Nanocellular Foams with a Superior Thermal Insulation Property

by

Mehdi Sanieisichani

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

© Copyright by Mehdi Saniei 2017
Nanocellular Foams with a Superior Thermal Insulation Property

Mehdi Sanieisichani
Degree of Doctor of Philosophy
Department of Mechanical and Industrial Engineering
University of Toronto
2017

Abstract

For the first time, it was demonstrated that a low-density nanoporous medium with a cell density in the order of $0.96 \times 10^{16}$ and the average cell size of ~70nm, out of isotactic polypropylene could be successfully prepared. This was accomplished by the introduction of a complex nano-fibrillar network into the matrix to alter the crystallization kinetics and to manipulate the nanostructure of polypropylene. Importantly, this recyclable medium had a remarkably 8-fold lower thermal conductivity compared to its solid counterpart owing to the diminution of the heat conduction through the solid fraction as well as the trapped air inside the nanopores with the Knudsen effect.

In the same context, polycarbonate is a special polymer that is not only strong but also it shows very unique characteristics that make it a promising candidate for the nanocellular foam fabrication. Among amorphous polymer, PC is the one that can be crystallized with the assistance of CO$_2$, and the nanocrystals can be harvested as the cell nucleating agent to increase the cell density. Moreover, in this study, it is shown that the solubility of CO$_2$ in PC increases dramatically at a very low temperature (e.g., up to -40 °C), where PC undergoes a transition from a solid to a rubbery state due to swelling and plasticization, so-called the retrograde vitrification behavior.
In this study, a theoretical model based on Henry’s law, Arrhenius equation, and Doolittle equation was developed to predict how the glass transition temperature depresses in the PC/CO₂ system at a different pressure. The experimentally measured solubility data were used to determine the coefficient of the model and to quantify the retrograde vitrification behavior of the PC/CO₂ system. To validate this model, the lower glass transition temperatures of PC/CO₂, at a few different pressures, were measured by using a high-pressure DSC. The results were in agreement with the theoretically predicted data. Furthermore, I demonstrated the rubbery state below the lower glass transitions by inducing foaming and crystallization in the theoretically predicted rubbery region.
To my beloved Bahareh and Ryan, awesome mom and dad for your patient and support through this journey. I could not have done it without you.
Acknowledgments

First, I feel extremely honored for the fulfillment of my Ph.D. degree under the supervision of Prof. Chul B. Park. I express my appreciation and deep gratitude to him for providing me with the guidance and support to get to this level. His scientific visions, deep insights, and valued suggestions not only enriched my research enormously but also will have a perpetual influence in my professional career.

I would like to thank Professor Tobin Filleter for his valuable comments and suggestions offered during my annual exams. Also, I am grateful for Professor David Sinton, and Professor Changchun Zeng for their valuable feedbacks in my Ph.D. final oral examination.

I would like to express my appreciation, and thank Mrs. Brenda Fung, Graduate Program Administrator at MIE department, for her assistance in various situations. I am grateful for the financial support and scholarships from Queen Elizabeth II Graduate Scholarship in Science and Technology, Consortium of Cellular and Micro-Cellular Plastics (CCMCP), and Auto 21.

My special thanks go to Mr. David Stirling, Mr. Mark Lindenfelzer, and Mr. Eric Fredrikson from ZOTEFOAM PLC and MuCell Extrusion LLC for their kind support.

I would like to thanks the other members of Microcellular Plastic Manufacturing Laboratory with whom I have lived five years as a family and will be living with their friendship. My Special thanks goes to Mrs. Kara Kim, Mr. Konstantin Kovalski, Dr. Saleh Amani, Dr. Changwei Zhu, Dr. Raymond Chu, Dr. Mehdi Hamidinejad, Dr. Amir Ameli, Dr. Reza Nofar, Dr. Reza Barzagari, Dr. Nemat Nossieny, Sasan Rezaei, Dr. Alireza Tabatabaei, Mohammed Alshrah, Dr. Vahid Shaayegan, Dr. Takashi Kuboki, Dr. Peter Jung, Dr. Anson Wong, Lun Howe Mark, Dr. Weidan Ding, Dr. Davoud Jahani, Dr. Hasan Mahmood, Dr. Ali Rizvi, Solmaz Karamikamkar,
Dr. Adel Kakroodi, Yasamin Kazemi, Azadeh Zandieh, Pavani Cherukupally, Piyapong Buahom, Sai Wang, Chongda Wang, Chongxiang Zhao, Eunse Chang, Jung Hyub Lee, Mayesha Binte Mahmud.
Table of Contents

Contents

Acknowledgments ............................................................................................................................. v

Table of Contents .......................................................................................................................... vii

List of Tables ................................................................................................................................... x

List of Figures ................................................................................................................................ xi

Chapter 1. Introduction .................................................................................................................... 1

1. Introduction ................................................................................................................................. 1

1.1 Preamble .................................................................................................................................. 1

1.2 Classification of Plastic Foams and their Applications ................................................................. 3

1.3 Plastic Foam Manufacturing Technology .................................................................................... 5

1.3.1 Batch Foaming ...................................................................................................................... 5

1.3.2 Extrusion Foaming ............................................................................................................... 5

1.3.3 Injection Foam Molding ....................................................................................................... 7

1.3.4 Bead Foaming ...................................................................................................................... 9

1.4 The Current Challenges and Future Outlook .............................................................................. 9

1.5 Objective of the Thesis .............................................................................................................. 13

1.6 Methodology and Approach ....................................................................................................... 14

1.6.1 Development of Polymer Blends and Composites with Nanostructures .............................. 16

1.6.2 Generation of Nano-Sized Cells .......................................................................................... 17

1.6.3 Expanding of Nanocellular Plastics ..................................................................................... 17

1.7 Overview of the Thesis .............................................................................................................. 18

Chapter 2. Theoretical Background and Literature Review .............................................................. 21

2. Theoretical Background and Literature Review .......................................................................... 21

2.1 Introduction ............................................................................................................................... 21
## 2.2 Fabrication of Nanocellular Plastics

2.2.1 Block copolymers, polymer blends, and Their Foams

2.2.2 Polymer Nanocomposites and Their Foams

2.2.3 Effects of Crystals on Foaming

## 2.3 Micro/Nanostructuring of Polypropylene using Clarifying Agent

## 2.4 Heat Transfer Mechanism in Cellular Materials

2.4.1 Solid conduction through the polymer matrix

2.4.2 Gas conduction in cellular structure

2.4.3 Radiation in cellular materials

2.4.4 Convection in cellular materials

## 2.5 Retrograde Vitrification Behavior in Polymeric Materials

### Chapter 3. From Micro/Nano Structured Isotactic Polypropylene to a Multifunctional Low-density Nanoporous Medium

#### 3.1 Abstract

#### 3.2 Introduction

#### 3.3 Experimental

3.3.1 Materials

3.3.2 Sample Preparation and Foaming Experiment

3.3.3 Thermal Characterization

3.3.4 Viscosity Measurement

3.3.5 Electron and Optical Microscopy

3.3.6 Thermal Conductivity Characterization

#### 3.4 Results and Discussion

3.4.1 Crystallization Behavior

3.4.2 Foaming Behavior
3.4.3 Thermal conductivity evaluation of the nanoporous samples..........................65

3.5 Conclusion .................................................................................................................68

Chapter 4. Retrograde Vitrification Behavior of Polycarbonate ........................................70

4. Retrograde Vitrification Behavior of Polycarbonate ....................................................70

4.1 Abstract ......................................................................................................................70

4.2 Introduction ..............................................................................................................70

4.3 Theoretical modeling of PC/CO₂ Retrograde Vitrification .........................................76

4.4 Experimental ..............................................................................................................80

4.4.1 Materials ...............................................................................................................80

4.4.2 Sample preparation and foaming experiments.......................................................80

4.4.3 Sample characterization ......................................................................................81

4.4.4 High pressure DSC measurement .....................................................................81

4.5 Results and Discussion ............................................................................................82

4.5.1 Foaming of PC/CO₂ mixture .............................................................................82

4.5.2 High-Pressure DSC .........................................................................................83

4.5.3 Crystallization Behavior ....................................................................................87

4.6 Conclusion ................................................................................................................95

Chapter 5. Summary and Concluding Remarks ..............................................................96

5. Summary and Concluding Remarks ............................................................................96

5.1 Summary ..................................................................................................................96

5.2 Significance and Benefits .......................................................................................96

5.3 How Will the benefits be realized? ........................................................................97

5.4 Key Contributions ...................................................................................................97

References.....................................................................................................................101
List of Tables

Table 3-1. Thermal conductivity evaluation data ......................................................................... 67

Table 4-1. different experimental methods to measure the thermal properties . ......................... 72
List of Figures

Figure 1-1. Thermal conductivity and service temperature range of various materials. .............. 2

Figure 1-2. (a) closed-cell structure, (b) open-cell structure, and (c) reticulated foam structure... 4

Figure 1-3. Schematic Diagram of Extrudate Expansion [7].......................................................... 6

Figure 1-4. Schematic of typical low-pressure foam molding [12]................................................ 8

Figure 1-5. Schematic of typical low-pressure foam molding[12]............................................... 8

Figure 1-6. Cell density of various cellular morphologies versus the expansion ratio for different cell size....................................................................................................................................... 11

Figure 1-7. Cell wall thickness in homogeneous microcellular and nanocellular morphologies versus the expansion ratio for different cell sizes................................................................. 12

Figure 1-8. Cell wall thickness in homogeneous microcellular and nanocellular morphologies versus the cell density for different expansion ratios............................................................. 13

Figure 1-9. Schematic of the Methodology .................................................................................. 16

Figure 2-1. Schematic of PP crystallization kinetics in the presence of nucleating agent and clarifying agent ...................................................................................................................... 30

Figure 2-2. Proposed schematic, monotectic phase diagram of the binary system of i-PP/DMDBS. Four relevant composition ranges are indicated. Sketches and actual optical micrographs (crossed nicols) of the various states of matter of representative mixtures of compositions in those ranges are inserted. REPRINTED (ADAPTED) WITH PERMISSION FROM REF[71]. COPYRIGHT (2003) AMERICAN CHEMICAL SOCIETY .................................................................................. 31
Figure 2-3. Schematic of the Knudsen effect within a cell......................................................... 34

Figure 2-4. Schematic of the radiation rays in low-density and high-density cellular plastics .... 35

Figure 2-5. Contribution of solid conduction, gas conduction, convection, and radiation versus the relative density of LDPE foams with an average cell size of 100μm[81,92]. ......................... 37

Figure 2-6. Contribution of solid conduction, gas conduction, and radiation versus the relative density of the foams for different cell sizes................................................................. 38

Figure 2-7. Fundamental types of T_g behavior as a function of pressure predicted by Condo[96] .................................................................................................................................................................. 39

Figure 3-1. Schematic of PP crystallization kinetics in the presence of nucleating agent and clarifying agent .......................................................................................................................... 46

Figure 3-2. Schematic of the transient plane-source test (TPS)................................................... 51

Figure 3-3. Crystallization temperature of iPP/CA mixture as a function of CA content .......... 53

Figure 3-4. (a) Isothermal TGA of the clarifying agent at 200°C for 30 min, (b) TGA of the clarifying agent, iPP/0CA, and iPP/0.5CA .............................................................................................................................. 54

Figure 3-5. (a) Complex shear viscosity of iPP/0CA & iPP/0.5CA, (b) Van-Gurp-Palmen plot. 55

Figure 3-6. DSC cooling (Left) & heating (Right) thermograms of iPP/0CA and iPP/0.5CA at a rate of 10°C/min ....................................................................................................................... 56
Figure 3-7. (a) Transmission electron microscopy of iPP/0.5CA, (b) Optical microscopy of the fibers were formed from iPP with 10wt% CA, (c) SEM of the pure CA particles that turned into fibers at 155°C.

Figure 3-8. Polarized Optical micrograph of the morphology of compression-molded films of (a) iPP/0CA and (b) iPP/0.5CA.

Figure 3-9. DSC melting thermograms of the iPP/0CA and iPP/0.5CA isothermally treated under 30 MPa for 15 min and 30 min at different temperatures.

Figure 3-10. SEM micrographs of iPP/0CA (a1, a2, and a3) and iPP/0.5CA (b1, b2, and b3) samples foamed by saturation in sc-CO2 at different temperatures for 15 min. The foaming temperature of the first (a1 and b1), second (a2 and b2), and third (a3 and b3) columns were 145°C, 147.5°C, and 150°C, respectively. Each row has the same magnification.

Figure 3-11. (a) Average cell density, (b) cell size, and (c and d) expansion ratios (with and without the skin) of the samples foamed at different temperatures.

Figure 3-12. SEM micrographs of nanoporous iPP/0.5CA sample foamed 149°C after saturation in sc-CO2 for 30 min (a and b) are from the core of the sample with two different magnifications, (b and c) are from the skin of the samples.

Figure 3-13. Thermal conductivity of the samples versus the expansion ratio and the average cell size.

Figure 4-1. The definition of the glass transition temperature as a slope change in (a). the volume, (b). enthalpy, (c). storage shear modulus, (d). volume coefficient of expansion which is the first.
derivative of the volume, (e). specific heat capacity which is the first derivative of enthalpy, and (f). the loss shear modulus versus temperature[174].

Figure 4-2. Theoretical model of the glass transition temperature of PC/CO$_2$ overlaid on the CO$_2$ phase diagram.

Figure 4-3. Optical microscopy (a$_1$, b$_1$, and c$_1$) were taken in a lateral direction, and SEM (a$_2$, b$_2$, c$_2$, and d$_2$) were taken in a longitudinal direction of the samples were introduced with cells at different T and P right after a rapid depressurization.

Figure 4-4. Specific heat capacity ($C_p$) of the PC/CO$_2$ system at low temperature and pressure of (a) at 80 atm, (b) at 90 atm, (c) at 100 atm, (d) at 110 atm, and (e) at 130 atm. A solid curve is drawn to show the trend of the $C_p$ data to elaborate the $T_{GL}$.

Figure 4-5. $T_g$-P profile of PC/CO$_2$. (a) HP-DSC experimental data points. Note that the HP-DSC data points here are different from those of Figure 4-3. (b) $T_{GL}$ data from HP-DSC experiment.

Figure 4-6. POM micrographs of the PC sample saturated at -30$^\circ$C and 100 atm. The sample thickness was 200 µm. The crystals were developed slowly over time.

Figure 4-7. Curves of constant fractional free volume for PC/CO$_2$.

Figure 4-8. Isothermal DSC curve of the saturated samples for different period of time, (a) at -30$^\circ$C and 100 atm, (b) at 130$^\circ$C and 100 atm, (c) at 130$^\circ$C and 120 atm, (d) at 130$^\circ$C and 150 atm, corresponding to “A, B, C, and D” in Figure 4-7, respectively.

Figure 4-9. Crystallinity of the samples (A, B, C, and D in Figure 4-7 & Figure 4-8) versus saturation time.
Figure 4-10. Crystallographic patterns of the PC samples, (a) saturated at -30°C and 100 atm for 0 hr, 72 hrs, and 2 weeks; (b) saturated at 130°C under 100 atm for different periods of time; (c) saturated at 130°C under different pressures for 24 hrs. In these figures, A, B, C and D correspond to A, B, C, and D in Figure 4-7, respectively. ................................................................. 94

Figure 5-1. Overview of characteristics (average cell size, porosity, expansion ratio, and cell nucleation density) of nanocellular foams achieved from various polymer systems. REPRINTED (ADAPTED) WITH PERMISSION FROM Journal of Applied Polymer Science Volume 131, Issue 23, 14 AUG 2014 DOI: 10.1002/app.41293[113]................................................................. 98
Chapter 1. Introduction

1. Introduction

1.1 Preamble

Every segment of our society uses plastics and plastic composites. In many applications, their excellent strength-to-weight ratios and processing ease have given them an undeniable advantage over other conventional materials such as metals and ceramics. However, due to the substantial increase in the price of crude oil, manufacturers who produce plastic products have made much effort to reduce their material costs, which account for about 70% of the production cost. In this context, plastic foaming offers a timely solution to the problem of the continuously rising cost of plastic resins. In the last decade, the emergence of microcellular plastics (i.e., plastics with micron-sized cells) has expanded the market for plastic products to include such high-value industrial and consumer applications as thermal insulation, soundproofing, impact absorption and safety harnesses, and high-end filtration and packaging products.

Advanced composite materials, such as polymer blends and composites with nanostructures, offer great promise for improving various physical properties. Taking the technology one step further, the introduction of nanocellular structures in these advanced composites through foaming will translate into unprecedented improvements in thermal insulation property, weight loss, and material cost reductions. So, systematic research on materials and processes is needed to produce innovative low-density nanocellular foam products. Fundamental studies of the following four most important parameters that govern the quality of nanocellular plastic products must be undertaken: morphology, crystallization, cell nucleation, and cell growth behavior of polymer blends and composites with nanostructures. An understanding of these parameters is crucial to the development of low-density nanocellular plastic foams. Such knowledge will provide strategic
guidance in identifying the most effective and efficient material compositions and processing conditions and will translate into the technological insights needed to develop novel, high-value plastic products. Figure 1-1. **Thermal conductivity and service temperature range of various materials.** shows the thermal conductivity of different materials for different service temperature.

In this thesis, I have tried to fabricate a new family of materials which is shown in Figure 1-1. In green color as nanocellular plastic foams.

**Figure 1-1.** Thermal conductivity and service temperature range of various materials.
Extensive research in the field of microcellular plastics has resulted in new insights that will help in the development of the next generation of high-performance cellular plastics, that is, “nanocellular plastics”. Nanocellular plastics are plastics with nanometer-sized cellular morphologies. It is reported that, as the cell size is reduced to the submicron and nanometer regions, the cellular plastic’s thermal insulation[1] and mechanical[2] properties will be dramatically improved. However, the production of nanocellular plastics is technologically challenging. This is mainly due to the thermodynamically unstable nano-sized cells and the short time span between cell nucleation and growth. Consequently, the majority of nanocellular plastics investigated have very limited foam expansion ratios[3,4] or open-cell morphologies[5]. In this project, I will develop low-density nanocellular plastics. As well as reducing weight, these will enhance the plastic’s thermal insulation. In the automotive and packaging sectors, the material weight reduction will reduce fuel consumption and lessen the carbon footprint of vehicles. Additionally, the superior thermal insulation property of the proposed low-density nanocellular plastics will significantly reduce the current high energy consumption and the 8.3-Gton greenhouse gas emissions of the heating and air-conditioning systems of the developed world’s buildings and high-rises.

1.2 Classification of Plastic Foams and their Applications

Foams are often characterized by three parameters. 1) volume expansion ratio ($\Phi$) which is the volumetric ratio of foam to the unfoamed material; 2) average cell size ($D_{avg}$); 3) cell density with respect to the unfoamed volume (N). The foam density categorized as high-density foams ($\Phi$<4), medium-density foams (4<$\Phi$<10), and low-density foams ($\Phi$>10). The foam morphology also can be categorized by closed-cells in which individual cells are completely separated by cell walls,
open-cells where pores exist on the cell walls, or by a reticulated structure where cells are completely devoid of cell walls as shown in Figure 1-2. Closed-cell foams often exhibit a better mechanical strength and thermal insulation properties since the heat transfer through the gas is limited to a very small space within the cells. Also, closed-cell foams exhibit a better barrier property when gas/liquid permeation is undesirable. Open-cell foams are often used for adsorption applications (e.g., sponge), sound insulation, filtration, cushioning due to the flexibility, and packaging because of energy absorption properties. Due to a very high porosity of reticulated foams, they can be used for filtration process with a high flow rate.

![Figure 1-2.](image)

*Figure 1-2.* (a) closed-cell structure, (b) open-cell structure, and (c) reticulated foam structure.

In terms of the cell density and cell size, foams are classified as conventional foams ($D_{avg} > 300\mu m$ and $N < 10^6$ cells/cc), fine-cell plastics ($10 < D_{avg} < 300\mu m$ and $10^6 < N < 10^9$ cells/cc), microcellular plastics ($0.1 < D_{avg} < 10\mu m$ and $10^9 < N < 10^{15}$ cells/cc), nanocellular plastics ($D_{avg} < 0.1\mu m$ and $N > 10^{15}$ cells/cc)[6]. Rigid foams and flexible foams are also two terms by which two more general types of foams can be categorized. The rigidity or flexibility of foams depends on the base polymer, open cell content, and foam density.
1.3 Plastic Foam Manufacturing Technology

1.3.1 Batch Foaming

In terms of the ease of control and setup, batch foaming is one of the most well-studied processing methods to fabricate a cellular structure. It consists of a high-pressure vessel wherein a polymer sample is placed and pressurized with a physical blowing agent (e.g., CO\textsubscript{2}). The pressure and temperature can be accurately controlled using a temperature controller and a high-pressure syringe pump. After the gas dissolution process, either a temperature increase or a pressure drop, as a thermodynamic instability which causes a sudden drop in gas solubility, can result in the cell nucleation. In the first scenario so-called one-step batch foaming, the polymer is being saturated at an elevated temperature and pressure. After the pressure released, since the temperature is high and the viscosity is low, the cells can nucleate and grow. In this method, an effective cooling strategy should be applied to prevent cell coalescence and deterioration. On the other hand, batch foaming can be performed by saturating a polymer at an elevated pressure and room temperature. Since the gas diffusivity at room temperature is lower than that of at a higher temperature, depending on the thickness of the sample, a fully saturated state might be reached after a long period of time (e.g., 24 hours or longer). After saturation, a temperature increase causes the foam expands as cells are nucleated and grow.

1.3.2 Extrusion Foaming

All continuous production methods of microcellular foams such as extrusion foaming are complex phenomena, which are only the result of high-temperature and low-moisture conditions. Bubble nucleation, bubble growth, and bubble collapse are the events which occur during the phase transition and transformation from the base resin to the foam state. Foam extrusion is shown schematically in figure 1-3.[7]
Extrusion is one of the most common continuous methods to fabricate polymeric foam. A gaseous or supercritical phase can be introduced into the molten polymer through direct injection of a physical blowing agent or decomposition of a chemical blowing agent. The plasticizing screw rotates and generates a polymer/gas solution during the foam extrusion process. This technology ensures that the pressure in the extrusion barrel is relatively constant and that consistent gas dosing is attained for uniform polymer/gas mixture regardless of pressure fluctuations in the plunger[8]. A homogeneous polymer-gas mixture is being extruded through a die where the temperature and geometry of the die can generate enough resistance to provide desirable pressure drop rate for foaming. The measure of gas dissolved in polymer melt governs the cell morphology. Therefore, accurate control of the amount of gas which is injected into the extruder's barrel is the most critical issue in the process. A syringe pump is an excellent device for steady and precision gas flow rates in advanced structural foam molding. These pumps deliver reliable feeds in both “constant pressure” mode during the start-up phase of the process, and “constant flow” mode throughout the injection process, providing stable and constant gas flow into the polymer melt[9]. The extrusion
process could be improved by adding a melt pump to stabilize the flow of material and increase the pressure in the extruder barrel. Pressure should be monitored by a pressure transducer where the melt enters the pump. The pressure reading coming from the transducer is used to control the screw speed to ensure a uniform melt output at the end of the extruder[10,11]. The foam characteristics and morphology (e.g., cell density, cell size, and foam density) for any specific application can be tailored by using various materials and controlling the processing parameters.

1.3.3 Injection Foam Molding

During the past decades, many special injection molding processes have been developed either to address the possible solutions for the well-known defects on the conventional injection molded parts (e.g., local shrinkage, warpage, and weakness of the welding line). Also, to produce parts with special features that cannot be achieved by the conventional injection molding process at economically beneficial rates. These developed processes include low- and high-pressure foam injection molding and gas-counter-pressure foam molding.

Low-pressure foam molding is a process in which the mold cavity is partially filled with the mixture of a polymer and a blowing agent under a high injection pressure. A schematic of typical low-pressure foam molding is shown in figure 1-4. This method is being used to produce about 90% of thermoplastic structural-foam production worldwide because of its low cost. On the other hand, some disadvantages of this method such as large cell size production (greater than 1 mm), non-uniform cell size distribution (less than 1000 cells/cm³), low void fraction (typically less than 15%), and poor surface quality of the foams have restricted it to broader application.
Figure 1-4. Schematic of typical low-pressure foam molding.[12]

Figure 1-5 shows a schematic of a high-pressure foam molding. In this process, the pre-measured shot of a foamable mixture is injected into the mold under high pressure and with complete filling. The blowing agent is not able to expand in the cavity due to the high pressure, and thus, less swirl is created. So, it produces parts with a better surface quality than the low-pressure foam molding. Yet, cells cannot nucleate in this stage. After solid skin establishes, the mold retracts or expands to allow the cell to nucleate, and blowing agents to expand inside the core of the part. The popularity of the high-pressure technique is not as same as the low-pressure one because of practical limitations on part geometry and mold investments (typically 15–45% higher than for low-pressure types).

Figure 1-5. Schematic of typical low-pressure foam molding.[12]
1.3.4 **Bead Foaming**

In this technology, the pre-expanded beads of expandable polystyrene (EPS) or polypropylene (EPP) are sintered into a specific 3D geometry using steam-chest molding. The production of expanded beads of EPP and EPS is, however, totally different. The unexpanded EPS beads are typically prepared using n-pentane in the polymerization step and have a limited shelf time because n-pentane is volatile and diffuses out of them gradually. The unexpanded beads undergo the expansion process inside a pre-expander prior to the steam-chest molding. In the meantime, the EPP beads are prepared after they are immersed in a rotating fluid mixture (e.g., water, dispersion agent, and surfactant) under the pressure of a blowing agent (e.g., CO₂) following by depressurization. Due to a very high expansion ratio of EPS foams which results in a low thermal conductivity, EPS foams are widely used for thermal insulation applications. However, EPS foams show a very low flexural strength. Compared to EPS, EPP possesses a good mechanical property due to the inclusion of crystals and is used generally for automotive parts and sport protective gears.[13–15]

1.4 **The Current Challenges and Future Outlook**

Producing nanocellular plastics is challenging due to (a). The difficulty of Inducing a proper nanostructure favorable for nanocell formation, (b). Thermodynamically unstable nano-sized cells, since they lead to a huge increment of the interfacial (surface) area which results in a lot of interfacial (surface) free energy, and (c). The extremely short time span between the nucleation and collapse/growth of the nano-sized cells. Consequently, the majority of nanocellular plastics investigated have very limited foam expansion ratios[3,4] or open-cell morphologies[5]. Moreover, they barely have the cell density more than 10^{14} cells/cm³ and the cell size below 100nm. The morphology of the homogeneous anisotropic cellular structure can be modeled mathematically, as equation 1-1, in terms of the cell density (N), average cell size (D), and the
expansion ratio (Φ) by which a cellular structure is characterized. Equation 1-2 mathematically represents a relationship between the cell wall thickness (δ) in terms of the cell density and expansion ratio.[16–18]

\[
D \approx [(\Phi - 1) \cdot \frac{1}{\pi N}]^{\frac{1}{3}} \quad \text{Equation 1-1}
\]

\[
\delta = \left(3 \sqrt[3]{\frac{\Phi}{\Phi - 1} - 1}\right) \cdot \frac{\Phi - 1}{N} \quad \text{Equation 1-2}
\]

Figure 1-6 depicts the relationship between these three competing parameters that define the morphology of the foams. The characteristic of a cellular structure which fits under the definition of nanocellular foams is presented with a green color. The cell wall thickness in a nanocellular structure is shown in figure 1-7, and figure 1-8 versus the expansion ratio and cell density, respectively. Based on a mathematical estimation using Equation 1 and Equation 2, the thickness of a cell wall in nanocellular structure falls in the order of less than 10 nm. Considering the viscoelastic behavior of the polymers and a high strain rate biaxial stretch that the cell wall experiences during the cell growth in a high-pressure batch foaming process, the cell walls are extremely prone to be ruptured. This makes it extremely challenging to fabricate a closed-cell nanocellular structure.
Figure 1-6. Cell density of various cellular morphologies versus the expansion ratio for different cell size.
Figure 1-7. Cell wall thickness in a homogeneous microcellular and nanocellular morphology versus the expansion ratio for different cell sizes.
Figure 1-8. Cell wall thickness in a homogeneous microcellular and nanocellular morphology versus the cell density for different expansion ratios.

1.5 Objective of the Thesis

The long-term objective of the proposed research is to develop an innovative nanocellular foaming technology for nanostructured materials with a high expansion ratio, using the environmentally-friendly blowing agents N₂ and CO₂. The technology will combine these three steps: (1) materials development for nanocellular foams; (2) generation of nano-sized cells; and (3) increasing the expansion ratio of nanocellular plastics. This advanced foaming technology is expected to result in unprecedented improvements in plastic products so that they both weigh less and cost less and have vastly improved thermal insulation. The scientific understanding obtained from this research will provide strategic guidance in identifying the most effective and efficient
To attain low-density nanocellular plastic foams, it will be essential to develop suitable material systems and processing technologies to nucleate a large number of nano-sized cells and to expand these nuclei without passing beyond the nanoscopic realm. The first phase of my research will develop nanostructured polymer blends and composites with different sizes and morphologies by changing the materials composition, the compounding conditions, the thermal treatment, etc. In the second research phase, the polymer blend and composite systems containing nanostructures will be introduced to a foaming apparatus. Although various foaming processes will be considered, a batch-type foaming process with numerous control parameters will be mainly
used to take advantage of the crystals to be induced during gas saturation[13]. A solid-state or melt-state foaming apparatus will also be used to systematically examine the nucleation of the nano-sized cells with the polymer blends and composites prepared earlier. The results from the cell nucleation experiments will be used to assist in identifying a viable processing window for the fabrication of polymer blends and composites with nano-sized, closed-cell nuclei.

The second phase of the project will also promote foam expansion of the polymer blends and composites with the nano-sized cells to the desired density levels. The nanocell-nucleated blend/composite foams produced earlier will be re-introduced into the solid-state foaming environment to allow the nano-sized cell nuclei to expand and to further reduce the density of the nanocellular plastics. During the refoaming process, it will be essential to control the processing conditions to prevent these nano-sized cells from degrading or expanding beyond the nanoscopic realm. A systematic study will be performed to elucidate the expansion and stabilization behaviors of the polymer blend/composite foams developed in the early stage of the second phase.

The third phase will evaluate the thermal insulation properties of the low-density nanocellular foam prototypes. The properties will be measured as a function of the cell-number density and the foam density to derive the structure-property relationship. To decrease heat transfer through the plastic matrix, I will develop strategies to foam the plastics to a high expansion. Based on the above research results, I will develop guidelines for choosing the optimal nanocomposite compositions and processing conditions in the fourth phase. These guidelines will be an important strategic tool in the development of new low-density nanocellular plastic products.
It has been reported that it is preferable to create nanostructures within the polymer matrix to nucleate and sustain nano-sized cells. In this regard, the use of polymer block copolymers and blends\cite{2,3,19–29} has been seen as a promising technique to create nanostructures with a variety of sizes and morphologies. Some recent studies\cite{30,31} reported that nanofiller materials (e.g., nanoclay, nanosilica, and carbon nanotube) could contribute significantly to the crystallization of the matrix, and thereby to cell nucleation. Therefore, selecting the proper polymer types, nanofillers, and thermal conditions is vital to the successful creation of the desired nanostructures in the development of low-density nanocellular plastic foam. I propose a systematic study of the effects of the materials composition, the compounding conditions, and the thermal treatment (temperature and time) on the sizes and morphologies of the dispersed heterogeneous polymer domains, nanofillers, and nanocrystal structures in the polymer matrix. Accordingly, I will develop the following: (i) materials with different nanostructures for nanocellular plastics production, and
(ii) an extensive database on the materials and processing conditions needed to create the desired nanostructures. Also, the generation of a high amount of residual stress in the polymer matrix can decrease the activation energy for cell nucleation[32–34].

1.6.2 Generation of Nano-Sized Cells

The production of cellular plastics has a long history and is technologically mature. Despite this, achieving and stabilizing cells in nanometer sizes is very challenging, primarily because of the extremely short time span between the nucleation, growth, and collapse of these cells, even after a successful introduction of a proper nanostructure favorable for nano-cell nucleation described in Section 1.6.1. The proposed project will approach this challenge by decoupling the control of the entire foaming process into two steps: the nucleation of nano-sized cells, and the foam expansion. For the first step, it will be essential to nucleate a high population density of nano-sized cells. A systematic study will be conducted by inducing a thermodynamic instability in various foaming processes such as thermally induced and pressure-induced foaming for the nanostructured materials at their solid and melt states. During the process, I will investigate the effects of the nanostructure morphologies, the gas impregnation pressure, and temperature on the resulting foam structure.

1.6.3 Expanding of Nanocellular Plastics

In our earlier microcellular foaming processes, refoaming of the foamed samples was observed to be very effective in decreasing the foam density as long as the cells are highly closed. This approach might be used to decouple the foam density control in nanocellular foaming process. During the refoaming step, the nucleated nanocellular plastics will be allowed to impregnate and expand with a blowing agent again. To prevent the cells from over-expanding and coalescing, it will be vital to control the viscosity of the polymer matrix. A series of experiments will be
conducted to examine the evolution of the cellular morphologies under a variety of processing conditions during this step.

1.7 Overview of the Thesis

Chapter 2 presents a literature review on nanocellular foams. It outlines the previous studies about the various approaches and efforts to fabricate submicron and nano-sized cells. It also outlines the methods for the preparation of micro- and nanostructured medium appropriate to be introduced with a nanocellular structure. It specifically discusses the inclusion of a clarifying agent to induce a nonfibrillar network in the polymer to manipulate the crystallization kinetics and prepare a nanostructured medium. Finally, it discusses the heat transfer mechanism in cellular materials and elaborates a dramatic improvement of the thermal insulation property after the introduction of a nanocellular structure in a polymeric medium.

Chapter 3 focuses on the fabrication of a multifunctional low-density nanocellular medium. It describes the development of a method to make a low-density nanocellular foam with an average cell size of ~60nm to ~70nm and the cell density in the order of $0.98 \times 10^{16}$ cells/cm$^3$. It discusses the preparation of a nanostructured clarified polypropylene matrix and manipulation of the crystallization kinetics. It presents experimental steps and characterization results. It also discusses the effects of processing parameters on the formation of a nanofibrillar network and crystal morphology in polypropylene. It elaborates on the effects of saturation time and temperature, as an isothermal treatment of a clarified polypropylene with supercritical CO$_2$, on the cellular morphology of the foamed samples. It also discusses the effect of various morphologies of the nanofoam samples, specifically the average cell size and expansion ratio, on the thermal conductivity of the nanofoam. In this context, polypropylene was chosen because it has not only a lower density compared to other polymers, but it also is a semicrystalline polymer which inherently
possesses a controllable crystallization kinetics (not too fast compared to polyethylene and not too slow like PLA)[14,35–37]. The aim is to develop an industrially viable method to fabricate nanocellular foams in a batch foaming process. Also, it can serve as a baseline and a road map for dynamic processes such as extrusion foaming and foam injection molding.

Chapter 4 focuses on the preparation of a unique nanostructured medium using polycarbonate and elaborates on an exclusive processing window in which the polycarbonate shows an uncommon behavior, called retrograde vitrification. There are a few substantial and decisive requirements in the fabrication of nanocellular medium through foaming with an inert and green physical blowing agent. Among those requirements, having a nanostructured medium and increasing the gas solubility are the most important ones by which the cell nucleation can be enhanced dramatically. In this context, polycarbonate is a special polymer that not only is strong but also shows a unique characteristic that make it a very promising candidate for the nanocellular foam fabrication. Among amorphous polymer, PC is the one that can be crystallized with the assistance of CO$_2$, and the nano-crystals can be harvested as the cell nucleating agent to increase the cell density.

Moreover, in this chapter, I have shown that the solubility of CO$_2$ in PC increases dramatically at a very low temperature (e.g., up to -40 °C) where PC undergoes a transition from a solid to a rubbery state due to swelling and plasticization. So far, there have been only few amorphous polymers that show this behavior and provide a unique processing window adjacent to the lower glass transition temperature, where the gas solubility and the amount of stress variation inside the polymer are considerably high.

In this chapter, a theoretical model based on Henry’s law, Arrhenius equation, and Doolittle equation were developed to predict how the glass transition temperature depresses in the PC/CO$_2$
system with pressure. The experimentally measured solubility data were used to determine the coefficient of the model and to quantify the retrograde vitrification behavior of the PC/CO₂ system. To validate this model, I measured the lower glass transitions of PC/CO₂ by using a high-pressure DSC and compared the results with the theoretically predicted data. Furthermore, I also demonstrated the rubbery state below the lower glass transitions by inducing foaming and crystallization in the theoretically predicted rubbery region. Also, systematic foaming experiments at low temperature were conducted, and the crystallization kinetics of PC with the assistance of CO₂ was studied and characterized.

Chapter 5 serves as a summary of this thesis. It discusses the significance of the work and how the benefits can be realized. The major contribution of this thesis is also outlined. Finally, this chapter provides a list of recommendation for future research.
Chapter 2.

Theoretical Background and Literature Review

2. Theoretical Background and Literature Review

2.1 Introduction

Advanced composite materials, such as polymer blends and composites with nanostructures, offer great promise for improving various physical properties. Taking the technology one step further, the introduction of nanocellular structures in these advanced composites through foaming will translate into unprecedented improvements in thermal insulation, weight loss, and material cost reductions. To produce innovative, low-density nanocellular foam products, systematic research on materials and processes is needed. Fundamental studies of the following four most important parameters that govern the quality of nanocellular plastic products must be undertaken: morphology, crystallization, cell nucleation, and cell growth behavior in polymer blends and composites with nanostructures. An understanding of these parameters is crucial to the development of a low-density nanocellular plastic foam. Such knowledge will provide strategic guidance in identifying the most effective and efficient material compositions and processing conditions and will translate into the technological insights needed to develop novel, high-value plastic products.

For many years, researchers have made considerable efforts to reduce the overall cell size and to increase the cell size uniformity of certain plastic foams. As a result, a category of foamed plastics known as “microcellular plastics” was born; these typically exhibit cell sizes smaller than 10 μm and cell densities larger than $10^9$ cells/cm$^3$ [38]. Microcellular plastics display substantially superior features compared with their unfoamed counterparts; they exhibit higher impact strength (up to a five-fold increase)[39–42], toughness (up to a five-fold increase)[17], and fatigue
properties (up to a fourteen-fold increase)[43]. Moreover, in comparison with conventional plastic foams or solid plastics, microcellular plastics have enhanced thermal properties[41], as well as improved optical[44] and insulation properties[45]. It is also important to note that microcellular foams exhibit superb surface qualities that have drastically improved the “touch sensation” of many plastic parts.

Recently, the reduction of cell size from microcellular to the nanoscale, the so-called “nanocellular plastics”, has received much academic and industrial research attention because of its further improved properties. As cell sizes decreased to nanometer regions, the thermal insulation characteristics were improved[1]. Also, the mechanical strength (e.g., strain to failure and impact energy absorption) of cellular plastics can also be dramatically improved[2], reaching or even surpassing the strengths of unfoamed plastics by taking advantage of crystallization[46]. The improved mechanical strength of nanocellular foams can be attributed to an increase in the cell surface area that is caused by a strength-enhancing molecular orientation. Also, the nanocellular foams of amorphous polymers can appear transparent, which is an important characteristic in some automotive or aerospace applications.

However, producing nanocellular plastics is challenging due to the difficulty of inducing a proper nanostructure favorable for nano-cell formation, thermodynamically unstable nano-sized cells, since they lead to a huge increment of the interfacial (surface) area which results in a lot of interfacial (surface) free energy, and extremely short time span between the nucleation and collapse of the nano-sized cells. Consequently, the majority of nanocellular plastics investigated have very limited foam expansion ratios [16, 17] or open-cell morphologies [18].
2.2 Fabrication of Nanocellular Plastics

Microcellular foams can be manufactured by several methods; for instance, sintering, stretching, removal of inorganic salts, phase separation of polymer solutions and polymer foaming. Microcellular foaming has been studied for years in order to decrease the cell size and to increase the cell density to manufacture high-performance polymeric foams[16,17,20,31,47–49]. Nanocellular foams have successfully manufactured by a few techniques; for instance, in batch foaming by rapid pressure quenching[48], using blends with high \( T_g \)[49], and taking advantage of organoclay-polymer nanocomposites[31].

2.2.1 Block copolymers, polymer blends, and Their Foams

Block copolymers and polymer blends provide a versatile platform for creating a wide variety of nanostructures. The nanostructures, which are different regarding the gas solubility and the viscoelasticity, were used to fabricate the nanocellular plastics. Yokoyama et al.[3,23], Li et al.[21], and Taki et al.[24], used a diblock copolymer and CO\(_2\) as a foaming agent, to fabricate nanocellular foam with the cell size of 20-50 nm. The rationale behind their method is to use nanoscale-ordered spherical morphology within block copolymers that act as a template for nucleation and growth. The self-organized micelles which serve as internal “soft segments” in polymer matrix not merely can induce heterogeneous nucleation and growth of CO\(_2\) bubbles but also serve as CO\(_2\)-philic reservoirs to trap CO\(_2\).

Yokoyama et al. used CO\(_2\)-philic fluorinated polymers as a block component[3,21,23,50]. A principle of this method is that the fluorinated block copolymer localizes CO\(_2\) in their CO\(_2\)-philic fluorinated block nanodomains, and the CO\(_2\) leaves empty voids in the nanodomains of the CO\(_2\)-philic fluorinated block after the CO\(_2\) is depressurized. Foaming can be restricted in the fluorine-containing nanodomains; therefore, an empty void is surrounded by a thin wall of the CO\(_2\)-philic
fluorinated domain. Taki et al.[24], in their piece of works, tried to avail themselves of a material with a very high CO₂ affinity[e.g., poly(ethylene glycol); PEG] in order to promote foaming in bulk polymer blends. However, large bubbles in the CO₂-philic part were appeared due to the incorporation of such CO₂-philic polymers in the stiff polymer matrix. Taki et al.[24] followed Yokoyama’s idea and fabricated nanoscale wells on the surface of a polystyrene (PS)-b-poly(methyl methacrylate) (PMMA) di-block polymer by CO₂ foaming. Yokoyama’s method of preparing nanocellular plastics was further used for other polymer blends, such as PS/PMMA blends[41], PP/propylene-ethylene rubber (PER)[26], polypropylene (PP)/hydrogenated styrene-b-butadiene-b-styrene rubber (HSBR), PP/hydrogenated styrene isoprene styrene (HSIS) copolymer blends[25], poly(ether ether ketone) (PEEK)/poly(ether imide) blends[27], and PMMA/poly(methyl methacrylate)-block-poly(butyl acrylate)-block-poly(methyl methacrylate) (MAM) blends[20]. Further, nanocellular structures were produced by manipulating the foaming temperature and the concentration of dissolved blowing agents for poly(ether imide) (PEI)[28,51], poly(ether sulfone) (PES)[28], and their blends[29].

Otsuka et al.[19] conducted their foaming experiments on polystyrene/poly (methylmethacrylate) (PS/PMMA) blend and prepared nanocellular structure with the cell size of 40-50 nm and the cell density of 10^{14} cell/cm^3. They tried to control the bubble nucleation and growth using a polymer blend with different CO₂ solubility and viscoelasticity. In their experiments, the foaming temperature was chosen lower than the T_g of the matrix which was polystyrene. Consequently, the bubble growth was confined within the nano-sized dispersed domain and was suppressed by the stiffness of the matrix.

Nemoto et al.[25] prepared nanocellular foam from a nanostructured medium with a morphology of the polymer blend in which the bubble nucleation and growth were controlled by
nano-scale dispersed domains. They exploited the differences in viscoelasticity and diffusivity of a semicrystalline polymer as a matrix and rubber as a dispersed phase to control the bubble nucleation site inside the dispersed phase of their polymer blend (PP/propylene-ethylene copolymer (PER)). In their work, the crystallinity of the matrix was considered to manipulate the viscosity and diffusivity of the matrix with the purpose of having a lower solubility and diffusivity of CO₂ within the matrix phase during the saturation. By setting the foaming temperature below the crystallization temperature of the PP and using pressure quench method, they were able to control the cellular structure within the rubber domain, and the cell sizes were in the range of 0.5 - 2 μm.

Nemoto et al.[26] extended their experiments with the aim of reducing the cell size to control the foam structure. They developed their previous work and made a lamellar structure with aligned bubbles in one direction in order to have light reflective nanocellular foam. In their study, they used PP as a matrix and thermoplastic polystyrene elastomer (TPS) as the nanoscale dispersed domain which was either a hydrogenated polystyrene-block-polybutadiene-block-polystyrene (HSBR) or a hydrogenated styrene isoprene styrene (HSIS) copolymer. They took advantage of the crystallinity of PP and prepared nanocellular structure at 120°C in which PP had an appropriate stiffness and CO₂ solubility. Furthermore, nanocellular foam with an oriented cellular structure was fabricated by stretching a blend film and resulted in a highly ordered morphology with nanoscale rubber domain.

Block copolymers have the ability to be structured with local segregation of different polymer blocks which results in nanometer-sized molecular scale aggregates[3,23]. Depending on the relative chain length of the polymers and proportion of each block, di-block and tri-block, copolymers can offer different distribution of self-assembly blocks in the nanoscale range; for
instance, commercially available copolymers based on PS and PMMA units[21]. Depending on the mixing condition, additive quantity, and chemical composition of the matrix and copolymer, di-block and tri-block copolymers are able to be dispersed into other appropriate polymers at a nanometric scale. Consequently, one kind of nano-structured materials can be developed by adding a small amount of di-block copolymers. Nevertheless, several limitations are in mentioned pieces of work:

- Nanocellular foams have been achieved using thin film samples with the thickness of below 200um which makes the analysis of mechanical and thermal properties very difficult.
- The range of application of these foams is limited greatly since a small density reduction is achieved.
- A rather long and non-trivial chemical synthesis is needed to produce the CO₂-philic di-block fluoropolymers, which involves the use of several monomers under well-controlled synthesis conditions[20].

2.2.2 Polymer Nanocomposites and Their Foams

Crystalline fillers, such as glass fiber and nano clay, are usually used to augment the mechanical properties of the polymeric products. Moreover, they can improve the mechanical properties of the polymer foams; however, the original values for yield and ultimate stress of the pure polymeric samples could not be recovered. The nanofiller materials (e.g., nano clay, nanosilica, and carbon nanotube) play three important roles in plastic foam products: (i) reinforcement of the polymer matrix, (ii) enhancement of the crystal nucleation, and (iii) enhancement of bubble nucleation.

Foaming of nanocomposite polymers based on an amorphous polymer and nano clay carried out by Ito et al.[52]. He conducted his studies on organoclay polymer nanocomposites and claimed nanocellular structure from polylactide with a cell size of 200 nm[53]. A key point to manufacture
micro and nanocellular structure from nanocomposites is to disperse and exfoliate the nanoparticles completely within the matrix resulting in the melt strength, thermal stability, and the mechanical properties to improve. Moreover, acting as nucleating agent, the dispersed nanoparticles are able to improve the cellular structure of the foam. A series of complex chemical treatments have been employed to modify nanoparticles, especially nanoclay and carbon nanotubes, which resulted in better dispersion and exfoliation into the polymer matrix[54].

2.2.3 Effects of Crystals on Foaming

Crystals help to induce cell nucleation and maintain foam structure, but an excessive volume of them causes the viscosity of the polymer-gas mixture to increase unnecessarily too high, which hinders foam expansion. Also, gas cannot be dissolved into the crystalline regions effectively. If the size of these crystals is too large, this produces a non-uniform cell nucleation and foam structure. Previous studies have shown that a proper selection of processing parameters make it possible to tailor the crystallization kinetics for different cell morphology and mechanical properties. For example, Xu[55] conducted an extensive study of polypropylene (PP) foaming with carbon dioxide (CO₂). He showed that by varying the temperature, saturation pressure and depressurization rate, different cellular structures (uniform or bimodal cellular structures) could be obtained with the presence of crystalline phases.

Pioneering work on the microcellular foam of a semicrystalline polymer was conducted by Colton[16], and foaming temperature was set in the vicinity of the melting temperature. In his article, Doroudiani et al.[56] investigated the effects of the crystallinity and the morphology of semicrystalline polymers on the cell structure. He conducted batch foaming experiments with high-density polyethylene (HDPE), polybutylene (PB), poly(propylene) (PP), and poly(ethylene terephthalate) (PET). He stated that a key factor to prepare microcellular foams of semicrystalline
polymers is to control the cooling rate during foaming. Moreover, the bubble nucleation behavior was changed by crystallization and resulted in a different cell structure. Park et al. [57] investigated on how crystallinity affects foaming. They showed that the polymer blend of HDPE/i-PP was able to produce a finer cell structure.

Koga and Saito [58] investigated the morphology of high-density polyethylene (HDPE), and poly (vinylidene fluoride) (PVDF) crystallized under high-pressure CO₂ with polarized optical microscopy and observed a fine-layered porous structure for both materials. Based on Oda and Saito’s study [59], crystallization attributed to the expulsion of CO₂ from the crystal growth to the intercrystalline amorphous region and contributed to the growth of bubbles due to the supersaturation of CO₂ in the constrained amorphous region. Taki et al. [60] demonstrated this mechanism by in-situ observation of the foaming processes of polylactide (PLA), where the majority of bubbles nucleated around crystal spherulites that had formed in the PLA. Reignier et al. [61] used an ultrasonic measurement to detect the onset of cell nucleation in the foaming of poly(ε-caprolactone) with CO₂. They demonstrated that the presence of crystals led to a five- to ten-fold increase in the degassing pressure (that is, the pressure at which cell nucleation occurred during the depressurization process) in contrast to the amorphous case. This further demonstrated that crystals could induce cell nucleation. Meanwhile, by comparing the crystallization kinetics and foaming behavior of linear and branched PP, Liao et al. [62] demonstrated that a large density of small-sized crystals was favorable for generating foams with a high cell density. They suggested that the crystals acted as heterogeneous nucleating sites to promote cell nucleation.

2.3 Micro/Nanostructuring of polypropylene using clarifying agent

One of the most challenging requirements in preparing polymeric nanocellular media using a physical blowing agent is the uniform introduction of nano-size heterogeneities into the polymer
matrix. This could be achieved by preparing nanocomposites with uniformly dispersed nanoparticles in the matrix[63,64], or by crystallization[65–69]. Semi-crystalline polymeric structures can be modified into a nanostructured medium by manipulating the crystallization kinetics. Compared with high-density polyethylene, polypropylene has a slow overall crystallization rate, which is followed by the formation of large spherulites during the cooling process[66]. Accordingly, polypropylene’s crystal structure could be altered by adding either a nucleating or a clarifying agent to the PP matrix. This increases the crystal nuclei and decreases the crystal size[67,70].

Sorbitol derivatives, which are a type of clarifying agent, are often added to PP to enhance the clarity. Thus, a nanofibrillar sorbitol crystal network is created during the cooling process, and it produces a PP matrix with nano size crystals. This creates a nanostructured medium with substantially decreased visible light diffraction[65,71]. As seen in Figure 2-1, the schematic of the crystal formation in PP shows the effects of the nucleating agent versus the clarifying agent on the kinetics of crystal nucleation and growth in PP. The first row shows the homogeneous nucleation in iPP that results in a large, complex aggregate of crystals. The second row shows how crystallization is affected by the addition of any non-organic heterogeneity. The third row, on the other hand, describes a different PP crystallization mechanism in the presence of the clarifying agent. During the cooling process, the clarifier phase will start to crystallize first, and it will induce a nanofibrillar crystal network[71]. Then, the polymer chains will begin to crystallize around this nanofibrillar crystal network, and thus shish-kebab crystals or trans-crystalline iPP will be formed[72–75]. This structure minimizes the visible light’s diffraction due to the crystals’ submicron or nanoscale size.
**Figure 2-1.** Schematic of PP crystallization kinetics in the presence of nucleating agent and clarifying agent.

Figure 2-2 shows the proposed schematic of the monotectic phase diagram of the binary system for i-PP/sorbitol. In previous studies [65,71,76] on the phase separation of the binary system of isotactic polypropylene (iPP)/clarifying agent (CA), there was a relatively broad and high concentration regime, as part III of Figure 2-2 also shows, in which the liquid-liquid phase separation takes place above the monotectic temperature. Clear observations of this phenomenon support earlier studies made of it. Below the monotectic temperature, while the iPP was still in its liquid phase, the clarifying agent had self-assembled into a relatively large solid fibrillar domain.
On the other hand, a specific regime was distinguished in which the CA formed a fibrillar network with nano size fibrils that resulted in an iPP with a nano size heterogeneous structure. The narrow window II, shown in Figure 2-2, represents the earlier noted low concentration binary system. In this regime of most interest to me, the iPP/CA formed a homogeneous mixture in the melt state (that is, in which the CA dissolved in the iPP) above the liquidus temperature. When the homogeneous mixture was cooled, the CA crystallized into nano size fibrils prior to the iPP
crystallization. This occurred without any preceding liquid-liquid phase separation. This aforementioned window will provide a unique processing condition during which the crystallization kinetics of PP can be manipulated to results in a fine crystal structure. The resulting crystal structure will be harvested as a nucleating site in nanocellular foaming process.

2.4 Heat Transfer Mechanism in Cellular Materials

One of the primary applications of foams is thermal insulation. Fundamentally, the heat transfer mechanism through structural foams consists of conduction through the gas phase, conduction along the cell walls and struts of the solid materials, convection within the cells, and thermal radiation, as Equation 2-1 represents[77–81]. It is known that the main structural characteristics affecting the conductivity in polymer foams are the relative density, fraction of materials in the edges, and the cell sizes[82]. Furthermore, the conductivity of the solid and gas phase, the material thickness, and optical properties of the polymer phase also have an influence[82].

$$\lambda_{Total} = \lambda_{Solid} + \lambda_{Gas} + \lambda_{IR-Radiation} + \lambda_{Convection}$$  \hspace{1cm} \text{Equation 2-1}

2.4.1 Solid conduction through the polymer matrix

There have been several models that give a theoretical estimation of the conduction term for cellular polymers[81,83–86]. In low-density foams, far away from cubic or polyhedral-like geometries, the cellular morphology exhibits cell imperfection, inhomogeneities, and anisotropy or cell orientation. The equation 2-2 is proven to give a realistic agreement for the prediction of the conduction term through the solid[45,81,84].

$$\lambda_{Solid} = \frac{1}{3} (1 - \varepsilon_{VF}) \left[ f_s \sqrt{\frac{1}{AR}} + 2 (1 - f_s) \left( \frac{1}{AR} \right)^{\frac{1}{3}} \right] k_{Solid}^0$$  \hspace{1cm} \text{Equation 2-2}
where $k_{S0}^0$ is the bulk solid conductivity, $\varepsilon_{VF}$ is void fraction, AR is the geometrical anisotropy, and $f_s$ is the volume fraction of the struts. In the cellular polymers with a high expansion ratio with an isotropic-like cellular structure, the heat transfer can be simplified follow the model by Glicksman[45,81,84]. In this model, the cells are assumed to have a cubic shape in which four faces and four struts contribute in conducting the heat flux. Consequently, the solid conductivity is expressed as equation 2-3.

$$\lambda_{Solid} = (1 - \varepsilon_{VF})(\frac{2-f_s}{3})k_{S0}^0$$  

Equation 2-3

2.4.2 **Gas conduction in cellular structure**

Inside the small cells, the amount of collision between the air molecules become minimized and limited to the collision of the gas molecules and cell walls. Consequently, it also affects the energy transfer which can be determined by the cell size. To address the dependency of the gas conductivity to the cell size, the Knudsen number $K_n$ is defined as follow[87]:

$$K_n = \frac{l_{mean}}{d}$$  

Equation 2-4

where $d$ is approximately the diameter of the cells and $l_{mean}$ is the mean free path of gas molecules, which is 68 nm for air at ambient pressure and room temperature. Accordingly, the gas conduction through the air is expressed by Equation 2-5 [88,89].

$$\lambda_{gas} = \varepsilon_{VF} \cdot \frac{1}{1+2K_nB} \cdot k_{gas}^0$$  

Equation 2-5

where $\varepsilon_{VF}$ is void fraction, $K_n$ is the Knudsen number, B is energy transfer efficiency between the gas molecules and cell wall (about 2 for air), and $k_{gas}^0$ is the bulk gas conductivity (26 W/m.K for air).
Moreover, it has been shown that if the cell size is further reduced to below the free path of the gas molecules inside the cells (e.g., ~ 70 nm for air), the heat conduction within the gas phase could be minimized due to the Knudsen effect, which is a result of the limited vibration of gas molecules within cells[90,91]. Figure 2-3 is a schematic of the Knudsen effect within a cell.

![Schematic of the Knudsen effect within a cell.](image)

**Figure 2-3.** Schematic of the Knudsen effect within a cell.

Nowadays, conduction through the gas is minimized by impregnating the polymer foams with environmentally hazardous gases, yet it is not permanently efficient. My proposed nano-cellular plastics insulation not only eliminates this shortcoming but it also significantly decreases heat transfer through gas molecules due to their confinement within the nano-sized cell volumes (Knudsen effect).

### 2.4.3 Radiation in cellular materials

To explain the contribution of radiation, a model by William and Aldao is adopted because it is shown a good agreement with the experimental results in previous literature[92–94]. The model which relies on the radiative term appears as Equation 2-6.
\[ \lambda_{IR} = \frac{4\sigma T^2 L}{1 + \left(\frac{L}{\varphi}\right)(\frac{1}{T_N} - 1)} \]  

Equation 2-6

where \( \sigma \) is the Stefan-Boltzmann constant, \( L \) can represent the cell wall thickness, \( \varphi \) represents the cell size, and \( T_N \) is the fraction of the energy which is radiated from a cell wall with the thickness of \( L \).

It has been both theoretically and experimentally shown that for plastic foams with sub-micron cells, the radiation term in heat transfer vanishes and that can decrease the thermal conductivity by about 30\%[82]. In addition, as the relative density of the foam decreases, the radiation term in heat transfer mechanism which is proportional to the cell wall thickness, on the other hand, increases [89]. Figure 2-4 represents the radiation rays in low-density and high-density cellular plastics.

![Figure 2-4. Schematic of the radiation rays in low-density and high-density cellular plastics.](image)

**2.4.4 Convection in cellular materials**

It is widely accepted that convection terms can be neglected if the cell sizes are less than 4mm in diameter[95]. This is due to the fact that the drag resistance to setting up a convection current is only overcome if sufficiently large space and high temperature are present[82]. Almost
all polymeric foams, independent of the expansion ratio, exhibits a morphology with cell sizes that are clearly below 4-5 mm. As a result, the contribution of the gas movement inside the cells can be considered as minimal when compared to the other contributors such as conduction and radiation.

Figure 2-5 depicts the contribution of solid conduction, gas conduction, convection, and radiation versus the relative density of LDPE foams with an average cell size of 100 μm[81]. Figure 2-6 describes the effects of cell size on the contribution of conduction and radiation in the heat transfer mechanism through cellular materials.
Figure 2-5. Contribution of solid conduction, gas conduction, convection, and radiation versus the relative density of LDPE foams with an average cell size of 100μm[81,92].
Figure 2-6. Contribution of solid conduction, gas conduction, and radiation versus the relative density of the foams for different cell sizes.

2.5 Retrograde Vitrification Behavior in Polymeric Materials

Since the mid-1980s, it has been figured out that dissolved CO\textsubscript{2}, as a diluent, changes the glass transition temperature (T\textsubscript{g}) of polymers.[96,97] The T\textsubscript{g} depression happens due to the CO\textsubscript{2} plasticization effect and lowering the fractional interaction between the polymer chains. The degree of T\textsubscript{g} downturn depends on the amount of dissolved CO\textsubscript{2}, or on the pressure of the gas. Most of the polymer/CO\textsubscript{2} systems exhibit a linear relationship between T\textsubscript{g} and the pressure, or amount of dissolved CO\textsubscript{2}.[98–101] Condo developed a model to predict the T\textsubscript{g} depression of a polymer after a compressed fluid is dissolved into its matrix.[96]. He combined lattice fluid theory[102,103] and the Gibbs-Di Marzio criterion of the glass transition.[104] Fundamental types of T\textsubscript{g} versus pressure were identified and classified by exploring the solubility of the compressed
fluid, the flexibility of the polymer molecules, and the critical temperature of the pure fluid. He identified four different fundamental types of $T_g$ versus pressure behavior as it is shown in Figure 2-7. **Fundamental types of $T_g$ behavior as a function of pressure predicted by Condo**.[96]

![Diagrams showing different types of $T_g$ behavior](image)

**Figure 2-7.** Fundamental types of $T_g$ behavior as a function of pressure predicted by Condo.[96]

The term “retrograde vitrification” was used, for the first time, by Condo et al.[96] when the polymer/CO$_2$ undergoes multiple transitions from a rubbery to a solid state and from a solid to a rubbery state. For example, as it can be inferred from Figure 2-7 type IV, at a certain constant gas pressure or solubility, polymers experienced their second transition from a solid to a rubbery state at a certain temperature which was called the lower glass transition temperature ($T_{gl}$). This
behavior, which was rationalized by an enhanced gas solubility at a low temperature and its high
degree of plasticization, has been shown experimentally for only few polymers. So far, retrograde
vitrification behavior has only been confirmed in poly(methyl methacrylate) (PMMA),[97]
poly(ethyl methacrylate) (PEMA),[105] and acrylonitrile-butadiene-styrene copolymer
(ABS).[106]

Various techniques have been used to measure the depressed $T_g$ and to generate a $T_g$-$P$
curve for a gas-laden polymer.[98,100] Creep compliance has been the only successful method of
measuring the $T_g$ and establishing the retrograde vitrification behavior. Almost all other methods
have shown a failure to generate the retrograde curve.[98,100,107,108] This is mainly because it
was almost impossible to maintain a thermodynamic equilibrium state during heating or cooling
runs. $T_g$ can be characterized by a constant pressure heat capacity ($C_p$) step-change. The pioneering
work to make this method more accurate was done by Mraw et al.[109] using stepwise heating or
enthalpy increment. Handa et al.[105] extended his work to establish the $C_p$ steps for the polymer-
gas system. The stepwise increment method ensures to maintain a thermodynamic equilibrium
state for a gas-polymer system throughout the experiment and is capable of establishing $T_g$-$P$
profile accurately and more efficiently compared to the creep compliance technique.
Chapter 3.
From Micro/Nano Structured Isotactic Polypropylene to a Multifunctional Low-density Nanoporous Medium

3. From Micro/Nano Structured Isotactic Polypropylene to a Multifunctional Low-density Nanoporous Medium

3.1 Abstract

Homogeneous nano-porous medium of isotactic polypropylene (iPP) was fabricated using supercritical carbon dioxide (scCO\textsubscript{2}). A unique complex 3-dimensional nano-fibrillar network, using sorbitol derivatives, was induced inside the iPP to gel the matrix. The nucleating/clarifying agent 1,2,3-trideoxy-4,6:5,7-bis-O-[(4-propylphenyl) methylene]-nonitol (TBPMN) was used to promote crystal nucleation, which in turn dramatically enhanced nanocell nucleation. This clarifying agent (CA) has been developed as a new generation of sorbitol derivatives to improve polypropylene (PP)’s clarity. Samples of iPP with clarifying agent (iPP/CA) were prepared using a twin-screw microcompounder, and its thermal stability was accessed. The crystallization behaviors of the neat iPP (iPP/0CA) and iPP with 0.5wt% CA (iPP/0.5CA) were studied using differential scanning calorimetry (DSC), polarized optical microscopy, and a rheometer. The percolation state of the sorbitol nano-fibrillar network in the iPP/0.5CA was also investigated by using the Van Gurp-Palmen-plot. The cellular morphology was characterized as a function of the processing conditions in both micro and nano-scales. A nanocellular structure with an average pore size of ~70 nm, a cell density of ~10\textsuperscript{15} cells/cm\textsuperscript{3}, and a void fraction of 86% (an expansion ratio of 7.56) was achieved by controlling the crystallization kinetics of iPP in the presence of CA. An

\textsuperscript{1} Chapter 3 has been published by the Royal Society of Chemistry in the Journal of RSC Advances and is referred in the reference section as ref #91
optimum foaming temperature was found wherein the smallest pore size with the highest cell
density could be produced. The thermal conductivity of nanoporous samples decreased
dramatically up to about 8-fold compared with its solid counterpart. Its viability stemmed from its
relative low density, the unique 3D nanocellular structure, and nanoscale confinement of the
gaseous medium inside the nanopores (i.e., the Knudsen effect).

3.2 Introduction

Microcellular[110] and nanocellular[111] foams have been developed and extensively
studied for the last few decades because of their unique properties. The interest of manufacturing
microcellular foams was developed to dramatically improve the foams’ properties such as impact
strength[40], fatigue resistance[43], light reflectability[44], toughness[18], thermal insulation[88],
and sound insulation.[112] The advent of nanocellular foams has opened a new window of
opportunities for making polymeric materials much more functional in the following advanced
applications: in porous materials with superior thermal insulation and better mechanical
properties[113–116], in implantable controlled drug delivery devices[117], in biofiltration[118]
and water filtration[119], in gas and oil separation[120,121], in battery or fuel cell
membranes[122], and in energy storage and electrical conductivity applications.[123,124] With
respect to their superior thermal insulation applications, based on the Knudsen effect[90], the gas
molecules’ contribution to heat conduction is very low. This is basically due to their collisions
being inhibited inside those pores which are smaller than the mean free path of the air.[125] Hence,
these foams have recently attracted much attention. The intensive research that has been
undertaken to develop this new generation of high performance nanocellular multifunctional foams
has shown great promise. The technology is capable of producing an alternative to aerogel products
at different service temperatures and which also has far better mechanical properties. Furthermore,
the manufacturing process is much more sustainable, in terms of the production time and energy,
and is based on using CO₂ as an environmentally greener blowing agent. Because the media is a thermoplastic, all of its products are recyclable. Additionally, in using biodegradable types or biocompatible grades of thermoplastics means their products offer green solutions for biomedical applications.[14] Unlike that used for aerogel products, this technology proposes both an eco-friendly and industrially viable manufacturing process.

Various approaches have been proposed to fabricate nanocellular polymeric media using CO₂ as a physical blowing agent. For example, Yokoyama et al. used CO₂-philic fluorinated polymers as a block component.[3] Similarly, Taki et al.[24] created nanowells on the surface of a di-block copolymer of PS-b-PMMA, and Ruiz et al.[126] used a PS-b-PFDA system. The idea was further developed on the use of immiscible blends system by Ohshima et al.[19,25] An extensive experimentation accomplished by Reglero-Ruiz et al.[127,128] and Pinto et al.[129,130] on the use of PMMA and PMMA-b-PBA-b-PMMA triblock copolymer (MAM) blends. A thorough investigation performed on the fabrication of nanoporous acrylate-based random copolymers by Costeux et al.[131] In order to increase the porosity of the nanofoams, Costeux et al. initially relied on the cell nucleating agents.[114,132] Costeux et al.[133,134] further prepared different MMA-based random copolymers containing such comonomers with higher CO₂ affinity than MMA as ethyl acrylate (EA), ethyl methacrylate (EMA), and terbutylmethacrylate (tBMA). The concept of PMMA impregnation with CO₂ at low temperatures and retrograde vitrification which ultimately resulted from a higher gas solubility was predicted and shown by Condo et al[96]. This concept was further used by Geol et al[135], Handa et al.[105], and Guo et al.[136,137] to obtain a finer cell structure. On the use of high T_g engineering polymers, Krause et al.[29,138] performed a pioneering work. Likewise, Miller et al.[2], Aher et al.[139], and Guo et al.[140] reported on polyetherimide, polysulfone, and polycarbonate nanofoam. Fujimoto et al.[141], Ema et al.[53], and Ito et al.[52] extended some studies on the use of polylactic acid/nano clay and
polycarbonate/clay nanocomposites to produce submicron cells. Making use of polymer nanocomposites, Lee et al.[57], and Ameli et al.[124] reported nano-size cells in high-density polyethylene/nanoclay and PP/carbon nanotubes system, respectively. In his research, Yeh et al.[142], studied thermoplastic polyurethane/clay nanocomposites towards the fabrication of elastic nanocellular foams. On the use of pure semicrystalline polymers, few groups have tried to fabricate nanocellular foams for which one of the following disadvantages applies: the expansion ratio is very low, the cell density is low, the saturation time is too long almost more than a couple of weeks, the pores are thinly dispersed or scattered, or the morphology does not fit the definition of nanocellular foams at all. Bao et al.[143] used highly oriented iPP, and Li et al.[144] used poly(ethylene terephthalate) to induce nano-size cells. Miyamoto et al.[145] performed a pioneering experiment on the use of clarifying agent and PP to fabricate nanoscale voids on the cell walls.

One of the most challenging requirements in preparing polymeric nanocellular media using a physical blowing agent is the uniform introduction of nano-size heterogeneities into the matrix. The purpose is to have a potential medium which can introduce a nanocellular structure in the polymer matrix. Such a nanostructured medium would provide nucleation sites that can be harvested through the heterogeneous cell nucleation mechanism which can control the pore structure’s morphology accordingly. This could be achieved by using the following different methods: By preparing polymer composites with uniformly dispersed nanoparticles in the matrix[146–148], by polymer blending using block copolymers[25,27,149], by the introduction of a second-phase fibrillar structure inside the matrix[150,151], or by manipulating the crystallization kinetics of such semi-crystalline polymers as PP and polylactic acid.[65,67,152] Compared with high-density polyethylene, PP has an overall slower crystallization rate, which is followed by the formation of large spherulites during the cooling process.[66] Accordingly, PP’s crystal structure
could be altered by adding either a nucleating or a clarifying agent to the PP matrix. This increases the crystal nuclei and decreases the crystal size.[67,70]

Some sorbitol derivatives, for instance, 1,2,3-trideoxy-4,6:5,7-bis-O-[(4-propylphenyl)methylene]-nonitol which are a type of clarifying agents, are often added to PP to enhance the clarity. Thus, a nanofibrillar crystal network is created during the cooling process, and it can produce a PP matrix with nano-size crystals. This creates a nanostructured medium with substantially decreased visible light diffraction.[65,71] As seen in Figure 3-1, the schematic of the crystal formation in PP shows the effects of the clarifying agent on the kinetics of crystal nucleation and growth in PP. The first row shows the homogeneous nucleation in iPP that results in a large, complex aggregate of crystals. The second row, on the other hand, describes a different PP crystallization mechanism in the presence of the clarifying agent. During the cooling process, the clarifier phase will start to crystallize first, and it will induce a nanofibrillar crystal network. Then, the polymer chains will begin to crystallize around this nanofibrillar crystal network, and thus shish-kebab crystals or trans-crystalline iPP will be formed.[71,73,74]
Figure 3-1. Schematic of PP crystallization kinetics in the presence of nucleating agent and clarifying agent.

In my study, which capitalized on the inclusion of nano and submicron size crystals, I examined the fabrication of a unique polymer-based nanoporous material within a semi-crystalline PP structure. A three-dimensional nanofibrillar crystalline structure, which had been induced by sorbitol derivatives inside a homopolymer iPP matrix, was used as a nanostructured template to manipulate the iPP’s crystalline structure. To investigate the possibility of creating a nanocellular structure in the presence of a clarifying agent, I used one-step batch foaming with scCO₂.[113] Specifically, the effects of the saturation temperature and time on the cellular morphology were studied for both iPP/0CA and iPP/0.5CA. The heat transfer mechanism inside the nanoporous media was studied. I evaluated the samples’ thermal conductivity with respect to their superior thermal insulation applications.
3.3 Experimental

3.3.1 Materials

The polymer matrix used in this study was homopolymer iPP, commercially available as Moplen HP400R, supplied by Lyondell Basell Inc., with a density of 0.9 g.cm\(^{-3}\) at 23°C and a melt flow rate (MFR) of 25 dg.min\(^{-1}\) at 230°C/2.16 kg. The clarifying agent (CA) was Millad NX8000, supplied by Milliken Chemical, with a processing temperature window of 190°C to 230°C. CO\(_2\) was supplied by Linde Gas with a purity of 99.8%, and was used as the physical blowing agent for foaming experiments.

3.3.2 Sample Preparation and Foaming Experiment

The iPP pellets were pulverized using liquid nitrogen and a grinder. Then, they were dry mixed and compounded with various clarifying agent (CA) contents ranging from 0.1 wt% to 2.5 wt% using a DSM Xplore co-rotating twin-screw micro-compounder with a recirculating back-flow channel. A compounding temperature and a screw speed of 200°C and 60 rpm, respectively, were used for 10 min of the residence time under a nitrogen blanket to create a well-dispersed composite. As received iPP underwent the same processing condition and the resultant processed iPP (iPP/0CA) provided the same processing history for both the iPP/0CA and iPP/CA samples. The extrudates were then compressed into a flat sheet with a 0.5 mm thickness (for foaming) or a 1.2 mm thickness (for rheological measurements) using the laboratory hydraulic press (Carver SC7620) at a temperature of 220°C and at a pressure of 10 MPa for 10 min followed by quenching in water.

The one-step batch foaming process was used to foam the samples. The compression-molded samples were pressurized up to 30 MPa with CO\(_2\) using a Teledyne ISCO high-pressure syringe pump at an elevated temperature ranging from 145°C to 150°C. Foaming was then induced
by a rapid depressurization of 30 MPa.s\(^{-1}\). The foaming chamber, which contained the foam samples, was then quenched in water to the room temperature to stabilize the foam structure.

### 3.3.3 Thermal Characterization

The melting behavior \(T_m\) of the iPP/0CA and the iPP/CA was studied with a sample of 5-10 mg in a nitrogen atmosphere using a differential scanning calorimeter (DSC, Q2000, TA Instrument). Using a heat-cool-heat cycle that alternated between the room temperature and 240°C at a standard heating or cooling rate of 10°C/min, the thermal properties of the materials were determined. The samples were held at 240°C for 5 min to remove the processing history before the cooling and second heating cycles, and also to prevent the self-seeding of iPP\[153\]. The crystallization and melting temperatures were determined based on the peak temperatures of the thermographs. The area under the peaks was calculated to determine the degree of crystallinity of the samples using Equation 3-1, wherein \(\Delta H_c\) is the heat of crystallization, \(\Delta H_m^0\) is a reference value, which represents the melting heat of the same polymer with a 100% crystalline structure.

\[
\text{Crystallinity\%} = \frac{\Delta H_c}{\Delta H_m^0} \times 100\% \quad \text{Equation 3-1}
\]

Isothermal thermogravimetric analysis (TGA) was performed on the CA in a nitrogen atmosphere to evaluate the amount of degradation as a function of time at 200°C by TGA Q50 from TA instrument. The sample was heated from room temperature to 200°C and was monitored for 30 min.
3.3.4 Viscosity Measurement

The rheology test samples were compression-molded into circular disks with a 1.2 mm thickness and a 25 mm diameter using the previously noted compression molding procedure. To evaluate the absolute value of the complex viscosity of the iPP/0CA and the iPP/0.5CA, an advanced rheometric expansion system (ARES) was used. The measurement was conducted using a cone-and-plate setup with a 25 mm diameter and a 5° cone angle. The rheology samples were initially heated to 220°C. This was followed by a 5 min isothermal treatment at the same temperature to achieve a thermal equilibrium as well as to erase the cooling history of the material. After this, the temperature steadily declined at a rate of 2°C/min until the test material had solidified. Throughout the test, the samples had undergone a 10% strain at an oscillation frequency of 1 rad/sec.

3.3.5 Electron and Optical Microscopy

To evaluate the shape and the dimension of the clarifying agent structure, a transmission electron microscopy (TEM) was carried out. The instrument used was FEI Quanta FEG. A compression-molded sample with a 5 mm thickness was prepared. A rectangular thin film (~50 nm in thickness) was sectioned from the compression-molded sample using the Microtome Leica Ultracut UCT and collected on a copper TEM mesh. The samples were stained over 0.5% ruthenium tetroxide aqueous solution for 2.5 h. The optical microscopy study samples were prepared by compressing a granule of mixed material between two micro cover glass slides at 240°C, followed by quenching in water. Using a Nikon Labophot-2 optical microscope equipped with a hot stage and a temperature controller Linkam TP93-HFS91, the optical micrographs of the crystals in the iPP were taken to study the formation and size of the crystals. The morphology of the foam samples was examined by two scanning electron microscopes (SEM), Jeol 6060 and FEI Quanta FEG 250. The SEM samples were cryofractured in liquid nitrogen to obtain a clean cross
section, and were sputter-coated with palladium. The cell density of the foams was calculated from
the SEM micrographs with ImageJ software using Equation 3-2 as follows[154]:

\[
\text{Cell Density} = \left(\frac{\text{number of cells}}{\text{Area}}\right)^{1.5} \frac{\rho_{\text{polymer}}}{\rho_{\text{foam}}}
\]

Equation 3-2

The average cell size of the foam samples was calculated as the mean value for at least 50
cell measurements. The volume expansion and bulk density of the samples were determined using
the water displacement method, according to the ASTM-D792. The solid skin on the foam samples
was kept for the density measurement. The thickness of the solid skin was in the order of 80-120
µm.

3.3.6 Thermal Conductivity Characterization

The thermal behavior of the foamed samples was evaluated based on the transient plane-
source method using a HotDisk TPS 2500S. A Kapton-insulated sensor with a diameter of 3.2 mm
was used to measure the samples’ thermal conductivity. Figure 3-2 shows the schematic of the
transient plane-source test, which measures the solid materials’ thermal conductivity. With this
measurement technique, a bifilar spiral resistive element is placed between two of the same solid
or foamed samples, which also have the same dimensions, to measure the through-plane thermal
conductivity. The procedure to measure the thermal conductivity using this equipment is well
established[155,156] but one critical requirement is that the probing depth shown in Figure 3-2
be within the sample’s thickness; that is, it should not be beyond the distance between the hot disk
and the boundary of the sample.
3.4 Results and Discussion

3.4.1 Crystallization Behavior

Sorbitol-based compounds are among those clarifying agents and α-nucleators for PP that are capable of accelerating the polymer crystallization. Unlike the dispersion-type nucleators, a sorbitol-based clarifying agent dissolves in the molten PP and disperses uniformly into the matrix[67]. The phase separation of the sorbitol derivatives from the iPP and the supermolecular self-assembly mechanism, by which the sorbitol molecules precipitate out into the iPP and form a fibrillar structure, strongly depend on the CA content and on the cooling rate. In the previous studies on the phase separation of the binary system of iPP/CA[65,71,76], there was a relatively broad and high concentration regime in which the clarifying agent self-assembles into a relatively large solid fibrillar domain. This fibrillar structure is developed below the monotectic temperature while the iPP is still in its liquid phase, and this gels the matrix.

On the other hand, a specific narrow and low concentration regime was distinguished in which the CA formed a fibrillar network with nano size fibrils that resulted in an iPP with a nano
size heterogeneous structure. In this regime of most interest to us, the CA crystallized into nano size fibrils prior to the iPP crystallization. The amphipathic molecular structure of the sorbitol-based clarifying agents leads to the self-assembling of the CA nanofibrils.[71] The wings of the molecule are hydrophobic and are capable of dissolving in organic liquids including some polymer melts. But the body of a CA molecule is hydrophilic and can form multiple hydrogen bonds in a linear fashion, which results in the formation of a fibrillar structure.[157] In this nucleation and growth structure transformation process, the nano size fibril heterogeneities contributed to the alteration of the iPP’s crystallization kinetics by providing an extremely large surface area for crystal nucleation. Thus, the iPP peak crystallization temperature will considerably increase and extremely fine crystals generated around the nanofibrils were used for inducing nanocell structures.

Figure 3-3 shows the peak crystallization temperature of the iPP/CA samples as a function of the CA content. The crystallization temperature of the iPP/CA increased dramatically when the CA content was increased from 0.1 wt% to 0.5 wt%. Accordingly, it was postulated that 0.1-0.5 wt% of CA in iPP must represent the aforementioned window in which the CA crystal fibrils were forming in the nano size dimension. Hence, I selected the iPP with a 0.5 wt% CA (iPP/0.5CA) for further experiments.
The major drawback of some sorbitol derivatives as clarifying agents is their rapid evaporation and degradation during processing. The clarifying agent used in this study, 1,2,3-trideoxy-4,6:5,7-bis-O-[(4-propylphenyl) methylene]-nonitol, commercially so-called Millad NX8000, has a modified structure and much better thermal stability compared to the other sorbitol derivatives. As shown in Figure 3-4(a), the clarifying agent’s isothermal degradation at 200°C for 30 min in the TGA was not more than 0.7%, indicating its stability in the chosen processing temperate range. Figure 3-4(b) also shows the degradation of iPP/0CA, iPP/0.5CA, and CA itself. All of the samples seemed stable up to 250°C. The iPP/0.5CA started to lose weight (associated with the CA) at around 250°C slightly earlier than the iPP/0CA, which was far beyond the clarifying agent’s processing temperature of 190-220°C.

**Figure 3-3.** Crystallization temperature of iPP/CA mixture as a function of CA content.
Figure 3-4. (a) Isothermal TGA of the clarifying agent at 200°C for 30 min, (b) TGA of the clarifying agent, iPP/0CA, and iPP/0.5CA.

Figure 3-5(a) represents both samples’ complex viscosity as a function of temperature at a cooling rate of 2°C/min. The viscosity behavior of the iPP/0.5CA sample was illustrated by two distinct increases in the complex viscosity during cooling. The addition of 0.5 wt% CA manifested as an initial boost in the melt’s complex viscosity. A similar observation was reported previously.[158] The first boost, which demonstrated two-orders of magnitude increase in the complex viscosity, indicated the CA’s crystallization into the fiber-shaped CA crystals within the molten iPP.[65,71,76] In this state, the homogeneous single-phase liquid of the binary system of the iPP/0.5CA experiences a significant isothermal reversible alteration to form a second liquid phase of iPP with a solid phase of sorbitol during cooling. The second boost was associated with the iPP’s crystallization. The frequency sweep data at 165°C is shown in a Van Gurp-Palmen plot[159] in Figure 3-5(b). The iPP/0CA showed a much less elastic behavior for small values of $|G^*|$ as the phase angle $\delta$ approached 90°. However, the iPP/0.5CA clearly showed a percolation of the fiber network that was expressed by the maximum of the curve.
Figure 3-5. (a) Complex shear viscosity of iPP/0CA & iPP/0.5CA, (b) Van-Gurp-Palmen plot.

Figure 3-6 shows the iPP/0CA and iPP/0.5CA DSC thermograms, which were cooled from 240°C at a rate of 10°C/min. The iPP/0.5CA’s crystallization occurred much earlier than the iPP/0CA’s. Another minor peak was observed at around 178.6°C, which implied the CA’s crystallization. The iPP’s peak crystallization temperature increased from 122°C to around 132°C when 0.5 wt% CA was added. When the samples were cooled at a rate of 10°C/min, the crystallinity of the iPP/0CA and iPP/0.5CA samples was calculated to be ~52.6% and ~52.4%, respectively. The degree of crystallinity was determined based on the value of 209 J/g for 100% crystalline iPP.[160] It should be noted that the crystallinity of the iPP/0.5CA sample was not high compared to the case of iPP/0CA. Although the crystallization kinetics was active with higher crystallization temperature and a larger number of crystal nuclei, the crystal-to-crystal interactions typically lower the degree of crystallinity.[161,162] The melting temperature, on the other hand, did not change much. Both the iPP/0CA and iPP/0.5CA samples showed a melting temperature of around 164°C. This was fully in agreement with previous studies that had showed the melting peak temperature did not shift in the iPP/0.5CA binary system.[71]
**Figure 3-6.** DSC cooling (Left) & heating (Right) thermograms of iPP/0CA and iPP/0.5CA at a rate of 10°C/min.

Figure 3-7(a) shows a TEM micrograph of the iPP/0.5CA. The micrograph shows the fiber-like crystals of the CA, which were phase-separated from the single-phase melt mixture and formed sorbitol fibers. The diameters of the fibrils were below 10 nm. When compared to the length of the fibers, which ranged from a couple of micrometers to 10 µm, the fibrils’ aspect ratio was very high. At higher CA concentrations, Figure 3-7(b), a microfibrillar network was self-assembled through the same mechanism as mentioned above. Figure 3-7(c) shows the micron size fibers that formed from the CA powders at 155°C. This might be due to their ability to flow at a lower temperature than the melting temperature and to form fibers over a narrow temperature range. The fibers melted as the temperature was increased.
To better investigate the effects of the sorbitol nanofibrillar network on the crystals’ size and structure, both samples were also studied using optical scanning microscopy. **Figure 3-8** shows the optical micrograph of the iPP/0CA and iPP/0.5CA samples. It is obvious that the addition of a clarifying agent had a strong effect on the iPP’s crystallization structure. That is, it functioned as a crystal nucleating site by introducing a nano size fiber-shaped network into the matrix. Through the van der Waals interaction, the nanofibrils of sorbitol are able to stabilize the iPP molecule.
chains in a helical arrangement and to promote crystal nucleation.[163] Recent studies assert that the boost in iPP crystal nucleation in this regime might be governed by graphoepitaxy rather than by any chemical interaction between the iPP and the clarifying agent’s molecules.[164] Explicitly, a single iPP crystalline layer forms and grows on the surface of the non-single crystalline sorbitol fibers. The orientation of the atoms in the grown iPP crystals is controlled by the clarifying agent’s crystal lattice. Consequently, a larger number of crystals were nucleated in the iPP/0.5CA matrix.[165] Due to the increased crystal density, and the CA fiber to fiber distance, as is shown in Figure 3-7(a), the growth of each individual crystal was significantly hindered by the surrounding crystals. Therefore, as seen in Figure 3-8(a), this resulted in a large number of submicron size crystals compared to the iPP/0CA’s complex crystal aggregates, which grew due to the slow crystallization kinetics. This complex and fine crystalline structure had been expected from the DSC results shown in Figure 3-6. The heat of crystallization ($\Delta H_c$) was calculated at the same amount for both samples which indicated almost the same crystallinity. Considering the higher temperature at which crystallization starts in iPP/0.5CA samples, the formation of a large number of small crystals had been anticipated. Again, as mentioned earlier, the degree of crystallinity of iPP/0.5CA samples was not high.[161,162]
**Figure 3-8.** Polarized Optical micrograph of the morphology of compression-molded films of (a) iPP/0CA and (b) iPP/0.5CA.

**Figure 3-9** shows the melting behavior of iPP/0CA and iPP/0.5CA, which were treated isothermally with CO₂ under 30 MPa at different temperatures for 15 and 30 min. Both materials showed the formation of double melting peaks starting from 150°C. It implies that with the assist of sc-CO₂ a portion of crystals could melt at a much lower temperature (around 150°C) than the original melting peak temperature around 164.5°C (as shown in Figure 3-6). The increase in the melting peak at a higher isothermal temperature was due to the formation of crystals with a more close-packed structure as a consequence of the rearrangement of the crystals.[13]
Figure 3-9. DSC melting thermograms of the iPP/0CA and iPP/0.5CA isothermally treated under 30 MPa for 15 min and 30 min at different temperatures.

3.4.2 Foaming Behavior

Figure 3-10 shows the SEM micrographs of the iPP/0CA in the first row (a1, a2, and a3) and the iPP/0.5CA samples in the second row (b1, b2, and b3). All samples were foamed in one step, after they had been saturated with supercritical CO2 under the pressure of 30 MPa for 15 min at an elevated temperature. The foaming temperature of the first, second, and third column were 145°C, 147.5°C, and 150°C, respectively. Overall, adding 0.5 wt% of the CA significantly altered the foam morphology of the iPP. Figure 3-11 shows the samples’ average cell sizes, cell densities,
and expansion ratios of the foam samples.

Figure 3-10. SEM micrographs of iPP/0CA (a₁, a₂, and a₃) and iPP/0.5CA (b₁, b₂, and b₃) samples foamed by saturation in sc-CO₂ at different temperatures for 15 min. The foaming temperature of the first (a₁ and b₁), second (a₂ and b₂), and third (a₃ and b₃) columns were 145°C, 147.5°C, and 150°C, respectively. Each row has the same magnification.
Figure 3-11. (a) Average cell density, (b) cell size, and (c and d) expansion ratios (with and without the skin) of the samples foamed at different temperatures.

A uniform microcellular structure (Figure 3-10 a₁) with an average cell size of 5 μm and a cell density in the order of $10^{10}$ cells/cm³ was achieved with the iPP/0CA at 145°C. However, no cellular structure (Figure 3-10 b₁) was obtained from the iPP/0.5CA at this temperature. The formation of a large number of tiny crystals in the iPP/0.5CA could have multiplied the rigid-amorphous fraction (RAF)[166] compared to the iPP/0CA. The increased RAF must have decreased the solubility[167], and also the chain’s mobility for foaming. Although the RAF does not count in crystallinity calculation, it increases the interaction between the crystals which might
have resulted in a percolated crystal structure in the iPP/0.5CA. Also, as Figure 3-5 shows, the complex viscosity of the iPP/0.5CA was almost two orders of magnitude higher than the iPP/0CA at 145°C. This was because the iPP matrix had formed into a gel due to the presence of sorbitol fibrils. It should be noted that the elastic behavior also showed the similar trend (Figure 3-5). Thus, not only was the amount of dissolved gas less than that in the case of iPP/0CA, but also the stiffness of iPP/0.5CA might have been large enough to have prevented the nucleation and growth of any cell at 145°C.

In the first row of Figure 3-10 (a1, a2, and a3), it is apparent that with the increased foaming temperature, the cell density deteriorated by two orders of magnitude. This behavior often happens at high foaming temperatures in which the melt strength is low. It is inferred from Figure 3-9(a) that the poor cell morphology of iPP/0CA at the 150°C was most likely from the lower crystallinity and the development of a non-uniform crystal structure during the saturation.

The iPP/0.5CA sample (Figure 3-10 b3), which was saturated for 15 min and was foamed at 150°C, had a unique bimodal cellular structure. It consisted of cells with a size less than 5 μm surrounded by submicron cells. These large bubbles may have been nucleated during gas saturation. Because of the more active crystallization with the sorbitol fibrils, the gas molecules expelled from the formed crystals[60] may have caused a high thermodynamic instability because of the lower gas solubility in the PP with sorbitol fibrils. The gas molecules could not be diffused back to the high-pressure gas source in the chamber quickly and some bubbles could have been developed during this gas saturation stage. Or the bicellular structure may have been developed by the non-uniform crystal structure. The larger cells could have been formed where no crystals existed, whereas the smaller cells could come into existence in the fine crystalline structure regions because of the high local stresses.[32,168]
Figure 3-12. SEM micrographs of nanoporous iPP/0.5CA sample foamed 149°C after saturation in sc-CO₂ for 30 min (a and b) are from the core of the sample with two different magnifications, (b and c) are from the skin of the samples.

I found that a uniform nanoporous structure with an average pore size of ~70 nm and a cell density in the order of 10^{15} cells/cm^{3} had been fabricated, as shown in Figure 3-12. This highly desired porous structure was obtained using iPP/0.5CA at the 149°C foaming temperature after 30 min saturation. Usually, the pressure is the critical parameter for controlling cell nucleation[14,154] and the temperature is for controlling the expansion ratio.[169,170] But the temperature was found the most critical parameter for cell nucleation in this study because of the crystallization kinetics governing the cell density. The nanostructure that was introduced by the
clarifying agent in the iPP enforced the promotion of nano/submicron crystal formation. This complex nanostructure served as bubble nucleating sites and boosted the nanocell nucleation up. The saturation time with sc-CO$_2$ for iPP/0.5CA at 149°C was elongated from 15 min to 30 min. This prolonged impregnation time had been considered based on the presumption that a fully saturated state would not be reached within 15 min. In this condition, a higher saturation time means that more gas might be dissolved in the polymer. Furthermore, the development of the crystals during isothermal treatment resulted in an increased chance for cell nucleation. The supersaturation caused by the expelled gas from the crystals[60], the high tensile stress from the shrinkage of the crystals[168], and the local stresses generated around the crystals from their rigid body motion[168] must have promoted cell nucleation by decreasing the critical radius of the nucleated bubbles.[32,33,168] Temperature reduction could also have contributed to the formation of a nanocellular structure.[171]

3.4.3 Thermal conductivity evaluation of the nanoporous samples

As mentioned previously, the bulk density of the foam samples was measured with and without removing the skin. A solid skin was formed around the foam samples due to the gas loss[172] and the temperature gradient. Based on the characteristics and morphology of all the foam samples, the one with an average cell size of ~70 nm and the cell density of $10^{15}$ cells/cm$^3$ was selected to study the heat transfer mechanism as a potential candidate that might exhibit a low thermal conductivity with the Knudsen effect.[90] The overall expansion ratio of this sample was measured 3.97 with the presence of the solid skin. The thickness of the skin was measured between 80-120 μm using SEM. After the skin removal, the expansion ratio of the sample was measured to be 7.56 by which the void fraction was calculated 86%.
It is widely accepted and well known that the functionality of the solid materials, such as the thermal conductivity and diffusivity, can be extensively enhanced or depressed depending on the structure, porosity, density, and electrical conductivity of the matrix. These properties are also strongly dependent on and determined by the pressure and temperature. [156,173] Figure 3-13 demonstrates the measured thermal conductivity of all samples versus the expansion ratio and average cell size. Overall, it is apparent that the thermal conductivity reduced dramatically as the expansion ratio increased. The average cell size of the samples (a) and (b) in Figure 3-13 are almost comparable. The expansion ratio of the samples (a) and (b) are 1.2 and 7.56 respectively. It is evident that even if the sample (a) had a small cell size (~100 nm), but its thermal conductivity did not change much compared to its solid counterpart. The sample (b) in Figure 3-13 showed a lower thermal conductivity compared to the sample (c). This would result from an order of magnitude smaller average cell size in the sample (b) even though the expansion ratios of both samples are comparable.
Figure 3-13. Thermal conductivity of the samples versus the expansion ratio and the average cell size.

Table 3-1. Thermal conductivity evaluation data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured thermal conductivity (W/m. °K)</th>
<th>STD DEV (W/m.°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid iPP/0.5CA</td>
<td>0.251(^{(1)})</td>
<td>0.0031016</td>
</tr>
<tr>
<td>Nanoporous iPP/0.5CA(^{(2)})</td>
<td>0.0313</td>
<td>0.002821</td>
</tr>
</tbody>
</table>

(1) This is a measured datum. (2) The sample is shown in Figure 3-12.
Table 3-1 shows the average of the experimental data of the tests for solid iPP/0.5CA and nanoporous iPP/0.5CA (see Figure 3-13(b)). The first set of experiments were performed on iPP/0.5CA solid blocks to measure the solid sample’s thermal conductivity. A set of adequately reproducible measurements could be obtained at the room temperature (25°C). This preliminary measurement is reported here. This dramatic improvement in the insulation property was mainly associated with the contribution of the sample’s unique 3D nanoporous morphology and the relatively high void fraction. First of all, due to the reduced density by achieving an expansion ratio of 7.56, the contribution of the solid part to transfer the heat energy could be minimized. Secondly, when the pore size is in the order of the free path of the air molecules, most of the air molecules’ collisions are inhibited inside the cells.[88,90] The nanoporous iPP/0.5CA sample had an average cell size of ~70 nm, which is comparable to the mean free path of the air molecules at room temperature.[125] Thus, the conduction through the air could be diminished to the greatest extent.

3.5 Conclusion

Neat iPP and iPP with 0.5 wt% clarifying agent were used in a one-step batch foaming process using sc-CO₂. A unique nanoporous medium with a cell density in the order of 10^{15} cells/cm³, an average cell size of ~70 nm, and an expansion ratio of 7.56 was fabricated by manipulating the iPP’s micro-structure and crystallization kinetics. This was done by the inclusion of nanofibrillar heterogeneities in the iPP matrix, and also by controlling the processing parameters. Upon evaluation, the thermal conductivity of the nanoporous iPP was found to have decreased by almost 8-fold compared with its solid counterpart. The cellular structure of the foam samples, as well as the crystallization behavior of both materials were characterized. The results showed that adding a very low percentage of the clarifying agent promoted the iPP’s crystallization
kinetics. This resulted in an increase of about 10°C in the peak crystallization temperature during cooling while the degree of crystallinity remained almost the same.
Chapter 4.
Retrograde Vitrification Behavior of Polycarbonate

4. Retrograde Vitrification Behavior of Polycarbonate

4.1 Abstract

In this study, I examined the retrograde vitrification behavior of polycarbonate/CO$_2$. This behavior is first of all modeled for a polycarbonate/CO$_2$ system, which applies the free-volume theory. I hypothesized based on the Doolittle Equation that the fractional free volume of polycarbonate/CO$_2$ at all depressed glass transition temperatures and under different pressures is equal to a constant. Theorizing on this hypothesis, I determined the locus of the points with the same fractional free volume at the glass transition temperature, this being a representative curve for the retrograde behavior. I verified the existence of this behavior in polycarbonate experimentally by observing the foaming phenomena when the temperature decreased from 0°C to -40°C at an elevated pressure, where the PC entered a rubbery state and CO$_2$ was liquid. The retrograde curve was also experimentally determined using a high-pressure differential scanning calorimeter. A crystal structure was developed inside the PC at a CO$_2$ pressure of 100 atm, as the temperature was decreased to -30°C. I studied the crystal structure using polarized optical microscopy, differential scanning calorimetry, and X-ray diffraction.

4.2 Introduction

Various techniques have been used to measure the glass transition temperature ($T_g$) of a polymer[160]. These have included the study of any significant slope change in the volume or enthalpy curve versus the temperature ($T$), and any discontinuities in the following: storage shear modulus, loss shear modulus, volume coefficient of expansion, and the heat capacity versus the T
as it is shown in Figure 4-1. The different experimental methods of measuring the glass transition and thermal properties of the polymers are listed in Table 4-1.

**Figure 4-1.** The definition of the glass transition temperature as a slope change in (a) the volume, (b) enthalpy, (c) storage shear modulus, (d) volume coefficient of expansion which is the first derivative of the volume, (e) specific heat capacity which is the first derivative of enthalpy, and (f) the loss shear modulus versus temperature[174].
Table 4-1. different experimental methods to measure the thermal properties[175].

<table>
<thead>
<tr>
<th>Method</th>
<th>Representative Instrumentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilatometry</td>
<td></td>
</tr>
<tr>
<td>Volume-temperature</td>
<td>Polymer confined by mercury (home made)</td>
</tr>
<tr>
<td>Linear expansivity</td>
<td>TMS + computer</td>
</tr>
<tr>
<td>Thermal</td>
<td></td>
</tr>
<tr>
<td>DSC</td>
<td>Modulated DSC 2920 (TA Instruments)</td>
</tr>
<tr>
<td>DTA</td>
<td>DuPont 900</td>
</tr>
<tr>
<td>Calorimetric, ( C_p )</td>
<td>Perkin-Elmer modulated DSC, Pyris 1</td>
</tr>
<tr>
<td>Mechanical</td>
<td></td>
</tr>
<tr>
<td>Static</td>
<td>Gehman, Clash-Berg</td>
</tr>
<tr>
<td>Dynamic</td>
<td>Rheometrics RDA2 (Rheometrics Scientific)</td>
</tr>
<tr>
<td>Torsional braid analysis</td>
<td>TBA (Plastics Analysis Instruments)</td>
</tr>
<tr>
<td>Dielectric and magnetic</td>
<td>DuPont Dielectric Analyzer, DEA 2920</td>
</tr>
<tr>
<td>Dielectric loss</td>
<td>Joel JNH 3H60 Spectrometer</td>
</tr>
<tr>
<td>Broad-line NMR</td>
<td>Weissenberg Rheogoniometer</td>
</tr>
<tr>
<td>Melt viscosity</td>
<td>HiRes TGA 2950 (TA Instruments)</td>
</tr>
<tr>
<td>TGA</td>
<td></td>
</tr>
</tbody>
</table>

The \( T_g \)s of polymers have been studied theoretically using the following three important models: The free-volume theory,[176] the kinetic theories of \( T_g \)[177–183] and the thermodynamic theories of \( T_g \).[184–187] In the free-volume theory the polymer’s expansion coefficients in a solid and a rubbery state relate.[188,189] Accordingly, the viscoelastic motion can be expressed by an equation which only involves the time and temperature.[190] However, the actual motion of the polymer chains is not clearly defined. That is, the onset of the molecular motion is assumed to be required by segment-size voids and these are collectively called the free volume. The kinetic theory quantitatively determines the polymer’s heat capacity in either the rubbery or the solid state, and also defines any variation in the \( T_g \) with a specific timeframe. On the other hand, it cannot predict the \( T_g \) on an infinite timescale. This is because in kinetic theory the \( T_g \) is the temperature at which the relaxation time is of the same order of magnitude as the experiment time scale.[175] Lastly, in thermodynamic theory, any \( T_g \) change with the inclusion of a diluent, a molecular weight change,
and any variation in cross-linked density can be successfully predicted. However, this measurement requires an infinite timescale. In other words, to be able to observe any thermodynamic transition, an extremely slow cooling rate is required.[175,186]

The glass transition depression of polymers with CO$_2$ due to the plasticization effect has been studied for years.[96,97] This plasticization, which occurs through the dissolution of a physical blowing agent, specifically CO$_2$, is very important in various applications.[135,191–197] Almost all of these investigations have tried to define a relationship between the $T_g$ of the polymer and the gas pressure ($P$), known as the $T_g$-$P$ profile. This profile provides essential data about the processing temperature for amorphous polymers that use physical blowing agents at different pressures. Supercritical CO$_2$ is typically used to increase the gas solubility and diffusivity simultaneously.[198–203] The $T_g$-$P$ profile follows a linear trend over a limited pressure and temperature range.[99,100,107,108,196,204]

Condo et al.[96] theoretically defined four fundamental types of the $T_g$ behavior over a wide range of the pressure and the temperature. Their model was developed based on the lattice fluid theory and the Gibbs-Dimarzio criterion, which states that the entropy equals to zero at the glass transition temperature. The $T_g$ behavior was modeled as a function of the solubility, polymer flexibility, and the critical temperature of the blowing agent. They[96] predicted that, at a certain low temperature, which was called the lower glass transition temperature ($T_{gl}$), polymers experience their second transition from a solid to a rubbery state. This was called the retrograde vitrification behavior. This can be rationalized by an enhanced gas solubility at a low temperature and its high degree of plasticization. It is well-known that the CO$_2$ solubility in the polymer-gas system increases, as the saturation temperature decreases in an isobaric condition.[200,201,205] This retrograde vitrification behavior has been verified experimentally for only a limited number
of polymers of poly(methyl methacrylate), poly(ethyl methacrylate), and acrylonitrile-butadiene-styrene copolymer.

In a polymer-gas system, sorption kinetics and a systematic solubility measurement have been used to show this behavior, which is experimentally validated by a sharp change in the solubility and the diffusion coefficient. The creep compliance method and stepwise differential scanning calorimetry (DSC) were successfully used by Condo et al. and Handa et al. respectively, to experimentally verify the retrograde behavior. The pioneering work was done by Mraw et al. using stepwise heating or enthalpy increment. Handa et al. extended their study further on gas-laden polymer. They successfully determined all the \( T_{gl} \) at different \( P \) by studying the significant slope change in the heat capacity curve of the two-phase polymer-gas system versus the \( T \). Due to limitations in the pressure and temperature ranges of high-pressure DSC (HP-DSC) systems, all of the studies on the retrograde behavior of the polymer/CO\(_2\) system have been constrained by temperature and pressure. This means that all of these studies have been limited to thermodynamic conditions where the CO\(_2\) is in either a gas or a supercritical state.

On the other hand, the crystallization behavior of a polymer/CO\(_2\) system has been actively studied because of its positive effect on foaming. First of all, Taki claimed that supersaturation at the boundary of the crystal and amorphous sections because of the excessive gas molecules expelled from the formed crystals promotes cell nucleation with visualized images. Wong et al. and Leung et al. also claimed that the tensile stresses from the shrinking crystals and the local stress variations around the rigid crystals in the flowing field can contribute to the cell nucleation rates. Also, the presence of crystals enhances bubble growth with an increased melt strength through the connection of molecules, providing the crystallinity is not too high.
Among amorphous polymers, polycarbonate has shown the ability to be crystallized with the presence of CO\textsubscript{2}.\cite{214,215} Because of its chain rigidity, pure PC shows an extremely slow isothermal crystallization kinetics at 190\degree C and a half-time crystallization of 12 days.\cite{216} With the assistance of CO\textsubscript{2}, the PC could crystallize much faster at an elevated temperature above the T\textsubscript{g}, and a crystallinity of up to 30\% has been achieved.\cite{215} The CO\textsubscript{2}-induced crystallization of amorphous PC at a high pressure and temperature was pioneered by Beckman \textit{et al.}\cite{217} Following this, the nature of the crystal formation in PC has been widely studied.\cite{214} Li, \textit{et al.}\cite{215} investigated the crystallization kinetics of PC at a wide, high-pressure and temperature range using a magnetic suspension balance. So far, all of the studies on the CO\textsubscript{2}-induced crystallization found in PC have been done at a temperature far above the higher glass transition temperature (T\textsubscript{gh}), where the PC is molten or rubbery. It has not been investigated, however, at the retrograde vitrification temperature yet. In the PC/CO\textsubscript{2} system, to the best of our knowledge, neither the existence of retrograde vitrification behavior nor its corresponding curve has been experimentally determined. There was even a study that the PC/CO\textsubscript{2} system does not exhibit retrograde vitrification behavior.\cite{218} The objective of this study is, to theoretically model and experimentally show the retrograde vitrification behavior of a PC/CO\textsubscript{2} mixture. First, the retrograde vitrification behavior of a CO\textsubscript{2}-laden PC is modeled using the free volume theory. Later, the existence of a PC retrograde vitrification behavior was confirmed by a systematic set of foaming experiments, as well as by the development of a crystal structure inside the PC at a very low temperature wherein the PC was in a rubbery state. Lastly, capitalizing on a more capable HP-DSC, the retrograde vitrification curve of the PC was experimentally determined. This is significant because at a lower temperature, the CO\textsubscript{2} solubility increases,\cite{215} and PC also enters a rubbery state. This can potentially provide a new processing window in which the crystallization
is active, and the nucleated crystals can enhance the foaming behavior. This might provide conditions that favour the fabrication of nanocellular foams.[91,219]

4.3 Theoretical modeling of PC/CO\textsubscript{2} Retrograde Vitrification

Based on the Free-Volume Theory which was first developed by Eyring,[176] molecular chain motion depends on the existence of voids within a polymer’s bulk state. These voids are collectively called free volume. Fox et al.[188,220] concluded that the glass transition temperature is an iso-free-volume state. Simha et al.[189] further concluded that the volume expansion in the glassy region occurs at a constant free volume. They defined the free volume at $T= T_g$ as a constant.[221]

Following the early work of Doolittle[222,223] on the correlation between the viscosity and fractional free volume of polymers, the Williams-Landel-Ferry (WLF) equation[190] was developed by which the correlation between the fractional free volume and the temperature could be defined. They further asserted that at the $T_g$, the fractional free volume in all of the polymers was constant.[190,221,224] The WLF equation was further developed to include the effect of pressure on the $T_g$. It was based on a study by Eisenberg,[225] which showed a corresponding increase in $T_g$ at an elevated pressure. This was rationalized by a decrease in the free volume after the pressure was increased.

Lee et al.[226] developed a model based on the Doolittle equation for the polymer/CO\textsubscript{2} mixture. They expressed the fractional free volume as a power law series, using mathematical fitting based on the Taylor series, in terms of the temperature ($T$), pressure ($P$), and gas solubility
(S). This was expressed mathematically as Equation 4-1, where $T_0$, $P_0$, and $S_0$ were the reference values of temperature, pressure, and gas concentration, respectively, as follows.

\[
\frac{1}{f} = \frac{A}{(T-T_0)} + B(P-P_0) + C(S-S_0) + D
\]  

Equation 4-1

The glass transition temperature of amorphous polymers depresses following the dissolution of any plasticizer, including physical blowing agents, inside the polymer. Assuming that there is a constant fractional free volume at the Tg for a polymer/CO2 mixture, a certain set of data might be defined as $(T_{gi}, P_{gi}, S_{gi})$. At each of these the fractional free volume would be the same. Accordingly, Equation 1 can be re-written as follows in Equation 4-2.

\[
\frac{A}{(T_g-T_0)} + BP_g + CS_g + D' = 0
\]  

Equation 4-2

Therefore, I proposed that in a specific polymer/CO2 mixture, the locus of the points, each of which had the same fractional free volume at different glass transition temperatures $(T_{gi})$ and pressures $(P_{gi})$, must define the glass transition curve of the gas-laden polymer at different pressures. This might also predict the retrograde vitrification behavior of an amorphous polymer.

When a polymer is in a melt state in a polymer/gas mixture, the dependency of the $S$ on the $P$ and the $T$ follows the Henrian behavior\cite{200,201,227} and Arrhenius equation\cite{228,229}, respectively. Mutually, this can be expressed by Equation 3, where $a$ and $b$ are constant values, and where $R$ is the molar gas constant, as follows.

\[
S = a \cdot P \cdot \exp\left(\frac{-b}{RT}\right)
\]  

Equation 4-3

Based on the experimentally measured data of CO2’s solubility in the PC at a different pressure and temperature,\cite{215,230} $a$ and $b$ in Equation 4-3 were determined in such a way that could satisfy all of the experimental solubility data. In this context, $a$ and $b$ were found to be: $a=$
0.023 and b= -10364, respectively. The $T_g$ of the PC/CO$_2$ mixture at different pressures was experimentally measured by Banerjee,[204] and Handa.[105] These data, however, did not include the lower glass transition temperature of the PC at various pressures. Using these data sets ($T_{gi}$, $P_{gi}$), the associated gas solubility for each condition at a glass transition temperature and pressure, $S_{gi}$, was calculated using Equation 4-3. Subsequently, all of the constant values in Equation 4-2 were determined to satisfy the data set for ($T_{gi}$, $P_{gi}$, $S_{gi}$), which appears in Equation 4-4. Ultimately, these constant values formed two equations with three variables by which the $T_g$ of the PC versus the $P$ could be plotted, as shown in Figure 4-2. This could potentially represent the retrograde vitrification behavior of the PC/CO$_2$.

\[
\frac{21170}{T_g} - 0.46P_g - S_g - 50.5 = 0 \quad \text{Equation 4-4}
\]

\[
S_g = 0.023 \cdot P_g \cdot \exp\left(\frac{10364}{RT_g}\right) \quad \text{Equation 4-5}
\]
Based on the theoretical model shown in Figure 4-2, which is overlaid on the CO₂ phase diagram, the PC might show a retrograde vitrification behavior when the polymer is impregnated with CO₂ at a relatively low temperature. It is notable from Figure 4-2 that the retrograde vitrification of PC would occur in a condition during which the CO₂ is in a liquid state. Accordingly, the PC must be in a glassy state inside the $T_g-P_g$ envelope, and in a rubbery state
outside the retrograde envelope. So, guided by this model, I set up a systematic series of one-step foaming experiments. These were to verify whether any bubble could be nucleated in PC upon depressurization when it was saturated with CO₂ under conditions that existed outside of the retrograde curve. Obviously, it would not get foamed in the glassy state.

### 4.4 Experimental

#### 4.4.1 Materials

The polymer matrix used in this study was a linear polycarbonate resin, commercially available as Makrolon 24058, supplied by Bayer MaterialScience, with a density of 1.2 g.cm⁻³ at 23°C, a melt flow rate (MFR) of 20 dg.min⁻¹ at 300°C/1.2 kg, a processing temperature of 280°C – 300°C, and a glass transition temperature of 144°C. The CO₂ was supplied by Linde Gas, grade 4 with a purity of 99.99% and was used as the physical blowing agent.

#### 4.4.2 Sample preparation and foaming experiments

Because of the hygroscopic nature of the PC, the pellets were dried at 120°C for 2 hours in a vacuum oven. The PC films with a thickness of around 200 μm were prepared using compression molding at 280°C under 1KN pressure for 3 min., and this was followed by annealing for relaxation at the same temperature for 3 min. under no pressure. The film was air-cooled and was kept at 70°C for 24 hours before each experiment.

The one-step batch foaming process was used to foam the samples. The foaming autoclave was placed inside a freezer capable of providing a temperature of as low as -40 °C. The compression-molded samples were pressurized up to 10 MPa with CO₂ using a Teledyne ISCO high-pressure syringe pump at a low temperature ranging from -40°C to +10°C. Foaming was then induced by a rapid depressurization of 100 MPa.s⁻¹.
4.4.3 Sample characterization

The morphology of the foam samples was examined by a scanning electron microscope (SEM), Jeol 6060. The SEM samples were cryofractured in liquid nitrogen to obtain a clean cross section and were sputter-coated with palladium. The PC’s crystallization kinetics were studied in the PC films, after the saturation process. A Nikon Labophot-2 optical microscope, equipped with a polarized lens, was used to investigate the crystals’ formations and sizes. A differential scanning calorimeter (DSC, Q2000, TA Instrument) was used to study the thermal behavior of the saturated samples, with 5–10 mg of the sample in a nitrogen atmosphere. The materials’ thermal properties were determined using a heating ramp of 50°C to 350°C at a standard heating rate of 10°C min.⁻¹. The effect of the saturation time on the formation and development of the PC crystals at a low temperature of -30°C and at a saturation pressure of 100 atm was investigated using X-ray diffraction analysis. The X-ray diffraction test was performed on a Siemens D5000 diffractometer system operating at 40 kV/40 mA. All tests were run in a 2.5 s/step scan mode within the range 10-30° (2θ). A line-focus Cu Kα source was used with a Kevex detector.

4.4.4 High pressure DSC measurement

The T胶 of the PC/CO₂ in a pressure range of 80 atm – 110 atm was assessed and measured using a HP-DSC, Sensys Evo Setaram. The machine was calibrated with In, Sn, Pb, and Zn under both ambient and high pressures. At the desired pressure, 21 mg of a PC sample with a thickness of 200 μm was held isothermally at the initial temperature inside the HP-DSC, to be exposed to the high-pressure gas and to become saturated. After starting the experiment, the sample was held for 15 min. to establish a baseline at the initial temperatures. All of the samples were scanned at a rate of +1°C/min. for each +3°C temperature increment. This was followed by a 15-minute isothermal hold to establish a new baseline.
4.5 Results and Discussion

4.5.1 Foaming of PC/CO₂ mixture

Figure 4-3 shows the SEM micrographs of the samples that were foamed through one-step batch foaming right after the depressurization process. All of the samples were saturated using CO₂ at relatively low temperatures ranging from -40°C to 0°C and at elevated gas pressures ranging from 80 atm to 110 atm, where the CO₂ was in a liquid state. Also, in Figure 4-3, the PC samples that were successfully introduced with a cellular structure are indicated by the symbol (●), and the ones in which no bubbles could be nucleated are indicated by the symbol (X). As anticipated, all of the samples, which were saturated under the conditions outside of the retrograde envelope, were able to be nucleated because the PC was expected to be in a rubbery state. Since the solubility of CO₂ in PC increases as the temperature decreases,[206,218] under certain conditions the gas solubility inside the PC is high enough to turn the polymer from a glassy state into a rubbery state. Our foaming experiment showed that the PC turned into a rubbery state at low temperatures. However, the samples which were saturated under the conditions inside the retrograde curve, where the PC was expected to be in the glassy state, remained as a solid PC. This process could indicate the existence of the retrograde vitrification behavior.
Figure 4-3. Optical microscopy (a1, b1, and c1) were taken in a lateral direction, and SEM (a2, b2, c2, and d2) were taken in a longitudinal direction of the samples were introduced with cells at different T and P right after a rapid depressurization.

4.5.2 High-Pressure DSC

Using the step-wise temperature scanning technique,[105] the saturated samples were held for 15 min. inside the high-pressure chamber to establish their initial temperature baselines for any of the pressures being investigated. Based on the modeled retrograde curve in Figure 4-2, in the HP-DSC experiment, I used the following temperature scan windows: (-40 °C to -20 °C), (-30 °C to -10 °C), (-15 °C to +15 °C), (-40 °C to +30 °C), and (-40 °C to +30 °C) for the respective gas pressures of 80 atm, 90 atm, 100 atm, 110 atm, and 130 atm. All of the samples were scanned at a
rate of +1 °C/min. for each +3 °C temperature increment, following a 15 min. isothermal hold, which was done to establish a new baseline. The data were corrected with the blank run data. Figure 4-4 shows the heat capacity versus the temperature (\(C_p-T\) data) for the polymer containing gas at each pressure of 80 atm, 90 atm, 100 atm, 110 atm, and 130 atm. As expected from the data in Figure 4-2, at 110 atm and 130 atm the PC was in a rubbery state in all temperature ranges. The \(C_p\) data versus the temperature in Figure 4-4d and Figure 4-4e showed a linear trend. This indicated that the phase change did not happen at this pressure. At lower pressures, however, the \(C_p\) versus the temperature showed a non-linear trend, and this can be correlated to the rubbery-to-glassy state transition. Therefore, the corresponding \(T_{gl}\) can be defined in the manner shown in Figure 4-4a.[105] The subsequent \(T_{gl}\) data at different pressures are shown in Figure 4-5, which can further confirm the validity of theoretical modeling. It should also be emphasized that the predicted \(T_{gl}\) values based on the HP-DSC results (Figure 4-4) are consistent with those from the foaming results (Figure 4-3).
Figure 4-4. Specific heat capacity ($C_p$) of the PC/CO$_2$ system at low temperature and pressure of (a) at 80 atm, (b) at 90 atm, (c) at 100 atm, (d) at 110 atm, and (e) at 130 atm. A solid curve is drawn to show the trend of the $C_p$ data to elaborate the $T_{gl}$.
Figure 4-5. $T_g$-$P$ profile of PC/CO$_2$. (a) HP-DSC experimental data points. Note that the HP-DSC data points here are different from those of Figure 4-3. (b) $T_{g_L}$ data from HP-DSC experiment.

4.5.3 Crystallization Behavior

Figure 4-6 shows the polarized optical microscopy (POM) micrographs taken from the crystals that developed over time inside the PC film. They were under a CO$_2$ pressure of 100 atm at a temperature of as low as -30$^\circ$C. The pressure was released in such a way that any bubble nucleation inside the PC film was avoided. Figure 4-6a shows the sample that was kept for 12 hours, and no crystal development was observed. A track in the formation of crystals was seen after 16 hours in the isothermal-isobaric condition. This means that the active motion of the frozen
PC chains, which had been facilitated by high-pressure CO₂ molecules acting as a plasticizer, had started to form PC crystals. Figure 4-6f shows the sample after 72 hours of isothermal treatment. After this time, the crystals seemed to have impinged upon each other, since all of the saturated samples for a duration of more than 72 hours showed a similar structure under the POM.

**Figure 4-6.** POM micrographs of the PC sample saturated at -30°C and 100 atm. The sample thickness was 200 µm. The crystals were developed slowly over time.

It is interesting to note that the crystallization rate was very low below the T_{gl} line. The fact that crystallization occurred indicates that this point is in a rubbery state for PC. But the low crystallization rate may indicate that the crystallization kinetics is more sensitive to the temperature than the fractional free volume increase with a high gas concentration. In order to study the effect of the temperature on the crystallization behavior at the same fractional free volume in the rubbery domain, constant fractional free volume curves were drawn in Figure 4-7. “A” and “B” had the same fractional free volume because of the higher solubility of the gas in the PC matrix for “A” although the temperature of “A” was much lower.
Inote with interest that the constant free volume fraction curves crossed the vertical isobaric lines at different temperature setting. For example, the constant free volume fraction curves of 0.029, 0.031, and 0.033 cut the 100 atm line at 109°C, 130°C, and 152°C, respectively, in the upper region. But in the lower region, they cut the 100 atm line at -26°C, -30°C, and -33°C, respectively. Compared with the lower region, the upper region required a larger value of $\frac{\Delta T}{\Delta f}$. Iascribed this to the gas’s higher solubility in polymer at a lower temperature. At a given pressure, the free volume fraction is a function of the temperature and the gas concentration. According to Equation 4-3, the gas concentration (that is, the gas solubility) increased more sensitively at a lower temperature. Thus, the change in the free volume fraction, with respect to the temperature, was higher in the lower temperature region.

![Figure 4-7. Curves of constant fractional free volume for PC/CO₂.](image-url)
The DSC heating curves, the degree of crystallinity versus time, and the wide-angle X-ray scattering (WAXS) of A, B, C, and D samples are shown in Figure 4-8, Figure 4-9, and Figure 4-10, respectively. All of these samples had been isothermally treated and were saturated for different amounts of time. The samples’ crystallinity was calculated based on the heat of fusion for a pure crystalline phase equal to 26.2 cal/g.[214] Figure 4-8a and Figure 4-10a show the DSC and XRD results at the same processing condition, corresponding to A in Figure 4-7, at which the crystallization behavior of Figure 4-6 was observed.

The crystallization kinetics of sample A was slow. Figure 4-10 shows the crystallographic patterns of: (i) the PC before saturation (i.e., PC-base), (ii) the PC that was saturated for 72 hours (PC-72hr) at -30°C at a pressure of 100 atm, and (iii) the PC that was saturated for 2 weeks (PC-2weeks) at the same pressure and temperature. All of these patterns have the same wide peak at 2θ=17.6°, which is representative of an amorphous structure. Although the POM micrographs explicitely show the formation of crystals in the samples after 16-18 hours, no clear crystallization melting peak was detected in the DSC graphs, even after 72 hours of treatment (Figure 4-8a). Since the chain mobility near the surface was higher than in the core of the samples,[231–236] the crystals might have developed first on the film’s surface. In this case, the crystallinity might have been so low as to have prevented both the manifestation of a melting peak in the DSC curve and a crystallization peak in the WAXS experiment (see Figure 4-10a). However, the sample that was treated for 2 weeks in the same isothermal-isobaric condition showed a DSC melting peak at a temperature of 284.5°C (Figure 4-8). The crystallinity for this sample was calculated at 2.4%. A sharper and narrower peak was found in the PC-2weeks’ sample (Figure 4-10a); specifically, at 2θ=27°. And this could be indicative of the formation of a highly ordered structure.
On the other hand, the crystals of the gas-treated samples, i.e., samples B, C, and D, were clearly shown in the DSC thermograms. More interestingly, the formation of a double melting peak was observed in these samples as shown in Figure 4-8. These samples all had a much lower melting temperature than sample A, implying that they all had developed a less perfect crystal structure than sample A.[36,162] Also, in Figure 4-8, the glass transition was less apparent as the crystallinity became higher than ~18%. Under a few conditions, a triple melting peak was seen. This is shown in Figure 4-8c, where the sample was treated for 6 hours at 130°C and 100 atm. In Figure 4-10b, the amorphous peak (at θ=17.6°) became narrower over time as crystals were developed. The presence of a peak at θ=27° clearly shows the PC’s crystalline structure.[215] As Figure 4-10c shows, another peak was present in a lower position (θ≈12°) in the C and D samples. This could be interpreted as the formation of either a different type of crystals or of less perfect crystals.

Figure 4-8a, Figure 4-8b, and Figure 4-9 show that the crystallization kinetics was much faster for sample B than sample A (shown in Figure 4-7), indicating that the higher temperature is more important for crystallization than the fractional free volume. Although samples A and B had the same fractional free volume which resulted in their having the same rheological behavior, their crystallization behavior was entirely different. This implies that the molecular mobility that governs the crystallization kinetics is highly sensitive to the temperature. Figure 4-8c, Figure 4-8d, and Figure 4-9 show the crystallization behavior of this system in samples C and D (shown in Figure 4-7). Samples B, C, and D were treated at the same temperature, but in C and D, the fractional free volume was larger due to their higher gas concentration. Thus, the fractional free volume also affected the crystallization kinetics.
Figure 4-8. Isothermal DSC curve of the saturated samples for different period of time, (a) at -30°C and 100 atm, (b) at 130°C and 100 atm, (c) at 130°C and 120 atm, (d) at 130°C and 150 atm, corresponding to “A, B, C, and D” in Figure 4-7, respectively.
Figure 4-9. Crystallinity of the samples (A, B, C, and D in Figure 4-7 & Figure 4-8) versus saturation time.
Figure 4-10. Crystallographic patterns of the PC samples, (a) saturated at -30°C and 100 atm for 0 hr, 72 hrs, and 2 weeks; (b) saturated at 130°C under 100 atm for different periods of time; (c) saturated at 130°C under different pressures for 24 hrs. In these figures, A, B, C and D correspond to A, B, C, and D in Figure 4-7, respectively.
4.6 Conclusion

The retrograde vitrification behavior of the polycarbonate/CO$_2$ was modeled based on the free volume theory with the Doolittle Equation, which is concerned with the rheological behavior of a polymer and a diluent. The experimentally measured solubility data of the PC/CO$_2$ mixture in the rubbery state that follows the Henrian behavior were used. It theorized that assuming a constant fractional free volume at all depressed glass transition temperatures would result in a model for the PC’s depressed glass transition temperatures. This model suggested a retrograde vitrification behavior in the PC/CO$_2$ mixture due to its increased solubility at lower temperatures. It determined this model’s validity through a series of systematic foaming experiments at a low temperature. It also observed crystal development in the PC matrix at a low temperature, and applied HPDSC tests to experimentally measure the lower $T_g$ of PC/CO$_2$ under different pressures. The results of our study of the PC’s crystallization kinetics in the presence of CO$_2$ suggested that temperature was a more important factor in crystallization than the fractional free volume. The increased fractional free volume at the same temperature, which was due to the increased gas solubility at a higher pressure, also further accelerated the crystallization kinetics.
Chapter 5. Summary and Concluding Remarks

5. Summary and Concluding Remarks

5.1 Summary

In addition to the inherent properties of a polymer which can also be manipulated by using additives (e.g., nanoparticles, modifiers, etc.), the final morphology of a cellular structure determines the functionality, and hence the foam’s application and quality. Since the advent of microcellular foams, it has been shown theoretically and experimentally that as the cell size decreases to a submicron size level, and the expansion ratio increases, few properties of the foam improve dramatically, such as thermal insulation. The successful development of high-quality nanocellular foams (e.g., closed-cell nanofoams with high cell density, open-cell nanofoams with high porosity, and the ones with large volume expansion) for specific applications pivots on the scientific advancement of microcellular foam technology. In this context, this thesis investigated the fundamental requirements to fabricate nanocellular foam as the next generation thermal insulation materials and low-density multifunctional polymer composites. This project aims to develop innovative, lightweight, nanocellular foaming technology for polymer nanocomposites using an environmentally-friendly blowing agent.

5.2 Significance and Benefits

It has been estimated that the world will require 50% more primary energy by 2030. In light of this energy crisis, it is imperative to determine effective ways to reduce energy consumption. In particular, space heating and air-conditioning account for over 50% and 40% of residential and commercial energy consumption, respectively. However, the effectiveness of the current thermal insulation materials, which are often produced from highly-expanded polystyrene foams, has already been optimized. Therefore, it is important to develop the next generation thermal insulation
materials to significantly reduce energy use in space heating and air-conditioning. These nano-
cellular plastics will be the next generation thermal insulation materials that will significantly
reduce energy consumption in the world. This technology could also be effectively applied to other
sectors such as automotive and aerospace applications. Successful completion of this project will
lead to the new generation thermal insulation products that would yield reduction in our total
energy consumption by up to 10%-20% annually. This will also result in significant reduction in
CO₂ and other emissions.

5.3 How Will the benefits be realized?

Using the fundamental knowledge obtained to tailor material compositions and processing
conditions, I can provide industries with guidelines on how to develop new nanocellular plastic
products or to improve the quality of their foams. The resulting value-added products, in particular,
lightweight automotive parts, building products for excellent thermal insulation, and lightweight
packaging will increase the global market competitiveness of various industries. Demand for these
value-added products will increase and will translate into increased employment opportunities for
highly qualified personnel in the area of competitive manufacturing and value-added products.
This will positively impact the economy as a whole. It will assist the important development of
lightweight automotive parts using nanocellular polymer blends and composites, which will
improve fuel economy and will reduce air pollution. In the long term, this project will be a major
step forward in our pursuit of sustainable development in the field of polymer foams.

5.4 Key Contributions

Figure 5-1 shows an overview of nanocellular foam’s characteristics from various
polymers. In this thesis, a nanocellular structure with an average cell size of ~70 nm, a cell density
of 9.6*10¹⁶ cells/cm³, and a void fraction of 86% (an expansion ratio of 7.56) was achieved by
controlling the crystallization kinetics of iPP in the presence of the clarifying agent. An optimum foaming temperature was found wherein the smallest pore size with the highest cell density could be produced. The characteristic domain of the achieved products in this thesis is shown in Figure 5-1. 

Overview of characteristics (average cell size, porosity, expansion ratio, and cell nucleation density) of nanocellular foams achieved from various polymer systems. REPRINTED (ADAPTED) WITH PERMISSION FROM Journal of Applied Polymer Science Volume 131, Issue 23, 14 AUG 2014 DOI: 10.1002/app.41293[113].

Figure 5-1. Overview of characteristics (average cell size, porosity, expansion ratio, and cell nucleation density) of nanocellular foams achieved from various polymer systems. REPRINTED (ADAPTED) WITH PERMISSION FROM Journal of Applied Polymer Science Volume 131, Issue 23, 14 AUG 2014 DOI: 10.1002/app.41293[113].
An industrially viable, inexpensive nanocellular manufacturing technology was developed. Using this technology, a nanocellular iPP foam was fabricated in which the thermal conductivity decreased dramatically up to about 8-fold compared with its solid counterpart, from 251 mW/m°C to 31 mW/m°C. Its viability stemmed from its relative low density, the unique 3D nanocellular structure, and nanoscale confinement of the gaseous medium inside the nanopores (i.e., the Knudsen effect). The contribution of solid conduction and gas conduction was experimentally evaluated and verified with existing models.

A theoretical model based on Henry’s law, the Arrhenius equation, the Doolittle equation, and the experimentally measured solubility data was developed and verified, to predict how the glass transition temperature depresses in the PC/CO₂ system at different pressures. This model was built on the pioneering work by Condo et al.[96] on the retrograde vitrification behavior of thermoplastics. Condo capitalized on the lattice fluid theory and the Gibbs-Di Marzio criterion of the glass transition.

For the first time, a retrograde vitrification behavior for PC/CO₂ was predicted using the aforementioned developed model. This behavior was experimentally verified by examining the PC transition from a solid state to a rubbery state. This behavior was also verified by introducing a cellular structure and crystal formation when PC became rubbery due to the plasticization at a very low temperature. So far, this behavior is confirmed for few polymers.

The lower glass transitions of PC at different pressures were experimentally measured by a high-pressure DSC using step-wise temperature increment method at a constant pressure. This work was built on the research conducted by Handa et al.[237] on the PMMA/CO₂ system in which specific heat capacity of the system is experimentally measured and characterized for any dramatic slope change in the \( C_p-T \) curve.
Crystallization kinetics of PC with the assistance of CO$_2$ were thoroughly studied at a very low temperature, below the $T_{gl}$ when PC undergoes a phase transition, as well as at different pressures and temperatures above the $T_{gh}$. The contribution of temperature and fractional free volume at different conditions on the CO$_2$ assisted crystallization of PC were compared and discussed.

There are a few substantial and decisive requirements in the fabrication through foaming with an inert and green physical blowing agent. Among those requirements, having a nanostructured medium and increasing the gas solubility are the most important ones by which the cell nucleation can be enhanced dramatically. A unique processing window for the fabrication of nanocellular foams using PC is introduced wherein

1. A large amount of CO$_2$ is dissolved in the matrix until it underwent a transition from a solid to a rubbery state.

2. A fine crystal structure was induced within the matrix which resulted in a submicron/nanostructured medium.

3. The melt strength of the polymer improved due to the existence of crystals, so it can prevent the cell walls from being ruptured in an abrupt foam expansion process.

4. The foaming temperature could be chosen in the vicinity of $T_{gl}$ where there is maximum amount of stress variation inside the system.
References


[15] Nofar M, Ameli A, Park CB. Development of polylactide bead foams with double crystal


[41] Shimbo M, Higashitani I, Miyano Y. Mechanism of strength improvement of foamed


Bernland K, Tervoort T, Smith P. Phase behavior and optical- and mechanical properties of the binary system isotactic polypropylene and the nucleating/clarifying agent 1,2,3-trIDEOXY-4,6:5,7-BIS-O-[(4-PROPYLPHENYL) METHYLENE]-NONITOL. Polymer (Guildf) 2009;50:2460–4. doi:10.1016/j.polymer.2009.03.010.


Meijer-Vissers T, Goossens H. The influence of the cooling rate on the nucleation efficiency


[82] Solórzano E, Rodriguez-Perez MA, Lázaro J, de Saja JA. Influence of Solid Phase


[121] Rizvi A, Chu RK, Lee JH, Park CB. Superhydrophobic and oleophilic open-cell foams from fibrillar blends of polypropylene and polytetrafluoroethylene. ACS Appl Mater Interfaces


[134] Costeux S, Bunker SP, Jeon HK. Homogeneous nanocellular foams from styrenic-acrylic


