Processing of Polyethylene and Polypropylene Foams in Rotational Molding

by

Fangyi Liu

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

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Processing of Fine Cell Polyethylene and Polypropylene Foams in Rotational Molding

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Abstract

The goal of this research is to develop a scientific and engineering basis needed for production of thermoplastic foams in rotomolding using a chemical blowing agent (CBA). Both polyethylene (PE) and polypropylene (PP) were used for the foaming process, but a special emphasis was given to PP, due to its many advantages. Two types of methods were utilized in the research, namely the dry blending method and the melt compounding method. Decomposition behaviors of different CBAs were analyzed with a Thermogravimetric Analyzer (TGA) and a Differential Scanning Calorimeter (DSC). The zero-shear viscosities of polymers that determine the sintering behavior of plastic powder particles were studied with a rotational rheometer. The mechanisms that govern the cell nucleation, sintering, and cell distribution for both the dry blending and the melt compounding methods were clarified. The critical processing parameters that govern the mixing, foaming and skin formation were outlined. Based on these investigations, conclusions were drawn on the selection of polymer material, application of CBA, and the determination of processing conditions.
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Nomenclature

\[\begin{align*}
\text{b} & = \text{channel width (m)} \\
\text{CBA} & = \text{chemical blowing agent} \\
D & = \text{diameter of the extruder screw (cm)} \\
\text{DSC} & = \text{Differential Scanning Calorimeter} \\
h & = \text{flight height (cm)} \\
h_{\text{skin}} & = \text{thickness of the skin layer in the formation of skin and foam core structure (cm)} \\
l & = \text{edge length of extruder screw (\(\mu\)m)} \\
L & = \text{length of the mold (cm)} \\
\text{MFR} & = \text{Melting Flow Index (g/10min)} \\
m & = \text{mass of foamed sample (g)} \\
m_{\text{CBA}} & = \text{amount of CBA material used (g)} \\
m_{\text{pellet}} & = \text{amount of compounded pellets used for rotomolding in compounding based method (g)} \\
m_{\text{polymer}} & = \text{weight of pure polymer material used in dry blending based method (g)} \\
m_{\text{skin}} & = \text{amount of powder materials used for the skin layer in the formation of skin and foam core structure (g)} \\
N & = \text{rotational speed} \\
N_0 & = \text{cell density (#/cm}^3\text{)} \\
n_b & = \text{number of bubbles}
\end{align*}\]
\[ P = \text{pressure (Pa)} \]
\[ p = \text{pitch (cm)} \]
\[ Q = \text{heat flow to the constantan pan of the DSC cell (w)} \]
\[ Q_D = \text{drag flow in a single screw extruder (m}^3/\text{s}) \]
\[ Q_{DL} = \text{leakage flow due to drag flow in a single screw extruder (m}^3/\text{s}) \]
\[ Q_L = \text{leakage flow in a single screw extruder (m}^3/\text{s}) \]
\[ Q_p = \text{pressure flow in a single screw extruder (m}^3/\text{s}) \]
\[ Q_{PL} = \text{leakage flow due to pressure in a single screw extruder (m}^3/\text{s}) \]
\[ R_1 = \text{first principle radius of curvature (cm)} \]
\[ R_2 = \text{second principle radius of curvature (cm)} \]
\[ R_D = \text{thermal resistance of the constantan pan of the DSC cell} \]
\[ t = \text{flight width of a single screw extruder (cm)} \]
\[ T_c = \text{crystallization temperature of polymer (°C)} \]
\[ T_{Room} = \text{room temperature (°C)} \]
\[ \text{TGA} = \text{Thermogravimetric Analyzer} \]
\[ V = \text{volume of the mold (cm}^3\text{)} \]
\[ V_c = \text{volume of gas generated by CBA decomposition (at polymer crystallization temperature, cm}^3\text{)} \]
\[ V_f = \text{expanded volume (cm}^3\text{)} \]
\[ V_{Room} = \text{volume of gas generated by CBA decomposition (at room temperature, cm}^3\text{)} \]
\[ \varepsilon = \text{extensional strain rate} \]
\[ \gamma = \text{shear strain rate} \]
\[ \varepsilon = \text{extensional strain} \]
\[ \lambda = \text{extensional viscosity} \]
\[ \eta = \text{shear viscosity} \]
\[ \tau = \text{shear stress} \]
\[ \delta = \text{extensional stress} \]
\[ \gamma = \text{shear strain} \]
\[ \phi = \text{helix angle} \]
\[ \Phi = \text{volume expansion ratio} \]
\[ \rho = \text{density of material (g/cm}^3\text{)} \]
\[ \varphi = \text{volume of gas generated per unit mass of blowing agent (cm}^3\text{/g)} \]
\[ \Delta P' = \text{pressure difference between the two cells} \]
\[ \rho_{\text{polymer}} = \text{density of polymer used (g/cm}^3\text{)} \]
\[ \varphi_{\text{STP}} = \text{volume of gas generated per unit mass of blowing agent at room temperature given by CBA manufacturers (cm}^3\text{/g)} \]
\[ \Delta T = \text{temperature difference between the two pans of the DSC cell} \]
Chapter 1

Introduction

1.1 Rotational Molding

Rotational molding is a method of producing stress-free parts with complicated shapes, especially those with hollow structures. The concept of the process can be described as follows: a metal mold, charged with a predetermined amount of cold plastic powders and additives, is put into a preheated oven and rotated bi-axially. Once in the oven, the metal mold is heated up very quickly and the plastic particles begin to melt and sinter while tumbling in the mold. After the designated time for rotation in the oven had elapsed, the mold is pulled out of the oven. At this point of time, the plastic powders have already formed a uniform melt structure. The mold is then cooled to room temperature, without stopping the rotation, until the part is fully solidified. Finally, the mold is opened and the formed part is removed. The rotational molding process is illustrated in Figure 1-1.

Although rotational molding has similarities with centrifugal casting, rotational molding is a distinct and unique process. The most important difference between the two is the magnitude of the rotational speed that is applied on the mold during the process. Rotational molding is characterized with much lower rotational speeds than the centrifugal casting. Normally, in rotational molding, the speed is in the range 5-20 RPM. Therefore, as opposed to centrifugal casting, the plastic particles remain at the bottom of the rotating cavity of the mold, due to the gravity. As a result of the higher range of rotational speeds applied, in centrifugal casting, a significant centrifugal force is developed. This is why, in centrifugal casting, the melted material is forced to flow in the radial direction in the mold.
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In contrast, with rotational molding the particles stay in loose powder form until the surface of the mold reaches the temperature level that is high enough for the particles to begin to adhere or sinter to the mold and/or to each other, at the layer nearest to the surface. As the temperature increases, a uniform plastic melt structure is formed. The sintering process in rotational molding is illustrated in Figure 1-2.

1.1.1 Historical Overview [1, 2]

The first work on producing hollow structures by heat and bi-axial rotation is recorded as early as in 1865, but the first equipment alike a rotational molding machine of today appeared in a British patent of 1935 [1]. However, at that time, suitable materials that could be used for the process were not available, except some cellulosics materials. This situation remained unchanged since 1961 when finely ground polyethylene by USI (Quantum Corporation of today) was used for the first time in rotational molding [2]. With the introduction of polyethylene, the industry experienced a great expansion. By the mid-1970s, rotational molding was already one of the primary plastics processing technologies in the industry. After the mid-1970s, the rate of growth of rotational molding market was much faster compared to the rest of the plastic industry. In recent years, the rotational molding market is growing with a rate of 10-12% per annum. Although the traditional toy industry is still the biggest part of the market, more applications are found in other areas such as tanks and containers, and automotive parts [3].

Nowadays, with the improvement of the technology of material manufacturing, polyethylene (PE), polypropylene (PP), polycarbonate, fluoropolymers, PVC, Nylon, and other materials find broad applications in the rotational molding industry. Among them, PE
is still the most popular material for rotational molding. PE accounts for about 85% of the application. PP covers only a small section of the market [3].

1.1.2 Characteristics and Application of Rotational Molding

As a unique plastic processing technology, rotational molding has many advantages over many other methods [1].

1. The process can be used to produce parts of a wide range of sizes and shapes. Currently, products made with this technology can be as small as a doll's eye or as big as a 79,500 liter tank [2].

2. The initial investments for molds and the necessary manufacturing equipment are relatively low. Since the rotational molding process is often under very low pressure, the molds are inexpensive and the difficulty of mold manufacturing is dramatically reduced. Expensive high-strength molds, which are essential for the injection molding process, are not necessary in rotational molding. As a result, reduction of overall production costs can be easily achieved.

3. Because of the low-pressure processing environment, it is easy to make stress-free parts, if necessary precautions were taken as appropriate.

4. The rotational molding process is especially suitable for making seamless hollow structures with a very uniform skin thickness. Very complicated profiles and structures, such as core-skin structure, can be easily generated from rotational molding, especially for large parts. In addition, parts of different sizes and structures can be processed simultaneously within one batch.
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However, rotational molding also has disadvantages that restrict its development and application. It is believed that the potential of the process has not been fully utilized yet because of these disadvantages.

1. The slow production rate, among all the disadvantages, is the most important one. Since the mold has to be heated to the processing temperature that will melt the plastic materials and then cooled down to room temperature again, the cycle time is long and is not suitable for small parts that have to be produced in large quantities.

2. The material used for rotational molding must be in fine powder form because the size of the powder plays an important role in determining the part quality. This increases the material costs dramatically.

3. The number of materials that can be used for rotational molding is limited. Currently, polyethylene is the most commonly used one.

4. Solid rib structures are difficult to produce using rotational molding. Therefore, extra attention should be paid to the design stage for structures that need stiffness.

1.1.3 Rotational Molding Machine

A rotational molding machine has a place where the mold is heated and cooled while being rotated. The rotational motion is usually in a bi-axial manner that can be provided by a straight-arm structure or cranked-arm structure of the mold arm (Figure 1-3). Electricity, hot oil, or gas can provide the heat. The electricity option is clean but less efficient. The hot-oil option is just the opposite, which is efficient but messy and extra maintenance is needed for the equipment. The gas option is the most popular method now [1].
1.2 Polyethylene and Polypropylene

1.2.1 Polyethylene

PE is a kind of thermoplastic that has a long chain (CH₂-CH₂) aliphatic hydrocarbon structure. It is wax-like and becomes softened at about 80 - 130 °C. Polyethylene is a tough material with a moderate tensile strength. There are many ways of characterizing PE, but the main categorizing feature is the density of the polyethylene [9]. The four categories of PE, specified in accordance with ASTM standard, are presented in Table 1-1.

The difference between LDPE and LLDPE originates from the differences in their production process. LDPE is produced under a high pressure and possess a very branched polymer structure [9]. The LLDPE is formed in a low-pressure process that yields a linear structure with short side branches by controlling the reactor conditions. HDPE is also developed by low-pressure processes. However, the branching structure in HDPE is achieved by adding varying amounts of comonomers such as butane and hexane during polymerization [10].

1.2.2 Polypropylene

PP has many advantages, compared with polyethylene. The two most important are: the higher melting temperature (usually about 150-175 °C [12]) and the higher tensile modulus, while the density is kept low. However, the characteristics of PP with different structures differ from each other dramatically.

1.2.3 Homopolymer and Copolymer

PP homopolymer is the result of polymerization of propylene molecules CH₂=CHCH₃, with catalysts under certain processing conditions. The first appearance of Polypropylene
that is valuable for an industry purpose was introduced in 1955 by Natta et al. from organo-metallic catalyst based on titanium and aluminum [5-7]. A PP homopolymer consists of only propylene segments: (CH$_2$-CHCH$_3$)$_n$. Three possible structures exist: head-to-tail, head-to-head, tail-to-tail (Figure 1-4) [6]. The steric effect of the methyl group highly favors the head-to-tail structure because of the high chemical regularity of the PP chains caused by the structure. When a co-monomer is added to the chain structure, a copolymer is obtained. Usually, ethylene is used as co-monomer. The introduction of ethylene modifies the chemical and physical properties of the copolymer, such as the thermal stability, stiffness, and strength. This is due to the introduction of the co-monomer that reduces the regularity of the chain structure and therefore reduces the material's ability to crystallize. With the decrease of the crystallization ability, the PP material becomes less stiff and the brittleness becomes reduced. The effect becomes more dramatic with increasing the content of ethylene. When the ethylene amount is higher than 10 percent of molecular weight, the material is called Ethylene-propylene Rubber (EPR) [6].

1.2.4 Linear and Branched Polypropylene

As discussed earlier for PE, branching structure can also be introduced into linear PP backbone chains [8,9]. When a long chain branch is attached to the main chain, the material will be referred to as High Melt Strength Polypropylene (HMSPP) [10]. By the branching structure, the HMSPP shows very high melt strength that is highly favored in processes such as foaming, blow molding, and extrusion coating.
1.3 Plastic Foams

1.3.1 Foams

Plastic foams, also known as expanded or sponge plastics, consist of at least two phases: a solid polymer matrix and a gaseous phase derived from a blowing agent [10]. Plastic foams can be found in a variety of densities ranging from 1.6 [kg/m³] to over 96 [kg/m³]. The type of foaming method and the combination of blowing agent and plastic material used for its production determine the density of the foam. The density of the foam mainly determines its application. With reference to the density of the foamed structure, foams are classified into three categories: flexible, rigid, and semi-rigid. Rigid foams are usually used for load-bearing purposes while low density or flexible foams are normally used for packing or thermal insulation.

In foaming processes, a physical or chemical blowing (foaming) agent can be used for nucleation of the gas bubbles. A Chemical Blowing Agent (CBA) refers to those materials that decompose under heat and generate either N₂ or CO₂, or both of them. A physical Blowing Agent can be a gas such as N₂ or CO₂, or a liquid like fluorocarbon or isopentane that has a very low boiling point. The blowing agent dispersed in the polymer can be brought out for foaming by reducing the pressure or heating up the mixture [11,16]. This is called a nucleation process. Sometimes, a nucleating agent such as talc will be added to the mixture to increase the number of bubble nuclei.

1.3.2 Principal Foam Production Technologies

Among all the foam production technologies that have been developed by now, the following are recognized as principal [12]:

- Reaction Injection Molding (RIM), usually by impingement mixing
• Extrusion foaming by using expandable beads, pellets or physical blowing agent [13, 14]
• Injection molding of expandable beads or pellets
• Spraying of foams
• Rotational foam molding
• Lamination of foams, or foam board production
• Compression molding of foams

1.4 Rotational Foam Molding [15]

In the rotational foam molding process, when the mixture of polymer powders and chemical blowing agent is charged into the mold and roto-molded, a rotational foam product is obtained. When observing a finished roto-foamed part, a solid (unfoamed) skin layer and a foamed core structure can usually be distinguished. This dual layer structure is achieved by a two-shot process, in which the skin material is charged and molded first. After the skin is obtained, the polymer and chemical blowing agent composition is added into the mold either through a vent or by using a special device called "Drop Box" (Figure 1-5). The dual layer structure can also be achieved in one-shot process by choosing a proper combination of materials. This is also one of the research objectives on which this thesis is based.

1.5 Purpose Statement

The objective of the thesis work is to develop a new rotomolding technology for manufacturing of fine-cell PE and PP foams with an unfoamed skin layer. To be able develop a process model to control the cell morphology of the PE and PP foams in
Chapter 1 Introduction

rotomolding, it is essential to identify the effects of the material properties and processing conditions on foam structures in rotomolding. Since the rotational foaming process is under a low pressure, the cell nucleation and growth processes are different from those in extrusion and injection foam molding. Therefore, a clear understanding of the foaming mechanism in the process is critical to promote the uniformity of the cell distribution and to reduce the cell size.

Above all, efforts should be made to control the nucleation process. It is desirable that a large number of micro-bubbles work as the nuclei. Their distribution and population density will determine the final foam cell size and structure. To achieve this goal, promotion of good mixing techniques, proper processing conditions, and proper selection of materials are the essential elements to be considered. Prevention of cell deterioration is another crucial factor that has to be considered in order to achieve fine cell structure. Cell coalescence and cell coarsening are major reasons that reduce the cell population density during the cell growth stage. It is also critical to prevent the gas loss during the roto foam molding process. Besides the economic factors, the gas loss may completely destroy the general foam structure.

To be able to control all these factors, it is important: (1) to promote a good mixing of PE or PP powders and the chemical blowing agent (CBA); (2) to induce a good wetting of the polymer melt onto the surface of the CBA particles; and (3) to select proper material and processing conditions to effectively control cell deterioration.

Finally, it is the ultimate objective of the project to develop a new technique for obtaining a skin-core dual layer structure, i.e., an unfoamed skin and a foamed core, within one-shot rotomolding by controlling the properties of the skin and core materials. A finished
part, like the example shown in Figure 1-6 (b), will have much better mechanical properties compared to parts molded in a traditional process.

1.6 Overall Strategy

The research was conducted in two directions: material control and processing condition optimization. Guidelines for choosing proper combinations of CBA and polymer materials were established. In addition, the mechanism of the process was investigated and the effect of processing condition variation was studied. A schematic illustration is presented in Figure 1-7.

1.7 Outline of the Thesis

Since the objective of the thesis is to develop new techniques of producing foam in rotational molding by experimentation, the foaming mechanism was investigated by analyzing the obtained results obtained from a series of experiments. In other words, the thesis is based on the experimental results and the related analysis.

The research was focused on the analysis and design of two distinct technologies that were applied on two different types of polymers. More specifically, both dry blending and melt compounding based technologies were applied for experimental production of PE and PP foams, respectively. Comparative analysis of the experimental results and conclusions are presented in the thesis.

Chapter 2 provides the theoretical background of related subjects including the polymer rheological properties, the CBA decomposition behaviors, a sintering theory in rotational molding, and the concepts of mixing technology.
Chapter 1 Introduction

In Chapter 3, the experimental results obtained from the analysis of polymer materials and CBAs are presented. The proper selection of blowing agents and matrix polymer materials is based on these analyses.

Chapter 4 describes the experimental results obtained while using the dry blending technology. The identified effects of material properties, processing parameters, selection of chemical blowing agents, and additives on PE and PP rotational foam molding presented in this chapter were experimentally verified. Also, the foaming mechanism for this particular process is studied in detail.

Chapter 5 shows the work on the experiments conducted on the melt compounding based technology. In the chapter, the compounding process as well as the roto foaming is described and analyzed. Since the use of a melt compounding based technique changes the nucleation mechanism, the foaming process is different from that in the dry blending based technology. The foaming mechanisms in the melt compounding based technique are thoroughly studied and discussed in this chapter.

Chapter 6 concentrates on the research on the skin formation. Based on the melt compounding process, preliminary investigation has been conducted to outline the critical conditions and parameters for controlling the skin formation.

In Chapter 7, a summary and conclusions of the research are made. Some future work recommendations are also suggested based on this research.
Chapter 2

Theoretical Background

2.1 Polymer Properties

2.1.1 Viscosity and Elasticity

When a liquid-like polymer melt is subjected to a stress, it will deform continuously as time goes on. When the stress is released, the liquid stays in its deformed state [22,23]. Unlike that of solid materials, the stress and strain relationship of liquids is time-dependent. In the case of extension, the strain rate can be expressed as:

\[ \frac{d\epsilon}{dt} = \dot{\epsilon} \]  \hspace{1cm} (2-1)

and the extensional viscosity is

\[ \lambda = \delta / \dot{\epsilon} \]  \hspace{1cm} (2-2)

When a shear force is applied to liquids, the property of the material is indicated by a shear viscosity:

\[ \eta = \tau / \gamma \]  \hspace{1cm} (2-3)

where \( \gamma \) is the shear strain rate.

For a Newtonian fluid, the viscosity is constant at a specific temperature. However, for a non-Newtonian polymer melt, the shear rate is no longer proportional to the shear stress. The viscosity becomes a function of shear rate and temperature. For example, for PP and PE, the viscosity declines when the shear rate is increased. Therefore, the zero-shear
viscosity, defined as the viscosity at the zero shear rate, may be used to indicate the property of the material.

A clear understanding of the polymer viscosity properties is critical in polymer processing. In rotational molding, the zero-shear viscosity of the material plays an important role in particle sintering and bubble removal, corner filling, and some final mechanical properties [1].

2.1.2 Melt Flow Index

Besides the shear or extension viscosity, the Melt Flow Index (MFI) or the Melt Flow Rate (MFR) is another parameter that indicates the viscosity of polymer melt at a certain temperature [1]. They are defined as the amount of polymer (in gram) extruded from plastometer for 10 minutes. A standard measurement can be done with the equipment shown in Figure 2-1, according to the ASTM standard. The material to be tested is put in a heated barrel (190 °C for MFI and 230 °C for MFR) and a dead weight is applied on the polymer melt through a piston. The extrudate is collected and weighed.

Usually, the higher the average molecular weight, the lower the MFI or MFR. Therefore, MFI or MFR can be used effectively in choosing materials with a designated viscosity.

2.1.3 Melt Strength

The melt strength is an indicator of how much extensional force a plastic melt can stand [23]. In plastic foaming, this parameter reflects the strength of the foam cell walls, which indicates the ability to resist wall collapse [24]. The higher the melt strength, the
Chapter 2 Theoretical Background

easier to maintain the cell population density and a small cell size as will be analyzed in detail in Chapters 4 and 5.

2.2 Chemical Blowing Agent

A chemical blowing agent (CBA) produces gases through a chemical reaction, which may be a thermal decomposition or a reaction between two or more components [12].

2.2.1 Classification of CBAs

As the most inexpensive and most traditional blowing agent, the CBAs can be classified as inorganic and organic according to the structure of the CBA molecules.

Inorganic CBAs

Two major types of inorganic CBAs fall into this category: ammonium carbonate and carbonates of alkali metals [13]. Generally, ammonium carbonate is a mixture of (NH₄)₂CO₃·H₂O, NH₄HCO₃, and ammonium carbonate, NH₄COONa. With the presence of water or an increase in the temperature up to 30-40 °C, ammonium carbonate begins to decompose at about 60 °C and liberates NH₃ and CO₂.

Among carbonates of alkali metals, sodium carbonates and bicarbonates are the most popular ones [17]. After being heated up to the range of 145-150 °C, sodium bicarbonates (NaHCO₃) will be completely decomposed within 30 minutes. The decomposition follows the following scheme:

\[ 2 \text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]

\[ \text{Na}_2\text{CO}_3 = \text{NaO} + \text{CO}_2 \] (2-4)
Chapter 2 Theoretical Background

The foaming activity of the sodium bicarbonates is relatively slow, which can be an advantage when the smoothness of the decomposition is a concern. With sodium bicarbonates, the pressure of generated gas increases slowly and the process is more stable [13].

The disadvantage of inorganic blowing agents lies in their tendency to disperse in polymer matrix poorly and usually to decompose at temperatures far below the melting temperature of some polymers with a high melting temperature. This restricts the application of this type of CBA to a very narrow range.

Organic Blowing Agents

Compared with inorganic blowing agents, organic blowing agents have many advantages. They usually start to decompose or reach their maximum gas yield at the temperature that is close to the melting temperature of the polymer [13]. In addition, the CBAs can be well mixed with the polymer matrix. However, the disadvantage of this type of blowing agent is its relatively high cost and the non-gaseous products of the decomposition.

There are many classes of organic blowing agents, including azo and diazo compounds, N-Nitroso compounds, sulfonylhydrazides, azides, triazines, triazoles and tetrazoles, sulfonyl semicarbazides, urea derivatives, and esters [17]. Among all types of organic blowing agents, azodicarboxamide is one of the most effective high-temperature blowing agents. When decomposing at 190-240 °C, azodicarboxamide generates CO₂ and N₂, the gas sources of the foam. The blowing agent can be well dispersed in many solvents and can be easily mixed with different polymers. One of the disadvantages of azodicarboxamide is the acid decomposition residue that may cause damage to the processing equipment such as mold or extruders.
2.2.2 Endothermic and Exothermic Behaviors

During the decomposition process of CBAs, the chemical reaction can be either absorbing heat (endothermic) or releasing heat (exothermic) (Figure 2-2). For foaming processes in rotational molding, which is normally under low pressure, the endothermic or exothermic reaction involved in the decomposition process is vital to the foam quality according to the research result. Therefore, a clear understanding of the endothermic or exothermic effect of the particular blowing agent used is also very important.

2.2.3 Decomposition Rate

The decomposition rate is the speed at which the CBAs generate gases. It can be indicated by the speed of weight loss, the temperature range of the weight loss, or the speed of the pressure increment (Figure 2-3). According to our research, the decomposition rate is another critical factor in low-pressure foaming processes and it will be discussed in detail in the following chapters. However, it should be mentioned that too high or too low a decomposition rate is harmful to the final foam structures.

2.2.4 Selection of CBAs

In Handbook of Polymeric Foams and Foam Technology [13], Daniel Klempner and Kurt C. Frisch mentioned nine principal requirements, while making clear that no industrially available CBAs can meet with all the requirements. As summarized in the book, the main criteria by which to judge CBAs are:

- Gas number or gas yield, which is the volume of gas (in cc) yielded by one gram of blowing agent per unit of time at the temperature of maximum gas liberation,

- The onset point of the decomposition of the CBA,
The temperature of the maximum rate of decomposition and the pressure developed by generated gases,

The rate and kinetics of the decomposition.

2.3 Mixing Technology

In polymer processing, in addition to the designated form, homogeneity in composition and properties is also necessary, especially when additives are involved [18, 19, 20]. Chris Rauwendaal defined mixing as "a process to reduce the nonuniformity of a composition by inducing physical motion of the ingredients, resulting in a reduction of the concentration gradients or temperature gradients" [19].

According to the nature and form of the materials in the mixing process, mixing can be placed into two categories: melt compounding and dry blending. In some processes, either during the shaping processes or prior to the processes, materials, especially the polymer material, are in shear conditions in a melt or softening state. This type of process is usually called melt compounding or intensive mixing [18,19]. In other conditions, when the mixing is adequate without melting or softening the material, it is usually called simple mixing, or dry blending in which "components or ingredients are physically intermingled without significant change of the physical state of the components" [18]. In dry blending, the material must be in suitable forms such as powders.

2.3.1 Dry Blending Equipment

There are many types of dry mixing devices that can be used depending on the difficulty of the mixing and the requirement for the mixing quality. Among them, vibratory or reciprocating blenders, tumbling blenders, stir mixers, intensive non-fluxing mixers, ribbon blenders and related mixers, Z-blade and related double-arm mixers, lough mixers,
roll mills etc. are very commonly used in the industry. In the project of roto-foaming, tumble blenders are used for the dry blending based method.

In tumble blenders, the mixing is achieved through the movement of the composition particles by pouring, rolling, or falling. The main mixing action comes from the gravity force. It can be simply achieved by partially filling a tumbling drum with the materials and rotating it. There are several ways to improve cross mixing qualities including different ways of mounting the drum and different choices in the shape and structure of the drum. (Figures 2-4 and 2-5) [18]. In Figure 2-4 (a), the cylinder drum is mounted in such a way that the rotation is eccentric. By such a means, a reciprocating tilting motion across the direction of rotation introduces an element of cross mixing. In the machines illustrated in Figure 2-4 (a), the mixing in the longitude direction is achieved by using a V-shape chamber. The cross mixing can also be improved by changing the shape of the mixing chamber, as illustrated in Figure 2-5. Sometimes, deflector plates are mounted in the double-cone blenders to further improve the mixing quality (Figure 2-6) [18].

2.3.2 Melt Compounding Equipment

Melt compounding can be done in either a batch processing manner or a continuous manner. A continuous compounding process is more economical for large-scale processes in the plastic industry and is also more desirable when a high degree of product uniformity is critical.

Two-Roll Mill

The two-roll mill is a typical piece of batch compounding equipment that was originally used by the rubber industry. The structure of the mill is illustrated in Figure 2-7
In the machine, two rolls made of cast iron or alloy steel are mounted on a massive end frame. When the mixture of the blended materials passes the adjustable gap between the two rolls, the mixing is achieved. Usually, the rolls are equipped with heating and cooling units to control the temperature. For example, blowing agents and polymers can be mixed in this way. The polymer will be melted by the heat from the heater as well as by the friction generated between the rollers and the materials.

Apart from the low capacity of this type of mixing, the method has the disadvantage of raising safety concerns. An unguarded structure is very dangerous because it may catch a operator's hair, clothes, or even fingers. For small machines, it is easy to cover the working section, but special efforts should be made to avoid the problem when a large machine is used.

**Single Screw Extruder**

A single screw extruder is the type commonly used in the industry [21]. The structure of a typical extruder is shown in Figure 2-8 [22]. Solid materials are added through a hopper and fed into the barrel by gravity. After entering into the barrel, the material will pass through three sections: the feeding, compressing and metering sections. In the feeding section, the material is kept in a solid form and transported; in the compressing section, the plastic begins to melt when the channel of the screw becomes shallow and the material is compressed and sheared; in the metering section, the channel becomes shallower to keep the output stable. The detailed picture of the structure of a typical extrusion screw is shown in Figure 2-9 [13].
The mass flow in the extruder channel can be grouped into four categories. The flow generated directly by the shear or the relative movement of the screw surface and barrel surface is the *Drag Flow*, which can be expressed by the following model [13,30]:

\[
Q_D = \frac{\pi^2}{2} D^2 N h \sin \phi \cos \phi
\]  

(2.5)

Where \( D \) is the diameter of the screw, \( N \) is the rotational speed in revolution per second, and \( h \) is the channel depth.

The pressure flow is a flow caused by the backpressure at the end of the screw, whose effect is to push the material backward to the feeding zone. The mass flow caused by the pressure can be expressed by the following equation [13]:

\[
Q_p = b h^3 \frac{dP}{12\eta \, dz}
\]  

(2.6)

In Figure 2-9, the flow that is perpendicular to the flow channel of the screw causes another flow, the *transverse flow*.

The pressure difference and transverse flow generated by shear force cause another flow which goes backward, the *leakage flow*. The amount of leakage flow due to drag is:

\[
Q_{DL} = \frac{U}{2} \frac{\pi D}{\cos \phi} = \frac{\pi^2 D^2 N \delta \tan \phi}{2} \text{ Per turn}
\]  

(2.6)

And usually expressed as a fraction of the drag flow [13]:

\[
\frac{Q_{DL}}{Q_D} = \frac{\frac{1}{2} \pi^2 D^2 N \delta \tan \phi}{\frac{1}{2} \pi D h (p-t) N \cos^2 \phi} = \frac{\pi D \delta}{(p-t) h \cos^3 \phi} = \frac{\delta}{h \cos^2 \phi}
\]  

(2.7)
In addition, a certain amount of leakage is also caused by pressure difference, including a longitude pressure gradient and a transverse pressure gradient. The leakage flow can be expressed by the following equation:

\[
Q_{PL} = \frac{\pi^2 D^2 \delta^3 dP}{12\pi \cos \phi} dZ
\]  

(2-8)

The total output flow can be expressed approximately as

\[
Q_{Total} = Q_D - Q_p - Q_l.
\]  

(2-9)

However, since \(Q_l\) is too small for normal extrusion screw designs, it can be neglected in most cases. Therefore, the output will be

\[
Q_{Total} = Q_D - Q_p
\]  

(2-10)

In single screw extruders, the mixing process starts from the material-conveying zone, but as has been shown above, because the flight clearance is so tight that there is very little leakage flow, the material is very unlikely to go backward. Consequently, the mixing quality is very poor. To improve the mixing quality, in addition to the common sections, a mixing section can be added in the front of the screw. For example, a mixing screw with a blockhead mixing section as shown in Figure 2-10 [20] is used in the present experiments. The shape of the mixing head can be changed according to requirements.

In a mixing extruder, the heat that melts the plastic comes from the band heaters and viscous heating. To balance the temperature, some heat is carried away by the moving material, by conduction, by radiation, and sometimes by the cooling of the screw. A proper choice and combination of heating and cooling conditions is critical to stabilize the temperature, especially when heat sensitive materials such as CBAs are processed. This will be discussed in detail in Chapter 5.
Twin Screw Extruder

Typically, a twin screw extruder is for compounding. Through the co-rotating or counter-rotating motion of the screw, the shear straining is increased intensively. For this reason, the mixing quality is superior to that of single screw extruders. However, the high shear force makes it difficult to maintain the plastic melt at the designated temperature even though the temperature gradient is reduced dramatically with the polymer melt. This may present a problem for the compounding of temperature sensitive materials like CBA.
Chapter 3

Analysis of Materials

3.1 Material Requirements of PE and PP in Rotational Foam Molding

As stated in Chapter 2, material properties are essential in polymer processing. It will determine the processing parameters, product qualities, and applications. For rotational molding, the material properties become even more crucial as will be shown in Chapters 4 and 5. In this context, this chapter describes in detail the properties of the materials used in the rotational foam molding experiments.

3.1.1 Viscosity and Elasticity

The viscosity of plastic materials determines the ability of polymer particles to merge with each other in rotomolding and the molten polymer's ability to flow in the mold under certain temperatures. A low viscosity material is easier to sinter at a relatively low temperature, allowing the processing temperature to be lowered and the processing time to be reduced. It is also easier for a low viscosity material to flow into the corners or tips of some parts with complicated forms and structures.

In the rotational foam molding process, the sintering ability of plastic powders becomes critically important, especially when a dry blending based technology is used. The gas loss, nucleation, and the final cell property of the foam will be governed by the sintering quality. This aspect will be discussed in detail in Chapter 4.

Another essential material parameter in rotomolding foam processing is the melt elasticity that represents the melt strength. When a material with a high melt strength is used, the wall of the gas bubble is relatively difficult to break during the process of cell
expansion. This will reduce the cell coalescence and increase the cell population density of
the foams. Therefore, high melt strength material should be used and attention should be
paid to control of processing conditions in order to maintaining a high melt strength of
material.

3.1.2 Plastic Powders

Since PE and PP materials are of a poor thermal conductivity, the speed at which heat
is transferred into the center of each particle depends on the size and volume of the particles
[1]. For example, a large particle of polymer material melts more slowly than a small one;
therefore, small particle sizes are preferable when a quick sintering is needed. For a normal
rotational molding process, the sintering speed will affect the surface finishing, bubble
removing and final mechanical properties. In roto-foaming processes, in addition to the
problems related to sintering, the powder quality is also critical for achieving a high mixing
degree which will also determine the final foam cell size and distribution. Among the
powder properties, the particle size and particle shape are the most critical ones in rotational
foam molding.

Particle Size

Since fine powders will melt more quickly than coarse powders, it is desirable to have
powders in a finer grade. Besides the melting rate, the trapped air pockets among particles
pose the most serious problem. When charged into a mold, the materials are a mixture of
plastic powders, additives, and air. The air will form air bubbles in the polymer melt later. It
seems reasonable to expect that the bigger the particles, the bigger the air bubbles will be
and the more difficult it will be to remove them. The existing bubbles will affect the
mechanical property and surface quality of the molded part in normal rotational molding processes. On the other hand, with the same amount of powders used, it is not difficult to understand that the bigger the powder sizes, the fewer the air bubbles. Because the air bubbles will act as cell nuclei in the roto foaming process, their distribution and population density determine the foam cell distribution characteristics. A few large bubbles will lead to huge cells in the final foamed products. This aspect will be discussed in detail in Chapter 5.

**Particle Shape**

The shapes of the plastic particles after being ground are usually irregular. Typical shapes of plastic powders are shown in Figure 3-1. There are different opinions on how the particle shape affects the sintering in rotational molding. In his *Rotational Molding of Plastics*, R. J. Crawford claimed that too regular shapes such as uniform spherical particles would be too easy to roll around before the melting and sintering started. As a result, all the problems related to poor sintering either in normal roto-molding or rotational foam molding would occur. In addition, easy rolling will also cause an uneven distribution of materials in the mold [1]. However, we believe that the tails or hairs of powder particles with irregular shapes increase the inter-particle distance and the free volume of powders. Consequently, the sintering process will become slower.

However, when improper grinding conditions are applied, the plastic particles are torn and shredded since plastics like PE and PP are tough materials. When this problem occurs, the powder particles will have fibrillation structures as shown in Figure 3-1 in which a tail is attached to the powder particle. Poor sintering will result in because the fibrillation structure obstructs the contact of neighboring particles. Long fibrillation structures will also cause a bridging effect. It is not easy for hairy particles to flow freely around in the mold. If there is
a narrow tip or corner on the mold, the intertwined hairs may block the passage and no powder particles can flow into it. Finally, there will be a void part existing in the molded part or even a defect on the surface. When foaming takes place in the mold, the air pressure can push the material into these types of corners.

3.2 Materials Used

PE and PP materials are used in this study. For experiments on PE, a rotational molding grade LLDPE is chosen as the base material. For research on PP, various PP materials with different grades of viscosity, different molecular structures, and different melt strengths were tested. Detailed information of the materials used is listed in Tables 3-1 and 3-2.

3.3 Viscosity Analysis of PE and PP

In current experiments, the melt flow index (MFI) or melting flow rate (MFR), and the zero-shear viscosity are used to indicate the viscosity properties of PE and PP. MFI or MFR can serve only as an indicator of the viscosity of the material at the standard testing temperature, which is 190 °C for PE (MFI) and 230 °C for PP (MFR). The viscosity decreases as the processing temperature increases. The viscosity of PE and PP materials also depends on the shear rate and the materials used in the experiments are shear-thinning materials of which the viscosity decreases when the shear rate is increased. Since rotational molding is a low shear process, the zero-shear viscosity would be the most important rheological property, and therefore, it was used to evaluate the material viscosity.
3.3.1 Experimental Setup

A cone-plate type dynamic stress rheometer from Rheometrics Scientific (S-200) is used in the experiment. The picture of the rheometer is shown in Figure 3-2.

Before the test, standard samples are made using the sample maker of the rheometer. In order to remove the air pockets that become trapped among the plastic powder particles, the plastic materials are melted in a 3/4" inch Brabender single screw extruder (Brabender 05-25-000). The polymer melt from the extruder is charged into the standard sample maker and pressed into the designated shape. Then, the sample is loaded in the gap between the cone and plate of the testing head. When the sample is molten and reaches the testing temperature, the gap is forced to be a standard testing gap (0.051 mm in the experiments) and the experiment is started. To prevent the plastic material from being degraded and oxidized, nitrogen is used as a protecting gas. To test high viscosity materials, the initial temperature of the heater should be a little higher than the testing temperature in order to facilitate the melting process and improve the melt quality. On obtaining the polymer melt, the temperature can be lowered to the testing temperature before conducting the experiment.

In this study, at a certain temperature, a shear rate sweep starting from $10^3$ to 1 was applied on the samples and the zero-shear viscosity was determined. In Figure 3-3 (a) the measured zero-shear viscosity of different material at 190 °C was plotted as a function of MFR that are provided by suppliers. An example of the effect of processing temperature on the viscosity was shown in Figure 3-3 (b), for SC873 (MFR 50).
3.4 DSC Analysis of PE and PP

To obtain the processing temperature window of plastic, it is very important to know the melting point and related thermal reaction during the heating process. A Differential Scanning Calorimeter (DSC) is one of the most widely used equipment for this purpose in the thermal analysis.

3.4.1 Experimental Setup

DSC works by measuring the heat flow changes into or out of materials as a function of temperature. There are two most commonly used methods in DSC analysis: the power compensation method and the heat flux method. For the TA 2910 DSC cell (Figure 3-4) that is used in this study, the heat flow flux method is applied. The principle by which the method works is illustrated in Figure 3-5. In the enclosed cell, a reference pan and a pan with sample encapsulated is put on a constantan thermoelectric disc. Preheated purging gas is injected into the cell so that a stable and uniform heat environment is created. Once the pans are heated up, the difference between the temperature of the reference pan and the temperature of the sample pan is analyzed. From the temperature difference, the heat flow into or out of the material is calculated according to the following equation:

\[
\frac{dQ}{dt} = \frac{\Delta T}{R_p}
\]  

(3-1)

where \(dQ/dt\) is the heat flow, \(\Delta T\) is the temperature difference between the two pans, and \(R_p\) is the thermal resistance of the constantan disc.

During DSC experiments, plastic materials averaging 3-5 mg are encapsulated in the aluminum pan, and a moderated heating rate such as 10 °C per minute is used to achieve results with proper accuracy and resolution. Before the tests, special attention was given to
the temperature calibration. A standard indium specimen with a known melting point was run on the DSC under different conditions and calibration curves were obtained. Through the temperature calibration, the temperature errors caused by a thermal lag were minimized.

3.4.2 Results and Discussion

A series of DSC experiments have been conducted on both PE and PP materials. Results are shown in Figures 3-6 and 3-7, respectively. The results were analyzed with the data processing software, Universal Analysis, which is provided by the TA Instrument. The onset temperatures were studied to identify the starting point of the melting process. From test results, it was found that LLDPE 8556 and LLDPE 8361 started to melt at about 119°C. For most of PP materials, the melting began at 152-155°C and reached its peak at about 165°C. The only exception is PF633, the one with the highest melt strength and melt viscosity. It started to melt at 149°C and was fully melted at 160°C. This would be helpful to reduce the processing temperature in rotomolding.

3.5 Thermal Analysis of CBAs

In order to maintain the highest melt strength, the system temperature should be maintained at the minimum level that the process allows. To achieve this goal, the decomposition of CBAs should occur as early as possible after a uniform polymer melt has been obtained. Therefore, a proper processing temperature can only be set after a clear understanding of the thermal characteristics of the CBAs.
3.5.1 Experimental Setup

Two types of experiments were conducted to determine the thermal activities of candidate CBAs. DSC was used to study the endothermic and exothermic behaviors of the materials, the heat generated by the decomposition, and the decomposition temperature range.

In addition to DSC, a Thermalgravimetric Analyzer (TGA) (TA2050, Figure 3-8) was used to test the decomposition behavior. The TGA monitors the decomposition behavior by measuring the weight of the sample that has not been decomposed. From the TGA results, the decomposition efficiency can be clearly identified, as can the decomposition temperature and the decomposition rate.

In the experiments, about 10 mg of sample materials was put on a platinum sample pan and loaded onto a very accurate balance. Then, the sample was enclosed in an oven. The sample was heated up to the designated temperature with a certain heating rate. A stream of Helium gas (40 cc/min) was injected into the oven so that the generated gas from decomposition could be purged. Another stream of Helium gas (60 cc/min) runs through the balance chamber to prevent the influence of gas and heat coming up from the oven. Nitrogen or argon can also be used as purging and protection gas. But the relatively low thermal conductivity of nitrogen or argon may increase the measurement error caused by thermal lag. Therefore, the Helium that has a high conductivity is chosen especially for high heating rate experiments. An additional water-cooling system surrounding the balance chamber was used to maintain the balance chamber temperature. The weight of the sample was recorded as a function of temperature or time. A number of CBAs were tested (see Table 3-3).
3.5.2 Results and Discussion

The results of DSC analysis are shown in Figures 3-9 and 3-10. Figure 3-9 shows the comparison of different CBAs, including their decomposition onset temperature, peak temperature, and endothermic or exothermic properties. Together with DSC information on polymer materials, this provides the basis for the initial selection of CBAs. In Figures 3-10, the kinetic properties of selected CBAs as a function of the heating rate are illustrated. The information developed from the results can be used as guidelines in the control of processing conditions.

The results obtained from the TGA analysis of CBAs are shown in Figures 3-11 to 3-15. From these results, the weight loss properties and decomposition temperatures of different CBAs were compared, the effect of the heating rate on the weight loss behavior was investigated, and the effect of catalysts on the decomposition temperature of selected CBAs was studied. Since the CBAs are normally of a low thermal conductivity, the particle size of the CBA and the size of the testing sample may all have an effect on the decomposition behavior. Experiments were also conducted to illustrate the effect of these two factors.

Comparison of Different CBAs

Celogen AZ3990 is a type of an azodicarboxamide blowing agent provided by Uniroyal Chemical. As shown in Figures 3-9 (a) and 3-11 (a), the decomposition temperature of Celogen AZ3990 is 210.4 °C, which is about 50 °C higher than the melting temperature of all the PP materials. Therefore, Celogen AZ3990 may be used for foaming of PP. Detailed experiments were conducted to understand the decomposition behavior of the blowing agent under different processing conditions.
ADC series is another type of azodicarboxamide CBA provided by Bayer. According to the information from the DSC results in Figures 3-9 (b)-(c), and 3-11(b)-(c), ADC series have properties very similar to those of Celogen AZ3990 with an onset temperature of 204 °C. They, therefore, can be another choice for PP foams. In addition, there are two grades of particle size available for this type of blowing agent and this series of CBAs could be used to illustrate the effect of CBA particle size on the decomposition behaviors of CBAs. Two ADC samples were tested: ADC/M-C1 and ADC/F-C2.

It should be noted that the DSC diagrams in Figure 3-9 (a), (b), and (c) are sharp and right skewed, especially (b) and (c). This phenomena is caused by the exothermic nature of the azodicarboxamide blowing agent. The heat generated in decomposition increased the local temperature around the sample pan to a level that was higher than the oven temperature. The decomposition was enhanced by the high local temperature and finished almost instantaneously. This was also indicated by the sharp weight loss in TGA diagram in Figure 3-11 (a). However, the temperature of the sample pan dropped back to the oven temperature after the decomposition. This explains why the temperature fell down after the peak in the DSC diagrams. This self-heating phenomenon and its impact on roto foaming will be discussed in detail in Chapters 4, 5 and 6. Similar decomposition behavior can also be identified when another azodicarboxamide blowing agent Celogen OT was tested.

Celogen OT (benzenenesulfonyl hydrazide) is another exothermic blowing agent that generates N₂ and H₂O. In Figure 3-9 (d), it can be seen that Celogen OT decomposed very quickly with an onset temperature of 159 °C. The blowing agent is suitable for PE foams but cannot be used for PP foams because of its low decomposition temperature.

Sodium bicarbonate is an endothermic blowing agent that starts to decompose at a relatively low temperature. As the TGA results of Figure 3-11(g) indicates that the onset
decomposition temperature is about 124 °C, and that the peak gas yield occurs at 172 °C. Obviously, the decomposition is too early for PP materials and most of the gas will be lost before the melting of polymer starts. However, it is just above the melting temperature of PE and therefore can be used for PE foam processing. It is also identified that the blowing agent decomposes at a wide temperature range of 48°C, which indicates that the decomposition rate of sodium bicarbonates is very slow.

**Effect of Decomposition Promoters**

Since it is desirable that the decomposition temperature be kept as low as possible, the CBA should decompose as soon as the sintering is completed in order to keep a high polymer melt strength. It is well known that catalysts can be used to lower the decomposition temperature of azodicarboxamide materials. In the experiments, ZnO was selected to modify the decomposition behavior of Celogen AZ3990. From Figure 3-13, it can be seen that with the increase of the amount of ZnO, the decomposition temperature decreases. The percentage of ZnO to CBA is calculated in weight ratio and expressed as the amount of ZnO in 100 parts of Celogen AZ3990 (100 phr). When 100 phr of ZnO was added, the decomposition temperature was lowered to 189 °C, which is about 20 °C lower than that of the unmodified AZ3990.

**Effect of Heating Rate**

The heating rate of CBA varies greatly under different processing conditions. For example, the one in rotomolding is very different from that in the melt compounding process. To control the decomposition temperature precisely, the effect of heating rate on decomposition must be studied. From the TGA results shown in Figure 3-12, it can be seen
that with an increase of heating rate, the decomposition was delayed. This is caused by the thermal lag resulting from the low thermal conductivity of CBA particles. The higher the heating rate, the more dramatic the temperature difference between the surface and the center of the CBA particles. When the center part of the blowing agent particle reaches the decomposition temperature, the surface temperature of the particle, which is the measured temperature, appears to be higher when the heating rate is higher. However, from the DSC results shown in Figure 3-10 (a), the exothermic effect became more dramatic when the heating rate increased. This brought a very high local temperature increase. From the figures it was found that the actual temperature of the area surrounding the decomposed CBA particles is normally 10 °C to 20 °C higher when the decomposition reached its peak point. Because of this local temperature increase, the decomposition will reach its peak point more quickly. In Figure 3-12, this is indicated by an increased rate of weight loss. This phenomenon becomes more obvious for Celogen OT when a very high heating rate of 200 °C per minute has been used (Figure 3-10(b)).

Effect of CBA Amount

In Figure 3-15, it is proved that when a different amount of CBA materials is used, the decomposition behaviors are of little difference. However, for exothermic blowing agents like Celogen AZ3990, when a larger amount of blowing agent is added, more heat is generated from decomposition. Because the time for the heat to escape is limited, with a large amount of heat released from the reaction, the heating rate in the local area is higher. As a result, as shown in Figure 3-15, the sample of 30gram decomposed more quickly than the one of 10 gram.
Effect of CBA Particle Size

In the experiments on ADC series, the two samples are of the same composition and produced with the same method (Method Registration No. 123-77-3). The main difference between the two samples is the particle size of the CBAs. ADC/M-C1 is similar to Celogen AZ3990 with an average size of 4.5 μm, while the size of ADC/F is 15.5 μm. The experiments on ADC samples show that the decomposition behavior was not significantly affected by the particle size.

3.6 Selection of CBAs

Based on the thermal behaviors of the plastic materials and CBAs investigated using DSC and TGA, a preliminary selection of CBAs was made. Accordingly, sodium bicarbonate and Celogen OT were chosen for processing of PE foam because they decompose after the melting of the polymer and their decomposition temperature is not very high so that a proper polymer melt strength can be maintained. However, their decomposition temperature is below the melting temperature of PP materials and cannot be used for PP foam processing. Therefore, Celogen AZ3990 was chosen for PP foaming. The effects of heating rate, endothermic and exothermic behavior, and other factors on the foam structure were investigated by changing the processing and material parameters in the rotational foam molding experiments, which will be discussed in detail in Chapters 4 and 5.
Chapter 4

Rotational Molding of PE and PP Foams with the Dry Blending Method

4.1 Introduction

It is well known that the mechanical properties of rotational molded parts are weak because of their hollow structure. Some practices have been developed for using polyurethane foam to fill the part. However, because polyurethane is not compatible with the thermoplastic materials commonly used in rotomolding, the interface between the skin and the foam is very weak. It would be desirable to have a foam core that is made of the same material as the skin layer. Needham introduced a chemical blowing agent (sodium bicarbonate) into polyethylene-based materials in rotational molding [25]. Uniroyal Chemical [26] used Celogen OT as the chemical blowing agent to develop low-density polyethylene foams in rotomolding. However, the obtained cell structure is not satisfactory because of a large cell size and a low cell density. In addition, the foaming mechanism in rotomolding has not been clearly understood and very little research on the foaming in rotomolding and its applications has been published in the literature.

Since polyethylene is the most popular material in rotational molding, initial efforts were made in developing high quality low-density polyethylene foams in our research. However, due to the outstanding mechanical properties of polypropylene materials, research was conducted on developing a technology for making fine-cell low-density polypropylene foams as well. The high melting point and high mechanical strength make PP a good candidate for high strength foams that can be used for structural materials. In contrast,
because of the weak melt strength of PP materials, it is difficult to achieve high quality foam cells. Due to the technological difficulties, PP foams typically have very large cells with a very low cell-population density, and consequently, very few applications can be found.

4.2 Overall Processing Technology

For the dry blending based technology, the polymer materials must be in a powder form. It is easy to get PE powders since they are the most often used materials in the rotational molding industry. However, PP is normally supplied in a pellet form and must be ground.

The PE or PP powders are mixed with CBAs and other additives before they are charged into a rotational mold. The mold is put into a hot oven and rotated. After the predetermined processing time elapse, the mold is being pulled out of the oven and cooled while still rotating.

4.3 Processing Steps in Rotational Foam Molding

4.3.1 Continuous Phase Formation by Sintering of Powder Particles

In Figure 4-1, a schematic of the typical morphology change in rotational foam processing is presented. The powder mixture of polymer particles and CBAs is tumbled inside the mold while the mold rotates in the oven. The polymer powder particles will melt and fuse with each other. Ultimately, the powder particles will be fully fused and a continuous phase will be formed. This is referred to as the sintering process.
4.3.2 Cell Nucleation in the Dry Blending Method

There are two possible mechanisms of nucleation related to the dry blending method. When the sintered polymer powders become fully molten, the polymer melt should flow and wet the surface of the dispersed CBA particles. If the polymer melt can wet the CBA particles well before the decomposition of the blowing agent, or the CBA particles are entirely isolated in a uniform polymer matrix, the bubbles generated from the fine CBA particles will act as cell nuclei for the foaming process. In contrast, if the polymer melt does not wet the CBA particles well before the decomposition, there will be air pockets trapped between the CBA particles and the polymer matrix. These air pockets will work as cell nuclei later and dominate the foaming process.

4.3.3 Cell Growth and Cell Coalescence

As soon as the decomposition of the CBA begins, gas is generated, and consequently, cell growth occurs. As a result of the continually generated gas, the pressure in the nucleated cells increases. At the same time, the pressure of the polymer matrix in rotomolding is maintained almost at the atmospheric pressure at all times. The resulting pressure difference is the main driving force for the growth of the cells. The high pressure gas in the cells causes them to expand. The rate of cell growth is determined by the gas generation rate, the heating rate, the processing time, the amount of gas that diffused into the polymer matrix, and the strength of the polymer matrix.

As the cells grow, adjacent cells will be in contact with each other. There will be a thin polymer wall formed between the neighboring cells (Figure 4-2(a)). The thickness and the strength of the wall will decrease as the cells grow. When the wall is broken, two cells become one big bubble (Figure 4-2(b)). This phenomenon is called cell coalescence.
According to thermodynamics, the two adjacent cells tend to merge due to the fact that, through coalescence, the reduced surface area of cells will reduce the surface energy [27-29]. In other words, through cell coalescence, the total free energy of the polymer system will be reduced. Since plastic foams of a smaller cell size and a narrower size distribution exhibit better mechanical properties [38], it would be desirable to prevent cell coalescence and prevent the cell density deterioration. The melt strength, which is a degree of resistance to extensional flow of the cell wall during the drainage of the polymer in the cell wall when the volume expansion occurs, should be high enough to prevent cell coalescence. It is known that the melt strength decreases while the temperature increases [23], so maintaining a low processing temperature during rotational foam molding is critically important in reducing cell coalescence and thereby for the production of high quality foams.

4.3.4 Cell Coarsening

During cell growth, when two bubbles of different cell sizes are adjacent to each other, the gas in the smaller one tends to diffuse into the larger one. This phenomenon is called cell coarsening. The size of the smaller bubbles will be further reduced until it collapses. As a result, the two cells will merge into one and the cell density will be lowered. This is because the pressure is higher in the smaller bubble, due to the surface tension effect [28]. The pressure difference between the two adjacent cells can be expressed as a function of the surface tension on the polymer layer that separate them [39]:

\[
\gamma \left[ \frac{1}{R_1} - \frac{1}{R_2} \right] = \Delta P'
\]

(4-1)

where \( R_1 \) and \( R_2 \) are the radii of the two cells, \( \gamma \) is the surface tension, and \( \Delta P' \) is the pressure difference.
In order to reduce cell coarsening, cell nucleation at all locations should occur as simultaneously as possible. Therefore, CBAs having a higher decomposition rate are preferred.

### 4.4 Experimentation

#### 4.4.1 Experimental Procedure

While performing roto foam molding experiments, the polymer materials used in the experiments are required to be in a powder form. PE is available in a powder form and is convenient to use, whereas PP is usually in a pellet form and must be ground before processing. The polymer powder is blended with CBAs and other additives, and the mixture is molded in an in-house designed rotational molding machine and foamed samples are produced. In order to understand the temperature variation in the mold, experiments were also conducted for measuring the temperature profiles in the mold.

#### 4.4.2 Experimental Setup

The uni-axial rotomolding machine used for the rotational foam molding experiments is presented in Figure 4-3. It consists of a cylindrical aluminum mold, a motor, a hollow shaft, an oven, a temperature controller, and a water cooling system. A thermocouple is used in the center of the hollow shaft to monitor the temperature in the center of the mold. The diameter of the mold is 1.25" and its length is 4.00".

#### 4.4.3 Grinding of Plastic Materials

PP pellets must be ground before use. The grinding was done in the facilities of WedTech, the industrial sponsor of the project. A schematic of the small scale grinding
machine is shown in Figure 4-4. Polypropylene pellets are fed into the grinding head at the center. There are two cutting plates with radial cutting blades. One of the plates can be changed so that the particle size can be varied. The ground small particles are collected at the bottom edge of the grinding head by a vacuum pump. The particles are sieved in a mesh with a specified mesh size. Those conforming to the size requirement are collected through the collecting channel. The remaining particles that are too big are recycled to the grinding head to be reground.

PP materials must be frozen before they are ground. Otherwise, the frictional heat gets accumulated and the temperature of the cutting blade and the surrounding air quickly reaches the polymer melting point. Therefore, before grinding, the materials were placed in a freezer with a temperature of −40 °C. In this way, the materials become more brittle and easier to grind.

4.4.4 Hot Stage Microscopic Analysis

The cell nucleation, growth, coalescence, and coarsening phenomena were observed using an optical microscopic system (Olympus BH2) with a hot stage (Mettler FP 80 HT). The mixture of polymers and CBAs were put on the hot stage and heated up to 200 °C with a heating rate of 10 °C/min.

4.4.5 Rotational Foam Molding

Rotational foam molding experiments were carried out on the uni-axial rotational molding machine illustrated in Figure 4-3. A series of experiments were conducted to determine the effect of processing parameters on the cell morphology of different material foams. The oven temperature was varied from 200 °C to 350 °C. When Celogen AZ was
used as a CBA for PP foams, ZnO was used to promote the decomposition of the CBA and its amount was changed to adjust the desired decomposition temperature. The amount of polymer materials and chemical blowing agent were determined by the desired volume expansion ratio, e.g., three-fold and six-fold expansion based on the gas yield of CBA (see Section 4.5.8).

The oven must be turned on and warmed up 15 minutes before the experiment to ensure that the temperature reaches the set temperature. At the same time, the mold should also be prepared. First, the ventilation tube must be checked to make sure it is not blocked by polymer material and is replaced if necessary. Otherwise, the accumulated gas pressure in the core of the mold will lead to a hollow structure in the final foamed products. The ventilation tube consists of a 3/8” teflon tube and glass fiber to prevent polymer powders from being lost through the tube. After checking the ventilation, a mold-releasing agent (Miller-Stephenson, MS-122N/CO2) is sprayed into the mold so that the foamed part does not stick to the surface of the mold. After the release agent has dried, the mixture of CBA (additives) and polymer is charged into the mold. Before mounting the mold onto the rotational shaft, the mold should be shaken in the longitudinal direction to evenly distribute the powder materials in the mold. The motor that rotates the mold is turned on and the speed is adjusted to about 5 rpm (revolution per minute). Then the mold is inserted into the oven and the processing timer is started. After the processing time has elapsed, the mold is pulled out of the oven and cooled with running tap water. At this stage, the mold should keep rotating so that a uniform cooling and thereby a uniform cell structure can be obtained. The cooling lasts about 10 minutes, and the tap water can then be shut off. Finally, the mold is removed to demold a foamed part.
By stopping the experiment at fixed intervals during the process, the sintering, cell nucleation, and cell growth behaviors of each material were monitored. Samples were collected and the structure of the samples was investigated using a Scanning Electronic Microscope (SEM). The foaming process was investigated by studying the SEM images. To ensure that the results were comparable, samples used for analysis were collected from the same position of the molded parts. In addition, experiments were repeated to confirm the repeatability of the results obtained.

4.4.6 Characterization of Foams

The cell structures of the roto-molded foams were characterized in terms of the cell density, the volume expansion ratio and the average cell size.

Referring to Park [33], the cell density (or cell population density) is defined as the number of cells (or bubbles) per cubic centimeter of unfoamed original material. Since the number of cells per square centimeter of foamed material can be easily counted, the cell density can be determined from this value followed by compensating for the volume expansion.

First, the number of bubbles, \( n_b \), in a square of edge length, \( l \), is counted from a micrograph of the sample. The value observed is then normalized to the number of cells in a 10 \( \mu m \) square, \( n_{b0} \). This normalized value is converted to the number of bubbles per volume of 1 cm\(^3\). Finally, this converted number is multiplied by the volume expansion ratio to determine the cell density, \( N_c \), which can be expressed by the following equation:

\[
N_c = \left[ \frac{n_b \times (10 \mu m/l)^2}{l^3/2} \times 10^9 \right] \times \Phi
\]  

\[(4-2)\]
where $\Phi$ is the volume expansion ratio of roto-molded foam and it was determined by measuring the expanded volume of foam, $V_f$, and the mass, $m$, and

$$\Phi = \frac{V_f}{V_i} = \frac{V_f}{m/p}$$

(4-3)

where

$p = $ density of material

$V_i = $ initial volume of unfoamed solid plastic.

A schematic of the calculation procedure is illustrated in Figure 4-5.

4.4.7 Temperature Profile

In order to determine the temperature profile within the mold during heating and cooling, a thermocouple was inserted into the mold through the hollow shaft. The tip of the thermocouple was positioned in the center of the mold cavity. The measured temperature was recorded every 15 seconds. Diagrams of temperature as a function of time were plotted.

4.5 Results and Discussion

Several factors that affect the foam quality were studied through the experiments. For polyethylene, foams of six-fold expansion with a fine cell structure were obtained when Celogen OT and sodium bicarbonate were used as the blowing agents (see Figure 4-6). In the case of polypropylene, Celogen AZ3990 was used as a blowing agent with ZnO as a promoter for three-fold expansion. Foams of six-fold expansion were also achieved.
4.5.1 Investigation of the Temperature Profile in Rotational Foam Molding

In Figure 4-7, temperature profiles in the mold under different conditions were shown. First, an empty mold was put in the oven and went through the normal molding process. In the figure, the curve "Outside, empty mold" indicates the temperature variation at the point close to the mold surface and the curve "Inside, empty mold" illustrates the temperature change at the center position of the mold. Then, the temperature curve was plotted when 15 grams of MT4390 (PP) was charged in the mold, which is marked as "Pure MT4390" in Figure 4-7. In the end, temperature profiles at the center of the mold were obtained when 1% 50ZnO/50AZ and 5% 50ZnO/50AZ were added. From these profiles, the foam process in rotational molding can be classified into five stages. In fact, the first stage represents the pure heating of the mixtures in the mold. This is why the obtained heating curve is almost linear after the process stabilizes. For this stage, there is not much difference between heating an empty mold and a charged one. If comparing the heating curves, the one developed from heating an empty mold is almost the same as the one from heating a charged mold within this stage. During the second stage, the speed of the temperature increase slows down. Also, the heating curve for the charged mold becomes lower than the one for the empty mold. It is believed that polymer sintering and melting begin in this period. On one hand, the polymer layer developed on the inner surface of the mold reduces the heat transfer to the powders. On the other hand, because the sintering and the melting of polymers is an endothermic processes, some heat is absorbed during melting. During the third stage, the CBA is decomposed. Since the CBA used in the experiments was an exothermic blowing agent, Celogen AZ, a large amount of heat was generated during the decomposition. Graphically, it was indicated by a rapid jump in the temperature profile. In about 15 minutes, the decomposition of CBA is completed and the system enters into the
fourth stage of cell growth. When the foam structure is developed, the heat transfer rate was reduced due to the insulation effect of foams. After it reaches the designated heating time, the mold is pulled out and cooled with running water, which represents the fifth stage of the entire process.

4.5.2 Investigation of Sintering of Powder Particles and its Relationship with Cell Nucleation

Six-Fold Expansion

In processing of PP foams of six-fold expansion, three materials with different viscosity were chosen: SC873 (50 MFR), SD242 (30 MFR), and MT4390 (20 MFR). Fully expanded foams were successfully produced from SC873 and SD242 while no good foam structure could be achieved from MT4390. To explain the different results in rotational foam molding of these three materials, the heating was stopped at 13, 14, and 15 minutes and samples were taken from the foamed parts to investigate the sintering quality of polymer powder particles. In order to verify the repeatability of the experiments, three sets of experiments were conducted at the same conditions for each material. Figures 4-8, 4-9, and 4-10 show the SEM pictures of the selected foam samples of SC873, SD242, and MT4390.

In Figure 4-8, we can see that when SC873 with a MFR of 50 dg/min was used, powder particles began to form a uniform polymer melt after being heated for 13 minutes in the oven, although some unsintered particles were still found. At 14 minutes, the sintering was completed although a number of small air pockets still existed in the polymer matrix. These air pockets are believed to be the entrapped air among the polymer particles as indicated by Liu et al. [35]. Due to the low-pressure processing condition of rotomolding,
these air pockets were very difficult to remove when polymer particles were dry blended with CBA particles. At 15 minutes, the decomposition started.

When SD242 with a MFR of 30 dg/min was used, the sintering is not as good as that with SC873. At 14 minutes, several large air pores still existed in the polymer matrix (see Figure 4-9).

When MT4390 with a MFR of 20 dg/min was rotomolded, the sintering quality became worse. As shown in Figure 4-10, at 13 minutes, polymer particles were still in the early stage of sintering and individual polymer particles were clearly identified. At 14 minutes, there were a large number of entrapped air pockets in the polymer matrix, some of which were connected with each other. When it reached 15 minutes, huge cavities were formed.

Comparison of the sintering behaviors of PP materials with various MFRs indicates that the sintering of powder particles plays an important role in the cell nucleation process as in the case of PE processing [35] in the dry blending method. When the sintering of the polymer powder particles is good, the entrapped pockets will be isolated in the molten polymer matrix before the decomposition of CBAs. These bubbles will behave as cell nuclei in the foam processing [35]. If the sintering of polymer powder is poor, the entrapped air pockets will not be easily isolated before the decomposition of CBAs. These connected air pockets are problematic in the foam processing. As the CBAs begin to decompose, the gas generated from the decomposition of CBAs will inflate the connected cavities, forming huge cavities or losing all the gas through these connected cavities eventually to a ventilation hole. So, when MT4390 with a relatively low MFR of 20 dg/min was used in the six-fold expanded foam processing, huge cavities were observed in the final foam structures because of the poor sintering behavior of plastic powder particles.
Therefore, in order to achieve a fine-cell foam structure, formation of big air pockets should be prevented. Since these big cavities are generated by the poor sintering of polymer powder particles, it will be critical to have a good sintering in the rotomolding of PE and PP foams.

**Three-Fold Expansion**

As presented in Figures 4-8 and 4-9 the sintering quality was improved when low viscosity PP materials with high MFR were used for six-fold expanded foams. Although it is extremely difficult to remove the entrapped air completely in rotational molding, a good sintering can easily isolate these air bubbles and prevent formation of huge cavities. As a result, better nucleation is formed and a better foam structure is obtained. The improvement of cell structure by using a high MFR PP was further verified by the detailed experiments on three-fold expansion foams.

From the cell morphology shown in Figure 4-11 (a), when PF633 of a high viscosity (MFR 3~6 dg/min) was used, no fully expanded foam structure was obtained, although a proper amount of blowing agent was added. It seemed that the viscosity was too high to promote good sintering, and as a consequence, most of the gas was lost. When SD812 with a higher MFR of 16 dg/min was used, a uniformly distributed fine-cell structure was obtained as shown in Figure 4-11 (b). With an increase of MFR (or equivalently a decrease of viscosity), the sintering was improved and better foam quality was achieved. In Figure 4-11 (c), the cell structure was further improved, especially the distribution of the cells, when MT4390 (MFR 20 dg/min) was used. Figure 4-12 (a) shows that the cell population density of MT4390 foams is four times as high as that of SD812 foams.
However, a low viscosity is also detrimental to the foam structure. If the viscosity is too low, the melt strength becomes low (see Section 3.3) and cell coalescence may govern the foam structure. In the other words, when the MFR is too high, the cell nucleation behavior will be satisfactory because of good sintering. However, because of the weak melt strength, severe cell coalescence can be promoted and the high nuclei density may not be successfully preserved during cell growth. As a result, big bubbles may be formed in the foam structure. Therefore, there is an optimum viscosity level (or optimum MFR level) to achieve the highest cell population density.

Since the sintering behavior of plastic powder particles strongly depends on the amount of the plastic powder and CBA charged into the mold, the optimum value of viscosity to achieve the highest cell density is a function of the desired volume expansion ratio of foam. For example, for processing of three-fold expanded foams, a MFR higher than 15 dg/min is necessary to achieve a good sintering behavior and the optimum level of viscosity was observed to be 20 dg/min (see Figure 4-12). On the other hand, for processing of six-fold expanded foams, the sintering behavior of SD812 (MFR 16) and MT4390 (MFR 20) were not satisfactory. A MFR higher than 30 dg/min was necessary to produce a uniformly distributed and fully expanded foam structure.

It is interesting to note that the sintering of behavior of PP powder material was better for three-fold expansion than for six-fold expansion. For example, when 25 g of MT4390 powders with 1% of Celogen AZ were charged into the roto-mold for three-fold expansion, good sintering was observed at the foaming stage. However, when 13 g of MT4390 powders with 2.5% of Celogen AZ were charged into the roto-mold for six-fold expansion, the sintering behavior of the powders was poor at the onset of decomposition of CBA.
It was not clear why the sintering was better when more plastic materials with relatively less amount of CBA were used in the rotational foam molding. However, it is believed that the larger thermal inertia of the greater amount of plastic materials was responsible for this difference. When a large amount of materials were charged into the mold, the heating rate was lower because of an increased thermal inertia. As a consequence, the decomposition of the exothermic blowing agent will be delayed (see Figure 3-12). In other words, more time will be given for the sintering of plastic powder materials before the decomposition of CBA. On the other hand, when a less amount of materials was charged into the mold for six-fold expansion, the heating rate would be higher, and the decomposition of exothermic CBA would be earlier. In other words, the plastic powder particles did not have enough time to sinter together before the decomposition of CBAs.

Another reason for the poor sintering of plastic powders may be due to the increased particle-to-particle distance of plastic powders for the larger expansion composition of materials. It should be noted that for larger expansion, the relative CBA amount is greater, and therefore, the powder-to-powder distance of plastic powder particles is greater.

### 4.5.3 Investigation of Effect of Powder Qualities on Cell Morphology

Figures 4-13 and 4-14 show the effects of physical shapes of polymer powders on the cell morphology of PP foams. Figure 4-13 is the foaming results of SD812 for two different particle sizes (see Figure 3-1). Figure 4-14 shows the foam morphology of samples made from SD812 powders with and without long tails. The long tails of powders were observed to be formed when the pellets were ground into powders without being frozen.

**Effect of Particle Size**
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Figure 4-13 shows that bigger polymer powder particles yielded a bigger cell size and lower expansion. Since the cell-to-cell distance is determined by the average particle size in the dry blending technique, the cell size would increase as the power particle size increases. Furthermore, it seems to be more difficult for larger particles to sinter each other. Because of the poor sintering, the released gas easily escaped and fully expanded foam structure could not be obtained. These results imply that a smaller particle size is favorable for developing a fine-cell structure in the dry blending based method. Unfortunately, the available particle size was limited and further investigation could not be made.

Effect of Particle Shape

Figure 4-14 illustrates the effect of long tails attached to the powders on the cell morphology. Poor foam cells were generated from those particles with long tails. The hair or tail of these particles caused a poor contact between particles and made it difficult to achieve good sintering. As a result, the generated gas was lost and huge cells were obtained.

4.5.4 Investigation of Effect of CBAs on Cell Morphology

In Figure 4-15, the effect of the CBAs on the foam quality of six-fold PE foams is shown. Celogen OT ("OT") was used in (a) while in (b) sodium bicarbonate ("SB") was the blowing agent used for the foaming. When Celogen OT was used, a finer cell structure was obtained. It was not clear whether the better cell structure of PE foams using Celogen OT was due to the rapid decomposition (see Figure 3-11) of Celogen OT or due to the higher decomposition temperature (see Figure 3-10). Since the sodium bicarbonate starts to decompose at 133 °C, the sintering behavior of PE particles at the foaming stage may not be as good as in the case of using Celogen OT. Therefore, the cell nucleation will be better in
the case of Celogen OT for PE foam processing. Furthermore, cell coarsening could have affected the foam structure. During cell nucleation and growth, the bubbles that nucleated first were inevitably larger than those that were developed later. The smaller bubbles will eventually merge into the bigger ones and cell coarsening becomes severe. In addition, cell coalescence may also occur if the decomposition lasts long. As a result, the cell population density is reduced. Therefore, for the CBAs that decompose over a wide temperature range such as sodium bicarbonate, it would be difficult to obtain fine cell structures. On the other hand, for blowing agents such as Celogen OT, the decomposition occurs very quickly and most of the cells nucleate simultaneously. Cell coarsening is relatively low, which allows cells to grow uniformly. Since it was not clear which of the two dominated the cell formation, a future study is required.

### 4.5.5 Investigation of Effect of CBA Particle Size on Cell Morphology

Figure 4-16 shows the results of SD812 foams obtained when another azodicarboxamide CBA ADC series from Bayer was used. The information contained in this figure is helpful to understand the effect of CBA particle size on the foam quality. Figure 4-16 (a) presents the foam generated by ADC/M-C1 (the CBA with a small particle size of 4.5 µm), while Figure 4-16 (b) presents the foam generated by ADC/F that has a particle size of 15.5 µm, three times larger than that of ADC/M-C1. As shown in the figure, no significant difference was identified between the morphologies of the two samples.

It seems that a blowing agent with a smaller particle size is easier to disperse into the polymer powder and therefore a better degree of mixing during dry blending can be achieved. Consequently, a better foam structure will be produced. However, since the nucleation in dry blending method more depends on the sintering quality of the polymer
powder particles and the CBA particle sizes were much smaller than that of the plastic powder particles, the effect of the CBA particle size on the resultant foam structure was not significant. It should be noted that there is no big difference between the decomposition behaviors of ADC/M-C1 and ADC/F (see Figures 3-9 and 3-11).

4.5.6 Investigation of Effect of ZnO on Cell Morphology

Figure 4-17 illustrates the effect of ZnO on the cell morphologies of PP (MT4390) foams when AZ3990 was used as the blowing agent. From previous work [35] and the TGA test on the effect of ZnO (see Figure 3-13), it is known that the decomposition temperature of azodicarboxamide blowing agent is lowered with the presence of ZnO. The rational behind using this catalyst as a decomposition promoter is that the melt strength of PP will be increased by lowering the processing temperature via the decomposition temperature control. When the melt strength of PP was increased by having early decomposition of CBA, cell coalescence will be reduced and improvement of cell structure is expected. The effect of ZnO on cell morphologies is depicted by the two extreme results shown in Figure 4-17. With only a 20 °C decrease in the decomposition onset temperature (see Figure 3-13), the average cell size was reduced from 3 mm to 0.7 mm (700 μm). However, it should be noted that the effect of lowering the decomposition temperature on the cell morphology will be good only when the sintering of the plastic powder particles is good at decomposition. If the decomposition is too early, the resultant cell structure will not be good because of the unfinished sintering of plastic powder particles.

4.5.7 Investigation of Effect of Processing Parameters on Cell Morphology
Effect of Blowing Agent Amount

A foamed product is made up of a solid polymer matrix and a gas phase. The gas is generated from the chemical blowing agent. To achieve a desired expansion ratio, a proper amount of chemical blowing agent should be used. Theoretically, this can be estimated using the following equations.

\[ m_{\text{polymer}} = \frac{V}{\Phi \rho_{\text{polymer}}} \]  

\[ m_{\text{CBA}} = \frac{\Phi - 1}{\Phi} V \]  

where

- \( m_{\text{polymer}} \) = weight of pure polymer material used, g,
- \( m_{\text{CBA}} \) = weight of blowing agent, g,
- \( V \) = total volume of the mold, cm\(^3\)
- \( \Phi \) = expansion ratio,
- \( \varphi \) = volume of gas generated per unit mass of blowing agent, cc/g,
- \( \rho_{\text{polymer}} \) = density of the polymer material, g/cc.

The percentage (by weight) of CBA used can be expressed as

\[ \% \text{ CBA} = \frac{m_{\text{CBA}}}{m_{\text{polymer}}} = \frac{\Phi - 1}{\rho_{\text{polymer}} \rho_{\text{polymer}}} \]  

According to the data provided by the CBA manufacturers, the amount of gas generated from Celogen AZ3990 is 220 cc (STP)/g and the density of PP is around 0.9 g/cc. It is
worth noting that the gas yield data provided by the suppliers is at room temperature. A
typical schematic of a measurement system for CBA characterization is given by Klempner
and Frish [13]. However, the expansion of foam occurs at a very high temperature, that is,
above the polymer melting temperature. As the temperature decreases during the cooling
process, the maximum possible gas volume will be reduced. Since the polymer will be
frozen at the crystallization temperature, the structure of the foam is fixed at this
temperature. In other words, the void fraction of the foam is determined by the occupied
gas volume at the crystallization temperature. Since the volume of gas at this high
temperature is larger than the volume at room temperature, the gas yield data provided by
the manufacturer should be corrected in calculating the required CBA amount in Equation
4-6:

\[ \phi = \phi_{\text{STP}} \times \frac{V_c}{V_{\text{room}}} = \phi_{\text{STP}} \times \frac{T_c}{T_{\text{room}}} \quad (4-7) \]

where \( V_{\text{room}}, V_c, T_{\text{room}} \) and \( T_c \) are the gas volume at the room temperature, the gas volume at
the crystallization temperature, the absolute room temperature and the absolute
crystallization temperature, respectively. The room temperature is 25 °C, or 298 K, and the
crystallization temperature of PP is approximately 135 °C, or 408 K. Therefore, for the 80cc
mold used in the experiment, it is estimated that the amount of chemical blowing agent
needed is 0.625% for three-fold expansion and 1.5% for six-fold expansion.

The effect of varying the chemical blowing agent amount on the foam structure was
investigated. For three-fold expansion, the experiments were conducted while varying the
CBA from 0.5% to 1.5%. In the case of six-fold expansion, the amount of CBA was varied
from 1.5% to 4.0%. \( \text{ZnO} \) was used to modify the decomposition behavior when it was
necessary and possible.
Figure 4-18 shows the cell morphologies as a function of the blowing agent amount and Figure 4-19 illustrate the effect of CBA amount on cell size, cell population density and expansion ratio. For the three-fold expansion samples of MT4390, it was clearly observed that, too little an amount of CBA resulted in big cell size due to a deficient amount of gas and the bubbles were over expanded to fill the mold cavity. Too much gas also resulted in a poor cell structure because of too high gas pressure. It was also believed that when a large amount of CBA was used, the decomposition occurred earlier before the completion of sintering. As a consequence, the cell structure was not desirable. The experimental results indicated that an optimum amount of CBA should be applied according to particular product requirement. For example, 0.625% AZ3990 together with 0.625% ZnO is found to yield best results for three-fold expansion in our experiments.

On the other hand, a much larger CBA amount was required for six-fold expansion. For six-fold expansion, approximately 2.5%~3.0% of AZ3990 gave the best result. It should be note that this is much higher than the theoretically predicted value (by Eq. 4-6) because of the lower blowing agent efficiency. First, the gas loss may be high when less polymer is used. In addition, the CBA may not have been fully decomposed during foaming. During experiments on six-fold expansion, the optimum amount of ZnO was reduced to 0% to increase the decomposition temperature so that there was enough time left for achieving better sintering of the polymer particles. With the reduced amount of decomposition promoter, the AZ may not have been fully decomposed at the particular time/temperature when the experiments were stopped. Figure 3-13 shows that with a reduced amount of ZnO, the residue increases. For example, at 250°C, there is still 20 percent residue for pure Celogen AZ3990, but only less than 10 percent residue is left at 190°C when ZnO was added. Therefore, more CBA materials were consumed with ZnO.
Effect of Processing Time

Figures 4-20 and 4-21 illustrate the effect of processing time on the foam morphologies of three-fold expanded MT4390 (PP) foams. The oven temperature used for the samples was 350 °C, and the blowing agent was 0.625% of Celogen AZ together with 0.625% of ZnO. The processing time was varied from 10 minutes to 25 minutes.

It turned out that the processing time is another critical parameter in the rotational molding of PP foams. When the processing time was too short, the foam was not fully expanded. Figure 4-20 clearly shows the unfoamed yet sintered polymer layer where the temperature was still below the decomposition temperature. However, when the processing time is too long, a coarse foam structure was obtained. This seemed to be due to cell coalescence. As the processing time increases, the temperature of the polymer becomes higher because of the longer exposure time of oven. The melt strength and viscosity of PP drop dramatically as the temperature increases over the melting temperature (see Figure 3-3). The possibility of cell coalescence and cell coarsening increases as the melt strength decreases. Therefore, it would be desirable that the processing be stopped as soon as the expected volume expansion is obtained.

Effect of Oven Temperature

The effect of oven temperature on the cell morphology of PP foams was also studied using SC873. Four different oven temperatures of 350 °C, 325 °C, 300 °C, and 275 °C were tested in the experiments. In all the experiments, 13 g of SC873 powders and 3% AZ3990 were charged into the mold for six-fold expansion. In Figure 4-22 shows the foams obtained under oven temperatures of 275 °C and 350 °C. For the same amounts of plastic
and CBA materials, the higher the oven temperature, the higher the heating rate. It was found that too high a heating rate yielded very coarse structures because of the unique thermal behavior of the exothermic CBAs under a high heating rate. From DSC analysis results shown in Figure 3-10, it can be seen that much more heat is generated when the heating rate is increased for Celogen AZ. The heat generated from the reaction will increase the local temperature, almost instantaneously. For example, in Figure 4-23, the effect of this exothermic heating is clearly depicted. The actual temperature can be 20.52 °C higher than the theoretical temperature under a heating rate of 76.35 °C/min. Consequently, the melt strength will be lowered at interface of the polymer melt and the growing gas bubbles. This will promote severe cell coalescence and reduce the cell population density.

However, a low oven temperature, or a low heating rate, is not practical in production due to economical reasons. Another important factor is that, under a low heating rate, polymer particles tend to stick to each other locally, instead of forming a uniform polymer layer on the wall of the mold (Figure 4-24). This “balling phenomenon” also leads to non-uniform structures because of non-uniform distribution of materials. Therefore, setting a proper oven temperature is also critical in achieving good quality foams. For the particular mold used in our experiments, it is determined that 300-350 °C is suitable for three-fold expansion and 275-300 °C for six-fold expansion.
Chapter 5

Rotational Molding of PE and PP Foams with the Melt Compounding Method

5.1 Introduction

A dry blended mixture of a chemical blowing agent (CBA) and polymer resins was used in the previously presented research for the manufacturing of fine-cell, low-density PE and PP foams using rotational molding. As a result of this research, PE and PP foams of up to six-fold expansion have been successfully produced, and the foaming mechanism and the critical factors that affect the foam quality have been clarified. In dry blending, cell nucleation and growth are primarily determined by the sintering behavior of the plastic resin particles during the rotational molding process. Since the sintering ability of the polymer material is directly related to the viscosity, the selection of materials was limited to those having a higher melting flow rate (MFR) at the expense of melt strength. In a poor sintering process, the trapped air pockets formed among the polymer particles result in a relatively coarse foam structure. It is also difficult to obtain a large expansion ratio due to the poor sintering properties or the weak melt strength of such materials.

Melt compounding is an alternative method for material preparation in the manufacturing of fine-cell PE and PP foams. Melt compounding refers to the process of mixing the chemical blowing agent and the polymer resin using an extrusion compounder. The extruded mixture is cut into pellets and used for the rotational molding. In the melt compounding process, the chemical blowing agent can be better distributed in the polymer matrix due to the high shear force produced in the compounder. This could be of great help
in achieving a uniform cell distribution later in the process. In addition, the melt compounding process ensures better wetting of the polymer melt on the CBA particles and removes all the trapped air pockets. Moreover, the CBA(s) are well distributed in the polymer matrix after compounding. Therefore, the sintering behavior of the polymer particles is no longer the dominant force in the foaming process. Under these circumstances, the nuclei will be the CBA particles, and cell nucleation will be totally controlled by the decomposition behavior of the chemical blowing agent(s) and other additives. Since cell nucleation no longer depends on the sintering quality or the viscosity of the material, a much wider range of materials can be used for the production of PP foams in rotational molding. Furthermore, by using high melt strength materials foam structures of large expansion ratios can be achieved; such structures were not easily obtained with the dry blending methods.

5.2 Overview of the Process

In compounding based rotational foaming, the first step is the dry blending of the polymer materials, CBA(s), and other additives. Good premixing helps improve the mixing quality in the melt compounding stage. After the materials enter the compounder, the high shear force in the extruder barrel induces further mixing. However, chemical blowing agents are heat sensitive materials. The viscous heat generated by the high shear may cause the decomposition of the CBA(s) at the extrusion compounding stage, which should be prevented. Therefore, the shear force should be maintained in a proper range. In the second stage, the mixture is extruded and then cut into pellets with a pelletizer. The final stage is the foaming of the compounded pellets in the rotational molding machine.
5.3 Processing Steps in Rotational Molding

5.3.1 Cell Nucleation

In the melt compounding process, air pockets among the polymer particles or on the surface of the chemical blowing agent particles are removed during compounding; therefore, controlling the cell nucleation during foaming is simpler than with the dry blending method. As a result, the cell nuclei come only from the chemical blowing agent particles. The size of the CBA particles and their distribution in the polymer matrix determine the cell population density and distribution. The shear force involved in the process of compounding produces a better quality mixture. In addition, since CBA particles tend to agglomerate together, it is desirable that a high shear force be applied to break the agglomerated particles in the compounding. Therefore, the distribution of CBA(s) is better in melt compounding. Generally speaking, because of the elimination of trapped air pockets and the better distribution of CBA(s), a better cell nucleation is obtained.

5.3.2 Sintering of Pellets and Cell Growth

The compounded pellets are loaded into a roto-mold, and the mold is placed into an oven and rotated. After being heated up, the compounded pellets begin to sinter together. When the temperature reaches the decomposition temperature of the CBA(s), decomposition begins. The gas bubbles generated by decomposition behave as cell nuclei. The cells continue to grow until the CBA(s) are fully decomposed. The pressure from the generated gas helps the pellets sinter better. Unlike in the dry blending based method, the sintering quality of the pellets affects only the structural and mechanical properties of the final products, with no significant effect on the foam quality. The cell size and population
density will be completely determined by the decomposition behavior of the chemical blowing agent(s) and by cell coalescence.

5.4 Experimentation

5.4.1 Experimental Setup

Figure 5-1 shows the compounding system used in the experiment. Part (a) is a schematic of the system and part (b) is a photograph of the actual equipment. A Brabender single screw extruder (05-25-000) that is driven by a DC motor carries out the melt compounding. The extrudate from the extruder is cooled in a water bath (WedTech). After the cooling section, the extrudate is dried and pelletized in a pelletizer (Brabender 12-72-000). The pellets are collected and used for the rotational molding.

The rotational molding is conducted on the same machine as shown in Figure 4-3.

5.4.2 Materials

Experiments were conducted on both PE and PP. For PE, LL8556 was chosen as the base polymer material. Both Celogen OT and Sodium Bicarbonate were tested as CBAs for PE foams. For PP foams, efforts were concentrated on medium and low MFR materials in order to investigate the possibility of using a wider range of materials in roto foaming. The materials used were MT4390, SD812, and PF633. Celogen AZ 3990 was used as blowing agent for the PP foams.

5.4.3 Melt Compounding

The melt compounding process involved several steps.
First, the heater was turned on to warm up the system to the designated processing temperature. This temperature is just above the melting temperature of PE or PP and lower than the decomposition temperature of the selected blowing agents. According to Stevens [23], the temperature profile along the barrel should be varied purposely so as to produce optimum melting as well as good material transportation. The temperature of the first section, i.e., the material transport section, should be lower than the melting temperature so that the material will not slide in the barrel. But the temperature should not be too low to make melting difficult.

Second, after the system temperature stabilized, the system was purged with pure polymer material at least for 10 minutes so that contaminants did not affect the quality of the mixture. At the same time, the system was re-stabilized under running conditions, including extrusion speed settings.

Third, the dry blended polymer and CBA(s) were put into the hopper and the materials were compounded in the barrel. The amount of CBA was determined according to Equations 4-5 and 4-6.

Fourth, the extrudate was pulled through the water bath and put into the pelletizer. The extrudate was dried before being cut. The pulling speed (or the feeding speed of the pelletizer) was adjusted so that pellets of proper diameter and length were obtained. A fast feeding rate results in a smaller pellet size.

The collected pellets were used for rotofoaming.
Chapter 5 Rotational Molding of PE and PP Foams with the Melt Compounding Method

5.4.4 Rotational Foam Molding

Compounded pellets were roto-molded with the same rotational molding machine used in the dry blending method. Processing parameters were studied and the final foam samples were analyzed. The amount of pellet used was calculated as:

\[ m_{\text{pellet}} = m_{\text{polymer}} + m_{\text{CBA}} = m_{\text{polymer}}(1 + \%\text{CBA}), \]  

where \( m_{\text{pellet}} \) is the amount of polymer material and \( m_{\text{CBA}} \) is the mass of CBA, which are determined by Equations 4-4 and 4-5, respectively.

5.4.5 Hot Stage Optical Microscope Analysis

Two samples were chosen to be analyzed with a hot stage optical microscope. Pellets of MT4390 with 0.5% of Celogen AZ 3990, with pre-decomposition, were studied first. Then, a study was carried out on pre-decomposed pellets of LLDPE 8556 and 3% Celogen OT. A thin layer of the mixture was cut from the compounded pellets and heated at the hot stage of the microscope. The nucleation and cell growth phenomena observed.

5.5 Compound Results and Discussion

The compounding quality is very important to the final foam quality in rotational foaming molding. Among all the issues of concern in the compounding process, the decomposition of CBA is the most serious problem that affects the compounding quality. Due to the shear and the heating environment in compounding, the CBA may decompose during this process. This is referred to as pre-decomposition in this thesis. One of the objectives of the compounding is to prevent the pre-decomposition, or to control the pre-decomposition throughout the process.
Chapter 5 Rotational Molding of PE and PP Foams with the Melt Compounding Method

Several factors that affect the pre-decomposition have been investigated during these experiments. However, the most significant parameters are the system temperature and the rotational speed. The pre-decomposition behavior at different settings of these parameters was investigated.

Figure 5-2 gives a schematic of the heat exchange process for a typical extrusion system from which the key factors for melt compounding can be outlined. The input of energy comes from two sources: the band heater and the mechanical power from the motor. The mechanical energy is converted to heat by viscous shear. The heat is lost through three channels: (1) some heat will be lost from the surface of the barrel through radiation and convection; (2) when the polymer melt leaves the barrel, a certain amount of heat is carried away in the melt; and (3) heat is lost through the external cooling system. Compressed air can be forced around the barrel to absorb heat, and cooling water is run around the feeding throat. Sometimes, screw cooling is also necessary. Only a proper balance between heat input and output can maintain system temperatures at a stable level.

Table 5-1 outlines the results of the experiment when the temperature settings and rotational speed were changed. From these results, optimum processing conditions for the particular experimental system were obtained. For PP materials, pellets without decomposition were successfully obtained. For PE, when Celogen OT was compounded with LLDPE 8556, the decomposition could not be eliminated although careful attention was paid to temperature control and rotational speed setup. However, when sodium bicarbonate was used, pellets without decomposition were successfully generated (see section 5.5.4). The mechanism behind the results are summarized in the following sections.

5.5.1 Effect of Barrel Temperature on Compounding Quality

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To compound the chemical blowing agent particles in the polymer melt, the processing temperature must be above the melting temperature of the polymer. However, the processing temperature must be below the decomposition temperature of the chemical blowing agent to prevent pre-decomposition. If pre-decomposition occurred in the compounding process, the bubbles that are generated would adversely affect cell nucleation in the foaming process [33]. In addition, a certain amount of the blowing agent is lost. Since it is impossible to know the amount of gas lost, it is difficult to control the amount of CBA used in the process.

5.5.2 Effect of Rotational Speed of the Extrusion Screw on Compounding Quality

Since a lot of heat is generated from the shear force in the extruder due to the screw motion, many local hot spots may exist in the barrel. Even though the barrel temperature is set low, the actual local temperature will be high if the rotational speed of the screw is too high; this will result in pre-decomposition during compounding. The rotational speed of the extruder screw should be low enough to prevent any unnecessary viscous heat from being generated by the screw motion. However, the screw speed should also be kept within a certain range. With a decrease in rotational speed, the flow rate drops and the time that molten polymers stay in the barrel (which is referred to as the residence time) is longer. A longer residence time may cause pre-decomposition of CBAs in the extruder even at a low processing temperature as shown in Figure 5-3. Furthermore, when mixing quality is a concern, it is desirable to have a high extrusion speed because a high rotational speed of the screw results in a higher shear force and better mixing quality. In addition, a higher screw speed results in a high flow rate. Therefore, there is an optimum rotational speed of the screw for compounding. A proper extrusion speed should be carefully selected for each
processed material. For the experiments we performed, a speed in a range of 30 to 60 RPM and a processing temperature in the range of 160 °C to 165 °C were found to be appropriate to prevent decomposition in the compounding of PP and Celogen AZ. A different speed may be required if the polymer and CBA are changed.

5.5.3 Effect of Screw Cooling on Compounding Quality

For a large-scale continuous process, it is not sufficient to control only the barrel temperature and the rotational speed of the screw. When the generated friction overheats the screw, hot spots may be created and decomposition will again appear in an uncontrollable manner. To prevent this, screw cooling is necessary. However, in order to install a screw cooling system, the screw has to be at least 3.81cm [36]. In addition, the degree of the screw cooling must be within a reasonable range because a cooled screw will increase the shear force and reduce the flow rate.

5.5.4 Exothermic and Endothermic Effect of CBAs on Compounding Quality

When PE (LLDPE 8556) was compounded with Celogen OT and sodium bicarbonate separately, very different results were obtained. Although the onset decomposition temperature of Celogen OT is about 160 °C (which is about 30 °C higher than the set environment temperature), severe decomposition could not be prevented. When 3~5% of sodium bicarbonate is compounded with PE, with a barrel temperature of 130 °C and a screw speed of 40 RPM, pellets with no pre-decomposition were successfully generated. Although the decomposition temperature of sodium bicarbonate is 133 °C (only 3°C higher than the environment temperature), the compounding process was much easier to control than that when OT was used. It is believed that the different thermal characteristics of OT
and sodium bicarbonate were the reason for this difference. As Figure 3-9 (d) indicates, the decomposition of Celogen OT is an exothermic process. Since there are many hot spots at regions within the barrel with high shear force, local decomposition may be inevitable. When the decomposition occurs, a large amount of heat is generated and local temperatures can easily increase by 15-20 °C instantaneously, as shown in Figure 4-23. This leads to a series of decompositions in the neighboring area and propagate the decomposition, which makes the whole system unstable. However, when sodium bicarbonate is compounded, the decomposition is an endothermic process. Even if decomposition occurs, the temperature of the neighboring region is lowered and the decomposition does not propagate.

5.5.5 Effect of Heating Rate on Compounding Quality

As the material is processed in the extruder, the temperature of the mixture increases from room temperature to the melting temperature of polymer within the time it takes for the material to travel from the feeding section to the melting section. In the experiments, a timer was started when the material was put into the feeding throat (25 °C) and was stopped when the material exited the third heating zone (melting zone, 165 °C) without a die attached. The time was about 63 seconds when the screw rotational speed was set at 40 RPM. To prevent any material residing in the barrel from affecting the measurement, a colored material is added. The exact time of traveling can be calculated [23], but the simple measurement in the experiment implies that the time required to heat the polymer from room temperature to melting temperature is less than one minute. This means that the heating rate of the CBA and polymer is extremely high. For example, for PP materials, with a rotational speed of 40 RPM, the temperature will rise from 25 °C to 165 °C within one minute, and the heating rate is above 100°C per minute. This high heating rate will
dramatically increase the heat generated by exothermic CBAs such as AZ3990. In Figure 3-10, it is clearly shown that the temperature jump is higher under a higher heating rate. This was why the system became unstable and was difficult to control when compounding PP with Celogen AZ or PE with Celogen OT.

5.6 Foaming Results and Discussion

During rotational foam molding, the influence of melt compounding on the material selection, foam quality, and expansion ratio was studied. It is believed that the foaming mechanism for compounding based rotofoaming is different from that of the dry blending based foam processing. The foaming mechanism also depends on the compounding quality. When there are air bubbles generated by decomposition in the compounded pellets, the nucleation process is not the same as when pre-decomposition is completely prevented.

5.6.1 Foaming with Non-Decomposed Pellets

When pellets without pre-decomposition are rotofoamed, only the dispersed CBA particles can be the source of cell nucleation. When tumbling in the mold while being heated, the pellets begin to sinter with each other. Although some CBA particles may decompose during this period, all the generated gas is entrapped in the polymer matrix and the amount of gas lost is very small. It should be noted that the cell nucleation rate is determined by the decomposition rate and dispersion of CBAs. Since the cell distribution depends entirely on the position of CBA particles, the effect of the mixing quality is more important. The striation thickness of the polymer and CBAs, i.e., the average distance between CBA particles in the polymer matrix, is much smaller in the compounding based process than the average distance between the entrapped air bubbles in the dry blending
based foaming process. As a result, the nuclei density is higher, and therefore, a finer and more uniform structure is expected from the compounding based processing. However, if the nucleated cells coalesce during the cell growth stage in the rotational foam molding, the final cell density of the foams will be lower. Therefore, the cell morphology of the rotomolded foams obtained in the compounding based foam processing may be governed by the degree of cell coalescence.

When the nucleated cells grow, the volume of each pellet increases and this volume expansion of pellets enhances the sintering behavior of the pellets in rotomolding. Although the normal plastic pellets without any blowing agent do not sinter well even for the high MFR materials according to our experiments, the sintering behavior of the foamable pellets is outstanding because of the soft foam structure and expanding behavior of the pellets. Unlike the expanded PS or PP bead processing [38], no welding lines were observed between the expanded pellets.

Figure 5-4 shows the comparison of the results from the dry blending method and those from the compounding method for three different materials of MT4390, SD812, and PF633.

For MT4390 (Figure 5-4 (a)), no improvement was found. Because the sintering ability of MT4390 is relatively good in the dry blending method, there was not much difference between the foam structures obtained in the dry blending technology and compounding technology. Since it was expected that the nuclei density would be higher for the compounding based technology, cell coalescence during foaming must have occurred to a certain degree. Further study is required to understand the cell coalescence behavior during rotational foam molding in the compounding based method.
In addition, because of the reduced thermal conductivity when pellets are used for rotational molding, the processing time is increased. For example, in the experiments of three-fold expansion of PF633 (with 1.4% 50 AZ/50 ZnO), it took 17 minutes to develop a fully expanded structure with the dry blending based method, but it took 21 minutes when compounded pellets were used. As a result, the compounded pellet sample as a whole tended to be overheated and the cell structure was poor as shown in Figure 5-5. The average cell size was 531 μm in dry blending based foams and 539 μm in compounding based foams. The cell population density was 26184/cm³ and 26176/cm³, respectively.

Figure 5-4 (b) presents the foam morphologies of the high melt strength (HMS) PP, SD812 (Montell), with a MFR of 16. SD 812 has long chain branching in the polymer structure and has a high melt strength according to the manufacturer of the resin. Because of its high melt strength, the degree of cell coalescence with SD812 was expected to be low during foam processing. Furthermore, because of the higher MFR of this material, the viscosity was lower and the sintering behavior of the plastic powders was adequate for producing a fine cell structure with the dry blending based method. When the compounding method was used, a finer cell structure was obtained (see Figure 5.4 (b)). This implies that the bubble nucleation behavior with the compounding method for SD812 was better than that with the dry blending based method, as expected. After the compounding process, the nucleation was governed only by the decomposition behavior of the chemical blowing agent, and polymer viscosity had relatively little influence on nucleation. The improved mixing quality of the chemical blowing agent particles in the polymer matrix also played an important role. The advantage of the compounding method over the dry blending method was evident using this HMS PP material.
The advantage of the compounding method was more distinct when HMS PP PF633 with a very low MFR of 3-6 g/10 min was tested. From Figure 5-4 (c), it can be seen that a fully expanded foam structure was not obtained in the dry blending case using PF633. Because of the high viscosity of the material, the sintering process was too slow to form a molten polymer matrix and to isolate the CBA particles before the decomposition of the blowing agents. As a result, most of the gases escaped through the connected air channels that were formed due to poor sintering. Because of the small amount of gas left, foams with very low expansion were obtained. On the other hand, after compounding, the chemical blowing agent particles were well isolated in the polymer matrix, and very little gas was lost. Consequently, a uniform fine-cell foam structure was achieved. The experiments with PF633 indicate that the appropriate range of MFR of PP materials for rotational foam molding is much wider in compounding-based processing.

The hypothesis that the melt strength of PP materials dominates the foam quality in the compounding based rotational foam molding process was further verified by the experimental results of six-fold expansion. Figures 5-6 gives the comparison between six-fold expansion foams of SD812 and PF633. With the complete removal of pre-decomposition, the problems related to poor sintering and the resultant nucleation behavior in the dry blending method have been eliminated in the compounding method. The properties of the material govern the foaming: a higher melt strength resulted in a smaller cell size and improved cell distribution by preventing cell coalescence.
5.6.2 Foaming with Pre-decomposed Pellets

During the compounding process, some extrudates were observed to have slight pre-decomposition of CBAs. Foaming experiments were conducted with the pellets that had micropores induced by the premature decomposition of CBAs.

When pellets with micropores generated by pre-decomposition were roto foamed, the quality of PE foams was improved dramatically compared to the results from dry blending based processes. The average cell size was reduced dramatically and the cell distribution was much better. On the other hand, no good foam structure could be obtained from the compounded PP pellets with micropores. Only large hollow structures were produced.

A hot stage optical microscope analysis (see Figure 5-7) was used to explain the different result from PE foaming and PP foaming. In Figure 5-7 (a), it can be seen that a large number of tiny bubbles exist in the PE matrix. They are very fine and uniformly distributed. On the contrary, the bubbles from pre-decomposed CBA in PP pellets are few in number and are poorly distributed as shown in Figure 5-7 (b).

To further understand how the bubbles in the compounded pellets affect the foaming process, more hot stage optical microscope observations were conducted on PE pellets. A sample of LLDPE 8556 with 3% OT was placed on the hot stage and heated from 100°C to 200°C with a heating rate of 10 °C/min. A picture of the morphology of the sample was taken whenever a significant change was observed. The stage temperatures were also recorded. Figure 5-8 shows the bubble formation procedure at each temperature measured from the optical microscope. From the figure, it can be seen that when the temperature was below 157 °C, no decomposition occurred and only pure cell growth could be found. Above 157 °C, decomposition started and the cells began to move because of
volume expansion. At 162°C, the decomposition reached its peak and the movement was so large that it was difficult to focus. After 168°C, the cells growth dominated the process again. When then temperature reached 180°C the cell coalescence was so severe that the cell size and population density decreased dramatically.

From these observations, we found that the bubbles formed from pre-decomposition worked as nuclei in the compounding based rotational foaming method. Those bubbles generated from the later decomposition in rotomolding diffused into these existing cells and became the source of growth of these cells.

For the sample of LLDPE8556 with Celogen OT, the population density of bubbles from pre-decomposition is very high and results in a foam structure of high cell population density. For PP pellets of MT4390 with Celogen AZ 3990, the extremely large cells and low population density from pre-decomposition govern the nucleation and lead to unacceptable structures.

5.6.3 Effect of the Oven Temperature on Cell Morphology

When foams of a larger expansion ratio such as six-fold expansion are to be developed, the cell wall is thinner because there is less polymer material and more gas to fill the cavity compared to the three-fold expanded foam processing. The thin wall makes the cell coalescence phenomenon more sensitive to the processing conditions, especially the temperature factors. It was found that the oven temperature is one of the most important parameters that determine the cell morphology of the foams.

Although nucleation of cells can be improved significantly using the compounding technique, the cell structure of PP foams may not be good because of cell coalescence if the temperature is too high, or the processing time is too long. Especially when an exothermic
blowing agent such as Celogen AZ 3990 was used, a high heating rate or high oven temperature was observed to be detrimental to the foam structure in our previous study of the dry blending based technology. As in the case of the dry blending method, we found that a high oven temperature induced a high heating rate and the decomposition heat under such a high heating rate increased the temperature of the neighboring area and promoted cell coalescence in the compounding method. As a result, large cells and a low cell population density were developed under a high oven temperature. Figure 5-9 shows the effect of varying the oven temperature on the six-fold expanded PP foams.
Chapter 6

Formation of an Unfoamed Skin

6.1 Introduction

As mentioned in Chapter 1, a dual layer structure with a foamed core and an unfoamed skin can be developed in rotational molding. Some current techniques use a two-step procedure. After the skin is formed, the foam materials are charged into the cavity and roto foamed again. Uniroyal Chemical developed a method using a drop box structure (Figure 1-6) [27]. With such a method, a foamable composition consisting of a blowing agent and polymer powders is put into a box in the center of the mold. The box opens at a certain time and the foamable composition drops into the mold and develops a foam structure. This two-shot technique has two drawbacks, however. For devices such as a drop box, special considerations have to be given to the mold design, which may be difficult for a complicated structure with thin walls. Moreover, the low production rate makes them inefficient for industrial applications.

In the research that this thesis is based on, for the first time an unfoamed skin layer was produced in rotational molding of PP foams with one shot. The concept of this new dual layer manufacturing technology was verified through a series of experiments. The effect of major processing parameters was investigated in the research, and the feasibility of the technology has been proven. However, the research is still in its preliminary stages, and a systematic study is required to identify the effects of materials and processing parameters on the formed skin and foam structures. It should be noted that by forming a skin, the
optimum processing parameters in the compounding based rotational foam molding technology will be different from those in the processing with no skin.

In previous chapters, the research efforts were focused on the producing of fine-cell foams to be filled in the core of rotomolded products. The investigation on skin formation will be described in detail in Chapter 6.

6.2 Overall Process

It is well recognized that during normal rotational molding, particles of different sizes tend to form layers [1]. Because of the tumbling effect and the vibration when the mold rotates, finer particles will be filtered down to the mold surface and coarser materials will rise to the top. As a result, if particles of two different sizes are used, two layers of material will be formed before the melt starts. In this one-shot method, materials used for the skin should be in a fine powder form so that they can move to the mold surface area. The material for the foam core should be in a big pellet or granulate form in order to delay the melting and foaming. The smaller particles that are closer to the mold surface will be heated first and melt first. Ideally, they will form a uniform layer of polymer melt before the pellets begin to melt. Through this method, a skin-core structure can be obtained in one shot. It is expected that the more dramatic the difference between the sintering ability of the skin and core materials, the more distinct the layer will be.

6.3 Experimentation

6.3.1 Experimental Setup

The rotational molding machine shown in Figure 4-3 was used in the experiments on skin formation. The pellets used were generated from the compounding system shown in Figure 5-1.
6.3.2 Materials

Two materials with a high and low MFR were used to produce the foam core: SD812 (MFR 16) and PF633 (MFR 3-6). For the skin, an extrusion coating grade PP material of SC1355 (MFR 18) was chosen. In order to investigate the effect of material viscosity of the skin material, SC873 (MFR50), a material with a very low viscosity, was also tested for the purpose of skin formation.

6.3.3 Procedures

Compounding

In addition to the temperature settings and rotational speed of the screws, the feeding speed of the pelletizer and the diameter of the die exit should also be controlled, because it is believed that the size of the pellets plays a role in determining the skin quality. The feeding speed should be limited so that the diameter of the extrudate is not too thin due to the extensional force applied on the polymer melt. If necessary, the diameter of the die should be enlarged.

Roto Molding

First, a specified amount of powder and pellets were charged into the mold separately. The amount of materials added was determined by the designated expansion ratio and skin thickness. For the cylindrical mold used in the experiment, the amount of skin material, $m_{skin}$, was determined by
Chapter 6 Formation of an Unfoamed Skin

\[ m_{\text{skin}} = \frac{\pi L \rho_{\text{skin}}}{4} \left[ d^2 - (d - 2h_{\text{skin}})^2 \right], \quad (6-1) \]

where \( L \) is the length of the mold, \( h \) is the thickness of the skin, \( d \) is the diameter of the mold, and \( \rho_{\text{skin}} \) is the density of the skin material. For the pellets used for the foaming purpose, the amount was determined by following equation:

\[ m_{\text{pellet}} = m_{\text{polymer}} + m_{\text{CBA}} = \frac{V}{\Phi} \rho_{\text{pellet}} + \frac{\Phi - 1}{\Phi} \frac{V}{\varphi}, \quad (6-2) \]

where

- \( m_{\text{pellet}} \) = weight of pellets needed, g
- \( m_{\text{polymer}} \) = weight of pure polymer material used, g
- \( m_{\text{CBA}} \) = weight of blowing agent, g
- \( V \) = total volume of the mold, cm\(^3\)
- \( \Phi \) = expansion ratio, and
- \( \varphi \) = gas yield of blowing agent cm\(^3\)/g

Since the rotational molding machine in Figure 4-3 can only rotate along one axis, the mold was shaken along the longitudinal direction in order to achieve a uniform distribution of material. The mold was then mounted on the shaft driven by the motor and turned. The motor was run for 10 minutes at 20 RPM to separate the powder and pellets before they were heated. After 10 minutes, the rotational speed was reduced to the normal rotational molding level of 5 RPM for these experiments, and the rotating mold was inserted in the pre-heated oven. The mold was left to rotate in the oven until the designated time lapsed. The mold is then pulled out and cooled in the running tap water. Once the mold was cooled, the sample was taken out and cut. The cross section of the resulting foam was investigated.
6.4 Results and Discussion

During the experiments, several factors were investigated, including the oven temperature, the pellet size, and the relative amount of skin material to core material. In Table 6-1, a detailed description of the experimental conditions and results is given.

6.4.1 Effect of the Relative Amount of Powder and Pellets

When too much material was added to the mold, no obvious skin was formed (see Figure 6-1, Tables 6-1 to 6-4). The more material in the mold, the more difficult it was for the powders to travel to the surface, in turn making it more difficult for the skin to form. The skin should be thick enough so that the molten skin layer has adequate strength and pellets can be restricted inside this layer and not penetrate to the surface (see Figure 6-1 (b)).

6.4.2 Effect of Oven Temperature

Based on the analysis described in Chapters 4 and 5, the higher the oven temperature, the more distinct the effect of thermal lag when larger particles such as pellets are used. As a result, in the skin formation process, the time difference between the melting of the skin material and the foaming of the pellets is increased. The effect was helpful in achieving a more distinct skin layer as shown in Figure 6-2. In addition, we expect that the oven temperature should be higher than the optimum oven temperature used in the pure compounding based rotofoaming process without any skin layer. This is due to the fact that the formed skin layer will retard the heat transfer. However, it should also be noted that the oven temperature should be limited. Otherwise, the exothermic effect of the blowing agent will cause severe cell coalescence (see Sections 4.5 and 5.5)
6.4.3 Effect of Material Viscosity

In Figure 6-3, the effect of material viscosity on the skin structure is shown. When SC873 (MFR 50), a material with an extremely low viscosity was used, no distinct skin was formed. From the experimental results in Figure 6-3 (b), we can see that the skin was formed initially during the process. However, due to the low viscosity of SC873, the pellets penetrated into the skin layer after foaming and expansion started. In the end, the formed skin layer was destroyed. When SC1355 (MFR18) was used, the relatively high viscosity made the skin stronger and a clear skin was maintained (Figure 6-3(a)). Another reason for having a higher viscosity material in the skin is the mechanical properties; a higher viscosity material exhibits better mechanical properties and it would be desirable to have stronger physical properties of the skin in the foam products. However, use of a high viscous powder material in the skin might cause poor sintering of powders which may affect the mechanical properties and aesthetic aspect the final product. Therefore, the viscosity of the skin material should be carefully selected within a specific range. A further study is required to determine the proper viscosity range for the skin layer.

6.4.4 Effect of Pellet Size

In Figure 6-4, it can be clearly seen that the skin is more distinct for the sample made from larger-sized pellets. The reason for this difference lies in the fact that when the pellet size is increased, the thermal conductivity and sintering behavior of the pellets become worse, leading to a delay in the foam formation. The delay allows a sufficient time for the plastic powders to form a uniform layer. But when the processing time is too long, then the skin temperature is too high and it becomes soft enough to be penetrated by foamed pellets.
Therefore, the pellet size also plays a role in determining the skin quality. However, the pellet size has to be kept within a specific range. Otherwise, it will be difficult for the pellets to reach corners or tips of some complicated structures and a void section will be developed. A further study is required to determine the proper pellet size range for the skin layer.

6.5 Concluding Remarks

The feasibility of forming an unfoamed integral skin layer for the roto-molded PP foam products has been successfully demonstrated. The effects of the skin material parameters and processing parameters on the skin layer quality and foam structure were investigated. Several critical parameters that affect the skin layer quality have been identified. It was observed that the optimum ranges of the processing parameters in the compounding based technology have been changed because of the formed skin layer with a high thermal inertia.

Although the skin layer formation was well demonstrated, the achieved foam structures were not satisfactory. A systematic further study is required to investigate the effects of processing parameters on the foam structure with the skin layer.
Chapter 7

Conclusions and Recommendations for Future Work

7.1 Conclusions on Dry Blending Based Technology

During the research upon which this thesis is based, fine cell foams with an expansion ratio up to six-fold were successfully developed for both PE and PP using a dry blending based rotational foam molding process.

Based on a fundamental investigation of the dry blending based foaming process in rotational molding, the following conclusions can be drawn:

1. Sintering Mechanism. The nucleation mechanism is determined by the sintering behavior of the polymer powder particles. If the entrapped air pockets can be completely removed in a well-sintered polymer matrix, the nuclei will be the decomposed chemical blowing agent particles. Therefore, the cell distribution and population density is determined only by the distribution of the CBA particles. However, it was experimentally verified that most materials could not show such a perfect sintering behavior. When entrapped air pockets are formed during sintering, these cavities will dominate the nucleation and cell growth. If the formed cavities are separated from each other by good sintering of polymer powders before the onset of CBA decomposition, then the isolated cavities become cell nuclei and the gas generated from the decomposed CBA will promote growth of these cavities. If the formed cavities are not separated from each other because of inadequate sintering before the onset of CBA decomposition, the connected cavities will form large cells and/or will form channels for gas to escape, resulting in
poor expansion. Therefore, the polymer material should be well sintered before the decomposition of the CBA.

2. **Material selection.** Material selection is critical to the foam quality especially when foams of a large expansion ratio are to be developed.

   (a) Due to the importance of the sintering ability of the polymer material, materials with a large zero-shear viscosity or a high MFR are desirable. However, to maintain high melt strength, the MFR should not be too high. Otherwise, cell coalescence and cell coarsening will occur.

   (b) The particle size of the polymer powders should be as small as possible. With smaller particles, better sintering can be obtained and fewer air pockets will develop. With reduced number of air pockets, cell nucleation is more controllable and the cell structure can be improved.

   (c) The shape of the plastic powder particles is also an important element to be considered when dealing with raw plastic materials. Long tail structures should be reduced to improve the sintering ability. Good powder shapes will reduce problems that are related to sintering.

3. **CBA Selection.** Many other factors have to be considered when selecting CBAs and some conclusions have been drawn about the decomposition characteristics of CBAs. Some guidelines on the selection of CBAs have also been made:

   (a) The decomposition behavior of the chemical blowing agent is essential to the foam quality. Since an early decomposition will lead to poor sintering and late decomposition will cause a weak polymer melt strength at high temperature, it is desirable that the CBA decompose as soon as the sintering is finished. Additives such as ZnO can successfully control the decomposition temperature. Therefore a
Chapter 7 Conclusions and Future Work Recommendations

proper amount of such additives should be determined according to the rheological properties of the particular material used in the process.

(b) The CBA material should have a quick decomposition rate so that nucleation and cell growth can start uniformly within the polymer matrix.

(c) An endothermic CBA is preferred if other decomposition characteristics can satisfy the processing requirements. Due to the local heating effect caused by the heat generated from the decomposition, exothermic CBAs tend to decrease the melt strength.

(d) The CBA particle size does not play a large role in determining the cell morphology in dry blending based technology. Since the sintering ability governs the nucleation and cell growth, the effect of CBA particle size is negligible when the dry blending method is applied.

4. **Oven temperature.** The oven temperature is another important parameter that affects the final foam structure. A high oven temperature will result in a high heating rate, which will accelerate the decomposition of exothermic CBA. If the decomposition occurs before the sintering of powders, poor foam cells will be generated. On the other hand, a low oven temperature will cause a "balling phenomenon" that will reduce the uniformity of the material and cell distribution. Therefore, a proper oven temperature is essential to the foaming process.

7.2 **Conclusions on Compounding Based Technology**

Very fine cell foams were successfully produced using compounding based rotational foam molding. The following conclusions can be made:
1. *Nucleation Mechanism.* Cell nucleation in the compounding based foaming technology is dominated by the distribution and decomposition behavior of the chemical blowing agents. Compared to the dry blending based technology, the zero-shear viscosity of polymer materials has a relatively lower effect on cell nucleation when the compounding technology is used. Therefore, to get a large cell population density and uniformly distributed cells, the polymer and CBAs should be well mixed initially.

2. *Plastic material selection.* The melt strength of the PP materials is another important factor in the compounding based foaming process. The degree of cell coalescence will determine the final cell density. Therefore, materials of high melt strength are desirable if a fine cell structure is expected. In addition, a foam structure with large volume expansion can be achieved when high melt strength materials are used. Since most PP and PE materials can be foamed through melt compounding based technology, the application of rotational molding is extended to a larger range of materials.

3. *CBAs.* The endothermic and exothermic characteristics of the CBAs affect the compounding quality. An exothermic CBA will lead to an unstable mixing system temperature and may cause uncontrollable pre-decomposition in the compounding process. The high heating rate involved in the extrusion process makes this heat more severe. On the other hand, the decomposition temperature should not be too high in order to maintain a high melt strength of polymer. Therefore, the properties of CBA materials are important in determining the cell quality.

4. *Compounding Parameters.* Careful attention should be paid to the processing parameters of the compounding process. The processing temperature and the
extrusion speed (flow rate of polymer) are key factors of the process. The temperature should be above the melting temperature and below the decomposition temperature. Within this range, the temperature should be as low as possible. The rotational speed of the extrusion screw should be high enough to improve the mixing quality and reduce the residence time. It should also be as low as possible to prevent the decomposition caused by the local heat generated by viscous heating.

5. **Pre-decomposition.** Preliminary conclusions have been made on the effect of pre-decomposition in the compounding process. It is believed that air bubbles generated from pre-decomposition act as nuclei. Therefore, the distribution and cell population density of the bubbles generated from pre-decomposition determine the final foam quality. In a high pressure and high shear environment, it is easier to achieve a high population density if the melt strength of the polymer is adequate, as shown by the dramatic improvement in cell structure in our experiments. However, nuclei bubbles should not be generated by partial decomposition of the during compounding. There is no way to control how much CBA should be decomposed in the compounding process and how much should be left for the roto molding process. When a small percentage of CBA decomposes in compounding, very few bubbles will be generated, and therefore, the population density of nuclei for the roto foaming will be very low. As a result, the cell population density of the foam will be low. On the other hand, if a large percentage of CBA decomposes in compounding, there will not be enough amounts CBA left for the gas needed for cell growth in the roto molding process. Therefore, pre-decomposition should be avoided.
6. **Rotational Molding Parameters.** Processing time, oven temperature, and the amount of CBA used are as important as in dry blending based processes. Proper selection of these factors is critical to the foam structure.

7. **Conclusions on Skin Formation**

1. **Material Selection.** The skin material should have an appropriate viscosity so that the skin material is strong enough to prevent the foamed pellets from penetrating the skin layer and destroying the skin. On the other hand, the viscosity of skin material should be low enough to reduce the size of the entrapped air pockets in the skin layer.

2. **Amount of material.** The amount of material used should be determined based on the desired skin thickness. But if too much material is charged into the mold it will be difficult for the skin material, which is in a powder form, to travel to the surface to form the skin layer. As a result no distinct skin layer will be formed.

3. **Pellet Size.** The pellets used for the core should not be too small. The particle size difference between the powder for the skin and the pellets for the core plays an important role in differentiating the thermal conductivity and the sintering time. However, it is more difficult for larger pellets to travel to tips and corners, resulting in voids or large cells at these places. Therefore, the pellet size should be within a certain range.

4. **Oven Temperature.** A proper oven temperature should be chosen to improve the distinction between the skin and core according to the size and shape of the mold used (For example, 350 °C was the optimum for the mold in this research). But it
Chapter 7 Conclusions and Future Work Recommendations

should be noted that the oven temperature variations should remain in a reasonable range so that foam quality can be maintained.

7.4 Suggestions for Future Work

Based on the results achieved during the present research project and considering the problems that have been encountered, the following suggestions are made for future work:

(1) Although preliminary conclusions have been reached on the effect of pre-decomposition, further investigation using a hot stage microscope is necessary.

(2) Pre-decomposition can be introduced into the compounding process to generate bubble nuclei before the rotational molding. When tiny cells with an extremely large cell population density produced in the compounded pellets act as cell nuclei during foaming in roto-molding, a very fine cell structure can be expected according to the conclusions presented in Chapter 5. Two potential methods can be applied:

(a) Two CBAs with different decomposition temperatures can be used. The one with a lower decomposition temperature can be used to produce a micropore structure in compounding extrusion. The CBA with a higher decomposition temperature can be used to induce cell growth in the later rotational foam molding process.

(b) A physical blowing agent such as CO₂ can be used as a substitute for the first blowing agent in the compounding stage.

(3) A systematic study on the mechanism of skin formation should be carried out to identify the effect of material and processing parameters on the formed skin and foamed structure.
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### Table 1-1 Density of Different Grades of PE

<table>
<thead>
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<th>Category</th>
<th>Density (g/cc)</th>
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<td>Linear Low Density PE (LLDPE)</td>
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### Table 3-1 Polyethylene Materials

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<th>MFR (g/10 min.)</th>
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<td>Nova</td>
</tr>
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<td>LL8361</td>
<td>5.2</td>
<td>Nova</td>
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### Table 3-2 Polypropylene Materials

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<td>Montell</td>
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<tr>
<td>PF633</td>
<td>3.6</td>
<td>Montell</td>
</tr>
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<td>Quantum</td>
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<tr>
<td>SD812</td>
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<td>SD242</td>
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<tr>
<td>SC873</td>
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<td>Montell</td>
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### Table 3-3 Chemical Blowing Agents Used in the Experiments

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<td>ADC/F</td>
<td>204.37</td>
<td>Exothermic</td>
<td>Bayers</td>
</tr>
<tr>
<td>ADC/F-C2</td>
<td>206.30</td>
<td>Exothermic</td>
<td>Bayers</td>
</tr>
<tr>
<td>Sodium Bicarbonate</td>
<td>133.35</td>
<td>Endothermic</td>
<td>Exxon</td>
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<tr>
<td>Celogen OT</td>
<td>165.80</td>
<td>Exothermic</td>
<td>Uniroyal Chemical</td>
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<tr>
<td>Hydrocerol</td>
<td>149.48</td>
<td>Endothermic</td>
<td>BI Chemical</td>
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Table 5-1 Processing Parameters and Results

<table>
<thead>
<tr>
<th>Zones</th>
<th>Feeding</th>
<th>Compressing</th>
<th>Metering</th>
<th>Die Adapter</th>
<th>Die</th>
<th>Screw Speed (RPM)</th>
<th>Result</th>
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</thead>
<tbody>
<tr>
<td>MT4390 + AZ 3990</td>
<td>140</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>165</td>
<td>10</td>
<td>Pre-decomposition</td>
</tr>
<tr>
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<td></td>
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<td>Little Decomposition</td>
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<td>30</td>
<td>No Decomposition</td>
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<td>40</td>
<td>No Decomposition</td>
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<tr>
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<td></td>
<td></td>
<td>50</td>
<td>Pre-decomposition</td>
</tr>
<tr>
<td>LLDPE 8556 + OT</td>
<td>120</td>
<td>130</td>
<td>130</td>
<td>130</td>
<td>130</td>
<td>10</td>
<td>Pre-decomposition</td>
</tr>
<tr>
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<td></td>
<td>20</td>
<td>Pre-decomposition</td>
</tr>
<tr>
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<td>Pre-decomposition</td>
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<td></td>
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<td>Pre-decomposition</td>
</tr>
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<td>50</td>
<td>Pre-decomposition</td>
</tr>
<tr>
<td>LLDPE 8556 + SB</td>
<td>120</td>
<td>130</td>
<td>130</td>
<td>130</td>
<td>130</td>
<td>10</td>
<td>Pre-decomposition</td>
</tr>
<tr>
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<td>20</td>
<td>No decomposition</td>
</tr>
<tr>
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<td>No decomposition</td>
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<td>No decomposition</td>
</tr>
<tr>
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<td></td>
<td>50</td>
<td>Some Pre-decomposition</td>
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</tbody>
</table>
Table 6-1 Effect of Material Amount

<table>
<thead>
<tr>
<th>Skin</th>
<th>Foam</th>
<th>Heating Time (min)</th>
<th>T_{oven}(°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1355 (10 g)</td>
<td>PF633+1.25% AZ(25 g)</td>
<td>17</td>
<td>325</td>
<td>Fine foam structure, no clear skin</td>
</tr>
<tr>
<td>SC1355 (10 g)</td>
<td>PF633+3% AZ(15 g)</td>
<td>17</td>
<td>325</td>
<td>Fine foam structure, no clear skin</td>
</tr>
<tr>
<td>SC1355 (15 g)</td>
<td>PF633+3% AZ(10 g)</td>
<td>18</td>
<td>325</td>
<td>Coarse foam cell, distinct skin</td>
</tr>
<tr>
<td>SC1355 (15 g)</td>
<td>PF633+1.25% AZ(20 g)</td>
<td>17</td>
<td>325</td>
<td>Fine foam structure, no clear skin</td>
</tr>
</tbody>
</table>

Table 6-2 Effect of Material Viscosity

<table>
<thead>
<tr>
<th>Skin</th>
<th>Foam</th>
<th>Heating Time (min)</th>
<th>T_{oven}(°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1355 (15 g)-MFR18</td>
<td>PF633+3% AZ(15 g)</td>
<td>13</td>
<td>325</td>
<td>Distinct skin formed, no decomposition starts</td>
</tr>
<tr>
<td>SC1355 (15 g)-MFR18</td>
<td>PF633+3% AZ(15 g)</td>
<td>14</td>
<td>325</td>
<td>Skin is destroyed</td>
</tr>
<tr>
<td>SC1355 (15 g)-MFR18</td>
<td>PF633+3% AZ(15 g)</td>
<td>18</td>
<td>325</td>
<td>No distinct skin obtained</td>
</tr>
<tr>
<td>SC1355 (15 g)-MFR18</td>
<td>PF633+3% AZ(15 g)</td>
<td>18</td>
<td>325</td>
<td>Distinct skin</td>
</tr>
<tr>
<td>SC873 (15 g)-MFR50</td>
<td>PF633+3% AZ(15 g)</td>
<td>18</td>
<td>325</td>
<td>No obvious skin</td>
</tr>
</tbody>
</table>

Table 6-3 Effect of Oven Temperature

<table>
<thead>
<tr>
<th>Skin</th>
<th>Foam</th>
<th>Heating Time (min)</th>
<th>T_{oven}(°C)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1355 (15 g)</td>
<td>PF633+3% AZ(15 g)</td>
<td>34</td>
<td>250</td>
<td>Fine foam structure, no clear skin</td>
</tr>
<tr>
<td>SC1355 (15 g)</td>
<td>PF633+3% AZ(10 g)</td>
<td>18</td>
<td>325</td>
<td>Clearer skin layer</td>
</tr>
<tr>
<td>SC1355 (15 g)</td>
<td>PF633+3% AZ(10 g)</td>
<td>16</td>
<td>350</td>
<td>Very distinct layer, fine foam cells</td>
</tr>
</tbody>
</table>

Table 6-4 Effect of Pellet Size \( (T_{oven}=325°C) \)

<table>
<thead>
<tr>
<th>Skin</th>
<th>Foam</th>
<th>Heating Time (min)</th>
<th>Pellet Size</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1355 (15 g)</td>
<td>PF633+3% AZ(15 g)</td>
<td>18</td>
<td>Small</td>
<td>No distinct skin is formed</td>
</tr>
<tr>
<td>SC1355 (15 g)</td>
<td>PF633+3% AZ(10 g)</td>
<td>18</td>
<td>Large</td>
<td>Clearer skin layer formed</td>
</tr>
</tbody>
</table>
Figure 1-1 Schematic of Rotational Molding Process

Figure 1-2 Sintering in Rotational Molding
Figure 1-3 Examples of Rotational Molding Machine
(Courtesy of Crawford [1])

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(b) Exothermic Effect

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(b) Pressure Increase Rate (After Klemmper and Frisch [13])

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(a) Cylinder Drum Mixer

(b) Cylinder Drum Mixer

Figure 2-4 Cylinder Drum Mixer
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Figure 2-6 Blender with Deflectors

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(b) Effect of Temperature on Viscosity
   (Testing Sample: SC873 (MFR50))

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(Illustration Courtesy of TA Instrument)

Figure 3-5 Schematic of DSC Module
(Illustration Courtesy of TA Instrument)
Figure 3-6 DSC Thermograms of PE Materials
Figure 3-7 DSC Thermograms of PP Materials
Figure 3-7 DSC Thermograms of PP Materials (cont'd)

(c) SD242

(d) MT4390
Figure 3-7 DSC Analysis of PP Materials (cont'd)
Figure 3-8 TA 2050 Thermogravimetric Analyzer
Figure 3-9 DSC Analysis of CBA Decomposition
Sample: ADC/F
Size: 3.9000 mg
Method: hr 10 fast

Operator: F. Liu
Run Date: 11-Mar-98 22:39

---

Sample: Celogen OT
Size: 10.0000 mg
Method: hr 10 fast
Comment: hr10

Figure 3-9 DSC Analysis of CBA Decomposition (cont'd)
(c) Hydrocerol Compound

(f) Sodium Bicarbonate

Figure 3-9 DSC Analysis of CBA Decomposition (cont'd)
Figure 3-10 Effect of Heating Rate on DSC Thermogram of CBAs
Figure 3-11 TGA Analysis of CBA Decomposition Behaviors
Figure 3-11 TGA Analysis of CBA Decomposition Behaviors (cont'd)
(e) Celogen OT

(f) Sodium Bicarbonate
Figure 3-12 Effect of Heating Rate on the Decomposition Behavior

Figure 3-13 Effect of ZnO on Decomposition of Celogen AZ3990 (Heating Rate 10 °C/min)
Figure 3-14 Effect of CBA Particle Size on Decomposition of ADC Series CBA (Heating Rate: 10 °C/min)

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(Illustration Courtesy of Crawford [1])

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Figure 4-9 Cross Sections of Sintered Samples of SD242 (MFR30) + 3% Celogen AZ 3990 (Six-fold)

Figure 4-10 Cross Sections of Sintered Samples of MT4390 (MFR 20) + 3% Celogen AZ 3990 (Six-fold)
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(SD812 + 0.625% AZ3990 + 0.625% ZnO, Three-Fold, Scale 1:1)

(a) Particle size 1.5 mm  (b) Particle size 0.4 mm

Figure 4-14 Effect of Long tails on Cell Morphology
(SD812 + 0.625% AZ3990 + 0.625% ZnO, Three-Fold, Scale 1:1)

(a) From particles with Long Tails  (b) From particles without Long Tails

Figure 4-15 Effect of CBAs on the Cell Morphology of PE Foams

(a) LL8556+OT (Six-fold)  (b) LL8556 + SB (Six-fold)
Figure 4-16 Effect of CBA Particle Size on the Cell Morphology (Scale 1:1) of SD812 Foams in the Dry Blending Method

(a) ADC/M-C1 (4.5 μm)  (b) ADC/FC (15.5 μm)

Figure 4-17 Effect of ZnO on the Cell Morphology of MT4390 Foams

(a) 1.0% AZ  (b) 1.0% AZ + 1.0% ZnO
Figure 4-18 Effect of CBA Amount on Cell Morphology of Three-Fold Expanded MT4390 Foams
(AZ = Celogen AZ3990)
Figure 4-19 Effect of CBA Amount on the Cell Size, Cell Population Density and Volume Expansion Ratio of MT4390 Foams
Figure 4-20 Effect of Processing Time on Cell Morphology of MT4390 Foams
(MT4390 + 0.625% AZ3990 + 0.625% ZnO, Three-Fold)
Figure 4-21 Effect of Processing Time on the Cell Size, Cell Population Density and Volume Expansion Ratio
(MT4390 + 0.625% AZ3990 + 0.625% ZnO, Three-Fold)
Figure 4-22 Effect of Oven Temperature on the Cell Morphology
(SD242 + 3% AZ3990, Six-fold, Scale 1:1)

Figure 4-23 Self Heating Behavior of Exothermic CBAs
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Figure 5-2 Schematic of Heat Exchange in Extrusion (Courtesy of Stevens [23])

Figure 5-3 Effect of Residence Time on Decomposition of Celogen AZ3990
Figure 5-4 Comparison of the Cell Morphologies Obtained from the Dry Blending and Compounding Methods (Three-fold Expansion)
Figure 5-5 Comparison of Dry Blending and Compounding (Three-fold Expansion)
Figure 5-6 Comparison of the Cell Morphologies Obtained from the Dry Blending and Compounding Methods. The Foams Were to be Expanded Six-fold. (Scale 1:1)
(a) MT4390 (PP) + 1% AZ3990

(b) LLDPE 8556 + 3% Celogen OT

Figure 5-7 Comparison of Compounded Pellets of PP and PE
(Size of Sample: 2.0 mm x 1.5 mm)
Figure 5-8 Foaming Process of Pre-decomposed Pellets
(LLDPE 8556 + 3% Celogen OT, Size of Sample: 2.0 x 1.5 mm)
Figure 5-9 Effect of Oven Temperature on Cell Morphology
(PF633 + 2.5% AZ3990, Six-fold expansion, Scale: 1:1)
Figure 6-1 Effect of Material Amount (Scale 1:1)

(a) Skin: 10 g SC1355
     Foam: 15g PF633 + 3% AZ3990

(b) Skin: 15 g SC1355
     Foam: 10g PF633 + 3% AZ3990

Figure 6-2 Effect of Oven Temperature (Scale 1:1)
(Skin: 15g SC1355, Foam: 10g PF633 + AZ3990)

(a) 250 °C
(b) 320 °C
(c) 350 °C
Figure 6-3 Effect of Material Viscosity (Scale 1:1)

(a) Skin: SC1355 (MFR16)  
(b) Skin SC873 (MFR50)  
(Skin Formed Initially)  
(c) Skin SC873 (MFR50)  
(Skin Destroyed Later)

Figure 6-4 Effect of Pellet Size (Scale 1:1)  
Oven Temperature 325 °C  
(Skin: 15g SC1355, Foam: PF633 + 3% AZ3990)