EXTRUSION OF FINE-CELLED PLASTIC/WOOD-FIBER COMPOSITE FOAMS USING CO$_2$ AS A BLOWING AGENT

by

Haiou Zhang

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Mechanical & Industrial Engineering
University of Toronto

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0-612-50426-3
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ABSTRACT

This thesis is intended to investigate the feasibility of continuous extrusion processing of fine-celled plastic/wood-fiber composite foams using CO₂ as a physical blowing agent. The plastic/wood-fiber composites utilize wood-fibers as a reinforcing filler in the plastic matrix and are known to be advantageous over the neat plastics in terms of the materials cost and some improved mechanical properties such as stiffness and strength. However, these improvements are usually accompanied by sacrifices in the ductility and impact resistance. These shortcomings can be highly reduced by fine-celled and microcellular foaming of these composites to create a new class of materials with unique properties. An innovative tandem extrusion system with continuous and stable feeding, on-line moisture removal and CO₂ injection was successfully developed. The effects of both wood-fibers and CO₂ contents on the cell morphology and foam properties were studied. The cell morphology and foam properties modified by a coupling agent was greatly improved compared to unmodified composites. The tandem extrusion system was compared with a single extruder system to demonstrate the significant improvement in cell morphology resulting from uniform mixing and effective moisture removal. A scanning electron microscope (SEM) and a digital optical camera were used to characterize the cell morphology and extrudate profiles. The experimental results clearly proved that it is feasible to create fine-celled structures in the plastic/wood-fiber composite foams using environmentally-friendly CO₂.
DEDICATIONS

To my grand motherland of China

I am so proud to be a Chinese. Whatever I do, whenever I grow, wherever I go, I miss and love you so strongly. I know how much you have been suffering in the past, now you are waking up and opening to the world. Best wishes to you for the New Year 2000, the New Decade, the New Century, and the New Millennium.

To my dear parents Rongguo Zhang and Shanshan Pu

I am so happy and lucky to be your son, papa and mama. Thank you for your endless love, moral, spiritual, and financial support throughout my life. I really don’t know what my life would be without all sacrifices you have made for the life and education of your child. I love you forever.

To my sisters, uncles, aunts, friends and all whom
I deeply missed when I was abroad

Without the continuous encouragement and great help from all of you in my life, I can’t go so far.
I love all of you, and I pray for all of you.

To Ms. Brianna B. Shen

Your invaluable understanding, caring, help and support have made my life so enjoyable and memorable. So nice to meet and know you at the University of Toronto. I really want to say thank you and good luck for your future. Up over the world so high, like a diamond you are sure to shine!
ACKNOWLEDGEMENTS

This thesis would not have been accomplished without the guidance of my supervisor, Professor Chul B. Park. His suggestions, ideas and thoughtful insights during my research work and while reviewing drafts at different stages of development are greatly appreciated. I would like to express my sincere gratitude to Professor C. B. Park for providing support and encouragement throughout my study and especially at my most difficult and depressed times. His initiative, patience and personality will not be forgotten.

I would like to acknowledge the contribution of the Materials and Manufacturing Ontario (MMO), The Plastic Lumber Company Inc., CertainTeed Corp., CRF Technologies Group Ltd., Dupont Canada Inc., and Anderson Corp. for their sustained sponsorship of this project.

My gratitude is extended to the Department of Mechanical and Industrial Engineering at the University of Toronto for providing the University of Toronto Master's Open Fellowships and Frank Howard Guest Graduate Bursary. Special thanks are due Prof. J. Mostaghimi and Ms. B. Fung. I want to acknowledge the professional and technical support from Mike Smith, Jeff Sansome and Dave Esdaile in the Machine Tool Laboratory.

I would like to thank my past and present colleagues and fellow researchers working in the Microcellular Plastics Manufacturing Laboratory for their great help and friendship. They include Ghaus Rizvi, Dmitry Ladin, Simon Park, Amir Behravesh, Laurent Matuana, Anthony Yeung, Fangyi Liu, Remon Pop-Iliev, Xiang Xu, Cunning Xie, Xiaoyang Guan, Hani Naguib, Dr. Yuejian Liu, Gangjian Guo, Linda Lin, Esther Richards, Patrick Lee and Chris Ozolins.

Finally, I have tried to make the acknowledgement list as complete as possible, and regret any unintentional omissions. Those who feel that their names should be here, but it is not, please accept my unwritten thanks.
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<thead>
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<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>( A )</td>
<td>An Arbitrary Area on a SEM Micrograph (cm(^2))</td>
</tr>
<tr>
<td>( c_s )</td>
<td>Solubility of Gas in a Plastic (cm(^3)/g or g(gas)/g(plastic))</td>
</tr>
<tr>
<td>( C_0 )</td>
<td>Concentration of Gas Molecules in Solution (#/m(^3))</td>
</tr>
<tr>
<td>( D )</td>
<td>Diffusivity (cm(^2)/s)</td>
</tr>
<tr>
<td>( D_o )</td>
<td>Diffusivity Coefficient Constant (cm(^2)/s)</td>
</tr>
<tr>
<td>( D )</td>
<td>Diameter (m)</td>
</tr>
<tr>
<td>( d_N )</td>
<td>Nozzle Diameter (mm)</td>
</tr>
<tr>
<td>( f_o )</td>
<td>Frequency Factor of Gas Molecules Joining the Nucleus (1/s)</td>
</tr>
<tr>
<td>( H )</td>
<td>Henry’s Law Constant (cm(^3)[STP]/gPa)</td>
</tr>
<tr>
<td>( h )</td>
<td>Thickness of Sample (mm)</td>
</tr>
<tr>
<td>( K )</td>
<td>Consistency Parameter (Pa\cdot s(^n))</td>
</tr>
<tr>
<td>( k )</td>
<td>Boltzman Constant (J/K)</td>
</tr>
<tr>
<td>( L )</td>
<td>Laminar Factor for Static Mixer (m(^3))</td>
</tr>
<tr>
<td>( L_N )</td>
<td>Nozzle Length (mm)</td>
</tr>
<tr>
<td>( M )</td>
<td>Magnification Factor of a SEM Micrograph</td>
</tr>
<tr>
<td>( \dot{m}_o )</td>
<td>Injected Gas Flow Rate (g/min)</td>
</tr>
<tr>
<td>( N )</td>
<td>Cell Density (#/cm(^3))</td>
</tr>
<tr>
<td>( \dot{N} )</td>
<td>Rate of Nucleation (#/cm(^3)/s)</td>
</tr>
<tr>
<td>( n )</td>
<td>Power Law Index (dimensionless)</td>
</tr>
<tr>
<td>( n_o )</td>
<td>Number of Cells in an Area ( A ) on a SEM Micrograph (#)</td>
</tr>
<tr>
<td>( p_s )</td>
<td>Saturation Pressure (Pa)</td>
</tr>
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</table>
\( Q \) = Volumetric Flow Rate (m³/s)

\( R \) = Injected Gas Flow Resistance

\( Re \) = Reynolds Number

\( S \) = Specific Gravity

\( T \) = Temperature (K)

\( T_m \) = Melt Temperature (°C)

\( T_n \) = Nozzle Temperature (°C)

\( t_D \) = Diffusion Time (s)

\( V_d \) = Various Dead Volume

\( vl\% \) = Volumetric Percent

\( wt\% \) = Weight Percent

\( \alpha \) = Volume Expansion Ratio

\( \dot{\gamma} \) = Shear Rate (s⁻¹)

\( \dot{\gamma}_{\text{app}} \) = Apparent Shear Rate (s⁻¹)

\( \gamma_{ob} \) = Interfacial Surface Tension (mJ/m²)

\( \delta \) = Relative Injection Flow Variation

\( \eta \) = Shear Viscosity (Pa·s)

\( \rho_f \) = Bulk Density of the Foam Sample (g/mm³ or kg/m³)

\( \rho_0 \) = Bulk Density of the Raw Experimental Mixture (g/mm³ or kg/m³)

\( \Delta E_D \) = Activation Energy for Diffusion (J)

\( \Delta G \) = Gibbs Free Energy of Bubble Nucleation (J)

\( \Delta P \) = Gas Saturation Pressure (Pa)

\( \Delta P \) = Pressure Loss (Pa)
LIST OF ABBREVIATIONS

Ar = Argon
ASTM = American Society of Testing and Materials
CA = Coupling (or Compatibilizing) Agent
CBA = Chemical Blowing Agent
CFC = Chlorofluorocarbon
CTMP = Chemithermomechanical Pulp
CO₂ = Carbon Dioxide
FC = Fluorocarbon
HCFC = Hydrochlorofluorocarbon
HDPE = High Density Polyethylene
HIPS = High Impact Polystyrene
MFI = Melt Flow Index (g/10 min)
N₂ = Nitrogen
PAN = Polyacrylonitrile
PBA = Physical Blowing Agent
PE = Polyethylene
PET = Polyethyleneterephthalate
PP = Polypropylene
PS = Polystyrene
PTFE = Polytetrafluoroethylene
PVC = Polyvinyl Chloride
RPM = Revolution Per Minute (Rotational Speed of Extruder Screw)

SEM = Scanning Electronic Microscope

TGA = Thermalgravimetric Analyzer

WF = Wood Fibers or Wood Flour
CHAPTER 1

INTRODUCTION

This century is characterized by the ever-increasing consumption of plastics as a vital family of engineering materials, among which thermoplastics represent more than 80% of all plastics manufactured. Thermoplastics have been steadily replacing various metals in a wide range of applications, and this trend results in a continuous increase in their prices. Creating cell structures to produce foamed thermoplastics and utilizing inexpensive fillers to manufacture thermoplastic composites become two effective ways to address the price challenge and meanwhile improve the material properties.

1.1 Plastic/Wood-Fiber Composites

A composite is any combination of two or more materials in any form and for any use. Composites take advantage of the beneficial characteristics of each component material, and often have more useful properties than any of the constituents on its own. Within the next decade, composites are expected to constitute the most prominent segment of the plastics industry [1].

The use of wood fibers (WF) as a reinforcing filler in thermoplastics with the aim of reducing the cost as well as improving the mechanical and thermal properties has been
extensively studied in recent years due to the attractive benefits of WF. The main advantages of WF are their low density and cost, high specific strength and modulus, abundant availability and biodegradability, renewability and recyclability, and reduced equipment wear and good processability [2].

Filled thermoplastics represent a huge and growing market for all types of manufactured products. It is estimated that each year 20 million tons of fillers are used in plastic materials [1]. Currently, the most important fillers are calcium carbonate, talc, silica, mica, clay, alumina trihydrate, glass fibers, starch and cellulosic powders. Fillers have a variety of purposes and play an important role in reducing the cost and tailoring the performance of plastic resins to meet various industry specifications. The low cost and high strength-to-weight ratio of cellulosic fibers give such fibers considerable promise as reinforcing fillers in plastic composites [1].

However, the use of WF in thermoplastics as a reinforcing agent is restricted. Normally several problems arise in the manufacture of these composites as follows: (1) Difficulties occur in uniformly premixing the WF/thermoplastics feed because of the different bulk densities of WF and plastics; (2) The incompatibility of the hydrophilic WF and the hydrophobic plastic matrix causes poor dispersion and poor surface wetting of the WF. Poor dispersion of the fibers into the matrix results in a higher degree of variation in the ultimate properties of the composite; (3) No chemical bonding at the interface occurs since the WF and plastics are not chemically reactive with each other; (4) Poor adhesion with the plastic matrix due to water sorption on the WF surface makes total wetting impossible; (5) The chemical instability of the WF at a high temperature (greater than 200°C) and their tendency to give off volatiles causes numerous voids and poor interfacial bonding [2].
Therefore, most of the ongoing researches on plastic/WF composites have focused on the above mentioned problems, and conclusions are reached as: (1) use of effective processing systems to promote rapid dispersion and wetting of the WF by the molten plastics; (2) modification of the polar cellulosic fiber surface by grafting with compatible thermoplastic segments and vinyl monomers, or coating and/or reacting with compatibilizing or coupling agents prior to the compounding step; (3) addition of various additives, vinyl monomers, compatibilizing agents or coupling agents during the compounding step; (4) modification of non-polar plastic matrix with hydrophilic monomers or polar groups [2-9].

1.2 Plastic Foams

Foamed plastics (cellular plastics) can be defined as plastic materials that contain at least two phases: a solid plastic matrix and a gaseous phase. It is possible to have extra solid phases in plastic foams, such as a blend of plastics or fillers [10]. In other words, they have voids or cavities or cellular structures. Because of the voids present in the material, foamed plastics have less material in a given volume than neat plastics. Therefore, the production cost of foamed plastic products can be significantly reduced since the material cost can constitute up to 70% of the total cost of a plastic product [11].

Foamed plastics can be produced in many different methods. In the field of thermoplastic foams, the main stream method for creating cellular structures can be described as follows. First, gases are introduced into the melted plastic to create a plastic/gas solution (or mixture). This can be achieved by mixing a chemical blowing agent (CBA) or injecting a physical blowing agent (PBA) into the plastic matrix. CBAs release gases as a result of chemical reactions such as thermodecomposition, while PBAs are used directly as blowing agents.
Sometimes a nucleating agent is also added into the plastic to enhance the nucleation (i.e., bubble formation). The plastic/gas solution (or mixture) is conveyed forward in the extruder barrel by the screw motion until it reaches the die where it is subjected to a pressure drop and extruded out from the die. Due to the pressure drop, the gas is separated from the plastic matrix and forms nucleated bubbles. The bubbles continue to grow until there is no additional gas available in the plastic for further expansion or the plastic is cooled and solidified. The shape of the die exit can control the shape of the extrudate [10,12-13].

Foamed plastics offer many distinctive advantages over unfoamed plastics and other traditional materials, such as their cost effectiveness, unique insulating properties, impact-resistant characteristics, buoyancy and outstanding strength-to-weight ratios. Therefore they have an important economic impact on almost every aspect of life and account for more than 10% of the entire products of the plastic industry today. High-density foams are basically used in furniture, transportation, building products, wires and cables, automotive and structural applications, while low-density foams are used for shock mitigation, insulation, and rigid packaging [10,14-15].

The cell morphology of the plastic foams influences their characteristics, such as mechanical, thermophysical, dielectric and other properties. Plastic foams produced by conventional processes generally yield non-uniform cells with an average cell size greater than 300 μm, a cell density lower than $10^6$ cells/cm$^3$, a volume expansion ratio up to 50 and a broad cell size distribution. These result in a direct deterioration in the mechanical and other material properties of the conventional plastic foams [10,16-22].

The concept of creating a microcellular structure in a plastic matrix was invented by Suh et al. [23] at the Massachusetts Institute of Technology in the early 1980's. The development of these materials is based on the idea that the creation of a very large number of
microbubbles, which are smaller than the pre-existing natural flaws in a plastic, can reduce the material cost and consumption in mass-produced plastic parts without major compromise to the mechanical properties.

Microcellular plastics are foamed plastics characterized by a cell density greater than \(10^9\) cells/cm\(^3\), a fully grown cell size on the order of 10 \(\mu\)m and a specific density reduction in the range of 5 to 95%. The basic approach to the production of microcellular structures is to continuously form a complete plastic/gas solution, nucleate a large number of bubbles using rapid pressure drop, shape a nucleated plastic/gas solution under pressure, and induce a volume expansion to a desired expansion ratio. Successful completion of the above steps in extrusion will enable the manufacture of microcellular foamed plastics with a high cell-population density [23-24]. Typically, microcellular plastics exhibit high impact strength (up to a five-fold increase over unfoamed plastics), high toughness (up to a five-fold increase over unfoamed plastics), high stiffness-to-weight ratio (three to five times larger than unfoamed plastics), high fatigue life (up to a five-fold increase over unfoamed plastics), high thermal stability, low dielectric constant, and low thermal conductivity. These improvements are due to the presence of bubble cells which are much smaller than those of conventional foams. Such small bubbles inhibit crack propagation by blunting the crack tip and increasing the amount of energy needed to propagate the crack [25-26]. The presence of these cells can also reduce the specific density of the plastic in the range of 75% or higher. Due to such unique properties, there are a large number of innovative potential applications of microcellular plastics. These include food packaging with reduced material costs, airplane and automotive parts with high strength-to-weight ratio and acoustic damping, sporting equipment with reduced weight and high energy absorption, insulative fibers/filaments for fabric, molecular grade filters for separation processes, surface modifiers for low friction, and biomedical materials.
Since microcellular plastics are known to exhibit higher impact strength, higher toughness, higher ductility and increased fatigue life, microcellular foaming of plastic/WF composites would also improve these properties as well. Especially, it is expected that the deteriorated impact strength of plastic/wood-fiber composites will be improved significantly. Therefore, microcellular foaming of plastic/WF composites would lead to the creation of a new class of composite materials with enhanced and unique properties and characteristics.

As a first step, production of a fine-celled structure, a cell size between 10 μm and 100 μm, a cell density ranging from $10^6$ cells/cm$^3$ to $10^9$ cells/cm$^3$ and a cell uniform distribution, is intended in this study.

1.3 Blowing Agents

Blowing agents and other additives for foamed products are used to produce porous or cellular plastics. The amounts and types of blowing agents influence the densities of the finished products and their porous structures. There are two major types of blowing agents: physical and chemical. Physical blowing agents (PBA) are volatile liquids or compressed gases that change the state during processing to form a cellular structure. Chemical blowing agents (CBA) are solids that start to decompose thermally above a certain processing temperature to form gaseous decomposition products. The produced gases are finally distributed in the plastic melt to provide the foam structure [27].

CBAs are primarily used in applications where a high-density foamed product is required, while PBAs can be used in both high and low-density product lines. Current technologies for extrusion processing with CBAs are limited as follows: (1) On-line adjustment of foam densities is difficult to achieve without changing CBA concentration; (2)
Residual CBA in the extrudate can hinder recycling of scrap into process; (3) Migration of CBA in the dry-blended mix during transport may cause density variations in the product; (4) Relatively high cost of CBAs. Therefore utilizing PBAs in foam processing has been becoming the trend in plastics industry. However, conventional PBAs such as halocarbons (CFCs and HCFCs) and hydrocarbons are subject to strict environmental regulations today. An alternative group of inert-gas blowing agents such as carbon dioxide (CO₂), nitrogen (N₂) and argon (Ar) are currently generating much interest since they are more "environmentally friendly" without depleting the ozone layer [28].

1.4 Motivation of the Thesis

Since fine-celled and microcellular foams have superior properties to conventional foams, it is desirable to develop a cost-effective continuous foaming process to produce fine-celled and microcellular foamed products. To date, researches on continuous processing have focused on achieving a high-cell population density and a high volume expansion from the pure plastic foams [24, 29, 30-37]. Little work has been carried out to construct fine-celled and microcellular structures in plastic/WF composites, which is obviously an unexplored research field. Especially, all the plastic/WF composite foam processing has been conducted with a CBA. Processing with a PBA has not been studied for plastic/WF composite foaming.

The motivation of this thesis is: (1) to study the feasibility of creating fine-celled structures in plastic/WF composite foams with CO₂ as strategies to reduce the cost, the weight, the brittleness of the composites while improving their impact strength and ductility, (2) to develop and experimentally verify an innovative cost-effective continuous extrusion system
with injection of environmentally-friendly CO\textsubscript{2} as a PBA, and (3) to establish process-structure relationships for these composites.

1.5 Structure of the Thesis

Chapter 1 gives a general overview on the plastic/WF composites, plastic foams, blowing agents, motivation and structure of the thesis.

Chapter 2 involves the literature survey and theoretical background. It starts with a review of the plastic/WF composites, their fillers and the current research of interest. Then conventional foams and their production process are briefly reviewed followed by a detailed review of microcellular foams and their foaming processes.

Chapter 3 describes the detailed design of an innovative tandem extrusion system. It mainly includes a twin-screw feeder, a counter-rotating twin-screw extruder, a devolatilizing vent, a vented single-screw extruder with CO\textsubscript{2} injection system, a dissolution-enhancing device with inner static mixer, a heat exchanger with inner static mixer, a nucleation nozzle die and a temperature and pressure control panel.

Chapter 4 presents a series of well designed experiments conducted for studying the feasibility of fine-celled foaming of plastic/WF using CO\textsubscript{2} as a blowing agent. The devolatilizing characteristics of wood fibers were studied using TGA. After the preliminary experiments conducted for both HDPE/WF and HIPS/WF composites at a low WF content of 10 wt\% to investigate the operation of the developed tandem extrusion system, most of the efforts were focused on the foaming of fine-celled HDPE/WF composites at higher WF contents (20 wt\%, 30 wt\% and 40 wt\%) and various CO\textsubscript{2} contents (0 wt\%, 1 wt\%, 2 wt\% and 4 wt\%) to identify the effects of both WF and CO\textsubscript{2} contents on the cell morphology and foam
properties. Two system configurations (tandem extrusion system vs. single extruder system) were experimented to demonstrate the system effect on the cell morphology and foam properties. A suitable coupling agent (CA) was selected to modify the interface of HDPE and WF and effectively improve the bonding between HDPE and WF. The results were compared with those without CA modified to study the effect of CA on cell morphology and foam properties. Finally a set of supplementary experiments, suggested by the industrial companies for this research project at the third half-yearly sponsor meeting, were further performed to better understand the stronger effect resulting in the poor composite foams obtained from the single extruder system.

Chapter 5 summarizes the grand conclusions, introduces a number of possible extensions that can be drawn from the research work presented in the thesis, and identifies potential directions for future research.
CHAPTER 2

LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 Plastic/Wood-Fiber Composites

Within the next decade, composites are expected to constitute the most prominent segment of the plastics industry. Competition in high-volume markets has focused attention on low-priced materials that offer a more favorable balance of product quality, performance and cost. Wood fibers are of particular interest because of their low density, abundance and favorable strength-to-weight ratio. Plastic/WF composites also have the lowest material cost compared to other plastic composites [1].

Filled thermoplastics represent a huge and growing market for all types of manufactured products. The primary purposes for using a filler in a thermoplastic composite are its potential abilities to modify the properties of plastic materials such as stiffness, impact strength, abrasion resistance, electrical attributes and dimensional stability, and to typically reduce the material cost. The fillers applied can be either solid particulate or fibrous materials [38-40].

Reinforcing fillers, which implies that the fillers increase strength, must own the shapes of fibers or flakes, with one dimension being significantly longer than the other. Mica, talc and clay represent an intermediate class of low-cost mineral reinforcing fillers that owe their reinforcing action to the "flake aspect ratio" (the mean diameter of the flakes divided by their
mean thickness for any particular filler grade). Similarly, the "fiber aspect ratio" is the mean fiber length divided by the corresponding diameter [1].

2.1.1 Fiber-Reinforced Composites

Fiber-reinforced composites occupy a central role in the development of new materials and overcome many of the limitations of traditional materials. All classes of materials can now be reinforced and improved by the incorporation of fibers. A fiber is a long fine filament of matter, with a diameter generally of the order of 10 μm and an aspect ratio of length to diameter usually between 100 to 1000 and virtually infinity in the case of continuous fibers. Fibers are not only strong, stiff in tension and flexible in bending, but also they often combine these qualities with a low weight [38].

Fibers are ubiquitous and exist in both natural and synthetic forms. One can classify fibers in a variety of ways. One may divide the whole field of fibers into apparel and nonapparel fibers, i.e., based upon the final use of fibrous materials. The apparel fibers include synthetic fibers such as nylon, polyester, spandex, and natural fibers such as cotton, jute, sisal, ramie, silk, etc. Nonapparel fibers cover aramid, polyethylene, steel, copper, carbon, glass, silicon carbide, alumina and so on. These nonapparel fibers are used for making cords and ropes, geotextiles, and structural applications such as fiber reinforcements in a variety of composites [41].

Another classification of fibers can be made in terms of fiber length, continuous or staple fiber. Figure 2.1 shows such a classification based on the fiber size and the different product forms that are commonly available. Continuous fibers have practically an infinite length while staple fibers have short, discrete lengths (10-400 mm) [41].
Yet another convenient classification of fibers is based on natural and synthetic fibers, as shown in Figure 2.2. Natural fibers occurring in the vegetable or animal kingdom are polymeric in terms of their chemical constitution, while natural fibers in the form of minerals are akin to crystalline ceramics. A distinctive feature of natural fibers is that they are generally a mixture (chemical or physical) of different compounds. There are many natural fibers, organic and inorganic. Examples of organic fibers include silk, wool, cotton, jute, sisal and of inorganic fibers are asbestos and basalt. There are a large variety of synthetic fibers available commercially. Polymeric fibers such as polypropylene, polyethylene, polyamides, polyethyleneterephthalate, polycrylicanitrile, polytetrafluoroethylene, aramide, etc. are well established fibers. Metallic wires or filaments have been available for a long time. Examples include steel, aluminum, copper, tungsten, molybdenum, gold, silver, etc. Among ceramic and glass fibers, glass fibers for polymeric reinforcement have been available since the 1940s, while ceramic fibers such as carbon, silicon carbide, alumina, etc. became available from the 1960s onward [41].

Fiber-reinforced composites are finding ever-increasing applications in engineering and in consumer goods. They can offer a unique combination of properties or may be used simply because they are more economical than competing materials. The matrix material is usually polymeric and in many applications they compete with unreinforced polymers. Fiber reinforced composites improve their stiffness and strength, and for many polymers increase their toughness. In addition, the dimensional stability is improved, and benefits such as creep resistance and better ageing and weathering properties are usually obtained [42].

2.1.2 Fiber-Reinforced Plastics
Reinforcing Fibers

Glass fiber has been the major reinforcement for the fiber reinforced plastics industry, which is supplied in a variety of forms, e.g., continuous rovings, woven rovings, cloths and random chopped fiber mats. The drive for lighter, stronger, stiffer structures has seen the introduction of carbon and polyaramid fibers. The high strength and stiffness-to-weight ratios of carbon and polyaramid fibers make them particularly attractive for the manufacture of lightweight structural components. Other applicable reinforcing fibers include polyester, nylon and boron fibers for specialized applications.

Natural fibers such as jute and sisal have also been used to reinforce thermosetting resins, but their application has been limited by their poor long-term environmental performance [43, 44].

The use of wood fibers in thermoplastic composites has been limited due to poor compatibility between hydrophilic wood fibers and hydrophobic plastic matrix. If this problem is completely solved, wood fibers would be very well suited for thermoplastic reinforcement because of their strength and modulus properties which compare favorably with those of glass fibers. Furthermore, they display several advantages if one compares them to inorganic fibers, e.g., a lower density (1.5 g/cm$^3$ as compared to 2.5 g/cm$^3$ for glass fibers); flexibility during processing; no health hazard; non-abrasiveness of processing equipment; much lower costs than silane-treated glass fibers and an opportunity to use abundant wood fibers. In general, hardwood fibers have an especially high potential for reinforcement because they are shorter and stiffer than softwood fibers in addition to having a high fiber aspect ratio (50-150) [45].

Plastic Resin Matrix

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The most frequently used resins for the manufacture of fiber-reinforced plastics are polyester, vinyl ester and epoxy resins, along with other thermosetting resin systems including phenolic, silicone, polyimide, furane, melamine and urea-formaldehyde resins [43].

There is a growing interest in the use of thermoplastics in fiber-reinforcing applications because their excellent toughness, resilience and corrosion resistance. The key difference between such composites and the more traditional thermoset based composites lies in the behaviour of the matrix during processing. The thermoplastic matrix is not required to undergo a "cure" process to achieve its final mechanical properties - all that is required is melting, shaping and subsequent solidification. In consequence, such composites can offer the potential for extremely rapid forming [44]. However, these straight chain plastics, such as polycarbonate, polyethylene, polypropylene, polystyrene and nylon, do have fundamental disadvantages compared with thermosetting resins, in that they have to be molded either at elevated temperature, i.e., they are softened, or above their melting points. They are very viscous under molten conditions and in the finished state have lower levels of heat and solvent resistance [43].

2.1.3 Plastic/Wood-Fiber Composites

The concept of incorporating fibrous materials derived from cellulose or wood into a plastic matrix has been studied extensively, and different cellulosic fibers are more widely used in polyolefins (polyethylene and polypropylene) than in other thermoplastics [45-51]. They possess low specific gravities (about 0.9-1.4) and offer significant cost savings when filled to extend plastic matrices. The main reason for using fibrous cellulose materials lies in
the fact that these fibers are more able to resist degradation of their aspect ratio during processing, which is important for fibers to transfer stresses effectively in the composites. Most of the available literature on cellulosic-fiber filled plastics can be classified into three categories: (a) study of the processing parameters, (b) effects of the nature/type of fibers, and (c) effects of coupling agents/adhesion promoters on the performance of the composites.

Wood and plastics are becoming best friends these days. Dozens of firms are seeking to exploit these materials for manufacturing tough, light-weight window profiles, plastic lumber, and interior auto panels.

Wood-filled plastics or plastic/wood-fiber composites go back 25 years to a proprietary process, called Woodstock, for mixing 50% wood flour in PP. Woodstock was patented by extrusion machinery builder ICMA San Giorgio in Italy and processor G. O. R. Applicazioni Speciali SpA. The process went into production in 1971 at G. O. R. for Fiat cars [52]. Putting wood fillers into plastic lumber and window profiles started in the early 1990s. Andersen Corp. launched the first wood-fiber reinforced PVC profiles, called Fibrex, in 1993 [52]. An even newer market for wood fillers is commercial pellet-compounds and masterbatches according to custom formulations [52].

The difference between wood fibers and wood flour is that wood fibers have an aspect ratio (length/diameter) of 10:1 to 20:1, while wood flour generally has an aspect ratio of 1:1 to 4:1. Commercial wood flour generally comes in mesh sizes of 20 to 100, but most thermoplastic applications fall in the 40 to 80 mesh range. Fine-mesh wood flour adds stiffness but lowers impact strength, whereas longer wood fibers contribute strength and light weight but are trickier to bind into the composite. Beside the mesh size and uniformity, it also makes a difference by the original wood species such as pine, spruce, hemlock, maple, oak, birch, etc. Wood flour is very sensitive to moisture and temperature. Temperatures over 395°F (200°C)
begin to degrade it. Moisture levels above 0.5-0.7% in the flour will make the composite foamed in the extrusion process. In addition, plastics and wood do not mix easily, so they are more likely to need modification [52].

Beshay and Kokta [47] studied the performance of wood-fiber of aspen in the form of grafted chemithermomechanical pulp as reinforcement in a polyethylene (PE) matrix. The secant modulus, tensile strength, energy and elongation at yield were measured. It was found that the mechanical properties of the composite were higher than those of pure PE by a factor of 2.6 for modulus, 2.3 for stress, and 2.1 for energy at yield, while elongation at yield of grafted wood fiber composites did not significantly change compared to PE. In addition, compared to glass fiber composites, the chemithermomechanical pulp composites showed higher elongation, 100 percent higher energy, 106 percent higher stress, and 75 percent higher modulus. However, the cost of treated wood fibers was several times lower than that of treated glass fibers.

The use of wood fibers in thermosetting resins is well established. Wood flour has been used as filler/extender in phenol, urea and melamine formaldehyde resins to improve their toughness, limit resin shrinkage and reduce the cost. However, they have received only little attention as a filler/reinforcing agent in high volume thermoplastics (PE, PP, PVC and PS). This can be attributed to a number of drawbacks arising from the use of wood fibers: increased difficulty in compounding in thermoplastic matrices, weak adhesion between the polar, hydrophilic wood fibers and the non-polar, hydrophobic plastics, thermal degradation at higher processing temperature and poor moisture resistance. Raj and Kokta [49] believed that many of the above mentioned problems can be overcome to a greater extent by the modification of fiber surface with suitable additives and the use of coupling agents. The degree of interaction between filler and plastic is largely affected by the nature of the interface. The ultimate
properties of the composite are greatly influenced by the choice of additive/coupling agent, their concentration and the method of application. They examined the effects of additives/coupling agents in mechanical properties of high density polyethylene (HDPE) filled with different concentrations of wood fibers. The wood fibers were pretreated with isocyanate or silane coupling agents before incorporated into the plastic matrix. Their research showed that pretreatment of wood fibers with suitable additives improved the performance of wood fibers in HDPE. Compared to untreated-fiber (no additive) filled HDPE composites, a significant increase in tensile strength was obtained by the silane-pretreated wood fibers. The best increase in the composite properties was achieved at a lower concentration of silane. The elongation, tensile modulus, and Izod impact strength were more affected by the concentration of wood fibers in the composite and were less influenced by the fiber treatment.

Mckenzie and Yuritta [53] reported improvement in tensile strength by using wood fibers as a filler for PE and other plastics by lamination or impregnation. Sarma et al. [54] claimed successful use up to 40 percent of hardwood and softwood sawdust as fillers for phenolformaldehyde sulfonic resin. Seymour [55] reviewed use of cellulosic fillers in plastic composites. He used wood flour as reinforcement in different plastics including HDPE. He also considered the use of other cellulosic fillers such as ground wood waste, bark, nut shells, bagasse, corncube, bamboo and cereal straws. Belmares et al. [56] found that there were great improvements in the tensile strength and modulus along with low elongation at break when the natural hard fibers were used as fillers. Lawniczak [57] prepared composites from low density hardwood-polystyrene, called "lignomer" by using an autoclave for bonding of styrene impregnated wood. He concluded improvement in bending and compressive strength and lower hygroscopicity. Young and Nguyen [58] prepared composites from either mechanical or thermomechanical grafted pulps by the xanthation method using different vinyl monomers. He
proved an increase in the dry or wet strength after hot pressing. Coran and Patel [59] prepared composites of 2-55 weight percent (wt%) of cellulosic fibers and grafted olefin plastics by using bonding agents such as phenolformaldehyde resin, poly-isocyanate, etc. The cellulosic fibers were rayon, cotton, hardwood and kraft pulp. Some improvement of strength properties as well as swelling resistance was observed. Goettler [60] grafted hardwood fibers with vinyl chloride in the presence of isocyanate as a bonding agent. He declared that the composites can be molded or extruded to produce useful articles, e.g., floor tile, tubing, etc. Mansour et al. [61] prepared composites using both organic and inorganic fillers. They grafted bagasse and semi-chemical pulp of bagasse mixed with clay and methylmethacrylate using a sodium bisulfite system. The composites showed improvement in compression strength and water resistance.

The available literature indicates that wood fibers are the most favored reinforcing fillers among the various experimented cellulosic fibers. In detail, chemithermomechanical pulp and wood flour are the two most often chosen fillers in many researches. The main difficulty of dealing with fibrous cellulose materials is their tendency to entangle and form fiber agglomerates during processing. The formation of fiber agglomerates tends to prevent complete fiber dispersion, and affects the properties and appearance of the finish products. This problem limits the use of such fibrous fillers and favors wood flour and chemithermomechanical pulp. Moreover, the long, twisted cellulosic fibers tend to tangle and pack together, making conventional mixing procedures that employ gravity feed very difficult. For this reason, compounders prefer to use granular wood flour, which is wood or sawdust ground to a certain mesh size. The grinding process reduces the wood to a relatively dense, free-flowing powder that is more easily compounded with plastics. High intensity or high shear compounding applied in the industry minimizes this problem [1].
The literature survey implies that most of the research work carried out on plastic/cellulosic fiber composites up to now are focused on the areas including improvement of interfacial interaction and adhesion between fibers and plastic matrix, enhancement of dispersion of fibers into the plastic matrix, and testing of the material properties of composites. Different combinations and concentrations of fibers and plastics were investigated, various coupling agents, additives and dispersants were examined, and different cellulose treatments such as coating by latex and grafting with polymer/vinyl monomer were also studied.

However, little work has been conducted on fine-celled foaming of plastic/wood-fiber composites. Matuana et al. [62] reported that the microcellular structure was successfully created in the PVC/WF composite based on batch processing. Ghaus et al. [63] presented the research progress on the fine-celled foaming of plastic/wood-fiber composites using chemical blowing agents. A more effective and continuous processing based on extrusion for fine-celled foaming of plastic/wood-fiber composites with a physical blowing agent has not been effectively studied yet.

### 2.2 Plastic Foams

The idea of using a less material by creating bubbles (cells) in the plastic matrix to produce foams has become a desirable solution to address the challenge of material cost provided that the functionality of the product is not compromised. Besides this advantage, plastic foams usually offer superior properties which make them highly favored in diverse applications such as transportation, packaging, sports facilities, furniture, building and construction, thermal and electrical insulation, shock and sound attenuation, etc. Foamed plastics can often be stronger than their non-foamed analogues and, because of the reduced
weight, can achieve outstanding cost-to-performance and favorable strength-to-weight ratios [14].

There are different criteria to classify plastic foams. Based on the average cell size and cell density, plastic foams can be divided into three categories: conventional foams (cell size > 300 μm and cell density < 10^6 cells/cm³), fine-celled foams (10 μm < cell size < 300 μm and 10^6 cells/cm³ < cell density < 10^9 cells/cm³), and microcellular foams (cell size < 10 μm and cell density > 10^9 cells/cm³) [64].

The relationship between the glass transition temperature and the room temperature of the plastic foams can also be used as a classifying criterion. This kind of classification recognizes flexible, semi-flexible (or semi-rigid), and rigid foams. Flexible foams are associated with glass transition temperatures below the room temperature, semi-flexible foams are defined as an intermediate state between flexible and rigid foams, while rigid foams are associated with glass transition temperatures above the room temperature [13].

Another way of classifying plastic foams employs the fact that the cell morphology of the foam, comprising cell geometry, cell size and cell shape, strongly affects plastic foam properties. Thus, cells may be interconnected and/or discrete and independent. This method defines open-celled and close-celled foams [13].

The foam bulk density and the void fraction can also serve as a criterion for classifying plastic foams. According to this criterion, plastic cellular structures can be classified as high-density and low-density foams [14]. High-density foams assume a density of over 240 kg/m³, while low-density foams possess a density lower than 240 kg/m³ [10].

2.2.1 Conventional Foams
In a traditional extrusion process, foams are produced by mixing the plastic melt with a blowing agent under pressure. The blowing agent can be either physical (gas or liquid) or chemical (a substance decomposes to produce gas when heated). The gas or liquid is mixed with the plastic melt and dissolved in it. The mixture is then forced toward the die exit at the head of the extruder where it experiences a drop in pressure. The pressure drop causes bubble nucleation, and the nucleated bubbles continue to grow, resulting in foam expansion.

Foams produced in a state-of-the-art conventional extrusion process typically have cells larger than 300 μm, a cell-population density lower than 10^6 cells/cm³, and a broad cell size distribution. Because of the large cell size and non-uniform cell structure, conventional plastic foams exhibit relatively poor mechanical properties [10, 16-21]. However, in their favor, the expansion ratio of conventional foams can be high, i.e., up to 50 [13]. Production of fine-celled plastic foams is limited with available processing technologies.

A good review of conventional plastic foams and their processes is provided in [10, 64-65]. Plastic foams can be produced in such processes as extrusion, injection molding and compression molding. The selection and design of an appropriate process are governed mainly by the material characteristics, and thus it is impossible to offer a single process for all plastic materials. However, fundamentally, all foaming processes are similar.

In general, a foaming process consists of three main steps: formation of a plastic and blowing agent solution/mixture, cell nucleation, and cell growth. One of the conventional foam processes is called "Celuka Process" [66] and a schematic of this process is shown in Figure 2.3 [67]. In this process, a plastic is melted in an extruder, and a blowing agent is then injected which mixes with the plastic and dissolves in it. In some foaming process, the injected blowing agent may not completely dissolve in the plastic melt. The melt containing the blowing agent
is forwarded to the head of the extruder, which is partially plugged with a torpedo or mandrel. The melt then flows into a cooled shaper connected to the head of the extruder. The outer layer of the extrudate is therefore cooled and forms a skin layer. The foaming proceeds inward from the outer layer to the center of the extrudate. In this process, virtually no cell nucleation occurs in the melt before it flows into the shaper. Cell nucleation is initiated in the shaper, where cell growth also proceeds. In fact, in all the conventional processes, cell nucleation and cell growth take place simultaneously and thus are coupled with each other.

The Celuka process is a controlled foam extrusion process in which the foam product consists of a solid skin and a cellular core. In this process, the extrudate is mechanically constrained by a cooled shaper and thus is formed in the shaper's profile. Moreover, since the outer layer of the foam product is cooled and a solid skin is formed, the diffusion of the blowing agent from the outer surface to the atmosphere (or blowing agent escape) is prevented. However, the blowing agent can be still lost through the hot inner surface where foam growth occurs. This process can be used to produce foam parts with a wall thickness of over 6 mm [10].

In contrast to a controlled foam extrusion process, a conventional free foaming extrusion process allows the foaming article to expand without constraint. A schematic of this process is shown in Figure 2.4. The temperature of the melt at the die exit plays an important role in determining the final foam properties and the amount of expansion [68]. This process is suitable for products with a wall thickness in the range of 2-6 mm [10].

In a conventional foam process, foam products of various densities can be produced. However, the state-of-the-art foams have a fully grown cell size greater than 100 μm, a cell population density lower than $10^6$ cells/cm$^3$, and a nonuniform cell size distribution [10, 69]. Hence, the mechanical properties of the conventional foams are poor.
In conventional foam processing, the most commonly used blowing agents are FCs, CFCs, n-pentane, and n-butane [64]. These agents can dissolve into the plastic resin in large quantities due to their high solubility. For instance, the solubility of FC-114, a commonly used blowing agent, in polystyrene is above 20% by plastic weight at a pressure of 1000 psi and a temperature of 200°C [70]. This suggests that a foam product with a high void fraction can be produced at a relatively low pressure in the system. In addition, the loss of blowing agent from the extrudate during expansion is insignificant since the diffusivities of such agents are low due to their large molecular size, which allows the extrudate to expand significantly [64]. As a result, the final product will have a low foam density. Despite the favorable properties of the conventional blowing agents, there are major concerns in utilizing them. For instance, CFCs are known to deplete the ozone layer and their use has been stopped by the Montreal Protocol [71]. The other long-chain blowing agents such as n-pentane and n-butane are also hazardous because of their high flammability. Therefore, alternative blowing agents should be developed in plastic foam processing.

2.2.2 Microcellular Foams

It is well known that plastic foams with a smaller cell size and more uniform cell size distribution exhibit better mechanical properties such as a higher strength, a greater toughness and a better thermal insulation. The need to produce foams with smaller and uniformly distributed bubbles has become another interesting and challenging research direction, which generated a new category of plastic foams - microcellular foams [10, 16-21, 25]. Microcellular foamed plastics were invented with a cell size on the order of 10 μm and a cell density higher than 10⁹ cells/cm³ [25]. As a result, the mechanical properties of such foams are significantly
improved. When the cell size is extremely small, the impact strength and toughness of the foam are superior even to those of unfoamed neat plastics [16-21, 25]. Therefore, it is desirable to produce foams with a uniformly distributed fine-celled structure. A low material cost together with superior mechanical properties can make microcellular plastics suitable materials for a large number of innovative applications such as food packaging, sporting equipment, automotive components, building and construction, etc., provided that a cost-effective continuous manufacturing process for these materials is developed.

**Batch Processing of Microcellular Foams**

Microcellular plastics were first produced in a batch process [25] and have been extensively studied in batch processing. A schematic of the batch process is shown in Figure 2.5. In this process, a plastic sample is placed in a high-pressure chamber connected to a gas reservoir. The gas can be either nitrogen (N\textsubscript{2}) or carbon dioxide (CO\textsubscript{2}). The plastic sample then absorbs the gas and becomes saturated with it when a sufficient time is given for the absorption process. The amount of gas dissolved in the plastic plays an important role in the final foam qualities. When the sample is fully saturated with the gas, the pressure is rapidly decreased to cause a sudden drop in the solubility of the gas in the plastic. This initiates thermodynamic instability which drives nucleation of billions of microcells. These microcells cannot grow much due to a large amount of gas lost during cell growth. The foaming of the sample in the batch process is initiated by heating the surface of the sample. Since the temperature of the foam skin is always the highest during the foaming process, the gas can easily escape through the hot skin to the atmosphere. As a result, the sample expands to a certain size, which depends on the amount of gas left in the sample and used for the cell
growth. However, the foam products have a small cell size on the order of 10 µm due to the presence of a large number of nuclei generated in the plastic matrix.

In a batch process, cell nucleation and growth are decoupled. Cell nucleation is mainly governed by the saturation pressure or pressure drop, and cell growth is dominated by the heating temperature and time. Hence, the number of nucleated cells and the amount of expansion can be independently controlled. It must be noted that in a batch process, the foaming temperature is in general chosen to be the lowest to make the cell growth step highly controllable [72]. When the nuclei are generated, their growth is retarded due to the high stiffness of the plastic matrix at the low temperature. This prevents cell coalescence which degrades the foam product. Cell growth can be controlled by modulating the temperature and the time of the sample exposed to heat.

A major disadvantage of the batch process is that a very long time is required for saturation of gas in the plastic. This is due to a low rate of gas diffusion into the polymer at room temperature. For instance, the diffusivity \( D \) of CO\(_2\) in polystyrene at room temperature is \( 6 \times 10^{-8} \text{ cm}^2/\text{s} \) [73]. The diffusion time can be estimated using the following equation:

\[
t_D \equiv \frac{h^2}{4D},
\]

where \( h \) (mm) is the thickness of the sample. For a sample 1 mm thick, the diffusion time will be about 12 hours. As a consequence, the total processing time is too long, and thus the batch process is not cost-effective.

Clark and Seeler [74] introduced a sintering method to reduce the saturation time. In this method, a plastic resin is used in the form of powder instead of the net-shaped sample. Because the diffusion distance (powder radius) is much smaller for powders than for a net-shaped sample, the saturation time is significantly reduced. When the powders are saturated
with gas, they are loosely packed in a mold which is then heated to initiate cell growth and foam expansion as well as sintering. The powders tend to sinter together due to the heating and the expansion. In this approach, the gas absorption is quick because of the small powder size, but the gas desorption is also quick for the same reason. Thus, during foaming in the mold, a considerable portion of the gas would be desorbed. Also in the time period between the saturation step and the mold filling step, some portion of the gas is desorbed. Because a small amount of gas is preserved in the powders, the amount of foam expansion is low. The other shortcomings of this process include: presence of voids in the loosely packed powders, improper welding between powders, low strength of the sintered part, etc.

Seeler et al. [75] improved the sintering process by compacting the plastic powders in the mold. When the powders/particles are compacted, the diffusion distance during desorption becomes greater, and therefore, the amount of lost gas is reduced. In addition, compaction reduces the presence of voids and improves the welding between particles. Moreover, the gas loss in the time period between saturation and foaming is reduced by quickly purging the particles into the mold using a pressurized gas. The compacting pressure continues during heating until the desired temperature is reached; it is then released to allow foam expansion. Using this method, Seeler et al. produced microcellular parts with a volume fraction from 0.4 to 0.8. On the other hand, foaming did not take place uniformly throughout the product, and some locations did not even foam. They did not mention the processing time specifically, but it was noted that the total processing time has been considerably reduced. The reported results of this process were preliminary.

_Semi-Continuous Processing of Microcellular Foams_
Kumar and Schirmer [76] developed a semi-continuous process for production of solid state microcellular PET foams. In this process, layers of plastic sheet are interleaved with gas permeable materials (such as gauze, porous paper sheet, etc.). The roll of the interleaved plastic and gas permeable material is saturated with an inert gas in a high pressure vessel. The plastic sheet is taken out from the vessel, unrolled, and separated from the gas permeable material. The saturated sheet is drawn through a heating station and resides sufficiently to achieve a desirable foam density. In this process, the gas tends to escape from the sheet after its removal from the vessel. Therefore, the foaming must be processed promptly to avoid excess gas loss. In other word, only a finite length of the sheet can be foamed at one time, and hence, the process is called "semi-continuous".

**Continuous Processing of Microcellular Foams**

In order to overcome the shortcomings of the batch process, a cost-effective, continuous microcellular process has been developed in extrusion [24, 29, 30-37, 77-78]. A schematic of the microcellular extrusion process is shown in Figure 2.6. In this process, a much shorter time is needed for the saturation of the plastic with gas. When the plastic is melted in the extrusion barrel, a metered amount of gas is injected to the plastic melt [78]. The injected gas diffuses into the plastic matrix at a much higher rate because of the convective diffusion induced in the extruder barrel at elevated temperatures [77]. For example, the diffusivity of CO₂ in polystyrene at a temperature of 200°C is estimated to be 10⁻⁵ cm²/s. Thus, the time of gas diffusion into a 1mm thick melt (or a diffusion distance of 0.5 mm) is about 4 minutes (Equation 2.1). This represents a significant reduction in the diffusion time which results in a much shorter processing time.
There are three essential steps in a continuous microcellular extrusion process: (a) uniform plastic/gas solution formation, (b) cell nucleation and (c) cell growth.

**Solution Formation**

The formation of a uniform plastic/gas solution is essential in continuous microcellular foam processing since undissolved gas pockets can generate undesirably large voids. In other words, undissolved gas would appear as bubbles in the melt, which can cause heterogeneous nucleation later in the nucleation stage and result in an undesirable, non-uniform cell structure. The number of nucleated bubbles is greatly dependent on the quality of solution formation. A uniform solution can be achieved if the amount of injected gas is below the solubility limit [78], and dissolution of gas into the plastic is enhanced [31,77]. It must be noted that even if an appropriate amount of gas is injected into the plastic melt, this does not necessarily guarantee that all gases will be completely dissolved into the plastic. Moreover, complete dissolution of gas into the plastic melt must be ensured before the melt reaches the nucleation die, and this can be achieved by reducing the gas diffusion distance in the plastic (i.e., the striation thickness of the plastic and gas). The diffusion distance is reduced due to the shear field generated by the motion of the screw. In a shear field, the bubbles are stretched, giving a larger interfacial area and a lower striation thickness. Complete dissolution can be achieved by mounting a dissolution enhancing device in which static mixers are placed to enhance shear mixing [77].

Three strategies are applied to assist the complete dissolution of the injected gas in the plastic melt.
The first strategy is to inject and diffuse the gas at an elevated temperature. The gas diffusivity $D$ is mainly a function of temperature. The influence of temperature on the diffusivity can be explained using the following equation [79, 80]:

$$D = D_o \exp\left(-\frac{\Delta E_D}{RT}\right),$$

(2.2)

where $D = \text{diffusivity, cm}^2/\text{s}$,

$D_o = \text{diffusivity coefficient constant, cm}^2/\text{s}$,

$\Delta E_D = \text{activation energy for diffusion, J}$,

$R = \text{universal gas constant, J/K}$, and

$T = \text{temperature, K}$.

As shown in the equation, the diffusion coefficient increases as the temperature increases. Thus, the diffusion rate can be increased by processing the plastic/gas mixture at a higher temperature.

The second strategy is to use convective diffusion [81, 82]. The idea of convective diffusion is to bring the low gas-concentrated plastic melt and the high gas-concentrated gas bubbles into contact. To achieve this, the bubbles are stretched by the shear field generated by the screw motion; the stretched bubbles have a larger interfacial area and a lower striation thickness in the plastic melt. The diffusion distance is greatly reduced, and thus, the gas can be diffused into the plastic more easily. Static mixers can be added downstream of the extruder to enhance the shear mixing and ensure the homogeneity of the plastic/gas solution.

The third strategy is to raise the pressure in order to increase the solubility of gas in the plastic. The maximum amount of gas that can be dissolved into the plastic (i.e., the solubility) depends on the system pressure and temperature and can be estimated by Henry's law. The
relationship between pressure and gas solubility can be expressed by the following equation [79]:

\[ c_s = H \times p_s, \]  

(2.3)

where \( c_s \) = solubility of gas in the plastic, cm\(^3\)/g or g(gas)/g(plastic),

\( H \) = Henry’s law constant, cm\(^3\) [STP]/gPa, and

\( p_s \) = saturation pressure, Pa.

As shown in the equation above, the solubility of gas increases with pressure. If the processing pressure is too low, all of the injected gas may not dissolve in the plastic melt because of the low solubility.

**Cell Nucleation**

Microcell nucleation occurs in a rapid-pressure-drop nucleation nozzle [83, 84]. The rapid drop in pressure causes a rapid drop in the solubility of gas in the plastic melt, thus inducing thermodynamic instability as in the case of batch processing which drives nucleation of a great number of microcells. In a microcellular foaming process, generating a large number of gas bubbles is a critical step to achieve small cells of micron size. Nucleation of bubbles in a liquid has long been studied using the classical nucleation theory [85, 86]. Colton and Suh [87, 88] described the nucleation behavior in microcellular foaming using the classical nucleation theory and developed the following model for bubble nucleation rate:

\[ \dot{N} = f_o C_o e^{\frac{-\Delta G}{RT}}, \]  

(2.4)

where \( \dot{N} \) = rate of nucleation, #/cm\(^3\)s,

\( f_o \) = frequency factor of gas molecules joining the nucleus, 1/s,

\( C_o \) = concentration of gas molecules in solution, #/m\(^3\),

30
\[ \Delta G = \text{Gibbs free energy of bubble nucleation, J,} \]
\[ k = \text{Boltzmann constant, J/K, and} \]
\[ T = \text{temperature, K.} \]

and \( \Delta G \) can be expressed as:
\[
\Delta G = \frac{16\pi \gamma_{pb}}{3\Delta P^2}. \tag{2.5}
\]

where \( \gamma_{pb} = \text{interfacial surface tension, mJ/m}^2, \) and
\[ \Delta P = \text{gas saturation pressure, Pa.} \]

Therefore, a higher nucleation rate can be achieved by increasing the saturation pressure or blowing agent concentration. In addition, another important factor that affects the nucleation rate is the pressure drop rate. The investigation of Park et al. [28] has shown that the nucleation rate varies in direct proportion to the pressure drop rate. They explained this phenomenon by cell nucleation/growth competition for the dissolved gas. If the pressure drop rate is high, there is relatively less time for the gas to diffuse into the already nucleated cells, and the gas tends to nucleate an additional cell. Hence, a high pressure drop rate must be induced to produce a larger number of cells from the available gas concentration, and a nucleation die must be designed to promote a rapid pressure drop in a microcellular extrusion process.

**Cell Growth**

When cells are nucleated, they will grow as long as gas is still available in the plastic matrix to diffuse into the nucleated cells due to pressure difference, and the cell walls/membranes are pliant enough to sustain expanding. The nucleated cells continue to grow at the die exit and cell growth stops when all the gas dissolved in the plastic matrix is depleted.
or the matrix is too stiff to allow further growth. The growth dynamics is governed by a number of kinetic and system parameters such as the viscosity, the diffusion coefficient, the gas concentration, and the number of nucleated bubbles. For instance, when the plastic viscosity decreases via a temperature increase, the rate of growth increases due to the decrease in resistance against cell growth.

There are two critical issues involved in cell growth: cell coalescence and cell collapse. When a large number of nuclei are nucleated in a continuous process, they begin to grow very quickly due to the high diffusion of gas from the plastic matrix to the cells at high temperatures. In addition, the plastic matrix is softened at a high temperature, thus exerting less resistance against the cell growth. When the nucleated cells grow and contact with each other, contiguous cells tend to coalesce because the total free energy will be reduced through the coalescence of cells [10, 89]. Cell rupture is promoted when the stretched thin cell membrane separating two cells is not strong enough to sustain the tension developed during cell growth. It should be noted that the shear field generated during the shaping process tends to stretch nucleated bubbles, and this will further accelerate cell coalescence [32]. When cells are coalesced, the initial cell population density is deteriorated. In other words, although a cell nuclei density higher than $10^9$ cells/cm$^3$ has been achieved by the independent control of cell nucleation via a rapid pressure drop, the final cell population density of the produced foam might not be microcellular due to cell coalescence. In order to prevent the deterioration of the properties and to fully utilize the unique properties of microcellular plastics, cell coalescence should be effectively suppressed. Therefore, a strategy for preventing the coalescence of nucleated cells needs to be developed that preserves the high cell-population density obtained in the nucleation die. A schematic of cell coalescence is included in Figure 2.7.
On the other hand, cell collapse results in a low expansion ratio of a foam product. This phenomenon is caused by the escape of the dissolved gas into the atmosphere when the plastic melt is at a high temperature. In other words, most of the dissolved gas tends to diffuse externally into the atmosphere rather than diffusing internally into the nucleated cells in the plastic matrix. Moreover, the diffused gas in the cells will eventually diffuse into the atmosphere because ultimate separation of plastic and gas has the minimum free energy of the plastic-gas system [90]. Little gas remains in the plastic matrix, and the final expansion will be very low. A schematic of cell collapse is also included in Figure 2.7.

Cell growth must be carefully controlled because it affects not only the final foam density, but also the cell-population density. Carbon dioxide and Nitrogen, which are two commonly used gaseous physical blowing agents for the continuous process, have small molecular sizes. Therefore, they can easily escape from the plastic foam to the environment. If they escape from the foam, the cells will be collapsed and the foam density will be increased. If the melt strength of the plastic is too low, the cell walls will rupture due to the surface tension induced by cell growth. A schematic of this phenomenon is shown in Figure 2.7. Consequently, the adjacent cells will join together to form one single cell, and the cell density will be greatly reduced. Behravesh and Park [24, 35-36, 91] developed a process that can prevent cell coalescence and gas escape in the cell growth stage. Cell coalescence was suppressed by cooling the plastic/gas solution homogeneously to increase the melt strength, and gas escape was controlled by cooling the surface of the extrudate to form a solid skin layer, thereby blocking the gas from escaping the plastic.

In summary, cell growth is governed by many parameters which affect the final foam density, cell size and cell density. The amount of growth can be controlled by the temperature which influences two important parameters: the diffusivity and melt viscosity. By decreasing
the temperature, one can decrease the growth rate. It is important that the temperature control should be performed before cell nucleation since the rate of cell growth is much higher in the initial stage where the cells are small [92]. In the foaming process, it is important to consider the gas loss from the extrudate. Moreover, when smaller cells are present (more cells are nucleated), the wall separating the two cells turns thinner, and the rate of growth becomes faster. This may cause the cell wall to rupture, which results in cell coalescence [93]. This phenomenon is also undesirable, since the final cell density decreases. In microcellular foams, the cell size is very small and thus cells are more prone to coalesce.

2.3 Foaming of Plastic/Wood-Fiber Composites

There is very limited literature published regarding foam processing of plastic/WF composites. Several articles are found on production of plastic/WF composite foams based on injection molding, by which foaming process takes place in the molds [94, 95]. Pbedinskas et al. [96] described a continuous Celuka process for producing plastic/WF composite foams, however, the resultant cell structure was extremely poor.

The attempt to produce fine-celled and microcellular foamed plastic/WF composites has been continuously conducted in the Microcellular Plastics Manufacturing Laboratory at the University of Toronto. Matuana et al. [62] claimed that microcellular PVC/WF composite foams were successfully produced based on the batch processing, and Rizvi et al. [63] investigated the extrusion foaming feasibility of fine-celled plastic/WF composites using chemical blowing agents and promising experimental results were achieved. In Matuana's batch processing experiments, the compression-molded PVC/WF composite sheet samples were first placed in a high-pressure chamber and saturated with CO$_2$ at room temperature
for various saturation times, then these samples were quickly released from the chamber and
dipped in a glycerol bath at various elevated foaming temperatures to induce a thermodynamic
instability for microcellular foaming. Foamed samples were finally tested for the mechanical
properties such as notched Izod impact strength and tensile strength according to the ASTM
standards. The testing results showed that the deteriorated impact strength of PVC/WF
composites due to the WF presence was effectively improved by microcellular foaming
especially for treated WF, without significantly compromising other mechanical properties.

The batch processing of microcellular plastic/WF composite foams, however, was not
economical and very time-consuming. Therefore, an effective continuous extrusion foaming
of plastic/WF composites should be developed for the industrial applications. Because the
investigation of the foaming behavior of plastic/WF composites with gas injection has not
been conducted yet, the research described in this thesis is focused on extrusion foaming of
plastic/WF composites with CO₂ injection.
Chapter 3

Detailed Design & Construction of Experimental Equipment

3.1 Design Concept

This research is intended to produce fine-celled plastic/wood-fiber composites using CO₂ as a physical blowing agent based on a continuous foaming process. As one of the most widely used plastic processing techniques, extrusion covers a vast range of applications in which plastic resins are heated, melted and pumped for processing. Extruders accomplish these tasks by means of an internal screw. Extruders with single, twin or multiple screws are available. More elaborate extruder or extrusion system designs may be required if a process requires more steps to produce desirable products. Extruders all operate on the same principle: The material to be processed is sheared between the root of the rotating screw and the wall of the barrel which surrounds it. This process produces frictional energy which heats and melts the substance as it is conveyed down the barrel. Heat can also be applied to the outside of the barrel to promote and enhance melting by band heaters. Melted extrudate from the extruder is further processed after the extrusion process. The typical forms of the final products include
pellets, sheets, foam-sheets, cast-films, blown-films, fibers, coatings, pipes, profiles, and even molded parts [97].

The first microcellular foaming extrusion system was designed and constructed by Park [81] for filamentary processing of styrene plastics. Behravesh [36] used a similar extrusion system to produce low-density microcellular foams of HIPS and HDPE. Yeung [98] modified and constructed a tandem extrusion system for sheet processing of microcellular plastic foams. Similar to the above systems, a tandem extrusion system was specially designed and constructed for fine-celled foaming of plastic/wood-fiber composites.

Wood fibers are non-abrasive so that large concentrations may be incorporated into plastics without serious machine wear during extrusion. Melt-processing extrusion of plastic/wood-fiber composites facilitates wood fibers well dispersed into the plastic matrix to obtain an intimate mixture. However, when wood fibers are present, stable material feeding, uniform plastic/WF mixing and effective moisture removing become three challenging issues to be addressed in the continuous extrusion process.

The commonly used hopper, which employs gravity to feed the material into the extruder, is not suitable for the feeding of plastic/WF mixture. Continuous and stable feeding is one of the key points in extrusion process. However, wood fibers have low bulk density and tend to tangle together, they are easy to pack tightly and block the hopper exit preventing material-feeding. It is believed that the granular wood flour used in this research would be only better for easier compounding with plastics rather than material free-drop feeding. Therefore, a special feeding device such as a screw or vibratory feeder should be configured into the extrusion system.

Intensive and uniform distribution of wood fibers into plastic matrix is required in producing the uniform properties of the final plastic/WF composites. Any variation resulting
from the incomplete and non-uniform dispersion of wood fibers into the plastic matrix will greatly deteriorate the final composite properties, and the cell morphology of the composite foams. A twin-screw extruder, which is also widely applied in the industry as an effective mixer/compounder, should be integrated into the extrusion system.

On-line moisture removal from wood fibers should be also considered in the extrusion system design. Wood fibers inherently contain water in the form of moisture attached to their cell walls. If this moisture is not removed, the resultant foam structures will be deteriorated due to the existence of large bubbles. The water content in the commercially available wood fibers usually varies from 6-12%. The prevalent method for removing moisture is to dry wood fibers in a vacuum oven for 10-48 hours at temperatures ranging from 55-105°C. The duration of heating has to match the heating temperature so that the wood fibers do not degrade during the drying process. Another method is to blow hot dry air over the wood fibers to remove moisture [63]. Moreover, dried wood fibers are highly hygroscopic and quickly absorb moisture from the atmosphere. This necessitates the adoption of special handling procedures to prevent moisture absorption, such as providing dry ambient conditions during storing, mixing and feeding after drying process. This complicates the process and system, and increases the processing cost. Using the idea of an opening or vent to get rid of the volatile materials in the plastics, a devolatilizing vent is incorporated in the extrusion system to perform on-line moisture removal from wood fibers.

Thus, a tandem extrusion system is designed based on the following concepts: A first extruder is used as a compounder to uniformly mix wood fibers with thermoplastic resins, and to increase the mixture temperature for converting wood-fiber moisture into high energy vapor. A devolatilizing vent is then constructed between the first and second extruders to purge out the vaporized moisture. A second vented extruder is used for injecting a physical
blowing agent (PBA), such as CO₂ in this research, and promoting uniform diffusion of the blowing agent into the plastic matrix in its mixing section. A dissolution enhancing device with inside static mixer immediately follows the second extruder to facilitate complete dissolution of the PBA in the plastic matrix. The WF/plastic-gas system is then homogeneously cooled down through a heat exchanger with inside static mixer to increase the melt strength for preventing cell coalescence. Finally the WF/plastic-gas system passed through a nucleation die where the pressure is rapidly dropped causing a thermodynamic instability, which generates a large number of nucleated bubbles, and the surface temperature of the extrudate is reduced by a cooling sleeve surrounding the nucleation die to freeze the surface layer of the extrudate for preventing gas escape into the atmosphere. The nucleated cells continue to grow by the adjacent gas diffusing into these sites and cause volume expansion after the die.

3.2 System Overview

A complete setup of the designed tandem extrusion system for producing fine-celled plastic/WF composite foams includes: a twin-screw feeder, a first twin-screw extruder, a devolatilizing vent, a second vented extruder, a PBA injection system, a dissolution-enhancing device, a heat exchanger, a nucleation nozzle die, a temperature and pressure control panel and other auxiliary components. A schematic of this system is shown in Figure 3.1 and a photograph of this setup is presented in Figure 3.2. The objectives of this system design are: (1) to obtain a stable and continuous feeding of plastic/wood-fiber mixture; (2) to plasticate and uniformly compound plastic/wood-fiber mixture; (3) to remove moisture on-line; (4) to inject a PBA; (5) to completely dissolve the PBA into the plastic/wood-fiber composite melt;
(6) to avoid cell coalescence by cooling the melt temperature; (7) to induce cell nucleation in the composite melt at the die exit; and (8) to promote volume expansion of the extrudate. The major components of the tandem extrusion system are detailed as follows.

3.2.1 Twin-Screw Feeder

To effectively and precisely feed pre-mixture of plastic pellets and wood fibers, a twin-screw feeder (AccuRate 3006) with control panel (Danfoss Varispeed A2000) is configured in the tandem extrusion system for material feeding. This co-rotating twin-screw feeder with helix size 0.50" features a speed range of 50:1 and a feed rate from 1.0 to 185 lbs/hr. With the help of the co-rotation of the two screws, the plastic/WF mixture can be continuously and stably fed into the tandem extrusion system at a controllable feed rate.

3.2.2 First Twin-Screw Extruder

Mixing wood fibers or wood flour with thermoplastic resins is called compounding. Wood flour is easily compounded in conventional plastic mixing equipment, such as a twin-screw extruder. More fibrous fillers, such as ground or hammer-milled newspaper fibers, require high-intensity mixing to disperse and shred the fibers. Turbine mixers can effectively disperse wood fibers in the molten plastics in a relatively short time [1].

Through the years, twin-screw extruders have grown as the major compounding machines in the plastics industry. Twin-screw extrusion has been successfully applied to enhance the mixing and compounding of filled and unfilled plastics. There are two classes of modular intermeshing twin-screw extruders, co-rotating and counter-rotating. Generally co-
rotating twin-screw extruders have self-wiping screw design, which enables them to avoid the built-up of deposits. Research showed the rate of morphology evolution produced in the counter-rotating mode to be more rapid and to occur earlier along the screw axis. This is due to the higher shear stresses in the counter-rotating intermeshing region between the two screws, which brings about fast pellets pulverizing, earlier fusing and melt mixing [99, 100].

In order to uniformly melt and mix plastic pellets and wood flour in this research, a continuous counter-rotating intermeshing twin-screw extruder (C. W. Brabender: Model D6/2), which is driven by a 5 hp motor (Reliance Electric: Power Matched/RPM Rectified Power Motor) controlled by a variable speed drive unit (Canadian Drive Inc.) and equipped with a speed reducer (Hub City: Model 321, Ratio 15/1, Style C), is applied as the first compounding extruder in the designed tandem extrusion system. The 42mm (1.65”) parallel, counter-rotating, intermeshing screws create a high shear, high intensity mixing action. This design is ideal for intimate blending, mixing and compounding. Despite the relatively short L/D ratio (7:1), residence times are actually longer than extruders twice its length.

3.2.3 Devolatilizing Vent

On-line continuous wood-fiber moisture removal is designed to occur at the devolatilizing vent located at the intersection of the first and second extruders. By utilizing the existing hopper hole on the second extruder barrel as the devolatilizing vent, the first compounding extruder feeds perpendicularly to the side of the second extruder at the location of the hopper hole. Interconnecting parts are machined, mounted and heated by band heaters in processing.
3.2.4 Second Vented Extruder

The second vented extruder is used for providing an access port for PBA injection, and mixing the gas and plastic/wood-fiber composite melt. The extruder is a 3/4" laboratory extruder (C. W. Brabender: Model 3023-GR-8) equipped with a 5 hp motor (Allen Bradley: 1329 Inverter Duty Motor), which is controlled by a variable speed drive unit (Allen Bradley 1336 Impact). The extruder screw plays an integral role in the extrusion process. The screw RPM determines the shear rate, the extrusion rate and the residential time which the plastic is subjected to heat, and the screw compression ratio affects the extrudate quality and barrel pressure. The extruder screw used is a single-stage mixing screw (CWB 05-00-144) with a compression ratio of 30:1 (L/D). The purpose of the mixing section, which is located at the end of the screw and contains six rings of staggered mixing studs, is to enhance the mixing effect by chopping the blowing agent pockets into smaller bubbles to promote uniform distribution and diffusion of the blowing agent into plastic/wood-fiber composite melt.

3.2.5 PBA Injection System

The PBA injection system includes a gas cylinder, a freezer, a positive displacement syringe pump (ISCO DM260), a flow restrictor, an in-house designed and machined gas injection port, valves and fittings. The freezer is used to cool the liquified PBA in order to fill the syringe pump with more available gas amount. The two main components of the PBA injection system are the positive displacement syringe pump and the gas injection port.

It is essential that the correct and desirable amount of the physical blowing agent be continuously injected into the extruder barrel in order to achieve a consistent foam product. A
positive displacement pump is an appropriate device for injecting gas at a constant flow rate. In a positive displacement pump, adjusting the speed of the pump moving parts (either the piston or gears) can control the flow rate. However, due to PBA compressibility, the output flow rate can be affected by the variation/fluctuation in the downstream barrel pressure. As a result it causes variation in the flow rate of the fluid which deteriorates uniform foaming. In addition, if the downstream pressure increases, the amount of injected fluid decreases. The situation becomes worse when the downstream pressure exceeds the injecting pressure, causing a reverse direction of fluid flow. This results in the downstream plastic melt penetrating the fluid passage and clogging it. As a result, even though the injecting pump pushes the fluid into the extrusion system, no fluid is delivered to the extruder barrel. On the other hand, when the downstream pressure decreases, the pressure difference increases, and thus an excessive amount of fluid is injected into the barrel. The reason for the flow fluctuation is that the fluids in use are compressible, and therefore the pressures applied by the injecting pump and by the plastic melt compress the fluid while no net output flow of the fluid is given. The effect of compressibility is pronounced when the injected flow rate is small.

One solution to suppress the variations in the flow is to maintain a much higher injecting pressure above the downstream pressure (barrel pressure). In other words, a high pressure difference between the injection pump and the downstream barrel should be achieved. The rationale behind this can be illustrated by the following examples. If the gas injection pressure is 50 MPa and there is 10 MPa barrel pressure fluctuation, then the gas injection pressure could become 40 MPa or 60 MPa, a change of ±20%. However, if the gas injection pressure is 500 MPa, and the barrel pressure fluctuation remains the same, the gas injection pressure would change by only ±2%. Hence, in order to adjust the flow rate to the desired level while maintaining a high pressure difference, an appropriate flow restrictor must be employed and
mounted between the injection pump and the gas injection port. The resistance in the flow restrictor assures a high pressure difference between upstream (injection pump) and downstream (extruder barrel). The choice of flow restrictor depends on the required pressure difference and the desired gas flow rate.

The gas injection port connects the injection pump with the extruder barrel, and provides a mounting hole for pressure transducer for on-line continuous monitoring of the downstream barrel pressure.

3.2.6 Dissolution-Enhancing Device

The quality of extrudates depends mainly on the homogeneity of the melt during extrusion. This can be influenced by specially designed mixing zones or elements, where the melt flow is split, distributed and merged again. Immediately after the mixing stage of the second extruder, a dissolution enhancing device with inside static mixer is mounted to ensure the homogeneous diffusion and complete dissolution of the blowing agent into the plastic/wood-fiber composite melt via heating and shear mixing. Heating increases the diffusivity of the blowing agent into the plastic melt, and shear mixing enhances the convective mixing and reduces the striation thickness by generating a shear field. Band heaters are used to generate heat, and a static mixer is utilized to promote shear mixing. The static mixer selected (OMEGA FMX8441S) consists of 12 fixed, in-line baffles which cause the mixing fluids to shear and swirl clockwise and counterclockwise to promote a homogeneous output. This version of a static mixer has been found to be effective for enhancing dissolution in the microcellular extrusion process [30, 77-78].
The amount of pressure loss along the static mixer and the required number of static mixer elements (baffles) can be calculated based on the following formulas provided by the manufacturer's technical brochure [101]. For a laminar flow,

\[ \Delta P = \eta Q L, \]  

(3.1)

where \( \Delta P \) is the pressure loss (Pa), \( \eta \) the shear viscosity (Pa\cdot s), and \( Q \) the volumetric flow rate (m\(^3\)/s), and they must be converted to psi, cP, and gal/min, respectively, to use Equation (3.1). The parameter \( L \) (m\(^3\)) is the laminar factor for the static mixer given in the OMEGA specification table. According to OMEGA, the flow is laminar if the Reynolds number is below 500. The Reynolds number is given by:

\[ Re = \frac{3157 Q S}{D \eta}, \]  

(3.2)

where \( D \) is the diameter (m), and must be converted to inches to use Equation (3.2) and \( S \) is the specific gravity. The same units for \( \eta \) and \( Q \) must be used as for Equation (3.1). The parameters \( L \) and \( D \) for the selected static mixer are 0.1176 and 0.71 cm (0.28"), respectively [102]. The specific gravity \( S \) is about 1 for a wide range of plastic resins. A typical flow rate \( Q \) of this system is in the range of 5-12 cm\(^3\)/min (1.3-3.2x10\(^{-3}\) gal/min), depending on the processing conditions. Since the flow is a mixture or solution of the plastic/wood-fiber composite melt and the blowing agent, the viscosity \( \eta \) of the mixture or solution must be determined. On the other hand, the viscosity of plastic-blowing agent solution is difficult to measure, although some research has been carried out to determine the effect of adding solvent on the viscosity of a plastic resin [101, 103-105]. However, it is well known that the blowing agent plasticizes the plastic, and thus reduces its viscosity [106]. The amount of reduction in viscosity depends on the type of blowing agent and its concentration in the plastic. For the plastic/gas systems such as HDPE-CO\(_2\) and HIPS-CO\(_2\), no data are currently available.
The shear viscosity is influenced by the temperature and shear rate. The apparent shear rate in a circular channel is calculated by the following equation:

\[ \dot{\gamma}_{\text{app}} = \frac{32Q}{\pi D^3}, \]  

(3.3)

For a flow rate of 10 cm³/min and a diameter of 0.7 cm (0.28"), the apparent shear rate is about 0.6 1/s. The temperature of the dissolution enhancing device is typically maintained high up to 200°C. The viscosities of the pure HDPE and HIPS at 200°C with a shear rate of 0.6 1/s are approximately 10⁴ Pa·s (10⁷ cP) [107].

With these values, the Reynolds number can then be calculated using Equation (3.2) (where \( Q(\text{avg.}) = 8.5 \) cm³/min (2.2x10⁻³ gal/min), \( S = 1, \eta = 10^4 \text{ Pa}\cdot\text{s} (10^7 \text{ cP}), D = 0.71\text{ cm} \) (0.28")), which yields:

\[ Re = \frac{3157 \times 2.2 \times 10^{-3} \times 1}{0.28 \times 10^7} = 2.5 \times 10^{-6}, \]  

(3.4)

This Reynolds number is far below 500 (the upper limit for a laminar flow). The pressure loss is then calculated using Equation (3.1), which yields:

\[ \Delta P = 10^7 \times 2.2 \times 10^{-3} \times 0.1176 = 2590 \text{ psi} \equiv 18 \text{ MPa} \]  

(3.5)

This shows that increasing the number of mixing elements is undesirable because it increases the pressure loss. In the above calculation, the effects of the blowing agent and wood fibers on the viscosity are not considered because of the lack of data. Considering that the viscosity reduced by adding a blowing agent can be more than one-half [106] and neglecting the wood-fiber effect, it is expected that the pressure loss would be around 9 MPa (1300 psi), which is a reasonable fraction of the extrusion limit of 65 MPa (9400 psi).
3.2.7 Heat Exchanger

Cooling the composite melt will increase the melt strength and suppress cell coalescence. It is important to cool the composite melt homogeneously because non-uniform temperature distribution could induce non-uniform cell growth, resulting in a non-uniform cell structure. The heat exchanger was designed by Behravesh [36], which consists of a mild steel body and an inside static mixer (Labcore: H-04669-12). This static mixer is entirely different from the one used in the dissolution-enhancing device. The static mixer used for the dissolution-enhancing device is not appropriate for cooling since it does not promote a convectional heat transfer in the radial direction; it only rotates the flow clockwise and counterclockwise with no radial transportation of material. Therefore, the temperature distribution would not be affected by this version of static mixer. Instead, the Labcore static mixer can continuously direct the flow in the radial direction and exchange the melt material at the surface with the material at the core. It consists of guide vanes, which are bars intersecting at 30 degrees to the pipe axis. The vanes (elements) induce a transverse flow component which continuously transfers boundary material and heat to the center of the bulk stream and exchanges it with the core material. The radial convective transport of heat reduces temperature gradients across the melt. According to the calculation done by Behravesh [36], four elements are sufficient for mixing without sacrificing too high pressure drop.

Since the temperature can directly affect the foaming behaviour and quality, it is important to control the temperature of the heat exchanger precisely. Using band heaters and temperature controllers does not provide adequate control because of lack of a cooling source. For the heat exchanger, two common choices of the cooling media are circulating oil and pressurized air. The pressurized air offers comparatively simple, low cost systems with a
gradual response, which are preferred where small amounts of heat removal are required. Circulating oil system (oil bath) is more costly and have more heat removal capacity but respond more abruptly for small amounts of heat removal.

A pressurized air can be introduced to provide cooling for the heat exchanger. A temperature controller controls the air flow through the cooling channel in the heat exchanger using a solenoid valve. When the temperature is above the set point, the solenoid value opens to let the pressurized air expand and flow through the channel in the heat exchanger. Because of cooling induced during isentropic expansion [108], the temperature of air is reduced significantly and the cold air removes the heat from the heat exchanger. When the temperature is below the set point, the band heaters are switched on to provide the necessary heating. Using this band heater/pressurized air arrangement, temperature control of ±1°C was easily maintained.

In order to achieve a better control of the low temperatures, a high temperature oil (Labcore: Model H-01294-40) can also be applied to circulate in the cooling channel of the heat exchanger. The temperature of the oil is controlled by an oil bath controller (Grant: Model W6-KD) which is equipped with a pump to circulate the oil to the heat exchanger. A schematic of the heat exchanger is shown in Figure 3.3.

### 3.2.8 Nucleation Nozzle Die

Nucleation of numerous cells can be achieved by thermodynamic instability. Since the solubility of gas in the plastics is almost proportional to the processing pressure [109], a rapid pressure drop element is needed for the nucleation of a large number of microcells in extrusion foaming process. A nozzle is proposed as the nucleation die where a high pressure drop can be
produced due to high resistance. The pressure drop and the pressure drop rate can be controlled by the length $L_N$ and diameter $d_N$ of the nozzle [29]:

$$\Delta P = \left(\frac{L_N}{d_N^{3+3n}}\right)Q^n$$  \hspace{1cm} (3.6)

$$\frac{\Delta P}{\Delta t} = \left(\frac{1}{d_N^{3+3n}}\right)Q^{1+n}$$  \hspace{1cm} (3.7)

In these equations, $n$ (dimensionless) represents the power law index of a non-Newtonian plastic (power law model: $\eta = K\dot{\gamma}^{n-1}$, where $\eta$ is the shear viscosity with unit of Pa·s, $K$ is the consistency parameter with unit of Pa·s$^n$ and $\dot{\gamma}$ is the shear rate with unit of s$^{-1}$). According to Equations 3.6 and 3.7, the pressure drop depends on both length and diameter of the nozzle, while the pressure drop rate depends only on the diameter. Therefore, the nucleation nozzle die, which is characterized by a small diameter and short length, is designed to induce a rapid pressure drop to promote nucleation of a large number of cells. The dimension of the nozzle die used in this research for foaming plastic/WF composites is 1.27 mm (0.050") in diameter and 2.54 mm (0.1") in length.

The strategies for attaining foams that have a high cell-population density and desired expansion ratio are to cool the melt temperature and to freeze the extrudate surface at the die exit. Cooling the extrudate surface can be achieved by cooling the nozzle section with heat exchanging oil or pressurized air circulating around it. Thus, there is a need to provide a sealed channel around the nozzle to circulate the oil. It would be inefficient to make a channel for each nozzle, especially when a series of nozzles are to be experimented. An alternative design is to make a sleeve with a large circumferential groove inside it. When the sleeve is mounted on the nozzle and sealing is ensured using two O-rings at both ends, the heat exchanging oil can be circulated through the channel. A schematic of the cooling sleeve is given in Figure 3.4.
Although the effects of cooling and freezing are not clearly known, these issues are especially crucial for the processing of HDPE (a semi-crystalline plastic), which experiences a sudden change in viscosity at the temperatures close to its melting point. This could create an unpredictable processing condition such as sudden (local) freezing in the nozzle die, thus creating a pressure surge in the system. Therefore precise and quick-responding temperature control is essential especially for foaming of the HDPE/WF composites.

3.2.9 Temperature and Pressure Control Panel

All the temperature controllers and pressure meters of the tandem extrusion system are integrated into a control panel. OMEGA CN9000A Miniature Autotune Temperature Controllers and OMEGA DP25-S Strain Gage Panel Meters are well arranged and installed in the control panel. OMEGA Thermocouples (JMTSS-062G-6) and Dynisco Pressure Transducers (PT462E-10M-6/18), which are mounted in the critical points of the tandem extrusion system, are connected to their temperature controllers and pressure meters, respectively. Four pressure transducers are used in the tandem system, among which the first pressure transducer measures the flow pressure after the outlet of the first twin-screw extruder, the second one reads the downstream barrel pressure under the PBA injection port, the third one takes the maximum pressure at the end of the second extruder, and the fourth one obtains the nozzle pressure at the inlet of the nozzle die. Ten thermocouples are mounted in the tandem system, two for the first twin-screw extruder, one after the outlet of the first extruder, one at the inlet of the devolatilizing vent, three for the second extruder, one for the dissolution enhancing device, one for the heat exchanger and one for the nozzle die.
Experimental Verification for Foaming of Fine-Celled Plastic/Wood-Fiber Composites

Various experimental setups were designed and experiments were conducted to study the effects of material and processing parameters on the cell morphology and foam properties of the composite extrudates with a view to achieving fine-celled foaming of plastic/WF composites.

After a tandem extrusion system was constructed, preliminary experiments at a low WF content (10 wt%) were carried out to investigate the system operation. Two plastic materials, HIPS 3350 and HDPE 58G (both from Nova Chemicals), were both used as the plastic matrices in the composite foaming experiments.

Targeted experiments at higher WF contents (20 wt%, 30 wt%, and 40 wt%) focusing on HDPE at CO₂ 1 wt% were performed to identify the effect of WF content on cell morphology and foam properties. Two system configurations (tandem extrusion system vs. single extruder system) and two WF-treating conditions (WF with CA modified vs. WF without CA modified), which implied four categories of experiments, were designed and conducted to compare the effects of the system configuration and CA.

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Targeted experiments at other CO\textsubscript{2} contents (0 wt\%, 2 wt\%, and 4 wt\%) were further conducted to demonstrate the effect of CO\textsubscript{2} content on the cell morphology and foam properties based on WF with CA modified using the tandem extrusion system.

Supplementary experiments were designed and conducted to clarify whether the poor results from the single extruder system were mostly due to the moisture presence or a poor mixing by processing pre-dried WF/HDPE mixtures with CA modified in the single extruder system at CO\textsubscript{2} 1 wt\%, the results of which were compared with those in the above targeted experiments (undried WF with CA modified using the single extruder system).

4.1 Experimental Materials

Two types of plastic resins, high density polyethylene (HDPE 58G) and high impact polystyrene (HIPS 3350) both supplied by Nova Chemicals, were utilized in the related experiments. The wood fibers provided by American Wood Fibers, were Softwood Grade 12020 in the form of fine-mesh sized wood flour. The physical blowing agent (PBA) was Commercial CO\textsubscript{2} from Matheson Gas Products. The coupling agent (CA) selected for the targeted and supplementary experiments with HDPE was Fusabond\textsuperscript{®} E Modified PE provided by Dupont Canada. The talc powder, an inert and fine-particle material, was chosen as an effective nucleating agent provided by Stochem Inc. All the experimental materials remained unchanged and were used as received from the original manufacturers. Table 4.1 illustrates the main properties of these materials.

HDPE is a semi-crystalline plastic widely used for the production of bottles, drums, fuel tanks, toys, housewares, packaging, etc. HDPE is extruded as pipe, sheet, wire and cable and is also used for coating other extrudates [110].
HIPS, a modified polystyrene (PS) to improve the impact strength properties by the addition of rubber particles, is an amorphous plastic widely used for the production of appliances, housewares, cassettes, plates, bowls, cups, food trays, egg cartons, etc. [110].

4.2 Experimental Setup

To address the presence of WF in the plastic matrix, the tandem extrusion system was intentionally developed as described in detail in Chapter 3 and shown in Figure 3.1.

As a reference to the designed tandem extrusion system, a single extruder system, without the first twin-screw extruder as an effective compounding device and a devolatilizing vent as a moisture removal opening, was configured to compare the effect of system arrangement on the cell morphology and foam properties. Other components in the two systems remained the same. A schematic of the single extruder system was shown in Figure 4.1.

It was noticeable that the nozzle die acting as a rapid pressure drop device was fixed for all the experiments in this research project with a size of 0.05" in diameter and 0.1" in length.

4.3 Experimental Procedures

Experimental raw material mixtures were prepared in the following way: HDPE or HIPS pellets were weighed and CA of 5 wt% of wood fibers (in HDPE case) was added if applicable. 0.5 wt% of a commercial mineral oil (Life, Phamaprix) was used to wet the surface of the plastic pellets in order to facilitate uniform and complete distribution of the talc particles (2 wt% of HDPE and WF except for the preliminary experiments without talc added).
onto the surfaces of plastic pellets. After the plastic pellets and talc powders were mixed enough by intensive shaking and turning of a laboratory blending tumbler, wood fibers were weighed, added, and blended completely in the same way. The raw material mixtures were ready for the foaming extrusion experiments.

In the tandem extrusion system configuration, the blended mixtures were stored in the chamber of the twin-screw feeder. The mixtures were driven forward by the co-rotation of the twin screws, and fed down to the hopper of the first twin-screw extruder for plasticating and uniformly mixing through the intensive counter-rotation of the twin screws. The feed rate of the twin-screw feeder and the RPM of the first twin-screw extruder were properly adjusted and matched to ensure that no raw materials deposited in the extruder hopper and packed tightly, because the natural adhesiveness of the wood fibers would finally block the feeding. In other words, the amount of the mixture materials falling into the hopper was caught and conveyed instantly and continuously by the counter-rotation of the twin-screw extruder. The mixtures were plasticated and effectively mixed, and meanwhile the absorbed moisture in the wood fibers was converted into vapor. Then the mixtures were side-fed into the second extruder through the devolatilizing vent at the interconnection where the mixtures were exposed to the atmosphere and the vaporized moisture was purged out. PBA (CO₂) was metered and pumped into the mixture flow through the injection port two-thirds of the way down the second extruder barrel. The injected CO₂ was diffused and dissolved into the plastic matrix through the high shear field generated by the screw rotation especially at the mixing section in presence of high pressure and high temperature. The dissolution-enhancing device with inner static mixer following the end of the second extruder ensured complete dissolution of the injected CO₂ into the plastic matrix. The melt temperature of the WF/plastic-CO₂ system was homogeneously reduced in the heat exchanger with an inner static mixer. Finally, the cooled
composite melt entered the nucleation nozzle die where it experienced a thermodynamic instability caused by a rapid pressure drop, which produced a large number of nucleated bubbles. The available gas from the adjacent plastic matrix continued to diffuse into these nuclei and caused expansion. The temperature of the nozzle die was cooled so as to freeze the surface layer of the extrudate to block gas loss to the environment during the cell growth. Foamed extrudate samples were randomly collected at each processing condition when a stable state was achieved.

In the single extruder system arrangement, all the downstream procedures remained the same except that the raw mixture materials were directly fed into the single extruder through the twin-screw feeder.

The following conditions were maintained for all the foaming extrusion experiments:

1. The mass flow rate was set consistent at 12 g/min for all the experiments in either tandem extrusion system or single extruder system except for the preliminary experiments at a mass flow rate of 15 g/min.

2. The nozzle size remained unchanged for all the experiments with 0.05" in diameter and 0.1" in length.

3. All the upstream temperature profiles were kept the same, only the last two temperatures, melt temperature $T_m$ (heat exchanger) and nozzle temperature $T_n$ (nozzle die) were varied to study their effects on the cell morphology and foam properties. To simply the experiments, $T_m$ and $T_n$ were always set the same synchronously from the starting temperature down to the minimum temperature (except for HIPS/WF composite foaming in the preliminary experiments). For tandem extrusion system, the temperature profiles down the system were: 160°C and 170°C for the first twin-screw extruder, 190°C after the outlet of the first extruder and
200°C at the adapter to the devolatilizing vent, 165°C and 175°C for the zone 1 and zone 2 of the second extruder before the gas injection port, 195°C for the zone 3 after the gas injection port, 180°C for the dissolution-enhancing device, and $T_m$ and $T_n$ varied in the experimental processing window. For the single extruder system, the temperature profiles were the same if applicable.

4.4 Sample Preparation and Characterization

The foam samples were randomly collected at each processing condition when it was stabilized and characterized with a scanning electron microscope (SEM, Hitachi 510). Each sample was first dipped in the liquid nitrogen and then fractured freely to expose its cellular morphology. The fractured surface was then gold-coated using a sputter coater (E 50000C PS3) and the microstructure was examined using SEM. The cell density (i.e., the number of cells per unit volume of each foamed sample) and the volume expansion ratio $\alpha$ (or, equivalently, the foam density) were the structural foam parameters measured. The nozzle pressure was also recorded as a function of the varied foaming temperature. The volume expansion ratio $\alpha$ of each sample was determined by measuring the weight and volume of the sample, and calculated as the ratio of the bulk density of the raw experimental mixture ($\rho_0$) over the bulk density of the foam sample ($\rho_f$) [36]:

$$\alpha = \frac{\rho_0}{\rho_f}, \quad (4.1)$$

The cell density $N$ (cells per cm$^3$ of a foamed sample) was calculated using [36]

$$N = \left( \frac{n_e M^2}{A} \right)^{3/2} \times \alpha \quad \text{or} \quad (4.2a)$$
where \( A \) = an arbitrary area on the micrograph, \( \text{cm}^2 \),

\[
N = \left( \frac{n_o M^2}{A} \right)^{3/2} \frac{\rho_o}{\rho},
\]

\( n_o \) = number of cells in an area \( A \) on the micrograph, \#, 

\( M \) = magnification factor of the micrograph.

assuming an isotropic distribution of the cells (designated by factor 3/2).

In addition, samples were also arranged and photographed by a digital camera (DC260 Zoom Camera, Kodak Digital Science™) to record the foamed sample profiles.

**4.5 Thermogravimetric Analysis of Wood Fibers**

Water or moisture is inherently present in wood. There are three types of water in the wood products [111]. The contained water or free water is the water in the wood cells of the green state just like water in a container. The adsorbed water or bound water, which could constitute up to 40% of the weight of the dried wood, is the water attached through weak molecular forces. The water of constitution is the water of chemical composition. It exists as part of the molecular structure of the wood in the form of hydrogen and hydroxyl groups, which split off and form water under prolonged heating. For pre-treated wood products in the form of fibers or flour, the first type of contained water has already been removed. To dry the wood fibers or flour means to eliminate the adsorbed water, while the water of constitution should be unaffected otherwise the wood fibers or flour would be degraded.

Rizvi et al. [112] conducted a thermogravimetric analysis (TGA) to study the amount of residual moisture as a function of temperature in order to gain a fundamental understanding of
the devolatilization mechanism of the wood flour from the supplier using a TGA 2050 (TA Instruments). A heating rate of 100°C/min was applied. The wood flour sample used for testing was unchanged as received. The wood flour was initially heated up to 110°C and this temperature was maintained for 150 minutes. The temperature was then elevated to 200°C and maintained at this level during the remaining experiment for 150 minutes. The oven was continuously purged with nitrogen throughout the experiment to remove the released moisture and maintain the dry condition. The purging also prevented the degradation of the wood flour.

The thermogram of devolatilization of wood flour obtained by TGA analysis is illustrated in Figure 4.2. It was clearly seen that at 110°C, the initially undried wood flour started losing weight as soon as the experiment began. Approximately 8% of the moisture was removed when the wood flour maintained at this temperature for 150 minutes. However, it should be noted that most of the moisture loss (7.1%) occurred during the first 10 minutes of the experiment whereas an insignificant loss (0.9%) took place during a long period of the heating time (more than 140 minutes). The loss of moisture was mainly due to the drying of wood flour because the wood flour was heated up above the boiling temperature of water. The weight percent loss in moisture observed by the TGA analysis agreed well with the 8% value of the moisture content provided by the supplier.

After heating up wood flour at 110°C for 150 min, the temperature was quickly raised to 205°C and maintained at that temperature for 150 minutes while continuously purging with nitrogen. The thermogram of devolatilization of wood flour shown in Figure 4.2 clearly shows that even after wood flour were considered oven-dry, they could still release water. An additional 3% moisture was released when the temperature was raised from 110°C to 205°C. This moisture was believed to be the water of constitution or a small amount of remaining adsorbed water that required a higher energy to dislocate. This suggested that it was necessary
to control the maximum processing temperature not higher than 200°C to prevent wood flour from unexpected degradation.

4.6 Preliminary Experiments at a Low WF Content Using HDPE and HIPS

This set of experiments using two plastic materials, HDPE and HIPS, as the composite matrices, were carried out to investigate the operation of the constructed tandem extrusion system. Experimenting at a low WF content of 10 wt%, no coupling agent and nucleating agent were used, and CO$_2$ was continuously injected at 5 wt%.

4.6.1 Experimentation

HDPE or HIPS pellets were mixed with 10 wt% WF as raw materials and 5 wt% CO$_2$ was continuously metered and injected into the mixture melt. At such a low WF content and as initial experiments to investigate the tandem extrusion system operation, no coupling agent (for HDPE case) and talc were used. As stated before, the mass flow rate was maintained at 15 g/min for both cases.

4.6.2 Results and Discussion

Due to the accident of data lost, only the best results of both HDPE/WF and HIPS/WF were retrieved and saved. Figure 4.3 shows the SEM microstructures of a HDPE/WF composite foam obtained at the nozzle temperature and melt temperature both at 132°C with the nozzle pressure achieved at 3000 psi. Photographs (a) and (b) are for the same sample at
different magnifications of 30 and 100 times, respectively. The cell density reached $3.6 \times 10^6$ cells/cm$^3$ and the volume expansion ratio was up to 19 fold. Most cells were closed ones, and the cell size was well below 300 μm within a reasonable variation.

The SEM microstructures of a HIPS/WF composite foam, which was collected at the nozzle temperature down to 119°C and the melt temperature of 138°C with a nozzle pressure of 3500 psi, is shown in Figure 4.4. The cell density was very high on the magnitude of $10^8$ cells/cm$^3$ and the volume expansion ratio also reached as high as 19 fold. The cells were very uniformly distributed with a cell size less than 100 μm.

Regarding the cell morphology, it should be noted that the results of the HDPE/WF foams was different from the results of the HIPS/WF foams. Since HIPS has a high melt strength, cell coalescence was not dominant and the nuclei density (the cell density formed during the nucleation stage) was well maintained during cell growth. On the other hand, in the case of HDPE, the nuclei density would be severely reduced by vigorous cell coalescence and cell collapse during cell growth, and the final cell density of the extruded foams would therefore be much lower than the original nuclei density [36, 91]. Although it was not scientifically strict to compare the HDPE/WF and HIPS/WF foams because they were produced at different temperatures (even though they were with the same WF content and CO$_2$ content), we might still be able to observe the cell coalescence phenomena in the HDPE/WF foam compared with the HIPS/WF foam.

In spite of the data loss, another noticeable issue was that the ranges of the melt and die temperatures required to achieve the fine-celled morphology and high volume expansion in HDPE/WF foaming were very narrow compared with those for HIPS/WF foams. The difference stems from the structures of the two plastics. As mentioned earlier, HDPE is a semi-crystalline plastic, which shows a rapid change in its rheological properties around its freezing
point, whereas HIPS is an amorphous plastic showing a steady change in its rheological properties close to its glass transition temperature [36]. The difference between HDPE and HIPD indicates that the processing of HDPE/WF foams needs more precise control of the processing temperatures than that of HIPS/WF foams; in other words, it would be more challenging to deal with HDPE/WF foams.

4.6.3 Summary and Conclusions

Fine-celled composite foams of HDPE/WF and HIPD/WF were successfully achieved using the tandem extrusion system at a WF content of 10 wt%. It was observed that the addition of 10 wt% WF into the plastic matrices did not seem to change the plastic properties significantly. In other words, these composite foams seem to be able to be processed in a similar way to the pure plastic foams. Therefore, it may be concluded that a suitable coupling agent and nucleating agent did not seem mandatory to be applied at such a low WF content (10% in this research). Based on the structural differences between HDPE and HIPS, fine-celled foaming of HDPE/WF composites is more difficult and challenging than that of HIPS/WF composites.

4.7 Targeted Experiments at Higher WF Contents and Various CO₂ Contents Focusing on HDPE

To address WF at higher contents is the objective of this research project. In addition, the plastic industry, including the industrial sponsors for this research project, is more interested in HDPE than HIPS, since HDPE, with high corrosion resistance, high temperature stability and
outstanding comprehensive strength, has become the most important part of polyethylene (PE) and been most widely used in the industry [113]. Therefore, all the following experiments were focused on the HDPE/WF composite foaming.

Starting with CO₂ injected at 1 wt%, four categories of experiments (WF without CA modified using the tandem extrusion system, WF with CA modified using the tandem extrusion system, WF without CA modified using the single extruder system, and WF with CA modified using the single extruder system) were carried out to identify the effects of the system configuration and CA on the foam properties (cell morphology, extrudate profile, cell density, volume expansion ratio, etc.) and processability (flow stability, nozzle pressure change, processing temperature window, etc.).

Based on the promising results of fine-celled HDPE/WF composite foams achieved by WF with CA modified using the tandem extrusion system at CO₂ 1 wt%, this category of experiments (WF with CA modified using the tandem extrusion system) were further conducted at other CO₂ contents (0 wt%, 2 wt% and 4 wt%) to determine the effect of CO₂ content on the foam properties and processability.

Within each category of experiments, three WF contents (20 wt%, 30 wt% and 40 wt%) were used to study the effect of WF content on the foam properties and processability. At CO₂ 1 wt% with four categories of experiments, pure HDPE (WF 0 wt%) was also used as a reference to better understand the difference due to WF presence.

4.7.1 Experimentation

Wood fibers were mixed with HDPE at 20 wt%, 30 wt% and 40 wt% and CO₂ was continuously injected into the mixture flow at 1 wt% for high density product applications. A
coupling agent (CA) was selected and used by 5 wt% of the applied WF amount, and fixed for all the applicable experiments. Wood fibers without CA modified were also experimented in order to compare with those with CA modified. Moreover, the single extruder system was used for foaming of HDPE/WF composites, as a reference to the foamed composites produced from the tandem extrusion system. In addition, pure HDPE (WF 0 wt%) was foamed as a reference to further understand the differences from those with WF added. All the experiments were carried out at a mass flow rate of 12 g/min and a talc content of 2 wt% of HDPE and WF as stated before. Although both nozzle and melt temperatures had strong effects on the cell morphology and foam properties [36, 91], they were always adjusted the same to simplify experiments in the following experiments, and therefore, the foaming temperature is always mentioned in this thesis.

Then, further experiments were conducted by WF with CA modified using the tandem extrusion system. By keeping all the applicable conditions the same as the above stated, CO₂ was injected at other contents of 2 wt% and 4 wt% in addition to the already obtained results of CO₂ 1 wt%. Finally, the experiments without CO₂ injected (CO₂ 0 wt%) were also performed as a reference to those with CO₂ injected.

4.7.2 Results and Discussion

The experimental results for foaming of HDPE/WF composites at CO₂ 1 wt% with four categories of experiments are summarized in Figures 4.5-4.24 and Tables 4.2-4.5. Among these, Figures 4.5-4.17 show the cell morphology, Figures 4.18-4.21 show the extrudate profile, Figure 4.22 shows the volume expansion ratio, Figure 4.23 shows the cell density,
Figure 4.24 shows the measured nozzle pressure, and Tables 4.2-4.5 integrate all the experimental data.

The experimental results for foaming of HDPE/WF composites at other CO₂ contents of 0 wt%, 2 wt% and 4 wt% focusing on one category of experiments (WF with CA modified using the tandem extrusion system) are summarized in Figures 4.25-4.39 and Tables 4.6-4.8. Among these, Figures 4.25-4.30 show the cell morphology, Figures 4.31-4.33 show the extrudate profile, Figure 4.34-4.35 show the volume expansion ratio, Figure 4.36-4.37 show the cell density, Figure 4.38-4.39 show the measured nozzle pressure, and Tables 4.6-4.8 integrate all the experimental data.

### 4.7.2.1 Comparison of the Devolatilized Tandem Extrusion System with the Undevolatilized Single Extruder System

The effects of system configuration (tandem extrusion system vs. single extruder system) on the foam properties and processability can be clearly seen by comparing the results of the four categories of experiments at CO₂ 1 wt%.

**Cell Morphology**

From Figures 4.5-4.16 at CO₂ 1 wt%, it is observed that the effect of the system configuration on the cell morphology was pronounced when comparing the results of the tandem extrusion system with those of the single extruder system for both WF with CA modified and WF without CA modified at each WF content. When the single extruder system was used, the cell morphologies were very poor regardless of WF with CA modified or not. However, the cell morphologies were obviously improved using the tandem extrusion system,
although the results of WF with CA modified were much better than those of WF without CA modified. We could conclude that the system configuration had a strong effect on the cell morphology, and the tandem extrusion system is a prerequisite for fine-celled foaming of HDPE/WF composites. Without the help of the tandem extrusion system to achieve a uniform mixing and an effective moisture removal, it was believed that the effects of CA, CO₂ content, and WF content could not play important roles in fine-celled foaming of HDPE/WF composites.

*Extrudate Profile*

The extrudate profiles of the four categories' experiments are photographed and integrated in Figures 4.18-4.20 for WF 20 wt%, 30 wt% and 40 wt%, respectively. It was clearly observed that the effect of system configuration played a significant role in the extrudate profile. Especially during the foaming temperature range, the tandem extrusion system dramatically improved the surface quality of the extrudate profiles, while the single extruder system produced very poor extrudate profiles which were severely twisted and knotted, regardless of WF with CA modified or not.

*Volume Expansion Ratio*

The effect of system configuration on the volume expansion ratio can be studied by comparing (a) with (c), and (b) with (d), shown in Figure 4.22. Disregarding the difference in the foaming temperature range, the tandem extrusion system improved the maximum expansion ratio of WF 20 wt%, from about 4.3 fold (single extruder system) to about 6 fold for WF with CA modified, and from about 2.4 fold (single extruder system) to about 3.5 fold for WF without CA modified, while did not seem to increase the maximum expansion ratios of
WF 30 wt% and 40 wt%. However, it should be reminded that the tandem extrusion system produced much better extrudates with good volume expansion than the single extruder system, in which the extrudates were severely twisted and knotted. Therefore, it was believed that the tandem extrusion system facilitated the uniform volume expansion of all the three WF contents and improved the volume expansion ratio of WF 20 wt%.

**Cell Density**

The effect of system configuration on the cell density can be studied by comparing (a) with (c), and (b) with (d), referring to Figure 4.23, which shows the cell densities of the four categories' experiments.

Although all the cell densities were maintained on the order of $10^6$ cells/cm$^3$, it was observed that the cell densities were slightly increased when using the tandem extrusion system for both WF with CA modified and WF without CA modified, regardless of the difference in the foaming temperature range. This indicated that the tandem extrusion system had a positive effect on the cell density, probably due to the fact that the well mixed and dispersed WF particles into the HDPE matrix could act as an insignificant or aiding nucleating agent to increase the cell density to a limited extent, although the cell density was believed to be a weak function of the system configuration.

**Processability**

The effect of system configuration on the foaming processability is studied in terms of the flow stability, nozzle pressure ($P_n$) change, foaming temperature window, etc.
The flow was more stable with the tandem extrusion system resulting in the extrudates stably exiting the nozzle die and uniformly growing, while the flow was fluctuating with the single extruder system resulting in the extrudates twisted and knotted.

Figure 4.24 shows the change of $P_n$ with the foaming temperature ($T$), and the foaming temperature window with the minimum foaming temperatures for the four categories of experiments at CO$_2$ 1 wt%. The effect of the system configuration can be clearly identified by comparing (a) with (c), and (b) with (d) for WF with CA modified and WF without CA modified, respectively. Regarding the change of $P_n$ during the foaming temperature window, it was clearly observed that the tandem extrusion system had a smoother $P_n$ increase compared to the single extruder system, in which the $P_n$ surged steeply, when the foaming temperature was decreased. As for the foaming temperature window, the tandem extrusion system had a wider foaming window than the single extruder system.

Based on the results obtained, it was concluded that the tandem extrusion system effectively improved the foam processability with a smoother $P_n$ increase and a wider foaming temperature window compared to the single extruder system.

4.7.2.2 Effects of CA on the Foam Properties and Processability

The effects of CA (WF with CA modified vs. WF without CA modified) were also investigated using CO$_2$ 1 wt%.

Cell Morphology

The results, shown in Figures 4.11-4.16, indicated that CA had little effect on the cell morphology when using the single extruder system for both WF with CA modified and WF
without CA modified, probably due to the poor mixing of HDPE and WF. In other words, without good mixing of HDPE and WF, CA couldn't play an active role to improve the cell structures.

Using the tandem extrusion system, however, the effect of CA on the cell morphology was very strong when comparing the cell structures of each WF content between WF without CA modified (Figures 4.5-4.7) and WF with CA modified (Figures 4.8-4.10).

In the former case, because the interaction between HDPE and WF was very weak without the aid of the CA, HDPE tended to separate from WF to the skin area where the shear stress was the highest, while WF particles seemed to stay in the core area where the flow rate was the largest. This probably resulted in the fine-celled structures in the skin area where HDPE governed while poor-celled structures in the core area where WF concentrated. It may also be concluded that even though a uniform mixing of HDPE and WF was attained by the intensive shear of the counter-rotating twin-screw extruder, they were still easily separated from each other during the final foaming process without the aid of CA.

In the latter case, with the aid of CA to increase the interaction between WF and HDPE, the cell morphologies were greatly improved, and fine and uniform cell structures were achieved. One notable issue is that the dark areas of the SEM photograph of WF 20 wt%, shown in Figure 4.8(d), were due to the depressed areas of the sample cross-section, which were less gold-coated for SEM. Because the free-fractured sample surface could not be ensured even and smooth, resulting in both depressed and outstanding areas on the sample cross-section, accordingly the dark and bright areas on the SEM photograph, respectively. In fact, the whole cross-section was uniformly distributed with fine cells. The same explanation would also be given to that of WF 40 wt% shown in Figure 4.10(d). It was observed that the phenomena of skin and core separation were eliminated with the improved interaction between
HDPE and WF when CA was used. This implied that the effect of CA on the cell morphology was critical and a suitable CA was imperative for fine-celled HDPE/WF composite foaming. In other words, a effective bonding of HDPE and WF was crucial to achieve fine-celled HDPE/WF composite foams in addition to the uniform mixing and moisture removal, which was believed to be achieved by the tandem extrusion system as stated before.

In summary, CA had a strong effect on the cell morphology to achieve a fine-celled microstructure on the basis of the tandem extrusion system rather than the single extruder system, in which CA could hardly play an active role to effectively improve the cell morphology.

**Extrudate Profile**

It was also observed that CA had a stronger effect on the extrudate profile with the tandem extrusion system, in which the extrudates became much better in terms of straightness and smoothness, and the surface color became darker due to the fact that WF came to the skin layer.

**Volume Expansion Ratio**

It was observed that CA could make an active contribution to the volume expansion ratio based on both the tandem extrusion system and the single extruder system for WF 20 wt% and 30 wt%, while CA seemed to have little effect on that of WF 40 wt% probably due to the fact that the WF content could dominate the expansion ratio at such a high content. The scenario with the single extruder system for WF 20 wt% and 30 wt% could probably be assumed that even a small part of WF randomly and non-uniformly bonded with HDPE by the poor help of
CA, they could expand together with the HDPE to make a contribution to the volume expansion ratio.

**Cell Density**

Referring to Figure 4.23, it was also found that the effect of CA on the cell density could be hardly identified. The results indicated that the cell density was also a weak function of CA.

**Processability**

With the tandem extrusion system considered by comparing (a) with (b) of Figure 4.24, the effect of CA was so strong that the minimum foaming temperatures were shifted from the same 132°C up to 138°C, 140°C and 141°C for WF 20 wt%, 30 wt% and 40 wt%, respectively, which was believed to be due to the significantly increased viscosity of the melt flow resulting from the effective HDPE and WF bonding, and a higher viscosity of a higher WF content. It was also observed that for each WF content, $P_n$ increased more abruptly within an up-shifted and narrowed foaming temperature window when WF was modified by CA, however the maximum $P_n$'s before nozzle die choking remained in the range of 2000-2500 psi for both WF with CA modified and WF without CA modified. These results implied that CA had a strong effect on raising the minimum foaming temperature and narrowing the foaming temperature window rather than raising the maximum $P_n$ before nozzle freezing for each WF content.

When using the single extruder system, it was observed that $P_n$ increased in a similar way between (c) WF with CA modified and (d) WF without CA modified, and the lowest foaming temperatures only changed from 136°C, 137°C and 138°C (d) to 137°C, 139°C and 140°C (c) for WF 20 wt%, 30 wt% and 40 wt%, respectively, which also implied that without good mixing of HDPE and WF, CA could not play an effective role.
4.7.2.3 Effects of WF Content on the Foam Properties and Processability

The effects of WF content (0 wt%, 20 wt%, 30 wt%, and 40 wt%) were identified by comparing the results of various WF contents in each category of experiments at CO₂ 1 wt%.

Cell Morphology

It was generally observed that for each category of experiments, the results of WF 20 wt% exhibited better cell structures than those of WF 30 wt% and 40 wt%, in turn, those of WF 30 wt% showed better cell structures than those of WF 40 wt%. The SEM microstructures could be referred to Figures 4.5-4.7, Figures 4.8-4.10, Figures 4.11-4.13, and Figures 4.11-4.13 for the four categories of experiments, respectively. However, the cell morphologies were observed totally different from those of the pure HDPE results, which were processed in the same condition (CO₂ 1 wt% and talc 2 wt%), referring to Figure 4.17. This indicated that the presence of WF in the HDPE matrix significantly changed the cell morphology with the fibers connected and woven with each other in the cell structures. In other words, the presence of WF ruptured the continuous plastic matrix and deteriorated the cell morphology of the composite foams.

Extrudate Profile

By comparing the extrudate profiles of each category of experiments, shown in (a)s, (b)s, (c)s and (d)s of Figures 4.18-4.20, respectively, it was predicted that the best extrudate profiles were also obtained from WF 20 wt% in each category of experiments. On the other hand, all the extrudate profiles of pure HDPE (WF 0 wt%) foams, shown in Figure 4.21, had good
surfaces and the surfaces became shinier as the temperature was reduced. It was observed that the surface quality in terms of smoothness and shininess decreased with the increased content of WF in the plastic matrix.

**Volume Expansion Ratio**

Based on Figure 4.22 in each category of experiments, it was expected that WF 20 wt% also achieved the highest expansion ratio among the three WF contents in spite of the small difference in the foaming temperature. For the pure HDPE (WF 0 wt%), it reached its maximum expansion ratio up to about 4.5 fold at a much lower foaming temperature of 130°C, which was assumed to have a strong effect on preventing the pure HDPE from further expansion.

However, the effect of WF on the volume expansion ratio was observed to rely on the effects of the system configuration and CA. For example, WF content had a strong effect on the volume expansion ratio in (a) while the effect of WF content on the volume expansion ratio can hardly be identified in (d).

**Cell Density**

It was also clearly observed that WF content had little effect on the cell density in each category of experiments shown in Figure 4.23.

**Processability**

It was observed that the flow stability was decreased when the WF content increased, which was believed to be caused by the increased flow viscosity. From the devolatilizing vent, it was clearly noted that the mixture melt flow transformed from the soft flour-like material at
WF 20 wt% to the dense clay-like material at WF 40 wt%. In terms of volumetric percentage (v/l%), WF 20 wt%, 30 wt% and 40 wt% were equal to about WF 44 v/l%, 58 v/l% and 68 v/l%, respectively, in this research project based on the WF used. These data could help understand the material flow behavior that the melt flow probably transformed from the HDPE-dominated mixture to the WF-governed mixture. In other words, the composite flow became less extrudable or thrustable when the WF content increased.

In each category of experiments in Figure 4.24, it was found that the WF presence had a significant effect on the change of Pn and the foaming temperature window compared with the pure HDPE (WF 0 wt%), in which the Pn increased much more smoothly and the foaming temperature window were much wider with the minimum foaming temperature down to 130°C. Considering the three WF contents, it was also observed that the WF content had a direct effect on the Pn and the foaming temperature window in terms of the pressure increasing more abruptly and a narrower window range for the higher WF content.

4.7.2.4 Effects of CO2 Content on the Foam Properties and Processability

The effects of CO2 content on the foam properties and processability can be clearly seen by comparing the experimental results of WF with CA modified using the tandem extrusion system at different CO2 contents of 0 wt%, 1 wt%, 2 wt% and 4 wt%, which are shown in Figures 4.8-4.10, 4.25-4.39 and Tables 4.3, 4.6-4.8.

Cell Morphology

The extrudates of CO2 0 wt% did not achieve any foamed structures, therefore no cell morphologies (SEM photographs) were available.
With a considerable decrease of the minimum foaming temperature by around 4-5°C for each WF content when CO\textsubscript{2} was increased from 1 wt% to 2 wt%, the cell morphologies changed to a certain degree. The cross-sections of the foamed extrudates became slightly deteriorated for the CO\textsubscript{2} 2 wt% case, shown in Figures 4.25-4.27, in which cell coalescence was observed probably owing to the increased amount of CO\textsubscript{2}, compared with those of CO\textsubscript{2} 1 wt%, referring to Figures 4.8-4.10, in which the fine cells were uniformly distributed on the cross-sections for each WF content.

With the CO\textsubscript{2} content increased from 2 wt% to 4 wt%, it was observed that the cell structures became better in the skin area than in the core area, shown in Figures 4.28-4.30. However, these phenomena were believed to be different from the experimental results obtained by WF without CA modified using the tandem extrusion system at CO\textsubscript{2} 1 wt% shown in Figures 4.5-4.7. In the latter case, the poor cross-sections were caused by the separation of skin and core areas due to the bad interaction of HDPE and WF without CA modified, especially for WF 30 wt% and 40 wt%, whereas in the former case, the HDPE and WF were believed to be effectively bonded and the increased CO\textsubscript{2} amount probably resulted in the somewhat vigorous cell coalescence in the core area. The cross-sections of the former case were much better than those of the latter case.

Therefore, the increased CO\textsubscript{2} content could probably cause the cell coalescence in the later-solidified core area. However, the difference of cell morphologies between CO\textsubscript{2} 2 wt% and 4 wt% was not so obvious for each WF content, which implied that the maximum solubility of CO\textsubscript{2} into the HDPE/WF composite flow was probably in this range. A future study should be conducted to clarify this subject. Although the cross-sections of CO\textsubscript{2} 1 wt% exhibited the best cell morphologies, those of CO\textsubscript{2} 2 wt% and 4 wt% were observed to be promising.
Extrudate Profile

All the extrudate profiles at different CO$_2$ contents of 0 wt%, 1 wt%, 2 wt% and 4 wt% are integrated in Figures 4.31-4.33 for WF 20 wt%, 30 wt% and 40 wt%, respectively. Because the experiments of CO$_2$ 1 wt% were carried out earlier, the temperatures were started from 150°C gradually down to the lowest foaming temperatures for each experiment, while for the experiments of CO$_2$ 0 wt%, 2 wt% and 4 wt%, all the temperatures were started from 145°C slowly down to the minimum foaming temperatures for each experiment. It is worthy of noting that the extrudate profiles of CO$_2$ 0 wt% for WF 30 wt% seemed to be larger in diameter than those of CO$_2$ 0 wt% for WF 20 wt%. This illusion is caused by the more magnified image of WF 30 wt% with less samples in it than that of WF 20 wt%. As a matter of fact, the unfoamed extrudates without CO$_2$ injected (CO$_2$ 0 wt%) became more contracted as the WF content increased. In other words, at CO$_2$ 0 wt%, the higher the WF content, the smaller the extrudate diameter. Other possible illusions may be caused due to the same reason when integrating the four images (CO$_2$ 0 wt%, 1 wt%, 2 wt% and 4 wt%) together for each WF content.

Based on the four images of CO$_2$ 0 wt%, 1 wt%, 2 wt% and 4 wt% for each WF content, it was observed, especially during the low foaming temperature range, that the surface color changed from shining darkness for CO$_2$ 0 wt% to significant lightness for CO$_2$ 2 wt% and 4 wt%, which proved that the HDPE/WF composites transformed from dense unfoamed composites to significantly expanded foams with a much reduced density. Compared with the surface quality of CO$_2$ 1 wt%, it was also found that the surface quality was not much deteriorated and remained good for the extrudates of CO$_2$ 2 wt% and 4 wt%. These results
suggested that the CO$_2$ content had more effect on the surface color change due to the foam expansion rather than the surface quality such as smoothness and straightness.

It was encouraged by the results of WF 30 wt% and 40 wt%. With the help of increased CO$_2$ contents of 2 wt% and 4 wt%, the minimum foaming temperatures were significantly reduced by about 5°C compared with that of CO$_2$ 1 wt%, the composite foams at such high WF contents could also well expand with good extrudate profiles. The results strongly directed an effective way to address fine-celled HDPE/WF composite foaming with high WF contents such as 40 wt% or even more.

*Volume Expansion Ratio*

The volume expansion ratio is plotted in Figures 4.34 and 4.35 in terms of *for each WF% at various CO$_2$%* and *for each CO$_2$% at various WF%*, respectively.

From Figure 4.34, it was observed that the CO$_2$ content had a positive effect on the volume expansion ratio for each WF content.

Based on Figure 4.35, it was understandable that for CO$_2$ 0 wt% (a), the composite extrudates were intensively contracted with the expansion ratios less than 1 for the three WF contents, which was calculated on the basis of the densities of the HDPE/WF mixtures used as the raw experimental materials in this research project. It was found that CO$_2$ 1 wt% (b) only helped much on the volume expansion ratios of WF 20 wt% and 30 wt%, while CO$_2$ 4 wt% (d) also greatly improved the volume expansion ratio of WF 40 wt%, which also directed the way to effectively deal with the fine-celled foaming of HDPE/WF composites at a higher WF content, that is to inject more gas within a suitable range.

*Cell Density*
The cell density is shown in the Figures 4.36 and 4.37 in terms of for each WF% at various CO₂% and for each CO₂% at various WF%, respectively.

Based on the two figures, all the cell densities were observed to be still in the range of 10⁶ cells/cm³, which suggested that the cell density was also a weak function of the CO₂ content. In other words, the cell density was believed to be strongly determined by the talc content (nucleating agent) rather than the CO₂ content (blowing agent). However, the effect of talc content was not effectively investigated in this research.

Again because no cell structures were achieved from CO₂ 0 wt% experiments, no data of CO₂ 0 wt% were included in the two figures.

**Processability**

It was observed that the increased CO₂ content could facilitate the foaming processability such as the extrudates more freely exiting out of the nozzle die at a higher CO₂ content probably due to the decreased viscosity of the composite flow.

As stated before, a noticeable change was the significant decrease of the minimum foaming temperature (and/or the widening of the foaming temperature window), especially when CO₂ was increased from 1 wt% to 2 wt%, demonstrated that the increased CO₂ content tended to ease the foaming processability. However, the small difference of 1°C in the minimum foaming temperatures between CO₂ 2 wt% and 4 wt% for each WF content could probably be attributed to the fact that the maximum solubility of CO₂ into the HDPE/WF composite flow was achieved between these two CO₂ contents of 2 wt% and 4 wt%. No more CO₂ could be dissolved into the WF-dispersed HDPE matrix and the undissolved CO₂ would simply escape to the atmosphere through the foam skin. The solubility of CO₂ into the HDPE/WF composite flow, however, has been rarely investigated because of the difficulties
involved in measurement, a further study is required to quantify this phenomena. It was also clearly observed that the minimum foaming temperatures (or the foaming temperature windows) of CO₂ 0 wt% and 1 wt% were the same for each WF content, which implied that the 1 wt% injected CO₂ amount was completely dissolved into the HDPE/WF composite flow and such a CO₂ content did not seem to change the viscosity of composite flow significantly compared with that of CO₂ 0 wt%. The results indicated that the increased CO₂ content had a strong effect on the decrease of the minimum foaming temperature especially for CO₂ increased from 1 wt% to 2 wt%.

Regarding the P_n change, it was believed that several parameters affected P_n such as the foaming temperature, CO₂ content and WF content, which changed the composite flow viscosity resulting in the change of P_n when the effects of system configuration and CA were fixed.

From Figure 4.38, for each WF content, it was observed that the achieved maximum P_n's maintained in a small change for all the four CO₂ contents especially for WF 30 wt% and 40 wt%. For WF 20 wt% (a), the maximum P_n's were also almost unchanged if referred to the pressures at 134°C for CO₂ 2 wt% and 4 wt% compared with the maximum P_n's at 138°C for CO₂ 0 wt% and 1 wt%, we assumed that the further decrease of the foaming temperature caused the pressure increase from both about 2100 psi to 3000 psi and 3500 psi for CO₂ 2 wt% and 4 wt%, respectively. In other words, at such a low foaming temperature (below 134°C), it was believed that the maximum P_n was strongly affected by the foaming temperature rather than the CO₂ content. As stated before and also described in Behravesh's study [36], HDPE experiences a rapid change in its rheological properties close to its crystallization temperature, and the presence of WF and the dissolution of CO₂ into the HDPE matrix would both change the actual crystallization temperature of the WF/HDPE-CO₂ flow. Future research regarding
the properties of WF/HDPE-CO₂ flow is strongly suggested. Generally, we could conclude that the increased CO₂ content had little effect on the maximum nozzle pressure, which was believed to be the negative effects of the increased CO₂ content (reducing the flow viscosity) and the accordingly reduced minimum foaming temperature (raising the flow viscosity). The fact that the pressure jumped up below 134°C in WF 20 wt% case was assumed that the WF/HDPE-CO₂ flow was close to its rapid change window of the rheological properties, and therefore, the foaming temperature was believed to have a strong effect on the Pₙ.

Based on Figure 4.39, we could clearly see that the Pₙs of WF 30 wt% and 40 wt% behaved in a similar way at both CO₂ 2 wt% and 4 wt%, which also provided the strong clue for dealing with fine-celled HDPE/WF composite foaming at a high WF content (>30 wt%). In other words, injecting more CO₂ amount (>2 wt%) could significantly decrease the minimum foaming temperature while maintaining a suitable Pₙ range without a significant pressure surge. A future study to investigate a suitable range of CO₂ content is suggested.

4.7.3 Summary and Conclusions

A series of experiments were designed and conducted to study the processing and material parameters for fine-celled foaming of HDPE/WF composites. Wood fibers were mixed with HDPE at three contents of 20, 30 and 40 wt% and CO₂ was continuously injected into the mixture flow at a constant 1 wt% for all the foaming experiments. CA was used by 5 wt% (fixed for all the applicable experiments) of the applied WF amount and talc was added by 2 wt% of the HDPE and WF (fixed for all experiments). All the experiments were carried out at a mass flow rate of 12 g/min for the scientific rigidity, which was achieved by the suitable match of the feed rate of the twin-screw feeder and the RPM(s) of the extruder(s) for
the tandem extrusion system or the single extruder system. Four categories of experiments (WF without CA modified using the tandem extrusion system, WF with CA modified using the tandem extrusion system, WF without CA modified using the single extruder system, and WF with CA modified using the single extruder system) were carried out with WF at three contents of 20 wt%, 30 wt% and 40 wt% for each category. Pure HDPE (WF 0 wt%) with the same talc content of 2 wt% was also foamed at CO₂ 1 wt% to better understand the effect of WF presence.

Based on the above experiments, another set of experiments with other CO₂ contents of 0 wt%, 2 wt% and 4 wt% for the three WF contents (20 wt%, 30 wt% and 40 wt%) were designed and carried out focusing on one experimental category of WF with CA modified using the tandem extrusion system.

All the experimental studies lead to the following conclusions:

- Fine-celled HDPE/WF composite foams were successfully achieved by WF with CA modified using the tandem extrusion system in terms of the cell morphology, extrudate profile, volume expansion ratio, cell density, etc. These were believed to be the comprehensive effects of the uniform mixing, effective bonding and moisture removal. Among the three WF contents, WF 20 wt% had the best results with the maximum expansion ratio up to about 6 fold.

- By WF without CA modified using the tandem extrusion system, the foamed composites were not ideal because of the separation of the skin and core section. Fine-celled structures were only found in the skin area where HDPE governed rather than in the core area where WF concentrated. These results clearly indicated the importance of good bonding of HDPE and WF in addition to the good mixing and moisture removal. Among the three WF
contents, WF 20 wt% also had the best results with the maximum expansion ratio achieved at about 4.5 fold.

- Composite foams obtained from the single extruder system, by WF both with and without CA modified, were not acceptable in terms of the cell structure and uniformity, and the extrudate profiles which were severely twisted and knotted. The effect of CA on the foam properties could hardly be identified in these two cases, which suggested that CA could not perform effectively without the prerequisite of the uniform mixing of HDPE and WF. It was also observed that the WF content had a limited effect on the foam properties regarding the cell morphology and extrudate profile. These results strongly indicated that without uniform mixing and effective moisture removal with the single extruder system, fine-celled composite foams could not be achieved. In other words, uniform mixing and effective moisture removal were believed to be imperative for fine-celled HDPE/WF composite foaming.

- In addition to the effect of CA on the good bonding of HDPE and WF, CA had a strong effect on the increase of the minimum foaming temperature, which was believed to be the increased viscosity of the composite flow, resulting in the fact that the nozzle pressure increased more abruptly as the foaming temperature decreased within a narrowed foaming temperature window. These phenomena were very clear in the tandem extrusion system when comparing the results of WF with CA modified and WF without CA modified.

- Focusing on one category of experiments by WF with CA modified using the tandem extrusion system, it was observed that the CO₂ content had a strong effect on the decrease of the minimum foaming temperatures for the three WF contents with CO₂ content increased from 1 wt% to 2 wt%, while little effect with CO₂ content changed from 0 wt% to 1 wt% and from 2 wt% to 4 wt%.
Compared with the fine-celled HDPE/WF composite foams achieved at CO₂ 1 wt% for the three WF contents, cell coalescence was observed when CO₂ content was increased to 2 wt%. The difference of the cell morphologies between CO₂ 2 wt% and 4 wt% were not so obvious for each WF content, which implied that the maximum solubility of CO₂ into HDPE/WF composite flow would probably fall in this range. Support from future researches in this subject would be greatly appreciated. For CO₂ 4 wt%, it was found that the cell structures became better in the skin area than in the core area, which could be due to the somewhat vigorous cell coalescence in the later-solidified core area. In general, at CO₂ 2 wt% and 4 wt% the cell morphologies were still quite acceptable especially at the minimum foaming temperature for each WF content.

The CO₂ content also had an active effect on the extrudate color for each WF content. During the foaming temperature range, it was observed that the surface color became lighter when CO₂ content increased, which proved that the HDPE/WF composites transformed from the highly-integrated unfoamed composites with a increased density to the highly-expanded foamed composites with a significantly reduced density. The surface quality remained good for the extrudates of CO₂ 2 wt% and 4 wt%, which suggested that CO₂ content had more effect on the surface color rather than the surface quality such as smoothness.

It was encouraged by the results from WF 30 wt% and 40 wt%. With the help of increased CO₂ contents of 2 wt% and 4 wt%, the minimum foaming temperatures were significantly reduced by about 5°C compared with that of CO₂ 1 wt%, the composite foams at such high WF contents could also be well foamed with a good extrudate quality. These results strongly led a potential way to address fine-celled HDPE/WF composite foaming at high WF contents such as 40 wt% or even more. In other words, more CO₂ amount should be
injected in order to significantly decrease the minimum foaming temperature within a suitable CO$_2$ amount range because of the plasticating effect of CO$_2$, which needs further researches on this subject.

- It was found that CO$_2$ 1 wt% only made an active contribution to the volume expansion ratios of WF 20 wt% and 30 wt%, while CO$_2$ 4 wt% also greatly improved the volume expansion ratio of WF 40 wt% in addition to WF 20 wt% and 30 wt%, which also directed the potential way to effectively deal with fine-celled foaming of HDPE/WF composites at a higher WF content, that is to inject more gas within a suitable CO$_2$ range.

- When focusing on the experiments by WF with CA modified using the tandem extrusion system, the nozzle pressure $P_n$ was believed to be a function of the foaming temperature, CO$_2$ content and WF content, which changed the flow viscosity resulting in the change of $P_n$. The final $P_n$ was believed to be the comprehensive effects of the above three parameters. The maximum $P_n$s, however, only slightly changed for all the four CO$_2$ content at each WF content, which was believed to be the negative effects of the increased CO$_2$ contents (reducing the flow viscosity) and the accordingly reduced minimum foaming temperatures (raising the flow viscosity). At each CO$_2$ content, the maximum $P_n$s varied within a small range of 500 psi for the three WF contents except for WF 20 wt% at CO$_2$ 4 wt%, in which, however, the foaming temperature was so low as to be believed to have a strong effect on $P_n$. Therefore, it could be concluded that WF content had a small effect on $P_n$ for each CO$_2$ content, which was important for fine-celled HDPE/WF foaming at a high WF content without a significant $P_n$ surge.

- All the cell densities were well maintained in the range of $10^6$ cells/cm$^3$, which strongly suggested that the cell density should be governed by the talc content (nucleating agent)
rather than the system configuration, CA, WF content, and CO$_2$ content. In other words, the cell density was proven to be a weak function of all the investigated parameters.

4.8 Supplementary Experiments with Pre-Dried Wood-Fibers

Poor HDPE/WF composite foams were obtained in the two categories of experiments (WF with CA modified and WF without CA modified using the single extruder system). It was believed that the poor HDPE/WF mixing and moisture existing both caused the bad results. Thus the following supplementary experiments were designed and conducted to further identify which parameter had a stronger effect on the bad results based on the single extruder system. Because of no significant difference in the results between these two categories of experiments, the results from the experiments of WF with CA modified using the single extruder system were used as a reference. The foaming experiments of Pre-dried WF/HDPE composites (removing the effect of moisture existing) were carried out in the same applicable conditions at CO$_2$ 1 wt% by WF with CA modified using the single extruder system, and the results were compared with each other and analyzed to determine the stronger parameter which dominated the bad results.

4.8.1 Experimentation

Wood fibers were first pre-dried in a laboratory-type vacuum drying oven (VO-32D, ADVANTEC) at 105°C for 10 hours, and then rapidly weighed and added into the mixtures of HDPE, CA and talc which were already prepared in advance. Experiments were carried out in time using the single extruder system with a N$_2$ protected environment around the feeding
process. Wood fibers were also applied at 20 wt%, 30 wt% and 40 wt% and CO₂ was injected at 1 wt%. All the applicable experimental conditions remained the same as those stated in section 4.7.1.

4.8.2 Results and Discussions

The experimental results for foaming of pre-dried WF/HDPE composites at CO₂ 1 wt% by WF with CA modified using the single extruder system are summarized in Figures 4.40-4.48 and Table 4.9. The experimental results of undried WF/HDPE composite foams in the same experimental conditions could be referred back to Figures 4.14-4.16 (cell morphology) and were integrated in Figures 4.43-4.48.

Cell Morphology

Figures 4.40-4.42 shows the cell morphologies for dried WF 20 wt%, 30 wt% and 40 wt%, respectively. Compared with the cell morphologies of undried WF 20 wt%, 30 wt% and 40 wt% shown in Figures 4.14-4.16, respectively, it was observed that the cell structures were hardly improved even though the images of the cross-sections seemed to be a little better for the three WF contents. The results indicated that the HDPE/WF mixing had more effect on the cell morphology than the moisture existing when the single extruder system was used.

Extrudate Profile

Extrudate profiles for both dried and undried WF are integrated together in Figures 4.43-4.45 for WF 20 wt%, 30 wt% and 40 wt%, respectively. It was found that the extrudate profiles had a limited improvement for dried WF (a) compared with undried WF (b). Also the
extrudate color became a little darker because of the less expansion resulting from the moisture removed during the pre-drying process. The overall extrudate profiles, especially during the foamed products, however, were little improved due to the twisting and knotting still observed. These results also suggested that moisture existing or not only had a limited effect on the extrudate profiles, while the HDPE/WF mixing was believed to have a strong effect on the extrudate profiles.

**Volume Expansion Ratio**

Figure 4.46 shows the volume expansion ratio at different WF contents for dried WF (a) and undried WF (b). It was observed that the expansion ratio contributed from the moisture were obvious at the low foaming temperatures for each WF content. The maximum expansion ratios of undried WF were about 2 fold, 2 fold and 1 fold higher than those of dried WF for WF 20 wt%, 30 wt% and 40 wt%, respectively. We could probably conclude that the moisture effect played an active role in the volume expansion ratio considering the small CO₂ content of 1 wt% injected in these experiments. The maximum expansion ratio occurred at the minimum or second lowest foaming temperature for each experiment.

**Cell Density**

The cell density is presented in Figure 4.47 for dried WF (a) and undried WF (b), respectively. It was predicted that both the mixing and moisture effects should not affect the cell density at each WF content. All the cell densities were still remained in the range of 10^6 cells/cm³ with a small variation between dried and undried WF for each WF content. We could conclude on a high confidence level that both the mixing and moisture effects had no or very little effects on the cell density.
**Processability**

It was observed that the pre-dried WF/HDPE mixture did not seem to improve the composite flow stability significantly with the single extruder system.

Figure 4.48 shows the $P_n$ change for dried WF (a) and undried WF (b), respectively. It was found that the minimum foaming temperature (or the foaming temperature window) remained the same between dried WF and undried WF for each WF content. In addition, there was hardly difference in $P_n$ between dried WF and undried WF for each WF content, which implied that moisture existing or not had little effect on the $P_n$. It was assumed that the nozzle size (diameter and length) and the extruder RPM would have strong effects on $P_n$. These two parameters, however, have not been effectively investigated in this research. Nozzle die remained unchanged, and the extruder RPM only adjusted within a limited range to match the consistent flow rate at 12 g/min for all the experiments except for the preliminary experiments.

**4.8.3 Summary and Conclusions**

A set of supplementary experiments using pre-dried WF as the raw material were carried out by WF with CA modified using the single extruder system in order to better understand the mixing and moisture behavior on the final foam properties. These experiments led to the following conclusions:

- The results of pre-dried WF hardly improved the cell morphology and extrudate profile, which indicated that the HDPE/WF mixing parameter had more effect on the cell morphology and extrudate profile than the moisture parameter.
- The moisture effect was observed to make a considerable contribution to the maximum expansion ratio for each WF content at the low CO₂ content of 1 wt% used in the experiments.

- The cell density was proven to be a very weak function of both mixing and moisture effects. It was believed to be a strong function of the nucleating agent, which suggested the future experiments at different talc contents.

- The nozzle pressure Pₙ was observed to be a weak function of the moisture effect. It was assumed to be a strong function of the nozzle size and the extruder RPM, which implied the future experiments on the different nozzle sizes and extruder PRMs (using different flow rates within a suitable processing PRM window).
Chapter 5

CONCLUDING REMARKS AND FUTURE WORK

5.1 Concluding Remarks

The main contributions of the research presented in this thesis are the joint development of an innovative tandem extrusion system for continuous foaming of fine-celled plastic/WF composites flexible for using either physical blowing agent or chemical blowing agent, and a series of experiments well designed and carried out to study the fine-celled foaming of plastic/WF composites.

The innovative tandem extrusion system was developed initially by the concept and idea of uniformly and intensively mixing the raw material of HDPE/WF mixture as well as effectively on-line removing moisture which is inherent in WF. The first extruder targeted to address the former task was configured into a twin-screw counter-rotating extruder which is widely used as an intensive mixer or compounder in the plastics industry, and the devolatilizing vent at the interconnection of the two extruders was built up to deal with the latter task when the moisture was already converted into vapor ready for purging out. The second vented extruder and its following components were referred to the system setup developed by Behravesh [36] to handle the tasks of continuous and stable gas injection, gas uniform diffusion and complete dissolution, melt flow homogeneous cooling, and high
pressure drop rate to achieve fine-celled foam structures. After a number of testing experiments were carried out to investigate the system operation, continuous and stable feeding of the raw material of plastic/WF mixtures became a new challenging task. Then a twin-screw feeder was finally selected and incorporated into the tandem extrusion system to effectively solve the feeding problem. A suitable match between the feeding rate of the twin-screw feeder and the RPMs of the first and second extruders was achieved to effectively control the system mass flow rate. This refined tandem extrusion system was applied for all the applicable research experiments and is flexible for using either PBA or CBA by assembling or disassembling the gas injection system.

With the preliminary experiments conducted for both HDPE/WF and HIPS/WF composites at a low WF content of 10 wt% to investigate the operation of the tandem extrusion system, most of the efforts were focused on the foaming of fine-celled HDPE/WF composites at higher WF contents (20 wt%, 30 wt% and 40 wt%) and various injected CO$_2$ contents (0 wt%, 1 wt%, 2 wt% and 4 wt%) to identify the effects of WF content and CO$_2$ content on the cell morphology and foam properties. Two system configurations (tandem extrusion system vs. single extruder system) were experimented to demonstrate the system effect on the cell morphology and foam properties. A suitable coupling agent (CA) was selected to modify the interface between WF and HDPE and effectively improve the bonding between HDPE and WF. The results were compared with those without CA modified to study the effect of CA on the cell morphology and foam properties. Finally a set of supplementary experiments, suggested by the industrial companies for this research project at the third half-yearly sponsor meeting, were further performed to better understand the stronger effect resulting in the poor composite foams using the single extruder system.
All the research work including the system development and experimental results leads to the following grand conclusions:

- A tandem extrusion system with continuous and stable feeding, uniform and intensive mixing of plastic/WF mixture, on-line moisture removing and controllable mass flow rate was successfully developed for continuous extrusion foaming of fine-celled plastic/WF composites.

- With preliminary experiments at a low WF content of 10 wt% on both HIPS/WF and HDPE/WF, fine-celled composite foams have been successfully achieved without CA modified (for HDPE case) and talc added. At such a low WF content, the plastic/WF mixture was believed to still behave similarly to the pure plastic and WF content had little effect on the foamed results.

- With WF content increased on the targeted experiments, fine-celled foamability and easy processability of material flow were reduced. WF and HDPE tended to separate from each other because of their weak interaction without the aid of CA.

- With the aid of CA, WF and HDPE were effectively bonded without separating from each other. The cell morphology and extrudate profile were significantly improved. Fine-celled foam structures were attained for all the three WF contents at CO₂ 1 wt%. The maximum expansion ratios reached up to 5.9, 4.6 and 2.2 fold for WF 20 wt%, 30 wt% and 40 wt%, respectively. It was also observed that CA had a strong effect on the increase of the minimum foaming temperatures for the three WF contents, which should be attributed to the significantly increased flow viscosity when CA was applied.

- Using the single extruder system as a reference to the tandem extrusion system, fine-celled foam structures could not be achieved because of the poor mixing of HDPE/WF and the moisture existing. Without good mixing of HDPE/WF, CA could not play an active role in
effectively bonding HDPE/WF, and therefore, improvements in cell morphology and extrudate profile were hardly achieved when comparing the results with CA modified to those without CA modified.

- Fixed on the tandem extrusion system, with CO₂ content increased from 1 wt% to 2 wt%, there was a significant decrease of the minimum foaming temperature for all the three WF contents, whereas there was only a small difference by 1°C between CO₂ 2 wt% and 4 wt% and no difference between CO₂ 0 wt% and 1 wt%. Cell coalescence was observed in the cell morphologies due to the increased CO₂ contents. However, cell structures and extrudate profiles were still fine and very encouraging, which directed the future research to address the high WF contents by injecting more CO₂ within a suitable range to significantly move the minimum foaming temperature downwards. The maximum expansion ratios were achieved up to 8.3, 5.1 and 5.8 (experimental errors may occur in this value) fold for WF 20 wt%, 30 wt% and 40 wt%, respectively.

- With the supplementary experiments using pre-dried WF/HDPE mixture in the single extruder system, the poor mixing effect of WF/HDPE was clarified to dominate the bad foam results rather than the moisture effect. The contribution of moisture was found in the maximum expansion ratios, with the maximum expansion ratios increased by about 2, 2 and 1 fold for WF 20 wt%, 30 wt% and 40 wt%, respectively.

- The cell density was proven to be a very weak function of all the investigated material and processing parameters, such as the foaming temperature, WF content, CO₂ content, CA (modified vs. unmodified) and system configuration (tandem extrusion system vs. single extruder system). It was assumed to be a strong function of the nucleating agent content (talc in the research), which would require future experiments to verify this assumption.
The nozzle pressure $P_n$ was also believed to be a weak function of such parameters as WF content, $CO_2$ content, CA and system configuration considering the small pressure change range of 500 psi. Regarding the $CO_2$ content from 1 wt% to 2 wt%, the increased $CO_2$ amount tended to reduce the flow viscosity while the accordingly decreased minimum foaming temperature appeared to raise the flow viscosity, thus these two negative effects finally caused the maximum nozzle pressures changing in a limited scope. The foaming temperature was assumed to have a noticeable effect on the $P_n$ when the temperature was decreased close to the rapid change window of the composite flow properties, which demands the future research on the flow properties of WF/HDPE-$CO_2$ such as the actual crystallization temperature of such a flow. In addition, nozzle size and extruder PRM were supposed to have strong effects on the nozzle pressure, unfortunately these two effects have not been effectively investigated in this research.

5.2 Future Work

The following suggestions are made for the future direction of the research work in order to achieve fine-celled plastic/WF composite foams:

- The major goal of this research to achieve fine-celled HDPE/WF composite foams can be accomplished more effectively if the rheological properties of the HDPE/WF and HDPE-$CO_2$/WF material flow systems are well known. Once, the rheological properties of these material flow systems are obtained, proper die design can be established to attain optimum cell structures of the final composite foams, which is helpful for both PBA and CBA applications. Hence, an intensive study of the rheological properties of these material flow systems is strongly recommended. In detail, viscosities of HDPE/WF and HDPE-$CO_2$/WF
material flow systems should be measured as functions of WF content, CA content, CO₂ content (for HDPE-CO₂/WF), shear rate, temperature, pressure and system configuration (tandem extrusion system vs. single extruder system). A slit rheological die is recommended for the above-stated measurements. The slit rheological die, which can be easily mounted into the system setup and on-line measure the rheological properties of the material flow, was designed and developed by Ladin [114]. In addition, measurement of the melt flow index (MFI) of HDPE/WF is recommended, and the information acquired is believed to be useful for both PBA and CBA applications.

- For the system configuration, a third extruder should be considered to integrate into the tandem extrusion system. The main task of this third extruder is to highly improve the homogeneous cooling of the HDPE-CO₂/WF material flow while to maintain a significantly high pressure before the nucleation die, ready for rapid high pressure drop.

- A full parametric research of both processing and material parameters in a wider range is recommended for the future work. In detail, various temperature combinations in terms of \( T_n \) varies when \( T_m \) fixed and \( T_m \) varies when \( T_n \) fixed, various nozzle pressures achieved by different nozzle sizes and extruder RPMs, various injected CO₂ contents (0 wt%, 1 wt%, 2 wt% and 4 wt% used in this research), various coupling agents and contents (only one type and one content of CA used in this research), various PBA selections (N₂ and other long chain gaseous blowing agents in addition to CO₂ in this research), various WF contents (10 wt% for preliminary experiments and 20 wt%, 30 wt%, 40 wt% for targeted and supplementary experiments used in this research) and various material combinations of plastic/WF (most efforts focused on HDPE/WF in this research), etc.

- The experimental results for the production of fine-celled HDPE/WF composite foams achieved in this research can provide useful insights and information to extend the
filamentary extrusion process to profile extrusion (such as sheet extrusion), injection molding, compress molding and other possible processes for plastic/WF composite foam production. Using the standard die/mold and suitable technologies, the standard plastic/WF foamed parts are expected to be produced and applied for material properties testing such as ASTM testing.
REFERENCES


Table 4.1 Properties of Experimental Materials

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Table 4.2 Experimental Results of WF without CA Modified using the Tandem Extrusion System (CO₂ 1%)

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- WF: Foam Weight Fraction
- CA: Cell Agent
- Tandem Extrusion System
- CO₂ 1%
### Table 4.4 Experimental Results of WF without CA Modified using the Single Extruder System (CO₂ 1%)

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Table 4.6 Experimental Results of WF with CA Modified using the Tandem Extrusion System (CO$_2$ 2%)

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Table 4.7  Experimental Results of WF with CA Modified using the Tandem Extrusion System (CO₂ 4%)

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Table 4.8  Experimental Results of WF with CA Modified using the Tandem Extrusion System (CO₂ 0%)  

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Table 4.9 Experimental Results of Pre-dried WF with CA Modified using the Single Extruder System (CO₂ 1%)

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Figure 2.1 Classification of Fibers based on Fiber Length and Different Product Forms
Figure 2.2 Classification of fibers based on natural and synthetic fibers.
Fig. 2.3 Schematic of a Celuka Process (Controlled Foaming Extrusion)
Figure 2.4 Schematic of a Free Foaming Extrusion Process
Figure 2.5 Schematic of Batch Processing of Microcellular Foams
Fig. 2.6 Schematic of Continuous Processing of Microcellular Foams
Fig. 2.7 Schematic of Cell Collapse (Gas Escape) and Cell Coalescence in Extruded Foams at a High Temperature of Plastic Melt [37]
Figure 3.1  Schematic of the Designed Tandem Extrusion System
Figure 3.2 Photograph of the Constructed Tandem Extrusion System
Figure 3.3 Schematic of Heat Exchanger
Figure 3.4 Schematic of Cooling Sleeve Mounted Around Nucleation Nozzle Die
Figure 4.1 Schematic of the Single Extruder System
Figure 4.2 TGA Thermogram of Devolatilization of Wood Fibers [112]
Tn = Tm = 132°C, Pn = 3000 psi
Cell density = 3.6E06 cells/cm³, Expansion ratio = 19

**Figure 4.3** SEM Microstructures of HDPE/WF (10%) Composite Foams
Tandem Extrusion System, WF without CA Modified, CO₂ 5%, Mass Flow Rate 15 g/min
Tm = 138°C, Tn = 119°C, Pn = 3500 psi
Cell density = 2.1E08 cells/cm³, Expansion ratio = 19

Figure 4.4 SEM Microstructures of HIPS/WF (10%) Composite Foams
Tandem Extrusion System, CO₂ 5%, Mass Flow Rate 15 g/min
Figure 4.5 SEM Microstructures of HDPE/WF (20%) Foams
Tandem Extrusion System, WF without CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.6 SEM Microstructures of HDPE/WF (30%) Foams
Tandem Extrusion System, WF without CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.7 SEM Microstructures of HDPE/WF (40%) Foams
Tandem Extrusion System, WF without CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.8 SEM Microstructures of HDPE/WF (20%) Foams
Tandem Extrusion System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.9 SEM Microstructures of HDPE/WF (30%) Foams
Tandem Extrusion System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.10 SEM Microstructures of HDPE/IF (40%) Foams

Tandem Extrusion System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.11 SEM Microstructures of HDPE/WF (20%) Foams

Single Extruder System, WF without CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.12 SEM Microstructures of HDPE/WF (30%) Foams

Single Extruder System, WF without CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.13  SEM Microstructures of HDPE/WF (40%) Foams

Single Extruder System, WF without CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.14 SEM Microstructures of HDPE/WF (20%) Foams
Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.15 SEM Microstructures of HDPE/WF (30%) Foams

Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.16 SEM Microstructures of HDPE/WF (40%) Foams
Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.17  SEM Microstructures of Pure HDPE (WF 0%) Foams

\[ \text{CO}_2 \text{ 1\%, Mass Flow Rate 12 g/min} \]
Figure 4.18 Samples of HDPE/WF (20%) Foams

CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.19 Samples of HDPE/WF (30%) Foams

CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.20  Samples of HDPE/WF (40%) Foams

CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.21  Samples of Pure HDPE (WF 0%) Foams

CO$_2$ 1%, Mass Flow Rate 12 g/min
Figure 4.22 Effect of T on Expansion Ratio at Various WF Contents

\[\text{CO}_2\ 1\%,\ \text{Mass Flow Rate}\ 12\ g/\text{min}\]
Figure 4.23  Effect of T on Cell Density at Various WF Contents

CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.24 Effect of T on Pn at Various WF Contents

CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.25  SEM Microstructures of HDPE/WF (20%) Foams

Tandem Extrusion System, WF with CA Modified, CO₂ 2%, Mass Flow Rate 12 g/min
Figure 4.26  SEM Microstructures of HDPE/WF (30%) Foams
Tandem Extrusion System, WF with CA Modified, CO₂ 2%, Mass Flow Rate 12 g/min
Figure 4.27 SEM Microstructures of HDPE/WF (40%) Foams
Tandem Extrusion System, WF with CA Modified, CO₂ 2%, Mass Flow Rate 12 g/min
Figure 4.28 SEM Microstructures of HDPE/WF (20%) Foams
Tandem Extrusion System, WF with CA Modified, CO₂ 4%, Mass Flow Rate 12 g/min
Figure 4.29 SEM Microstructures of HDPE/WF (30%) Foams

Tandem Extrusion System, WF with CA Modified, CO₂ 4%, Mass Flow Rate 12 g/min
Figure 4.30  SEM Microstructures of HDPE/WF (40%) Foams
Tandem Extrusion System, WF with CA Modified, CO₂ 4%, Mass Flow Rate 12 g/min
Figure 4.31  Samples of HDPE/WF (20%) Foams at Various CO₂ Contents
Tandem Extrusion System, WF with CA Modified, Mass Flow Rate 12 g/min
Figure 4.32  Samples of HDPE/WF (30%) Foams at Various CO$_2$ Contents
Tandem Extrusion System, WF with CA Modified, Mass Flow Rate 12 g/min
Figure 4.33  Samples of HDPE/WF (40%) Foams at Various CO₂ Contents
Tandem Extrusion System, WF with CA Modified, Mass Flow Rate 12 g/min
Figure 4.34  Effect of T on Expansion Ratio for WF 20%, 30% and 40% at Various CO₂ Contents
Tandem Extrusion System, WF with CA Modified, Mass Flow Rate 12 g/min
Figure 4.35  Effect of T on Expansion Ratio for CO₂ 0%, 1%, 2% and 4% at Various WF Contents
Tandem Extrusion System, WF with CA Modified, Mass Flow Rate 12 g/min
Figure 4.36 Effect of T on Cell Density for WF 20%, 30% and 40% at Various CO₂ Contents
Tandem Extrusion System, WF with CA Modified, Mass Flow Rate 12 g/min
Figure 4.37 Effect of T on Cell Density for CO$_2$ 1%, 2% and 4% at Various WF Contents
Tandem Extrusion System, WF with CA Modified, Mass Flow Rate 12 g/min
Figure 4.38 Effect of T on Pn for WF 20%, 30% and 40% at Various CO₂ Contents
Tandem Extrusion System, WF with CA Modified, Mass Flow Rate 12 g/min
Tandem Exhaust System, WP with CA Modeled, Mass Flow Rate 12 g/min

Figure 4.39: Effect of CO2 for 1%, 2%, and 4% at Various WP Contents

(a) CO2 4%

(b) CO2 1%

(c) CO2 2%

(d) CO2 0%
Figure 4.40 SEM Microstructures of HDPE/Dried WF (20%) Foams

Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.41 SEM Microstructures of HDPE/Dried WF (30%) Foams
Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.42  SEM Microstructures of HDPE/Dried WF (40%) Foams
Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.43  Samples of HDPE/WF (20%) Foams (Dried vs. Undried)
Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.44  Samples of HDPE/WF (30%) Foams (Dried vs. Undried)

Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.45 Samples of HDPE/WF (40%) Foams (Dried vs. Undried)

Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.46 Effect of T on Expansion Ratio at Various WF Contents (Dried vs. Undried)

Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.47  Effect of T on Cell Density at Various WF Contents (Dried vs. Undried)
Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min
Figure 4.48  Effect of T on Pn at Various WF Contents (Dried vs. Undried)

Single Extruder System, WF with CA Modified, CO₂ 1%, Mass Flow Rate 12 g/min