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Evolution of Structure in Solid-State Microcellular and Nanocellular
Polyetherimide (PEI) Foams as a Function of Carbon Dioxide Concentration

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Abstract

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Evolution of Structures in PEI-CO₂ System

This study systematically investigates the evolution of structures in solid-state Polyetherimide (PEI) foams as a function of CO₂ concentration across a saturation pressure range of 0.5 to 5.5 MPa at room temperature. The PEI-CO₂ system produces a microcellular structure between the saturation pressure range of 0.5 (2.2 wt.% CO₂) to 3 MPa (8 wt.% CO₂), with cell sizes ranging from 1 to 5 μm . A rapid transition from a microcellular to a nanocellular (cell size ~ 10 nm) structure is observed between 3 and 3.5 MPa (10 wt.% CO₂), which is unique to the PEI-CO₂ system. The PEI-CO₂ system produces a nanocellular structure between the saturation pressure range of 3.5 to 5.5 MPa (12.4 wt.% CO₂) with average cell sizes ranging from 20 to 130 nm. At 5.5 MPa, the foams exhibit a uniform nanocellular structure with an average

cell size consistently around 20 nm across various foaming temperatures. A probabilistic model based on cell nucleation density is presented to predict the size distributions of the critical radius of cell nuclei based on the Laplace Equation. The model explains the mechanism of the structural transition from microcellular to nanocellular through progressive activation of smaller flaws by increasing saturation pressure.

Microcellular PEI foams exhibit a unique cellular structure, wherein secondary nanopores, ranging in size from 10 to 80 nm, develop on the cell walls of the primary microcells. This study experimentally characterizes the evolution of the secondary nanoporous structure as a function of primary cell expansion. The study comprises two parts: In Part I, the foaming temperature was varied independently at saturation pressures of 0.5 MPa, 2.5 MPa, and 3.3 MPa. In Part II, the foaming time was varied independently at different foaming temperatures under a saturation pressure of 1 MPa. The experimental results demonstrate that the growth of the primary cells directly influences the growth of the secondary nanopores. A modified classical nucleation theory framework based on strain energy due to primary cell expansion is presented to explain that the underlying nucleation mechanism of secondary nanopores is a coupled effect of polymer crazing and foaming.

Investigating the Effect of Cell Size on the Toughness of PEI Foams

This research is a collaborative effort involving Microcellular Plastics Lab, Meza Research Group in the Department of Mechanical Engineering, and the Multiscale Analysis of Materials & Structures (MAMS) Lab in the Department of Aeronautics and Astronautics. The title of the

project is “*Investigating Fundamental Toughness Mechanisms in Nanocellular Foams*,” which was funded by the National Science Foundation. The PI of the project is Dr. Lucas Meza from the Department of Mechanical Engineering. Dr. Vipin Kumar and Dr. Marco Salviato are the co-PIs from the Department of Mechanical Engineering and the Department of Aeronautics and Astronautics, respectively.

This investigation was conducted in collaboration with Kush Dwivedi, a Ph.D. student in Mechanical Engineering. Complete details of all the tensile and fracture experiments, along with numerical simulations, are to be provided in Kush Dwivedi’s Ph.D. dissertation.

The author contributed to the development of process space to fabricate microcellular and nanocellular foams, the fabrication of foam specimens for mechanical tests, the preparation of mechanical test specimens, the SEM characterization of foams before mechanical testing, and the SEM characterization of fracture surfaces.

Process space maps consisting of relative densities at different foaming temperatures were established for microcellular and nanocellular PEI foams. Process conditions were selected from the process space maps to fabricate microcellular PEI foams with cell sizes ranging from 3 to 5 μm and nanocellular PEI foams with cell sizes ranging from 15 to 40 nm. The relative densities of the foams ranged from 0.4 to 0.8. Uniaxial tensile and fracture tests were performed to investigate the effect of cell size on fracture toughness.

Tensile behavior was characterized using true stress–strain curves, while fracture behavior was characterized using load–CMOD (Crack Mouth Opening Displacement) curves. True strain and CMOD measurements were obtained using Digital Image Correlation (DIC).

In general, nanocellular foams demonstrated significantly higher toughness than microcellular foams at equivalent relative densities. These findings contradict the classical scaling law that predicts a reduction in fracture toughness with decreasing cell size. Notably, nanocellular foams with a relative density of 0.8 exhibited fracture toughness comparable to that of unprocessed PEI.

Post-test fracture surface analysis was conducted using SEM. Regions of stable crack propagation exhibited cell wall stretching, indicative of ductile failure. Conversely, unstable crack propagation regions exhibited flat fracture surfaces, characteristic of brittle failure. Overall, nanocellular foams exhibited larger regions of stable crack growth with cell wall stretching. This indicates plastic deformation occurring locally at the nanoscale level. Therefore, ductility at the nanoscale level leads to toughness enhancement, which is the underlying reason for the disruptive fracture behavior of the nanocellular foams.

Advanced Methods to Produce Skinless Solid-State Foams

Previous studies have shown that nanocellular PEI foams have an open-celled porous structure. However, access to these porous structures is limited by the presence of the solid skin layer. A novel plasma treatment-based solid-state process was developed in collaboration with Ankush

Nandi (Ph.D. student, ME) from the Vashisth Lab in the Department of Mechanical Engineering to produce skinless foams. The author contributed to designing, executing the experiments, and conducting SEM analysis. The author and Ankush Nandi contributed to tuning the plasma system parameters to achieve solid-state foaming.

This process involves plasma treatment of CO₂-saturated polymer sheets (with thicknesses ranging from 0.5 to 1.6 mm) using a commercially available low-temperature air plasma system. The resulting foams exhibit a porous surface on the plasma-treated side, with a gradient foam structure extending into the cross-section. Skinless microcellular foams were successfully fabricated in the PC–CO₂ system at saturation pressures of 1 MPa and 5 MPa. Additionally, skinless nanocellular foams with an average cell size of 90 nm were produced in the PEI–CO₂ system.

Selective foaming was achieved on the 15 µm-thick skin of a prefabricated open-cell porous nanocellular PEI sheet by partially re-saturating the skin with CO₂ and subsequently treating it with plasma. The SEM images revealed pores within the skin region and on the treated surface. The acetone-based dye penetration test confirmed that the treated surface is permeable, and the skin is now porous and interconnected with the core. Thus, we successfully demonstrated a new technique to selectively make the solid skin porous, thereby enabling a new way to access the porous structure at the core. Therefore, the plasma treatment-based solid-state foaming process is a promising method for producing skinless solid-state foams to access the core.

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DEDICATION

To my beloved sister, Sri Shabari Sridhar

Chapter 1. INTRODUCTION

1.1 SOLID-STATE FOAMING PROCESS

The Solid-State Foaming process was invented at MIT in the 1980s. The core rationale was to reduce plastic usage in the manufactured parts. Traditional foams, manufactured by blowing gas into a molten polymer matrix, are low-density foams with cell sizes typically greater than 100 μm . Many commercial plastic parts are thin-walled, with a thickness of the order of 1 mm. Introducing bubbles of size greater than 100 μm across 1 mm using the traditional foaming method shall drastically reduce the strength of the parts. The solid-state foaming process successfully introduced bubbles with a diameter of approximately 10 μm across a polymer sheet, resulting in microcellular foams. The strength of the microcellular foams scales with the reduction in the relative density, offering superior mechanical properties compared to conventional foams.

The solid-state foaming process involves saturating thermoplastic polymer sheets with high-pressure gas inside a pressure vessel, typically CO_2 or N_2 , depending on the solubility of the gas in the polymer. At the end of saturation, the polymer-gas system reaches an equilibrium. The vessel is depressurized at this point, and the sheets are removed. These super-saturated sheets are finally quenched in a hot liquid bath at a specific temperature for foaming. The thermodynamic instability during the foaming process leads to the formation and growth of bubbles across the polymer matrix. A typical cell nucleation density for microcellular foam is approximately 10^8 cells/ cm^3 . The initial process development was conducted in the PS- N_2 system³. Over the years, the process has been successfully implemented in several polymer-gas systems such as PC- CO_2 ^{4,5}, PLA- CO_2 ⁶, ABS- CO_2 ⁷, PMMA- CO_2 ⁸⁻¹⁰, and PEI- CO_2 ¹¹⁻¹³, to name a few.

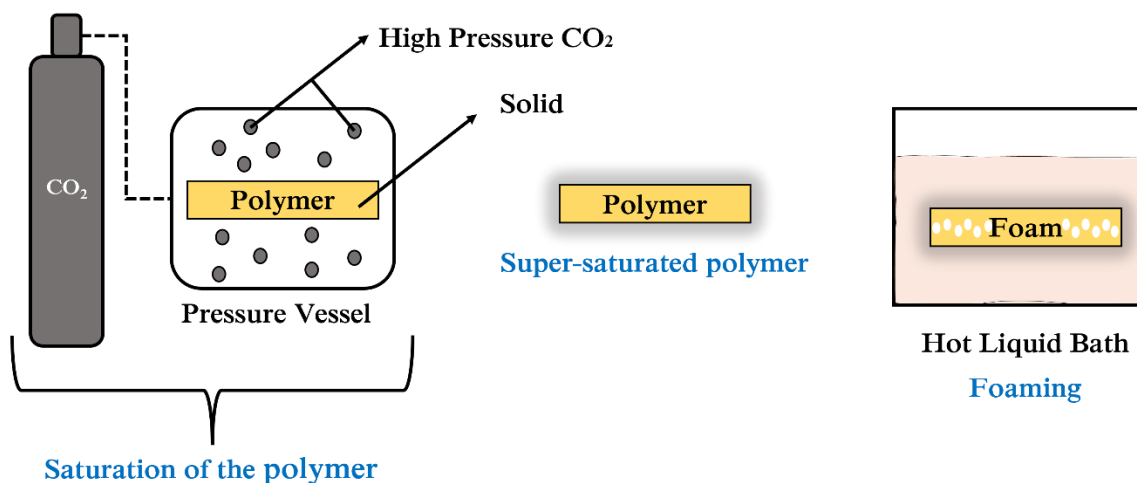


Figure 1.1 Schematic of the solid-state foaming process illustrating different stages of the process

1.2 PROCESS PARAMETERS AND EFFECTS ON STRUCTURE

During the saturation process, the gas diffuses into the polymer sheet under high pressure. At the end of saturation, the gas sorption stops, and the polymer-gas is in equilibrium. The key variables are the saturation pressure (P_{sat}) and the saturation temperature (T_{sat}). They are varied to achieve a desired gas concentration at equilibrium (C_{eqbm}). This is illustrated in Figure 1.2. The concentration of gas in the polymer at the time of foaming determines the cell nucleation density in the foam.

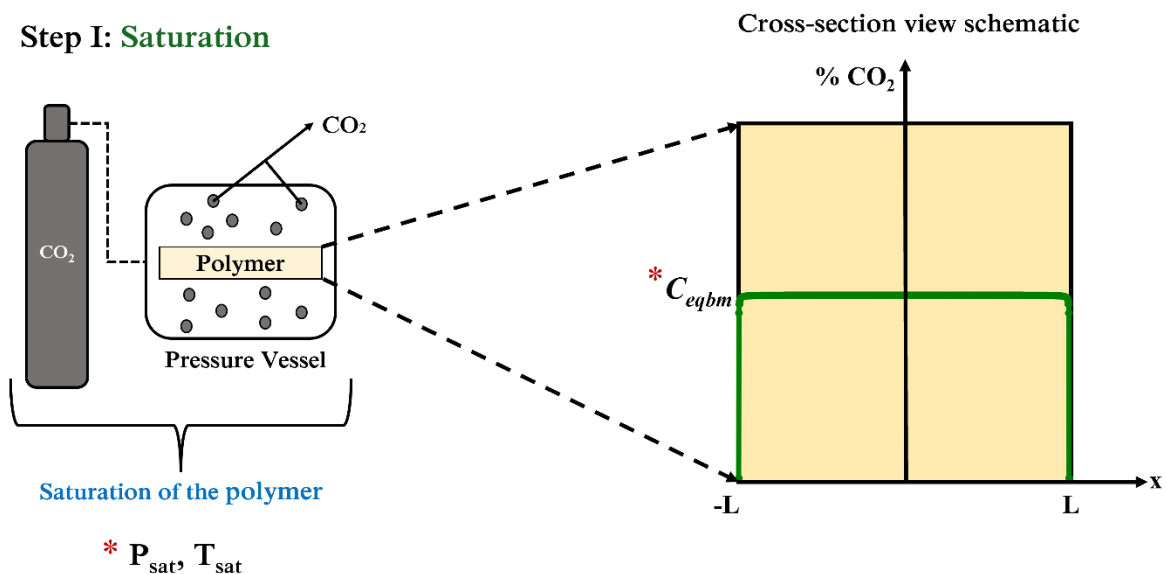


Figure 1.2 A schematic illustrating the saturation of the polymer with CO₂. The schematic view of the cross-section on the right shows an estimated CO₂ concentration profile across the sheet thickness ($2L$) for reference. The CO₂ concentration is uniform at the end of saturation.

Once the saturated polymer is removed from the pressure vessel, it is in a supersaturated state under atmospheric conditions. The gas begins to diffuse out from the polymer through the surface; as a result, the gas concentration in the polymer decreases. This process is called desorption. The time between depressurization and foaming is considered as desorption time ($t_{desorption}$). This is illustrated in Figure 1.3. The gas desorption results in the formation of the solid skin on the outer layer of the foam, as shown in the SEM image in Figure 1.4. A longer desorption time results in a thicker skin¹⁴.

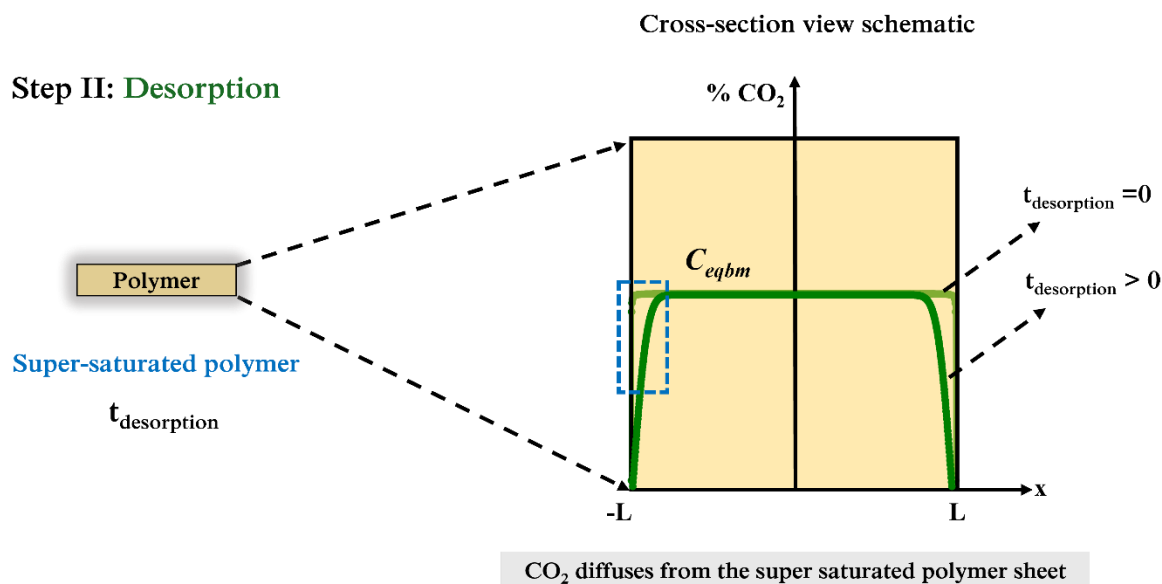


Figure 1.3 A schematic illustrating the effect of desorption of CO_2 from the sheets. The schematic view of the cross-section on the right shows an estimated CO_2 concentration profile across the sheet thickness ($2L$) after a finite desorption time for reference. The CO_2 concentration decreases at the edge.

The supersaturated polymer-gas is quenched in a hot liquid bath set at a temperature called the foaming temperature (T_{foam}). The presence of gas in the thermoplastic polymer lowers the glass transition temperature (T_g) of the polymer due to the plasticization effect. The foaming temperature is always above the T_g of the polymer-gas system, which is referred to as the effective T_g . Heating the polymer-gas system above the effective T_g causes a drastic reduction in the solubility of the gas in the polymer, leading to thermodynamic instability and the nucleation and growth of bubbles. Higher foaming temperature leads to larger bubble growth, resulting in lower relative densities. A higher foaming temperature also leads to thinner solid skin; further discussion on this topic can be found in Chapters 5 and 6.

Step III: Foaming

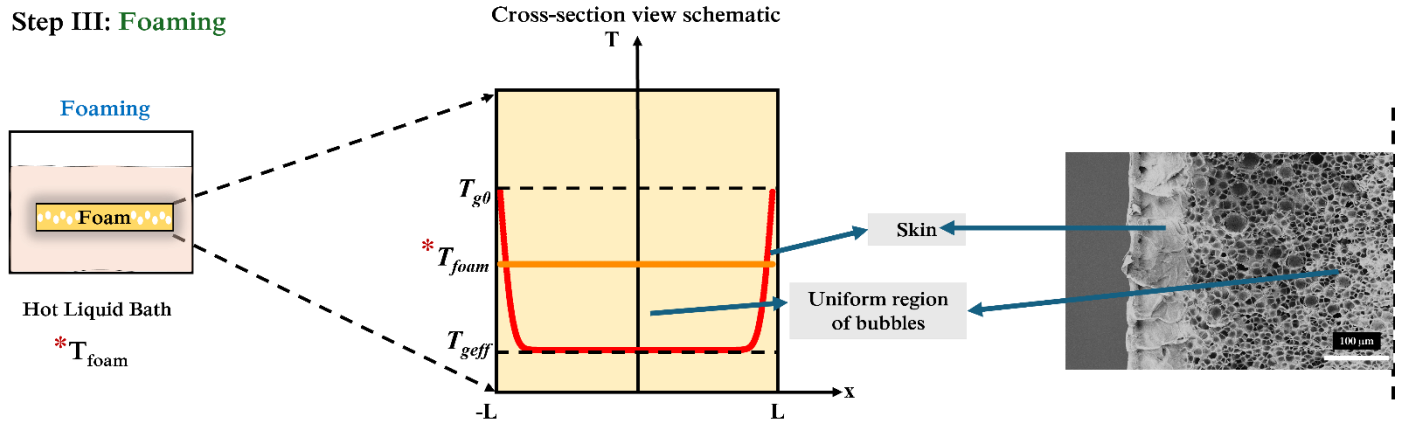


Figure 1.4 A schematic illustrating the underlying principle of the foaming process. The schematic view of the cross-section on the right shows an effective T_g profile across the thickness ($2L$). The horizontal line corresponds to a foaming temperature. The SEM image captured at the ` illustrates the skin and the cellular core.

Overall, in the solid-state foaming process, we vary the P_{sat} to control the cell nucleation density. T_{sat} is generally fixed at room temperature. The T_{foam} is varied to achieve different relative densities. In general, we establish a process-space map for a given polymer-gas system, which consists of relative density vs T_{foam} and cell size vs T_{foam} at different P_{sat} .

1.3 CELLULAR STRUCTURES CHARACTERIZATION

Over the years, the solid-state foaming process has advanced to produce nanocellular foams. Nanocellular foams have an average cell size of less than 100 nm. Krause et al.¹⁵ successfully produced nanoporous bi-continuous open structures in the PES- CO_2 and PEI- CO_2 systems with a pore size as small as 40 nm. The study characterized the transition from microcellular to open-celled nanocellular structure through helium-based gas permeation measurements. Over the years,

the feasibility of producing nanocellular foams was studied in several polymer-gas systems. The standard strategy was to substantially increase gas solubility in the polymer by either increasing the P_{sat} or decreasing the T_{sat} or both simultaneously. Enhancing gas solubility in the polymer increased the cell nucleation density, leading to the production of nanocellular foams. The two notable polymer-gas systems are the PMMA-CO₂^{8–10} and PEI-CO₂^{11–13} systems. Krause et al.¹⁵ achieved a nanocellular structure at a saturation pressure of 5 MPa under room temperature saturation conditions. However, Guo¹⁶ demonstrated that PMMA-CO₂, PC-CO₂, PSU-CO₂, and PPSU-CO₂ systems produce nanocellular foams when the saturation temperature is lowered below room temperature. Nicole¹⁷ has shown that the PEI-CO₂ system produces transparent foams at sub-zero saturation temperatures.

Fukasawa et al.¹⁸ discovered that the PC-CO₂ system produces microcellular foams with secondary nanopores on the cell wall, leading to a unique microstructure. Miller et al.¹² reported the presence of secondary nanopores in the PEI-CO₂ system. Guo's¹⁶ work reported the presence of secondary nanopores in COC-CO₂¹⁹, PSU-CO₂, and PPSU-CO₂. Gong et al.²⁰ characterized the secondary nanopores in the PC-CO₂ system. The study attributes the mechanism of secondary nanopores to crazing. It also revealed that microcellular foams are open-celled through the secondary nanopores at low relative densities.

Chapter 2 presents an investigation of the evolution of structures in the PEI-CO₂ system as a function of CO₂ concentration. The PEI-CO₂ system is unique in that it produces microcellular and nanocellular foams within the saturation pressure range 0.5 to 5.5 MPa under room temperature

saturation conditions. In this study, the saturation pressure is systematically varied to achieve different CO₂ concentrations in PEI to characterize the evolution of structure.

Chapter 3 presents the experimental characterization of the secondary nanopores in microcellular PEI foams. The study comprises two parts: 1. Effect of Saturation Pressure, and 2. Effect of Foaming Time. In Part 1, we characterize the development of secondary nanopores on the cell wall as a function of foaming temperature across different saturation pressures in the PEI-CO₂ system. Part 2 investigates the development of secondary nanopores on the cell wall as a function of foaming time at different foaming temperatures for a given saturation pressure.

1.4 EFFECT OF CELL SIZE ON THE TOUGHNESS OF NANOCELLULAR PEI FOAMS

The effect of reducing cell size to nanometers on bulk mechanical properties is a significant area of interest. Preliminary studies by Miller et al.²¹ and Martin De Leon et al.²² showed that nanocellular foams exhibit improved fracture properties at the same relative densities compared to the microcellular foams. A recent review paper on the effect of cell size reduction on mechanical properties by Le Barbenchon and Kopp²³ highlighted the challenges of foams at a given relative density across different cell size ranges. In a collaborative research effort, we fabricated microcellular PEI foams with cell sizes ranging from 3 to 5 μm and relative densities between 0.5 and 0.8. We fabricated nanocellular PEI foams with cell sizes ranging from 15 to 40 nm and relative densities between 0.4 and 0.8. We conducted systematic tensile tests and fracture tests to characterize the effect of cell size on tensile properties and fracture properties of the PEI foams. Chapter 4 summarizes the tensile and fracture properties as a function of relative density and cell size. The tensile and fracture test results were analyzed using Digital Image Correlation (DIC).

SEM analysis of fracture surface areas is presented, offering new insights into crack propagation across cells in microcellular and nanocellular PEI foams.

1.5 SKIN THICKNESS AND SKINLESS FOAMS

The integral solid skin forms in the solid-state foaming process due to gas desorption. As gas diffuses from the sheets through the thickness, the local gas concentration drastically decreases at the outer edge. Weller¹⁴ proposed that bubbles will not nucleate during foaming when the local gas concentration in the polymer matrix decreases below a specific minimum value. Therefore, an unfoamed layer of solid skin develops on the outer edge, and the thickness of the solid skin grows with desorption. Weller¹⁴ studied the effect of desorption time on the skin thickness in the PC-CO₂ system. The study led to the development of a 1D mass diffusion model²⁴ to predict skin thickness based on the minimum gas concentration required for bubble nucleation. Mohyeddin and Fereidoon²⁵ validated a similar model on the PS-N₂ system. Wesseling et al.²⁶ and Adams et al.²⁷ developed an effective T_g -based model to predict skin thickness, based on the theory that bubbles will nucleate in the polymer matrix only when the foaming temperature exceeds the effective T_g . A recent study by Sridhar et al.²⁸ further experimentally validated the effective T_g -based model in the PC-CO₂ system at different foaming temperatures, which predicts skin thickness as the point where the temperature profile generated by heating during the foaming process first intersects the effective T_g profile. Chapter 5 of this document is based on this work. The experimental results indicate that increasing the foaming temperature significantly reduces skin thickness during the solid-state foaming process. At higher foaming temperatures, a higher degree of reduction in solubility leads to the nucleation of more bubbles, thereby increasing cellular core thickness and decreasing skin thickness. This effect is discussed in detail in Chapters 5 and 6.

In Chapter 6, we experimentally characterize the development of skin during the foaming process as a function of foaming time. The central question is whether skin evolves during the foaming process as a function of foaming time. The study was conducted at low and high desorption times. The results highlight how the behavior of the polymer-gas system changes with the desorption time and how it affects the evolution of the skin as a function of the foaming time. The effective T_g -model from Sridhar et al. was implemented to compare model predictions as a function of foaming time with experimental results. The chapter presents key insights into skin formation in solid-state foaming, which are essential for designing foams with varying skin thicknesses and developing a comprehensive prediction model.

The skin is a barrier that prevents access to the cellular core. Over the years, the solid-state foaming process has produced nanocellular polymers, including transparent foams in PEI and PMMA. Due to the presence of skin, characterizing the cellular structure has been challenging. Nicolae¹⁷ has machined the skin and characterized the transportation properties of PEI nanocellular foams. There is an emerging area of research where researchers are aiming to produce skinless foams directly in solid-state foaming. Nanoporous polymers have several applications in the field of filtration and other, yet unexplored, potential applications. The common approach presented involves sandwiching a thin sacrificial layer^{29–31} on the surfaces of the polymer sheet; the sandwich is then saturated and foamed. The skin forms on the sacrificial layer, which acts as a gas barrier for the base polymer sheet. After foaming, the sacrificial layer is removed using a solvent, leaving a skinless foam of the base polymer. In Chapter 7, we demonstrated a novel system and method for producing skinless microcellular and nanocellular foams using a low-temperature atmospheric

plasma-induced solid-state foaming process. Overall, Chapters 5-7 have advanced the research area of solid skin, offering new insights into skin formation and a promising technological advancement for producing skinless foams.

Chapter 2. EVOLUTION OF STRUCTURES IN SOLID-STATE PEI FOAMS AS A FUNCTION OF CO₂ CONCENTRATION

2.1 ABSTRACT

This chapter investigates the evolution of structures in solid-state PEI foams as a function of CO₂ concentration across a saturation pressure range of 0.5 to 5.5 MPa at room temperature. The PEI-CO₂ system produces a microcellular structure between the saturation pressure range of 0.5 (2.2 wt.% CO₂) to 3 MPa (8 wt.% CO₂), with cell sizes ranging from 1 to 5 μm . A rapid transition from a microcellular to a nanocellular (cell size ~ 10 nm) structure is observed between 3 and 3.5 MPa (10 wt.% CO₂), which is unique to the PEI-CO₂ system. The PEI-CO₂ system produces a nanocellular structure between the saturation pressure range of 3.5 to 5.5 MPa (12.4 wt.% CO₂) with average cell sizes ranging from 20 to 130 nm. At 5.5 MPa, the foams exhibit a uniform nanocellular structure with an average cell size consistently around 20 nm across various foaming temperatures. A probabilistic model based on cell nucleation density is developed to predict the size distributions of the radius of critical nuclei based on the Laplace Equation. The model explains the mechanism of the structural transition from microcellular to nanocellular through progressive activation of smaller flaws due to increasing saturation pressure.

2.2 INTRODUCTION

The Solid-State Foaming process was developed and invented at MIT in the 1980s¹⁻³ to introduce micro-sized bubbles into thin-walled plastics. The process involves two primary steps: 1. Saturate the polymer sheets with gas, typically CO₂ or N₂, under high pressure in a pressure vessel. 2. Once the polymer-gas system reaches equilibrium, remove it from the pressure vessel and quench it in a hot liquid medium. In this step, the increase in temperature decreases the solubility of the gas in the polymer, inducing a thermodynamic instability that results in the nucleation and growth of micro-sized bubbles, creating a microcellular polymer foam. The first experiments were conducted on the PS-N₂ system¹⁻³. Over the years, the solid-state foaming process has been expanded to several polymer-gas systems, including PC-CO₂^{4,5}, PLA-CO₂⁶, ABS-CO₂⁷, PMMA-CO₂⁸⁻¹⁰, and PEI-CO₂¹¹⁻¹³ to name a few. For each system, a process space was established where the saturation pressure and foaming temperature are varied to produce foams with the desired cell size range and relative density.

Over the years, the solid-state foaming process has been advanced to produce nanocellular foams^{11,12,15,16}. The underlying principle is to increase the gas concentration in the polymer by increasing the solubility to enhance the nucleation density, thereby decreasing the cell size, and producing nanocellular foams. There are two common strategies: (1) increasing the saturation pressure, and (2) decreasing the saturation temperature below room temperature, either individually or in combination. Guo¹⁶ has conducted an extensive feasibility study to assess the ability of different polymer-CO₂ systems to produce nanocellular foams through low-temperature saturation experiments. Krause et al.¹⁵ investigated the solid-state foaming behavior of PEI and PES-CO₂ systems. Remarkably, the study showed that the PEI-CO₂ system can produce

microcellular and nanocellular foams under room temperature saturation conditions. In a 75 μm -thick PEI film, they achieved a bi-continuous nanocellular structure with an average cell size as small as 40 nm at a saturation pressure of 4.6 MPa. The study evaluated the PEI-CO₂ across a pressure range of 0.2 MPa to 4.6 MPa. Krause et al.¹⁵ reported a threshold CO₂ concentration at which the structure becomes nanocellular. Interestingly, even at a low saturation pressure of 0.2 MPa, PEI foams had an average cell size of approximately 10 μm . The study also shows PEI and PES foams have an open-porous nanocellular structure at higher foaming temperatures close to the T_g of the unprocessed polymer. They report gas permeation through the porous structure as a measure of the open-cell content. To avoid the solid skin, the flux was measured in the lateral direction through the nanoporous structure.

Miller et al.¹² further investigated the PEI-CO₂ system. At 1 MPa and 4 MPa (3.6 wt.% CO₂ and 9.4 wt.% CO₂), PEI produced microcellular foams with a cell nucleation density of approximately 10^{10} cells/cm³. Miller et al.¹² reported that upon increasing the saturation pressure to 5 MPa (11 wt.% CO₂), the structure became nanocellular. The average cell size ranged from 30 to 120 nm, exhibiting considerable variation. Correspondingly, the cell nucleation density increases to 10^{14} cells/cm³. These studies show that PEI is unique in that it nucleates 10^{10} cells/cm³ even at low saturation pressures of 1 MPa and 0.2 MPa. They do not report structures with a cell size greater than 10 μm . Zainab et al.³² demonstrated that varying CO₂ concentrations in PEI films result in structures ranging from microcellular to nanocellular. For instance, the 70 μm film produces a microcellular structure when saturated at 5 MPa. Due to the high rate of CO₂ desorption in thin films within 1 min of desorption, the CO₂ concentration decreases, which results in a microcellular

structure. This study aims to characterize the structures that can be achieved in the PEI as a function of CO₂ concentration.

The research goals that this study explores are as follows

1. Establish the conditions for microcellular and nanocellular structures as a function of CO₂ concentration in PEI
2. Characterize the region in process space where the transition from microcellular to nanocellular structure occurs
3. Develop a theoretical framework to understand the nucleation mechanism

2.3 MATERIALS

0.5 mm-thick 1" x 1" PEI specimens (Ultem 1000) were saturated with high-pressure CO₂ in a pressure vessel at respective set pressures under room temperature conditions. Once equilibrium was achieved in the PEI-CO₂ system, the vessel was depressurized, and the specimens were removed and immediately stored in liquid nitrogen (LN₂) to minimize CO₂ loss. The specimens were foamed in hot oil at respective foaming temperatures for 30s. The foamed specimens were freeze-fractured in liquid nitrogen (LN₂) to expose the cross-section. The cross-section is coated with a 4-5 nm platinum (Pt) layer and analyzed under a Scanning Electron Microscope (SEM). The density of foams was measured using the weight displacement method.

2.4 EXPERIMENTAL

Table.2.1 A list of saturation pressures and corresponding foaming temperatures

P_{sat} (MPa)	T_{foam} (°C)
0.5	180 °C, 190 °C and 200 °C
2.5	160 °C, 170 °C, 180 °C, 190 °C and 200°C
3	160 °C, 180 °C and 200°C
3.2	160 °C, 180 °C and 200°C
3.3	160 °C, 180 °C and 200°C
3.5	160 °C, 180 °C and 200°C
4	160 °C, 180 °C and 200°C
4.5	160 °C, 170 °C, 180 °C and 190°C
5.5	160°C, 180 °C and 200°C

2.5 RESULTS

2.5.1 Summary of Process Space Data

Table.2.2 Summary of relative density and cell size at various saturation pressures

Microcellular PEI Foams					
P _{sat} (MPa)	CO ₂ (wt.%)	T _{foam} (°C)	Relative Density	Avg. Cell Size (μm)	SD (μm)
0.5	2.2	180	0.96	2	0.3
		190	0.87	2.6	0.5
		200	0.72	4.5	1.1
2.5	6.95	160	0.83	0.9	0.3
		170	0.74	—	—
		180	0.64	2.1	1.5
		190	0.55	—	—
		200	0.4	2.9	2.7
3	8	160	0.8	1.3	0.2
		180	0.64	1.9	0.4
		200	0.4	2.1	1.7
Nanocellular PEI Foams					
P _{sat} (MPa)	CO ₂ (wt.%)	T _{foam} (°C)	Relative Density	Avg. Cell Size (nm)	SD (nm)
3.5	10	160	0.71	42	18
		180	0.6	72	42
		200	0.48	56	26
4	10	160	0.69	53	27
		180	0.53	130	65
		200	0.32	45	19
4.5	10.6	160	0.7	57	24
		170	0.67	36	13
		180	0.54	56	22
		190	0.49	58	22
5.5	12.4	160	0.68	19	8
		180	0.5	23	7
		200	0.49	21	8

*CO₂ concentration is the average of three specimens measured immediately after depressurization of the pressure vessel.

2.5.2 Process Space for Microcellular PEI Foams

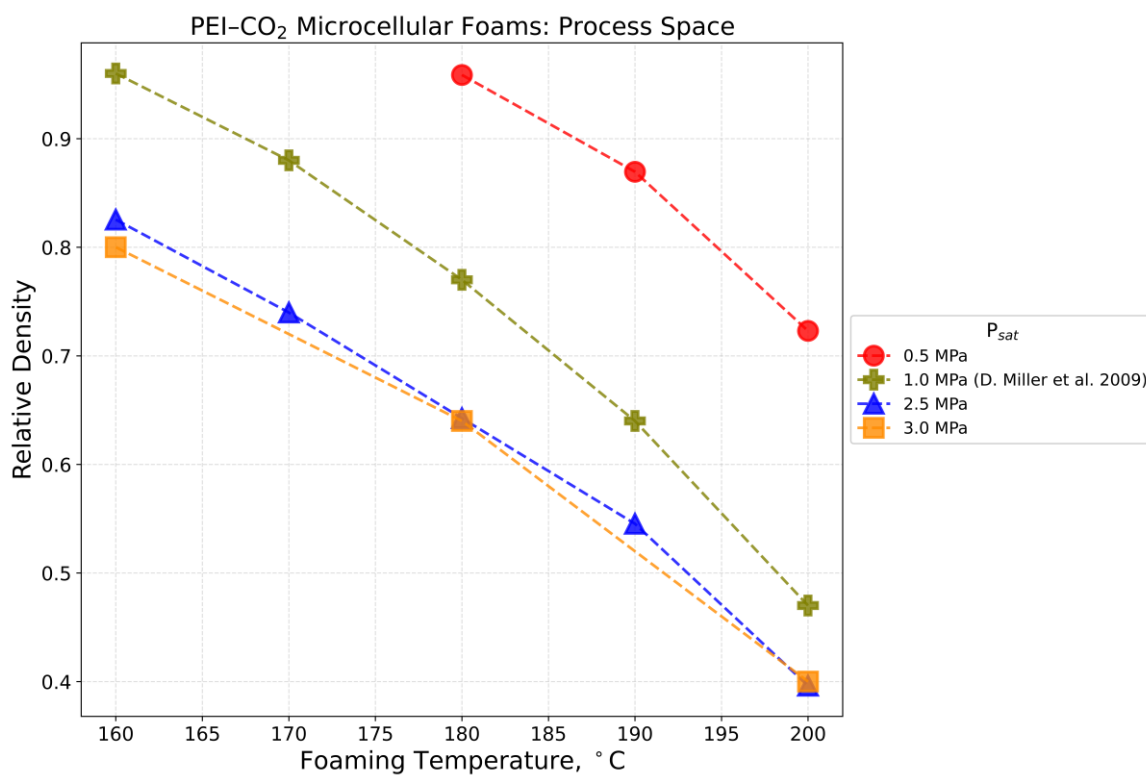


Figure 2.1 Relative density vs. Foaming temperature in PEI-CO₂ system for the saturation pressure range 0.5 to 3 MPa

2.5.3 Process Space for Nanocellular PEI Foams

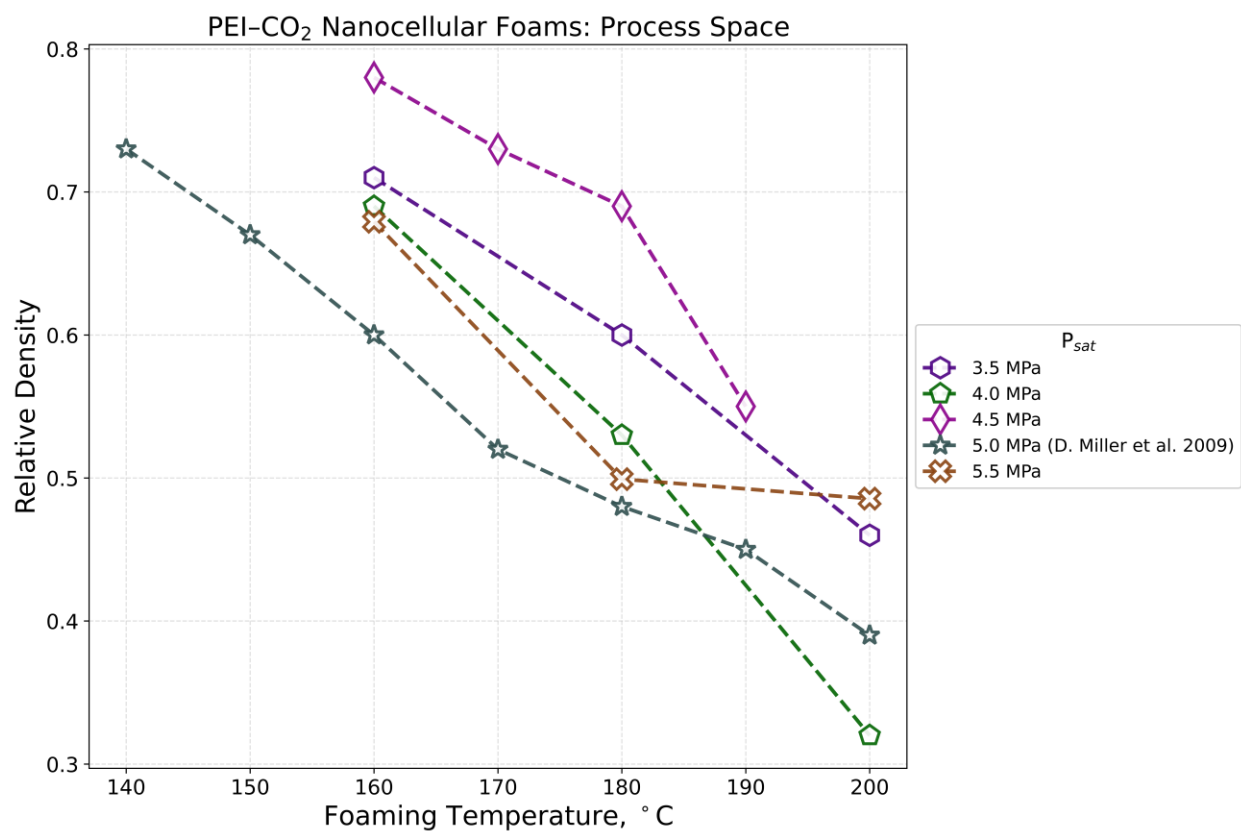


Figure 2.2 Relative density vs. Foaming temperature in PEI-CO₂ system for the saturation pressure range 3.5 to 5.5 MPa

2.5.4 SEM Analysis of the Microcellular PEI Foams

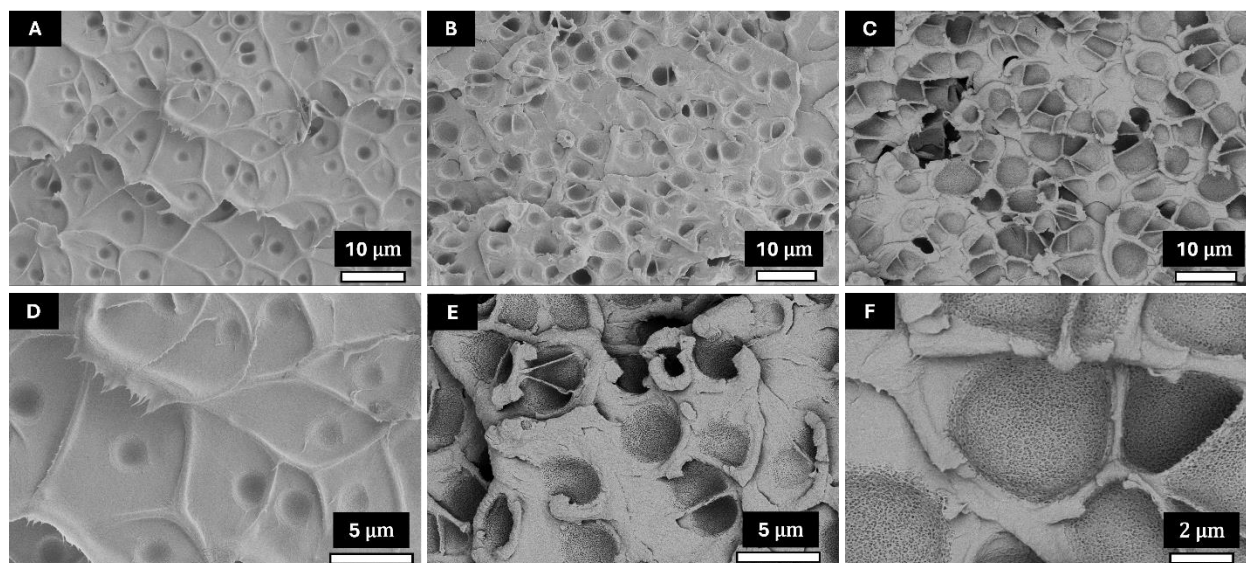


Figure 2.3 (A-C) SEM images of cellular structures of PEI foams saturated at 0.5 MPa and foamed at 180°C, 190°C, and 200°C, respectively. (D-F) Corresponding high magnification SEM images

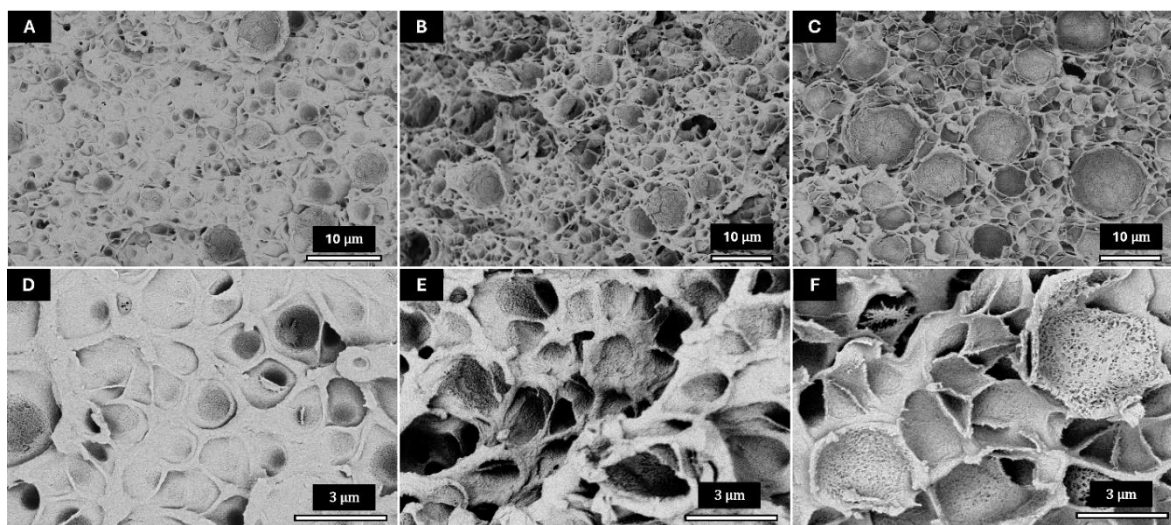


Figure 2.4 (A-C) SEM images of cellular structures of PEI foams saturated at 2.5 MPa and foamed at 160°C, 180°C, and 200°C, respectively. (D-F) Corresponding high magnification SEM images

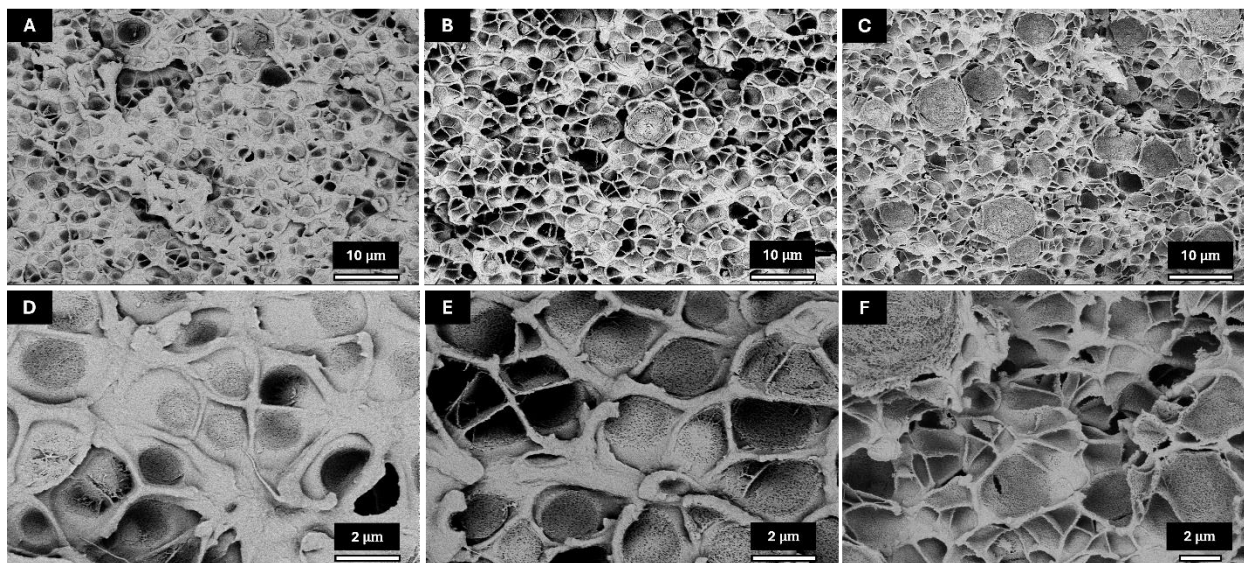


Figure 2.5 (A-C) SEM images of cellular structures of PEI foams saturated at 3 MPa and foamed at 160°C, 180°C, and 200°C, respectively. (D-F) Corresponding high magnification SEM images.

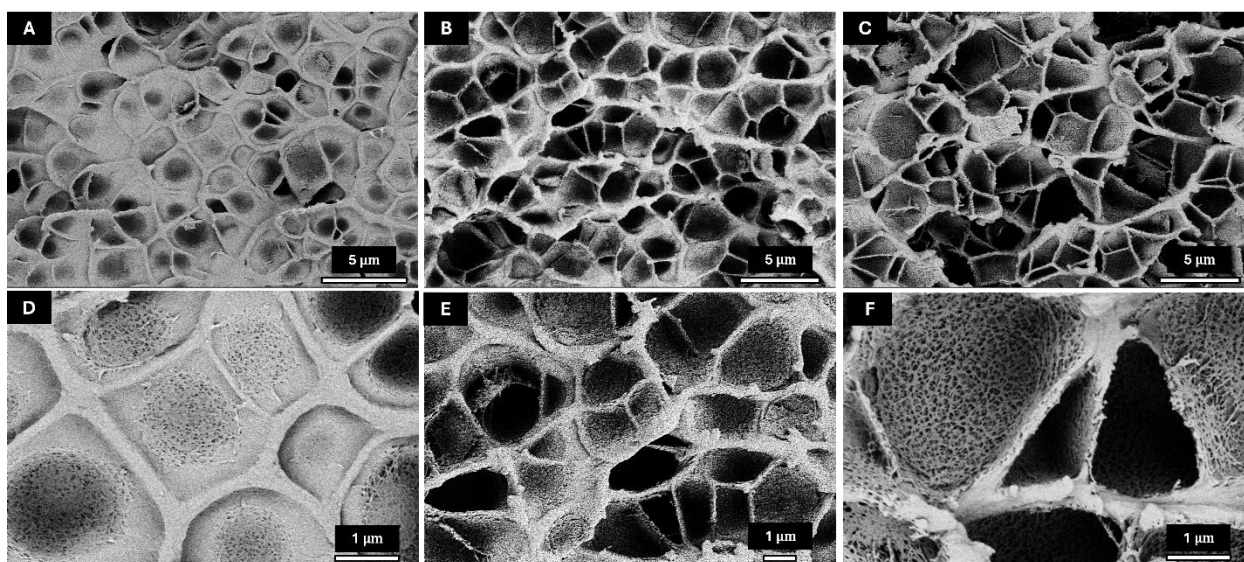


Figure 2.6 (A-C) SEM images of cellular structures of PEI foams saturated at 3.2 MPa and foamed at 160°C, 180°C, and 200°C, respectively. (D-F) Corresponding high magnification SEM images.

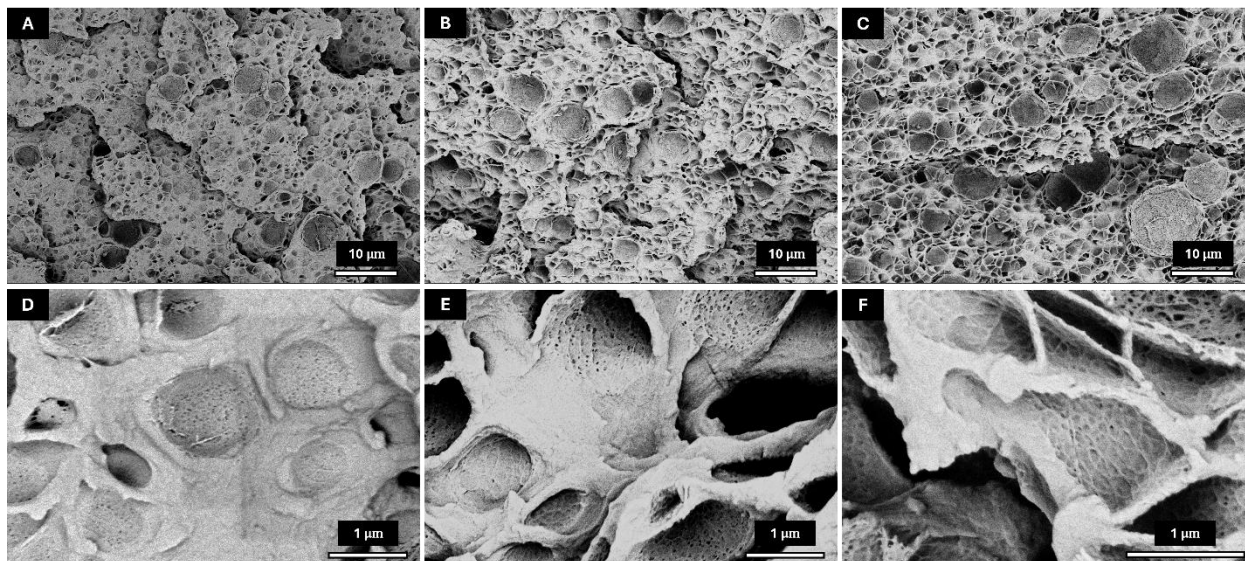


Figure 2.7 (A-C) SEM images of cellular structures of PEI foams saturated at 3.3 MPa and foamed at 160°C, 180°C, and 200°C, respectively. (D-F) Corresponding high magnification SEM images.

2.5.5 SEM Analysis of the Nanocellular PEI Foams

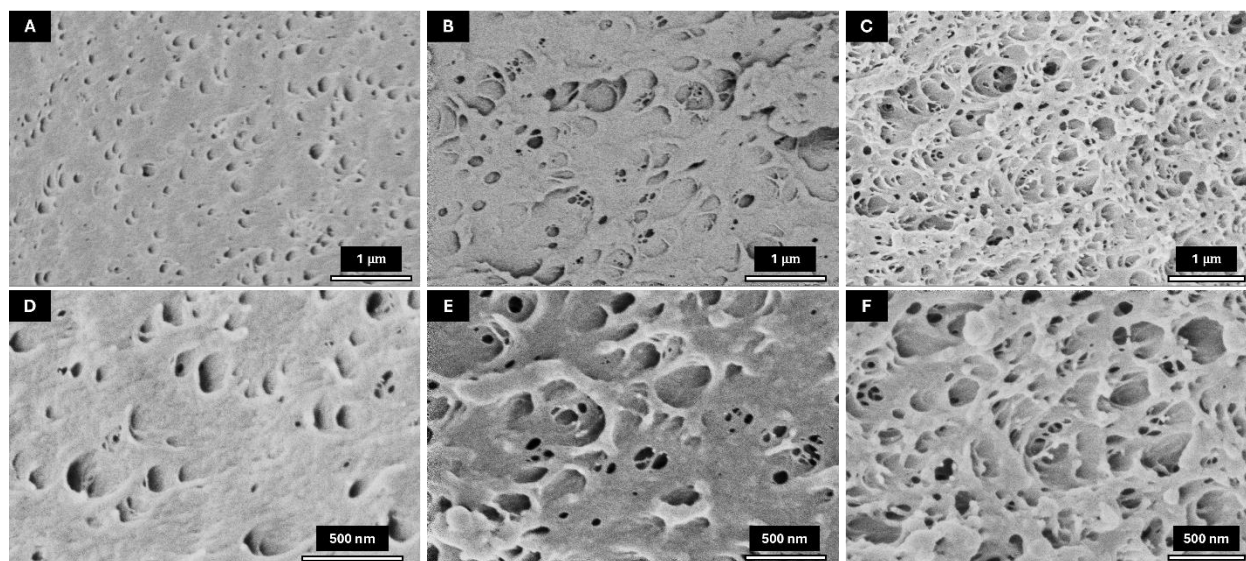


Figure 2.8 (A-C) SEM images of cellular structures of PEI foams saturated at 3.5 MPa and foamed at 160°C, 180°C, and 200°C, respectively. (D-F) Corresponding high magnification SEM images illustrating the details of the pores.

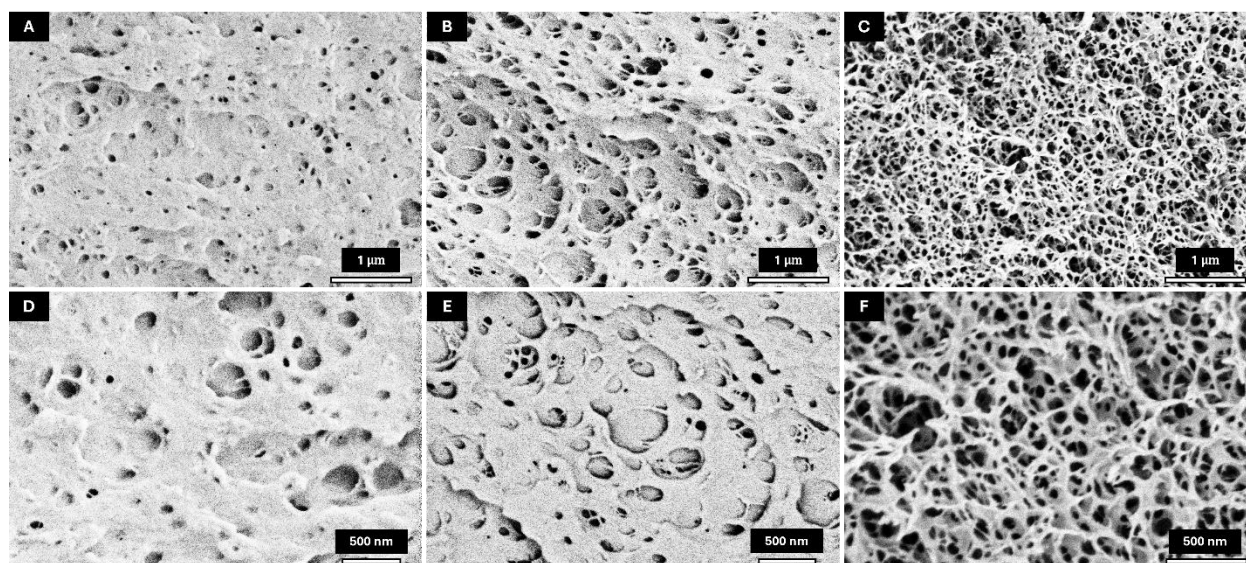


Figure 2.9 (A-C) SEM images of overall cellular structures of PEI foams saturated at 4 MPa and foamed at 160°C, 180°C, and 200°C, respectively. (D-F) Corresponding high magnification SEM images illustrating the details of the pores.

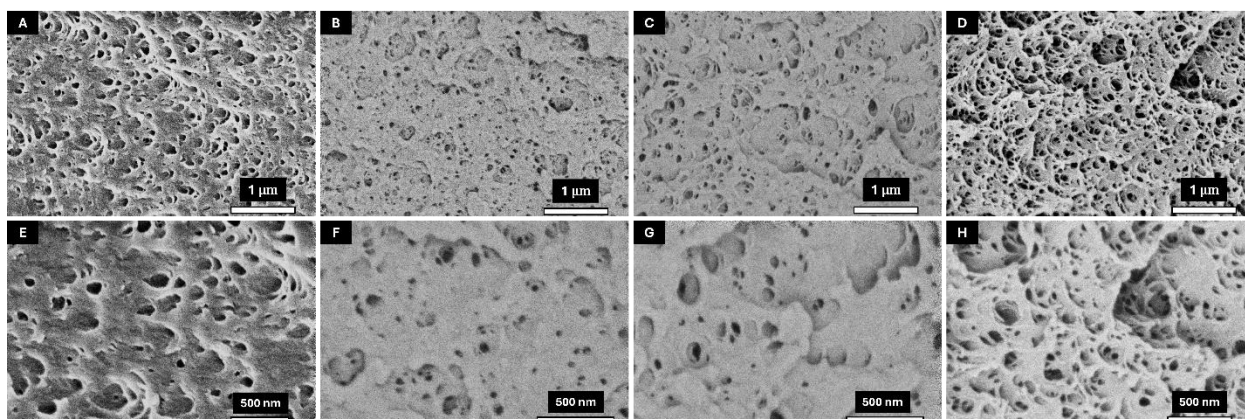


Figure 2.10 (A-D) SEM images of overall cellular structures of PEI foams saturated at 4.5 MPa and foamed at 160°C, 170°C, 180°C, and 190°C, respectively. (E-H) Corresponding high magnification SEM images illustrating the details of the pores.

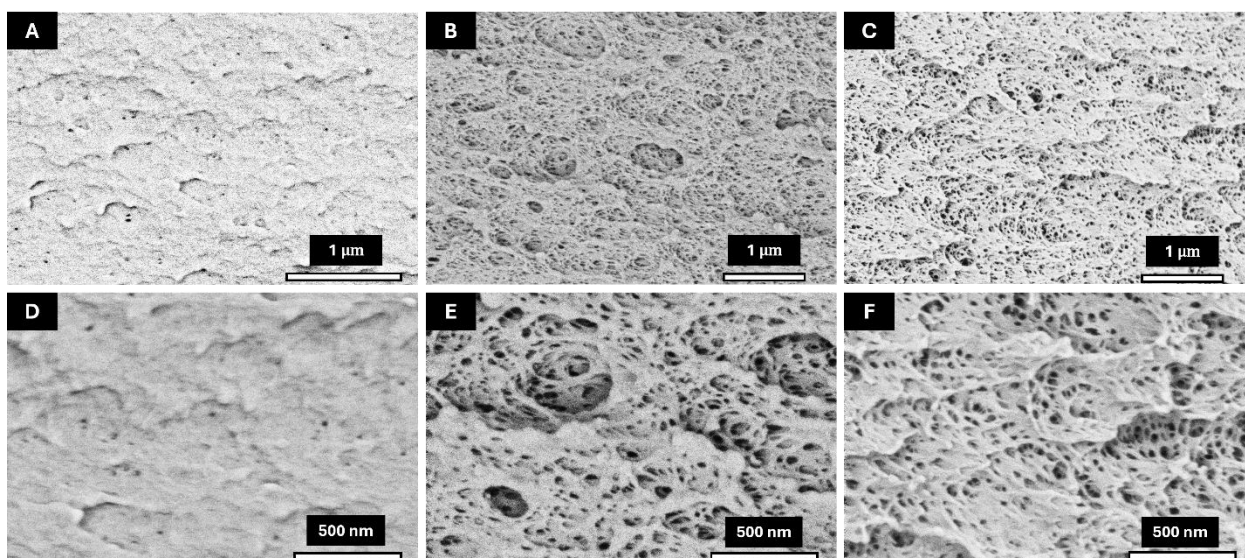


Figure 2.11 (A-C) SEM images of overall cellular structures of PEI foams saturated at 5.5 MPa and foamed at 160°C, 180°C, and 200°C, respectively. (D-F) Corresponding high magnification SEM images illustrating the details of the pores.

2.5.6 Cell Size Distribution in Microcellular and Nanocellular PEI Foams

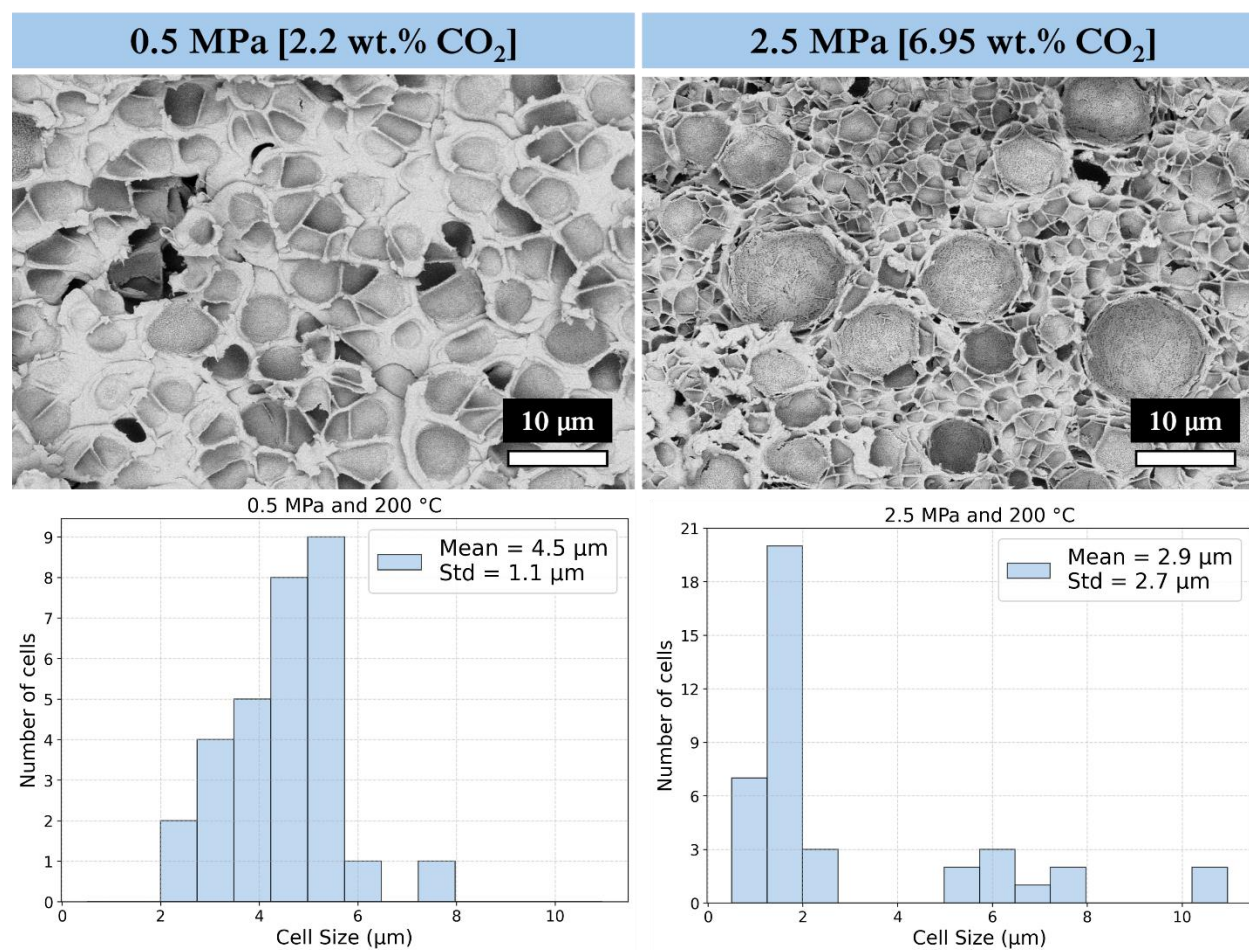


Figure 2.12 SEM images and cell size distribution of microcellular PEI foams saturated at 0.5 and 2.5 MPa and foamed at 200°C.

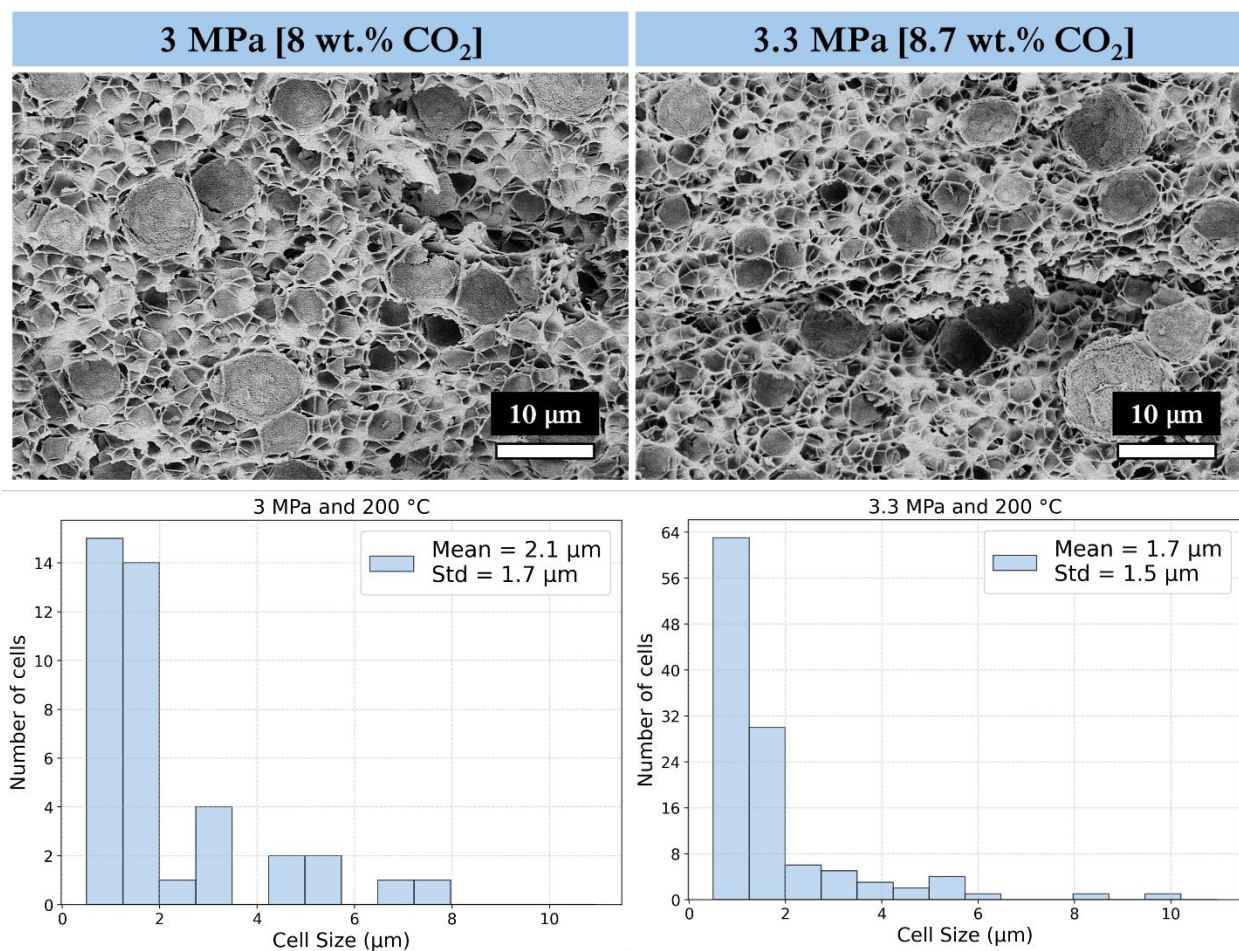


Figure 2.13 SEM images and cell size distribution of microcellular PEI foams saturated at 3 and 3.3 MPa and foamed at 200°C.

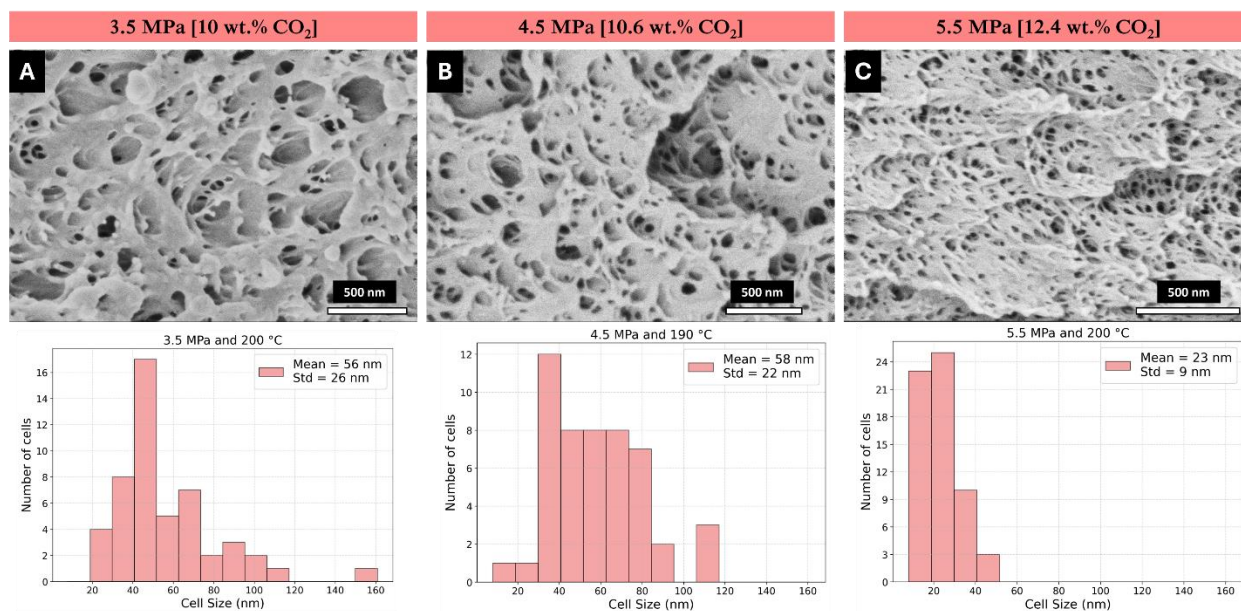


Figure 2.14 SEM images and cell size distributions of nanocellular PEI foams. A) Saturated at 3.5 MPa and foamed at 200°C, B) Saturated at 4.5 MPa and foamed at 190°C. C) Saturated at 5.5 MPa and foamed at 200°C.

2.5.7 Solubility of CO₂ in PEI as a function of saturation pressure

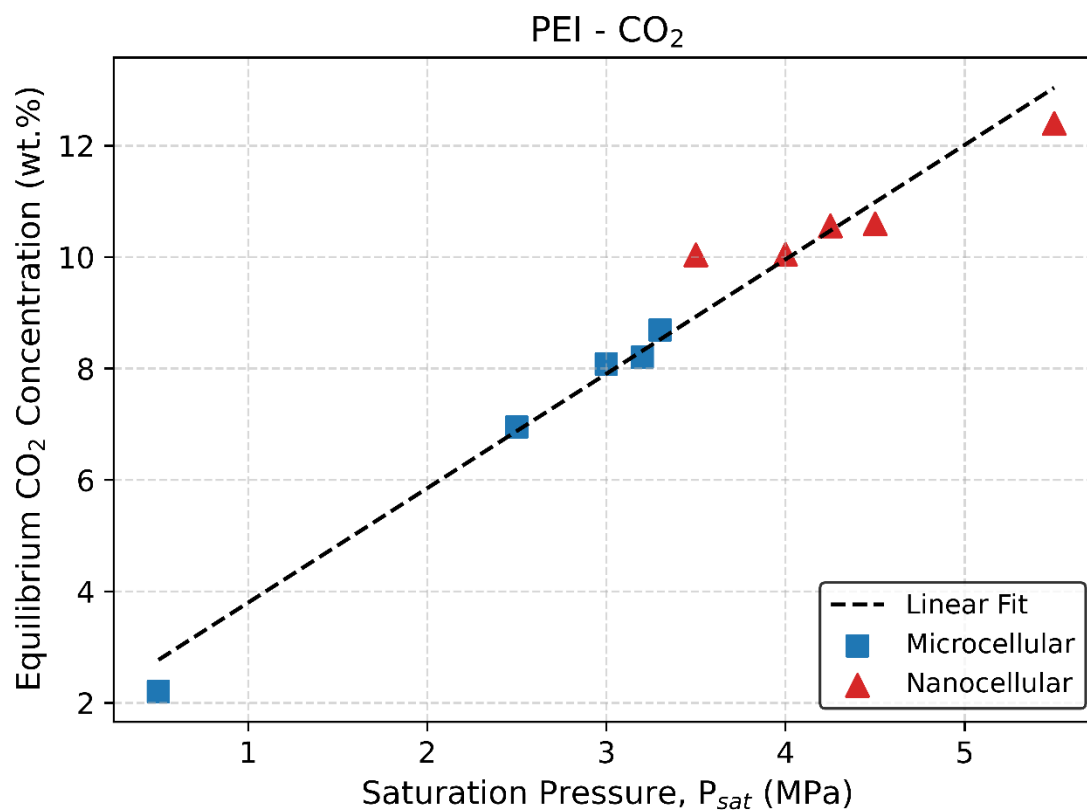


Figure 2.15 Measurements of the CO₂ concentration in PEI at different saturation pressures. The structure becomes nanocellular at 3.5 MPa (10 wt.% CO₂).

2.5.8 Cell Nucleation Density in PEI-CO₂ System

The cell nucleation densities at various saturation pressures were estimated based on the method described in Weller and Kumar (2010)³³.

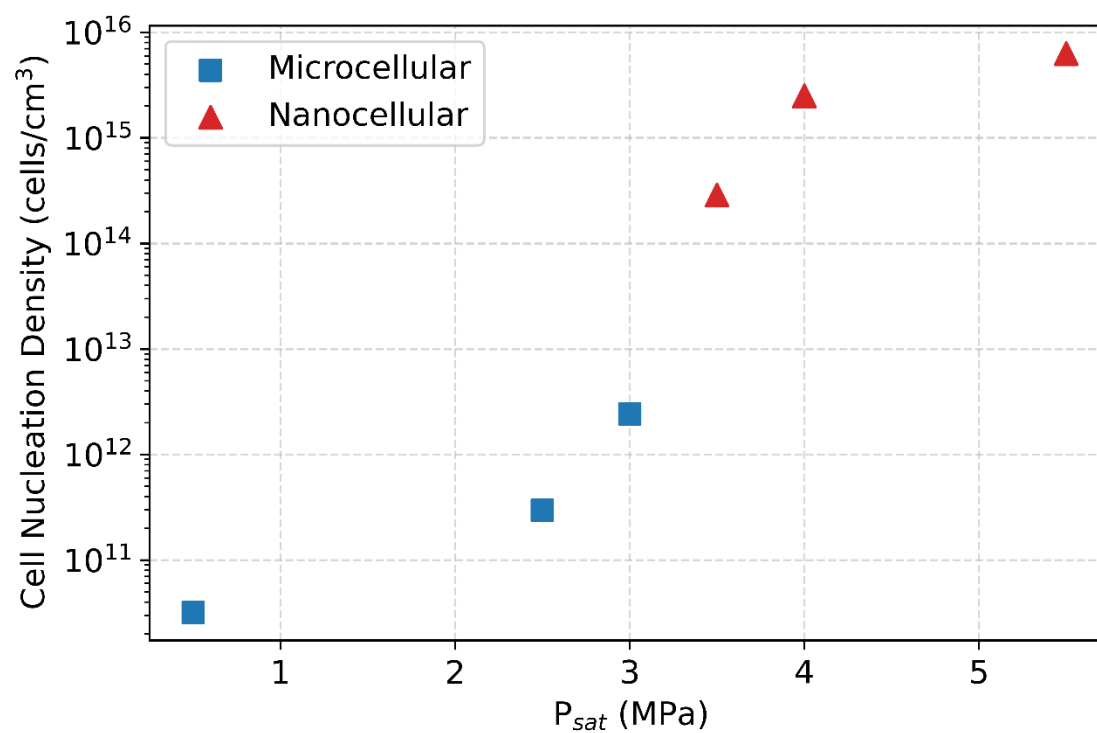


Figure 2.16 Plot reporting estimated cell nucleation density in the PEI-CO₂ system at different saturation pressures at a foaming temperature of 200°C.

2.6 DISCUSSION

2.6.1 *Relative Density Vs. Foaming Temperature in PEI-CO₂ System*

There is a trend in variation of relative density among the microcellular PEI foams across the saturation pressure range of 0.5 –3.3 MPa. The rate of reduction in relative density with foaming temperature increases with saturation pressure (Figure 2.1). For instance, at a foaming temperature of 200 °C, the relative density produced at a saturation pressure of 0.5 MPa is 0.72, compared to 0.47 at 1 MPa and 0.4 at 2.5 MPa. The corresponding average cell size is 4.5 µm at 0.5 MPa, 4 µm at 1 MPa, and 2.9 µm at 2.5 MPa. The average cell size is comparable, but the cell nucleation density increases with increasing saturation pressure, which affects the resulting relative density. From 0.5 MPa to 2.5 MPa, there is an order of magnitude increase in the cell nucleation density for the same foaming temperature reported in Figure 2.16. There is no clear trend across the saturation pressure range for nanocellular foams between 3.5 and 5.5 MPa. The relative density reaches a limit of 0.5 at 5.5 MPa as the foaming temperature increases. Theoretically, relative density ρ_{rel} as a function of cell nucleation density N_0 and cell size φ is described by equation 2.1.

$$\rho_{rel} = \frac{1}{N_0 \frac{\pi}{6} \varphi^3 + 1} \quad (2.1)$$

To reduce the relative density of nanocellular foams, since the cell size φ is in the nanometer scale, it requires a corresponding significant increase in cell nucleation density N_0 such that it can compensate for the effect of φ^3 . The required increase in N_0 is practically unachievable. As shown in Figure 2.16, the N_0 begins to plateau at 10^{16} cells/cm³, highlighting the difficulty in increasing

the cell nucleation density. A cyclic gas dissolution foaming approach was developed to simultaneously reduce cell size and relative density³⁴.

2.6.2 *Microcellular Structure in PEI Foams*

The PEI-CO₂ system produces microcellular foams at a saturation pressure range of 0.5 MPa (2.2 wt.%) to 3.3 MPa (8.69 wt.%). The overall average cell size range across the microcellular is between 1 μm and 5 μm (Figure 2.3, Figure 2.12Figure 2.13). The cell nucleation density in this case increases by two orders of magnitude (from 10^{11} to 10^{13} cells/cm³) between 0.5 MPa and 3.3 MPa (Figure 2.16), the average cell size shows minimal variation across the saturation pressure range. PEI is unique in that it can nucleate a substantially high number of cells with 2.2 wt.% CO₂ was not observed in PC-CO₂¹⁶ or PMMA-CO₂¹⁶ systems.

It has been observed in previous studies of other polymer-gas systems by Weller et al.³⁵ and Guo¹⁶ that after the cell nucleation density reaches a threshold value of 10^{10} cells/cm³ the variation in average cell size across the saturation pressures and foaming temperatures becomes minimal. Since where N_0 is inversely proportional to φ^3 for a 100 times increase in N_0 from 0.5 to 3.3 MPa, the estimated cell size decrease is approximately 5 times, which aligns with the experimental results. The structure in PEI is microcellular between the CO₂ concentration range 2.2 wt.% to 8.7 wt.%.

2.6.3 *Transition Structure in PEI Foams*

There is an order of magnitude increase in the cell nucleation density when the saturation pressure increases from 3 MPa (8 wt.% CO₂) to 3.5 MPa (10 wt.% CO₂) (10^{14} cells/cm³ - refer to Figure 2.16). At 3.5 MPa, the foam structure becomes nanocellular (refer to Figure 2.8Figure 2.17), with an average cell size as low as 42 nm. Previously, Miller et al.¹² obtained a nanocellular foam at a saturation pressure of 5 MPa, with a reported equilibrium CO₂ concentration of 11 wt.%, and a microcellular foam at a saturation pressure of 4 MPa, with a reported equilibrium CO₂ concentration of 9.43 wt.%. The discrepancy can be attributed to CO₂ desorption in the specimens in Miller's study. Additional evidence indicates that the specimens saturated at 5 MPa exhibited a cell size range of 30 to 120 nm, indicating structural changes resulting from CO₂ desorption. Krause et al.¹⁵ reported a threshold CO₂ concentration of 7.8 wt.%, at which the morphology becomes nanoporous, with an average cell size of less than 100 nm. Krause et al.¹⁵ had observed 40 nm cells at a saturation pressure of 4.6-5 MPa. According to this study, the transition in the structure occurs between a CO₂ concentration range of 8.7 wt.% to 10 wt.%. The transition in the structure is rapid, with an increase in CO₂ concentration as shown in Figure 2.17. During the transition, the average cell size reduces by a factor of 10, entering the nanoscale regime. The SEM images from Zainab et al.³² show that the morphology transitions from microcellular to nanocellular at a CO₂ concentration of 10 wt.%, aligning with the findings of this study.

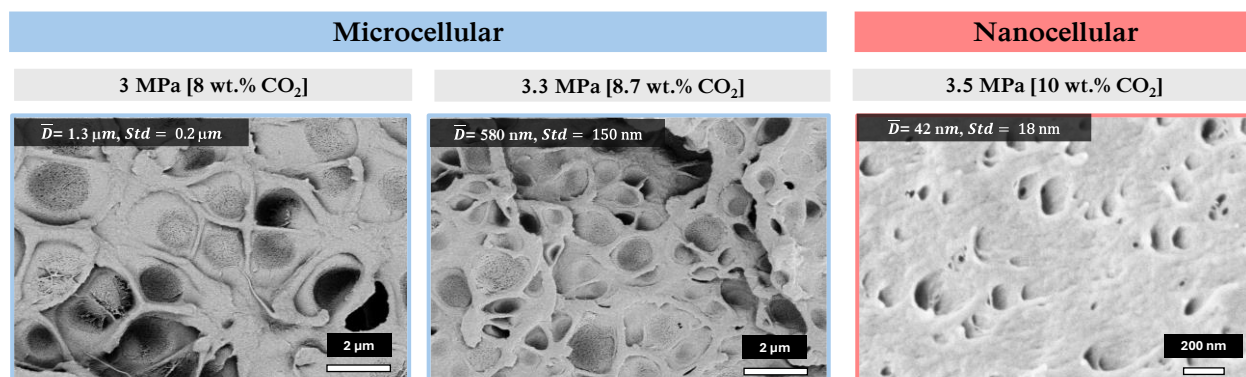


Figure 2.17 SEM images illustrate the transition from microcellular to nanocellular structure in PEI as the CO₂ increased from 8.7 wt.% to 10 wt.%. The SEM images correspond to a foaming temperature of 160°C.

2.6.4 Nanocellular Structure in PEI Foams

In general, the average cell size of nanocellular foams does not show a significant variation in cell size analogous to microcellular foams across a saturation pressure range of 3.5 MPa (10 wt.% CO₂) to 4.5 MPa (10.6 wt.% CO₂). The average and standard deviation of cell size increases at the foaming temperature of 180°C (Table 2.2). The SEM images at 160 °C show that the structure is beginning to form, with nanopores distributed sporadically, as shown in Figure 2.8Figure 2.9,Figure 2.10A. This is attributed to the transition of the structure towards an open structure as the cells grow. The gas permeation measurements performed by Krause et al.¹⁵ show that the open-cell content peaks around 180 °C–190 °C, as they report peak permeability within this range. The SEM images also show the overall qualitative structural change with the increase in the foaming temperature at each saturation pressure.

At 5.5 MPa (12.4 wt.% CO₂), we consistently observe a uniform nanocellular structure with minimal variation in cell size across the entire foaming temperature range (Figure 2.11). The average cell size is approximately 20 nm across the entire foaming temperature range. (Table.2.2). The cell nucleation density at 5.5 MPa is reaching approximately 10^{16} cells/cm³ (Figure 2.16) and it is plateauing.

2.6.5 *Cell Size Limit*

Can we continue to increase the cell nucleation density to reduce the cell size? This remains a key question. The smallest average cell size observed in PEI is 20 nm at 12.4 wt.% CO₂. A recent study by Lizalde-Arroyo et al.³⁶ demonstrated that at 13.8 wt.%, the PEI foams become optically transparent, suggesting a significant increase in cell nucleation density and corresponding reduction in the cell size below 20 nm. Based on the relation between the cell nucleation density and cell size, as shown in Figure 2.18 the cell size approaches the order of radius of gyration of the polymer when the cell nucleation density exceeds 10^{16} cells/cm³. The PEI-CO₂ system suggests that there are fundamental limits to increasing cell nucleation density and reducing cell size.

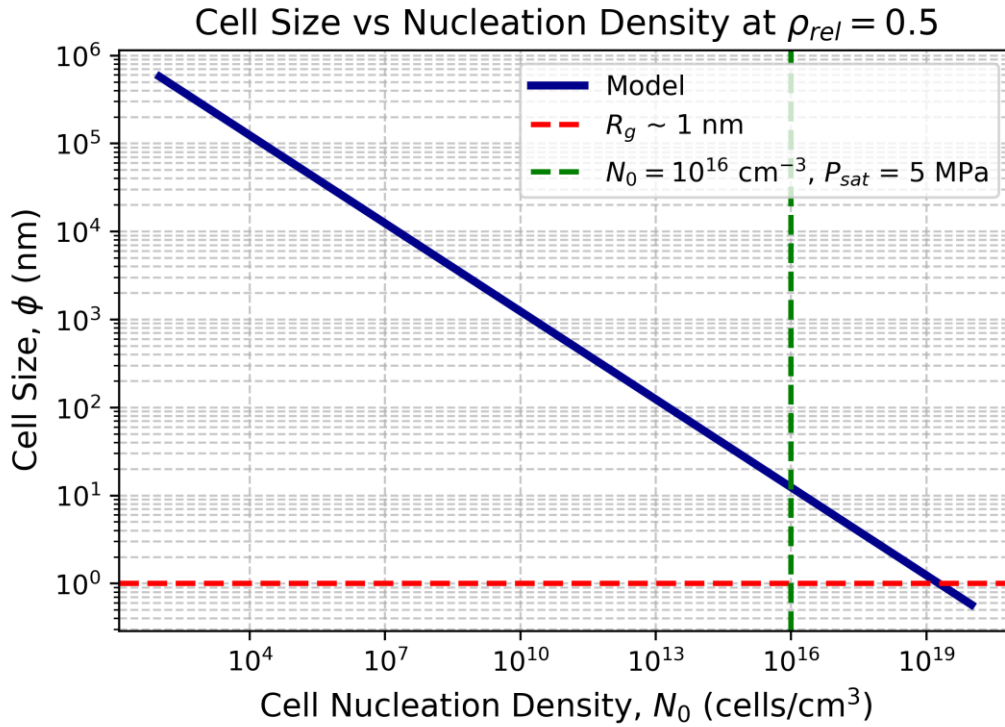


Figure 2.18 Theoretical plot showing reduction in cell size as a function of increasing cell nucleation density at a relative density of 0.5. The vertical green line indicates the approximate value of maximum cell nucleation density observed in nanocellular PEI foam in this work. The red horizontal line indicates 1 nm, which is typically of the order of the radius of gyration of the polymer.

2.6.6 Cell Nucleation Mechanism

The study shows that increasing the CO₂ concentration enhances the cell nucleation density in PEI. To understand the cell nucleation mechanism, it is helpful to consider that there is a random distribution of flaws within the polymer, as illustrated below in Figure 2.19. The flaws are potential nucleation sites, and their activation depends on the saturation pressure. During the saturation process, different sizes of flaws get activated depending on the CO₂ concentration. At higher saturation pressure, the smallest of the flaws can be activated. The critical radius of a cell nucleus

r_c is inversely proportional to the pressure inside the cell P , as expressed in the Laplace equation (2.2),

$$r_c = \frac{2\gamma}{P} \quad (2.2)$$

An increase in P reduces the critical radius. Consequently, high saturation pressures result in large cell nucleation densities by enabling the formation of smaller stable nuclei, ultimately producing a nanocellular structure.

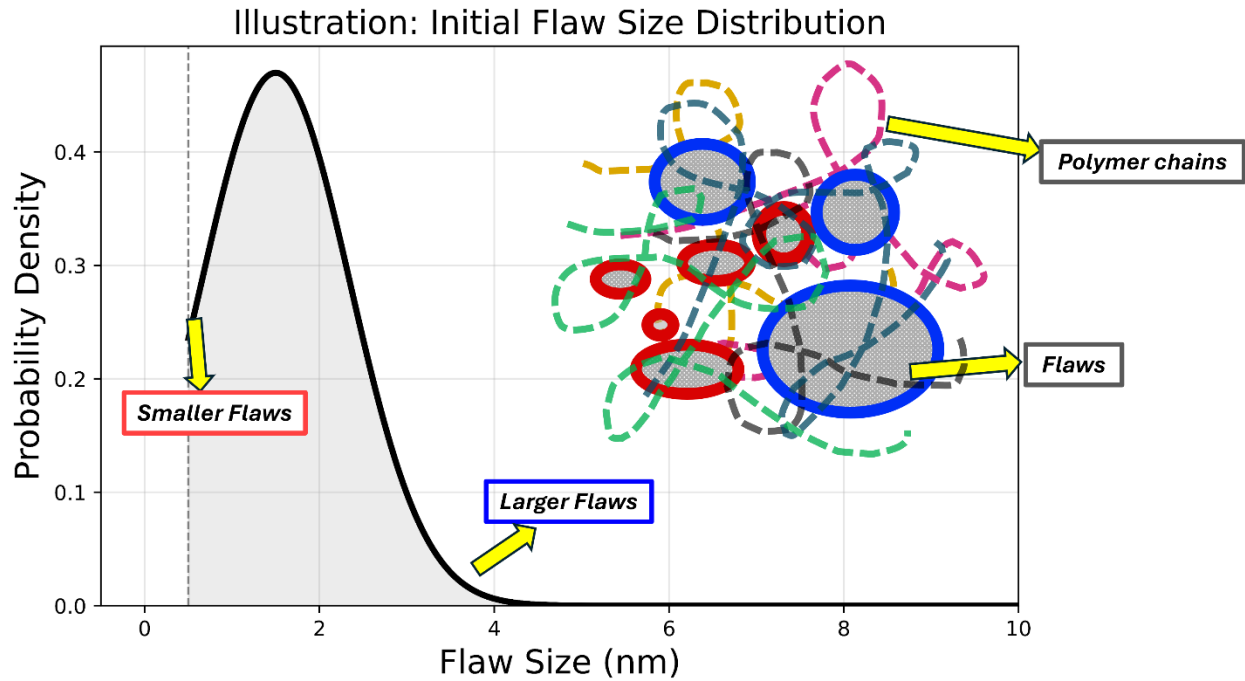


Figure 2.19 Plot illustrating the random distribution of flaws in a typical polymer. The inset illustrates larger and smaller flaws at the polymer chain level.

To verify this hypothesis, experimental data on cell nucleation density as a function of saturation pressure were analyzed. The sigmoidal trend observed in the data is fitted as a logistic function. Equation (2.3) gives the general form of the model.

$$CN(P) = \frac{CN_{max}}{1 + \exp[-k(P - P_0)]} \quad (2.3)$$

CN_{max} is the maximum cell nucleation density

k is the steepness parameter

P_0 is the critical pressure at $CN_{max}/2$

A non-linear regression analysis using the least squares method was performed to determine the best-fit values. The equation is displayed on the plot (refer to Figure 2.20).

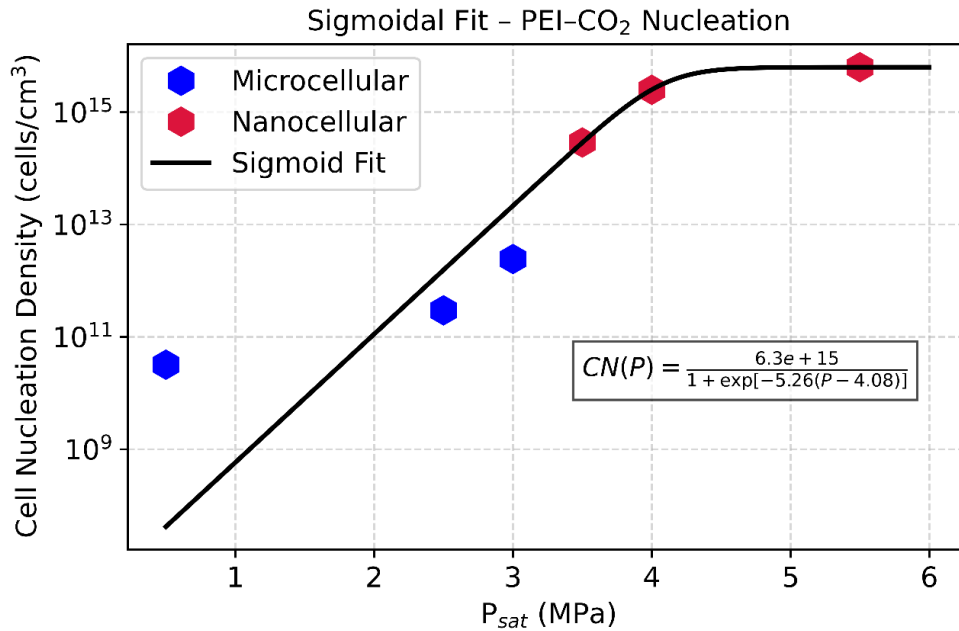


Figure 2.20 Plot showing the estimated cell nucleation density at various saturation pressures, curve fitted with a logistic function. The cell nucleation density values are from the experiment reported in Figure 2.16.

The fitted sigmoidal curve is interpreted as a Cumulative Distribution Function of cell nucleation densities, representing the activated cells. A corresponding Probability Density Function was then generated. Using equation (2.2), the Probability Density Function can be reformulated as a function of the estimated radius of cell nuclei. The surface tension of PEI is taken as 49.3 mN/m^{37} , estimated based on the contact angle method. For more accurate predictions, however, the surface tension of PEI in the presence of CO_2 should be considered. In most cases, the pressure inside the cell nuclei can be assumed equal to the saturation pressure. Nevertheless, heating during the foaming process can initially increase the internal pressure. Holl³⁸ reports about a twofold increase in gas pressure compared to saturation pressure during the foaming process (see Figure VI 26c in Holl's thesis). To account for this effect, three cases were considered for the internal pressure: $P = P_{\text{sat}}$, $2P_{\text{sat}}$, and $3P_{\text{sat}}$, in estimating the distribution curves for the radius of the activated nuclei (refer to Figure 2.21).

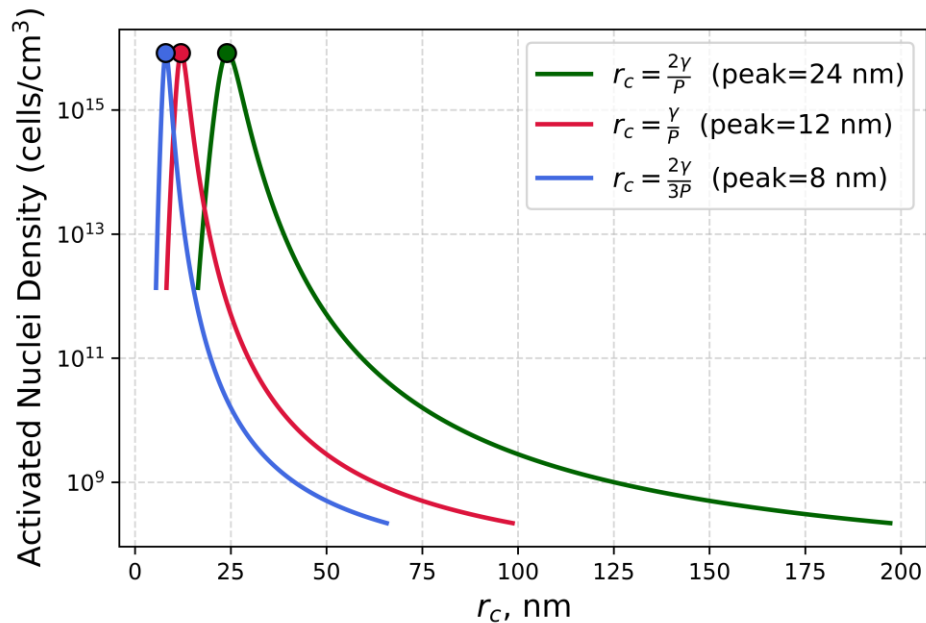


Figure 2.21 Plot showing the predicted distribution curves for the radius of activated nuclei for the PEI- CO_2 system.

The predicted distribution curves for the radius of activated nuclei indicate that increasing saturation pressure decreases the critical radius required for the formation of a stable cell nucleus. At higher saturation pressures, smaller cell nuclei with radii of the order of 1 to 10 nm can be activated. As a result, higher pressures promote high cell nucleation densities and nanocellular structures. Beginning with a random size distribution of flaws in the polymer, an increase in the saturation pressure leads to activation of a larger number of smaller flaws, which can subsequently form stable nuclei and contribute to the overall cell nucleation density. Therefore, the foam structure becomes nanocellular with increasing saturation pressure.

2.7 CONCLUSION

The CO₂ concentration plays a critical role in determining the structure of the PEI foams. Microcellular foams are produced across a saturation pressure range of 0.5 MPa (2.2 wt.% CO₂) to 3.3 MPa (8.7 wt.% CO₂) with average cell sizes ranging from 1 to 5 μm . The PEICO₂ system is unique and exhibits higher cell nucleation density. Even at 2.2 wt.% CO₂, the cell nucleation density is estimated as 10^{10} cells/cm³. The structure rapidly transitions from microcellular to nanocellular as the CO₂ concentration increases from 8.7 wt.% to 10 wt.%, (corresponding to 3.5 MPa). Nanocellular foams are produced across a saturation pressure range of 3.5 MPa (10 wt.% CO₂) to 5.5 MPa (12.4 wt.% CO₂) with average cell sizes ranging from 20 to 130 nm. At the saturation pressure of 5.5 MPa, PEI consistently produces a uniform structure with an average cell size of 20 nm across the foam temperature range, and the cell nucleation density approaches 10^{16} cells/cm³. Overall, the cell nucleation density increases by six orders of magnitude as the CO₂ concentration increases from 2.2 wt.% to 10 wt.%. As the cell nucleation density reaches 10^{16} cells/cm³, it begins to plateau; correspondingly, the cell size and relative density are approaching a limit as the foaming temperature increases. The predicted distribution curves of the radius of

activated nuclei indicate a transition from microcellular to nanocellular structures as increasing saturation pressure enables the formation of smaller, stable nuclei. Therefore, increasing saturation pressure progressively activates smaller flaws in the polymer, which become stable nuclei, contributing to the cell nucleation density, consequently leading to the formation of a nanocellular structure.

Chapter 3. EXPERIMENTAL CHARACTERIZATION OF SECONDARY NANOPOROUS STRUCTURES IN MICROCELLULAR PEI FOAMS

3.1 ABSTRACT

Microcellular PEI foams produced through the solid-state foaming process exhibit a unique cellular structure, wherein secondary nanopores, ranging in size from 10 to 80 nm, develop on the cell walls of the primary microcells. This study experimentally characterizes the evolution of the secondary nanoporous structure as a function of primary cell expansion. The study comprises two parts. In Part I, the foaming temperature was controlled independently at different saturation pressures of 0.5 MPa, 2.5 MPa, and 3.3 MPa. In Part II, the foaming time was controlled independently at different foaming temperatures under a saturation pressure of 1 MPa. The experimental results demonstrate that the growth of the secondary nanopores is directly influenced by the growth of the primary cell. A modified classical nucleation theory framework based on strain energy due to primary cell expansion is presented to explain that the underlying nucleation mechanism of secondary nanopores is a coupled effect of polymer crazing and foaming.

3.2 INTRODUCTION

The solid-state foaming process was developed at MIT in the 1980s¹⁻³. The rationale was to reduce plastic usage by introducing bubbles of approximately 10 μm in size across the thin-walled plastic parts. The process involves saturating the thermoplastic polymer sheets with a gas under high pressure in a pressure vessel, typically CO_2 or N_2 , depending on the gas's solubility in the polymer.

At the end of saturation, the polymer-gas system reaches equilibrium. The vessel is depressurized at this point, and the sheets are removed. These super-saturated sheets are finally quenched in a hot bath at a specific temperature for foaming. The thermodynamic instability during the foaming process leads to the uniform nucleation and growth of bubbles across the polymer matrix. The process was initially developed using the PS-N₂ system¹⁻³, where the bubble size was approximately 10 μm , hence the name "Microcellular foams." Since then, the process has been successfully implemented in various polymer-gas systems, including PC-CO₂⁴, PET-CO₂³⁹, PMMA-CO₂^{8-10,40}, PEI-CO₂^{11-13,15,32}, PLA-CO₂⁶, and PVC-CO₂⁴¹, among others.

Microcellular foams of some thermoplastic polymers produced through solid-state foaming exhibit a unique structure, where the walls of the primary bubbles consist of secondary nanopores with diameters less than 100 nm. These secondary nanopores have been reported in various polymer-gas systems, including PEI-CO₂¹², PC-CO₂¹⁸, COC-CO₂¹⁹, PSU-CO₂¹⁶, and PPSU-CO₂¹⁶. The exact mechanism behind the formation of these cells has yet to be thoroughly established. Fukasawa et al.¹⁸ first reported this novel structure in the PC-CO₂ system. Gong et al.²⁰ further investigated the PC-CO₂ system and proposed a mechanism for the secondary cells by combining craze and bubble nucleation theories. The study proposed that nanopores are voids resulting from crazing, which occur due to the stretching of cell walls during the foaming process, suggesting a strain-induced phenomenon. They have observed that the nanoporous structure grows on the cell wall, coalesces, and transforms into fibrils under high tension. This finding is significant because controlling the nanoporous structure on the cell wall provides a way to create interconnected open-celled microcellular foams, which are generally closed-celled.

The study by Gong et al.²⁰ integrates craze and bubble nucleation theories to develop a mechanism for the occurrence of secondary nanopores in the PC-CO₂ system. A detailed description of the theory can be found in their work. At the core of the theory, the study claims that the development of strain energy due to the high tension on the wall during bubble expansion results in crazing⁴², rather than yielding, which creates secondary nanopores. To support the theory, they conducted a uniaxial tensile test at elevated temperatures above the T_g of the unprocessed PC. They used various strain rates and final strains to simulate cell wall stretching caused by bubble expansion during foaming. At temperatures exceeding the T_g , the polymer chains tend to relax, preventing craze. However, the high strain rate favors crazing. The competing effects of strain rate and temperature determine whether crazing can occur. The SEM analysis of the fracture surface reveals that a high strain rate (60 mm/min) and moderate strain (80 mm) or moderate strain rate (40 mm/min) and high strain (100 mm) at a moderate temperature (167 °C) result in crazing-induced nanopores. However, at a lower temperature (162 °C), a moderate strain rate (40 mm/min) and moderate strain (80 mm) also lead to crazing-induced nanopores. The fracture surface was clean without nanopores at the highest temperature, 170 °C, and at the lowest strain rate, 5 mm/min. This indicates that crazing occurs when the strain energy effect due to polymer stretching dominates over chain relaxation at elevated temperatures, resulting in the formation of nanopores on the cell walls during the foaming process.

The study also characterizes the time evolution of nanopores as the bubble expands in the PC-CO₂ + acetone system. The results show a gradual development of secondary nanopores on the cell wall with foaming time. They explore the effect of plasticization on the formation of nanopores. Increasing the concentration of the plasticizer, in this case, acetone, which acts as a crazing agent, lowers the surface energy required to form new voids, thereby enhancing the

nucleation of nanopores and increasing the measured pore density. They conclude that the secondary nanopores nucleate if the strain energy released due to bubble expansion exceeds the surface energy required to create the new pores.

They report no significant variation in the average nanopore diameter at different acetone concentrations and foaming temperatures. Increasing the foaming temperature beyond the T_g of the unprocessed PC drastically reduces nanopore density, with peak nanopore density observed at an optimal foaming temperature below the T_g of the unprocessed PC. The study reveals that annealing the foams at 170 °C for 2 minutes results in the disappearance of nanopores due to chain rearrangement, suggesting that nanopores form as a result of crazing. The study shows that as the foaming temperature increases towards the T_g of the unprocessed polymer, the cell wall expands more, resulting in a reduction in cell wall thickness. As a result, cell wall thinning results in complete rupture, and secondary nanopores interconnect the primary bubbles. The measured open-cell content peaks at 100% when the foaming temperature reaches 150 °C, which is close to the T_g of the unprocessed PC.

Miller et al.¹² reported secondary nanopores in microcellular PEI foams, as shown in Figure 3.1. The SEM images in Figure 3.1 provide a detailed description of the secondary nanoporous morphology typically observed in microcellular PEI foams. Zainab et al.³² demonstrated that by varying the CO₂ concentration in PEI, the cellular structure can be tuned from microcellular with a secondary nanoporous structure to nanocellular. Therefore, there is a threshold CO₂ concentration above which the occurrence of secondary nanopores on the cell walls diminishes, which needs to be investigated.

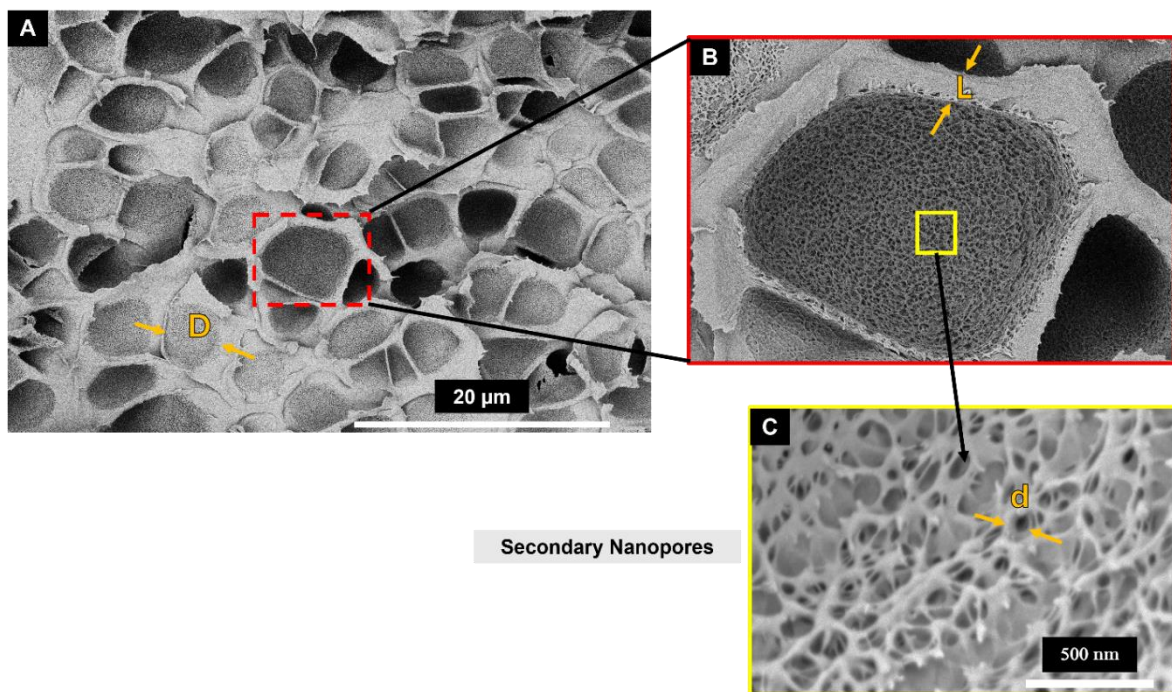


Figure 3.1 A representative set of SEM images of a microcellular PEI foam showing the details of the secondary nanoporous structure. A) Each primary cell consists of a secondary nanoporous network covering its cell walls. B) A single primary cell is highlighted to show the uniformity of the nanoporous network covering the entire cell wall. C) A close-up SEM image of the nanoporous network on the cell wall. “D” – primary cell size, “L” – primary cell wall thickness, and “d” – the size of the nanopores are the key characteristics analyzed.

In this study, we focus on further investigating and experimentally characterizing the secondary nanoporous structures that develop in the PEI–CO₂ system. The study has been divided into two parts. In the first part, we investigate the effect of saturation pressure on the secondary nanopores at different foaming temperatures. In the second part, we characterize the effect of foaming time on the growth of secondary nanopores at different foaming temperatures. In the end, we present a modified classical nucleation theory framework based on strain energy due to primary cell expansion to explain that the underlying nucleation mechanism of secondary nanopores is a coupled effect of polymer crazing and foaming.

3.1 PART I: EFFECT OF SATURATION PRESSURE: FOAMING TEMPERATURE CONTROLLED GROWTH

3.1.1 *Objective*

The saturation pressure is systematically varied to study its effect on the secondary nanoporous network. The process space indicates that when the saturation pressure is increased from 0.5 MPa to 3.3 MPa, the average size of the primary cells in microcellular PEI foams remains relatively constant, exhibiting minimal variation. The saturation pressure affects the CO₂ concentration in the polymer matrix. Therefore, it influences the pressure in the primary cell nuclei and the amount of CO₂ in the cell wall, which affects the surface tension. The foaming temperature is used as the variable that controls primary cell expansion, and foaming time is held constant.

3.1.2 *Experimental*

In a pressure vessel, 0.5 mm-thick, 1" x 1" PEI specimens (Ultem 1000) were saturated with CO₂ at 0.5 MPa, 2.5 MPa, and 3.3 MPa, respectively. Once equilibrium was achieved in the PEI-CO₂ system, the vessel was depressurized, and the specimens were removed and immediately stored in liquid nitrogen (LN₂) to minimize CO₂ loss. The specimens corresponding to 0.5 MPa were foamed in hot oil at 180°C, 190°C, and 200°C for 30s. The specimens corresponding to 2.5 MPa were foamed in hot oil at 160°C, 180°C, and 200°C for 30s. The specimens corresponding to 3.3 MPa were foamed in hot oil at 160°C, 180°C, and 200°C for 30s. The foamed specimens were freeze-fractured in liquid nitrogen (LN₂) to expose the cross-section. The cross-section is coated with a 4-5 nm platinum (Pt) layer and analyzed under a scanning electron microscope (SEM).

3.1.3 Results

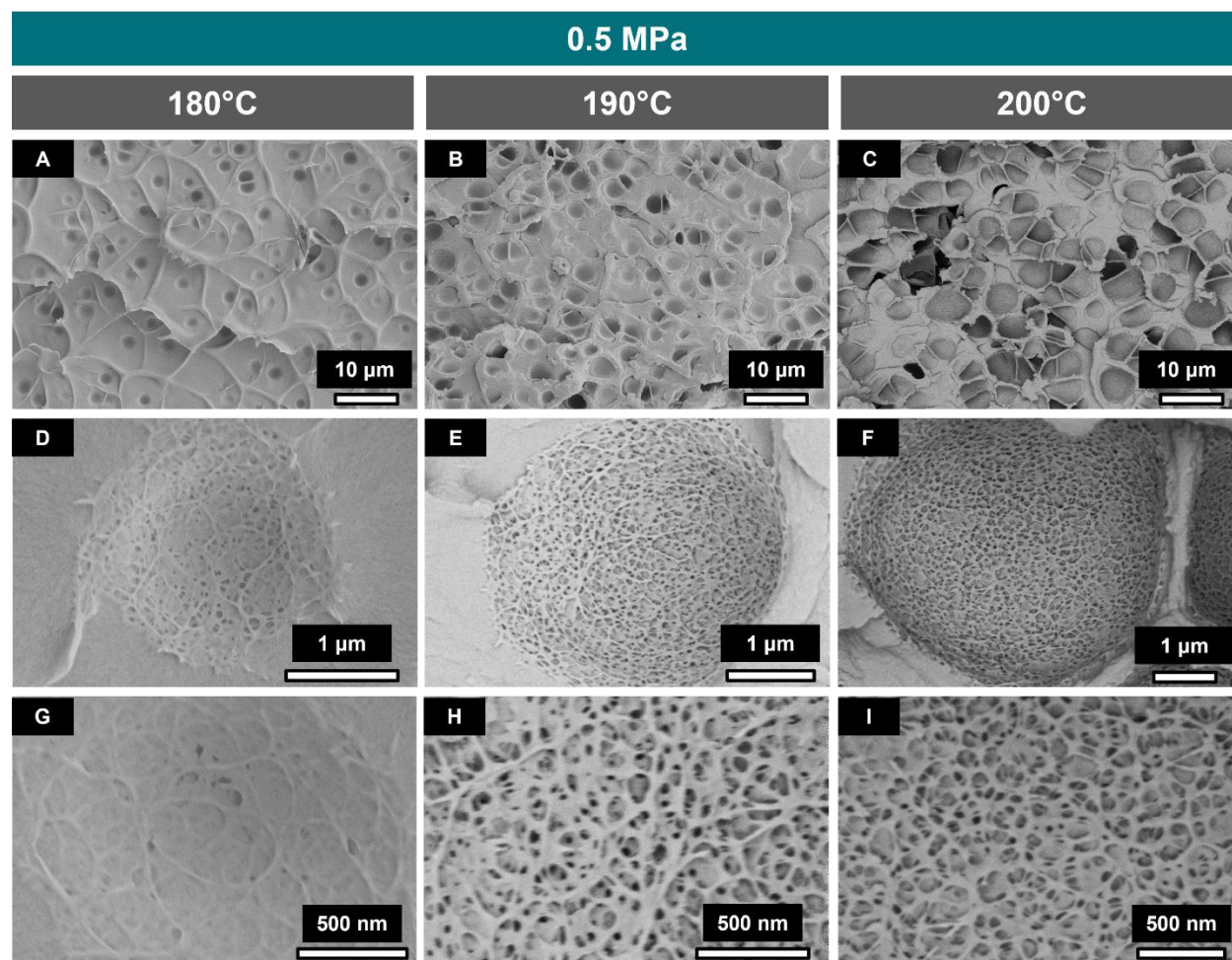


Figure 3.2 (A-C) SEM images of overall cellular structures of PEI foams saturated at 0.5 MPa and foamed at 180°C, 190°C, and 200°C (each column), respectively. (D-F) Representative SEM images of a single primary cell from the microstructure showing the development of a secondary nanoporous network on the cell wall. (G-I) Representative zoomed-in SEM images of the nanoporous network on the cell wall

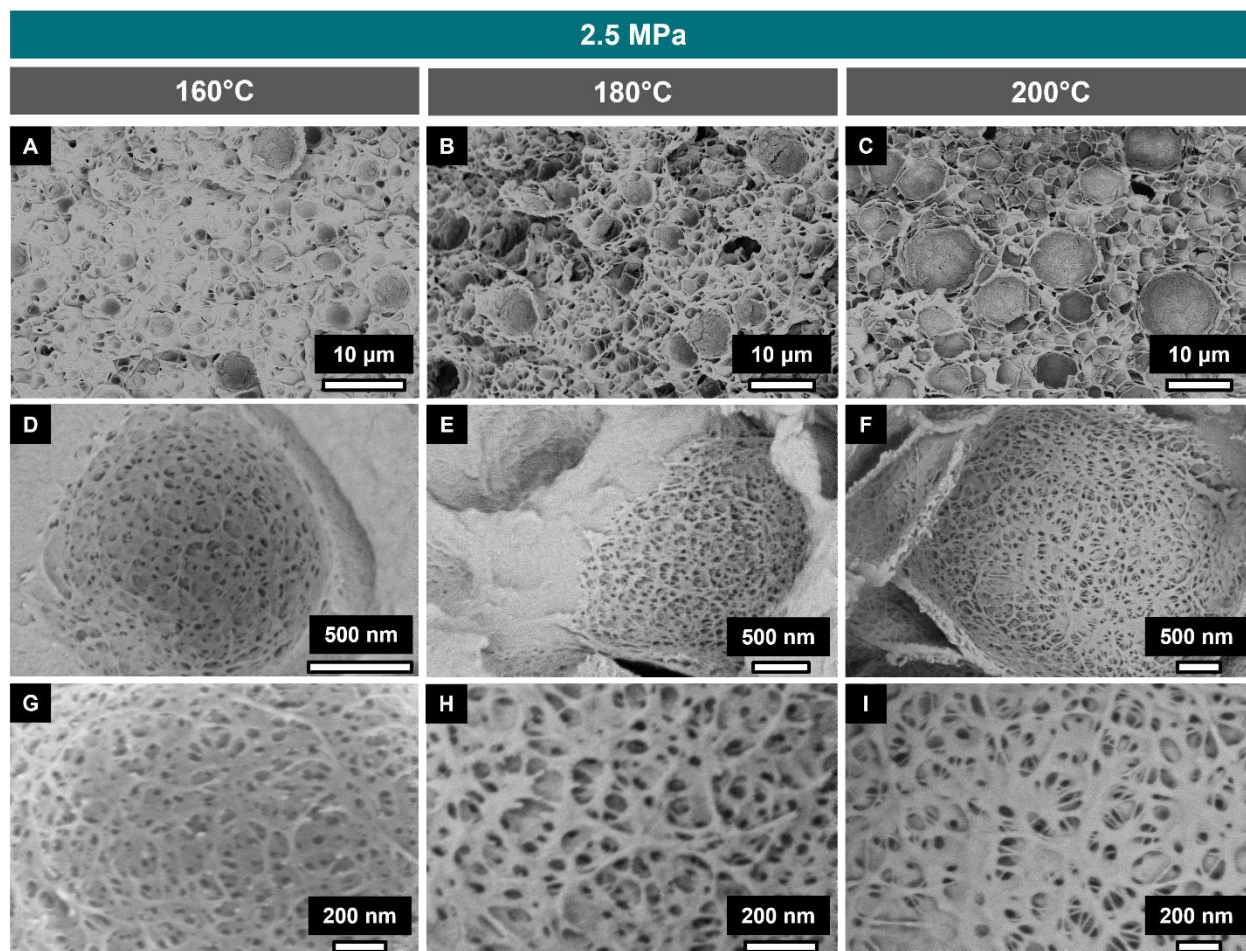


Figure 3.3 (A-C) SEM images of overall cellular structures of PEI foams saturated at 2.5 MPa and foamed at 160°C, 180°C, and 200°C (each column), respectively. (D-F) Representative SEM images of a single primary cell from the microstructure showing the development of a secondary nanoporous network on the cell wall. (G-I) Representative zoomed-in SEM images of the nanoporous network on the cell wall.

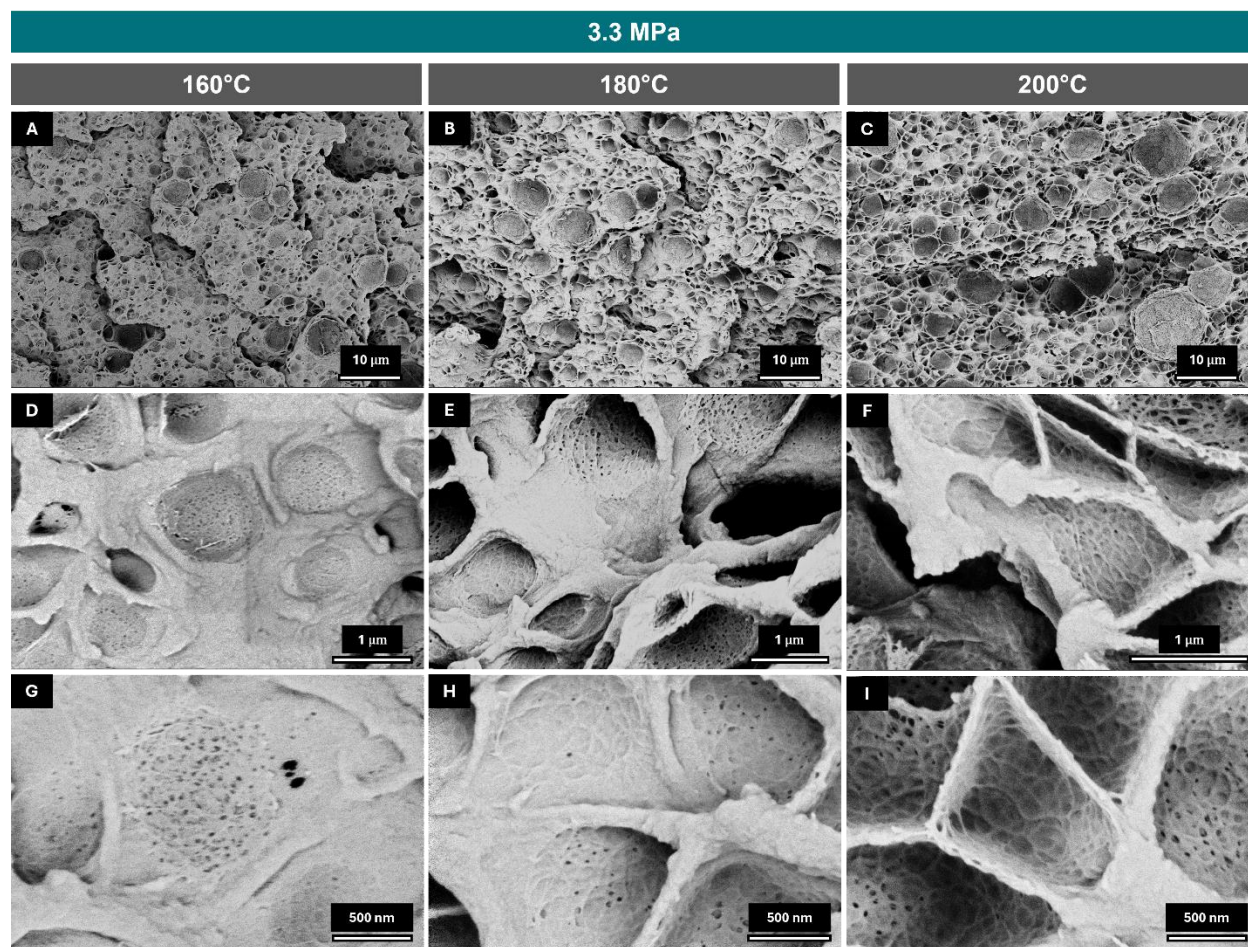


Figure 3.4 (A-C) SEM images of overall cellular structures of PEI foams saturated at 3.3 MPa and foamed at 160°C, 180°C, and 200°C (each column), respectively. (D-F) Representative SEM images of a single primary cell from the microstructure showing the development of a secondary nanoporous network on the cell wall. (G-I) Representative zoomed-in SEM images of the nanoporous network on the cell wall.

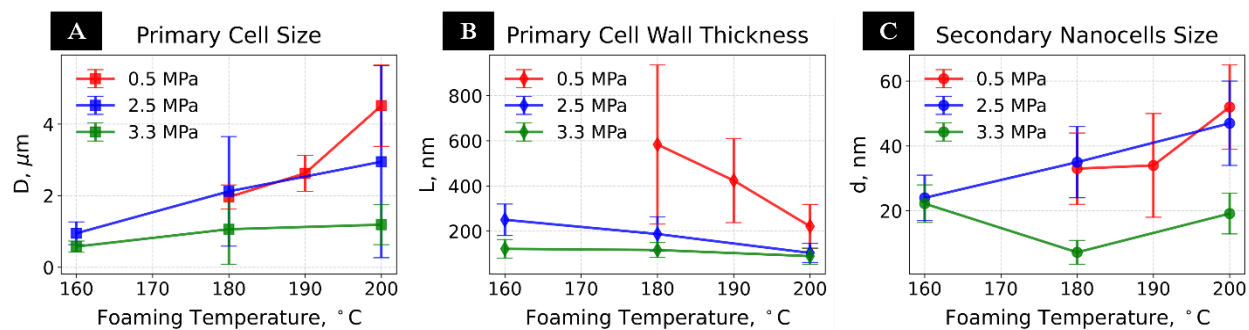


Figure 3.5 A) Plot showing primary cell size growth as foaming temperature increases at saturation pressures of 0.5 MPa, 2.5 MPa, and 3.3 MPa. B) The corresponding reduction in the primary cell wall thickness as the primary cell grows. C) The size of the secondary nanopores as the primary cell wall expands. (Data represents Avg. $\pm$ SD)

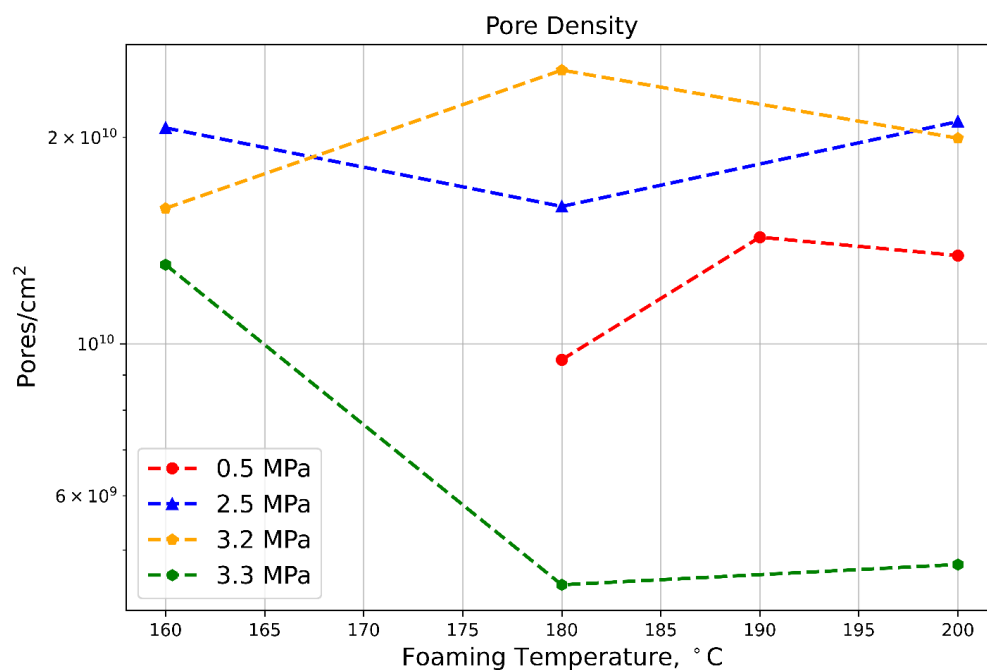


Figure 3.6 Secondary nanopore density per cm^2 in PEI- CO_2 system at saturation pressures 0.5 MPa, 2.5 MPa, 3.2 MPa, and 3.3 MPa at different foaming temperatures estimated based on the method proposed by Gong et al.²⁰.

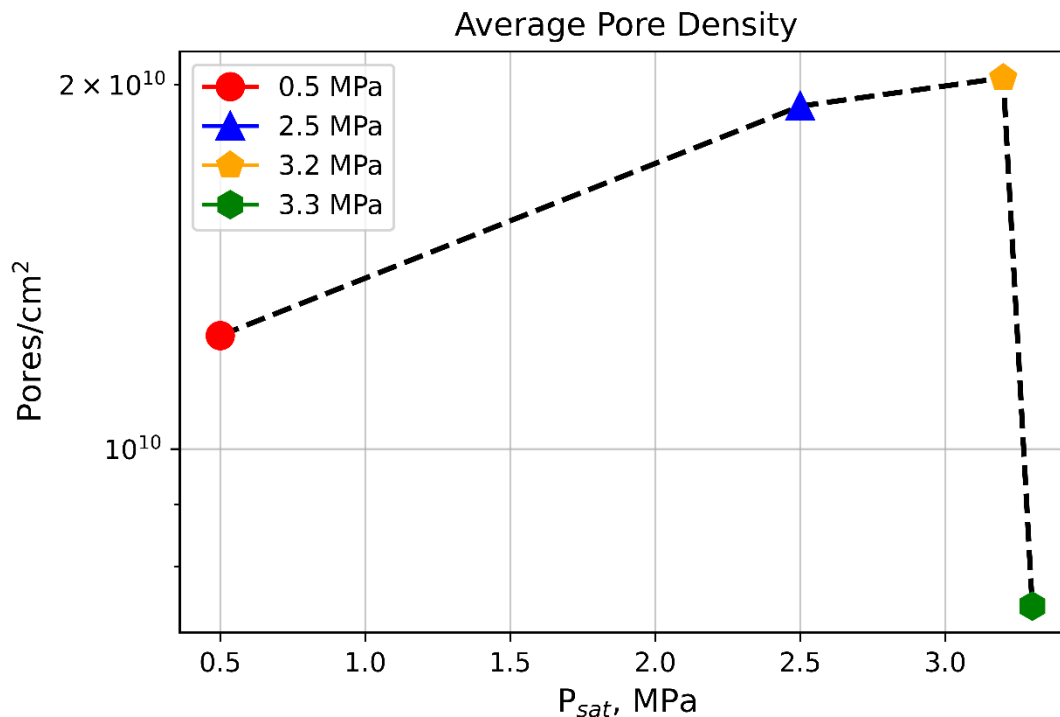


Figure 3.7 Average secondary nanopore density per cm^2 in PEI- CO_2 system at saturation pressures 0.5 MPa, 2.5 MPa, 3.2 MPa, and 3.3 MPa.

3.1.4 Discussion

Secondary Nanopores at 0.5 MPa

At a saturation pressure of 0.5 MPa (2.2 wt.% CO_2) and a foaming temperature of 180°C , the secondary nanoporous network initially forms as uniformly distributed circular regions across the cross-section on the sites of primary bubble nucleation. The zoomed-in SEM image in Figure 3.2G reveals fibrillation and scission, indicating polymer crazing as the primary cell wall is drawn under high tension during expansion. SEM in Figure 3.2A shows that the bubble nucleation partitions cross-section at the primary cell level, resembling a random Voronoi tessellation. As the primary cell walls expand with increasing foaming temperature, the secondary nanoporous network grows

along the wall, eventually occupying the entire cell wall by the end of the growth process. This is evident in the SEM images in Figure 3.2D-F.

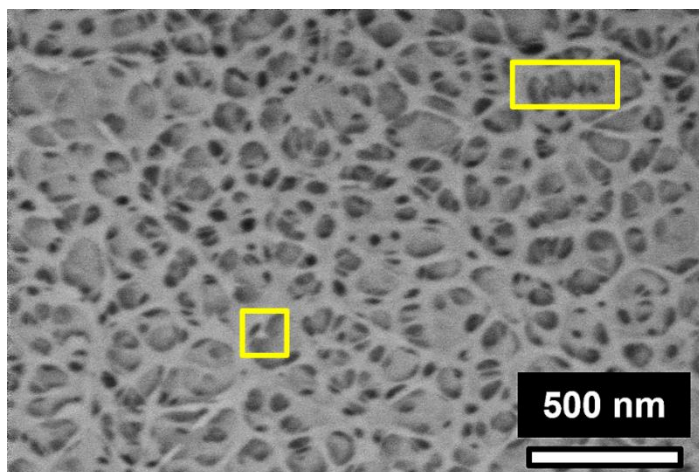


Figure 3.8 The SEM image of microcellular PEI foam, saturated at 0.5 MPa and foamed at 200°C, shows a zoomed-in view of the secondary nanoporous network, where selected regions of scission leading to pore coalescence are highlighted.

Secondary Nanopores at 2.5 MPa

At a saturation pressure of 2.5 MPa (6.95 wt.% CO₂) and a foaming temperature of 160 °C, the cell walls consist of secondary nanopores. Interestingly, the cellular structures at 2.5 MPa exhibit sporadic, highly stretched giant primary cells (average size ~ 10 μm) with secondary nanoporous networks, as shown in Figure 3.3A-C and Figure 3.9. The number of these giant cells increases with foaming temperature. The high stretching leads to the formation of secondary nanopores covering the strut, as shown in Figure 3.3F, which potentially interconnect the cells. At 2.5 MPa, the cell nucleation density increases, resulting in neighboring cells hindering each other's

expansion and limiting the development of the secondary nanoporous network. As shown in Figure 3.9B, the limited expansion of the primary cell caused by the competing growth of neighboring cells leads to incomplete development of the secondary nanopores. This effect is more pronounced in the case of 3.3 MPa as discussed in the next section.

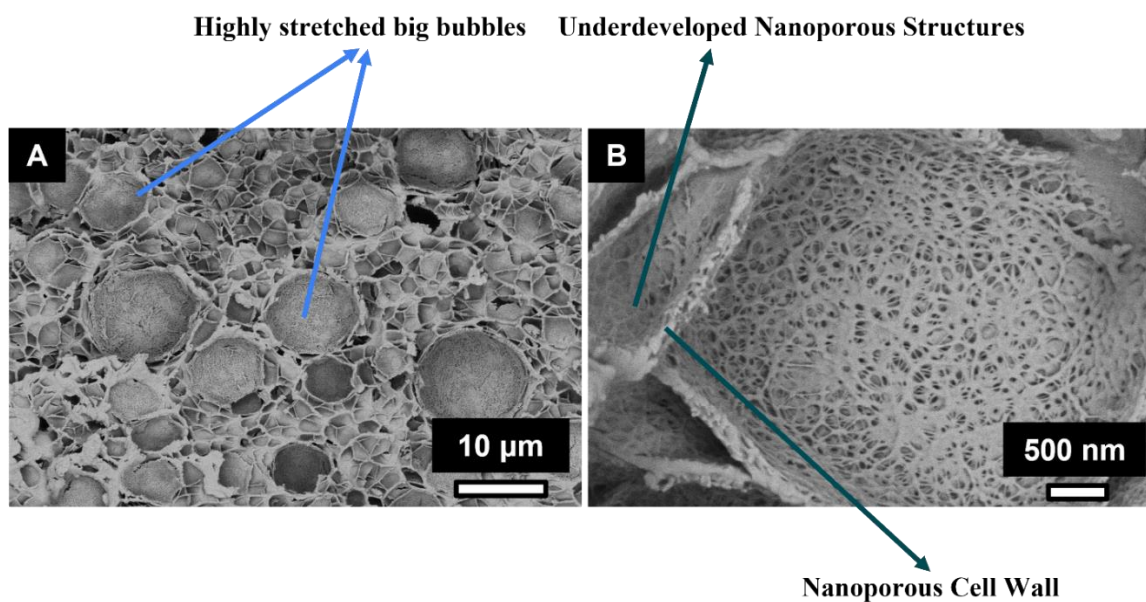


Figure 3.9 SEM images of microcellular PEI foam saturated at 2.5 MPa and foamed at 200°C. A) A micrograph showing the occurrence of highly stretched cells. B) A micrograph showing the underdeveloped nanoporous structure on the cell wall due to diminished growth of the primary cell, hindered by the neighboring cells. The micrograph also shows that the cell wall becomes nanoporous.

Secondary Nanopores at 3.3 MPa

Secondary nanoporous structures are present but underdeveloped at a saturation pressure of 3.3 MPa (8.69 wt.% CO₂). SEM image of a primary cell in Figure 3.10, where the cell wall exhibits a Voronoi-like tessellation pattern⁴³. This pattern signifies the initial stage of secondary nanopore formation. Notably, the nanopore nuclei appear to self-organize in a manner analogous to the Voronoi-like arrangement observed during the nucleation of primary cells, highlighting a similarity in structural development. This suggests that the underlying nucleation mechanism of secondary nanopores and primary microcells is the same. In this case, the density of secondary nanopores is low due to the high nucleation density observed at 3.3 MPa, which results in smaller primary cell sizes compared to those at 0.5 MPa and 2.5 MPa. For secondary nanopores to develop, sufficient stretching of the cell wall is required. Our observations suggest that when the final primary cell size is below approximately 1 μm , the nucleation and growth of secondary nanopores are significantly suppressed. A similar microstructural trend was reported by Zainab et al.³², who observed sparse secondary nanopores on the cell walls of a 120 μm PEI film with an average CO₂ concentration of 8.32 wt.%. In their study, the corresponding primary cell size was approximately 333 nm.

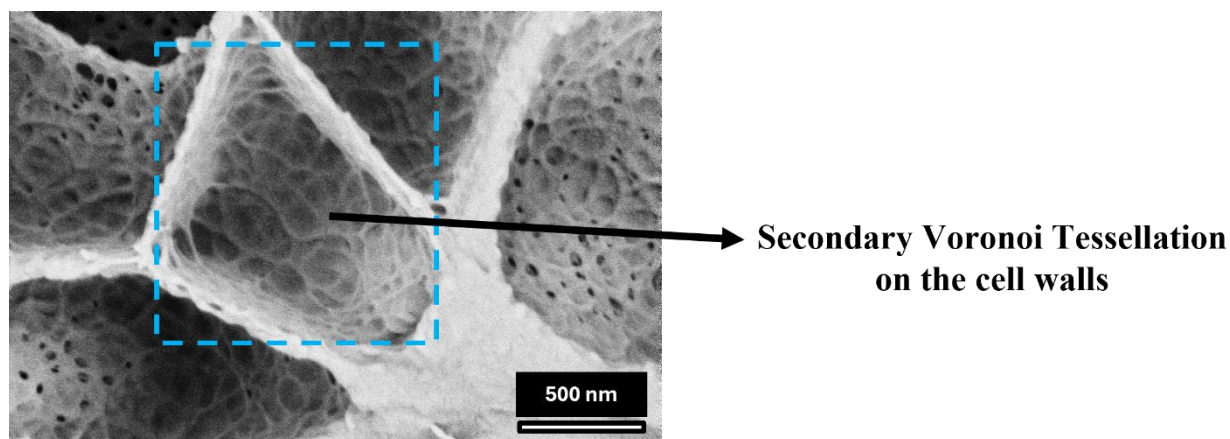


Figure 3.10 SEM image of microcellular PEI foam saturated at 3.3 MPa and foamed at 200°C, showing a zoomed-in image of a primary cell highlighting the Voronoi-like tessellation formation of nucleated secondary nanopores on the cell wall.

Effect of Saturation Pressure on Secondary Nanopore Density

In the PEI-CO₂ system, as shown in Figure 3.6 and Figure 3.7, the nanopore density on the cell wall increases marginally as saturation pressure increases from 0.5 MPa to 2.5 MPa. The increase is attributed to the increased plasticization effect. However, there was a sudden reduction at 3.3 MPa. The average primary cell size is lower at 3.3 MPa due to enhanced primary cell nucleation density, as shown in Figure 3.4 and 3.5A. By increasing the saturation pressure, the primary cell nucleation density increases, resulting in smaller primary cells and thinner cell walls (Figure 3.5A and B). The impedance to growth from the neighboring cells also influences the local strain on the cell walls. Simultaneously, higher saturation pressures increase the CO₂ concentration in the polymer, which acts as a plasticizer. Gong et al.²⁰ demonstrated that plasticizers (e.g., acetone) lower the surface tension, thereby reducing the energy barrier for forming new surfaces and

promoting the nucleation of secondary nanopores. However, in their study, they maintained a constant CO₂ concentration (~10–11 wt.%), resulting in no significant effect on primary cell nucleation density; all their foam specimens had a primary cell nucleation density of approximately 10¹⁰ cells/cm³. The acetone promoted crazing as a crazing agent. In contrast, the system in this study has a broad CO₂ range (2.2–8.69 wt.%). Although there is a drastic increase in plasticization within this range, the increase in nanopore density is marginal. In our study, the primary cell nucleation density ranges from 10¹⁰ cells/cm³ to 10¹² cells/cm³. The increase in primary cell nucleation density and plasticization has a competing effect on secondary nanopore development.

At the cell wall level, there is competition between the release of strain energy and surface tension in creating secondary nanopores. For example, as discussed earlier, despite a reduced surface tension at 3.3 MPa, the lower strain energy release due to insufficient expansion of primary cells resulted in a reduced secondary nanopore density compared to that at 0.5 MPa.

Effect of Saturation Pressure on the Secondary Nanopore Size

The increase in saturation pressure from 0.5 MPa to 3.3 MPa has a minimal impact on the average pore size of the secondary nanoporous network, as shown in Figure 3.5C. The size of the secondary nanopores increases Marginally with the foaming temperature, establishing a correlation between the growth of primary cells and the final size. Increasing the foaming temperature stretches the cell wall further as the cell expands, causing polymer fiber scission, which leads to pore coalescence and thus increases the average cell size and variation, as shown in Figure 3.5. This indicates that more stretching occurs as the foaming temperature increases, leading to scission, suggesting the occurrence of crazing on the cell wall. The average nanopore size at 3.3 MPa is lower than at saturation pressures of 0.5 MPa and 2.5 MPa, as shown in Figure 3.5. This, as discussed earlier, is due to the lower primary cell size and less stretching of the cell wall, resulting in smaller nanopores. Overall, across a pressure range of 0.5 – 3.3 MPa, the nanopore size averages 10 nm to 60 nm.

3.1 PART II: EFFECT OF FOAMING TIME

3.1.1 Objective

In this study, we experimentally characterize the growth of secondary nanoporous structures on the cell walls as a function of foaming time at various foaming temperatures at a constant saturation pressure, using SEM analysis. The objective is to understand when the secondary nanopores start to form and how they grow during the foaming process.

3.1.2 *Experimental*

0.5 mm-thick 1" x 1" PEI (Ultem 1000) specimens were saturated with CO₂ at a pressure of 1 MPa in a pressure vessel. Once equilibrium was achieved in the PEI-CO₂ system, the vessel was depressurized, and the specimens were removed and immediately stored in liquid nitrogen (LN₂) to minimize CO₂ loss. The specimens were foamed in hot oil at 175°C, 185°C, and 195°C at specific foaming times, as reported in the table below. The foamed specimens were quenched in liquid nitrogen (LN₂) at the end of foaming to arrest cell growth. The experiment aimed to characterize the development of hierarchical secondary nanopores on primary cell walls as the foaming process progressed over time. The foamed specimens were freeze-fractured in liquid nitrogen (LN₂) to expose the cross-section. The cross-section is coated with a 4-5 nm platinum (Pt) layer and analyzed under a scanning electron microscope (SEM).

Table 3.1 List of foaming temperatures and corresponding foaming times considered to characterize the evolution of the secondary nanoporous network with foaming time.

Foaming Temperature, °C	Foaming Time, s
175	7
175	10
175	15
185	5
185	7
185	10
185	15
195	5
195	7
195	10
195	30

3.1.3 Results

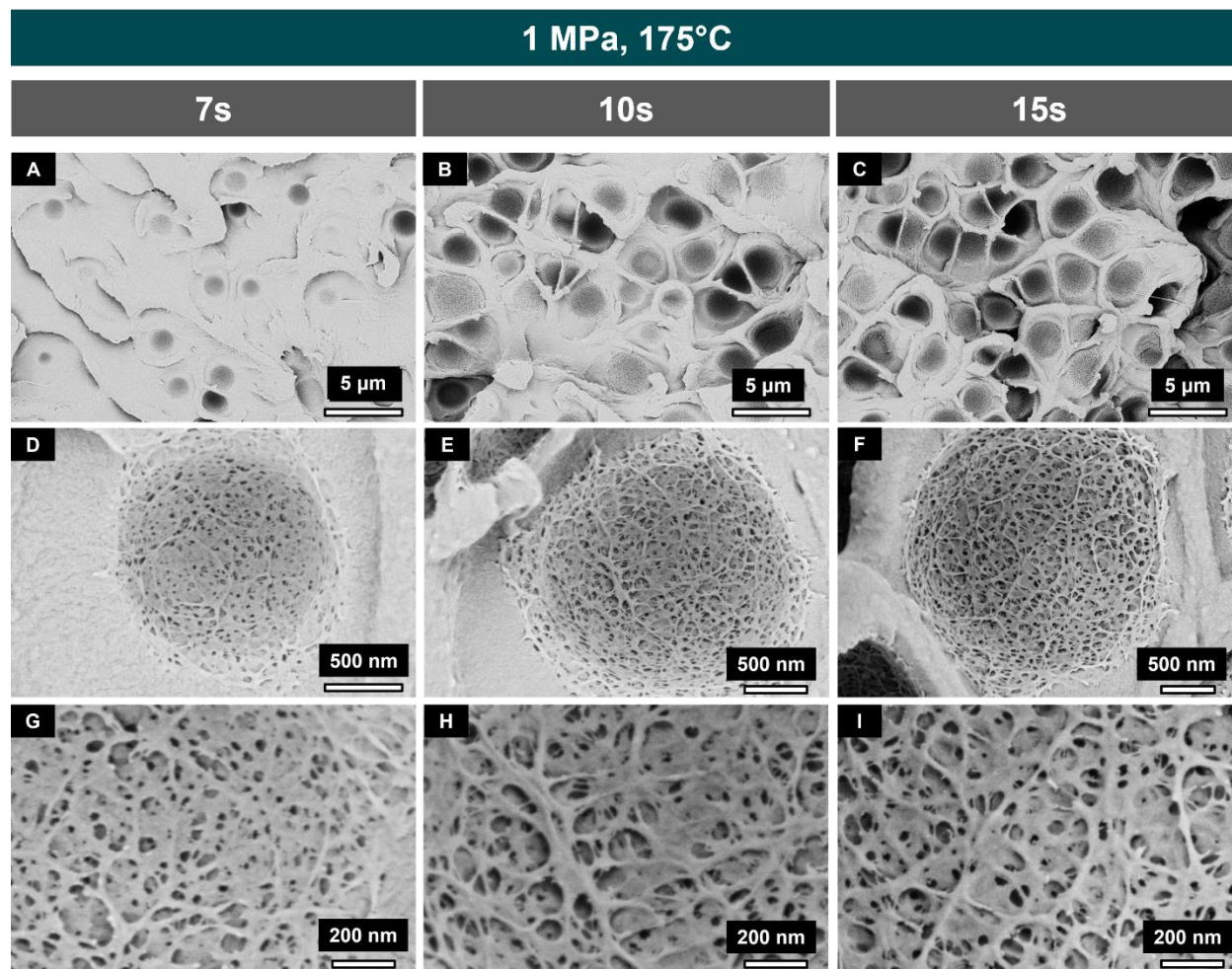


Figure 3.11 (A-C) SEM images of cellular structures of PEI foams saturated at 1 MPa and foamed at 175°C; each column corresponds to a foaming time of 7s, 10s, and 15s, respectively. (D-F) Representative SEM images of a single primary cell from the microstructure showing the development of secondary hierarchical nanoporous structures on the cell wall. (G-I) Representative SEM images of secondary hierarchical nanoporous structures on the cell wall.

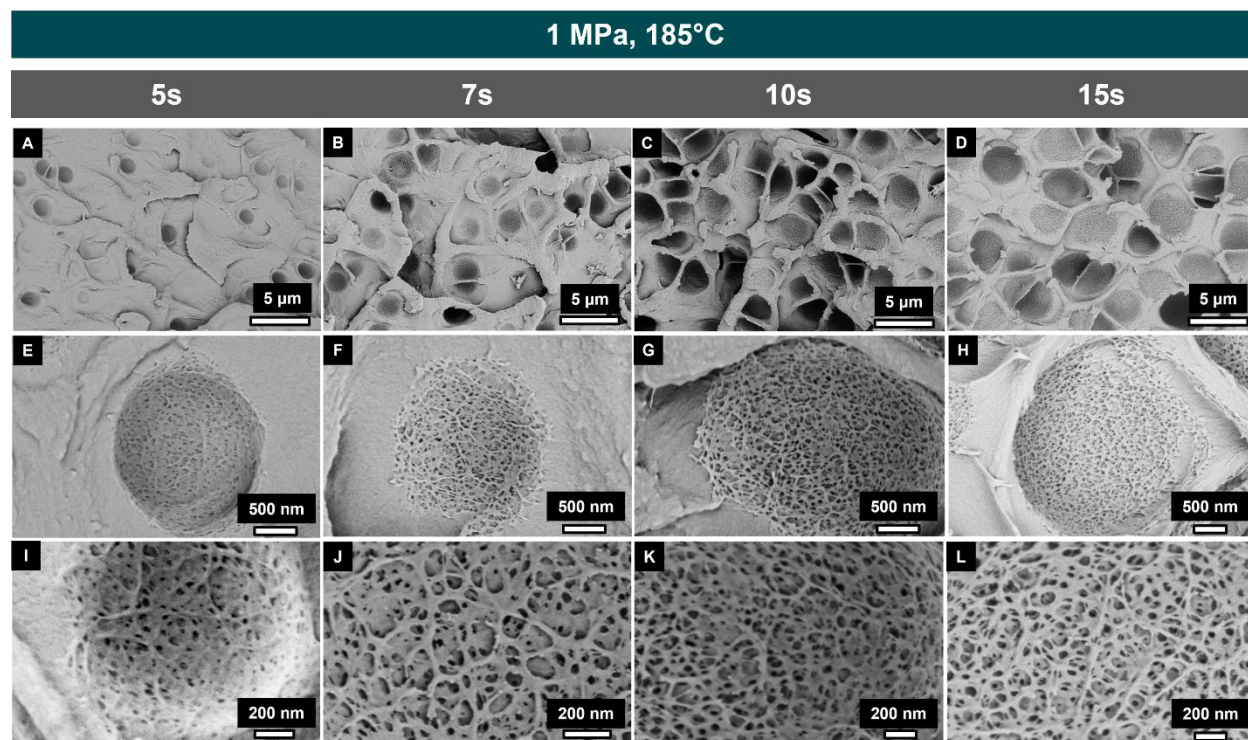


Figure 3.12 (A-D) SEM images of cellular structures of PEI foams saturated at 1 MPa and foamed at 185°C; each column corresponds to a foaming time of 5s, 7s, 10s, and 15s, respectively. (E-H) Representative SEM images of a single primary cell from the microstructure showing the development of secondary hierarchical nanoporous structures on the cell wall. (I-L) Representative SEM images of secondary hierarchical nanoporous structures on the cell wall.

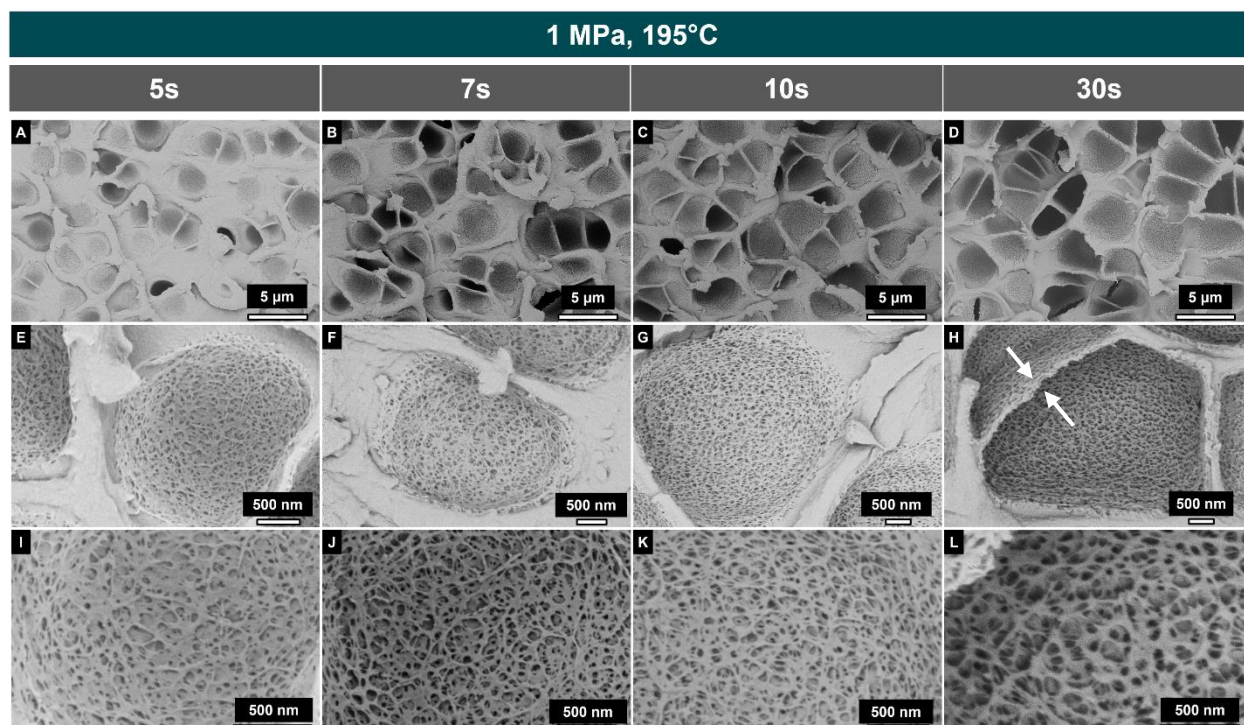


Figure 3.13 (A-D) SEM images of cellular structures of PEI foams saturated at 1 MPa and foamed at 195°C; each column corresponds to a foaming time of 5s, 7s, 10s, and 30s, respectively. (E-H) Representative SEM images of a single primary cell from the microstructure showing the development of secondary hierarchical nanoporous structures on the cell wall. (I-L) Representative SEM images of secondary hierarchical nanoporous structures on the cell wall.

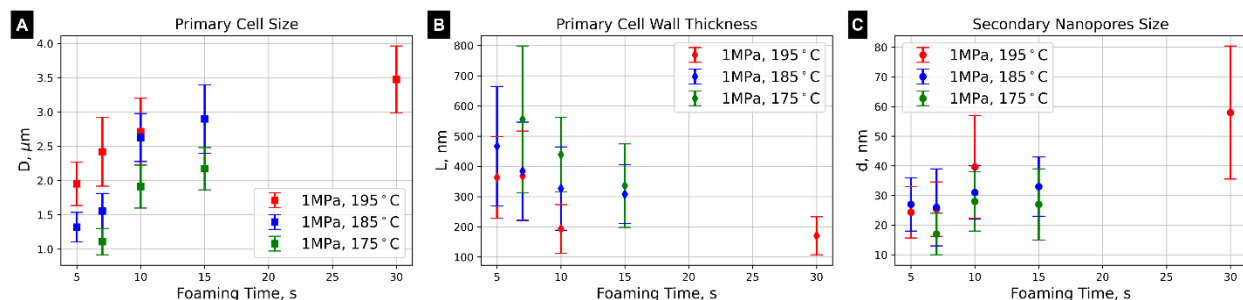


Figure 3.14 A) Plot showing primary cell size growth with foaming time at foaming temperatures 175°C, 185°C, and 195°C. B) The corresponding reduction in the primary cell wall thickness as the primary cell grows. C) The size of the secondary nanopores as the primary cell wall expands. (Data represents Avg $\pm$ SD)

3.1.4 Discussion

Time Evolution of Secondary Nanopores

There is no visible foaming below a foaming time of 5s for all foaming temperatures. The specimens became partially opaque, indicating bubble formation, at a foaming time of 7 seconds for the 175 °C foaming temperature and at 5 seconds for the 185 °C and 195 °C temperatures. At these foaming times, the SEM images in Figure 3.13 show nanopores on the cell wall with a primary cell size in the range 1-2 μm . This suggests that cell expansion is rapid during the initial stages of the foaming process, which aligns with predictions made by the bubble growth model in the PMMA-CO₂ system by Van Loock et al.⁴⁴ Secondary nanoporous structures are nucleated on the cell wall during the rapid expansion period and continue to grow as the cell expands with increasing foaming time.

As expected, lower foaming temperatures result in longer foaming times for cell growth. The average primary cell size is higher at foaming temperatures of 195°C, followed by 185°C and 175

°C, as shown in Figure 3.14A. The SEM image in Figure 3.13H, corresponding to a foaming temperature of 195°C, in one of the primary cells, we observe that the nanoporous network covers the entire cell wall after 30s of foaming, and the cell wall completely ruptures (indicated by the arrow), resulting in interconnected cells. The same effect is observed in PC by Gong et al.²⁰ at a foaming temperature of 150 °C. There is a specific final cell size limit for PEI at the end of growth, where the cell walls have sufficiently stretched and thinned to the point of complete rupture, facilitating primary cell elongation. Hence, a high foaming temperature close to the T_g of the unprocessed polymer is necessary to create interconnected microcellular PEI through the secondary nanopores.

The average pore size of the nanoporous network increases with foaming time as the primary cell expands, as shown in Figure 3.14C. There is no significant variation in pore size during the initial stages of foaming, when the foaming time is less than 15s, across the entire foaming temperature range. This suggests that the nanopores are primarily controlled by the stretching of the cell walls due to primary cell expansion. The significant variation in nanopore size observed at 15s and 30s for the case of 1 MPa and 195°C is attributed to pore coalescence, resulting from polymer fiber scission as the primary cell expands more rapidly at a higher foaming temperature. Overall, the average nanopore size ranges from 20 nm to 60 nm across the foaming temperature range.

In the first part of the study, we observed that the nucleation density of primary cells plays a crucial role in forming a porous cell wall. In this case, the saturation pressure is constant, so that the cell nucleation density is of the same magnitude. Therefore, the influence of neighboring cells growing simultaneously on the stretching of a given cell wall does not vary significantly as the foaming

temperature is varied. However, there will still be a slight increase in nucleation density with foaming temperature.

Role of Primary Cell Nucleation Density

To highlight the role of primary cell nucleation density, for example, consider two cases: 0.5 MPa at 200°C and 1 MPa at 195 °C. The average primary cell sizes and cell wall thicknesses are 4.5 μm and 221 nm for the first case, and 3.5 μm and 170 nm for the second. Although these values are relatively close, SEM images show that the cell walls are fully ruptured at 1 MPa. This example highlights the importance of cell nucleation density. A higher nucleation density leads to more neighboring cells, which impinge on each other and create thinner walls. These thinner walls are more likely to rupture, which is necessary to achieve an open-celled microcellular foam. Therefore, an optimal nucleation density, combined with a high foaming temperature, can create an interconnected microcellular foam through the formation of hierarchical secondary nanopores.

Nucleation Mechanism of Secondary Nanopores

As shown in Figure 3.10, the secondary nanopores are randomly distributed on the cell wall, resembling a Voronoi tessellation. The experiments indicate that the secondary nanopores are strongly dependent on the primary cell expansion. The random flaw distribution hypothesis described in 2.6.6, which was previously used to explain the structural transition from microcellular to nanocellular in PEI, can be extended to the nucleation of secondary nanopores.

Under a typical saturation pressure that produces a microcellular structure, smaller flaws are not activated. However, the strain energy that develops in the cell wall due to high tension from stretching lowers the activation energy, enabling the activation of smaller flaws and leading to the secondary nucleation of nanocells.

The mechanism is captured using equation (3.1), a modified expression for the free energy of a bubble.¹ nucleation ($\Delta G_{nucleation}$) that incorporates the strain energy due to cell expansion, as formulated by Gong. et.al²⁰.

$$\Delta G_{nucleation} = 4\pi R_b^2 \gamma - 8\pi E_{elastic} R_b^2 \zeta - \frac{4}{3}\pi R_b^3 (P_{int} - P_{sys}) \quad (3.1)$$

$$\Delta G_{surface} = 4\pi R_b^2 \gamma \quad \text{Eq. 3.2}$$

$$\Delta G_{strain} = 8\pi E_{elastic} R_b^2 \zeta \quad \text{Eq. 3.3}$$

$$\Delta G_{volume} = \pi R_b^3 (P_{int} - P_{sys}) \quad \text{Eq. 3.4}$$

γ is the surface tension

R_b is the radius of the bubble

$E_{elastic}$ is the shear modulus

ζ is the initial spacing in the polymer that is deformed to become a bubble

P_{int} is the internal pressure of the bubble

P_{sys} is the system pressure

¹ The term “bubble” is used interchangeably for a “cell”

Equation (3.1) demonstrates that the strain energy released during bubble expansion reduces the activation energy for cell nucleation, driving the nucleation of secondary nanocells. This model provides a good explanation for experimental observations on secondary nanopore formation. Gong et al. argue that the formation of microvoids due to crazing in polymer at high strain rates has a similar nucleation mechanism. Therefore, secondary nanopores may result from a combination of foaming and crazing.

3.2 CONCLUSION

The key driving force of nucleation of secondary nanopores on the cell wall is the stretching of the cell wall due to primary cell expansion. Increasing primary cell growth either by increasing foaming temperature at constant saturation pressure or by increasing foaming time at constant foaming temperature results in an increase in the area of cell wall covered by the nanopores, and the size of nanopores increases by 10 to 80 nm. The strong influence of primary cell expansion is evident in Part I of this study. However, increasing the saturation pressure reduces the surface tension, favoring nucleation of secondary nanopores, and it also enhances the primary cell nucleation density. This results in a smaller primary cell, resulting in diminished expansion. As a result, the secondary nanopore nucleation density on the cell wall is lower at 3.3 MPa compared to 0.5 MPa.

Part II shows that higher foaming temperatures lead to faster primary cell growth, which promotes secondary cell nucleation. Incorporating strain energy due to cell expansion into the classical nucleation theory framework, analogous to craze nucleation theory, explains the mechanism of secondary nanopore nucleation. Secondary nanopores likely nucleate due to both crazing of the polymer and foaming.

Chapter 4. EFFECT OF CELL SIZE ON THE TOUGHNESS OF PEI FOAMS

This work is a collaborative effort with the Meza Research Group in the Department of Mechanical Engineering and the Multiscale Analysis of Materials & Structures (MAMS) Lab in the Department of Aeronautics and Astronautics, focusing on the experimental characterization of the toughness in microcellular and nanocellular PEI foams as a function of cell size, funded by the National Science Foundation. Details of all the tensile and fracture experiments to be found in Kush Dwivedi's (Department of Mechanical Engineering) Ph.D. dissertation. This work has been submitted for publication under the title “Breaking Down the Exceptional Size-Dependent Toughness of Nanocellular Foams” by Dwivedi et al.⁴⁵ in which I am serving as a co-author.

My contributions are as follows:

- 1. Developing the process space map that enables the fabrication of microcellular and nanocellular PEI foams at specific relative densities*
- 2. Developing protocols for the fabrication of foam specimens for mechanical tests*
- 3. Detailed SEM characterization of the cellular structures before mechanical testing*
- 4. SEM characterization of fracture surfaces post-mechanical testing*

4.1 ABSTRACT

PEI microcellular foamed sheets with cell sizes ranging from 3 to 5 μm and nanocellular foams with cell sizes ranging from 15 to 40 nm were fabricated. The relative densities of these foams ranged from 0.8 to 0.4. Uniaxial tensile tests were performed to obtain the true stress-strain curves from which we estimated values of the Elastic Modulus (E), Strength (σ_y), Failure Stress (σ_f), and Failure Strain (ϵ_f). Single Edge Notch Tension (SENT)-based fracture tests were performed, and the load-Crack Mouth Opening Displacement CMOD curves were obtained from which we estimate the values of Energy Absorbed (E_a) and Fracture Work (W_f). The true strain and CMOD were accurately measured using a Digital Image Correlation (DIC) technique.

The nanocellular foams exhibited significantly higher toughness compared to the microcellular foams at the equivalent relative densities. These results contradict the classical scaling law $K_{IC} \propto \sqrt{l}$ that predicts a decrease in fracture toughness K_{IC} with a decrease in cell size l . Notably, nanocellular foams with a relative density of 0.8 exhibited fracture toughness comparable to that of solid PEI. Scanning Electron Microscopy (SEM) analysis of fracture surfaces along the path of crack propagation revealed distinct failure mechanisms at the microscale and nanoscale levels. The stable crack propagation regions showed cell wall stretching, a key characteristic of ductile failure. In contrast, areas of unstable crack propagation exhibited flat fracture surfaces and no cell wall stretching, consistent with brittle behavior. In general, fracture surfaces in nanocellular foams exhibited larger areas of stable crack growth, supporting the observed enhancement in toughness. The disruptive fracture behavior of nanocellular PEI foams is attributed to nanoscale-level ductility. Complete details of all the tensile and fracture experiments, along with numerical simulations, will be provided in Kush Dwivedi's Ph.D. dissertation.

4.2 INTRODUCTION

Weller and Kumar³³ conducted a study on the effect of cell size on the tensile properties of microcellular PC. They observed no significant effect of cell size on tensile properties, such as tensile modulus, tensile strength, elongation at break, and toughness, over a cell size range of 4 μm to 40 μm . Miller²¹ reported that nanocellular PEI foams, with an average cell size of 30 nm, exhibited significantly greater toughness compared to microcellular PEI foams, which had an average cell size of 3 μm for the same relative densities. In a separate study, Martin-de-Leon et al.²², reported a substantial improvement in fracture toughness of nanocellular PMMA foams compared to their microcellular counterparts at the same relative densities, contrasting with the traditional Gibson and Ashby model prediction⁴³. The classical model scales fracture toughness K_{Ic} as shown in equations (5.1) and (5.2). The model predicts that fracture toughness should decrease as cell size decreases, contrary to what is observed in these studies.

$$K_{Ic} = C_1 \sigma_f \sqrt{\pi l} (\rho_{rel})^{3/2} \text{ (open-celled) } (5.1)$$

$$K_{Ic} = C_2 \sigma_f \sqrt{\pi l} (\rho_{rel})^2 \text{ (closed-celled) } (5.2)$$

where ρ_{rel} is relative density, l is the cell size, σ_f is the fracture strength and $C_{1,2}$ are constants.

The classical scaling law predicts that fracture toughness should decrease as cell size decreases, contrary to what is observed in these studies. Therefore, a fundamental shift in mechanical behavior occurs when the average cell size reaches the nanoscale. This study systematically investigates the effect of reducing cell size to the nanoscale on the toughness of PEI foams.

4.3 EXPERIMENTAL

4.3.1 Process Space of PEI-CO₂ System

The motivation for establishing the process space is to produce microcellular and nanocellular foams at the same relative densities while the cell size varies by a factor of 100. This enables decoupling the effect of cell size on bulk material properties by holding the relative density constant.

Table.2.2 consists of a detailed summary of the process conditions for producing microcellular foams and nanocellular foams at different relative densities and cell sizes.

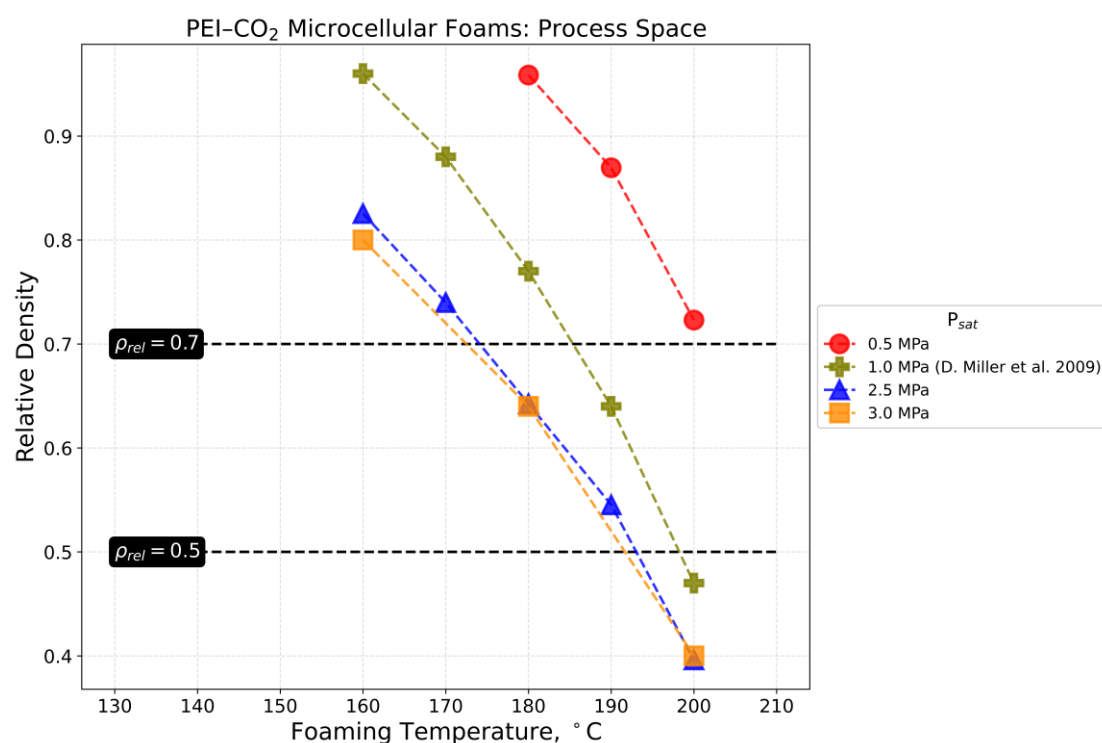


Figure 4.1 Process space map for microcellular PEI foams for room temperature saturation conditions. Horizontal lines corresponding to relative densities 0.7 and 0.5 are overlaid on the plot to illustrate that the intersection points represent conditions that produce microcellular foams at constant relative densities.

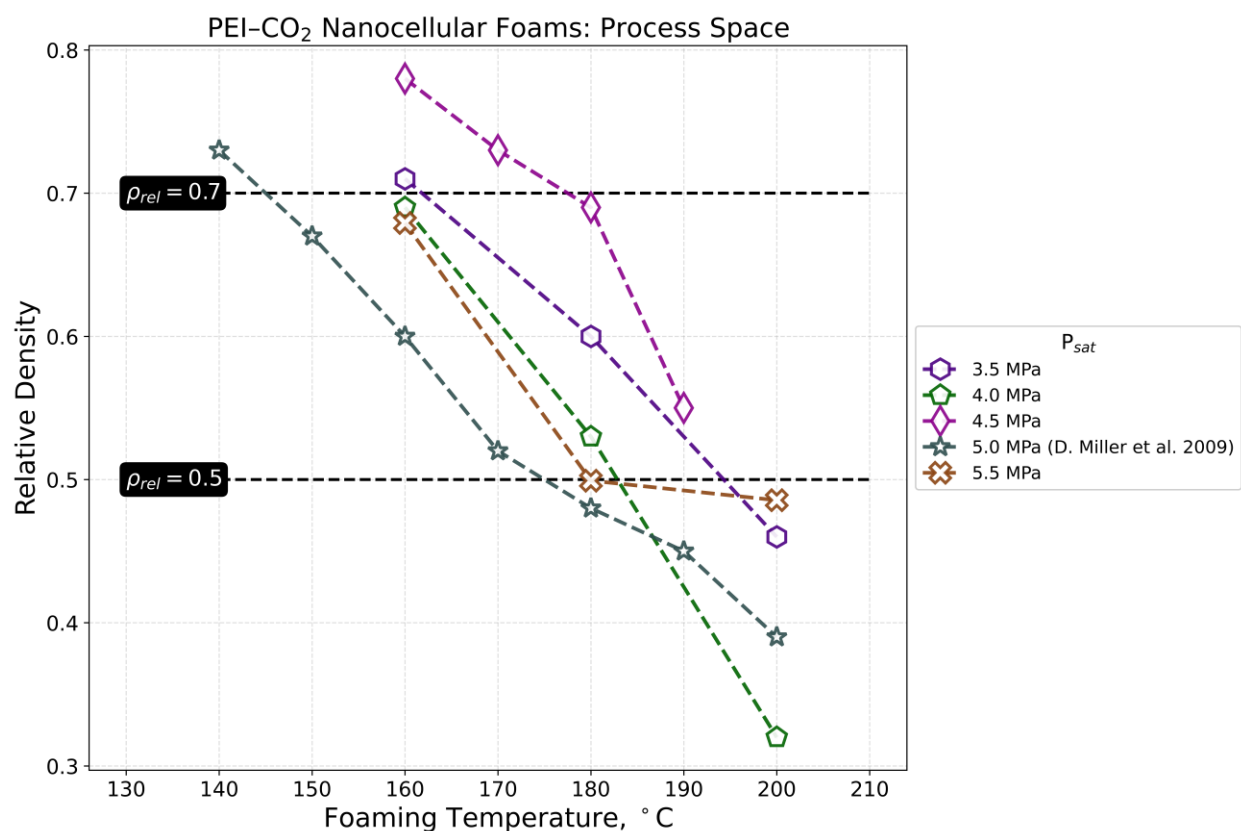


Figure 4.2 Process space map for nanocellular PEI foams for room temperature saturation conditions. Horizontal lines corresponding to relative densities 0.7 and 0.5 are overlaid on the plot to illustrate that the intersection points represent conditions that produce microcellular foams at constant relative densities.

Table 4.1 lists all the process conditions. For microcellular foams, a saturation pressure of 1 MPa was selected, and 5 MPa for nanocellular foams. Flat specimens were prepared for the test using the technique described in section AI in the Appendix.

Table 4.1 Process conditions for tensile and fracture test specimen fabrication

Saturation Pressure, MPa	Foaming Temperature, °C	Press Temperature, °C	Relative Density
1	175	175	0.80
1	185	185	0.71
1	195	195	0.63
1	195	205	0.49
5	130	140	0.77
5	145	145	0.72
5	165	165	0.58
5	160	180	0.42

4.3.2 *Structure of Fabricated PEI Foams*

Microcellular PEI foams exhibit an average cell size ranging from 3 to 5 μm , with secondary nanopores on the cell walls, measuring sizes from 20 to 80 nm, as shown in Figure 4.5. At high relative densities, structure is likely closed-cell. At low relative densities, the secondary nanoporous network extends to cover the entire cell wall as the cell wall stretches during cell expansion. This results in partial or complete cell wall rupture and can potentially transform the foam into an open-celled structure. A similar behavior in microcellular PC foams was reported by Gong et al.²⁰, confirming that microcellular PC foams, which also exhibit secondary nanopores, are open-celled at low relative densities. In the present study, SEM images of microcellular PEI foams at relative densities of 0.6 and 0.5 show ruptured cell walls, indicating a possible transition

to an open structure. A detailed study is yet to be conducted to confirm whether the microcellular PEI foams with secondary cells are open-celled.

The nanocellular PEI foams have cell sizes ranging from 15 to 40 nm. These nanopores appear in small clusters of two or three and are sporadically distributed, as illustrated in the SEM image in Figure 4.5. In some cases, the inter-pore wall thickness was observed to be as low as 16 nm, as shown in the Figure 4.5 below, leading to nanoconfinement effects^{46,47} on the cell wall. The inter-pore distance between the secondary pores in microcellular PEI foams was observed to be as low as 11 nm, which can lead to nanoconfinement effects as well.

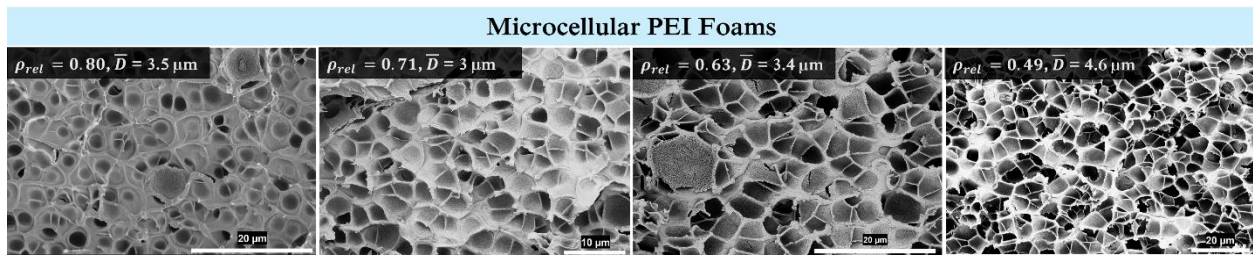


Figure 4.3 SEM images showing structures of microcellular PEI foams of different relative densities (0.8-0.5) fabricated for tensile and fracture tests.

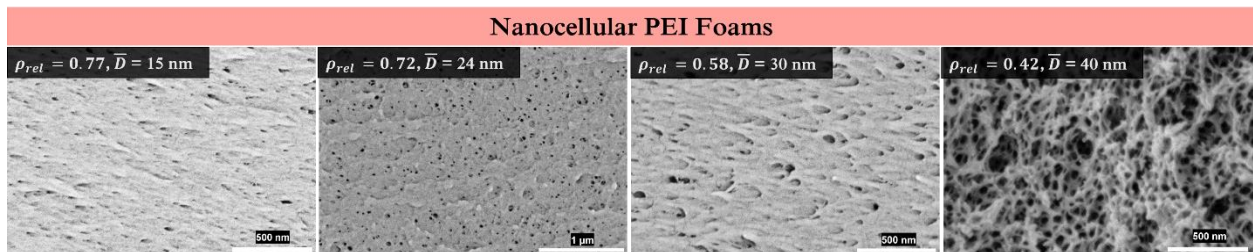


Figure 4.4 SEM images showing structures of nanocellular PEI foams of different relative densities (0.8-0.4) fabricated for tensile and fracture tests.

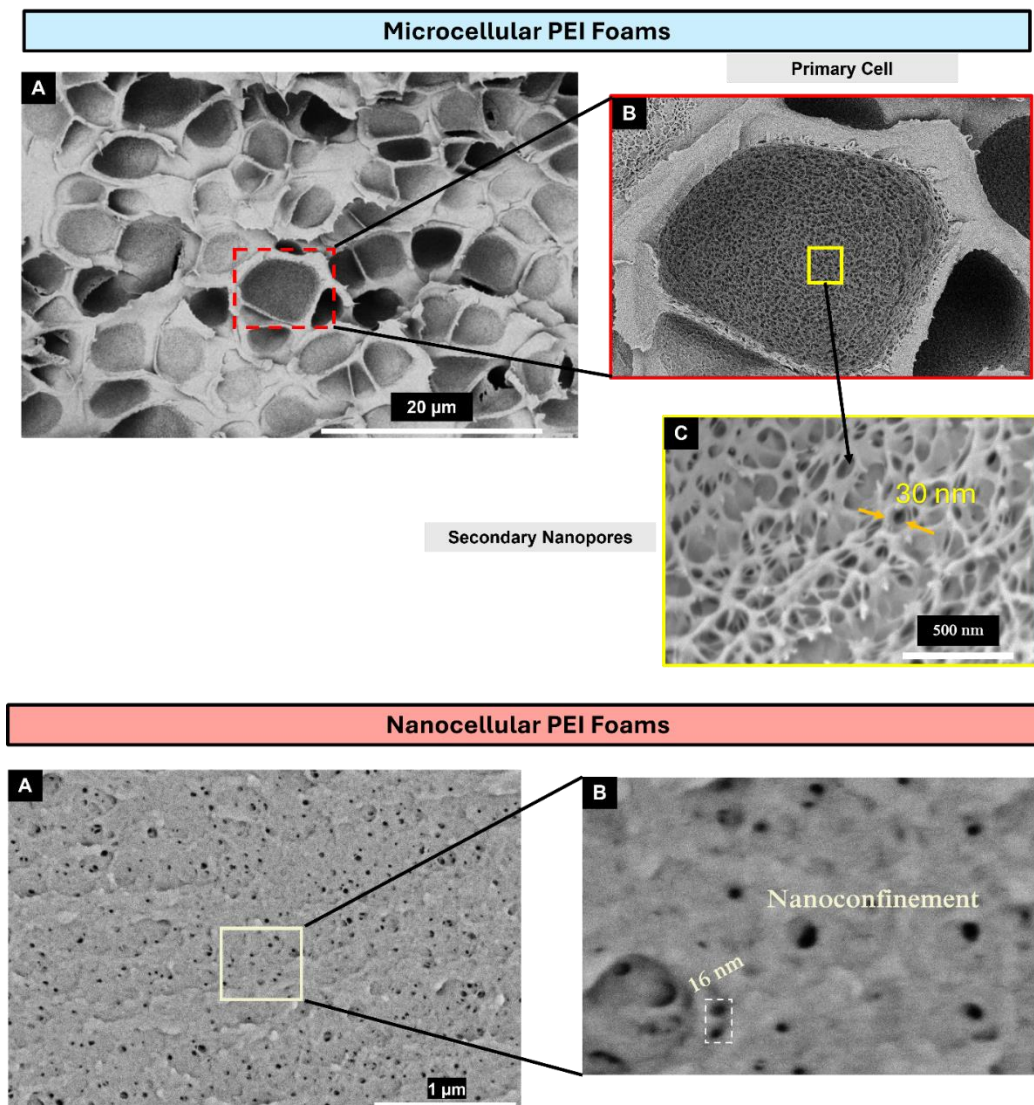


Figure 4.5 (Upper) SEM images showing the hierarchical morphology of microcellular PEI foams. A) Overview of the cellular microstructure consisting of closed, regularly shaped primary cells. B) Zoomed-in view of a representative primary cell, revealing the presence of secondary nanopores on the cell wall. C) Further magnification of the cell wall region, highlighting the nanoporous network, with an average pore size of approximately 30 nm. (Lower) SEM images showing the morphology of nanocellular PEI foams. A) Overview of the nanocellular architecture with uniformly distributed nanopores. B) Higher magnification of a selected region, showing a cluster of nanopores where the cell wall thickness is reduced to ~16 nm, indicating nanoconfinement effects at the wall level.

4.4 RESULTS

4.4.1 Tensile Behavior of Microcellular and Nanocellular PEI Foams

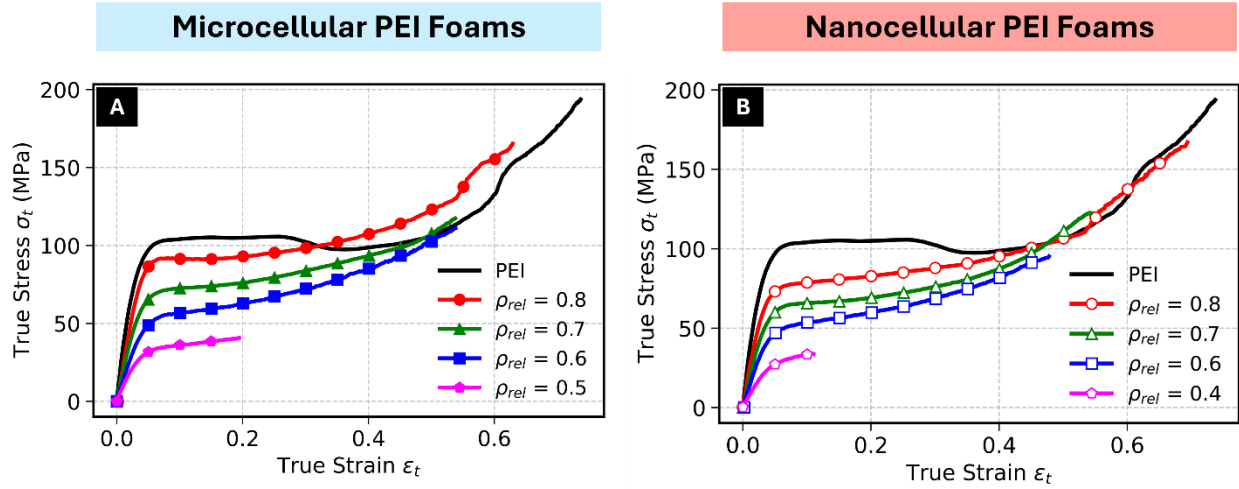


Figure 4.6 A) True Stress-True Strain tensile curves for solid PEI and microcellular PEI foams with a relative density range of 0.8 – 0.5. B) True Stress-True Strain tensile curves for solid PEI and nanocellular PEI foams with a relative density range of 0.8 – 0.4.

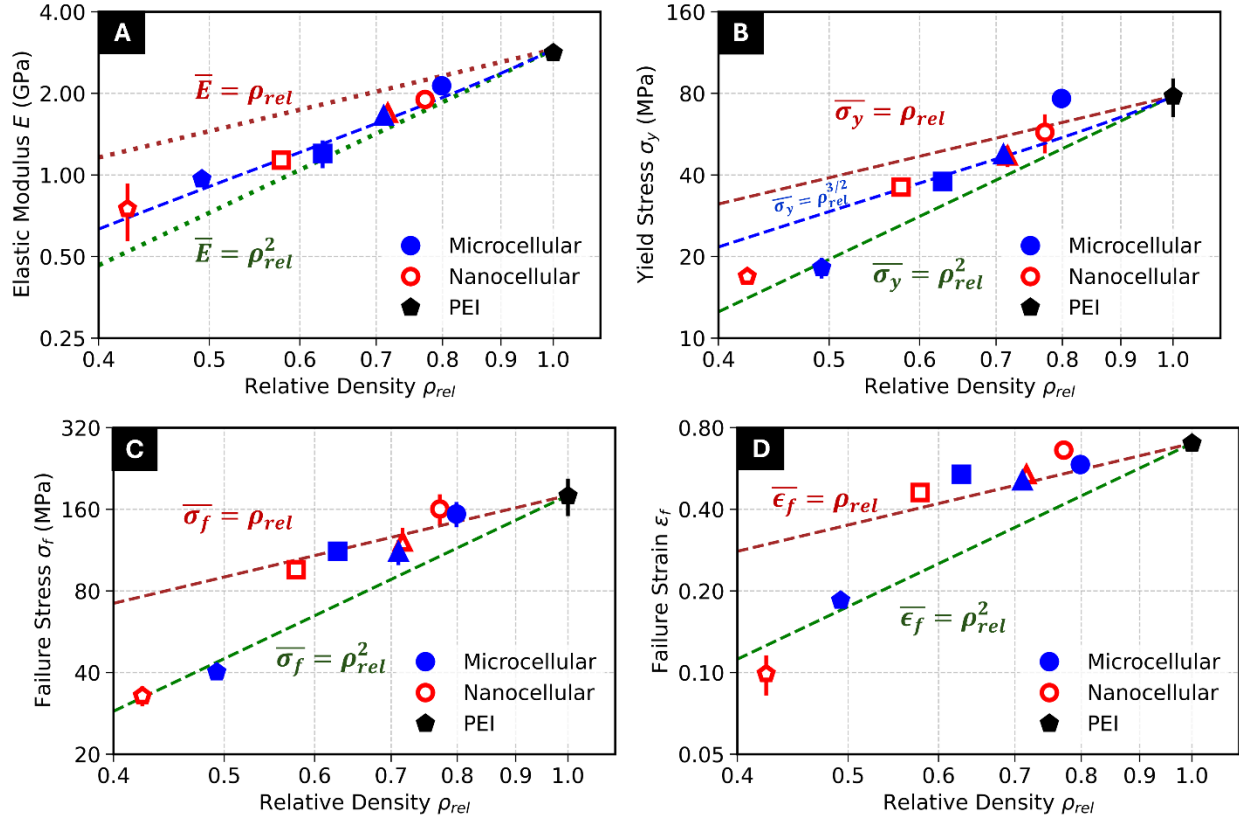


Figure 4.7 Tensile properties were measured from the true stress–true strain curves. A) Elastic Modulus (E) of microcellular and nanocellular PEI foams at different relative densities at different relative densities. B) Yield Stress (σ_y) of microcellular and nanocellular PEI foams at different relative densities. C) Failure Stress (σ_f) of microcellular and nanocellular PEI foams at different relative densities. D) Failure Strain (ϵ_f) of microcellular and nanocellular PEI foams at different relative densities. Dashed lines overlaid on the plots represent classical power-law scaling relations of mechanical properties with relative density (ρ_{rel}) for cellular solids. The location of experimental data relative to these scaling laws provides insight into the mechanical behavior of PEI foams.

4.4.2 Fracture Behavior of Microcellular and Nanocellular PEI Foams

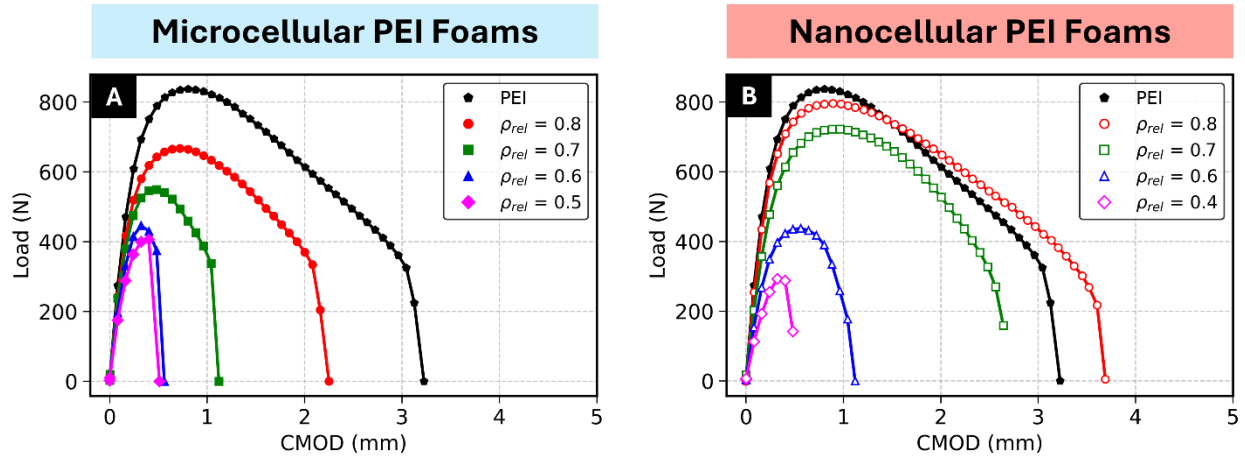


Figure 4.8 A) Load vs. CMOD (Crack Mouth Opening Displacement) from the fracture tests for microcellular PEI foams of different relative densities. B) Load vs. CMOD (Crack Mouth Opening Displacement) from the fracture tests for nanocellular PEI foams of different relative densities. The results are compared with the solid PEI.

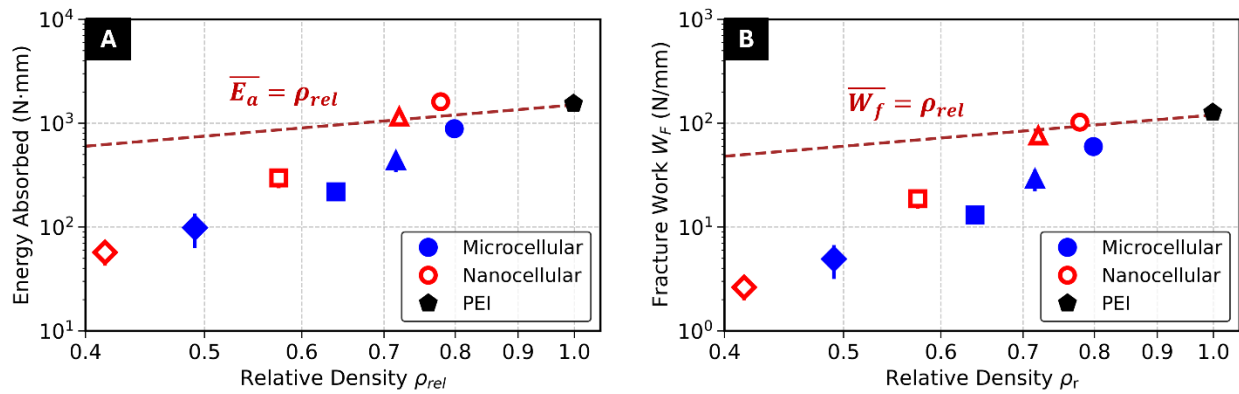


Figure 4.9 A) Energy absorbed by microcellular and nanocellular PEI foams estimated from fracture test results and compared against the solid PEI. B) Fracture Work (W_F) by microcellular and nanocellular PEI foams estimated from fracture test results and compared against the solid PEI.

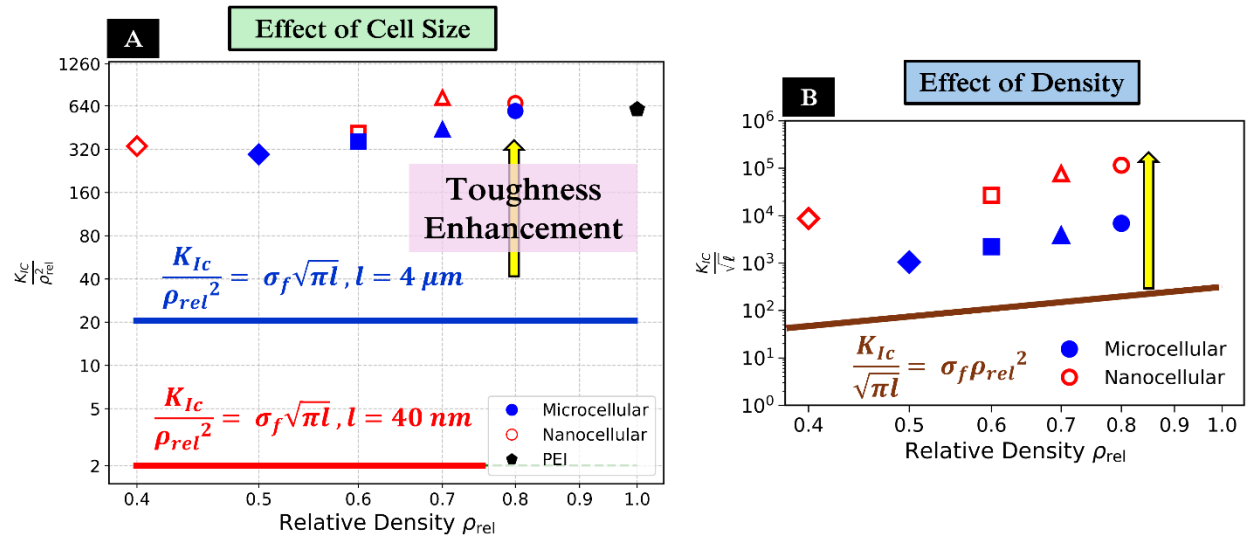


Figure 4.10 Fracture behavior of microcellular and nanocellular foams as a function of relative density compared to the classical scaling law.

4.4.3 SEM Analysis of Fracture Surface

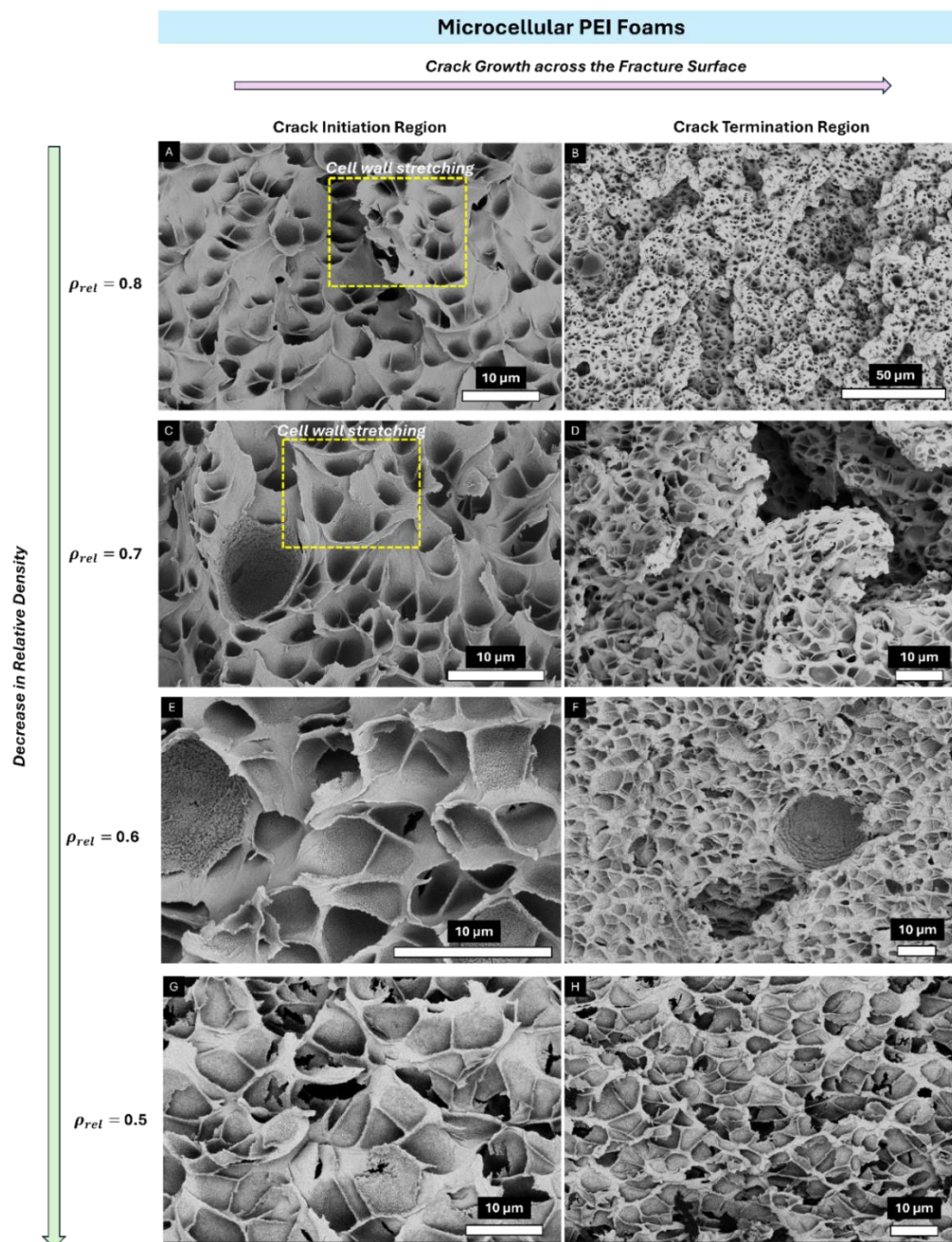


Figure 4.11 SEM images of fracture surfaces of microcellular PEI foams with relative densities ranging from 0.8 to 0.5 after fracture testing. SEM images (A, C, E, G) show regions near the notch where crack initiation occurred. SEM images (B, D, F, H) correspond to regions on the unnotched side where crack propagation terminated. Yellow dashed regions on the SEM images (A) and (C) highlight localized cell wall stretching near the crack initiation zone, indicating stable crack growth and ductile behavior.

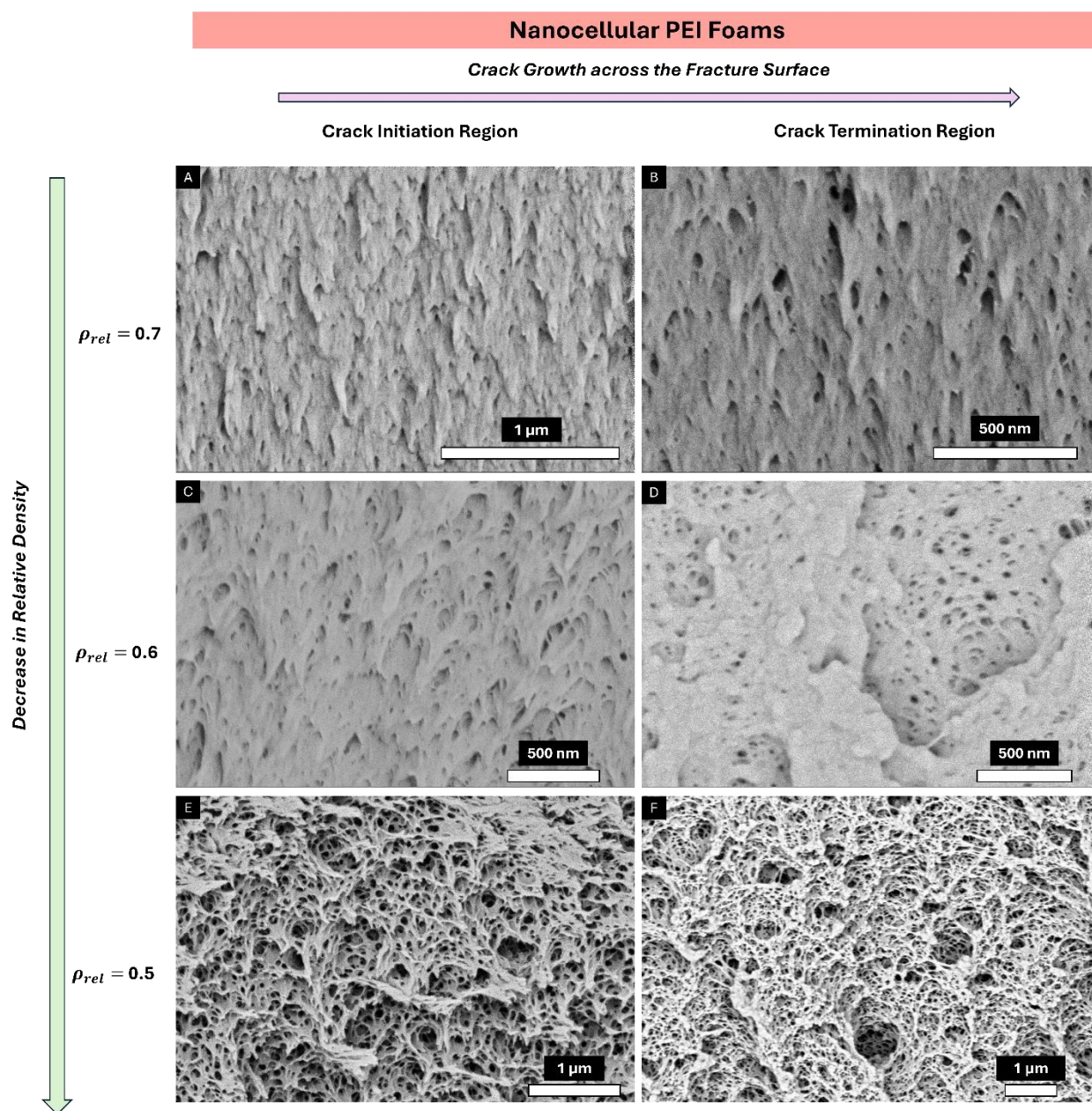


Figure 4.12 SEM images of fracture surfaces of nanocellular PEI foams with relative densities ranging from 0.7 to 0.5 after fracture testing. SEM images (A, C, E) show regions near the notch where crack initiation occurred. SEM images (B, D, F) correspond to regions on the unnotched side where crack propagation terminated.

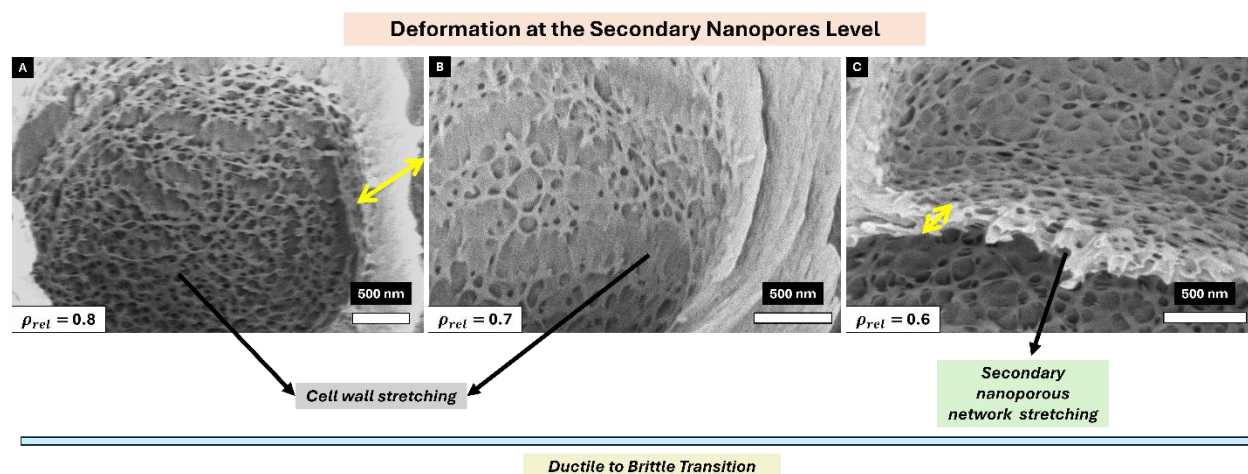


Figure 4.13 SEM images of fracture surfaces of microcellular PEI foams with relative densities ranging from 0.8 to 0.6 that exhibited ductile to brittle transition, captured at the walls of primary cells. Images A and B show the evidence of cell wall stretching and partial disintegration of the secondary nanoporous network. Image C shows a fractured cell wall where individual nanopores appear stretched, indicating localized deformation. The yellow double-headed arrow highlights the reduction in wall thickness, indicating the change in the cellular architecture.

4.5 DISCUSSION

4.5.1 *Tensile Behavior of Microcellular and Nanocellular PEI Foams*

The elastic modulus E , for both microcellular and nanocellular foams, the trend is similar. There is no impact due to the cell size difference. The elastic modulus scales in such a way that the data lies between the classical bounds $E \sim \rho_{rel}$ (upper bound) and $E \sim \rho_{rel}^2$ (lower bound).

The yield strength σ_y , of microcellular and nanocellular foams follow the same trend, with no significant difference. There is no impact due to the cell size difference. The yield strength scales in such a way that the data follows $\sigma_y \sim \rho_{rel}^{3/2}$. However, low-density microcellular and nanocellular foams are outliers as they lie on the bound, $\sigma_y \sim \rho_{rel}^2$. This can be attributed to the structure shifting towards an open-celled architecture.

The failure stress σ_f of both microcellular and nanocellular foams follow the same trend, with no significant difference. There is no impact due to the cell size difference. The failure stress scales in such a way that the data follows $\sigma_f \sim \rho_{rel}$. However, low-density microcellular and nanocellular foams are an outlier as they lie on the bound $\sigma_y \sim \rho_{rel}^2$. This can be attributed to the structure shifting towards an open-celled architecture. Note that the high-density nanofoam exhibits failure stress comparable to that of the solid PEI, demonstrating ductility enhancement at a reduced density.

The failure strain ε_f , of both microcellular and nanocellular foams follow the same trend without any significant difference. There is no impact due to the cell size difference. The failure strain scales in such a way that the data follows $\varepsilon_f \sim \rho_{rel}$. However, low-density microcellular and nanocellular foams are an outlier as they lie on the bound $\varepsilon_f \sim \rho_{rel}^2$. This can be attributed to the structure transitioning towards open-celled architecture. Note that the high-density nanofoam exhibits a failure strain comparable to that of the solid PEI, demonstrating ductility enhancement at a reduced density. The true stress–true strain curves show that the microcellular and nanocellular foams exhibit ductile behavior, except at relative densities of 0.5 and 0.4, respectively. These results contrast with those of Miller et al.²¹, where microcellular foams with a relative density as high as 0.9 failed at a low strain, exhibiting low ductility. We must also note that they reported engineering stress-strain curves. Compared to Miller et al.²¹, our study has produced consistent results with less variation due to our systematic sample preparation technique.

4.5.2 *Fracture Behavior of Microcellular and Nanocellular PEI Foams*

The load vs. CMOD shows that, in general, nanocellular foams have higher peak loads and larger CMOD compared to microcellular foams in the relative density range 0.8-0.6. The nanocellular foams, with a relative density of 0.8 and a corresponding cell size of 15 nm, exhibit comparable toughness to solid PEI, as reported in Figure 4.8. The post-peak load decline is gradual, indicating slow progress of the crack across the nanocellular surface. This is remarkable because it demonstrates that we can reduce the density of PEI and enhance its toughness by introducing nanopores. The behavior is reflected in the Energy Absorbed and Fracture Work estimations in Figure 4.9. The Energy Absorbed is calculated as the total area under the curve minus the recoverable elastic energy, the energy required to break. The Fracture Work is Energy Absorbed

normalized by the area of the section, which is the energy required by the crack to create a new surface. The low relative density (0.4) nanocellular foam fails immediately after peak load, indicating a ductile-to-brittle transition. From Chapter 2, we know that in nanocellular foams, there is no significant increase in cell size as the relative density decreases. At a relative density of 0.7, the average cell size is ~ 30 nm, and at a relative density of 0.4, the average cell size is ~ 40 nm. Yet, there is a ductile-to-brittle transition. This demonstrates the need to quantify the effect of architecture. Consider the cell wall thickness, which reduces from 38 ± 30 nm at a relative density of 0.7 to 22 ± 10 nm. Therefore, the remaining surface area of the solid through which the crack must propagate decreases with relative density; as a result, the toughness decreases. Microcellular foams exhibit considerable toughness at high relative densities, ranging from 0.8 to 0.6, and we also observe a gradual post-peak decline, indicating slow crack propagation. However, the low-density microcellular foams fail immediately after the peak load, indicating a ductile-to-brittle transition. However, the transition happens earlier compared to nanocellular foams. The behavior is reflected in the Energy Absorbed and Fracture Work calculations in Figure 4.9. Figure 4.10A and B show that both microcellular and nanocellular PEI foams exhibit higher toughness compared to predictions by classical models. The results show that nanocellular foams exhibit higher toughness than the microcellular foams in disrupting the classical model predictions. This highlights the importance of the effect of architectural features and toughness-enhancing mechanisms due to nanoscale ductility on the fracture behavior of nanocellular foams.

4.5.3 SEM Analysis of Fracture Surface

The fracture surface was analyzed at two different regions under the SEM – Crack Initiation Region and Crack Termination Region. The fracture surface analysis results for microcellular PEI foams are illustrated in Figure 4.11. The load-CMOD plots (Figure 4.8A) indicates that at relative densities 0.8 and 0.7, the behavior is ductile, and the crack propagation is gradual. This is reflected on the fracture surface. The crack propagation is resisted by the cell wall stretching, showing ductile characteristics during the initial stages of crack propagation, which is referred to as stable crack growth. The cell wall stretching in the crack initiation region for the corresponding microcellular foams is shown in Figure 4.11 A and C. Towards the end, after the onset of peak load, the crack propagation becomes unstable; therefore, we don't observe cell wall stretching in the crack termination region, with the fracture surface exhibiting brittle characteristics. This is illustrated in Figure 4.11 B and D. For microcellular foams at relative densities 0.6 and 0.5, the Load-CMOD plots (Figure 4.8A) indicates brittle behavior. Consequently, no cell wall stretching is observed in the crack initiation and termination regions, indicating completely brittle characteristics as illustrated in Figure 4.11 E, F, G, and H.

Further, SEM analysis was conducted on the cell walls to examine the role played by the secondary nanopores. There is no evidence of stretching secondary nanopores in microcellular foams with relative densities of 0.8 and 0.7, as shown in Figure 4.13 A and B. This is because the secondary nanopores only partially cover the primary cell wall. However, at a low relative density of 0.6, due to enhanced cell expansion, the secondary nanopores cover the cell wall, resulting in nanopore stretching as the crack propagates, as shown in Figure 5.9C. However, the effect of low relative

density leads to brittle failure with no significant enhancement of ductility due to nanopore stretching.

The Load-CMOD curves indicate that nanocellular foams exhibit ductile behavior, except for the low-density foam, which exhibits brittle failure (Figure 4.8B). The nanocellular foams are also consistently ductile than the microcellular foams within the relative density range 0.8-0.6. The SEM images of the fracture surface area show individual pore wall stretching at both the crack initiation region and the crack termination region at relative density 0.7, as shown in Figure 4.11. This is in line with the gradual post-peak decline of load-CMOD curves. The crack propagation remains stable from initiation to termination. However, for relative density 0.6-0.4, there is pore wall stretching at the crack initiation region exhibiting ductile characteristics. The absence of stretching at the crack termination region indicates that the crack transitions from a stable growth mode to an unstable growth mode. This is illustrated in Figure 4.12. Note that even at a relative density of 0.4, the nanocellular foams exhibit a certain degree of ductility, which is remarkable, showcasing the nanoscale cell size effect.

4.6 CONCLUSION

In general, the nanocellular foams are tougher than microcellular foams for the same relative density. This behavior is unconventional and disrupts the classical scaling law. The enhanced toughness in nanocellular foams is evident from fracture test results. The load-CMOD curves in the case of nanocellular foams had a higher peak load and a gradual decline in post-peak load, indicating plastic deformation and a higher degree of energy absorption leading to ductility. The nanocellular foam with a relative density of 0.8 exhibits failure stress, failure strain, energy

absorbed, and fracture work comparable to those of solid PEI. The fracture toughness of 0.8 relative density foam is comparable to that of solid PEI. This is a remarkable result as it showcases the effect of reducing cell size in enhancing toughness while reducing density. In general, low-density materials exhibit less ductility and undergo brittle failure. Both microcellular and nanocellular foams exhibit a ductile-to-brittle transition as the relative density decreases. However, the transition happens in microcellular foams at a much higher relative density. The SEM analysis of the fracture surfaces along the crack propagation path revealed that the ductile microcellular foams exhibit cell wall stretching in the crack initiation region and no stretching in the crack termination region, indicating moderate ductility, except for the low-density foam, which did not have any stretching. Currently, the effect of secondary nanopores is not decoupled. SEM analysis on cell walls of microcellular foams indicates that there is no evidence of any effect associated with secondary nanopores on the fracture behavior. High-density nanocellular foams show cell wall stretching in both the crack initiation and termination regions. Notably, even the low-density nanocellular foam had cell wall stretching in the crack initiation region, exhibiting some ductility. The fracture surfaces of nanocellular foams show a high degree of cell wall stretching, indicating plastic deformation at the nanoscale level due to local ductility, which contributes to a high degree of energy absorption. The findings of this study show how nanoscale features can improve toughness in foams while providing lightweight.

Chapter 5. EXPERIMENTAL VALIDATION OF EFFECTIVE GLASS TRANSITION TEMPERATURE-BASED MODEL FOR PREDICTING SKIN THICKNESS IN SOLID-STATE MICROCELLULAR AND NANOCELLULAR FOAMS

Part of this work was published in a peer-reviewed journal, and I am the first author of the paper published under the title “Experimental Validation of Effective Glass Transition-Based Model for Predicting Skin Thickness in Solid-State Microcellular and Nanocellular Foams” by Sridhar et al. (2025)²⁸.

5.1 ABSTRACT

The solid-state foaming process produces foams with an outer layer of solid skin that encapsulates a cellular core. We implement a one-dimensional heat and mass transfer model in PC–CO₂ to predict skin thickness as a function of foaming temperature, based on the effective glass transition temperature (T_g) of the polymer-gas system. Effective T_g values are measured across a saturation pressure range of 0.1 to 5 MPa, and a correlation is established to predict T_g accurately. The model is validated using experimental results, showing good agreement. Both experimental and predicted skin thickness values decrease with increasing foaming temperature. The study reveals a significant new insight: skin formation occurs during the early stages of the foaming process.

5.2 INTRODUCTION

The process of solid-state foaming was developed in the 1980s¹⁻³ to reduce density and plastic usage by introducing bubbles in thin-walled plastics without drastically affecting their mechanical properties. The process is two-stage, as illustrated in Figure 5.1. The first stage involves saturating the polymer sheets under high pressure inside a pressure vessel, typically with CO₂ or N₂. At the end of saturation, the vessel is depressurized, and the sheets are removed. The polymer sheets with dissolved gas are then quenched in a hot bath to induce foaming at a specific temperature, typically for a fixed amount of time. The process results in the formation of bubbles across the polymer cross-section, as illustrated in Figure 5.1. The typical bubble size is of the order of 10 μm ; therefore, these are referred to as microcellular foams. Over the years, the process has been successfully implemented in several polymer-gas systems, including PC-CO₂^{4,5}, PLA-CO₂⁶, ABS-CO₂⁷, PMMA-CO₂⁸⁻¹⁰, and PEI-CO₂¹¹⁻¹³, among others.

A representative microstructure of a microcellular PC foam is shown in the SEM image in Figure 5.1. A microcellular foam comprises an unfoamed solid skin layer on the outer edge that encapsulates the cellular core. A portion of the region on the outer edge always remains unfoamed after the foaming process because, after depressurization, the supersaturated polymer sheets desorb gas under ambient conditions. As gas diffuses from the thin sheets through the thickness, the local gas concentration decreases at the outer edge. Weller¹⁴ proposed that bubbles will not nucleate during foaming when the local gas concentration in the polymer matrix decreases below a specific minimum value. Therefore, an unfoamed layer of solid skin develops on the outer edge, and the thickness of the solid skin grows with desorption. Weller¹⁴ studied the effect of desorption time

on the skin thickness in the PC-CO₂ system. The desorption time is the interval between depressurization and the onset of foaming. The study led to the development of a 1D model to predict skin thickness based on the minimum gas concentration required for bubble nucleation. The model diverges from the experimental results at lower desorption times. Recent work by Mohyeddin A and Fereidoon A²⁵ on the PS-N₂ system, which employed the minimum gas concentration approach, also demonstrates that the model fails to predict skin thickness at low desorption times accurately. The hypothesis of the minimum gas concentration required for bubble nucleation can be revisited by examining the fundamental physics of the solid-state foaming process.

We know that bubble nucleation occurs in the solid-state foaming process when the foaming temperature exceeds the effective T_g of the polymer-gas system. Effective T_g is the reduced T_g of the polymer due to the presence of gas in the polymer matrix that leads to a plasticization effect. Therefore, the skin is the local region where the specimen temperature during the foaming process does not exceed the effective T_g of the polymer matrix. Now, we can model skin thickness directly based on the effective T_g of the polymer-gas system.

Wesseling et al.²⁶ and Adams et al.²⁷ developed an effective T_g -based model to predict skin thickness. They predicted the effective T_g profiles across the polymer cross-section at different desorption times. They modeled the evolution of the temperature profile across the specimen during the foaming process. They compared the two profiles and predicted the skin thickness as the first intersection point where the local specimen temperature exceeds the local T_g . Adams et al.²⁷ and Wesseling et al.²⁶ consider the first intersection point as the skin thickness because it

represents the onset of foaming. However, there is no further experimental evidence that skin thickness does not vary during the foaming process. The critical step is predicting the effective T_g profile based on the gas concentration profile across the polymer cross-section. The effective T_g depends on the amount of gas dissolved in the polymer matrix. The higher the gas concentration, the lower the effective T_g . Wesseling et al.²⁶ assumed a linear correlation between gas concentration and effective T_g . Adams et al.²⁷ used Chow's equation⁴⁸ to predict the effective T_g for a given gas concentration. However, Chow's equation's parameters z and ΔC_{pp} are unavailable for many polymer-gas mixtures. A model must accurately predict the effective T_g profile at low gas concentrations because the skin forms on the outer edge, where the gas concentration decreases rapidly to the extent that it is negligible at the surface. In the PC-CO₂ system⁵, Chow's equation deviates from the experiment when the saturation pressure is reduced to 1 MPa. There is no proper study on the trend of effective T_g at low gas concentrations. It is necessary to experimentally measure the effective T_g at low gas concentrations to establish a better correlation between gas concentration and effective T_g .

Wesseling et al.²⁶ validated the model at different desorption times for a given foaming temperature. In contrast to minimum gas concentration-based models, the model shows deviation when desorption increases. The desorption times reported in the work are of the order of a few seconds. The first intersection point-based method had not been validated for long desorption times of the order of hours. Adams et al.¹¹ varied foaming temperature and desorption time but lacked experimental data to validate the model. In this work, we implemented the effective T_g -based model to predict skin thickness in the PC-CO₂ system. We have compared the experimental and

model results at both short and long desorption times to validate the model. We also experimentally verify the validity of predicting the skin thickness as the first intersection point in the model.

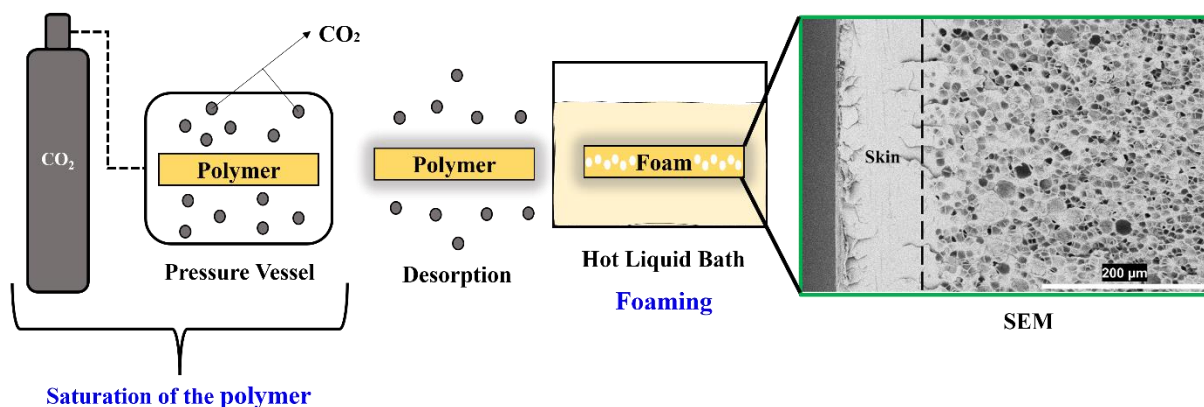


Figure 5.1 Schematic of the Solid-state foaming process along with a representative SEM image of a microcellular PC foam showing the solid skin and the cellular cores

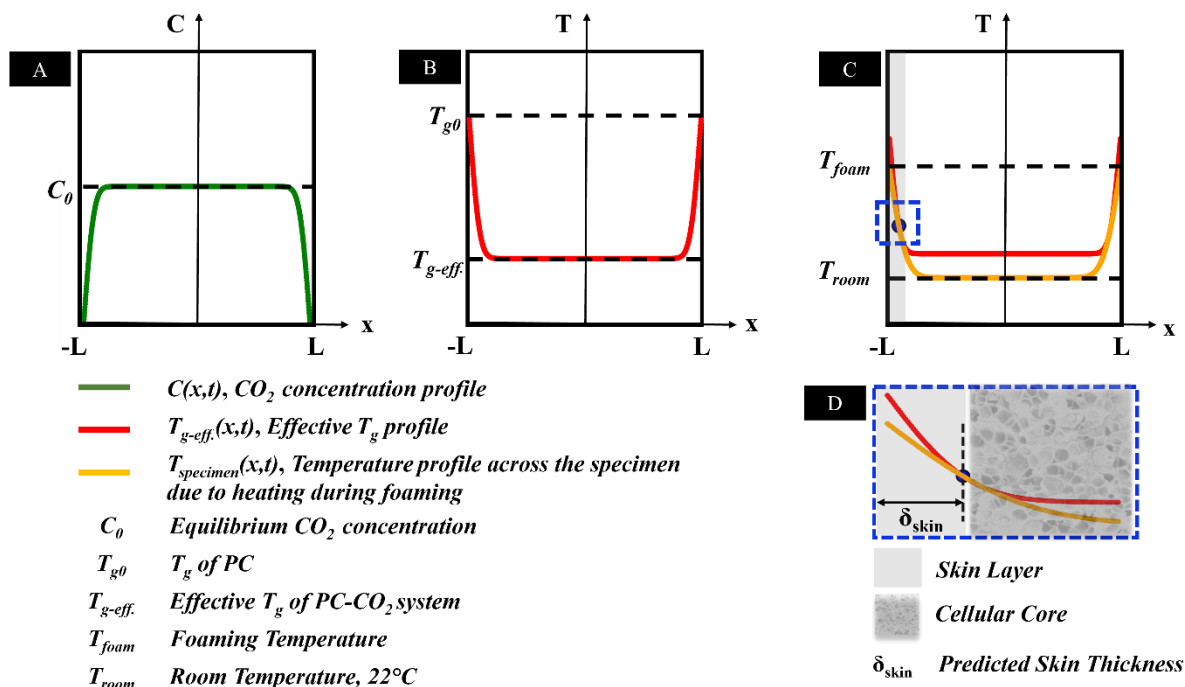


Figure 5.2 The analytical model to predict skin thickness is illustrated using a visual representation of the polymer sheet cross-section. A) Schematic showing a typical CO_2 concentration profile of a polymer-gas system after a finite desorption time. B) Schematic showing the effective T_g profile of a polymer-gas system corresponding to the CO_2 concentration profile. C) Schematic showing skin thickness being predicted as the first intersection point of the effective T_g profile and

temperature profile developed due to heating during the foaming process. D) The enclosed schematic shows the intersection point; the distance from the edge to the intersection point is predicted as skin thickness.

5.3 THEORY

Consider the cross-section of the polymer sheet thickness, as illustrated in Figure 5.2. At saturation, the CO₂ concentration is uniform across the cross-section. However, it becomes non-uniform due to diffusion after a finite desorption time, as illustrated in Figure 5.2A. Dissolving gas in the polymer reduces its glass transition temperature, T_g , to an effective T_g due to plasticization. The reduction in the T_g depends on the amount of gas dissolved in the polymer. The higher the gas concentration, the higher the reduction. The foaming temperature should be higher in the solid-state foaming process than the effective T_g for bubble nucleation to occur. However, the effective T_g is non-uniform across the cross-section due to the non-uniform gas concentration profile. This is illustrated in Figure 5.2B.

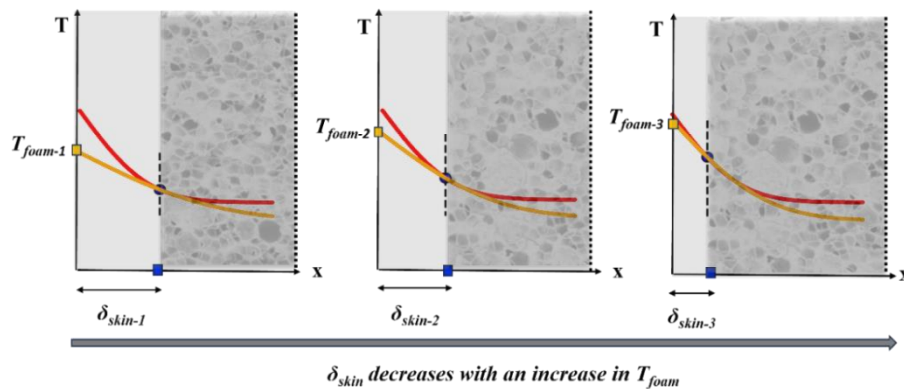


Figure 5.3 A schematic illustration of the model predicting that the skin thickness decreases with increasing foaming temperature ($\delta_{skin-1} > \delta_{skin-2} > \delta_{skin-3}$ for $T_{foam-1} < T_{foam-2} < T_{foam-3}$)

Heating during the foaming process results in an evolving temperature profile across the cross-section, as illustrated in Figure 5.2C. After a finite time during the foaming, the evolving temperature profile will intersect the effective T_g profile, as illustrated in Figure 5.2C. This is where the local specimen temperature exceeds the local effective T_g for the first time. Bubble growth begins at this point in the core region, and the outer edge remains unfoamed, forming a solid skin. Hence, skin thickness is the distance from the edge to this point. This is illustrated in Figure 5.2D. The theory also predicts that increasing the foaming temperature decreases skin thickness, as illustrated in Figure 5.3. Therefore, we can produce microcellular foams with the desired skin thickness by varying foaming temperatures.

5.4 MODEL

- a) Calculate the CO_2 concentration profile for a given diffusion coefficient, D ; desorption time, t ; and equilibrium concentration, C_0 , using the analytical solution for 1D gas diffusion across a plane sheet, equations (AII.1)²⁴ and Eq. (AII.2)²⁴. Refer to the Appendix for boundary conditions. This is illustrated in Figure 5.2A.
- b) Develop a mathematical correlation between CO_2 concentration and effective T_g . Use the correlation to convert the CO_2 concentration profile into the effective T_g profile. This is illustrated in Figure 5.2B.
- c) Calculate the evolving temperature profile, T_{specimen} , in the specimen due to heating during the foaming process for the given thermal parameters and foaming temperature, T_{foam} , by considering 1D heat diffusion across a plane sheet, Eq. (AIII). Refer to the Appendix for boundary conditions. This is illustrated in Figure 5.2C. Thermal parameters of the unprocessed polymer are used to model the heat transfer.

- d) Find the first intersection point where the T_{specimen} exceeds the effective T_g .
- e) The model parameters are listed in Table 5.1.

Table 5.1 The model for skin thickness input parameters and constants

Parameters	Value
Diffusion constant, D , cm^2/s ¹⁴	5e-08
T_g of PC ⁵ , °C	150
Thermal conductivity of PC ⁴⁹ , K , $\text{W}/\text{cm}\cdot\text{s}$	0.2e-3
Heat Capacity of PC ⁴⁹ , $J/\text{kg}\cdot\text{K}$	1.255
Density of PC ⁵⁰ , ρ , g/cm^3	1.2
Avg. Equilibrium CO_2 concentration, $\text{g}/\text{g}\%$	10.8
Nominal Desorption time, t , min	3

5.5 MATERIALS

For all the experiments, we used 1.54-mm-thick 1" x 1" square PC sheets (GE LEXAN 9030). Medical-grade CO_2 (purchased from Praxair) was used as the diluent, and silicone oil (DOWSILTM 710) was used as the foaming medium. All the foam specimens were freeze-fractured in Liquid Nitrogen (LN_2). The fractured foam cross-sections were sputter-coated with Au/Pd or Pt (4 nm – 6 nm). Then, they were analyzed under an SEM (FEI Apreo S) for imaging.

5.6 EXPERIMENTAL

5.6.1 *Effective T_g Measurement*

The effective T_g can be measured directly in a foaming experiment. It is simply the temperature at which the polymer specimen begins to foam, where the specimen's appearance changes from transparent to translucent (due to bubble nucleation and growth). The gas concentration is low near the outer edge of the sheet cross-section where the skin forms. The model must accurately predict an effective T_g profile where the skin thickness intersection point lies. Therefore, measuring the effective T_g data at low saturation pressures below 1 MPa is essential. The data will strengthen the mathematical correlation, enabling accurate prediction of the effective T_g at low gas concentrations.

In separate batches, the specimens were saturated at pressures of 0.1 MPa for 91 hours, 0.5 MPa for 119 hours, 1 MPa for 70 hours, 3 MPa for 95 hours, and 5 MPa for 69 hours. The specimens from each batch were foamed at a set of incremental foaming temperatures.

All specimens were stored in liquid nitrogen (LN_2) before foaming to minimize CO_2 loss. Upon removal from LN_2 for foaming, the specimens were allowed to thaw at room temperature for 2-3 minutes. All the specimens were weighed before foaming to record the CO_2 concentration. Any moisture condensation was removed before CO_2 concentration measurements. A foaming time of 5 minutes was set for the remaining experiments to ensure complete bubble growth throughout the cross-section.

5.6.2 *Effect of Foaming Temperature on Skin Thickness*

All the specimens were saturated at 5 MPa at room temperature for 69 hours. Immediately upon depressurization, the CO₂ concentration of one specimen from the batch was measured and taken as a reference. They were then stored in liquid nitrogen (LN₂) to minimize CO₂ loss. There was no planned desorption time. The nominal duration of depressurization and quenching in LN₂ is 3 minutes, which is considered the desorption time. Upon removal from LN₂, the specimens were allowed to thaw at room temperature for 2-3 minutes before foaming. The CO₂ concentrations were measured before foaming each specimen. The specimens were foamed at 100 °C, 110 °C, 120 °C, 130 °C, and 140 °C for 5 minutes.

5.7 RESULTS

5.7.1 Effective T_g Measurements as a function of CO_2 concentration

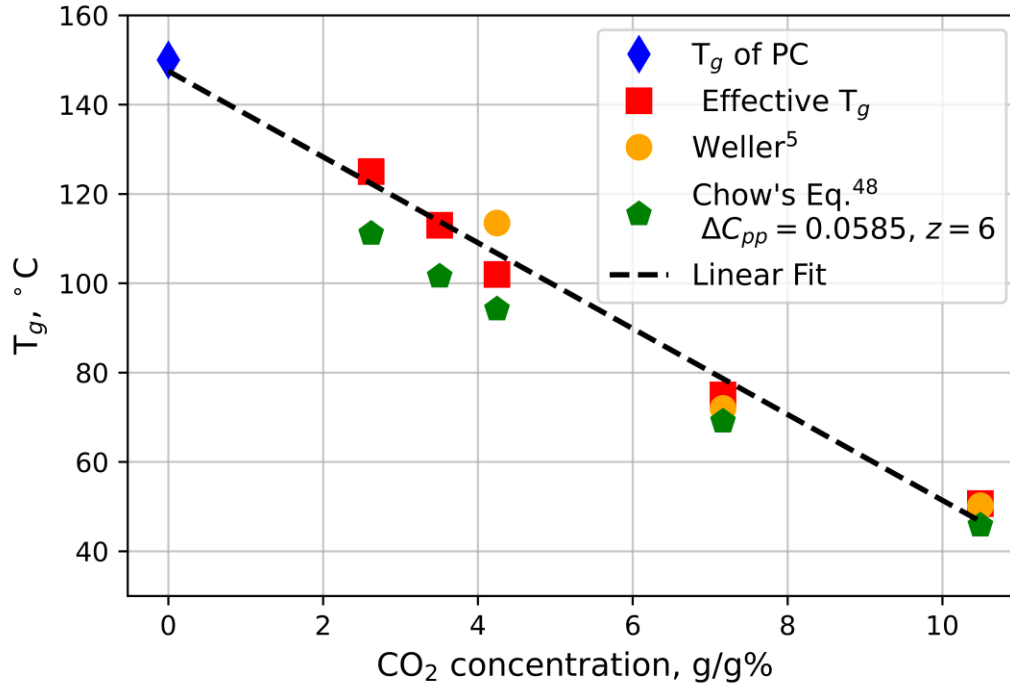


Figure 5.4 Measurements of the effective T_g of the PC- CO_2 system at different CO_2 concentrations. The measurements are compared with predictions from Chow's equation and literature data.

$$T_{g-eff}(c) = -9.6c + 147.5 \quad (5.1)$$

Where c is CO_2 concentration g/g% and T_{g-eff} is the effective T_g , °C.

Table 5.2 Experimental values of skin thickness measurements

Foaming Temperature, °C	Measured CO₂, wt.% in specimen	Average Skin Thickness, μm
100	10.22	83.9
110	10.28	53.9
120	10.26	37.0
130	10.25	27.3
140	10.29	22.3

The SEM images of the skin at different foaming temperatures are shown in Figure 5.5. To characterize the skin thickness, the SEM images were captured at three different locations on the cross-sections of each specimen. Lines perpendicular to the foam edge were drawn until they intersected the bubbles, allowing for the measurement of skin thickness. The distance from the edge to the intersection point is skin thickness. An average of 60 measurements is reported for each specimen, i.e., 20 measurements per micrograph. Figure 5.6A-C shows the model results. Figure 5.7 shows the comparison between the experimental and model results.

5.7.2 SEM Images of Skin at Various Foaming Temperatures

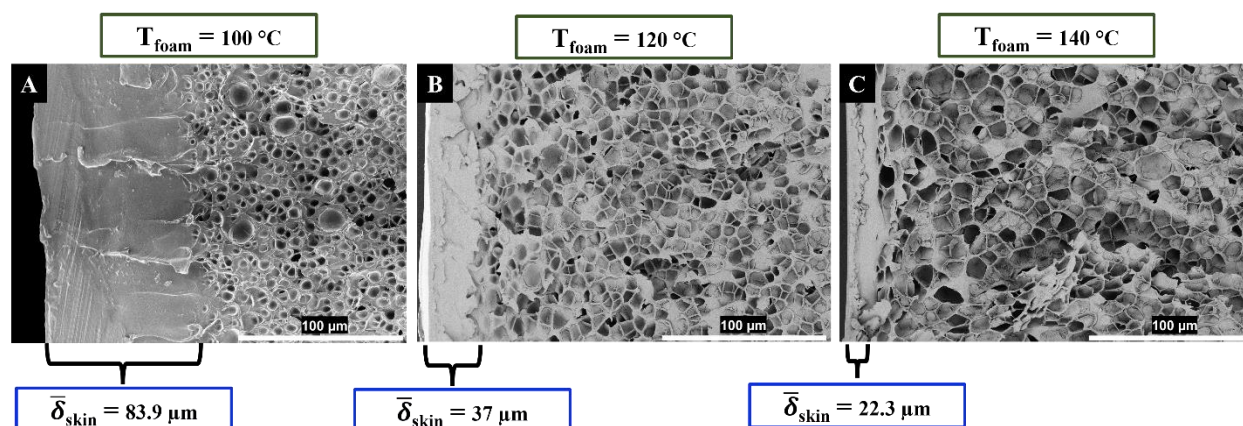


Figure 5.5 A-E) SEM images of the skin regions of microcellular PC foams. They were foamed at 100 °C, 110 °C, 120 °C, 130 °C, and 140 °C respectively. The skin thickness is decreasing with increasing foaming temperature. The values are reported in Table 5.2.

5.7.3 Model Predictions of Skin Thickness at Various Foaming Temperatures

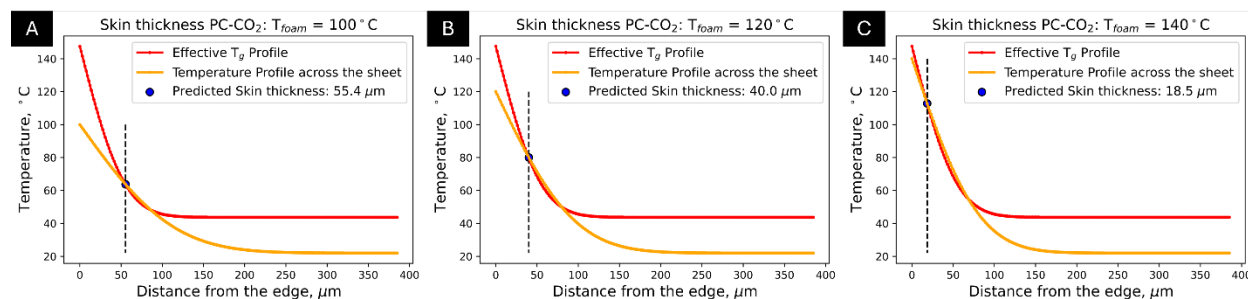


Figure 5.6 A-C) Model results at foaming temperatures 100 °C, 120 °C, and 140 °C, respectively.

The plots show the intersection point of the effective T_g profile and evolving specimen temperature profile. Increasing foaming temperature shifts the intersection point closer to the edge; therefore, predicted skin thickness decreases. Only a quarter of the cross-section is shown to highlight the intersection points.

5.7.4 Skin Thickness: Experiment Vs. Model Comparison

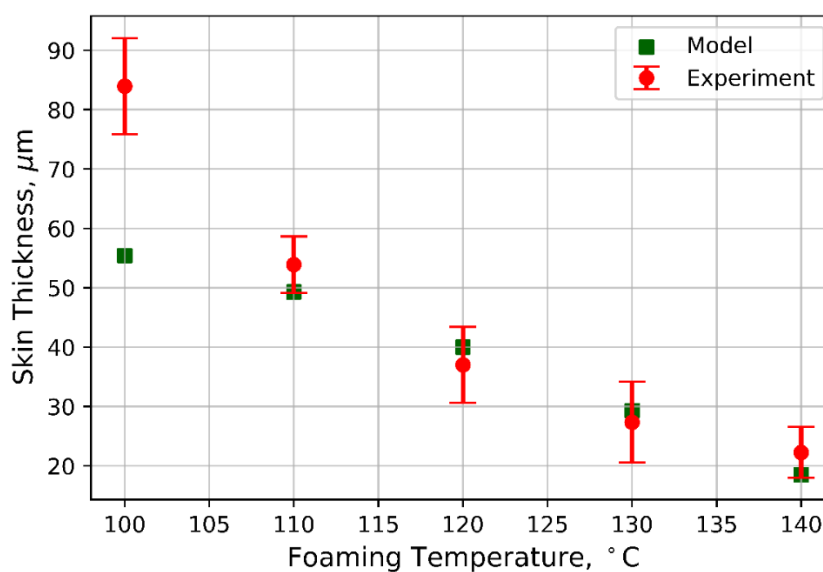


Figure 5.7 Plot compares experimental measurements and model predictions of skin thickness at various foaming temperatures.

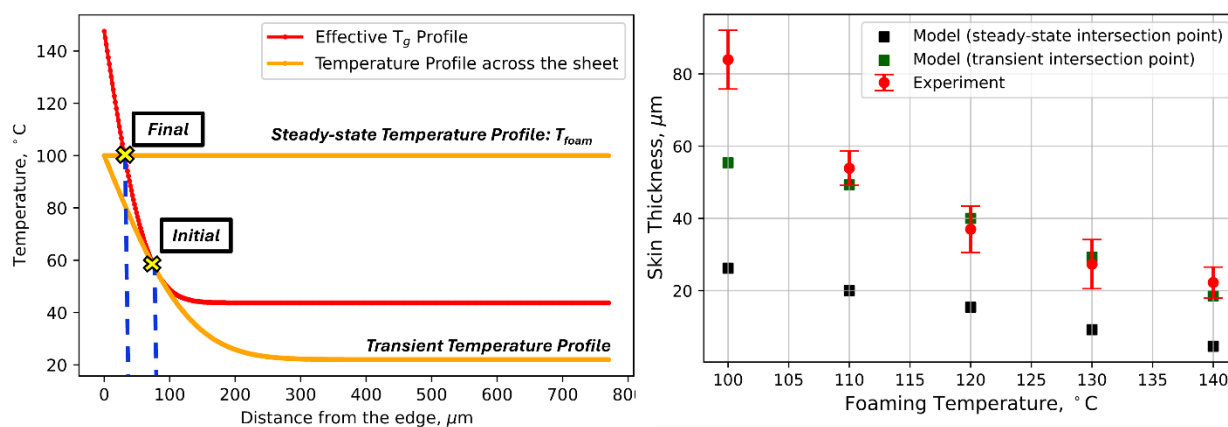


Figure 5.8 A) Plot from the model illustrating two different methods to predict skin thickness. The initial intersection point method involves the transient temperature profile intersecting the effective T_g profile. The final intersection point method involves the steady-state temperature profile

intersecting the effective T_g profile. B) Plot compares the experimental results against the model results for the two different approaches described in A).

5.8 DISCUSSION

5.8.1 *Effective T_g model as a function of CO_2 concentration*

We developed an experiment-based linear correlation to predict the effective glass transition temperature (T_g) in the PC- CO_2 system. Chow's equation⁴⁸ using parameter values reported by Weller⁵, underpredicts effective T_g values at saturation pressures below 1 MPa (refer to Figure 5.4). Therefore, Chow's equation is unsuitable for predicting effective T_g at low CO_2 concentrations. Accurately establishing effective T_g values in this low-concentration regime is critical for predicting skin thickness. The new linear correlation (5.1) presented in this work enables accurate prediction of effective T_g values in the low-concentration edge region where skin formation occurs.

5.8.2 *Experiment Vs. Model Comparison*

Experimental results indicate that skin thickness decreases as the foaming temperature increases from 100 °C to 140 °C (Figure 5.5 and Figure 5.6, and Table 5.2). When the foaming temperature increases from 100°C to 140°C, the reduction in skin thickness is 73.5%. The model shows the same trend and predicts a 66% reduction in skin thickness. The experiment and model are in good agreement. The model prediction is significantly higher than the experimental measurements at 100°C . This is due to the discrepancy in the predicted CO_2 concentration profile. This is evident from the difference between the predicted average (10.33 wt.%) and the measured CO_2 concentration (10.22 wt.%) in the specimen corresponding to 100 °C before foaming (refer to

Table 5.2). The specimen has a higher degree of desorption compared to the model. Therefore, the model under-predicts skin thickness because it predicts less CO₂ loss. This difference is expected because the desorption rate is higher during the initial period, and the diffusion coefficient used in the model is an average value. Given the dynamic nature of the skin formation during the initial desorption period, the key to reducing the error is accurately predicting the CO₂ concentration profile.

5.8.3 *Insights on Skin Formation Process*

The effective T_g model shows that the initial intersection point, where the transient temperature profile in the polymer sheet crosses the effective T_g profile, more accurately predicts skin thickness than the steady-state intersection point (refer to Figure 5.8). This offers a significant new insight into skin formation, which the previous works failed to observe and explicitly highlight. The skin formation is dynamic, and it occurs during the initial stage of the foaming process. This leads to the idea that we may be able to decouple the skin formation process from the core formation process. We can envision an experiment where we initially select a high foaming temperature to achieve a small skin thickness, followed by foaming at a desired foaming temperature to achieve different cell sizes. The foaming time study presented in Chapter 6 further investigates the skin formation process during the foaming process.

5.9 CONCLUSION

Skin thickness decreases with increasing foaming temperature. This study successfully implements and validates a one-dimensional heat and mass transfer-based effective T_g model for the PC–CO₂ system. A correlation was experimentally developed to estimate effective T_g at low

CO₂ concentrations, where predictions from Chow's equation significantly deviate from experimental observations. The model and experimental results show good agreement. Two modeling approaches were evaluated: (1) predicting skin thickness based on the initial intersection point using the transient temperature profile, and (2) predicting skin thickness based on the final intersection point using the steady-state temperature profile. Comparison with experimental data indicates that the initial intersection point method provides more accurate predictions of skin thickness. This finding reveals a key insight: skin formation occurs during the early stages of the foaming process, highlighting its dynamic nature and offering new possibilities to decouple skin formation from the formation of core structure in the foam.

5.10 ACKNOWLEDGMENTS

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Chapter 6. EVOLUTION OF THE UNFOAMED SKIN AS A FUNCTION OF FOAMING TIME IN THE SOLID-STATE FOAMING PROCESS

6.1 ABSTRACT

Foams produced through the solid-state foaming process have an outer layer of unfoamed solid skin encapsulating the cellular core. In this work, we characterized the evolution of the skin as a function of the foaming time in the PC-CO₂ system. The experimental results indicate that skin formation is instantaneous, and skin thickness is independent of foaming time when the polymer is foamed immediately after a 3-minute desorption period. However, skin formation is a continuous process, and skin thickness decreases with increasing foaming time, particularly when the desorption time is 60 minutes. The experimental results are compared with a 1D heat and mass transfer model to understand the underlying mechanism.

6.2 INTRODUCTION

The process of solid-state foaming was developed in the 1980s¹⁻³ to reduce density and plastic usage by introducing bubbles in thin-walled plastics without drastically affecting their mechanical properties. The process involves saturating the thermoplastic polymer sheets with high-pressure gas in a pressure vessel, typically CO₂ or N₂, depending on the degree of solubility. At the end of saturation, the polymer-gas system reaches equilibrium. The vessel is depressurized at this point, and the sheets are removed. These super-saturated sheets are finally quenched in a hot bath at a

specific temperature for foaming. The thermodynamic instability during the foaming process leads to the formation and growth of bubbles across the polymer matrix. This process has been studied in several polymer-gas systems, such as PC-CO₂^{4,5}, PLA-CO₂⁶, ABS-CO₂⁷, PMMA-CO₂⁸⁻¹⁰, and PEI-CO₂¹¹⁻¹³, to name a few.

Foams produced through this process have an outer layer of solid skin that encapsulates the cellular core. The development of skin is primarily due to gas desorption from the sheets upon depressurization, until foaming occurs. The time between depressurization and foaming is defined as the desorption time. Increasing desorption time leads to thicker skin as more gas diffuses from the polymer sheet. Weller¹⁴ proposed a model based on a hypothesis that bubbles cannot nucleate in the polymer matrix when the gas concentration decreases below a specific minimum limit. The model was validated on the PC-CO₂ system. Mohyeddin and Fereidoon²⁵ validated a similar model on the PS-N₂ system.

The presence of gas in the polymer matrix reduces the T_g of the polymer due to plasticization⁴⁸. The reduced T_g of the polymer-gas system is defined as an effective T_g . The bubbles will nucleate in the polymer matrix only when the foaming temperature exceeds the effective glass transition temperature (T_g). Based on this theory, Wesseling et al.²⁶. and Adams et al.²⁷ developed an effective T_g -based model to predict skin thickness. The model predicts gas concentration profiles at different desorption times across the polymer sheet using the solution to the one-dimensional mass transfer equation for an infinite planar sheet²⁴. The corresponding effective T_g profiles are predicted based on Chow's equation⁴⁸ or experimentally developed correlations. The temperature

profile across the specimen as a function of foaming time is computed using the solution to the one-dimensional heat diffusion equation for an infinite planar sheet²⁴.

The model identifies the point where the effective T_g and growing temperature profile intersect to predict skin thickness. The intersection point physically represents the point in the polymer matrix where the local temperature has exceeded the local effective T_g , facilitating bubble nucleation. Hence, the distance from the edge to this point is predicted to be the skin thickness. As the growing temperature profile reaches the steady-state temperature, the foaming temperature, there is more than one possible intersection point.

In the recent study by Sridhar et al.²⁸ to validate the model, skin thickness is predicted as the intersection point where the temperature profile generated due to heating during the foaming process first intersects the effective T_g profile. Locally, this is the point in the cross-section where the local temperature exceeds the effective T_g for the first time during the foaming process. The study reports an overprediction of skin thickness; however, the prediction and experimental results generally agreed.

However, whether the skin thickness is established at this first intersection point remains to be verified. The model assumes that the gas concentration profile remains constant during the time it takes for the specimen to achieve a uniform temperature. Hence, the effective T_g profile remains unaffected during the foaming process in the model. As foaming proceeds, the temperature profile develops until it reaches a steady state, where the temperature becomes uniform throughout the cross-section, equal to the foaming temperature. When the temperature profile grows, the

intersection points shift toward the edge of the cross-section. Therefore, according to the model, theoretically, there is a possibility that the skin thickness should decrease with the foaming time and reach a final value when the temperature reaches a steady state. This is illustrated in Figure 6.1, using the model results.

In this study, we experimentally characterize the evolution of skin in the PC-CO₂ system during the foaming process by measuring skin thickness at different foaming times. We considered two cases for desorption time: small desorption times, where the saturated specimens were foamed immediately after depressurization, and larger desorption times, where the saturated specimens were allowed to desorb for a specific amount of time before foaming. We utilize the model developed by Sridhar et al.²⁸ to predict skin thickness at different foaming times. The model facilitates an understanding of the skin formation mechanism as the foaming process is completed.

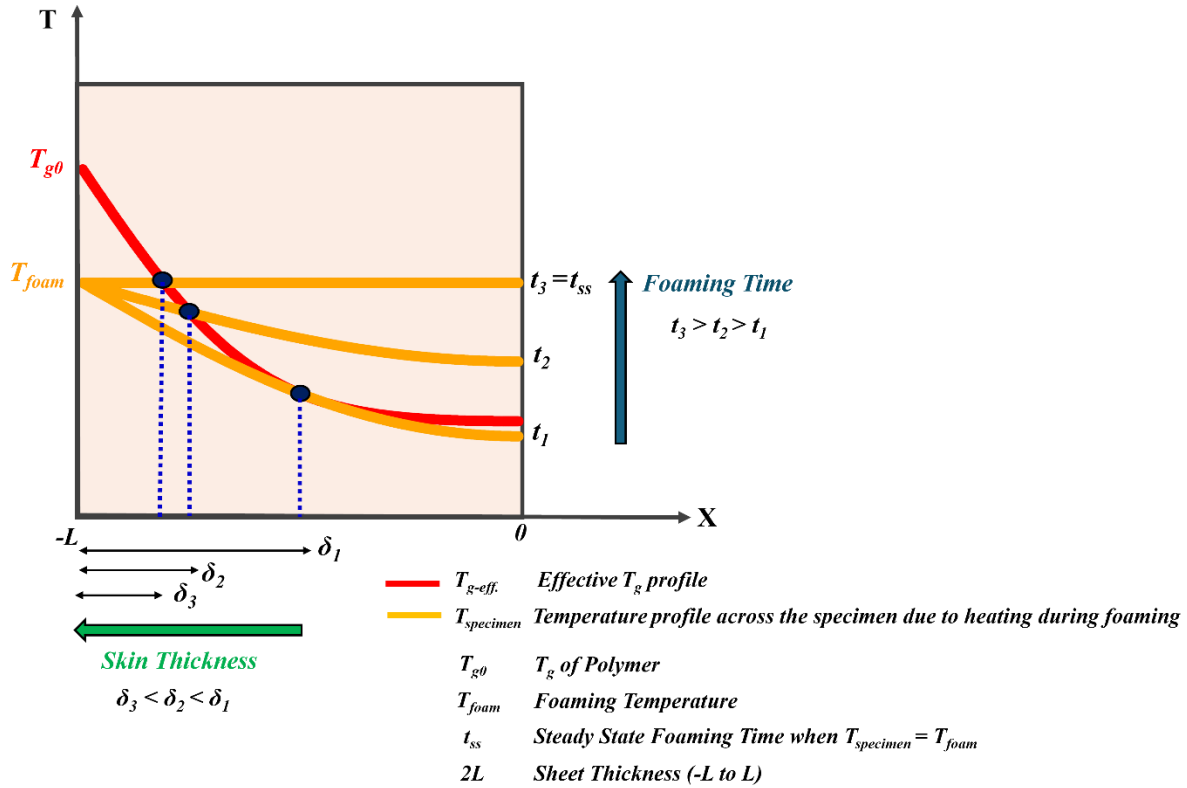


Figure 6.1 A model showing the predicted skin thickness variation with foaming time, with an example of the PC-CO₂ system, is shown in the figure. The computed temperature profiles across the sheet at different foaming times are shown against the effective T_g profile. The intersection points denote the skin thickness, which decreases with foaming time as the temperature profile reaches a steady state. δ_3 is the final skin thickness.

6.3 MATERIALS

For all the experiments, we used 1.54-mm-thick 1" x 1" square PC sheets (GE LEXAN 9030). Medical-grade CO₂ (purchased from Praxair) was used as the diluent, and silicone oil (DOWSIL™ 710) was used as the foaming medium.

6.4 EXPERIMENT

The effect of foaming time was characterized by considering two different desorption time cases. PC specimens were saturated at 5 MPa for 70 hours to achieve equilibrium. At the end of equilibrium, they were removed from the pressure vessel and separated into two batches. In Case 1, the specimens were foamed immediately with a nominal desorption time of 3 min. In Case 2, the specimens were foamed after a desorption time of 60 min. As listed below, they were foamed in the oil bath at 100°C for different foaming times.

Case 1 - Foaming time: 3s, 10s, and 300s

Case 2 - Foaming time: 3s, 5s, 10s, 30s and 300s

All the specimens were freeze-fractured in Liquid N₂ to expose the cross-section. The cross-section was sputter-coated with a 4 nm-5nm thick layer of Pt and analyzed under the SEM (FEI Apreo). Skin thickness measurements were made at two different locations on the cross-section.

6.5 MODEL

The model and the input parameters used are from an earlier study by Sridhar et al.²⁸, except for the equilibrium CO₂ concentration in this experiment, which was measured at 11% g/g.

6.6 RESULTS

6.6.1 Case 1

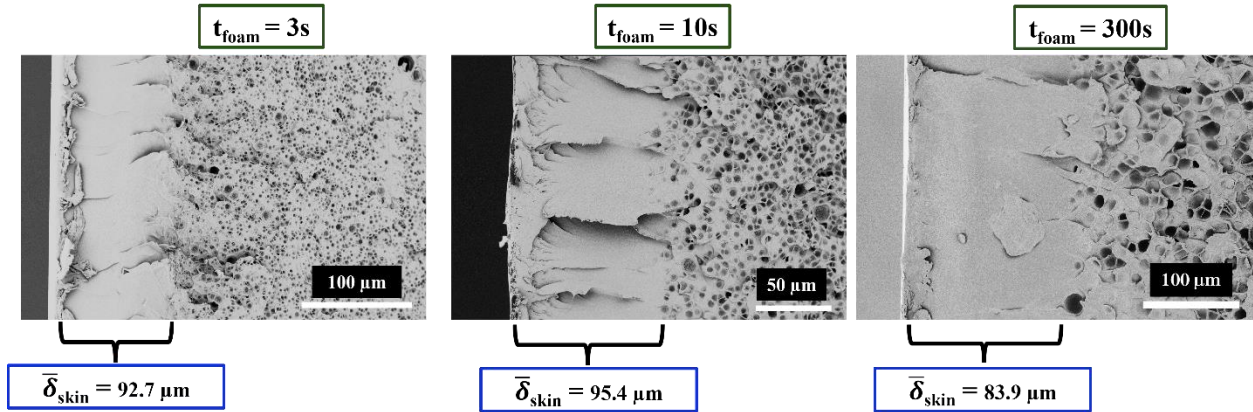


Figure 6.2 SEM micrographs showing the skins of microcellular PC foams foamed at 100°C for 3s, 10s, and 300s, respectively, after a nominal desorption time of 3 min (Case 1).

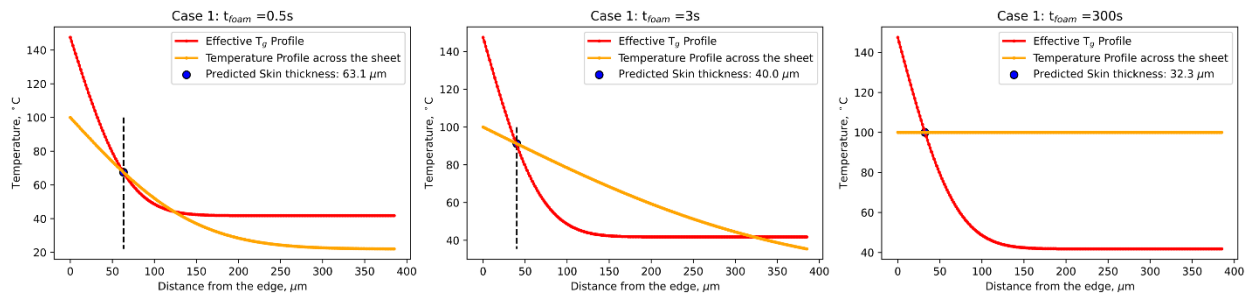


Figure 6.3 Predicted skin thickness values at the set foaming times of 0.5s, 3s, and 300s for a desorption time of 3 min (Case 1).

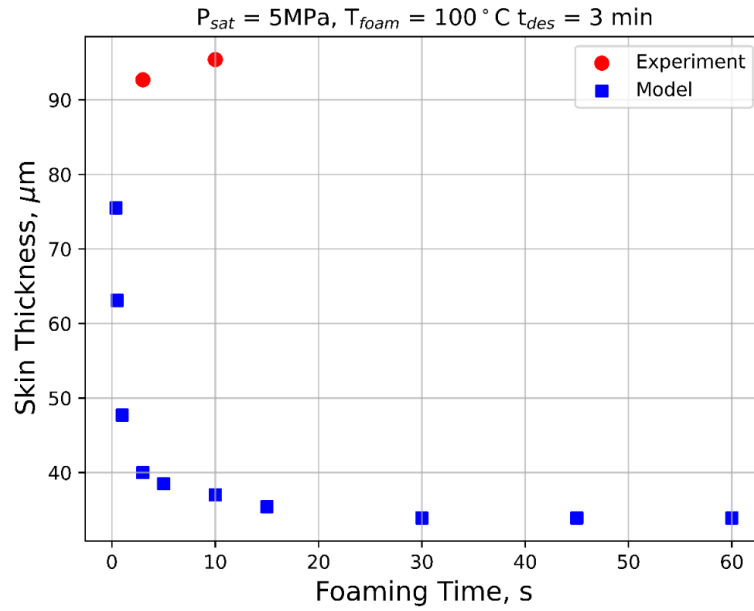


Figure 6.4 A plot compares the experiment and model skin thickness values at different foaming times for the PC-CO₂ system saturated at 5 MPa and foamed after a nominal desorption time of 3 min (Case 1) at a foaming temperature of 100°C.

6.6.2 Case 2

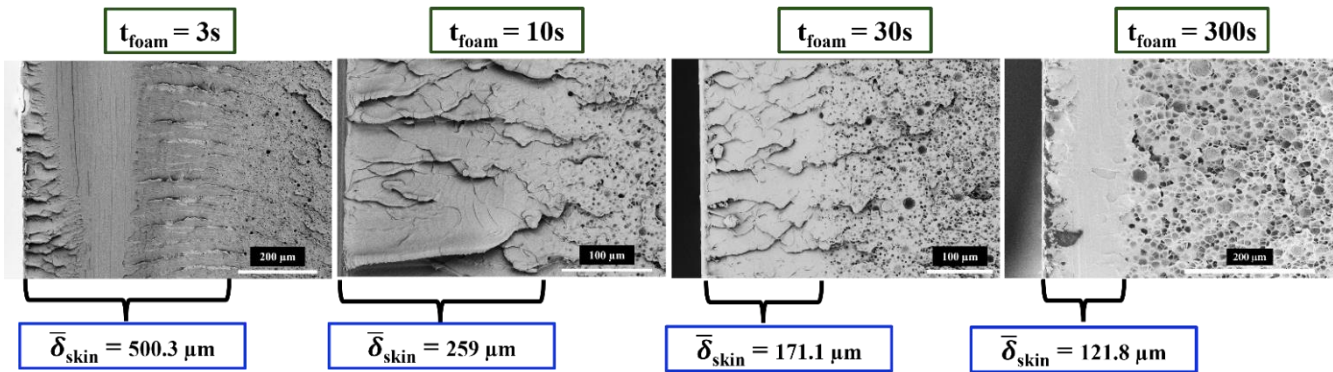


Figure 6.5 SEM micrographs showing the skins of microcellular PC foams foamed at 100°C for 3s, 5s, 10s, and 30s, respectively, after a desorption time of 60 min.

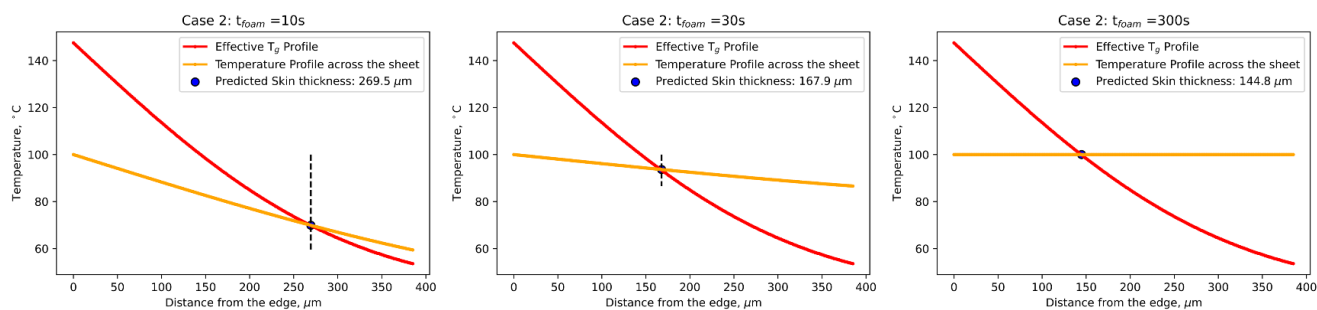


Figure 6.6 Predicted skin thickness values at set foaming times of 10s, 30s, and 300s for a desorption time of 60 min (Case 2).

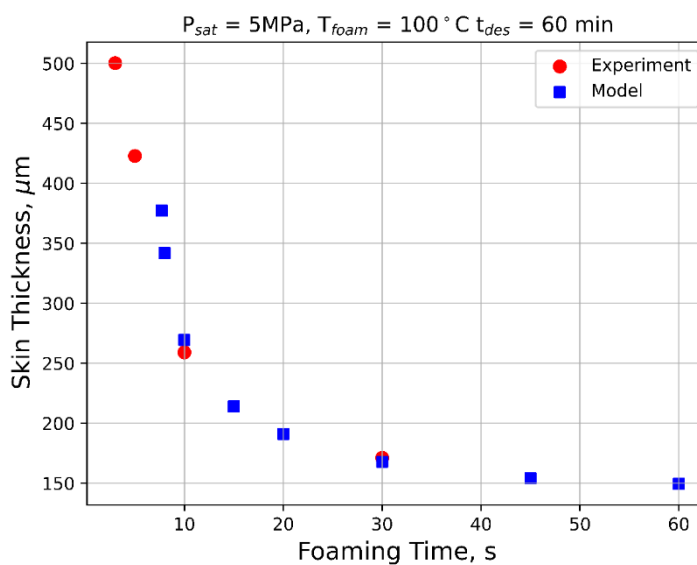


Figure 6.7 Plot comparing the experiment and model skin thickness values at different foaming times for the PC-CO₂ system saturated at 5 MPa, foamed after a desorption time of 60 min at a foaming temperature of 100°C.

6.7 DISCUSSION

6.7.1 *Effect of Foaming Time: Experiment and Model Comparison*

The model predicts a decrease in skin thickness with foaming time in Cases 1 and 2. However, the key difference is that the predicted rate of decrease is significantly higher in Case 1 than in Case 2, as shown in the FiguresFigure 6.4 and Figure 6.7.

Case 1: 3 min of CO₂ Desorption

The SEM images in Figure 6.2 show that skin thickness does not change significantly with foaming time. Experimental results show that skin thickness is established instantaneously and independently of foaming time and does not follow the predictions shown in Figure 6.4. This implies that at low desorption times, the skin thickness is established during the initial stages of the foaming process when the local temperature in the polymer matrix exceeds the local effective T_g for the first time. In the model, this is the point where the temperature profile intersects the effective T_g profile for the first time. Therefore, the experimental results validated the proposed model to predict skin thickness in the previous study²⁸, where the desorption time was 3 min.

Case 2: 60 min of CO₂ Desorption

In Case 2, according to the model, the first skin thickness is established only after a foaming time of 8s, whereas experimentally, we observe skin at a foaming time of as low as 3s. However, the model and the experiment agree at higher foaming times. The SEM images from the experiment in Figure 6.5 show a continuous evolution of skin thickness and a decrease with foaming time. The

experimental results closely follow the predicted skin thickness at different foaming times. Skin development is complete, and the skin thickness reaches a final value when the growing temperature profile in the specimen reaches a steady state. Therefore, the model implemented by Sridhar et al.²⁸ It is not validated if the desorption time is in the order of hours, and skin thickness at the steady-state intersection point should be used as the prediction.

6.7.2 *Skin Development in Solid-State Foaming Process*

The skin thickness should decrease with foaming time as the growing temperature profile in the specimen becomes uniform and reaches a steady state. As the temperature reaches the steady state in the polymer, the intersection points between the temperature and effective T_g profiles shift towards the edge during the foaming process. New bubbles nucleate and grow in the polymer, expanding the cellular core region towards the edge. Therefore, skin thickness decreases with foaming time. The extent of the expansion of the cellular core towards the edge at the end of the foaming process determines the final skin thickness for the given conditions. This is described in Figure 6.8.

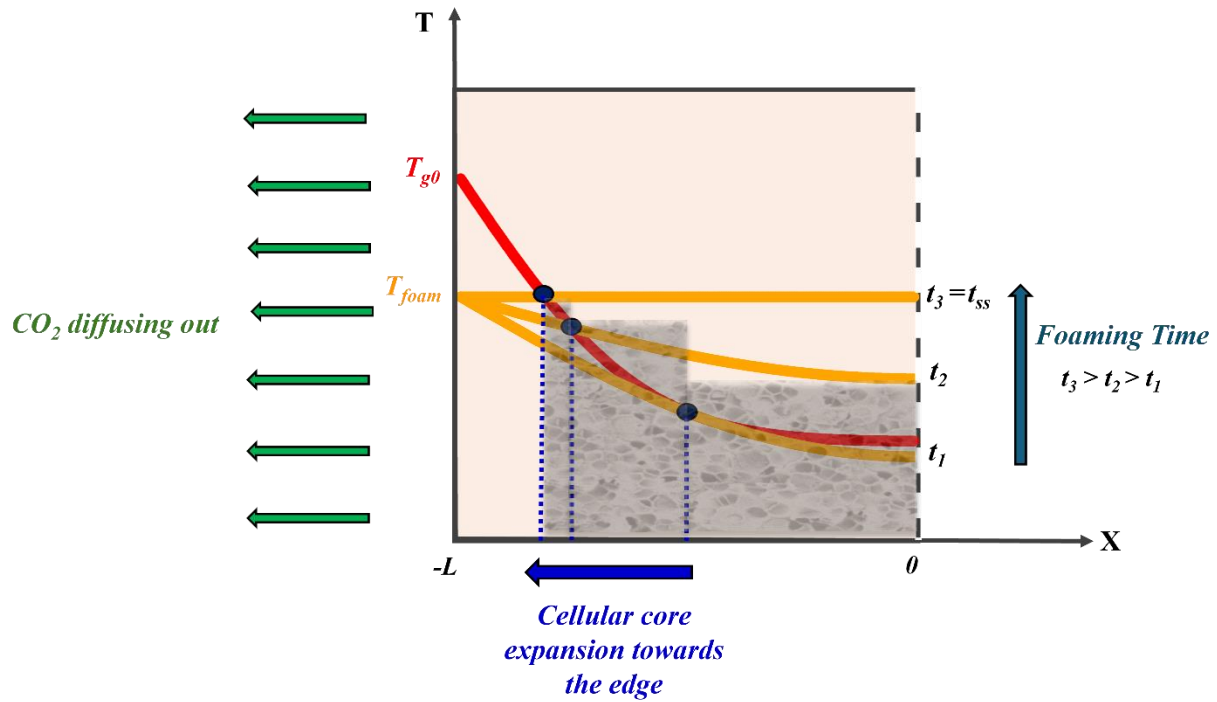


Figure 6.8 This figure depicts the expansion of the cellular core towards the edge during the foaming process, using model results based on the PC-CO₂ system.

6.7.3 Evolution of Skin: Case 1 and Case 2 Comparison

Case 1

The diffusion rate is higher during the initial desorption period as the CO₂ concentration decreases exponentially. The rate of CO₂ diffusion is relatively faster in Case 1 due to the short desorption time, and the CO₂ concentration decreases drastically at the edge. The predicted CO₂ concentration profile in the model is based on an average diffusion coefficient. Therefore, the predicted CO₂ concentration closer to the edge will be more than the actual concentration. As a result, the actual effective T_g is higher than predicted, implying that the temperature required to nucleate bubbles closer to the edge is also higher. Furthermore, the linear correlation²⁸ used to predict the effective

T_g is based on data measured at saturation pressures ranging from 0.1 MPa to 5 MPa, with no data available below 0.1 MPa, where CO_2 concentrations are very low. However, we extend this correlation, assuming its accuracy, to predict the effective T_g profile at severely low CO_2 concentrations within the polymer matrix, specifically in the region close to the edge where the skin forms.

In Case 1, the model predicts a final skin thickness of 34 μm at the end of the foaming process when the temperature in the polymer reaches a steady state. To establish this skin thickness, we must note that the process should produce bubbles close to the edge. However, the observed skin thickness at the end of foaming, corresponding to a foaming time of 300s, is 84 μm ²⁸, which is higher than the prediction. The skin thickness, as observed, does not decrease significantly with the foaming time. This shows that a foaming temperature of 100°C cannot nucleate bubbles and cause core expansion towards the edge to reduce skin thickness below 84 μm . Therefore, the core stops expanding during the initial stages of the foaming process, and the skin thickness is established early. To further propagate the core expansion towards the edge to reduce skin thickness, the temperature should be above 100°C. Skin thickness decreases with increasing foaming temperature as more bubbles nucleate due to an enhanced decrease in CO_2 solubility in the polymer at higher temperatures (Figure 6.9A,B). Experimental results show that skin thickness as low as 22.3 μm can be achieved by increasing the foaming temperature to 140°C (Figure 6.9A)²⁸. The experimental skin thickness values are reported in Figure 6.9A for different foaming temperatures for desorption times 3 min (Case 1)²⁸ and 60 min (Case 2). The differences in skin thickness values between the two cases decrease as we increase the foaming temperature. Hence, foaming temperature has a dominant effect on reducing skin thickness. The skin thickness values

plateau at higher foaming temperatures, indicating a lower limit. The impact of temperature on CO₂ solubility at different temperatures in PC is shown in Figure 6.9B¹⁴. The CO₂ solubility in PC decreases with an increase in temperature³⁵.

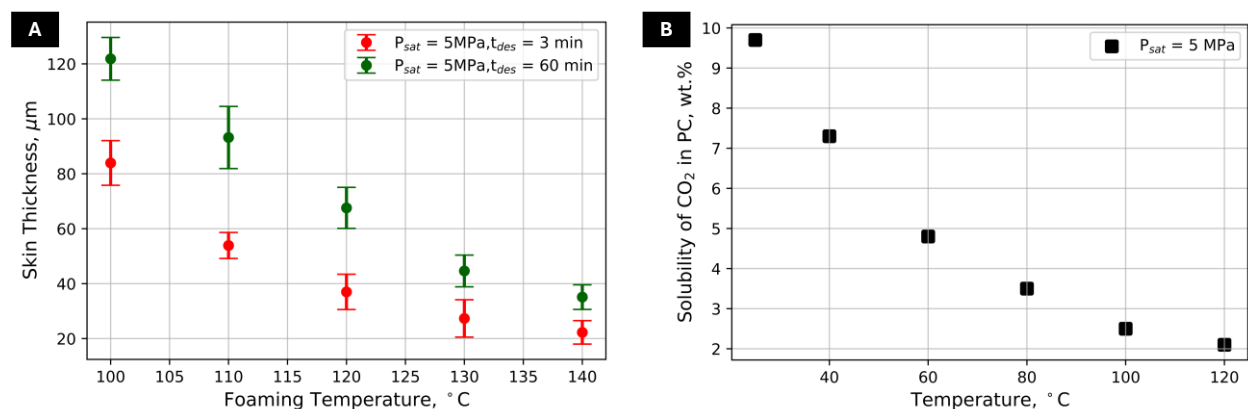


Figure 6.9 A) Experimental skin thickness values at different foaming temperatures after 3 min of desorption (Case 1)²⁸ and 60 min of desorption (Case 2). B) CO₂ solubility in PC³⁵ at different temperatures.

Case 2

In Case 2, the diffusion rate is slower. However, after 60 minutes of desorption, a substantial amount of CO₂ is lost, influencing the effective T_g profiles. Due to the characteristics of these profiles, core expansion toward the edge initiates later in the foaming process. It occurs further from the edge in Case 2 compared to Case 1, as illustrated in Figure 10. This is supported by the experimental results, where after 3 seconds of foaming, the observed skin thickness in Case 2 is 500 μm (Figure 6.5), in contrast to 93 μm in Case 1 (Figure 6.2). This considerable difference facilitates continuous core expansion and a progressive reduction in skin thickness throughout the foaming process in Case 2, as depicted in Figure 6.10 .

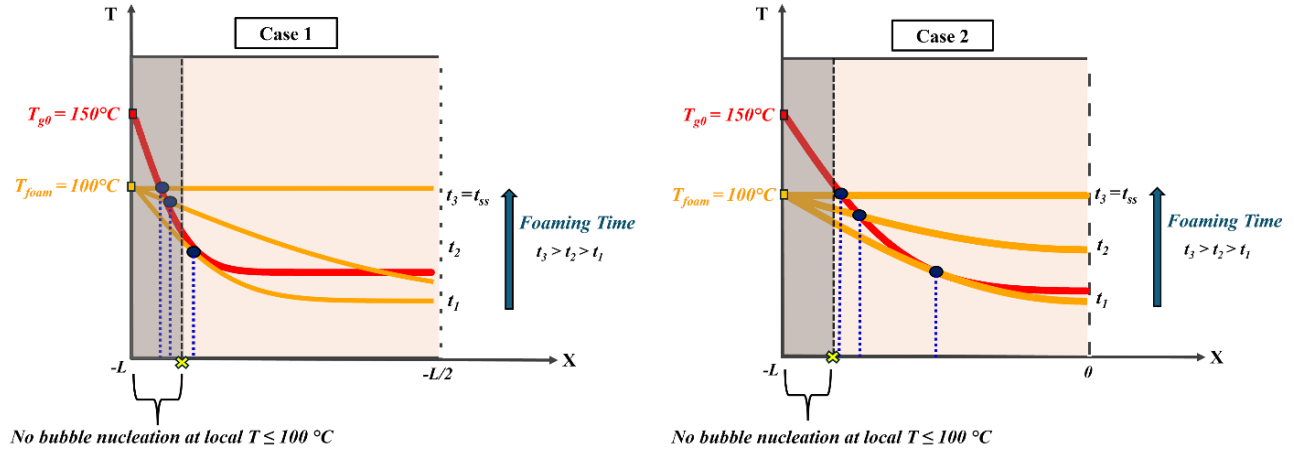


Figure 6.10 Model results show skin evolution in Cases 1 and 2. *Left*: Shows a quarter of the thickness of the polymer cross-section with the calculated effective T_g and temperature profiles for Case 1 conditions, highlighting that the core expansion starts closer to the edge and ends during the initial stages of the foaming process, as bubbles cannot nucleate at a local temperature of 100°C . *Right*: Shows half of the thickness of the polymer cross-section with the calculated effective T_g and temperature profiles for Case 2 conditions, highlighting that the core expansion starts farther away from the edge and ends when the temperature profile reaches the steady-state stage.

6.8 CONCLUSION

This study highlights the challenges in nucleating bubbles closer to the edge to reduce skin thickness. We compared the effect of foaming time on the evolution of skin thickness in two cases for a saturation pressure of 5 MPa and a foaming temperature of 100°C . In Case 1, the desorption time is 3 min. The model predicted a rapid decrease in skin thickness with foaming time. The experimental results did not agree with the model, and skin thickness remained constant with the foaming time. The model indicates that the bubble nucleation and subsequent core expansion

towards the edge begin closer to the edge. As the core region expands towards the outer edge, the CO_2 concentration rapidly decreases. Foaming temperature of 100°C is insufficient to nucleate bubbles in the vicinity of the outer edge. The experimental results clearly show that to reduce skin thickness, the foaming temperatures should be higher and closer to the T_g of the unprocessed polymer. Since skin thickness does not decrease with foaming time, using the initial intersection point method to predict skin thickness at short desorption times agrees well with the experiment.

In Case 2, the desorption time is 60 min, and the experimental results show that skin thickness reduces with foaming time. The model shows that bubble nucleation and subsequent core expansion towards the edge begin relatively far away from the edge. This allows the core expansion to occur in a region with sufficient CO_2 concentration to cause a continuous reduction in skin thickness with foaming time. The skin formation also begins relatively later during the foaming process. Since skin thickness decreases with foaming time, using the steady-state intersection point method to predict skin thickness at long desorption times will agree well with the experiment.

Chapter 7. SKINLESS MICROCELLULAR AND NANOCELLULAR FOAMS THROUGH NOVEL PLASMA TREATMENT- BASED SOLID-STATE FOAMING PROCESS

7.1 ABSTRACT

Microcellular and nanocellular foams produced through the solid-state foaming process have a solid skin encapsulating the cellular core. Over the years, solid-state foaming has enabled the fabrication of various microcellular and nanocellular structures across several polymer-gas systems. These include transparent foams, open-celled nanocellular foams with specific pore sizes ranging from 10 to 100 nm, and microcellular foams with unique secondary nanopores (10-80 nm) on the cell walls. The presence of a solid skin layer obstructs access to the internal cellular structure, which could otherwise be characterized for filtration properties. We present a novel method to produce skinless microcellular and nanocellular polymer foams through a plasma treatment-based solid-state foaming process using a low-temperature atmospheric plasma system. We demonstrate a decoupled method for reprocessing prefabricated foam with a solid skin, making the skin porous and allowing access to the open-porous core structure by partially re-saturating the skin with CO₂, followed by plasma treatment. An Acetone dye penetration test confirmed that the newly created porous skin is interconnected to the open-porous core. This powerful technique is a promising way forward to access the core by making the skin porous. The novel plasma treatment-based solid-state foaming process can be used to produce skinless foams with unique structures, suitable for advanced filtration applications.

7.2 INTRODUCTION

The solid-state foaming process produces foams with a solid skin¹⁴ that encapsulates the cellular core. The solid skin prevents direct access to the internal microcellular and nanocellular structures. Hence, it is challenging to characterize the internal micro- and nanostructures and understand how they affect the material properties. Through years of research, we have established processes that can produce unique microcellular and nanocellular structures in various polymer–gas systems. However, eliminating the solid skin remains a significant challenge. To fully characterize the internal cellular structure and study the transportation properties for applications such as filtration, it is essential to eliminate or avoid skin formation. There are two main approaches: (1) remove the skin layer during or after foaming, or (2) develop process conditions that directly produce skinless foams.

Typically, researchers machine the skin from the foamed sheets to measure properties such as open-cell content, density, and transport properties. This process is tedious and can damage the underlying porous structure. Nicolae¹⁷ machined holes in the skin to access the nanocellular structure produced in PEI foams and characterized the transportation properties. The other approach is to laminate the primary polymer sheet between solvent-soluble or removable sacrificial thin secondary polymer sheets, which act as a gas diffusion barrier and help reduce gas desorption. This sandwiched polymer stack is then saturated and foamed. Cuadra-Rodriguez et al.³¹ produced skinless PMMA foam using a water-soluble 50 μm PVOH film as the gas barrier. Jiang et al.⁵¹ produced skinless TPU foam using 40–50 μm PI film as the gas barrier. Wang et al.³⁰ produce skinless PVDF foaming using an elastic film with a gas barrier. Kakumanu and Srinivas

Sundaram⁵² covered the PEI sheets with 3 layers of 10 μm PVC films to reduce CO_2 loss, saturated them, and foamed using a laser after 45 minutes of desorption. The PVC films were removed before laser irradiation. The SEM images⁵² reveal a conical-shaped foamed channel along the laser path, indicating laser ablation, and surface pores are present, but with excessive roughness and damage due to the ablation process. Another approach is to perform an in-situ foaming inside the pressure vessel when the polymer sheets are saturated with gas. Theoretically, this process can prove effective as in-situ foaming can produce uniformly porous foam without solid skin.

This chapter presents our recent advancements in producing skinless microcellular and nanocellular foams through a novel plasma treatment-based solid-state foaming process utilizing a commercially available atmospheric pressure low-temperature plasma jet system.

7.3 EXPERIMENTAL

7.3.1 Plasma Treatment-Based Solid-State Foaming Process

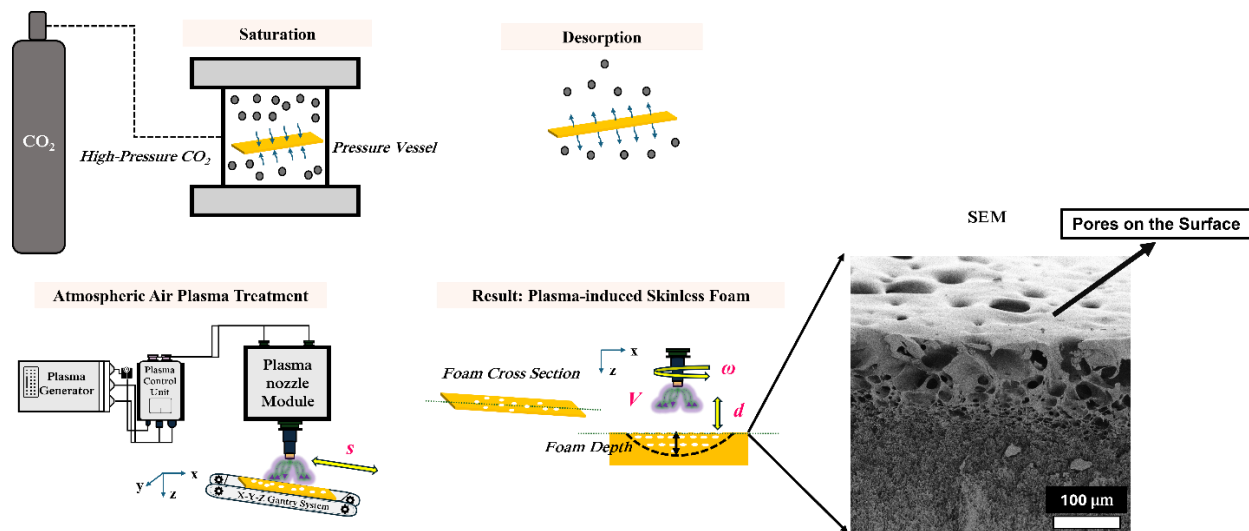


Figure 7.1 A schematic of the Plasma Treatment-based Solid-State Foaming Process illustrating different steps involved. A representative SEM images showing a porous surface created by plasma

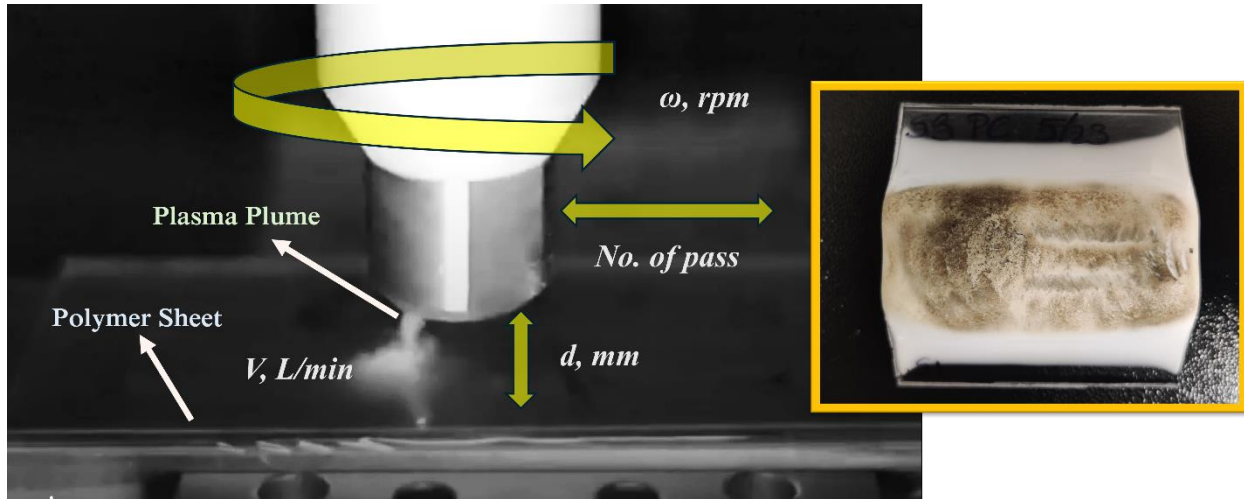


Figure 7.2 An actual illustration of the experimental setup of the air plasma treatment of a polymer sheet. The key parameters controlled during the Plasma-Induced Foaming Process are shown. V – Flow Rate L/min, ω – RPM, d – Standoff Distance mm, and s – Speed of Translation mm/s. The inset shows the surface of a microcellular PC foam produced through plasma treatment.

7.3.2 Plasma Treatment in PC-CO₂ System

Five specimens of 2 in x 2 in - 1.56 mm-thick PC (GE Lexan 9030) sheets were saturated with CO₂ under a pressure of 5 MPa in a pressure vessel at room temperature. After 72 hours, the specimens reached equilibrium and were removed from the pressure vessel. The specimens were stored in liquid N₂ to reduce CO₂ loss due to desorption until the foaming process. Before foaming, the specimens were thawed at room temperature for 1 to 2 minutes.

The specimen surface was exposed to an atmospheric plasma jet (Plasmatrete OpenAIR) system, which translated across the surface to induce foaming, as shown in Figure 7.1 and

Figure 7.2. To achieve the required surface temperature conditions, the key parameters of the plasma system, including initial standoff distance, flow rate, and number of passes, were varied. At the same time, the nozzle rpm and speed were fixed across the specimens. The plasma system parameters are listed in Table 7.1.

Table 7.1 Parameters to produce skinless microcellular PC foam

Specimen ID	Nozzle RPM, ω	Flow Rate (L/min), V	Number of Pass, N	Initial Standoff Distance (mm), d	Translation Speed (mm/s), s
PC_1	1000	23	6	11	50

7.3.3 Plasma Treatment in PEI-CO₂ System

Five specimens of 2 in x 2in - 0.5 mm-thick PEI (SABIC Ultem 1000) sheets were saturated with CO₂ under a pressure of 5 MPa in a pressure vessel at room temperature. After 48 hours, the specimens reached equilibrium and were removed from the pressure vessel. The specimens were stored in liquid N₂ to reduce CO₂ loss due to desorption until the foaming process. Before foaming, the specimens were thawed at room temperature for 1 to 2 minutes.

The specimen surface was exposed to an atmospheric plasma jet system (Plasmamatreat OpenAIR), which translated across the surface as shown in Figure 7.1 and

Figure 7.2. To achieve the desired surface temperature conditions, the key parameters: initial standoff distance, flow rate, and number of passes, were varied. At the same time, the nozzle rpm and speed were fixed across the specimens. The plasma system parameters are listed in Table 7.2.

Table 7.2 Parameters to produce skinless nanocellular PEI foam

Specimen ID	Nozzle RPM, ω	Flow Rate (L/min), V	Number of Pass, N	Initial Standoff Distance (mm), d	Translation Speed (mm/s), s
PEI_1	1000	23	4	5	50

7.3.4 *Selective Plasma Treatment-based Foaming of Skin to Access the Core*

The goal was to create porous skin from a prefabricated foamed sheet with a known skin thickness, cell structure, and density. The foam sheet will be partially re-saturated, so only the solid skin can absorb CO₂. The partially saturated sheet will then be subjected to plasma treatment to create a porous skin and surface.

Three specimens of prefabricated nanocellular PEI sheets with solid skin were partially re-saturated with CO₂ under a saturation pressure of 5 MPa for 2 hours. Following this, the specimens are stored in liquid N₂. The partially saturated foam sheets were exposed to an atmospheric plasma jet system (Plasmatreat OpenAIR), which was translated across their surface, as shown in Figure 7.1 and

Figure 7.2. The nanocellular PEI sheets were previously prepared by saturating the unprocessed PEI sheets at 4.5 MPa and then foaming them in a hot bath at 170°C using the conventional solid-state foaming process. The foam sheet has a skin thickness of approximately 15 µm, as shown in Figure 7.3. The plasma parameters are listed in Table 7.3.

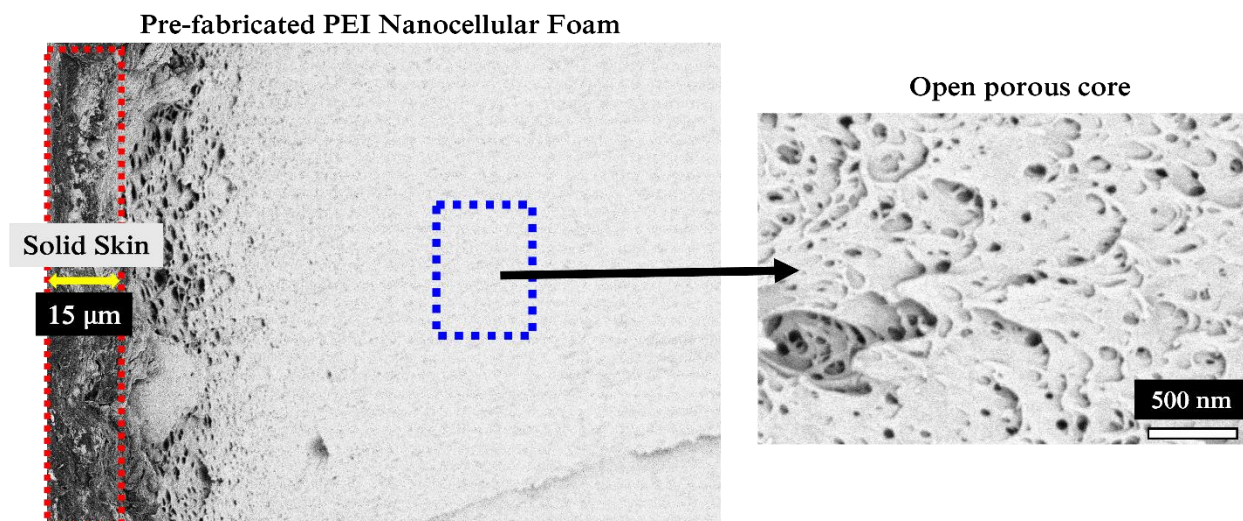


Figure 7.3 SEM image of PEI nanocellular foam sheet with a solid skin of approximately 15 μm , saturated at 4.5 MPa, and foamed at 170°C. The core structure is open-porous.

Table 7.3 Parameters to create a porous skin to access the core in the nanocellular PEI sheet

Specimen ID	Nozzle RPM, ω	Flow Rate (L/min), V	Number of Pass, N	Initial Standoff Distance (mm), d	Translation Speed (mm/s), s
PEI_2	1000	23	4	11	50

7.3.5 Effect of Saturation Pressure on Plasma Treatment-based Solid State Foaming Process

Two specimens of 1.56 mm-thick PC (GE Lexan 9030) sheets were saturated with CO₂ under a pressure of 1 MPa in a pressure vessel at room temperature. After 72 hours, the specimens reached equilibrium and were removed from the pressure vessel. The specimens were stored in liquid N₂ to reduce CO₂ loss due to desorption until the foaming process. Before foaming, the specimens were thawed at room temperature for 1 to 2 minutes. The specimen surface was exposed to an

atmospheric plasma jet (Plasmatreat OpenAIR) system, translating across the surface to induce foaming, as shown in Figure 7.1 and

Figure 7.2. The plasma system parameters are listed in Table 7.4.

Table 7.4 Plasma system parameters for plasma-induced foaming of microcellular PC at 1 MPa

Specimen ID	Nozzle RPM, ω	Flow Rate (L/min), V	Number of Pass, N	Initial Standoff Distance (mm), d	Translation Speed (mm/s), s
PC_2	1000	23	6	11	50
PC_3	1000	23	12	11	50

7.4 RESULTS

7.4.1 *PC-CO₂ System: Skinless Microcellular PC*

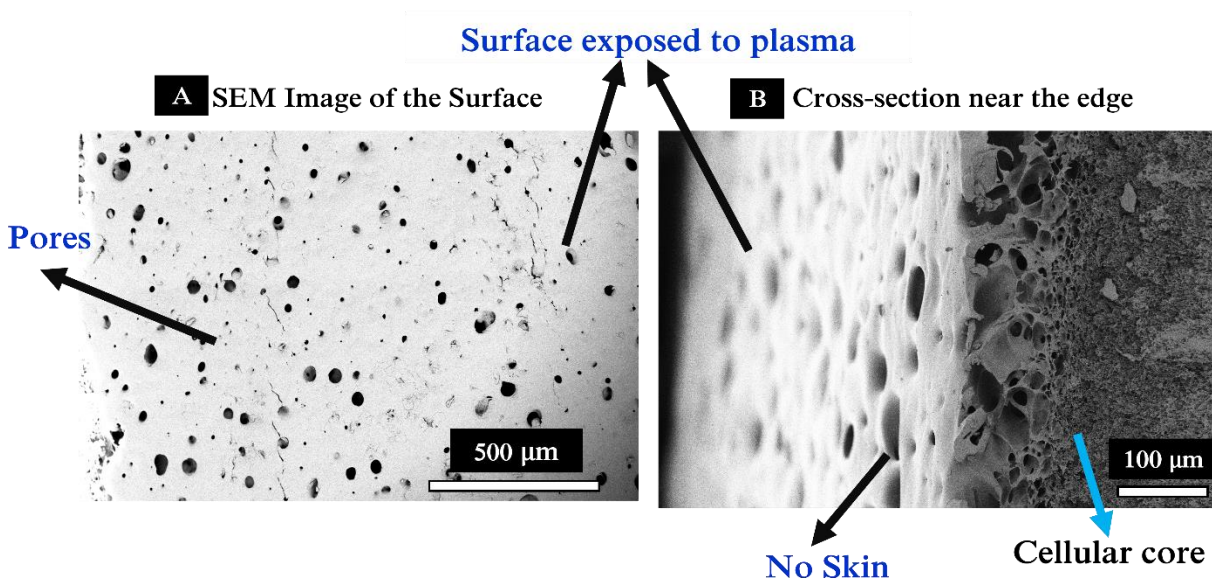


Figure 7.4 A) SEM image of the top surface of plasma treatment-based solid-state microcellular PC foam showing pores. B) A SEM image of the outer layer of a plasma treatment-based solid-state microcellular PC foam showing no skin and a porous surface. The surface has been treated with plasma. The SEM shows relatively large cells on the outer edge compared to the cellular core.

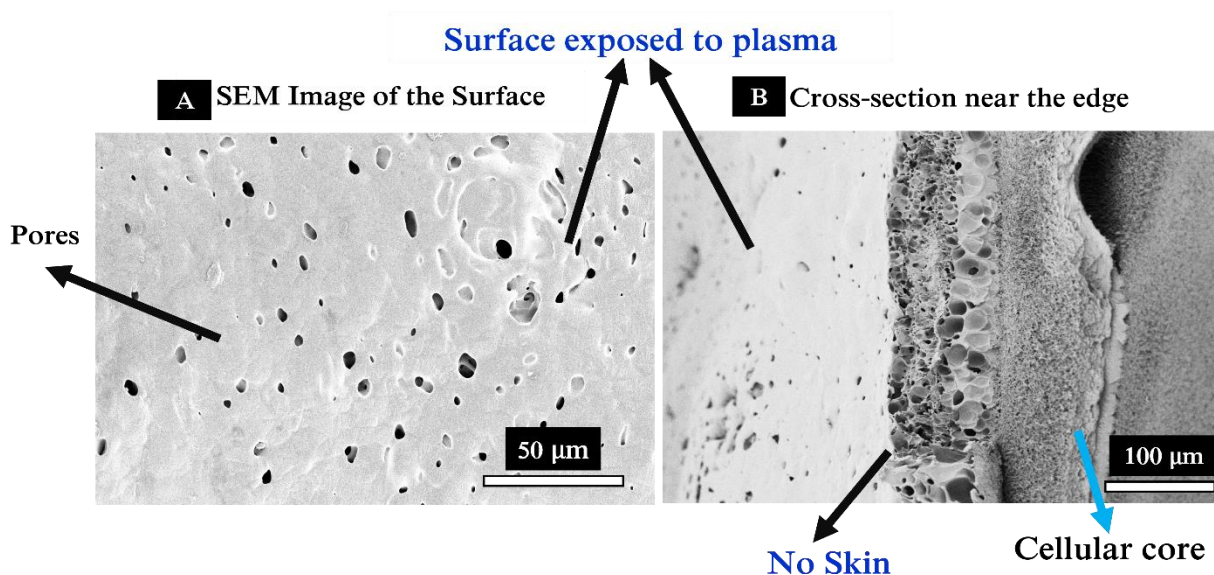
7.4.2 PEI-CO₂ System: Skinless Nanocellular PEI

Figure 7.5 A) SEM image of the top surface of plasma treatment-based solid-state nanocellular PEI foam showing pores. B) A SEM image of the outer layer of a plasma treatment-based solid-state nanocellular PEI foam reveals no skin. The surface has been treated with plasma. The SEM shows relatively large cells on the outer edge compared to the cellular core.

7.4.3 *Selective Plasma Treatment-based Foaming of Skin in a Prefabricated Nanocellular PEI Foam to Access the Core*

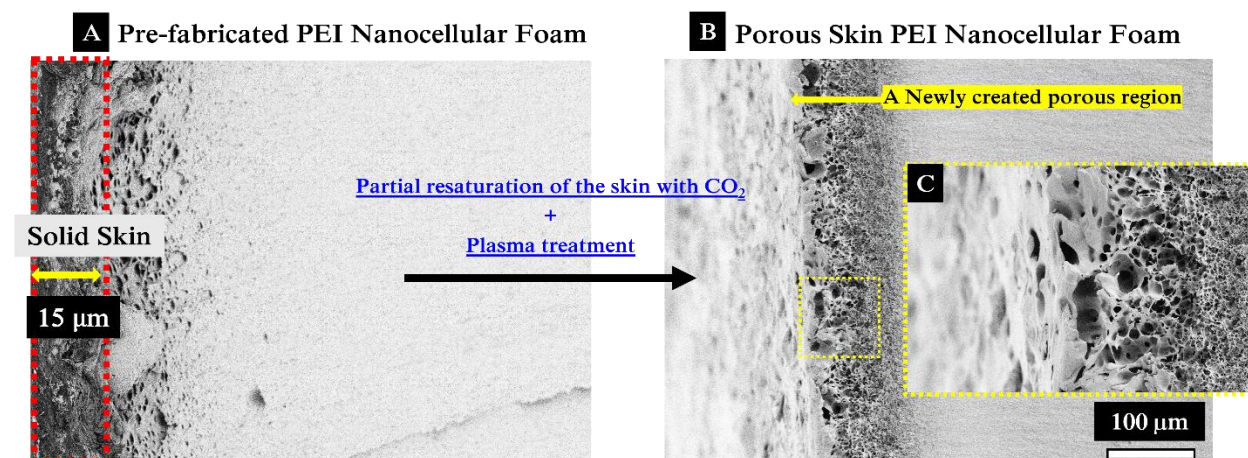


Figure 7.6 A) SEM of the solid skin of the prefabricated PEI nanocellular foam sheet with an open porous core. B) A SEM image of the outer edge of the nanocellular PEI foam, whose skin layer is porous. The SEM shows a layer of bubbles on the edge. C) Zoomed-in SEM image of the outer edge region showing large bubbles.

7.4.4 Effect of Saturation Pressure on Plasma Treatment-based Solid State Foaming Process

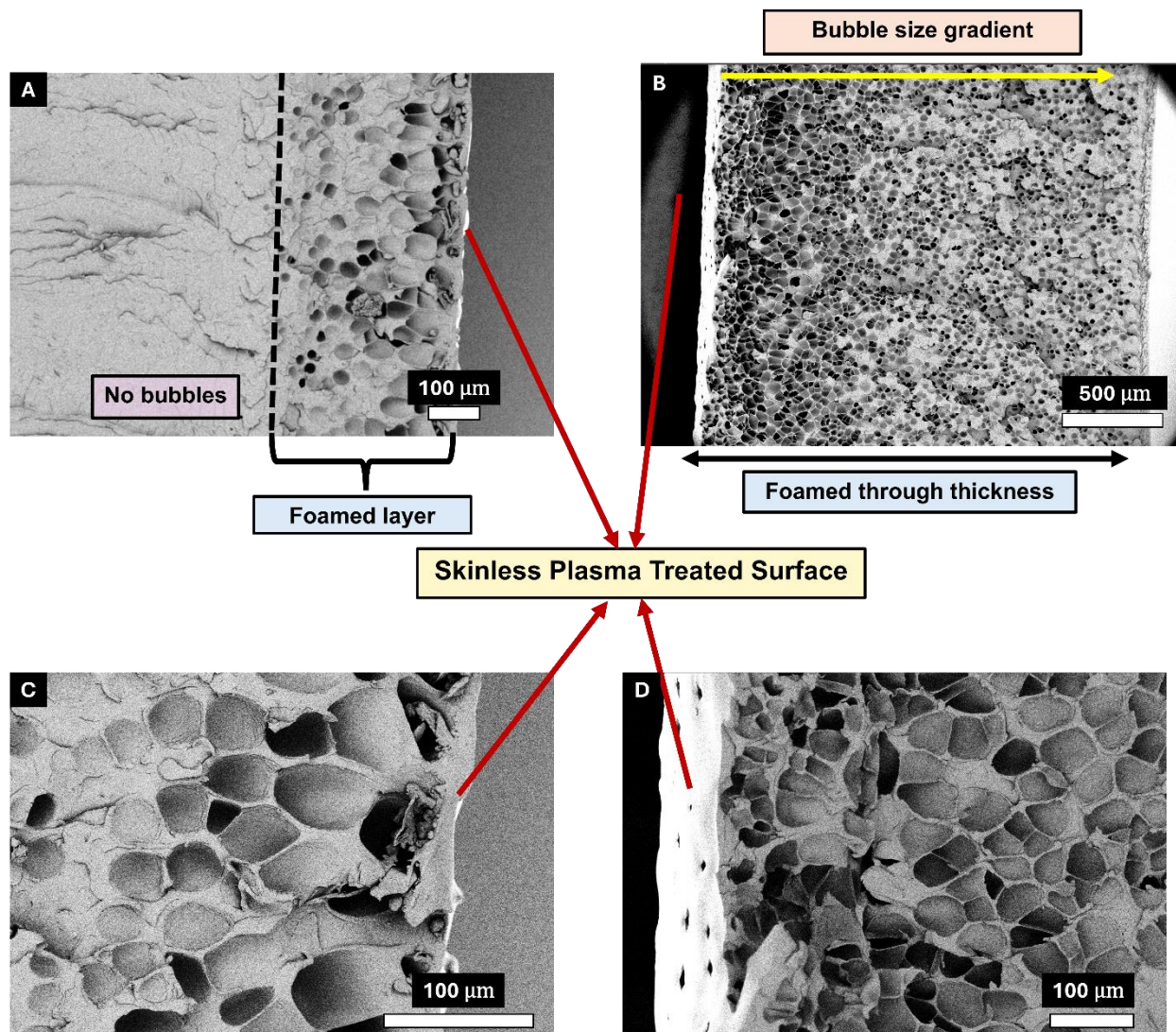


Figure 7.7 A) An SEM image of the plasma-induced microcellular PC foam (#PC_2) saturated at 1 MPa shows the foamed region near the outer edge. B) An SEM image of the skinless plasma-induced microcellular PC foam (#PC_3) saturated at 1 MPa shows the foamed region near the outer edge. C) Zoomed-in SEM image of the outer edge region showing a “cell wall” thick skin; the cells have formed close to the edge. D) Zoomed-in SEM image of the outer edge region shows no skin and a porous surface.

7.5 DISCUSSION

7.5.1 *PC-CO₂ System*

Skinless Microcellular PC Foam

Plasma treatment-based foaming produced skinless microcellular PC foam, as shown in the SEM image in Figure 7.4. At the outer edge, the cells are larger, and the surface is porous. As the plasma interacts with the surface, heat is transferred into the bulk, resulting in foaming through the cross-section. The depth of foaming depends on the surface temperature and exposure time. The SEM analysis also reveals that the foam structure is identical to that of the conventional solid-state foaming process, as shown in Figure 7.8. This indicates that plasma primarily affects the surface and does not directly interact with the bulk. Through further experiments, we observed that increasing the number of passes (N) enhances heat transfer through the bulk, resulting in foaming of the entire cross-section. The following section will discuss the effect of plasma system parameters on the foaming process based on preliminary experiments.

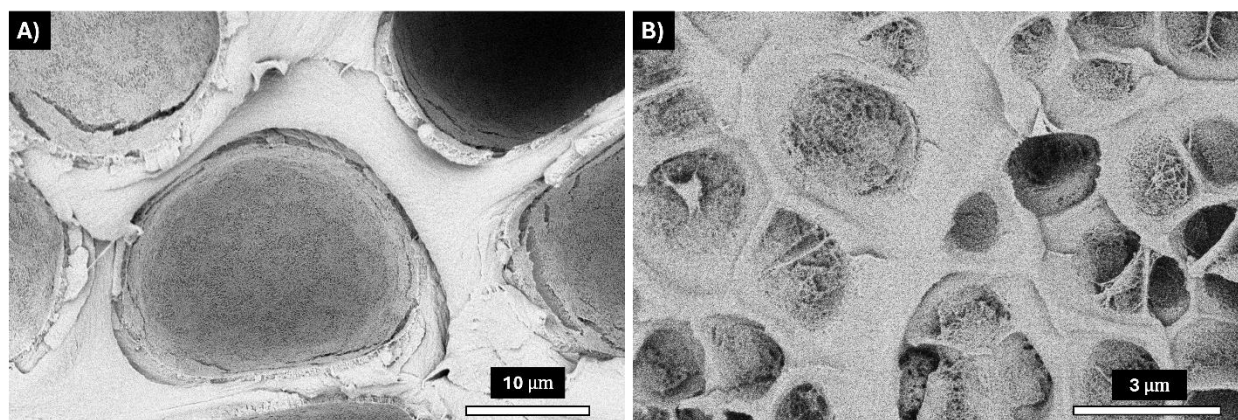


Figure 7.8 A) An SEM image of a microcellular PC foam produced through conventional solid-state foaming. B) An SEM image showing the cellular structure of the core of plasma treatment-based microcellular PC foam (#PC_1). The structure reveals primary cells with secondary nanopores on the cell wall, which is typically observed in microcellular PC foams produced through the conventional hot bath foaming process.

Effect of Saturation Pressure: PC-CO₂ System

The effect of saturation pressure on skin thickness remains to be fully established in the conventional solid-state foaming process. Experimental results show that the average skin thickness is larger at lower saturation pressures. For example, in the PC-CO₂ system, the average skin thickness is 180 μm for the processing conditions of 1 MPa and 120°C, compared to 37 μm for the processing conditions of 5 MPa and 120°C. The underlying reason is that the saturation pressure affects the effective T_g of the polymer-gas system. Decreasing saturation pressure decreases the CO₂ concentration in the polymer, increasing the effective T_g of the polymer-gas system. As a result, the reduction in solubility is less pronounced at 1 MPa, which is the driving force behind cell nucleation, leading to the nucleation of fewer bubbles and, consequently, a larger skin.

To evaluate the effect of reducing the saturation pressure on the plasma system's ability to produce skinless microcellular foams, samples were saturated at 1 MPa and subsequently treated under the same foaming conditions that had previously produced skinless foams at 5 MPa (refer to Table 7.1). The SEM images are presented in Figure 7.7 A and C. SEM image A reveals thin skin on the foam, with a thickness comparable to that of the cell wall thickness. Additionally, the foamed region depth extends only a few hundred micrometers from the surface, significantly less deeply than the foamed layer observed at 5 MPa. The depth of the foamed layer is reduced due to the higher effective glass transition temperature (T_g) at lower saturation pressure, which requires higher temperatures and longer times (as discussed in Chapter 6) for cell growth.

The SEM analysis reveals that the foam becomes skinless, and foaming progresses through the bulk cross-section as the number of passes (N) increases, as shown in Figure 7.7 B and D. This experiment indicates that increasing the number of passes (N) propagates the heat through the bulk, analogous to cycling heating. SEM image B shows that the foamed region has expanded to the other side of the polymer cross-section. The SEM image D shows pores on the surface. These preliminary results suggest that nucleating cells close to the surface to create a porous surface depends predominantly on the Initial Standoff Distance (d). This can be seen in the case of PEI, where a lower standoff distance is required because PEI is a high-temperature, aerospace-grade polymer that is generally more inert than PC. When we compare the effect on skin thickness at 1 MPa and 5 MPa (refer to the SEM images in Figure 7.7), the plasma system produces a significantly thinner skin of the order of cell wall thickness at 1 MPa and no skin at 5 MPa. This shows that plasma treatment-based foaming has two effects. The first is the surface effect, where the exact mechanism that produces a porous surface is yet to be explored. The surface temperatures measured using an infrared camera varied from 150 to 200 °C for each pass, as shown in Figure 7.9. Note that the measurement indicates that the surface temperature is above the T_g of the unprocessed PC, and the effect of plasma treatment appears to be confined to the surface. We hypothesize that the heat transfer rate exceeds the mass transfer rate of diffusing CO₂ due to the unique nature of plasma and polymer surface interaction. Plasma may also weaken the polymer surface, plasticize the chains, and promote bubble nucleation as the CO₂ diffuses through the surface. We verified that there is also an effect of polymer etching due to plasma. Unprocessed PC specimens were treated with plasma under the same conditions that produce skinless foam. We estimate the etched layer thickness to be around 0.5-1 μm based on the weight difference before

and after plasma treatment. A detailed study is needed to understand the exact mechanism of how plasma treatment produces a porous surface and decouple the contribution from etching.

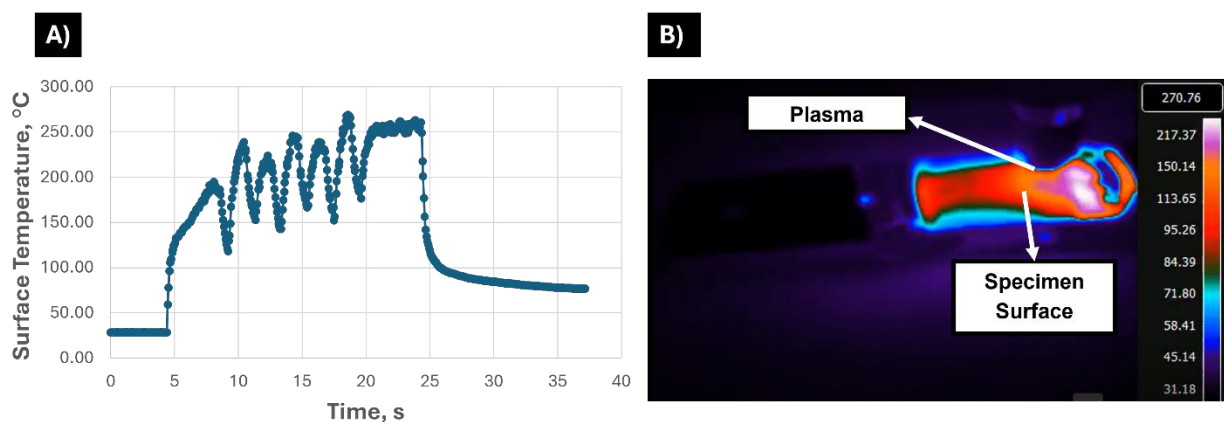


Figure 7.9 A) Surface temperature measurements from an IR camera during the plasma-induced foaming of PC. The peaks correspond to each pass. B) A corresponding temperature map of the surface.

The second effect is the effect of heat transfer into the bulk, which determines the microstructure in the core. The primary goal of this study is to identify the conditions that produce skinless foams. As mentioned, the foam structure created during the plasma treatment-based foaming process will depend on the extent of heat transfer into the bulk. The current plasma treatment-based foaming process is not decoupled to produce skinless foams and the desired foam structure. The plasma system does not produce skinless foam under all conditions. However, we observed that skin thickness is generally thinner than that of the conventional solid-state foaming process.

7.5.2 *Skinless Nanocellular PEI Foam*

Under the conditions listed in Table 7.2, plasma treatment-based foaming produced skinless nanocellular PEI foam, as shown in the SEM image in Figure 7.5. Compared to the PC-CO₂ system, the initial standoff distance was reduced by half to achieve a higher surface temperature and induce greater plasma-polymer interaction. The SEM image shows that the surface exposed to plasma is porous. The pores on the surface have diameters ranging from 1 to 10 μm . There is a layer of large bubbles whose average size is 14 μm beneath the surface, as shown in Figure 7.10 below. Microcellular PEI typically has a cell size of 1–5 μm ; larger cell sizes are expected near the surface due to low CO₂ concentrations and high temperatures resulting from plasma exposure. There is a gradient in cell size in the structure near the surface. There is a layer of cells just below the surface that consists of smaller cells, which transition into larger cells. This offers some key insights based on the fundamentals of bubble formation. Bubbles that nucleate near the polymer surface have two distinct types of bubble surfaces. The upper half has a surface that has an interface with the atmosphere, and the lower half has an interface with the polymer bulk⁵³. The surface bubbles also have slightly higher internal pressure⁵³. The stability of the bubble depends on the surface of the polymer. We hypothesize that the plasma treatment is plasticizing the polymer surface to promote bubble nucleation near the surface, but the exact mechanism is yet to be completely understood.

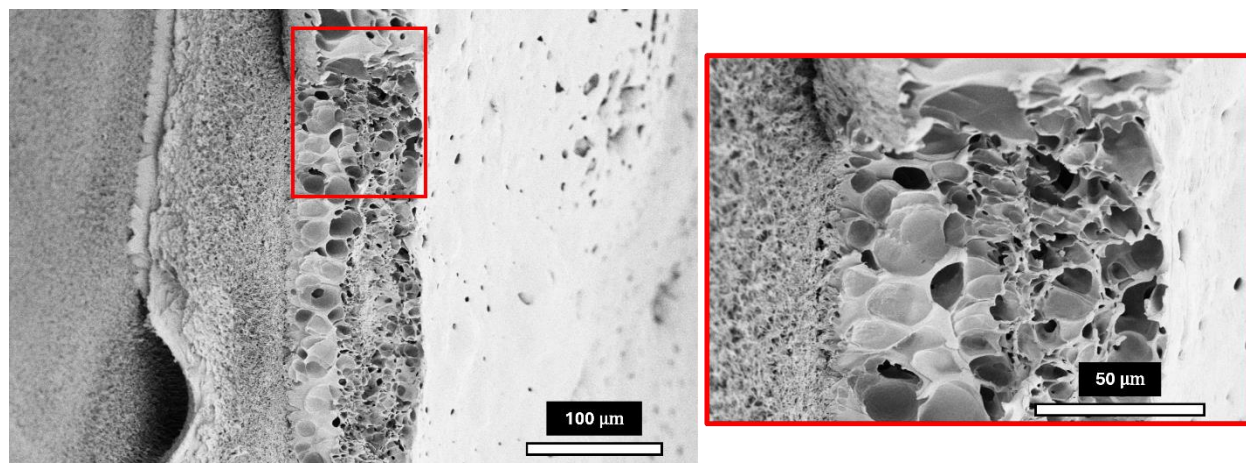


Figure 7.10 An SEM image showing the zoomed-in image of the cellular structure beneath the plasma-treated surface. The SEM shows a layer of large bubbles formed beneath the surface.

The core has a nanocellular structure, which is open-celled. The average cell size is 94 nm, with a standard deviation of 52 nm. SEM images of nanocellular structures obtained in the plasma treatment-based foaming process and the solid-state foaming process are compared in Figure 7.11 below. Consistent with the PC–CO₂ system observations, the PEI–CO₂ system exhibits an identical structure in plasma treatment-based foaming compared to conventional solid-state foaming, as shown in Figure 7.11.

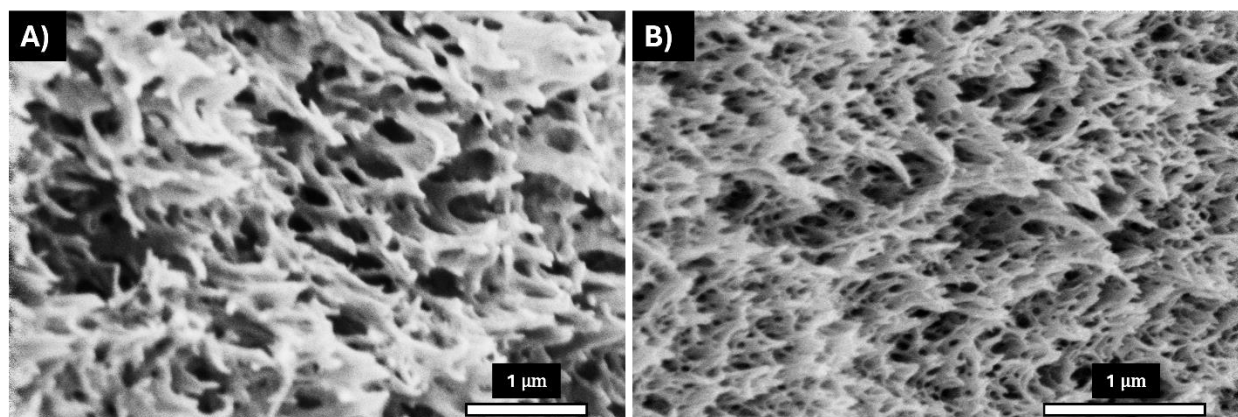


Figure 7.11 A) An SEM image of the nanocellular structure produced using a plasma treatment-based foaming process. B) An SEM image of the nanocellular PEI produced using the conventional solid-state foaming process saturated at 5 MPa, foamed in an oil bath at 160°C, and flattened in a hot press at 180°C with a relative density of 0.42. The process has retained the same morphology as the traditional bath foaming process.

A temperature measurement was conducted on the PEI-CO₂ system, and the results are shown in Figure 7.12. As observed in the PC-CO₂ system, each peak represents a pass, and the peak shifts towards higher temperatures in the later passes due to specimen curling and consequent reduction in the initial standoff distance.

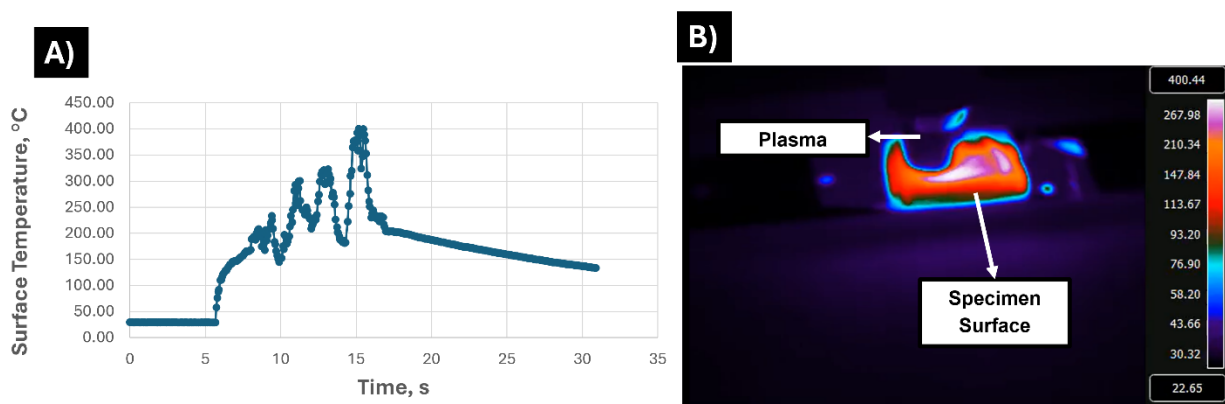


Figure 7.12 A) Surface temperature measurements from an IR camera during the plasma treatment-based foaming of PEI. The peaks correspond to each pass. B) A corresponding temperature map of the surface.

To investigate the behavioral differences between the PC and PEI-CO₂ systems, the PEI-CO₂ system was subjected to plasma treatment-based foaming under the same conditions (refer to Table 7.2), resulting in skinless foam in the PC-CO₂ system. The objective is to determine whether these conditions can also yield skinless foam in PEI, and if not, to identify the skin thickness, considering that PEI is typically inert. The SEM results are shown below in Figure 7.13.

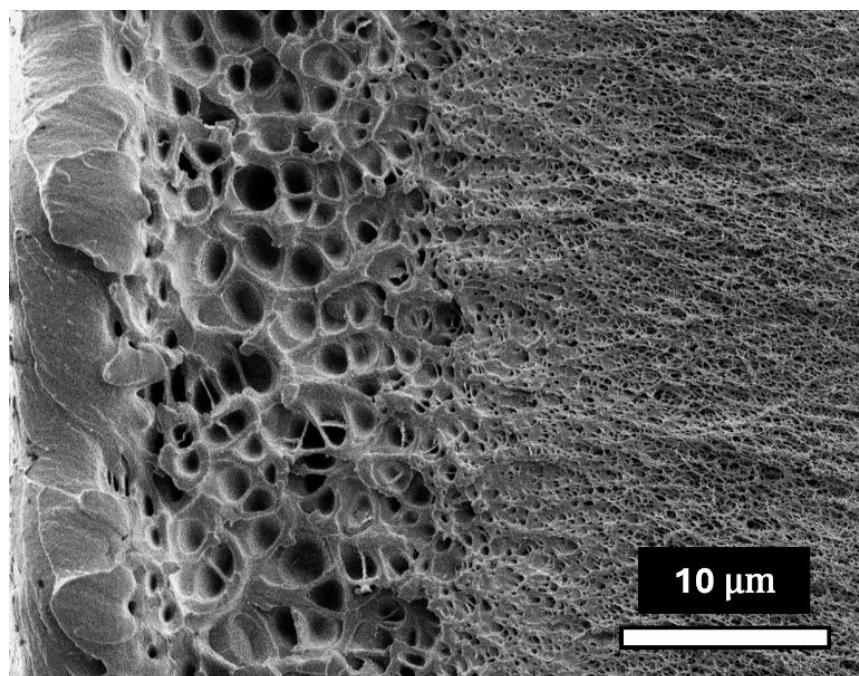


Figure 7.13 An SEM image of the skin region of plasma treatment-based nanocellular PEI foam subjected to conditions that resulted in skinless foam in the PC-CO₂ system.

The SEM shows the PEI foam has a thin layer of solid skin when subjected to the same conditions, resulting in skinless foam in the PC-CO₂ system. The average skin thickness is 5 μm, typically less than what is observed in the PEI-CO₂ system. This comparison illustrates the effect of the initial

stand-off distance on the ability to create a skinless, porous surface. A lower distance allows more plasma-polymer interaction; a detailed study must be conducted to uncover the exact mechanism.

An unprocessed PEI was plasma-treated using the conditions in Table 7.2 and the surface was analyzed under the SEM. The SEM image is shown below in Figure 7.14. *The surface has no pores. This is proof that we need a gas-saturated polymer to nucleate pores on the surface. Plasma treatment itself cannot create a porous surface.*

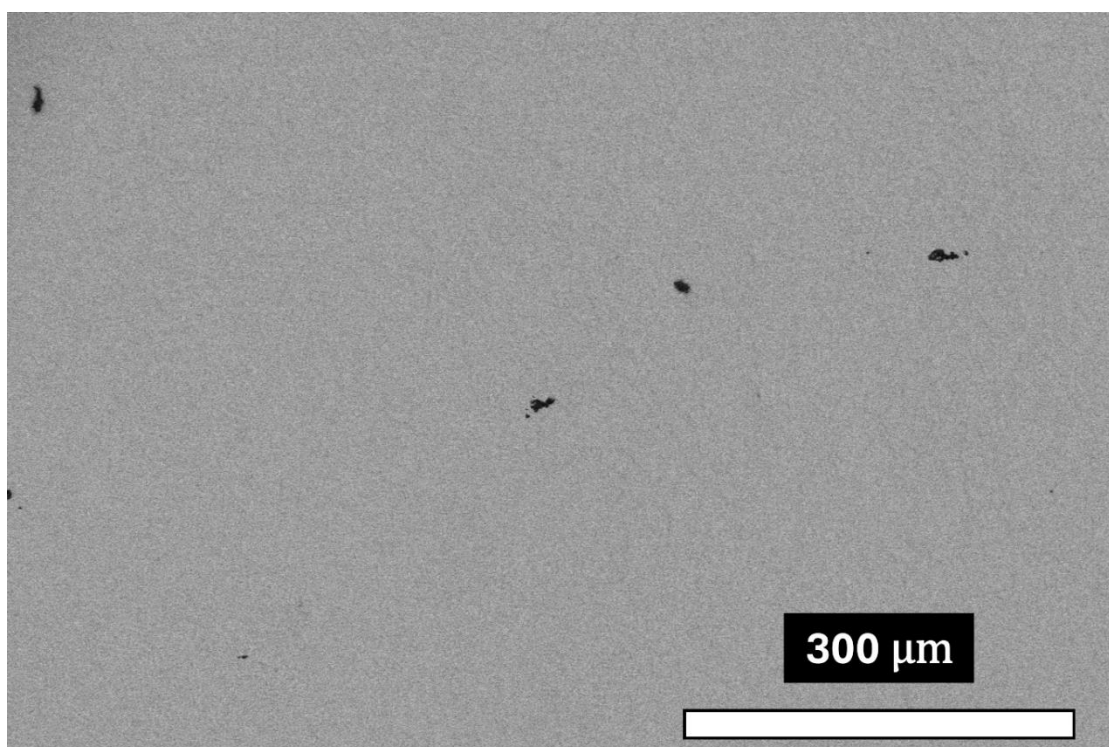


Figure 7.14 An SEM image of a plasma-treated surface of an unprocessed PEI under the conditions in Table 7.2 that produce skinless PEI foams.

7.5.3 *Selective Plasma Treatment-based Foaming of Skin in a Prefabricated Nanocellular PEI Foam*

SEM images in

Figure 7.6 confirm that the plasma-treated sheet has resulted in a porous layer on the outer edge and pores on the surface. The core structure from prefabrication remains unaffected because the core temperature during the plasma treatment stayed below the T_g of unprocessed PEI. Through this experiment, we successfully demonstrated that a prefabricated foamed sheet with a solid skin and the desired morphology can be partially re-saturated and plasma-treated to create a porous surface, thereby accessing the core. Nicolae's¹⁷ previous work showed that nanocellular PEI structures are permeable to acetone. We performed an acetone dye penetration test to verify surface porosity and check whether the dye could pass through the foam's cross-section. The results are presented in the following section.

7.5.4 Dye Penetration Test

After the plasma treatment, a few drops of blue food color-based acetone dye were added to the porous surface. The cross-section of the dye-absorbed foam sheet is shown below in Figure 7.15. The cross-section has turned blue, revealing that the dye has penetrated the plasma-treated surface.

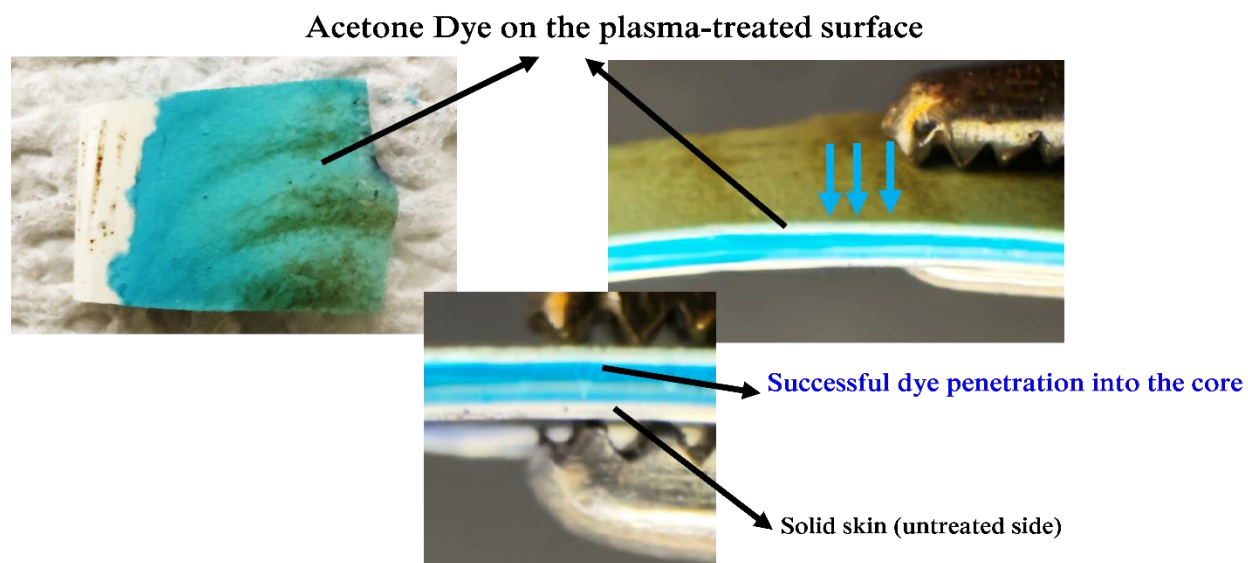


Figure 7.15 Results of the acetone-based dye penetration test on the prefabricated PEI nanocellular foam subjected to selective plasma treatment-based foaming of skin.

We have years of research on solid-state foaming processes across various polymer–gas systems, enabling the production of foams with diverse micro- and nanocellular structures. This approach offers a powerful and effective way forward. The ability to selectively foam the skin by plasma treatment and create a porous surface to access the core position makes this technique a promising strategy for characterizing various morphologies produced in the solid-state foaming process.

7.6 CONCLUSION

This study demonstrated a novel plasma treatment-based solid-state foaming process to produce skinless microcellular and nanocellular foams using a commercial low-temperature atmospheric air plasma system. Notably, the process produced skinless microcellular foams in the PC-CO₂ system at both saturation pressures, 5 MPa and 1 MPa. The parameter Number of Passes (N) plays the key role in propagating the heat through the specimen to increase the foam depth. The process produced skinless nanocellular foams in the PEI-CO₂ system when the stand-off distance was reduced by half compared to the PC-CO₂ system. Stand-off distance plays a key role in achieving skinless foams; the lower the distance from the nozzle, the greater is the plasma-polymer interaction. The optimal parameters to produce skinless foams of two different polymer systems were established.

As an extension of the process, an innovative decoupled method was demonstrated where a solid skin of prefabricated nanocellular PEI sheet was made porous by partial re-saturation with CO₂ and subsequent plasma treatment. An acetone-based dye penetration test confirmed that the surface and skin have become porous. Examination of the cross-section revealed dye infiltration through the core, proving that the porous skin is interconnected with the open-celled nanostructure in the core. This powerful technique now leads the way forward to reprocessing the prefabricated foam sheets with solid skin and desired structure for different applications, making the skin porous using plasma treatment and accessing the core.

Preliminary experiments show that plasma has a unique ability to enhance bubble nucleation in the region close to the surface where the CO₂ concentration is extremely low. Results clearly show that the polymer sheets need to be saturated with CO₂ to nucleate bubbles on the surface. Therefore, this novel plasma treatment-based solid-state foaming process is a promising way forward to producing skinless foams for various filtration applications.

7.7 ACKNOWLEDGMENTS

The author acknowledges Ankush Nandi for his assistance with operating the plasma system and for providing insights into plasma system parameters to design experiments. The author also acknowledges Dr. Vipin Kumar, Dr. Anirudh Vashisth, Dr. Lucas Meza, Dr. Marco Salviato, and Dr. Krishna Nadella for their valuable insights. The author thanks Amitha Rani Mulastham and Andrea Exil for helping with the SEM imaging. The author also thanks Shaunak Deshpande for assistance with the experiments.

Chapter 8. CONCLUSIONS AND RECOMMENDATIONS

8.1 EVOLUTION OF STRUCTURES IN PEI-CO₂ SYSTEM

The CO₂ concentration plays a critical role in determining the structure of the PEI foams. Microcellular foams are produced across a saturation pressure range of 0.5 MPa (2.2 wt.% CO₂) to 3.3 MPa (8.7 wt.% CO₂) with average cell sizes ranging from 1 to 5 μm . The PEI-CO₂ system is unique and exhibits higher cell nucleation density. Even at 2.2 wt.% CO₂, the cell nucleation density is estimated as 10^{10} cells/cm³. The structure rapidly transitions from microcellular to nanocellular as the CO₂ concentration increases from 8.7 wt.% to 10 wt.%, (corresponding to 3.5 MPa). This is unique to the PEI-CO₂ system. Nanocellular foams are produced across a saturation pressure range of 3.5 MPa (10 wt.% CO₂) to 5.5 MPa (12.4 wt.% CO₂) with average cell sizes ranging from 20 to 130 nm. At the saturation pressure of 5.5 MPa, PEI consistently produces a uniform structure with an average cell size of 20 nm across the foam temperature range, and the cell nucleation density approaches 10^{16} cells/cm³. Overall, the cell nucleation density increases by six orders of magnitude as the CO₂ concentration increases from 2.2 wt.% to 10 wt.%. As the cell nucleation density reaches 10^{16} cells/cm³, it begins to plateau; correspondingly, the cell size and relative density are approaching a limit as the foaming temperature increases. The predicted size distribution curves of the radius of nuclei indicate a transition from microcellular to nanocellular structures as increasing saturation pressure enables the formation of smaller, stable nuclei. Therefore, increasing saturation pressure progressively activates smaller flaws in the polymer, which become stable nuclei, contributing to the cell nucleation density, consequently leading to the formation of a nanocellular structure.

The sub-room temperature saturation process space needs to be explored and established for the PEI-CO₂ system. Nicoale¹⁷ has shown that the PEI-CO₂ system produces transparent foams at a saturation pressure of 5 MPa and a saturation temperature of -32 °C. Lizalde-Arroyo et al.³⁶ recently characterized the transparent PEI foams by increasing the saturation pressure above 5 MPa, as well as saturation temperatures below room temperature. There is a challenge in characterizing the pore size of transparent foams, as the SEM is unable to image the porous structure. However, the pore size can be estimated through various indirect characterization methods. For instance, Lizalde-Arroyo et al.³⁶ estimated the cell size of transparent foams based on observed optical transmittance.

Another area of interest is developing a protocol for analyzing SEM images to facilitate advanced statistical quantification. For example, defining the distance between the pores in PEI nanofoams when they are distributed sporadically is a challenge. Estimating the surface area from SEM images can provide new insights and aid in developing better structure-property correlations.

8.2 SECONDARY NANOPORES CHARACTERIZATION

The key driving force of nucleation of secondary nanopores on the cell wall is the stretching of the cell wall due to primary cell expansion. Increasing primary cell growth either by increasing foaming temperature at constant saturation pressure or by increasing foaming time at constant foaming temperature results in an increase in the area of cell wall covered by the nanopores, and the size of nanopores increases by 10 to 80 nm. The strong influence of primary cell expansion is evident in Part I of this study, although increasing the saturation pressure reduces the surface

tension, favoring nucleation of secondary nanopores, it also enhances the primary cell nucleation density. This results in a smaller primary cell, resulting in diminished expansion. As a result, the secondary nanopore nucleation density on the cell wall is lower at 3.3 MPa compared to 0.5 MPa. Part 2 shows that higher foaming temperatures lead to faster primary cell growth, which promotes secondary cell nucleation. Incorporating strain energy due to cell expansion into the classical nucleation theory framework, analogous to craze nucleation theory, provides an explanation for the mechanism of secondary nanopore nucleation. It is likely that secondary nanopores nucleate due to both crazing of the polymer and foaming.

The mechanics of the bubble growth has been modeled for the solid-state foaming process have been modeled in the literature^{44,54}. The models can be implemented for PEI to estimate stress and strain developing on the cell wall due to stretching. This setup enables investigation into whether the predicted stress and strain levels are consistent with the proposed mechanism of crazing in the cell wall.

In general, microcellular foams are closed-celled. Gong et al.²⁰ reported that the open-cell content in microcellular PC foams containing secondary nanopores increases with foaming temperature. This observation suggests that nanopores on the cell walls contribute to enhanced interconnectivity between primary cells. Accordingly, controlling the development of secondary nanopores is a new strategy for producing open-celled microcellular foams with tunable interconnectivity.

8.3 FRACTURE BEHAVIOR OF MICROCELLULAR AND NANOCELLULAR FOAMS

This work is a collaborative effort with the Meza Research Group in the Department of Mechanical Engineering and the Multiscale Analysis of Materials & Structures (MAMS) Lab in the Department of Aeronautics and Astronautics, focusing on the experimental characterization of the toughness in microcellular and nanocellular PEI foams as a function of cell size, funded by the National Science Foundation. Details of all the tensile and fracture experiments to be found in Kush Dwivedi's (Department of Mechanical Engineering) Ph.D. dissertation. This work has been submitted for publication under the title “Breaking Down the Exceptional Size-Dependent Toughness of Nanocellular Foams” by Dwivedi et al.⁴⁵. It is currently under peer review, and I am serving as a co-author.

My contributions are as follows

- 1. Developing the process space map that enables the fabrication of microcellular and nanocellular PEI foams at specific relative densities*
- 2. Developing protocols for the fabrication of foam specimens for mechanical tests*
- 3. Detailed SEM characterization of the cellular structures before mechanical testing*
- 4. SEM characterization of fracture surfaces post-mechanical testing*

In general, the nanocellular foams are tougher than microcellular foams for the same relative density. This behavior is unconventional and disrupts the classical scaling law. The enhanced toughness in nanocellular foams is evident from fracture test results. The load-CMOD curves in the case of nanocellular foams had a higher peak load and a gradual decline in post-peak load,

indicating plastic deformation and a higher degree of energy absorption leading to ductility. The nanocellular foam with a relative density of 0.8 exhibits failure stress, failure strain, energy absorbed, and fracture work comparable to those of solid PEI. The fracture toughness of 0.8 relative density foam is comparable to that of solid PEI. This is a remarkable result as it showcases the effect of reducing cell size in enhancing toughness while reducing density. In general, low-density materials exhibit less ductility and undergo brittle failure. Both microcellular and nanocellular foams exhibit a ductile-to-brittle transition as the relative density decreases. However, the transition happens in microcellular foams at a much higher relative density. The SEM analysis of the fracture surfaces along the crack propagation path revealed that the ductile microcellular foams exhibit cell wall stretching in the crack initiation region and no stretching in the crack termination region, indicating moderate ductility, except for the low-density foam, which did not have any stretching. Currently, the effect of secondary nanopores is not decoupled. SEM analysis on cell walls of microcellular foams indicates that there is no evidence of any effect associated with secondary nanopores on the fracture behavior. High-density nanocellular foams show cell wall stretching in both the crack initiation and termination regions. Notably, even the low-density nanocellular foam had cell wall stretching in the crack initiation region, exhibiting some ductility. The fracture surfaces of nanocellular foams show a high degree of cell wall stretching, indicating plastic deformation at the nanoscale level due to local ductility, which contributes to a high degree of energy absorption. The findings of this study show how nanoscale features can improve toughness in foams while providing lightweight.

This study highlights two significant aspects: 1) The effect of reducing the cell size on enhancing the toughness of nanocellular foams in comparison to microcellular foams. 2) The dominant effect

of relative density on fracture toughness. The effect of reducing density exceeds the effect of reduction in cell size, as both microcellular and nanocellular foams exhibit brittle behavior at low relative densities. In simple terms, we can define toughness as the resistance a propagating crack encounters when creating a new surface. The surface area of microcellular and nanocellular foams is not yet fully characterized. Correlating the surface area with ductility can be an interesting direction.

Results show that the nanocellular foam with a relative density of 0.8 exhibited comparable toughness with solid PEI. However, a more accurate comparison would be with saturation-cycled PEI. Saturation cycling refers to the process in which solid PEI undergoes a complete cycle of CO₂ sorption followed by desorption. A previous study by Seeler and Kumar⁵⁵ reports that the fatigue life of saturation cycled PC increased by a factor of 30 when compared to unprocessed PC. The base polymer in the foams is essentially saturation-cycled. We need to compare the ductility exhibited by the high-density foam and saturation-cycled PEI.

The effect of secondary nanopores on the fracture behavior remains decoupled. There is no conclusive evidence that the presence of secondary nanopores on the cell wall enhances toughness. We can explore the region 3.3 MPa – 3.5 MPa in the process space where the secondary nanopore density decreases, and the cell size is slightly below 1 μm . A study of tensile and fracture properties comparing foams at 1 and 3.3 MPa can offer insight into the effect of secondary nanopores.

8.4 SKIN FORMATION IN SOLID-STATE FOAMING PROCESS

Skin thickness decreases with increasing foaming temperature. This study successfully implements and validates a one-dimensional heat and mass transfer-based effective T_g model for the PC-CO₂ system. A correlation was experimentally developed to estimate effective T_g at low CO₂ concentrations, where predictions from Chow's equation significantly deviate from experimental observations. The model and experimental results show good agreement. Two modeling approaches were evaluated: (1) predicting skin thickness based on the initial intersection point using the transient temperature profile, and (2) predicting skin thickness based on the final intersection point using the steady-state temperature profile. Comparison with experimental data indicates that the initial intersection point method provides more accurate predictions of skin thickness. This finding reveals a key insight: skin formation occurs during the early stages of the foaming process, highlighting its dynamic nature and offering new possibilities to decouple skin formation from the formation of core structure in the foam. This study led to the question of whether skin formation is a continuous process as foaming proceeds, or does the skin form at the beginning of the foaming process?

Chapter 6 delves into this question by characterizing the evolution of skin as a function of foaming time for two cases: 1) Short desorption time of 3 mins. and 2) Long desorption time of 60 mins. The model predicted a decrease in skin thickness with increasing foaming time in both cases. The rate of decrease is higher at 3 minutes compared to 60 minutes. However, the experimental findings suggest that at 3 minutes, skin thickness remains relatively constant through the foaming process, indicating that skin formation is independent of the foaming time. At 60 minutes of desorption, the skin thickness decreases with foaming time as predicted by the model. This provides a new

insight into the behavior of polymer-gas systems. Depending on the desorption time, the model must consider the initial skin thickness or the final steady-state skin thickness.

The study compares experimental skin thickness vs. foaming temperature data for the PC-CO₂ system. The skin thickness values for the case of 3 minutes desorption and 60 minutes desorption tend to converge as the foaming temperature increases. This shows the importance of reducing solubility in reducing skin thickness. The model should incorporate the reduction in solubility to improve the accuracy of skin thickness predictions. The effective T_g model is not yet validated for lower saturation pressures. The effective T_g model is not yet validated for other polymer-gas systems.

8.5 PLASMA TREATMENT-BASED SOLID STATE FOAMING PROCESS FOR SKIN-LESS FOAMS

This study demonstrated a novel plasma treatment-based solid-state foaming process to produce skinless microcellular and nanocellular foams using a commercial low-temperature atmospheric air plasma system. Notably, the process produced skinless microcellular foams in the PC-CO₂ system at both saturation pressures, 5 MPa and 1 MPa. The parameter Number of Passes (N) plays the key role in propagating the heat through the specimen to increase the foam depth. The process produced skinless nanocellular foams in the PEI-CO₂ system when the stand-off distance was reduced by half compared to the PC-CO₂ system. Stand-off distance plays a key role in achieving skinless foams; the lower the distance from the nozzle, the greater is the plasma-polymer

interaction. The optimal parameters to produce skinless foams of two different polymer systems were established.

As an extension of the process, an innovative decoupled method was demonstrated where a solid skin of prefabricated nanocellular PEI sheet was made porous by partial resaturation with CO₂ and subsequent plasma treatment. An acetone-based dye penetration test confirmed that the surface and skin have become porous. Examination of the cross-section revealed dye infiltration through the core, proving that the porous skin is interconnected with the open-celled nanostructure in the core. This powerful technique now leads the way forward to reprocessing the prefabricated foam sheets with solid skin and desired structure for different applications, making the skin porous using plasma treatment and accessing the core.

Preliminary experiments show that plasma has a unique ability to enhance bubble nucleation in the region close to the surface where the CO₂ concentration is extremely low. Results clearly show that the polymer sheets need to be saturated with CO₂ to nucleate bubbles on the surface. Therefore, this novel plasma treatment-based solid-state foaming process is a promising way forward to producing skinless foams for various filtration applications.

A systematic study should be conducted on the effect of variable No. of Pass, Stand-off Distance, Flow Rate, and RPM on skin thickness. Systematic SEM analysis of the plasma-treated surface, with varying standoff distances, is crucial for understanding the underlying mechanism.

There is a limit on the thickness of the sheet that can be treated with the plasma system. Thin films of the order of typical skin thickness ($<100\text{ }\mu\text{m}$) can be degraded on exposure to plasma. Preliminary tests on $120\text{ }\mu\text{m}$ PC and PEI films suggest that increasing the nozzle RPM may aid in achieving skinless foam, although process conditions require further optimization. Laminating the film onto a thicker polymer substrate is one potential solution. We have observed that saturating a laminated PEI film with a PC substrate by heat pressing above the T_g of PC results in delamination due to gas-saturation-induced warping of the PC. Expanding the process of producing skinless thin film foam under the plasma is a challenge.

We selectively foamed a $15\text{ }\mu\text{m}$ -thick skin of a prefabricated open-cell, porous nanocellular PEI sheet by partially re-saturating the skin with CO_2 and subsequently treating it with plasma. The SEM images showed that the treated surface and the skin region have become porous. Acetone-based dye penetration test confirmed that the treated surface is permeable and that the skin region is porous and interconnected with the core. Thus, we successfully demonstrated a new technique to selectively make the solid skin porous, thereby enabling access to the porous structure at the core. This versatile approach should be validated for a broader range of polymers and optimized for varying skin thickness.

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APPENDIX A

AI: PRELIMINARY EXPERIMENTS

Method to Produce Flat Foamed Sheets

The gas-saturated polymer specimens are typically foamed in a hot-liquid bath, and we use silicone oil as the medium. An example of a curled and warped foamed sheet is shown below. Figure AI.2 A) Image of a warped foam sheet foamed in a hot oil bath. B) Image of the same sheet flattened in the press following the steps in Figure A.1. After foaming, the sheets will have a certain amount of residual gas in the polymer matrix. Since the presence of gas will reduce the T_g , the newly foamed sheets will have a slightly lower T_g than the unprocessed polymer. Therefore, curled or warped sheets can be flattened by applying heat and pressure. Based on this hypothesis, a two-step protocol was developed, as described below and illustrated in Figure AI.1.

In the first step, the curled or warped foamed sheets will be immediately pressed in the hot press for 1 min. The platen temperature is significantly essential. The platen temperatures are the same as those used in the oil bath for foaming. There are two major requirements: (1) The temperature should be sufficiently high to flatten the specimen. (2) The temperature should not be high enough to cause further foaming during the flattening, as it might alter the relative density of the foam. The other secondary factors are pressing pressure, heating, and cooling time. We decided not to apply any pressure under the press. The platens will just come into contact with the specimen. The heating and cooling times were determined through preliminary experiments.

In the first step, the warped or curled specimen is pressed under the platen for 1 minute, at a temperature set to the foaming temperature at which the specimens were foamed in the oil bath. In the second step, after 1 minute, the heaters will be turned off. Then, using external fans, the flattened foamed sheets will be allowed to cool for 7 minutes while still in the press. This method is illustrated in Figure AI.1. The relative densities of flattened sheets were compared with those of oil-foamed sheets at different foaming temperatures to verify whether flattening adversely affects the foams by causing cell collapse. The results are shown in Figure AI.3.

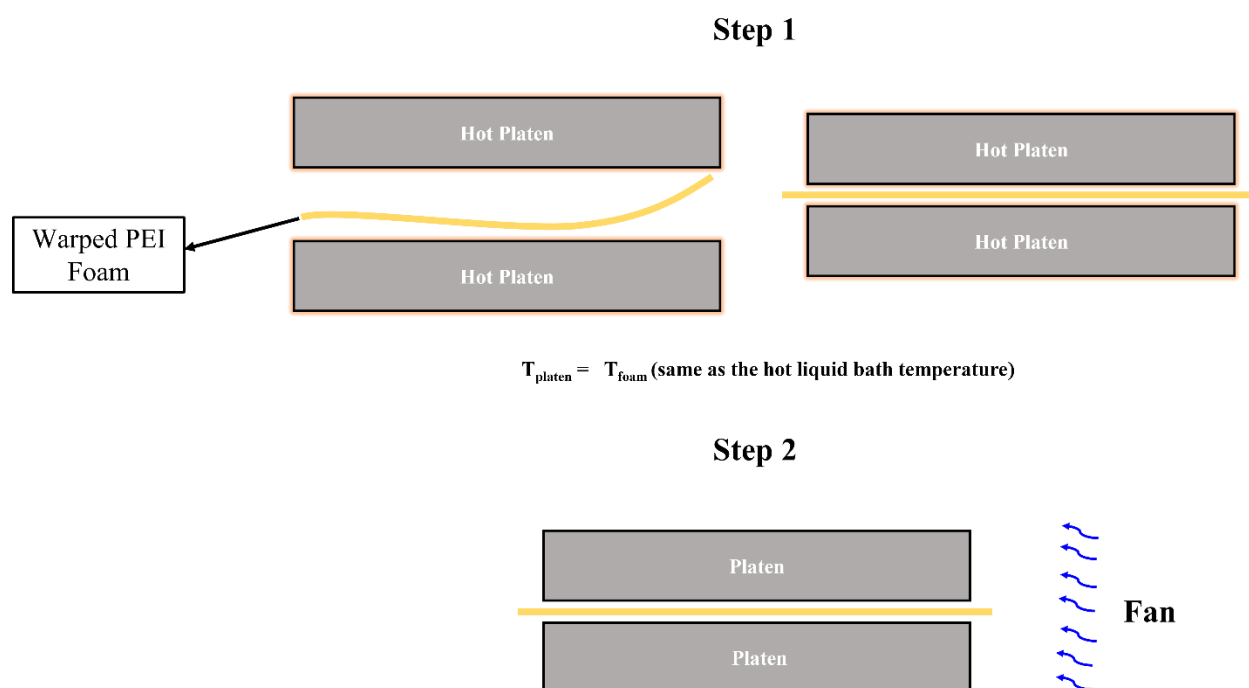


Figure AI.1 A schematic illustrating the steps to flatten the warped foamed sheets.

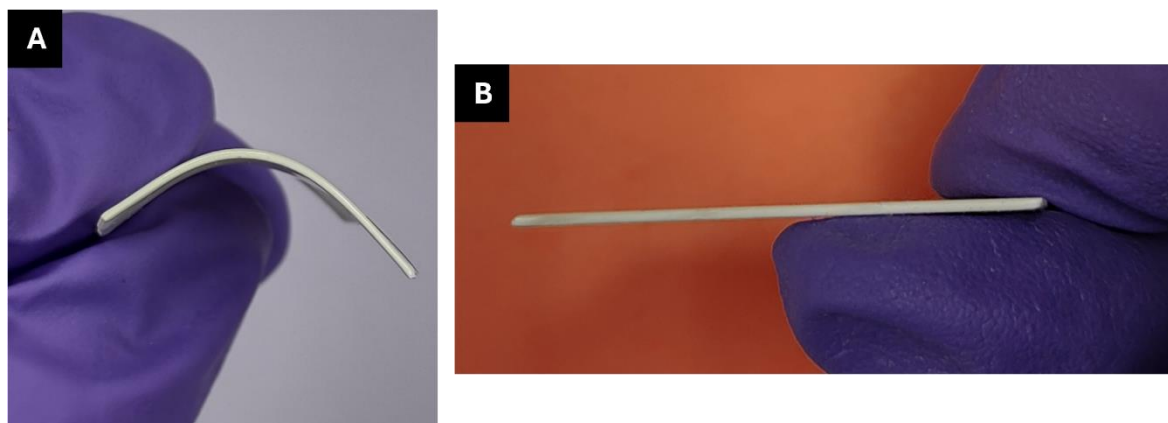


Figure AI.2 A) Image of a warped foam sheet foamed in a hot oil bath. B) Image of the same sheet flattened in the press following the steps in Figure A.1

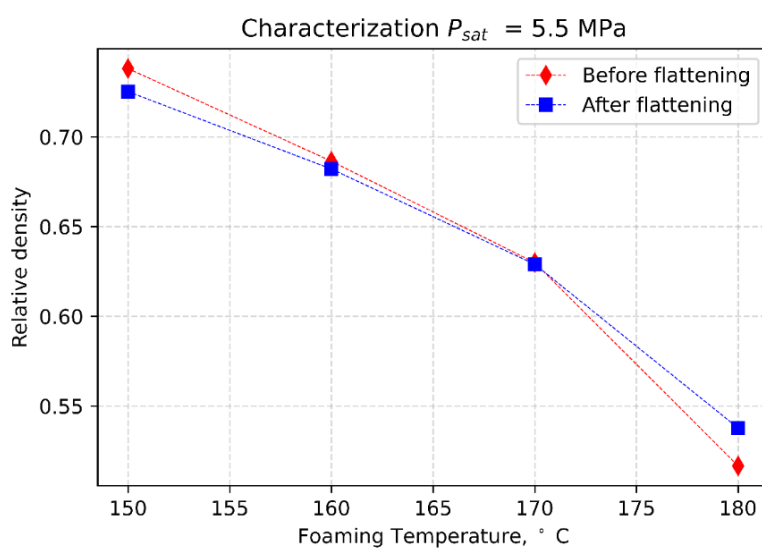


Figure AI.3 Relative densities of foams at different foaming temperatures processed at $P_{sat} = 5.5$ MPa for oil-foamed and flattened sheets.

No significant variation exists in the relative densities of oil-foamed and flattened foam sheets. However, we explored whether increasing the platen temperature above the foaming temperature

enhances flattening. To confirm, the press temperature was increased by 5°C. Similarly, the relative densities of flattened foam sheets were compared with the oil-foamed sheets at different foaming temperatures to verify the effect of increasing the platen temperature. The results are shown in Figure AI.4.

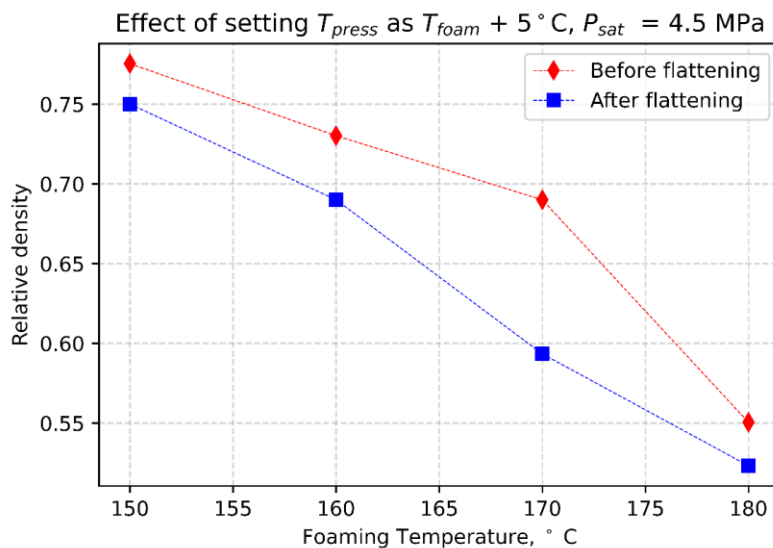


Figure AI.4 Relative densities of foams at different foaming temperatures processed at $P_{sat} = 4.5$ MPa for oil-foamed and flattened sheets when the platen temperature is 5°C higher than the intended foaming temperature.

The results show that increasing the platen temperature by 5°C reduces the relative density, which is undesirable. This can be attributed to the potential for additional cell growth resulting from the higher temperature during the hot-pressing step. Therefore, the hot press temperature during the flattening process should be set to the foaming temperature used in the oil bath.

Method To Produce Low-Density and High-Density Flat Foamed Sheets

The foaming temperature for the given saturation pressure determines the relative density of the foam. Increasing the foaming temperature decreases the relative density of the foam. While using the protocol for flattening the specimens, we encountered two issues: The platen temperature was high enough to flatten the specimens at low foaming temperatures for high-density foams. The specimens warped severely in the oil bath for low-density foam due to high foaming temperatures, making them unable to be flattened at all.

Flattening High-density Foams

For high densities, the foaming temperature range will be closer to the effective T_g of the polymer-gas system, given the saturation pressure. Preliminary experiments suggested that setting the platen temperature equal to the foaming temperature is insufficient to flatten high-density foam specimens. The solution was to increase the temperature of the platen. However, this can induce further bubble growth and decrease relative density. A study was conducted on the PEI-CO₂ system at 5 MPa to produce a flat specimen at a relative density of 0.8. We developed a two-step process in which we foamed the sheet at 130°C, the temperature corresponding to the target relative density. The image of the specimen after the oil bath foaming is shown in Figure AI.5. We observed a slight warp. The foamed sheet was then pressed at 140°C according to the flattening protocol, except that the platen temperature was 10°C higher than the foaming temperature. We

flattened the specimen, and its relative density was measured as 0.77. The image of the specimen is shown in Figure AI.5.B.

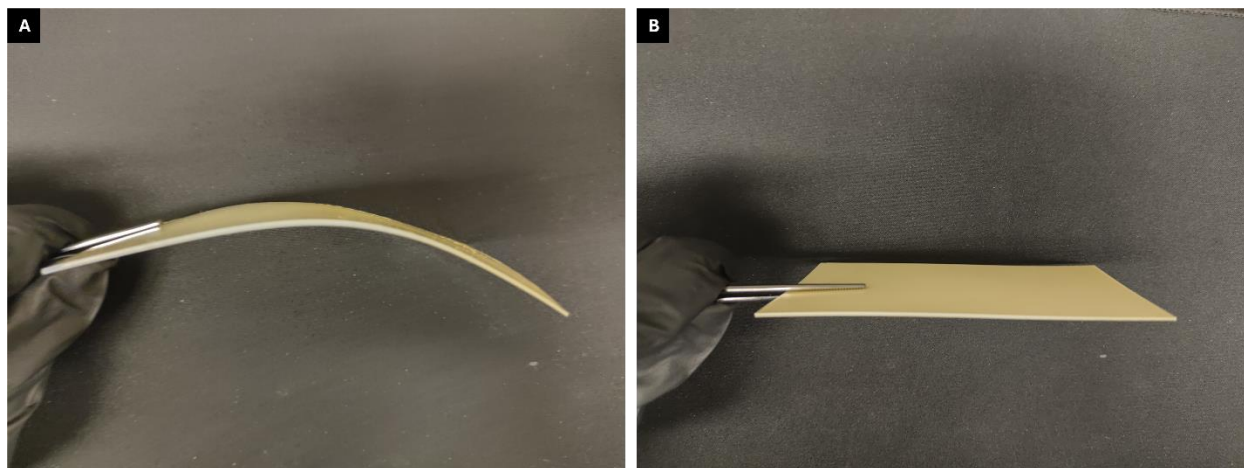


Figure AI.5 A) High-density PEI sheet foamed in an oil bath at 130°C. B) The foamed sheet is flattened in a press at 140°C.

Flattening Low-density Foams

For low-density foams, the foaming temperature will be closer to the T_g of the unprocessed polymer. The warping, as shown in Figure AI. 6. A, makes it practically impossible to flatten the specimen under the hot press. The solution is to foam the specimen at a lower temperature than required to achieve the target relative density in the oil bath. Select a temperature that is low enough to make warping manageable. Now flatten the sheet under the press at a temperature higher than the foaming temperature to induce foaming and reduce the density to the desired final relative

density. A study was conducted on the PEI-CO₂ system at 5 MPa to identify the foaming temperature and the required increase in the platen temperature.

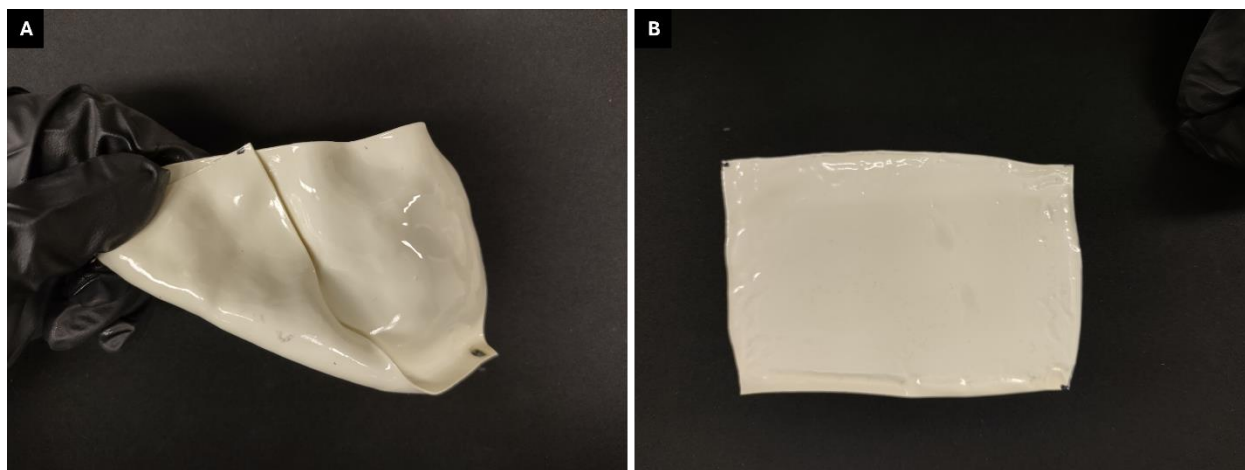


Figure AI.6.A) Low-density PEI sheet foamed in an oil bath at 180°C. B) A PEI sheet foamed in an oil bath at 160°C and flattened at 180°C in the press.

We developed a two-step process where we foamed the sheet at 160°C first in the oil bath. We observed a slight warp. The foamed sheet was then pressed at 180°C to induce secondary foaming and flattening. The image of the flat specimen is shown in Figure AI.6.B. The image of the specimen foamed directly at 180°C is shown in Figure AI.6. For reference, this shows severe warping. Through this two-step process, we have achieved the target relative density of 0.42. We extended the process to produce a low-density microcellular flat sheet at 1 MPa by foaming at 195 °C in an oil bath and then pressing the sheet at 205 °C. We produce a flat microcellular sheet with a relative density of 0.5.

Method To Reduce Gas Loss in Saturated Specimens Before Foaming

The diffusion coefficient of CO₂ in the polymer decreases with decreasing temperature. Therefore, preserving the saturated specimens at room temperature decreases the rate of CO₂ diffusion from the polymer. The CO₂ loss from saturated specimens was measured in two different cold environments: in a lab-grade freezer maintained at -30°C (verified using a laboratory thermometer) and in liquid N₂. The results are shown in Figure AI.7.

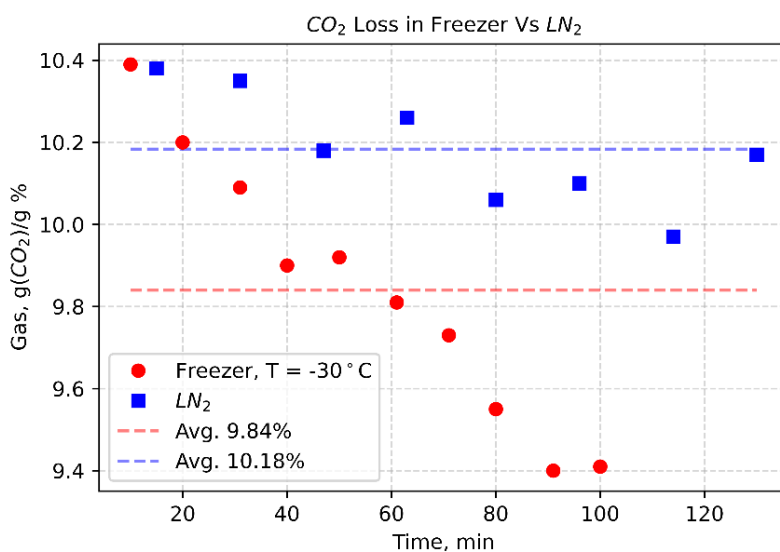


Figure AI.7 Measurements of CO₂ concentration in the PEI at different desorption times in the freezer and in Liquid N₂.

Results indicate a steady loss of CO₂ in the freezer. However, in liquid N₂, the rate of CO₂ loss is relatively lower. Note that after retrieval from the cold storage, the specimens were wiped with lint-free wipes before each weight measurement to remove any condensed moisture. The effectiveness of removing moisture was verified on neat polymer sheets without gas by subjecting them to the same process and measuring their weight periodically.

In another study, the saturated specimens were periodically retrieved and foamed at the same temperature to compare the effect of CO₂ loss on the relative density for both freezer and liquid N₂. The results are shown in Figure AI.8.

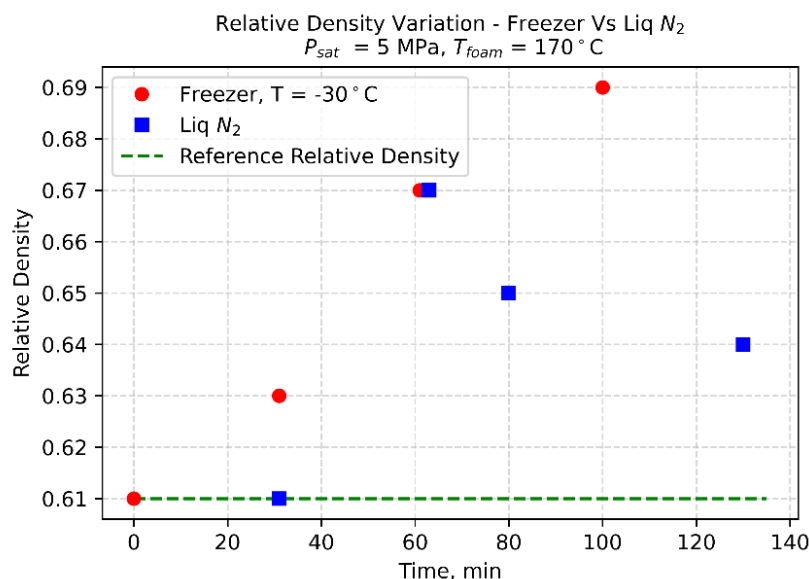


Figure AI.8 A plot shows the relative density variation of PEI foams caused by CO₂ loss in the freezer versus liquid N₂.

The relative density of the freezer-stored specimen when foamed after 100 minutes increased by 13% compared to the target relative density. The relative density of the liquid N₂-stored specimen

was measured after foaming, and it increased by only 5%. Therefore, when preparing flat-foamed sheets for mechanical tests, all the saturated specimens will be stored in liquid N₂ after being removed from the pressure vessel until the foaming process is complete. After being removed from liquid N₂, the specimens will be allowed to thaw for 2 minutes to reach room temperature before foaming. This ensures that we don't introduce a starting temperature profile to specimens; instead, we want every point of the specimen to be at room temperature before foaming, and it is also safe to quench in hot oil.

AII. EQUATIONS FOR THE EFFECTIVE T_g-BASED MODEL TO PREDICT SKIN THICKNESS (CHAPTERS 6 AND 7)

Analytical Solution for Gas Concentration Profile in Polymer Sheet

1D Gas Diffusion

$$\frac{\partial^2 C(x,t)}{\partial x^2} = D \frac{\partial C(x,t)}{\partial t} \quad (\text{AII.1})$$

D is the average diffusivity of CO₂ in polymer, cm^2/s .

C is gas concentration, *wt. %* of the polymer.

x is the distance across the thickness, cm .

t is the desorption time, s .

Boundary conditions for desorption

$C(x, t = 0) = C_0$ (Uniform initial gas concentration)

$C(x = -L, t) = C(x = L, t) = C_1 = 0$ (Instantaneous loss of gas from the edge surfaces at the onset of desorption)

$2L$ is the thickness of the specimen.

Solution

$$C(x, t) = C_0 + (C_1 - C_0) * \left(1 - \frac{4}{\pi} * \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-D * \left(\frac{2n+1}{2L} \right)^2 * t} * \cos \left(\frac{(2n+1) * \pi * x}{2L} \right) \right) \quad (\text{AII.2})^{24}.$$

Analytical Solution for Temperature Profile in the Polymer Sheet during Foaming

1D Heat Diffusion

$$\frac{\partial^2 T(x,t)}{\partial x^2} = \frac{\rho c_p}{k} \frac{\partial T(x,t)}{\partial t} \quad (\text{AII.3})$$

k is the thermal conductivity of the neat polymer, $W/cm^\circ C$.

ρ is the density of the neat polymer, g/cm^3 .

c_p is the heat capacity of neat polymer, $J/g^\circ C$.

T is temperature, $^\circ C$.

x is the distance across the thickness, cm .

t is desorption time, s .

Boundary conditions

$$T(x, t = 0) = T_0 = 22^\circ C \text{ (Uniform temperature)}$$

$$T(x = -L, t) = T(x = L, t) = T_1 = T_{foam}$$

$2L$ is the thickness of the specimen.

Solution

Replace D with $\frac{\rho c_p}{k}$ and $C(x, t)$ with $T(x, t)$ in Eq.(A2), C_0 with T_0 and C_1 with T_1

AIII. PLASMA TREATMENT-BASED SOLID-STATE FOAMING PROCESS

Effect of Plasma Etching on Skin

A microcellular PC specimen was subjected to cold oxygen plasma etching under a vacuum using a commercially available plasma etcher. The specimen was saturated at 5 MPa and foamed in a hot oil bath at 150°C. The goal is to decouple the effect of plasma etching on the skin and help understand the impact of etching in eliminating skin in the plasma-induced foaming process.

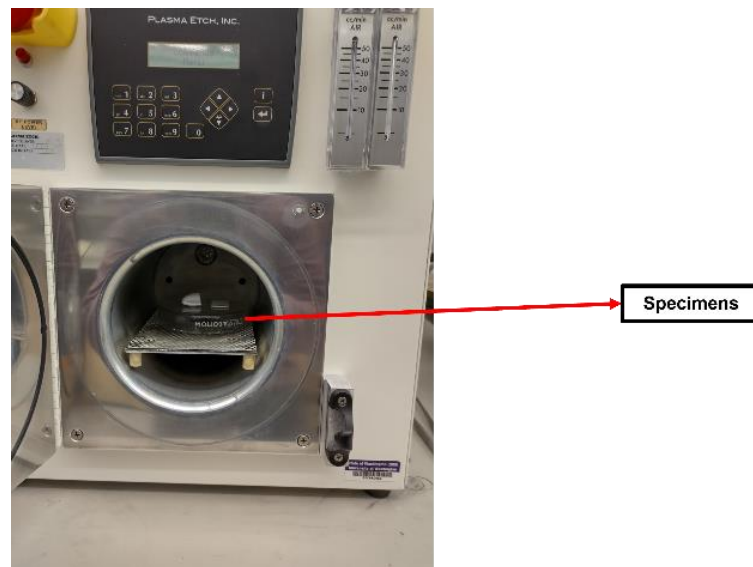


Figure A1: An oxygen gas plasma etcher

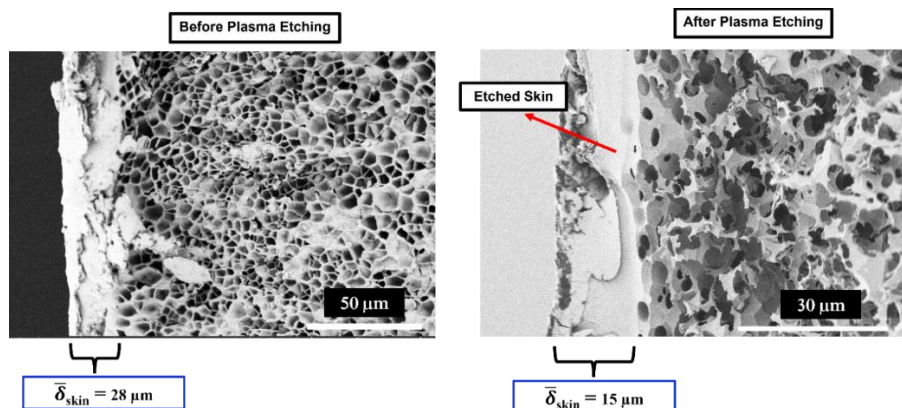


Figure AIII.2: The SEM images show that plasma treatment can etch the PC. In this case, plasma etching reduced the skin thickness by 50%.

Therefore, skin in solid-state microcellular and nanocellular foams can be etched by plasma treatment. The etching conditions required will vary depending on the base polymer

