durril and Griskey, 1966 and 1969; Weinkauf and Paul, 1990). The heat of solution calculated from the data measured at temperatures lower than \( T_g \) is not useful because the solubility changes dramatically near \( T_g \) (Moisan, 1985; Weinkauf and Paul, 1990). Durril and Griskey's data (1966 and 1969) was used to estimate the solubilities of \( \text{CO}_2 \) and \( \text{N}_2 \) in various polymers at 200 °C and 27.6 MPa (4,000 psi), which are a typical processing temperature and pressure, respectively. At these processing conditions, the solubilities of \( \text{CO}_2 \) and \( \text{N}_2 \) in most polymers are approximately 10% and 2% by weight, respectively. The estimated solubilities are summarized in Table IV.1.

### IV.2 Flow Control of a High Pressure Gas

#### IV.2.1 Overview

In order to produce a two-phase polymer/gas mixture with a constant weight ratio, the flow rate of the gas and polymer streams must be controlled. The functional requirements (FRs) for maintaining a constant weight ratio of the gas and the polymer melt can be stated as

\[
\text{FR}_{211} = \text{metering of the polymer flow rate} \\
\text{FR}_{212} = \text{metering of the gas flow rate.}
\]

The polymer flow rate is easily controlled by the rotational speed of the extruder screw. The metering of the gas flow rate is more difficult because the
Table IV.1: Estimated Gas Solubility in Polymers
at 200 °C and 27.6 MPa (4,000 psi)
(Durril and Griskey, 1966 and 1969)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CO₂ weight gain (%)</th>
<th>N₂ weight gain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td>PP</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>PS</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>PMMA</td>
<td>13</td>
<td>1</td>
</tr>
</tbody>
</table>
flow rate is very small, the working pressure is very high, and the viscosity of gas is very low.

From the previous section, the weight ratio of the gas flow rate with respect to the polymer flow rate was estimated to be 10%. If the polymer flow rate is $Q_p$ g/min, the gas flow rate should be $0.1 \ Q_p \ g/\min$. Since the pressure at which the gas is delivered into the extrusion barrel is typically 27.6 MPa (4,000 psi), the specific volume of CO$_2$ is approximately 3 cc/g at 200 °C (IUPAC, 1973). Therefore, the volume flow rate of the gas is approximately $0.3 \ Q_p \ cc/\min$. For a 3/4 inch extruder with a 0.025 inch diameter finnament die, as used in the experiments, a typical polymer flow rate is $Q_p = 20 \ g/\min$. The corresponding gas flow rate is 6 cc/min. Considering the low viscosity of the gas and the sealing difficulty, controlling a gas flow rate this low at such an elevated pressure is very difficult.

IV.2.2 Design I: Flow Control by a Positive Displacement Pump

One way of controlling the gas flow rate is by using a positive displacement pump/compressor. Figure IV.1 shows a schematic diagram of using a positive displacement pump to meter the gas flow. One characteristic of the positive displacement pump is that the output is unaffected by variations of system pressure because a positive internal seal against leakage is present (Ogata, 1978). The gaseous volumetric output is controlled by the pump, thereby allowing the flow rate of the gas to be controlled independently of the barrel pressure.

The design parameters (DPs) for the set of FRs stated in Section IV.2.1 can be chosen as
Figure IV.1: Schematic of Polymer/Gas Mixture Formation Using a Positive Displacement Pump and a Plasticating Screw
DP_{211} = \text{rotational speed of the screw}

DP_{212} = \text{volumetric output of the positive displacement pump.}

Then, the design equation for metering each flow becomes

\[
\begin{bmatrix}
\text{Polymer flow rate control} \\
\text{Gas flow rate control}
\end{bmatrix} = \begin{bmatrix} X & 0 \\ 0 & X \end{bmatrix} \begin{bmatrix}
\text{speed of the plasticating screw} \\
\text{volumetric output of the pump}
\end{bmatrix}
\] (IV-4).

First, the polymer melt flow rate is not affected by the gaseous volumetric output of the positive displacement pump. Also, the gas flow rate has no relationship with the barrel pressure which is determined by the speed of the screw. According to these observations, the design matrix is diagonal, and therefore, the designed metering process is uncoupled. Equation (IV-4) is the design equation of the third level in the FR-DP hierarchy of Figure III.2.

The design equation does not tell us anything about the information content of the designed system. Information content is defined as the measure of knowledge required to satisfy a given functional requirement at a given level of the FR hierarchy (Suh, 1990). According to the second axiom, a design with less information is better. Because the information content is related to complexity, the second axiom simply states that a simpler design is better. Due to the sealing difficulty of high pressure gas, the dynamic internal seal in the pump would be very complex. As a result, the cost of the pump would be very high. For example, a commercial positive displacement pump for CO\textsubscript{2} costs about $15,000. This, however, would be appropriate for an industrial application because the marginal cost of the pump per product
would be low when parts are mass-produced.

IV.2.3 Design II: Flow Control by a Porous Material

Another method for controlling the flow rate of the gas is to use a porous material that is highly resistant to the flow of gas. The difference between the upstream and downstream pressures is the driving force for the gas flow. Figure IV.2 shows a schematic diagram of the flow through a porous material. The gas flow rate through the porous material to a first order approximation can be expressed as

\[ Q_g = \frac{P_i - P_b}{R} \]  \hspace{1cm} (IV-5)

where

- \( P_i \) = gas injection pressure, Pa
- \( P_b \) = barrel pressure, Pa
- \( R \) = "resistance" of the porous material, Pa-min/g.

If the upstream gas injection pressure is chosen as the design parameter to control the gas flow rate, then the design parameters (DPs) for the set of FRs given in Section IV.2.1 can be stated as

- \( DP_{211} \) = rotational speed of the screw
- \( DP_{212} \) = upstream gas injection pressure.

Then the design equation for the metering of each flow is as follows:
Figure IV.2: Gas Flow through a Porous Material
\[
\begin{bmatrix}
\text{Polymer flow rate control} \\
\text{Gas flow rate control}
\end{bmatrix} =
\begin{bmatrix}
X & 0 \\
X & X
\end{bmatrix}
\begin{bmatrix}
\text{speed of the plasticating screw} \\
\text{upstream gas injection pressure}
\end{bmatrix}
\] (IV-6).

First, the polymer melt flow rate is not affected by the gas injection pressure. However, the rotational speed of the screw affects the barrel pressure, thereby affecting the gas flow rate. According to these observations, the design matrix is triangular, and therefore, the designed metering process is decoupled. Equation (IV-6) is the design equation of the third level of the FR and DP domains in Figure III.2.

The designed metering process is shown in Figure IV.3. 35 gas injection ports are used to increase the interfacial area of the gas and polymer melt in the early mixing stages.

**IV.3 Calibration of the Gas Flow Rate through the Porous Material**

An experimental set-up was designed to calibrate the gas flow rate through a porous material (model #: Mott 5000-1/4-10) as shown in Figure IV.4. The upstream gas injection pressure is controlled by the pressure regulator, and the downstream pressure is controlled by a metering valve (model #: Whitey SS31RF2-G). The design equation for this experimental apparatus is

\[
\begin{bmatrix}
\text{Upstream pressure control} \\
\text{Downstream pressure control}
\end{bmatrix} =
\begin{bmatrix}
X & 0 \\
X & X
\end{bmatrix}
\begin{bmatrix}
\text{pressure regulator} \\
\text{metering valve}
\end{bmatrix}
\] (IV-7).
Figure IV.3: Control of the Gas Flow Rate Using a Porous Material
Figure IV.4: Set-up for the Calibration of the Gas Flow Rate through the Porous Material
When the flow rate and the pressures are at steady state, the flowing gas is collected for one minute and measured. The gas flow rates were measured for a range of upstream pressures and downstream pressures. Figure IV.5 (a) shows the calibration curve for CO\(_2\) flow rate through the porous material in terms of the gas injection pressure (p\(_i\)) and the barrel pressure (p\(_b\)). For example, if the barrel pressure is 27.6 MPa (4,000 psi) and the gas injection pressure is 34.5 MPa (5,000 psi), then the flow rate of CO\(_2\) is 2 g/min. So when the flow rate of the polymer melt is 20 g/min, the gas injection pressure should be tuned to be 34.5 MPa (5,000 psi) to maintain a 10% weight ratio. The gas flow rates of N\(_2\) through the porous material were also measured for a range of upstream pressures and downstream pressures. The calibration curve for N\(_2\) is shown in Figure IV.5 (b).

Because the porous material is easily contaminated by impurities in the gas, a filtering element (model #: Nupro SS4TF-05) was used. Metering the gas flow rate using a porous material is a good design because of its simple geometry, its nearly linear resistor behavior, and its decoupled characteristic.

### IV.4 Design of a High Pressure Pump for CO\(_2\)

#### IV.4.1 Overview

In order to inject a gas at a desired rate into the extrusion barrel, the gas should be supplied upstream under a desired high pressure. According to the calibration curves of Figure IV.5, gas at a pressure of at least 34.5 MPa (5,000 psi) is needed to maintain a 10% weight ratio of gas for a typical barrel pressure, P\(_b\) = 27.6 MPa (4,000 psi), and a typical polymer flow rate, Q\(_p\) = 20...
(a) CO\textsubscript{2} Calibration Curve

(b) N\textsubscript{2} Calibration Curve

Figure IV.5: Calibration Curves of the Gas Flow Rate through the Porous Material
g/min. However, carbon dioxide is commercially available only up to 5.9 MPa (850 psi) at room temperature. A simple pump for supplying high pressure CO₂ needs to be designed.

IV.4.2 Design of a Pneumatic High Pressure Pump for CO₂

Since high pressure (6,000 psi) nitrogen is commercially available, the injection of nitrogen as a blowing agent is not problematic. Moreover, a simple pneumatic system using nitrogen as a driving power fluid can also be designed.

Figure IV.6 shows a schematic diagram of a design for producing high pressure CO₂ using high pressure N₂. Carbon dioxide at 5.9 MPa (850 psi) enters the pump and is pressurized by high pressure N₂ through a piston. Then, the highly pressurized CO₂ is supplied to the extrusion barrel. Since the CO₂ pressure is equal to the N₂ pressure, the CO₂ pressure can be controlled by the pressure regulator (model #: Matheson 3066-1/4) of the N₂ cylinder.

An undulated surface on the piston would prevent the seizure of the piston (Suh, 1986). However, the manufacturing of the piston and the inside wall of the pump would be difficult. This design is modified to a simpler one as described in the following section.

IV.4.3 Modified Design of the Pneumatic High Pressure Pump for CO₂

The modified design is illustrated in Figure IV.7. Because this design does not use a piston, the modified design is simpler and better. The CO₂ is
Figure IV.6: Design of a High Pressure Pump for CO₂
Figure IV.7: Modified Design of a High Pressure Pump for CO₂
still pressurized by high pressure N₂. The first task is to change the phase of CO₂ from gas to liquid. First, the pump is filled with gaseous CO₂ at 5.9 MPa (850 psi). The wall temperature of the pump is lowered using ice while the CO₂ inlet valve (valve 1) is opened. The N₂ inlet valve (valve 2) and the CO₂ outlet valve (valve 3) are closed at this time. The CO₂ gas is liquified locally at the wall of the pump because the equilibrium phase of CO₂ at 5.9 MPa (850 psi) and 0 °C is liquid (IUPAC, 1973). Gravity causes the liquified CO₂ to collect at the bottom of the tank. More CO₂ flows into the pump during the liquidification of the CO₂ (Cha et al., 1991). When the CO₂ is liquified at the wall, the specific volume of the CO₂ decreases and the pressure inside the pump tends to decrease. Since the pump is connected to a 5.9 MPa (850 psi) pressure source, the local liquidification of CO₂ causes more CO₂ to flow into the pump in order to maintain the pressure. The states of CO₂ during this process can be seen in Figure IV.8. Since the CO₂ gas cylinder provides saturated gas at 5.9 MPa (850 psi), the pump is filled with the saturated gas at this pressure (state "A"). Then some of the saturated gas becomes locally liquified (state "B") at the wall because the temperature of the wall is 0 °C and the pressure is 5.9 MPa (850 psi). More CO₂ flows in to compensate for the specific volume difference until the entire volume of the pump is filled with the liquid at state "B".

When the whole volume is filled with liquid CO₂ at 5.9 MPa (850 psi), valve 1 is closed and valve 2 is opened. Then the liquified CO₂ is pressurized as the high pressure N₂ flows in. The liquid CO₂ can be pressurized up to a desired pressure using the pressure regulator of N₂ as in the previous design. This pressurized CO₂ is metered and injected into the barrel.
Figure IV.8: Pressure - Specific Volume Diagram of CO₂
Since N₂ is in a gaseous phase, liquid CO₂ and gaseous (more precisely supercritical) N₂ are not mixed together unless there is a sudden flow of the N₂ into the CO₂ when valve 2 is opened. A flow restrictor (model #: Mott 5000-1/4-250) is placed next to the opening of valve 2 to prevent a sudden incoming flow of N₂. When the liquid CO₂ is pressurized as a separate phase, diffusion of N₂ into the CO₂ bath occurs at the phase boundary.

Contamination of the CO₂ bath by the N₂ molecule diffusion is considered here. The total volume of the pump is designed to be 110 cm³. The desired CO₂ flow rate was estimated as 2 g/min for a typical polymer flow rate \( Q_p = 20 \) g/min. Because the specific volume of CO₂ at 5.9 MPa (850 psi) and \( 0 \) °C is 1.06 cc/g (IUPAC, 1973), the equivalent volumetric flow rate is 2.1 cc/min. If the entire volume of the pump is initially filled with the CO₂ liquid at 5.9 MPa (850 psi) and \( 0 \) °C, then the pump can inject the CO₂ into the extrusion barrel for 52 minutes. The diffusion depth of N₂ during this time can also be estimated.

A typical diffusion coefficient of gas in a liquid is approximately \( 1.0 \times 10^{-5} \) cm²/s (Bird et al., 1960a), and the diffusion depth, \( l_D \), of N₂ molecules for 52 minutes is estimated as

\[
l_D = \sqrt{D t_D} = \sqrt{(1 \times 10^{-5}) (52 \times 60)} \text{ cm} = 0.2 \text{ cm}
\]  

(IV.8)

where

\[
D = \text{diffusion coefficient, cm}^2/\text{s}
\]

\[
t_D = \text{diffusion time, s.}
\]

Since the diffusion depth is very small compared to the length of the pump, 18.3 cm, the contamination of CO₂ by diffused N₂ can be neglected.
Figure IV.9 shows the actual high pressure pump for CO₂. The pump was designed according to the ASME Boiler and Pressure Vessel Code (ASME, 1989).
Figure IV.9: Pneumatic Pump for Injecting High Pressure CO₂
Chapter V

COMPLETION OF SINGLE-PHASE POLYMER/GAS SOLUTION FORMATION

V.1 Overview

One of the critical steps in the continuous production of microcellular plastics is the completion of polymer/gas solution formation at a reasonable rate. Formation of a homogeneous single-phase solution from a two-phase mixture of polymer and gas is governed by gas diffusion.

Diffusion of gases in polymers is known to be very slow. For example, the diffusion coefficient of CO₂ in most thermoplastics at room temperature is approximately 5x10⁻⁸ cm²/s (van Krevelen, 1976). The time, \( t_D \), required for a gas to diffuse through a distance of 0.5 mm is estimated as

\[
t_D = \frac{D}{\bar{D}} = 50,000 \text{ s} = 14 \text{ h}
\]

(V-1)

where

\( \bar{D} = \text{diffusion distance, cm} \)
D = diffusion coefficient, cm²/s.

This means that it takes approximately 14 hours to saturate a 1 mm thick sheet of plastic with a gas in the batch process described in Section II.1.

In order to produce microcellular plastics at industrial processing rates, a technique for rapid formation of a polymer/gas solution needs to be developed. The two basic strategies for rapid solution formation are increasing the diffusion coefficient by increasing the temperature and reducing the diffusion distance through convective diffusion.

V.2  Estimation of the Diffusion Coefficient at Elevated Temperatures

In general, the diffusion coefficient of a gas in a polymer changes with temperature, pressure, and gas concentration (Newitt and Weale, 1948; Durril and Griskey, 1966 and 1969; van Krevelen, 1976; Koros and Paul, 1980), and can be approximated as

\[ D = D_0 \exp \left( -\frac{\Delta E_D}{kT} \right) \]  

(V-2)

where

\[ D_0 = \text{diffusion coefficient constant, cm}^2/\text{s} \]
\[ \Delta E_D = \text{activation energy for diffusion, J/mol.} \]

In this expression, the effect of the concentration dependence on the diffusion coefficient is neglected. Since the diffusion coefficient increases as the
temperature increases, the rate of gas diffusion is enhanced by processing the polymer/gas mixture at elevated temperatures, for example in the heated extrusion barrel.

Only limited data is available for gas diffusion in polymers at high temperatures (Newitt and Weale, 1948; Durril and Griskey, 1966 and 1969; van Krevelen, 1976). The estimated diffusion coefficients are summarized in Table V.1. At 200 °C, a typical diffusion coefficient of CO$_2$ or N$_2$ in a thermoplastic is approximately 10$^{-6}$ cm$^2$/s, which is two orders of magnitude greater than a typical diffusion coefficient, 10$^{-8}$ cm$^2$/s, at room temperature.

V.3 Basic Concept of Convective Diffusion: Mixing and Diffusion

Mass transfer by molecular diffusion is analogous to heat transfer because the heat conduction and diffusion equations have the same form (Bird et al., 1960b). The heat transfer rate is enhanced by convection. A convective flow causes fluid particles of lower (or higher) temperature to be brought into contact with the heat source resulting in a higher temperature gradient near the source. The heat transfer rate is promoted by the higher temperature gradient. Similarly, the diffusion rate can also be enhanced by convection. Convection brings low gas concentration polymer into contact with high gas concentration bubbles. This convective flow induces a high concentration gradient which promotes diffusion.

When the diffusion source is stationary and exhibits a simple shape, such as a flat plate as shown in Figure V.1, the concentration profile is similar to the temperature profile associated with a similar heat source. Therefore, the concentration profile may be expressed from known heat transfer
Table V.1: Estimated Diffusion Coefficient of Gases in Polymers at Elevated Temperatures

<table>
<thead>
<tr>
<th>Polymer</th>
<th>D of CO₂ (cm²/s) at 188 °C</th>
<th>D of CO₂ (cm²/s) at 200 °C</th>
<th>D of N₂ (cm²/s) at 188 °C</th>
<th>D of N₂ (cm²/s) at 200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>-</td>
<td>1.3 x 10⁻⁵</td>
<td>-</td>
<td>1.5 x 10⁻⁵</td>
</tr>
<tr>
<td>PP</td>
<td>4.2 x 10⁻⁵</td>
<td>-</td>
<td>3.5 x 10⁻⁵</td>
<td>-</td>
</tr>
<tr>
<td>PET</td>
<td>-</td>
<td>2.6 x 10⁻⁶</td>
<td>-</td>
<td>8.8 x 10⁻⁷</td>
</tr>
<tr>
<td>HDPE</td>
<td>5.7 x 10⁻⁵</td>
<td>2.4 x 10⁻⁵</td>
<td>6.0 x 10⁻⁵</td>
<td>2.5 x 10⁻⁵</td>
</tr>
<tr>
<td>LDPE</td>
<td>-</td>
<td>1.1 x 10⁻⁴</td>
<td>-</td>
<td>1.5 x 10⁻⁴</td>
</tr>
<tr>
<td>PTFE</td>
<td>-</td>
<td>7.0 x 10⁻⁶</td>
<td>-</td>
<td>8.3 x 10⁻⁶</td>
</tr>
<tr>
<td>PVC</td>
<td>-</td>
<td>3.8 x 10⁻⁵</td>
<td>-</td>
<td>4.3 x 10⁻⁵</td>
</tr>
</tbody>
</table>

* Durril and Griskey (1966 and 1969)
† Van Krevelen (1976)
Figure V.1: Diffusion Boundary Layer on a Flat Plate
solutions with an appropriate change in notation. Typical examples are the concentration boundary layer on a flat plate, the concentration profile in a flow between the parallel plates, and the concentration profile in a flow through a circular pipe. The diffusion rates are promoted by a forced convective flow.

When the diffusion source is also moving, the analysis of the problem becomes complicated. In investigating the local concentration profile, the first step is to trace the shape of the source boundary. Since the diffusion sources in this study are the gas bubbles which are moving along the polymer melt, the dynamic behavior of the gas bubbles and the polymer melt should be investigated first. The diffusion phenomena will then be analyzed based on the mixing behavior of the gas bubbles and the polymer melt.

As the gas molecules diffuse into the polymer matrix, the total volume of the gaseous phase diminishes in size until the gas completely dissolves into the matrix. Since the size of one phase component is changing, the mixing behavior of the two-phase mixture is far more complicated than simple mixing. It is very difficult to investigate the mixing behavior of the two-phase mixture and the flow fields of each phase. Since the diffusion phenomenon strongly depends on mixing behavior, the analysis of the mass transfer phenomena of diffusion is also complicated. The diffusion of gas into the polymer matrix may not be completely analyzed.

Despite the complication of modeling the dynamic behavior of the mixture of the two fluids, the diffusion rate is greatly enhanced when the diffusion source is also moving. As the degree of mixing increases, more polymer melt is brought into contact with the source of the high gas concentration which increases the effect of convective diffusion. This
convective diffusion effect is enhanced through an increase in the interfacial area per unit volume, a reduction of the diffusion distance, and a redistribution of the local gas concentration profile in the polymer matrix. In addition, since the diffusion rate strongly depends on the mixing behavior, the diffusion time can be controlled by varying the degree of mixing.

V.4 Convective Diffusion in an Extrusion Barrel

V.4.1 Overview

One technique for rapid solution formation using convective diffusion employs laminar mixing in the molten polymer shear field. The shearing action of the extrusion screw draws small bubbles of gas into the molten polymer shear field. The mixing action of the shear field slowly disperses the gas bubbles into the polymer matrix. The gas eventually diffuses into the polymer, forming a single-phase solution. At typical industrial processing rates, the mixing of the polymer and gas must result in striation thicknesses such that the gas will diffuse into the polymer melt within a reasonable length of time.

When the gas and polymer melts are mixed in an extrusion barrel, the gas bubbles are stretched by the generated shear field, resulting in the increase in the gas-polymer interfacial area. As this interfacial area between the gas and the polymer melt increases, the diffusion of gas into the polymer melt is promoted. The movement of the concentration source and the diminishing of the total volume of the gaseous phase component causes the analyses of
the mixing behavior of the two-phase mixture and the diffusion phenomena to be very difficult.

However, we can still estimate the diffusion time for completing the solution formation based on the estimated striation thickness of the gas and polymer mixture.

As an order of magnitude, the diffusion distance, $l_D$, is estimated as

$$l_D = \sqrt{D t_D}$$

(V-3)

where

$D =$ diffusion coefficient, cm$^2$/s

$t_D =$ diffusion time, s.

The time at which the diffusion distance is of the same order as the striation thickness of the mixture (see Section V.4.2) can be estimated as the diffusion time:

$$t_D = \frac{l_D^2}{D} = \frac{s^2}{D}$$

(V-4)

where

$s =$ striation thickness of the mixture, cm.

The estimated diffusion times are shown in Table V.2 for various striation thicknesses and diffusion coefficients. For example, if the striation thickness is less than 100 μm, the diffusion of gas would be completed within 2 minutes for a typical diffusion coefficient of $10^{-6}$ cm$^2$/s at 200 °C (see Section V.2).
Table V.2: Estimated Diffusion Time at Various Striation Thicknesses and Diffusion Coefficients

<table>
<thead>
<tr>
<th>Striation Thickness (s)</th>
<th>Diffusion Coefficient (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{-5} \text{cm}^2/\text{sec}$</td>
</tr>
<tr>
<td>1 $\mu$m</td>
<td>$1 \times 10^{-3}$ sec</td>
</tr>
<tr>
<td>10 $\mu$m</td>
<td>0.1 sec</td>
</tr>
<tr>
<td>50 $\mu$m</td>
<td>2.5 sec</td>
</tr>
<tr>
<td>100 $\mu$m</td>
<td>10 sec</td>
</tr>
<tr>
<td>250 $\mu$m</td>
<td>63 sec</td>
</tr>
<tr>
<td>500 $\mu$m</td>
<td>4 min</td>
</tr>
<tr>
<td>750 $\mu$m</td>
<td>9 min</td>
</tr>
<tr>
<td>1 mm</td>
<td>17 min</td>
</tr>
</tbody>
</table>
The estimation of striation thickness is based on the dispersive mixing theory, and the basic experiments for investigating the stretching behavior of gas and polymer in a shear field are described in the following sections.

V.4.2 Striation Thickness: Degree of Mixing

Because the diffusion rate strongly depends on the degree of mixing, the mixing behavior of the gas and polymer melt is investigated. The mixing theory of highly viscous fluids describes the growth of interfacial areas in different types of shear flows. The interfacial area per unit volume is a key measure of mixing (Spencer and Willy, 1949). Related to this interfacial area per unit volume is the striation thickness, s, which is defined as the average distance between similar interfaces of the components in the mixture. These two parameters representing the degree of mixing are related by the expression (Schrenk et al., 1963):

$$ s = \frac{2V}{A} = \frac{2}{A/V} \quad (V-5) $$

where

- $A =$ interfacial area of gas bubbles and polymer melt matrix, m$^2$
- $V =$ total volume of the polymer melt matrix and gas bubbles, m$^3$.

From Equation (V-5), the striation thickness as a function of stretching can be expressed as (Mohr et al., 1957; Kim et al., 1972)

$$ s = \frac{s_0}{\Phi_v \gamma} \quad (V-6) $$
where

\[ s_o = \text{initial striation thickness, m} \]
\[ \Phi_V = \text{volume fraction of the minor component} \]
\[ \gamma = \text{mean stretching ratio of the minor component}. \]

Therefore, the initial striation thickness, the volume fraction of gas, and the mean stretching ratio should be estimated in order to estimate the striation thickness.

V.4.3 Estimation of the Disintegrated Bubble Size and the Initial Striation Thickness

The mixing behavior of a gas in a polymer melt follows the dispersive mixing theory (Bolen and Colwell, 1958; Tadmor and Gogos, 1979). This theory states that the minor components, gas bubbles in the present case, are stretched by the shear forces and disintegration of the bubbles takes place when the stretching exceeds a critical value of the Weber number (Taylor, 1934; Rumscheidt and Mason, 1961, Mutsakis et al., 1986). The Weber number, \( \text{We} \), is defined as

\[
\text{We} = \frac{\gamma d_b \eta_p f(\lambda)}{2 \sigma} = \frac{\text{shear forces}}{\text{surface forces}}
\]  

(V-7)

where

\[
f(\lambda) = \frac{19 \lambda + 16}{16 \lambda + 16}
\]  

(V-8)
\[ \lambda = \text{viscosity ratio} \left(= \frac{\eta_g}{\eta_p} \right) \]
\[ \eta_g = \text{dynamic viscosity of gas, Pa-s} \]
\[ \eta_p = \text{dynamic viscosity of polymer matrix, Pa-s} \]
\[ \gamma = \text{shear rate in mixer, s}^{-1} \]
\[ d_b = \text{bubble diameter, m} \]
\[ \sigma = \text{surface tension, N/m}. \]

For typical values of \( \eta_p \) and \( \eta_g \) (Vukalovich and Altunin, 1968), the disintegrated bubble diameter can be estimated as follows:

\[ \eta_p = 2 \times 10^2 \text{ Pa-s} \]
\[ \eta_g = 3 \times 10^{-5} \text{ Pa-s} \]
\[ \lambda = \frac{\eta_g}{\eta_p} = 1.5 \times 10^{-7} \quad (V-9) \]
\[ f(\lambda) = 1 \quad (V-10) \]

The critical Weber number for a viscosity ratio of \( 1.5 \times 10^{-7} \) in a simple shear field is estimated as (Karan and Bellinger, 1968) \( \text{We} = 390 \).

The surface tension of polystyrene at 200 °C is (Wu, 1970)

\[ \sigma = 40.7 - 0.072 \ (T-293) = 28 \text{ dyne/cm} = 0.028 \text{ N/m} \quad (V-11). \]

The shear strain rate in an extrusion barrel for the screw RPM of 90 min\(^{-1}\) and the screw channel depth of 0.8 mm is estimated as
\[
\dot{\gamma} = \frac{u}{b} \frac{r_s (2\pi \Omega / 60)}{b} = \frac{8.7 \text{ mm} \times (2\pi \times 90 / 60)}{0.8 \text{ mm}} = 100 \text{ s}^{-1}
\]  
(V-12)

where

\[u = \text{linear speed of the tip of the screw flight, m/s}\]

\[b = \text{channel depth of the screw, m}\]

\[r_s = \text{radius of the screw, m}\]

\[\Omega = \text{RPM of the screw, min}^{-1}\]

Finally, the disintegrated bubble size is determined as

\[
d_b = \frac{2 \sigma \text{We}}{\dot{\gamma} \eta_p f(\lambda)} = \frac{2 \times 0.028 \times 300}{100 \times 2 \times 10^2 \times 1} = 8.4 \times 10^{-4} \text{ m} = 1 \text{ mm}
\]  
(V-13)

Therefore, when the gas is injected into the extrusion barrel, the large injected bubbles are stretched and disintegrated into 1 mm diameter bubbles in the shear field generated by the screw.

Figure V.2 shows a hypothetical model of the polymer melt and the disintegrated gas bubbles. Because the large bubbles are stretched and disintegrated into 1 mm diameter bubbles, these bubbles remain stretched. The hypothetical model considers unstretched 1 mm bubbles for estimating the initial striation thickness.

Let's consider a two-dimensional case. For a disintegrated bubble size of 1 mm and a gaseous volume fraction of 0.22 (see Appendix B), the initial striation thickness in Equation (V-6) can be derived as follows:
Figure V.2: Hypothetical Model of the Unstretched Disintegrated-Bubbles and the Polymer Melt for Estimation of the Initial Striation Thickness
\[
\Phi_v = 0.22 = \frac{3 \times \frac{1}{6} \pi \frac{d_b^2}{4}}{\frac{\sqrt{3}}{4} s_o^2}
\]  
(V-14)

or

\[
s_o = 2 d_b
\]  
(V-15)

Therefore, the initial striation thickness is approximately double the disintegrated bubble size.

V.4.4 Estimation of the Bubble Stretching Ratio

In order to estimate the bubble stretching ratio in the shear field of the extrusion barrel, an experimental apparatus which generates a simple shear field was used as shown in Figure V.3. The stretching behavior of a 1 mm diameter air bubble in a silicone fluid (Dow Corning #200 Fluids) bath was investigated. The rotating disk and the container are transparent so that the stretching behavior of the air bubble can be observed.

The bubble stretching ratio, \( \gamma_b \), is defined as

\[
\gamma_b = \frac{d_{\text{max}}}{d_b}
\]  
(V-16)

where \( d_{\text{max}} \) is the maximum length of the elongated bubble in the shear field as shown in Figure V.4. The bubble stretching ratio was measured at various shear strain rates of the silicone fluid bath. The bubble was not stretched
Figure V.3: Experimental Apparatus for Generating a Simple Shear Field
Figure V.4: Stretching Behavior of a Gas Bubble in a Shear Field
proportionally to the total shear strain/deformation of the silicone fluid bath. Instead, the bubble maintained a stretched shape at the steady state as the silicone matrix was being sheared at a certain rate. This implies that the mixing of gas and polymer does not follow the distributive mixing theory. This theory states that the minor component follows the streamlines of the matrix fluid (major component) and that the distribution depends on the total deformation of the system (Tadmor and Gogos, 1979; Naka-sim and Harrel, 1984). In fact, the mixing behavior of the polymer/gas system follows the dispersion mixing theory as discussed in Section V.4.3.

The bubble stretching ratio was measured at various shear strain rates of the silicone matrix. According to the experimental results, the maximum length of the stretched bubble, i.e., the bubble stretching ratio, increased as the shear strain rate of the silicone matrix increased. The bubble stretching ratio was also affected by the viscosity of the silicone fluid. Two different viscosity fluids of 600 Pa-s and 10 Pa-s were used in the experiment. Higher bubble stretching ratios were observed in the higher viscosity fluid for the same stretching rates. The measured bubble stretching ratios at various shear strain rates for the two viscosity fluids are plotted in Figure V.5. For a typical polymer matrix viscosity of, $\eta_p = 200$ Pa-s, the bubble stretching ratio is estimated to be about 100 for the equivalent shear rate of 100 $s^{-1}$ in the extruder.

V.4.5 Estimation of the Striation Thickness and the Diffusion Time

From Equation (V-6), the striation thickness is estimated as
Figure V.5: Stretching Ratio of 1 mm Diameter Air Bubbles in Silicone Fluid Baths
\[ s = \frac{s_0}{\Phi_v \gamma_g} = \frac{2 \text{ mm}}{0.22 \times 100} = 90 \mu\text{m} \] (V-17).

Therefore, the required diffusion time is estimated as

\[ t_D = \frac{s^2}{D} = \frac{(90 \times 10^{-4})^2}{1 \times 10^{-6}} = 80 \text{ s} \] (V-18).

The order of magnitude analysis shown above predicts that the solution formation will be completed in 80 seconds when the polymer/gas system is fully mixed and the striation thickness is 90 \( \mu\text{m} \). Therefore, continuous solution formation can be achieved in extrusion systems without substantially decreasing the processing rates.

Since the mixing accomplished by the simple screw motion is limited, efforts were made to enhance the mixing effectiveness by introducing various mixing sections in the extruder (Erwin, 1978; Mokhtarian and Erwin, 1983; Bigio et al., 1985; Elmendorp, 1991; Raunwendaal, 1991). The idea behind the mixing section is that reorientation of the mixture during processing will enhance the effectiveness of shear mixing. Using the mixing section, the diffusion time would decrease due to the enhanced degree of mixing.
Chapter VI

DESIGN OF A NUCLEATION DEVICE
FOR CONTINUOUS PROCESSING

VI.1 Overview

The next critical step in the continuous production of microcellular plastics is the promotion of high bubble nucleation rates in the polymer/gas solution. Nucleation of bubbles is the transformation of small clusters of gas molecules into energetically stable pockets of molecules with distinct walls. The microcellular process requires that the nuclei density be larger than $10^9$ cells/cm$^3$ so that the fully grown cell size will be less than 10 μm. The key to producing the required cell density is inducing a very high rate of cell nucleation in the polymer/gas solution.

High nucleation rates have been achieved in batch processes by using a thermodynamic instability of the gas and polymer system. In order to make use of a thermodynamic instability in a continuous process, a rapid drop in gas solubility as in the batch process must be induced in the polymer/gas
solution. The solubility of gas in a polymer changes with pressure and temperature (Newitt and Weale, 1948; Lundberg et al., 1966; Veith et al., 1966; Durril and Griskey, 1966 and 1969; van Krevelen, 1976; Koros and Paul, 1980; Weinkauf and Paul, 1990). Therefore, a thermodynamic instability can be induced by rapidly varying the pressure, temperature, or both. Since, in the typical range of interest, the solubility of a gas in a polymer decreases as the pressure decreases, a high cell nucleation rate can be promoted by subjecting the polymer/gas solution to a rapid pressure drop.

The greatest possible number of cells for a given pressure difference would be nucleated out of a given polymer/gas solution if the pressure drops instantaneously. However, in reality the pressure drops over a finite time period as shown in Figure VI.1. It is expected that the more rapidly the pressure drops, the greater the number of cells that would be nucleated, because a greater thermodynamic instability would be induced. A rapid pressure drop element consisting of a nozzle (shown in Figure VI.2) is utilized in this study. When a viscous polymer/gas solution passes through the long, narrow nozzle, the pressure drops linearly with distance due to friction. In order to be able to maximize the pressure drop rate and therefore to induce the greatest thermodynamic instability, the pressure drop and the pressure drop rate are analyzed in an order of magnitude analysis. To compensate for the error involved in the theoretical model, an experimental calibration is performed in Section VII.4.

In this Chapter, the analytical aspects of a rapid pressure drop nucleation device in continuous processing of microcellular plastics are studied. First, the effect of the pressure drop rate on nucleation is qualitatively analyzed using the classical nucleation theory and the concept of
Figure VI.1: Pressure Drop Profile in a Rapid Pressure Drop Device
Figure VI.2: Typical Pressure Drop Element
the competition between the nucleation of new cells and the growth of existing cells for gas molecules in Section VI.2. In order to design a microcell nucleation device that utilizes a rapid drop in the pressure, the pressure change of a flowing polymer/gas solution in the device need to be analyzed. In Section VI.3, a detailed analysis that considers the rheological behavior of a non-Newtonian fluid is described. Based on the analysis, a rapid pressure drop element is designed as a nucleation device for continuous processing of microcellular plastics in Section VI.4.

VI.2 Effect of the Pressure Drop Rate on Nucleation

The homogeneous nucleation theory (Colton and Suh, 1987a) predicts that the cell nucleation rate is given by

\[ N_{\text{hom}} = f_0 C_0 \exp \left( -\frac{\Delta G_{\text{hom}}}{kT} \right) \]  

\[ \Delta G_{\text{hom}} = \frac{16\pi \sigma^3_{\text{sp}}}{3\Delta P^2} \]  

where \( N_{\text{hom}} \) is the homogeneous nucleation rate and \( \Delta P \) is the pressure drop of the gas/polymer solution. Equations (VI-1) and (VI-2) predict that, for a larger pressure drop, the cell nucleation rate will increase. If an instantaneous pressure drop and instantaneous homogeneous nucleation are assumed, then the nucleation rate and the number of nucleated cells correspond. Thus for a constant pressure drop with an instantaneous pressure drop rate, the cell density should be constant. However, in reality the pressure drop is not instantaneous but happens over a finite time period.
It is expected that the nucleation time period is affected by the time period over which the thermodynamic instability is induced in the system, and that the pressure drop rate will affect the nucleation time period, and therefore, will affect the nucleation rate.

To explain the pressure rate effect, one must consider both microcell nucleation and the growth of the cells with respect to the competition between these mechanisms (Martini, 1981). The basic concept is the following. During the course of the pressure drop, which instigates a thermodynamic instability, some stable cells nucleate early during the residence time of the polymer in the nozzle. The gas in solution will diffuse to the nucleated cells to lower the free energy of the system. As the gas diffuses to these cells, low gas concentration regions where nucleation cannot occur are generated adjacent to the stable nuclei as shown in Figure VI.3. As the solution pressure drops further, the system will either both nucleate additional microcells and expand the existing cells by gas diffusion or only expand the existing cells. To determine whether further microcells are nucleated, one must look closely at the depleted gas regions around the previously nucleated cells. If the depleted regions of adjacent cells impinge upon each other, then no further nucleation will tend to occur. This follows since the gas has preferentially diffused to the existing cells, depleting the gas between cells. In this state, the gas concentration between the existing cells is below the critical level needed to nucleate additional cells. However, if the size of the depleted gas regions is less than the dimension between existing cells, then additional cells will tend to nucleate between existing cells.

Here, the effect of the pressure drop rate on the competition of nucleation and cell growth is considered. Consider the pressure drop for
Figure VI.3: Competition between the Nucleation of New Cells and the Growth of Existing Cells
Figure VI.4: Comparison of Pressure Drop Profiles for Nozzle i and Nozzle j
Nozzle i and Nozzle j as shown in Figure VI.4. At time $t_1$, where $t_0 - t_1$ is an arbitrarily small time period, the pressure drop for Nozzle j, $\Delta P_{j1}$, is larger than the pressure drop for Nozzle i, $\Delta P_{i1}$. Since the nucleation rate is inversely sensitive to $\Delta P$ [according to Equations (VI-1) and (VI-2)], the nucleation rate in Nozzle j is higher than the nucleation rate in Nozzle i as illustrated in Figure VI.5 (a) and (b). At the next time step $t_2$, the previously nucleated cells have grown thus reducing the available gas for nucleating additional cells. In the region of the polymer/gas solution where the gas has not been depleted, the nucleation rates for Nozzle i and Nozzle j increase exponentially. However, for any given time, the nucleation rate for Nozzle j is higher than that for Nozzle i due to the additional pressure drop experienced by Nozzle j. This is illustrated in Figure VI.5 (c) and (d). Since the nucleation rates for Nozzle j are much higher than for Nozzle i, the total nucleation time for Nozzle j will be less than for Nozzle i. This follows since the number of cells nucleated increases exponentially as the sizes of the depleted gas regions increase with time. Thus the depleted zones impinge upon one another more rapidly for Nozzle j than Nozzle i as illustrated in Figure VI.5 (e) and (f). For Nozzle i, the depleted zones impinge upon one another at a much later time. Since the nucleation for Nozzle i takes place over a long time period, the depleted zones of the previously nucleated cells must have grown significantly by the time the nucleation stops. Therefore, some of the gas that could have been used for additional nucleation was used for cell growth for Nozzle i. In other words, more gas was used for cell growth in Nozzle i. Since in Nozzle j, nucleation took place over a short time period with high nucleation rates, more gas was used for nucleation of cells. Therefore, the total number of nucleated cells should be higher for
Figure VI.5: Nucleation of New Cells and Growth of the Depleted Zones in Nozzle \( i \) and Nozzle \( j \) at Each Time Step
Nozzle \( j \) than Nozzle \( i \). This competition between microcell nucleation and cell growth for gas molecules is determined by the rate of the pressure drop, and results in the different total numbers of nucleated cells even from an identical polymer/gas solution. Based on this concept, a rapid pressure drop element is analyzed and designed in the following sections. The effect of the pressure drop rate on the cell density is examined experimentally in Chapter VII.

### VI.3 Analysis of the Pressure Change of a Polymer/Gas Solution Flowing in a Circular Nozzle

The pressure change of a flowing, non-Newtonian fluid in a nozzle is analyzed in this section. As a first order approximation, it is assumed throughout the analysis that the rheological properties of the fluid are independent of the gas concentration. However, experimental work shows that the polymer/gas solution has a lower viscosity because of the plasticizing effect of gas (Baldwin and Suh, 1992). In order to compensate for this error, the nozzles theoretically determined are calibrated experimentally in Section VII.4.

The governing equations for a non-Newtonian fluid that describe the fluid flow and the heat transfer are (Bird et al., 1977)

\[
\nabla \cdot \mathbf{v} = 0 \quad \text{(VI-3)}
\]

\[
\rho \frac{D\mathbf{v}}{Dt} = -\nabla p + [\nabla \cdot \mathbf{\eta} \mathbf{\dot{\gamma}}] \quad \text{(VI-4)}
\]
\[ \rho \ c_p \ \frac{dT}{Dt} = k \ V^2 \ T + \frac{1}{2} \ \eta \ \dot{\gamma} \cdot \dot{\gamma} \]  \hspace{1cm} \text{(VI-5)}

where

\( v \) = velocity vector, m/s

\( \rho \) = density, kg/m\(^3\)

\( t \) = time, s

\( p \) = pressure, Pa

\( \eta \) = non-Newtonian viscosity of polymer/gas solutions, Pa-s

\( \dot{\gamma} \) = rate-of-strain tensor, s\(^{-1}\)

\( c_p \) = specific heat at constant pressure, kJ/kg\(^\circ\)C

\( k \) = thermal conductivity, W/m\(^\circ\)C

\( T \) = temperature, \(^\circ\)C.

Equations (VI-3),(VI-4), and (VI-5) are the continuity equation, the equation of motion, and the energy equation, respectively. The non-Newtonian viscosity depends strongly on both velocity gradients and the temperature. The velocity distribution cannot be obtained from Equation (VI-4) unless the temperature distribution is known, and the temperature distribution cannot be obtained from Equation (VI-5) unless the velocity distribution is known. Therefore, the temperature and the velocity distribution couple the equations.

However, the velocity and pressure profiles can be estimated for certain flow fields by some simplifying assumptions. A flow of a polymer/gas solution through a circular nozzle of radius \( r_0 \) and length \( L \) is considered in this study as shown in Figure VI.6. An estimate of the pressure profile can be
Figure VI.6: Fluid Flow in a Circular Nozzle
obtained by considering a simplified rheological behavior of a non-Newtonian fluid in the nozzle.

The pressure distribution in a flow field strongly depends on the velocity profile. Therefore, the velocity profile must be investigated first to estimate the pressure drop rate in the nozzle flow. Assume that the viscosity of the polymer/gas solution is shear-rate dependent, described by a "power law" (de Waele, 1923; Ostwald, 1925) as follows:

\[ \eta = m \dot{\gamma}^n \]  

(VI-6)

where

\[ m = \text{characteristic constant of a non-Newtonian fluid over a temperature range, N-s}^n/m^2 \]

\[ n = \text{dimensionless characteristic constant of a non-Newtonian fluid over a temperature range} \]

\[ \dot{\gamma} = \text{velocity gradient of a non-Newtonian fluid, s}^{-1}. \]

Then, for the fully developed flow through the nozzle, Equation (VI-4) reduces to

\[ \frac{dp}{dz} = - \frac{1}{r} \frac{dr}{dz} \left[ r m \left( \frac{dv_z}{dr} \right)^n \right] \]  

(VI-7)

where

\[ z = \text{axial coordinate in the flow direction, m} \]

\[ r = \text{coordinate in the radial direction, m} \]

\[ v_z = \text{velocity component in z-direction, m/s}. \]
The boundary conditions are

\[ v_z(r_0) = 0 \]  \hspace{1cm} (VI-8)

\[ \frac{dv_z}{dr}(0) = 0 \]  \hspace{1cm} (VI-9).

Solving Equation (VI-7) with the boundary conditions, the velocity profile, \( v_z \), is expressed as

\[ v_z(r) = \left( \frac{r}{a+1} \right)^a \left( - \frac{r_0}{2m} \frac{dp}{dz} \right) \left[ 1 - \frac{r}{r_0} \right]^{a+1} \]  \hspace{1cm} (VI-10)

where

\[ a = \text{nondimensional characteristic constant (}= 1/n). \]

The volumetric flow rate of the polymer/gas solution, \( q \), is derived as

\[ q = \int_0^{r_o} v_z 2\pi r dr = \frac{\pi r_0^3}{a+3} \left( - \frac{r_0}{2m} \frac{dp}{dz} \right)^a \]  \hspace{1cm} (VI-11).

Integrating Equation (VI-11) over the length of the nozzle yields

\[ -\Delta p = \frac{2m L}{r_0} \left( \frac{q}{\pi r_0^3} \right)^{\frac{1}{a}} \]  \hspace{1cm} (VI-12)

where \(-\Delta p\) is the difference between the inlet and outlet pressures.
A flow of impact grade polystyrene (Novacor/Monsanto 3350 HIPS) at 221 °C (430 °F) is considered as a typical application. The characteristic constants used in the calculation are $m = 17,420 \text{ N} \cdot \text{s}^{0.30} / \text{m}^2$ and $n = 0.30$. These values are from the rheological data supplied by Novacor Chemicals Inc. for the shear rate range of $10^1$ to $10^4 \text{ s}^{-1}$ at 221 °C (430 °F).

By substituting these values, Equation (VI-10) can be rewritten as

$$-\Delta p = 42,991 \left( \frac{L}{r_0^{1.9}} \right) q^{0.3}$$  \hspace{1cm} (VI-13).

For different values of the ratio ($L/r_0^{1.9}$), the flow rate is calculated in terms of the pressure drop as shown in Figure VI.7. Each line in the figure represents a group of nozzles that satisfy the relationship

$$\frac{L}{r_0^{1.9}} = \text{constant} \hspace{1cm} (VI-14).$$

It may be noted that, for these nozzles, the pressure drops across the nozzles would be equal for equal flow rates. The general form of Equation (VI-14) for other non-Newtonian fluids is

$$\frac{L}{r_0^{3n+1}} = \frac{-\Delta p}{2m} \left[ \frac{\pi}{q^{(a+3)}} \right]^n = \text{constant} \hspace{1cm} (VI-15).$$

Consider a group of nozzles which satisfy

$$\frac{L}{r_0^{1.9}} = 105,153 \hspace{1cm} (VI-16).$$
Figure VI.7: Theoretical Flow Rate Versus Pressure Drop for Various Nozzle Geometry Groups
For a pressure difference of 38.6 MPa (5,600 psi), the volumetric flow rate of the polymer through these nozzles would be

\[
q = \left( \frac{-\Delta p}{42,991 \frac{L}{r_0^{1.9}}} \right)^{0.3} = \left( \frac{38.6 \times 10^6}{42,991 \times 105,153} \right)^{0.3} = 1.28 \times 10^{-7} \text{ m}^3/\text{s}
\]

(VI-17).

Theoretically, all these nozzles, which are represented by Equation (VI-16), can be replaced by each other without affecting the pre- and post- flow conditions, i.e., upstream/downstream pressures and flow rates. This follows because all the flow rates and all the pressure drops across the nozzles are the same. It may be noted that the pressure changes at the sudden contraction (Kim-E et al., 1983; Coates et al., 1992) are not considered in this analysis; however, the effects are discussed in Section VII.6.

Next, consider three specific nozzles out of this group as a case study. The geometries of the three nozzles are shown in Figure VI.8. The average residence time, \( \Delta t \), of the flowing polymer/gas solution in the nozzle of length \( L \) is expressed as

\[
\Delta t = \frac{L}{v_{\text{avg}}} = \frac{L}{\frac{q}{\pi r_0^2}} = \frac{\pi r_0^2 L}{q}
\]

(VI-18)

where \( v_{\text{avg}} \) is the average velocity of the polymer/gas solution in the nozzle.

For each nozzle, the residence time is estimated as follows:
Figure VI.8: Calculated Geometries of Three Nozzles that Have the Same Pre- and Post-Flow Conditions
\[ \Delta t_1 = \frac{\pi r_o^2 L}{q} = \frac{\pi (0.60 \times 10^{-3})^2 (78.74 \times 10^{-3})}{1.28 \times 10^{-7}} = 0.666 \text{ s} \]  
(VI-19)

\[ \Delta t_2 = \frac{\pi r_o^2 L}{q} = \frac{\pi (0.39 \times 10^{-3})^2 (35.75 \times 10^{-3})}{1.28 \times 10^{-7}} = 0.136 \text{ s} \]  
(VI-20)

\[ \Delta t_3 = \frac{\pi r_o^2 L}{q} = \frac{\pi (0.23 \times 10^{-3})^2 (12.75 \times 10^{-3})}{1.28 \times 10^{-7}} = 0.016 \text{ s} \]  
(VI-21)

There is approximately an order of magnitude difference in the residence times between each of the nozzles.

Now, the pressure drop rate for each nozzle can be calculated. Because the residence time for each nozzle is different, the pressure drop rate in each nozzle is different, even though the pressure drops are equal. The average pressure drop rate is estimated as

\[ \frac{-dp}{dt} = \frac{-\Delta p}{\Delta t} = \frac{-\Delta p}{\pi r_o^2 L} \]  
(VI-22)

For each nozzle, the pressure drop rate is estimated as follows:

\[ \left(\frac{-dp}{dt}\right)_1 = \frac{-\Delta p}{\Delta t_1} = \frac{38.64 \times 10^6}{0.666} = 0.058 \text{ GPa/s} \]  
(VI-23)

\[ \left(\frac{-dp}{dt}\right)_2 = \frac{-\Delta p}{\Delta t_2} = \frac{38.64 \times 10^6}{0.136} = 0.284 \text{ GPa/s} \]  
(VI-24)
\[ \left( \frac{-dp}{dt} \right)_3 = \frac{\Delta p}{\Delta t_3} = \frac{38.64 \times 10^6}{0.016} = 2.355 \text{ GPa/s} \]

(VI-25).

There is also about an order of magnitude difference in the pressure drop rates between each nozzle, while the total pressure drop across the nozzle length is equal for each nozzle.

Since the gas solubility is approximately proportional to the pressure (Newitt and Weale, 1948; Durril and Griskey, 1966, 1969; van Krevelen, 1976), a larger solubility drop rate would be induced for a greater pressure drop rate. The drop rate of the gas solubility is expressed as

\[ \frac{dC_s}{dt} = \frac{\Delta C_s}{\Delta t} = \frac{\Delta C_s q}{\pi r_o^2 L} \]

(VI-26)

where \( \Delta C_s \) is the change of the gas solubility in polymer. For each nozzle, the solubility drop rate is estimated as follows:

\[ \left( \frac{dC_s}{dt} \right)_1 = \frac{\Delta C_s}{\Delta t_1} = \frac{0.14}{0.666} = 0.21 \text{ s}^{-1} \]

(VI-27)

\[ \left( \frac{dC_s}{dt} \right)_2 = \frac{\Delta C_s}{\Delta t_2} = \frac{0.14}{0.136} = 1.03 \text{ s}^{-1} \]

(VI-28)

\[ \left( \frac{dC_s}{dt} \right)_3 = \frac{\Delta C_s}{\Delta t_3} = \frac{0.14}{0.016} = 8.75 \text{ s}^{-1} \]

(VI-29).
There is also approximately an order of magnitude difference in the solubility drop rates between each nozzle while the solubility drops of the polymer/gas solutions across the total length of the three nozzles are the same. The estimated residence time, pressure drop rate and solubility drop rate for each nozzle are summarized in Table VI.1.

VI.4 Design of a Rapid Pressure Drop Element for Microcellular Nucleation

Based on the analysis of the pressure change in a nozzle, a decompressive nucleation element consisting of a nozzle is designed in this section. The design variables of the decompressive nucleation element are the radius and the length of the nozzle. Since the induced thermodynamic instability depends not only on the magnitude of the solubility drop but also on the rate of the solubility drop, both the magnitude of the pressure drop and the rate of the pressure drop are considered in the design of the decompressive nucleation element.

First, consider the three nozzles described in the previous section, since the pressures and the flow rates of this group of nozzles are in the processing range encountered in extrusion. Since the solubility drop rates are different, the induced thermodynamic instability for each nozzle is different, even though the solubility drops are the same. The greatest thermodynamic instability would result when the solubility drops most rapidly. Since the third nozzle with the smallest radius and the smallest length has the highest pressure drop rate and the highest solubility drop rate, the nucleation rate for the third
Table VI.1: Residence Times, Pressure Drop Rates and Solubility Drop Rates of the Nozzles for a Pressure Drop of 38.64 MPa (5,600 psi)

<table>
<thead>
<tr>
<th>Nozzle</th>
<th>Flow rate</th>
<th>Residence time</th>
<th>Pressure drop rate</th>
<th>Solubility drop rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle 1</td>
<td>1.28×10⁻⁷ m³/s</td>
<td>0.666 s</td>
<td>0.058 GPa/s</td>
<td>0.21 s⁻¹</td>
</tr>
<tr>
<td>Nozzle 2</td>
<td>1.28×10⁻⁷ m³/s</td>
<td>0.136 s</td>
<td>0.284 GPa/s</td>
<td>1.03 s⁻¹</td>
</tr>
<tr>
<td>Nozzle 3</td>
<td>1.28×10⁻⁷ m³/s</td>
<td>0.016 s</td>
<td>2.355 GPa/s</td>
<td>8.75 s⁻¹</td>
</tr>
</tbody>
</table>
nozzle would be the greatest, and therefore, it should be the most effective microcellular nucleation element among the three.

To maintain the pressure drop and the flow rate, the nozzle radius and the length should satisfy the following relationship

\[
\frac{L}{r_o^{3n+1}} = \frac{-\Delta p}{2m} \left[ \frac{\pi}{q(a+3)} \right]^n = \text{constant}
\]  

(VI-30).

According to Equations (VI-22) and (VI-26), higher pressure drop and higher solubility drop rates are achieved when the nozzle radius is smaller. Theoretically, when the nozzle radius becomes zero, the pressure drop rate and the solubility drop rate become infinitely large. With such an instantaneous pressure drop as shown in Figure VI.1, the greatest possible number of cells would be nucleated out of a given polymer/gas solution. However, the radius reduction is limited by the manufacturability of the hole and the mechanical strength of the nozzle. According to Equation (VI-30), the nozzle length decreases with the radius. The nozzle length cannot be arbitrarily reduced because the nozzle must have the mechanical strength to withstand the processing pressure of extrusion.

Considering the limit of the nozzle diameter and length, Nozzle 3 was chosen as a decompressive nucleation element to allow a rapid pressure drop in the flowing, viscous fluids. This rapid drop in gas solubility will induce a thermodynamic instability, and a high nucleation rate will be promoted in the polymer/gas solution. The designed decompressive nucleation device is experimentally examined in Chapter VII.
Chapter VII

EXPERIMENTS AND DISCUSSION

VII.1 Experimental Set-up

Based on the design proposed in Chapters III-VI, an experimental extrusion set-up was built. A schematic of the equipment is shown in Figure VII.1. The set-up used a 3/4 inch Brabender Type 2523 extruder with a filamentary die. The barrel was tapped near the end of the plasticating screw and was connected to high pressure CO$_2$ and N$_2$ gas cylinders. A mixing screw (Brabender 05-00-051) [or a venting screw (Brabender 05-00-048A)] and a six-element static mixer of diameter 6.8 mm (Figure VII.2) were used for enhancing the mixing of gas and polymer melt. The L/D ratio and the compression ratio of the screws are 25:1 and 3:1, respectively.

Six band heaters and temperature controllers were installed: three for the plastication extrusion barrel, two for the static mixers, and one for the die. A thermocouple was installed to measure the temperature of the flowing polymer melt. Two pressure transducers were also installed: one to measure
Figure VII.1: Schematic of the Experimental Set-up for Filamentary Extrusion of Microcellular Polymers
Figure VII.2: Six-Element Static Mixer Used in the Experimental Set-up
the pressure of the extrusion barrel where the gas is injected and one at the end of the mixing/diffusion device to measure the pressure of the single-phase solution flow. Figure VII.3 is a photograph of the experimental set-up.

VII.2 Experimental Materials

Both semicrystalline and amorphous polymers were processed. The polymers used in the experiments were Phillips 66 Marlex Polypropylene (PP), Novacor/Monsanto 3350 High Impact Polystyrene (HIPS), and GE Cycolac Acrylonitrile Butadiene Styrene (ABS). Polymeric pellets were plasticated in the barrel, and a metered amount of CO₂ or N₂ was injected into the polymer melt.

VII.3 Experimental Procedure

The experimental set-up required a warming up period in which each temperature controller was set to a desired temperature and the system was allowed to warm up for approximately 40 minutes. For experiments involving CO₂ injection, a high pressure CO₂ pump, as described in Section IV.4.3, was employed. For experiments involving N₂ injection, a high pressure pump was not used. Instead, a 6000 psi N₂ cylinder was directly connected to the barrel in order to supply the required high pressure N₂.

When the plasticating screw started to rotate, the pressure in the barrel started to build up. In order to maintain a constant gas to polymer ratio, the gas injection pressure had to be maintained about 500 psi higher than the barrel pressure (see Figure IV.5). If the gas injection pressure was incorrectly
Figure VII.3: Experimental Set-up for Filamentary Extrusion of Microcellular Polymers
adjusted, an incorrect amount of gas would be injected into the barrel. The barrel pressure increased as the rotational speed of the screw increased. As the rotational speed was adjusted to a desired RPM, careful attention was paid to maintain the desired difference between the gas injection pressure and the barrel pressure. In the worst case, when the barrel pressure became higher than the gas injection pressure, the polymer melt flowed into the porous material, clogging it.

Even when the screw RPM and the barrel pressure were stabilized, the whole system was still not in a steady state. An unfoamed polymer melt came out of the die for a limited time. After about 7-10 minutes the foamed polymer came out of the die. Since the flow rate increases with the die temperature, the settling time could be shortened by temporarily raising the temperature of the die. When a foamed polymer filament came out of the die, the flow rate and the barrel pressure were changed. In 1-2 minutes, a steady state was reached and a foamed filament with the desired cell structure was steadily produced. The machine was allowed to run for 30 minutes at the steady state to check for any variation in the temperature, the pressure, and/or the cell structure. The temperature and the pressure profiles were recorded throughout the experiment.

Extruded foam samples were randomly chosen and examined with a scanning electron microscope (SEM). The samples were dipped in liquid nitrogen, and then fractured to expose the microstructure. The fracture surface was then coated with gold and analyzed in an SEM to characterize the microstructure.
VII.4 Calibration of the Nozzles

The three nozzles, theoretically equivalent with respect to the pre- and post-flow conditions in Section VI.3, were experimentally calibrated so that they produced the same amount of flow rate for a given pressure difference. This calibration was needed because the actual experimental relationship between the flow rate and the pressure drop in a nozzle is different from the theoretically predicted value.

Nozzle 3 was chosen as a reference for the calibration of other nozzles. When Nozzle 3 was mounted, the nozzle pressure and the flow rate were measured as 38.64 MPa (5,600 psi) and $1.9 \times 10^{-7}$ m$^3$/s, respectively. It may be noted that the actual flow rate through Nozzle 3 was almost twice the predicted value. Next, the size of Nozzle 1 was calibrated as follows. Initially, a nozzle of a radius 0.60 mm (0.024 in) and a length 92.23 mm (3.631 in) was used. When the nozzle was mounted, the nozzle pressure and the flow rate were measured as 44.57 MPa (6,460 psi) and $1.5 \times 10^{-7}$ m$^3$/s, respectively. The nozzle length was then cut in stages until the flow rate and the pressure were measured to be 38.64 MPa (5,600 psi) and $2.0 \times 10^{-7}$ m$^3$/s. This completed the calibration of Nozzle 1. The length of Nozzle 2 was also determined in a similar manner. The geometry of the calibrated nozzles, the residence time, and the pressure drop rate for each nozzle are summarized in Table VII.1.
Table VII.1: Calibrated Geometries, Residence Times, and Pressure Drop Rates of the Nozzles for Unsaturated HIPS with a Pressure Drop of 38.64 MPa (5,600 psi)

<table>
<thead>
<tr>
<th>Nozzle</th>
<th>Radius</th>
<th>Length</th>
<th>Flow rate</th>
<th>Residence time</th>
<th>Pressure drop rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle 1</td>
<td>0.60 mm (0.024 in)</td>
<td>87.22 mm (3.434 in)</td>
<td>2.0×10⁻⁷ m³/s</td>
<td>0.510 s</td>
<td>0.076 GPa/s</td>
</tr>
<tr>
<td>Nozzle 2</td>
<td>0.39 mm (0.016 in)</td>
<td>36.32 mm (1.430 in)</td>
<td>1.9×10⁻⁷ m³/s</td>
<td>0.092 s</td>
<td>0.420 GPa/s</td>
</tr>
<tr>
<td>Nozzle 3</td>
<td>0.23 mm (0.009 in)</td>
<td>12.75 mm (0.502 in)</td>
<td>1.9×10⁻⁷ m³/s</td>
<td>0.011 s</td>
<td>3.500 GPa/s</td>
</tr>
</tbody>
</table>
VII.5 Experiments and Results

Five sets of experiments were carried out to investigate the effects of the experimental parameters on the cell morphology of the extruded polymers. In all the experiments other than the pressure-drop-rate experiments, Nozzle 3 was used as a nucleation device.

Effect of Gases on Cell Nucleation

First, the effect of different gases on the cell morphology was studied. The gases injected in these experiments were CO₂ and N₂, and the processed polymers were Polypropylene and High Impact Polystyrene. Approximately 10% by weight of CO₂ and 2% by weight of N₂ were injected into each polymer melt.

The extruded samples were examined by an SEM to characterize the microstructures. Figure VII.4 (a) and (b) show the scanning electron micrographs of the extruded PP. When N₂ and CO₂ were processed, the cell densities were 3 x 10⁷/cm³ and 6 x 10⁸ cells/cm³, respectively. Figure VII.5 (a) and (b) show the micrographs of the extruded HIPS. The cell densities were 9 x 10⁷ cells/cm³ and 8 x 10⁹ cells/cm³ for N₂ and CO₂ injection, respectively.
Figure VII.4: Scanning Electron Micrographs of Extruded PP
Figure VII.5: Scanning Electron Micrographs of Extruded HIPS
Effect of the Processing Pressure on Cell Nucleation

Next, the effect of the processing pressure on the cell morphology was studied. In these experiments, the maximum soluble amount of CO₂ was injected into the polymer melt at each processing pressure. The polymer used in these experiments was HIPS. Figure VII.6 shows the micrographs of the extruded HIPS at each processing pressure. When the processing pressures were 5.4 MPa (780 psi), 10.6 MPa (1,530 psi), 18.6 MPa (2,700 psi), and 28.3 MPa (4,100 psi), the cell densities were $7 \times 10^5$ cells/cm³, $2 \times 10^7$ cells/cm³, $2 \times 10^8$ cells/cm³, and $6 \times 10^9$ cells/cm³, respectively. These cell densities are plotted as a function of the processing pressure in Figure VII.7.

Effect of the Injected Gas Amount on Cell Nucleation

The effect of the amount of gas injected on the cell density was also studied. A series of experiments was conducted by varying the injected gas amount while the processing pressure was maintained at 27.6 MPa (4,000 psi) in these experiments. Figure VII.8 shows the micrographs of the extruded HIPS for each injected gas amount. When 1%, 5%, and 10% (by weight) CO₂ were injected, the cell densities were $10^7$ cells/cm³, $4 \times 10^8$ cells/cm³, and $6 \times 10^9$ cells/cm³, respectively. These cell densities are plotted as a function of the injected gas amount in Figure VII.9.
Figure VII.6: Scanning Electron Micrographs of Extruded HIPS at Different Processing Pressures
Figure VII.7: Effect of the Processing Pressure on the Cell Density of Extruded HIPS
Figure VII.8: Scanning Electron Micrographs of Extruded HIPS for Different Injected CO2 Amounts
Figure VII.9: Effect of the Injected CO$_2$ Amount on the Cell Density of Extruded HIPS
**Effect of the Pressure Drop Rate on Cell Nucleation**

In these experiments, the role of the nucleation device was examined. Using the nozzles calibrated in Section VII.4, a series of experiments was carried out for each nozzle to investigate the effects of the pressure drop rate on the cell morphology of the extruded microcellular HIPS. In all the experiments, the same amount of gas, 10% (by weight) CO₂, was injected to form identical polymer/gas solutions. Figure VII.10 shows the micrographs of the extruded HIPS for each nozzle. The cell densities for the nozzles from 1 to 3 were $1 \times 10^8$ cells/cm³, $1 \times 10^9$ cells/cm³, and $7 \times 10^9$ cells/cm³, respectively.

The rheological behavior of the polymer/gas solution was slightly different from that of the polymer melt. When the gas was injected, the nozzle pressure and the flow rate were measured as about 34.5 MPa (5,000 psi) and $4.6 \times 10^{-7}$ m³/s, respectively for each nozzle. It may be recalled that, without gas as in Section VII.4, the nozzle pressure and the flow rate were measured as 38.64 MPa (5,600 psi) and $1.9 \times 10^{-7}$ m³/s, respectively. The pressure decreased and the flow rate increased with gas injection. This could be due to a lower viscosity of the polymer/gas solution. The residence times of the polymer in the nozzles were 0.19 s, 0.038 s, and 0.005 s, respectively. The corresponding pressure drop rates for the nozzles were 0.18 GPa/s ($2.6 \times 10^4$ psi/s), 0.90 GPa/s ($1.3 \times 10^5$ psi/s), and 6.9 GPa/s ($1.0 \times 10^6$ psi/s), respectively. The cell densities for each nozzle are plotted as a function of the pressure drop rate in Figure VII.11.
(a) Nozzle 1

(b) Nozzle 2

(c) Nozzle 3

Figure VII.10: Scanning Electron Micrographs of Extruded HIPS for Different Nucleation Devices
Figure VII.11: Effect of the Pressure Drop Rate on the Cell Density of Extruded HIPS
Other Materials

Although HIPS was used in the experiments described above, some other materials were also tested. When ABS was processed with 10% (by weight) CO₂, the cell density was 9 × 10⁸ cells/cm³. Figure VII.12 shows the SEM pictures of the extruded ABS. When PP was processed with 10% (by weight) CO₂, the cell density was 6 × 10⁸ cells/cm³ as described before in Section Effect of Gases on Cell Nucleation.

VII.6 Discussion

The amount of gas dissolved in the polymer directly affects the cell density because a greater thermodynamic instability is induced by the gas solubility drop when the polymer has more dissolved gas. Since the weight ratio of dissolved gas to polymer in the polymer/gas solution is determined by the gas, the polymer, the processing pressure and the injected gas amount, the effects of these parameters on the cell density of the extruded foam were investigated.

Effect of Gases on Cell Nucleation

The thermodynamic instability induced through the solubility drop seems sufficient to produce a microcellular structure when the maximum soluble amount of CO₂ was injected. About 10⁹-10¹⁰ nucleated cells per cm³ of unfedfoamed material were found in the samples of PP and HIPS. However, when N₂ was processed, 10⁷-10⁸ cells/cm³ were found in the PP and HIPS
Figure VII.12: Scanning Electron Micrograph of Extruded ABS with 10% (by weight) CO$_2$ Injection
samples. The higher cell densities in the samples processed with CO₂ are likely to be due to the higher solubility of CO₂ in the polymers. In Section IV.1, the solubilities of CO₂ and N₂ in most polymers at 27.6 MPa (4,000 psi) and 200°C were estimated as 10% and 2% by weight, respectively. Because of the higher solubility, more gas was dissolved in the polymer when CO₂ was injected. It is believed that the larger amount of dissolved gas induced a greater thermodynamic instability, and thereby a higher cell density.

**Effect of the Processing Pressure on Cell Nucleation**

Next, the effect of the processing pressure on the cell density of the extruded HIPS was experimentally studied (Figure VII.6), and the results are plotted in Figure VII.7. The results show that the cell density increased with the processing pressure. When the processing pressure was 28.3 MPa (4,100 psi), the foam structure of the extruded HIPS was microcellular, and the cell density was 6 x 10⁹ cells/cm³.

Since the solubility of gas is approximately proportional to the processing pressure (Newitt and Weale, 1948; Durril and Griskey, 1966, 1969; van Krevelen, 1976), more gas can be dissolved in the polymer when the processing pressure is higher. The increased amount of dissolved gas induced a greater thermodynamic instability and a larger cell density. Therefore, a larger cell density is expected when the processing pressure is higher. However, the processing pressure is limited by the capacities of the high pressure gas pump and the extruder. Accordingly, a lower cell density is expected when the processing pressure is lower. In fact, when the processing
pressure fell below 6.9 MPa (1,000 psi), the cell density in the samples was on the order of $10^6$ cells/cm$^3$.

**Effect of the Injected Gas Amount on Cell Nucleation**

The effect of the injected gas amount on the cell density was also studied experimentally (Figure VII.8). In these experiments, the processing pressure was maintained as 27.6 MPa (4,000 psi) while the injected gas amount was varied. Figure VII.9 shows that the cell density increased as the injected gas amount increased. When the injected gas amount was 10\% by weight, the structure of the extruded HIPS foam was microcellular.

For the processing pressure of 27.6 MPa (4,000 psi), the 10\% weight ratio is the maximum soluble amount of CO$_2$ (see Section IV.1). Up to this amount, all the injected gas will be dissolved in the polymer. This dissolved gas amount again affects the cell density of the extruded HIPS foam.

The experimental results shown in Figure VII.7 predict that a microcellular structure with a cell density larger than $10^9$ cells/cm$^3$ can be produced when the processing pressure is higher than 22 MPa (3,200 psi). Since the gas solubility is approximately proportional to the processing pressure, the required gas amount for microcellular nucleation is estimated to be 7.5\% by weight. The experimental results shown in Figure VII.9 predict that the required gas amount is 6.5\% by weight.

There was a difficulty of processing the polymer/gas mixture with the gas amount larger than 10\% by weight. When the amount of the injected gas was higher than 10\% by weight, the barrel pressure decreased significantly and the extrusion system became very unstable. It is believed that the significant
pressure drop in the barrel was due to the lowered viscosity of the polymer/gas mixture since the volume fraction of gas in the mixture increased as the injected gas amount increased. The gas flow rate is inversely sensitive to the barrel pressure (see Figure IV.5). Therefore, the drop of the barrel pressure further increased the gas flow rate. The increased amount of the injected gas again further dropped the barrel pressure due to further viscosity drop. This cascading cycle continued until the barrel was filled with the gas and the system became unstable. To improve the stability of the system at a gas flow rate higher than 10% by weight, a screw of a larger L/D ratio or a tandem extrusion system is recommended.

Effect of the Degree of Mixing on Cell Nucleation

The degree of mixing of the gas and the polymer melt is also very important because it determines the diffusion time for the formation of the polymer/gas solution. When the gas and the polymer melt are not mixed well, the gas does not completely dissolve into the polymer matrix in the given processing time period. The residual air voids then affect the cell density because the existence of these voids prohibits the formation of nucleation sites. For example, when the speed of the plasticating screw fell below 35 RPM in the processing of HIPS with CO₂, the cell density was about 10⁶ cells/cm³, and large hollow cavities were observed in the samples.
Effect of Pressure Drop Rate on Cell Nucleation

Formation of polymer/gas solutions under identical processing conditions results in an equal amount of dissolved gas. However, the cell density can vary when the polymer/gas solution experiences different nucleation rates as described in Section VI.2.

Figures VII.10 and VII.11 clearly show the dominant effect of pressure drop rate on the continuous nucleation of microcells in microcellular extrusion. In each case shown, the processing conditions are identical except for the nozzle geometries. The nozzle geometries were selected such that the total pressure drop and the overall flow rate remained constant in each case studied.

The residence times of the polymer/gas system in Nozzle 1 and Nozzle 3 were 0.19 s and 0.005 s, respectively. The corresponding pressure drop rates for Nozzle 1 and Nozzle 3 were 0.18 GPa/s and 6.9 GPa/s, respectively. Since Nozzle 3 experiences a higher pressure drop rate, the nucleation rates for Nozzle 3 are higher than for Nozzle 1. Therefore, the total number of nucleated cells are larger for Nozzle 3 than for Nozzle 1, and the average cell size for Nozzle 3 (5 μm) is smaller than for Nozzle 1 (20 μm).

As discussed in Section VI.2, nucleation stops when all the depleted regions of adjacent cells impinge upon each other and the gas concentration in the polymer matrix is below the critical level needed to nucleate additional cells. The pressure drop rates that the nozzles experience affect this nucleation time period. For Nozzle 1, the pressure drop rate is low, and therefore, the nucleation rates are slow. Since the nucleation rates are
governed by the pressure drop rate, the nucleation time period would be shorter than the total time period over which the pressure drops.

Assume that the nucleation rates for Nozzle 3 are governed by the pressure drop rate and that nucleation is completed before the pressure drops completely to the downstream pressure as shown in Figure VII.13. In this case, the nucleation time period is shorter than the residence time period in the nozzle. If the residence time period decreases, then the pressure drop rate increases. This will induce higher nucleation rates, and the nucleation time period will decrease. However, the decrease of the nucleation time period is limited because for the depleted regions to impinge upon each other takes time. The growth of the depleted region is governed by gas diffusion in the polymer matrix. Therefore, the nucleation time period cannot be reduced infinitely small as the pressure drop rate increases infinitely. When the pressure drops almost instantaneously, the nucleation time period may be longer than the residence time period. In this case, the pressure drop rate does not affect the nucleation rate because most of nucleation takes place after the pressure drops completely. Figure VII.13 depicts the nucleation time period for Nozzle 3 to be less than the residence time period. It may be noted that this is a conservative estimate. The actual nucleation time period for Nozzle 3 may be longer than the residence time period. Additional work is required to determine the actual nucleation time period for each nozzle.

The previous argument predicts that some critical pressure drop rate exists above which the pressure drop rate does not affect the competition between microcell nucleation and cell growth. This would imply the graph in Figure VII.11 should reach a maximum constant value. Figure VII.11 shows that start of such a maximum; however, due to practical limitations in
Figure VII.13: Comparison of Residence Time Periods and the Nucleation Time Periods
the manufacture of small bore nozzles, as described in Section VI.4, data points verifying the maximum were unobtainable.

**Accounting for the Rapid Contraction Effect in the Nozzles Design**

Because the nucleation devices have a sudden contraction, there is an extra pressure loss at the entrance (Kim-E et al., 1983; Coates et al., 1992). This excess pressure drop, or Couette correction (Coates et al., 1992), is one of the reasons for the difference between the theoretically predicted nozzle size and the experimentally calibrated size since this entrance pressure loss was not considered in the theoretical estimation. However, to compensate for the errors involved in the theoretical analysis, the nozzles were experimentally calibrated as described in Section VII.4.

**Effect of the Viscous Heating on the Cell Morphology**

The temperature rise through viscous heating in the pressure drop element will affect the cell morphology. Since most shearing takes place near the nozzle wall, the viscous heating occurs mainly near the surface of the extruded filament. This forms a highly nonuniform temperature profile in the radial direction (Bird et. al, 1977). Furthermore, because cell nucleation and cell growth strongly depend on the temperature, this nonuniform temperature distribution will result in a nonuniform cell morphology. First, the temperature rise results in a decrease in the gas solubility. In addition to the pressure drop in a nozzle, this temperature rise may play a role in cell nucleation. Also, when the temperature is high, the rate of cell growth
increases because the polymer matrix softens and the diffusion coefficient increases. Therefore, the nuclei near the wall will grow faster. Furthermore, since the polymer matrix near the wall is subject to shear deformation, the grown cells might coalesce more easily. It is also believed that the temperature rise near the surface enhances the coalescence of the bubbles. Figure VII.14 shows a typical cell morphology of an extruded HIPS filament. The cells near the surface are larger than the cells in the core of the filament. It may be noted that some of the cells near the surface are connected to each other, which supports the possibility of coalescence of the cells near the surface. The cells in the core, by contrast, are uniformly distributed. The surface quality improves as the cell density increases.
Figure VII.14: Typical Scanning Electron Micrograph of Extruded Filamentary HIPS with a Different Cellular Structure Near the Surface
Chapter VIII

SUMMARY AND CONCLUSIONS

VIII.1 Summary

An extrusion process for manufacturing microcellular polymer filaments has been presented. In a manner similar to a batch process, this continuous process makes use of a thermodynamic instability. This was done by performing two major process steps: continuous formation of a polymer/gas solution and microcell nucleation by a thermodynamic instability in the polymer/gas solution. The main strategy for the process design was to integrate these two steps into an extrusion process such that the overall process had independently controllable functions.

An axiomatic design approach has been used for the design of the overall manufacturing process, and for the detailed design of the polymer/gas solution formation process. The resulting process comprises the following steps. First, the polymeric pellets are plasticated in the extrusion barrel. Then, a metered amount of gas is injected into the stream of the molten polymer to form a two-phase mixture. The two-phase mixture becomes a
single-phase solution when the gas dissolves into the liquid-polymer matrix. Microcell nucleation takes place in a nozzle via a pressure drop. Finally, cell growth occurs as the nucleated polymer/gas system exits the nozzle.

In order to meter a minute flow of high pressure gas, a porous material was used, and the gas flow rate through the porous material was calibrated. A convective diffusion device for enhancing the effectiveness of mixing and diffusion was designed for the rapid formation of a polymer/gas solution. The required processing time for solution formation was estimated from experimental data and the theory of dispersive mixing. The solubilities and the diffusion coefficients of CO₂ and N₂ at high temperatures and pressures were estimated from the published data.

The next critical step was to promote a high rate of bubble nucleation in the polymer/gas solution. This was achieved by rapidly lowering the solubility of gas in the solution by dropping the pressure. A rapid decompressive element, consisting of a nozzle, was employed as a microcell nucleation device. In order to maximize the pressure drop rate, and therefore, to induce the greatest nucleation rate, the pressure drop and the pressure drop rate of a non-Newtonian fluid flowing through a nozzle were analyzed based on the power-law model.

The kinetics of polymer/gas solution formation and microcell nucleation by a thermodynamic instability were examined through experimental work. Based on the proposed design, an experimental extrusion set-up was built. Experiments were carried out to verify the design and to identify the critical process parameters. Various semicrystalline and amorphous polymers were processed with high pressure carbon dioxide or nitrogen. About 10⁹-10¹⁰ cells/cm³ were nucleated when PP, HIPS, and ABS
were processed with 10% CO₂. Relatively low cell densities of 10⁷-10⁸ cells/cm³ were found in the samples of PP and HIPS when 2% N₂ was injected into the polymer melt.

In order to investigate the effects of the processing pressure and the injected gas amount on the cell morphology, a series of experiments on HIPS was carried out. The cell density increased as the processing pressure was increased. The cell density also increased as the injected gas amount was increased, up to the gas solubility. When the processing pressure was 27.6 MPa (4,000 psi) and the injected gas amount was 10% by weight, 6 x 10⁹ cells/cm³ were nucleated in the extruded HIPS.

The effects of the pressure drop rate on the cell morphology of the extruded HIPS were also studied. In these experiments, the same amount of gas, 10% by weight, was injected to form identical polymer/gas solutions. When the pressure drop rates in the nucleation device were 0.18 GPa/s, 0.90 GPa/s, and 7.0 GPa/s, the cell densities were 1 x 10⁸ cells/cm³, 1 x 10⁹ cells/cm³, and 7 x 10⁹ cells/cm³, respectively.

VIII.2 Conclusions

The analytical and experimental works presented in this thesis lead to the following conclusions:

1. A continuous extrusion process for microcellular polymer filaments has been designed. The main strategy for the process design was to integrate the polymer/gas solution formation and the cell nucleation steps into an
extrusion process such that the functions of the overall process were independently satisfied.

2. An experimental set-up has been constructed based on the proposed design, and microcellular polymer filaments have been successfully produced using the extrusion set-up.

3. A greater number of cells are nucleated using CO₂ injection than with N₂ injection. It is believed that the higher CO₂ nucleation density is due to the higher solubility of CO₂ in the polymers studied.

4. The amount of gas dissolved in the polymer directly affects the cell density, i.e., the number of cells nucleated, because a greater thermodynamic instability is induced when the polymer has more dissolved gas. Based on the experimental results, it is recommended that the dissolved gas amount be higher than 7% by weight to produce a microcellular structure.

5. The processing pressure affects the cell density because the maximum soluble amount of gas in the polymer is determined by the processing pressure. Experimental results indicate that the gas solubility increases as the processing pressure increases, thereby resulting in a larger cell density.

6. The injected amount of gas also affects the dissolved gas amount, and thereby the cell density. The cell density increases as the injected gas amount increases up to the solubility.
7. The mixing quality of the polymer melt and the gas is critical in microcellular processing because it determines the diffusion time required for the formation of the polymer/gas solution. The residual air voids due to poor mixing affect the cell density because the existence of these voids prohibits homogeneous nucleation.

8. The pressure drop rate in the nucleation device plays a strong role in determining the cell density of the extruded HIPS foam through its effects on the thermodynamic instability induced in the polymer/gas solution and the competition between cell nucleation and growth. Based on the experimental results, it is recommended that the pressure drop rate be higher than 0.9 GPa/s (1.3 x 10^5 psi/s).

9. The cells near the surface of extruded filaments are larger than those in the core. It is believed that the temperature rise near the surface due to viscous heating affects the cell morphology near the surface through its effects on the cell growth rate and bubble coalescence.
Chapter IX

FUTURE WORK AND APPLICATIONS

The filamentary microcellular extrusion process developed in this research can be readily adapted to other continuous processes, such as sheet extrusion and injection molding. Since this research has only focused on polymer/gas solution formation and microcell nucleation with a simple filamentary die, additional work is needed to accommodate the control of shaping and cell growth.

Experimental results of this research indicate that when prematurely grown cells are subjected to a shear field in a shaping device, such as a die or a mold, the coalescence of the bubbles is enhanced, especially at high temperatures. Therefore, nucleated cells must be prohibited from growing until shaping is completed in order to maintain a high cell density in the final product.

The concepts of polymer/gas solution formation and microcell nucleation developed in this research can also be applied to injection molding processes. One technical difficulty in developing an injection molding process is maintaining a sufficiently high barrel pressure so that the
requisite gas molecules diffuse into the polymer matrix. When the pressure is not high enough, the solubility of a gas in the polymer decreases, and the gas molecules will diffuse out of the polymer matrix. Since the screw in a reciprocating-screw injection unit (Berins, 1991) is subjected to discontinuous stop-move conditions, the barrel or the screw should be modified so that the barrel pressure can be maintained even when the screw is not rotating. It may be easier to use a screw-preplasticator injection unit (Berins, 1991) where the screw rotation and the barrel pressure can be controlled independently.

In the development of other continuous processes or in scale-up of the filamentary extrusion process, the mixing elements should be designed so that a desirable striation thickness of polymer and gas can be achieved, and the formation of a single-phase polymer/gas solution can be completed at a reasonable rate. To improve the model of continuous formation of a single-phase polymer/gas solution, fundamental research should be carried out on the diffusivity and the solubility of gases in polymers at high temperatures and pressures and on the polymer/gas mixing behavior in the mixing elements.

When sheet extrusion and injection molding processes are developed, a large number of innovative applications of microcellular plastics will emerge. These include food packaging with reduced material, airplane and automotive parts with high strength-to-weight ratio and acoustic damping, sporting equipment with reduced weight and high fracture toughness, insulative fibers/filaments for fabric, molecular grade filters for separation processes, low-friction materials, polymeric implants, safety helmets, etc. Furthermore, since the processing of microcellular plastics does not use CFCs, the process of the polymer/gas solution formation and microcell nucleation
described in this thesis could be used in replacing CFCs in the foam industry. It may be noted that the cell densities of the samples were greater than those of conventional foams even when N₂ was injected. As the capacities of the high pressure gas pump and the extruder are increased (see Section VII.6), the cell densities would increase, and even with N₂ injection microcellular foam structure could be obtained.
REFERENCES

ASME, 1989, ASME Boiler and Pressure Vessel Code, Section VIII, Division 1.


References


Appendix A

PROCEDURE FOR
DETERMINING THE CELL DENSITY

The cell density is defined as the number of cells (or bubbles) per cubic centimeter of unfoamed original material. When the cell density is higher than $10^9$ cells/cm$^3$, the fully grown cell size is on the order of 10 $\mu$m or less, and therefore, the resulting foam structure is microcellular. Since the number of cells per square centimeter of foamed material can be easily counted, the cell density can be determined from this value and by compensating for the volume expansion.

Figure A.1 shows a schematic of a procedure for determining the cell density. First, the number of bubbles, $n_b$, in a square of edge length $l$ is counted from a micrograph of the sample. An area having about 100 cells is normally used. The value observed is then normalized to the number of cells in a 10 $\mu$m square, $n_{bo}$. This normalized value is converted to the number of bubbles per volume of 1 cm$^3$. Finally, this converted number is multiplied by the volume expansion ratio to determine the cell density.
The Cell Density

\[
\text{The Cell Density} = \left( n_{bo}^{3/2} \times 10^9 \right) \times \frac{V_f}{V_i}
\]

\[
= (n_b \times 10 \mu m / l)^{3/2} \times 10^9 \times \frac{V_f}{V_i}
\]

**Figure A.1: Procedure for Determining the Cell Density**
The number of bubbles in a 10 μm square, $n_{bo}$, serves a quick check to see if the foam structure is microcellular. When $n_{bo}$ is greater than or equal to one, the structure is microcellular.
Appendix B

Calculation of the Initial CO₂ Volume Fraction in the Polymer/Gas Mixture

In Section IV.1, the weight ratio of the gas flow rate with respect to the polymer flow rate was estimated to be 10%. This value is based on the estimated solubility of CO₂ in various polymers at 200 °C and 27.6 MPa (4,000 psi), a typical processing temperature and pressure, respectively.

Let's calculate the initial volume fraction of the CO₂ in the flowing polymer/gas mixture when the soluble amount of CO₂ is injected into the polymer melt. The volume fraction of gas is expressed as:

\[ \Phi_v = \frac{\dot{V}_g}{\dot{V}_p + \dot{V}_g} = \frac{Q_g v_g}{Q_p v_p + Q_g v_g} = \frac{Q_g}{Q_p} \left( \frac{v_g}{v_p} \right) \left[ 1 + \left( \frac{Q_g}{Q_p} \frac{v_g}{v_p} \right) \right] \]

(B-1)
where
\[ \dot{V}_g = \text{volume flow rate of gas (Q}_g v_g), \text{cm}^3/\text{min} \]
\[ \dot{V}_p = \text{volume flow rate of polymer melt (Q}_p v_p), \text{cm}^3/\text{min} \]
\[ Q_g = \text{mass flow rate of gas, g/min} \]
\[ Q_p = \text{mass flow rate of polymer melt, g/min} \]
\[ v_g = \text{specific volume of gas, cm}^3/\text{g} \]
\[ v_p = \text{specific volume of polymer melt, cm}^3/\text{g}. \]

The solubility of a gas in the polymer melt, i.e., the weight ratio of the gas flow rate with respect to the polymer flow rate, is approximately proportional to the pressure (see Section IV.1). Based on the estimated solubility of 10% at 27.6 MPa (4,000 psi) and 200 °C, the weight ratio of the gas and the polymer flow rates in Equation (B-1) is approximated as

\[ \frac{Q_g}{Q_p} = 0.1 \times \frac{P_b}{27.6 \text{ MPa}} \]

(B-2)

where \( P_b \) is the barrel pressure. Then, Equation (B-1) becomes

\[ \Phi_v = \frac{0.1 \times P_b}{27.6 \text{ MPa}} \left( \frac{v_g}{v_p} \right) = \frac{1}{1 + \left( \frac{0.1 \times P_b}{27.6 \text{ MPa}} \right) \left( \frac{v_g}{v_p} \right) + 1} \]

(B-3)

The specific volume of most polymer melts is approximately 1 cc/g (Tadmor and Gogos, 1979). The specific volumes of CO\(_2\) at 200 °C at various pressures can be obtained from a thermodynamic table of CO\(_2\) (IUPAC, 1973).
Appendix E: Initial CO₂ Volume Fraction in the Polymer/Gas Mixture

For the processing temperature of 200 °C, the initial volume fraction of gas in the mixture was calculated at various pressures. For example, at the pressure of 27.6 MPa (4,000 psi) and the temperature of 200 °C, the specific volume of CO₂ is 2.85 cc/g (IUPAC, 1973). The volume fraction then becomes

\[ \Phi_v = \frac{0.1 \times 2.85}{1 + 0.1 \times 2.85} = 0.22 \]  

(B-4).

Table B.1 shows the specific volume, the estimated solubility, and the initial volume fraction of CO₂ in the mixture at various pressures. The solubility was calculated based on the estimated value of 10 % at 27.6 MPa (4,000 psi).

It may be noted that the initial volume fraction of the soluble amount of CO₂ in the flowing mixture is about 25 % regardless of the pressure.
Table B.1: Specific Volume, Estimated Solubility, and Initial Volume Fraction of CO₂ at 200 °C [Based on the estimated solubility of 10% at 27.6 MPa (4,000 psi) and 200 °C]

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Specific volume of CO₂ (cm³/g)</th>
<th>Estimated solubility of CO₂ (wt %)</th>
<th>Initial volume fraction of CO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 MPa (300 psi)</td>
<td>44.6</td>
<td>0.8</td>
<td>25</td>
</tr>
<tr>
<td>6.2 MPa (900 psi)</td>
<td>14.0</td>
<td>2.3</td>
<td>24</td>
</tr>
<tr>
<td>13.8 MPa (2,000 psi)</td>
<td>6.14</td>
<td>5</td>
<td>23</td>
</tr>
<tr>
<td>27.6 MPa (4,000 psi)</td>
<td>2.85</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>41.4 MPa (6,000 psi)</td>
<td>1.98</td>
<td>15</td>
<td>23</td>
</tr>
<tr>
<td>55.2 MPa (8,000 psi)</td>
<td>1.63</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>68.9 MPa (10,000 psi)</td>
<td>1.45</td>
<td>25</td>
<td>27</td>
</tr>
</tbody>
</table>
BIOGRAPHICAL NOTE

Chul B. Park was born on May 6, 1960 in Jungeup, Korea. He received a B.S. degree in Mechanical Engineering from Seoul National University in 1983, and a M.S. degree in Mechanical Engineering from the Korea Advanced Institute of Science and Technology (KAIST) in 1985. For three and a half years, he continued to work as a research engineer at KAIST. In 1988, he came to the Massachusetts Institute of Technology to pursue his doctoral studies in Mechanical Engineering. After completing his degree, he will join the faculty of the Department of Mechanical Engineering at the University of Toronto. He is a member of Sigma Xi, ASME, and SPE.