ROTATIONAL FOAM MOLDING

OF METALLOCENE CATALYZED POLYETHYLENE

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OF METALLOCENE CATALYZED POLYETHYLENE

By

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ABSTRACT

The foaming process has received increased attention by the rotational molding industry in recent years. The use of metallocene catalyzed polyethylenes for producing a cellular structure is a new development in rotational molding. The objective of this work was to investigate the effects of different chemical blowing agents, resin properties and processing conditions on the structure of foamed metallocene polyethylene and obtain a fundamental understanding of the parameters governing the foam structure and part properties.

An experimental study was conducted to produce metallocene polyethylene foams in dryblending-based rotational foam molding. The physical and cell structure properties of the final foamed parts were examined. The critical processing parameters that optimize the foam structure have been identified through adjustments to the molding conditions.

The foaming performance of exothermic and endothermic chemical blowing agents were examined and it was revealed that selecting an appropriate chemical blowing agent was crucial as the foam structure depends significantly on the properties of the blowing agent. Exothermic blowing agents resulted in greater foam density reduction compared to endothermic blowing agents.

The effect of rheological properties on the foaming process and foam properties was also examined. Rotomolding experiments were performed in monolayer and skin-foam moldings. Observations indicated that the final foam properties were profoundly influenced by the rheological properties of the polymer materials. There was a good correlation between the foam properties produced in both monolayer and two layer moldings. It was discovered that polymer materials with higher extensional viscosity could provide a promising foaming performance at different processing conditions.

The effect of the surface tension of the polymer materials was investigated. It was found that type of reaction of the blowing agent (exothermic/endothermic) and composition of gas generated determine whether the surface tension of the resin contributes to the trend of changes in foam properties.

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Nomenclature

Δ	Change in, Difference in
Ė	Extensional rate
γ̈́	Shear rate

- η Viscosity
- η_e Extensional viscosity
- η_0 Zero-shear viscosity
- $\eta^* \quad \text{Dynamic Viscosity} \quad$
- λ Cross model constant
- π Pi
- ρ Density
- σ Surface tension
- τ Shear stress
- φ Volumetric gas yield

- D Diffusion constant
- d_g Molecular Diameter of the gas
- M_w Molecular weight
- n Power low index
- P Permeation coefficient
- P_e Entrance pressure
- P_i Pressure of the gas inside the bubble
- P₀ Pressure in the surrounding liquid
- Q Flow rate
- r Radius
- R₀ Initial radius of the bubble
- S Solubility coefficient
- T_c Crystallization temperature
- T_{room} Room temperature
- V_c Gas volume at crystallization temperature
- V_{room} Gas volume at room temperature
- V_{foam} Volume of the foam
- V_i Volume of the solid unfoamed plastic
- VER Volume expansion ratio

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Chapter 1

Introduction

1.1 Rotational Molding

Rotational molding, also known as rotomolding, is a plastic processing technology designed for the manufacture of hollow, large-sized and stress-free plastic articles. Rotomolding is a very cost-effective molding method that can be used to produce complex parts with highly structured shapes and details. Nowadays, rotational molding is one of the fastest growing sectors of the polymer processing industry, with an annual growth rate of 12%. It has experienced a major transformation over the past decade with new types of machine control, mold designs and new types of plastics available. The advantages which it offers in terms of economic production have made it a very competitive alternative to blow molding or injection molding [Beall, 1998].

The primary operating principle of rotational molding is comprised of four manufacturing steps [Bellehumeur, 1997]:

- 1. The mold is charged with a pre-measured amount of a pulverized plastic resin.
- The charged mold is closed and subjected to biaxial rotation in a heated environment. As the temperature increases, the powder starts to melt and stick to the hot mold and achieves an even distribution over the mold surface.
- 3. When all of the powder has melted and formed a homogeneous layer on the walls of mold cavity, the mold is transferred to a cooled environment. The biaxial rotation continues until the plastic has solidified.
- 4. The rotation is stopped, the mold is removed from the cooling chamber and the final part is released from the mold.

These four stages are schematically shown in Figure 1.1.

Like all other manufacturing processes, rotational molding has its share of advantages and disadvantages. Rotational molding is a low pressure process that allows the use of light strength molds and machines. Consequently, the lower mold and machine costs allow the production of small quantities of very large or complex parts that would not be economically feasible by other processes. Also this process uses little or no pressure in comparison with other processes and as a result, the molded parts exhibit low levels of molded-in stress. Possibility of molding extremely large objects, excellent thickness uniformity and ability to produce two-color or two-material parts without multiple molds are some other advantages of rotational molding [Crawford, 1996; Beall, 1998].

On the negative side, cycle times in a rotomolding process are long because it requires the heating and cooling of both plastic material and mold. Also, as an open-molding process, there are no cores inside the hollow parts. Surface details and dimensions can







3. Mold Rotation and Cooling





2. Mold Rotation and Heating



4. De-molding

only be controlled on the mold side of the part. Some other disadvantages are limited material choices, high material cost due to pulverization, low production rate and the labor intensive loading/unloading operations [Crawford, 1996; Beall, 1998].

1.2 Rotational Foam Molding

The use of polymer foam products has received increased attention in recent years. This trend has had a strong impact on the rotational molding industry, where the production of foamed polymers has become a progressively important process. The strength-to-weight ratio of foamed materials would be the main reason for the growth of the foam industry. However, these materials possess some unique advantages over traditional non-cellular materials [Throne, 1996].

Plastic foams are mainly characterized by their low specific weight. Rotational foam molding provides a proven method for improvements of the thermal insulation properties and stiffness per unit weight of the part. Foamed plastics can also be used to improve mechanical, insulative and shock migration properties of hollow conventionally rotomolded structures [Aasen, 2001]. Also less warpage has been observed in foamed parts than non-foamed parts [Liu, 2001].

Foam is a disperse system of gas in solid polymer matrix. There are two basic ways of generating the gas phase in the matrix [Crawford, 2002]:

- 1. Physical blowing agents, which can be injected directly into the molten polymer, including hydrocarbons, or atmospheric gases like carbon dioxide and nitrogen.
- 2. Chemical blowing agents, which are thermally unstable and decompose relatively rapidly at a very specific temperature.



Figure 1.2: Rotationally molded foamed parts

Solubility of physical blowing agents in the melt polymer is sensitive to pressure and needs elevated mold pressure. Because of the low mold pressure in rotational molding, physical blowing agents are not appropriate for this application. Chemical blowing agents have been the most common method of generating cellular structure in rotational foam molding. Foams are produced by adding chemical blowing agents to the polymer, either by compounding them into the polymer prior to pelletizing and grinding, or by drymixing with the polymer powder.

Selecting a proper chemical blowing agent is very critical as the final foam structure depends greatly on the properties of the blowing agent. Using both compatible polymer material and chemical blowing agent can provide a unique performance or economic advantage.

In rotational molding different types of foam can be made: monolayer foam and multilayer foam [Beall, 1998]. The monolayer foam can be achieved by rotomolding the blend of required amount of blowing agent and polymer material, using standard processing conditions. Blowing agents decompose over a specific temperature range to release gases and produce the foamed part. Due to coarse the cell structure, the part appearance may be not quite satisfactory. As a result, techniques have been developed to rotationally mold multi-layer structures in which either or both part surfaces are made of compact surfaces (Figure 1.2). The foamed core layer adds rigidity, increases structural strength and reduces raw material costs.

Recently, metallocene catalyzed polyethylenes have been introduced to the rotational foam molding [Archer, 2004]. Metallocene are a new range of polyethylenes which have been found to improve processing and mechanical properties of rotationally molded parts (unfoamed). Due to their narrow molecular weight distribution, metallocene polyethylenes behave differently from conventional polyethylenes. This work was undertaken to study the performance of metallocene polyethylenes for producing foam in rotational molding.

1.3 Research Objectives and Thesis Outline

The present work investigates the use of metallocene catalyzed polyethylenes in the production of cellular rotationally molded parts. The purpose of this work is to characterize appropriate chemical blowing agents for rotationally molded foam applications and study parameters involved in the foaming process and their impact on the final foam properties. The ultimate goal is to identify efficient blowing agents and determine the correlation between the material properties and foam structure.

This thesis is comprised of seven chapters, including this introduction. Chapter 2 presents a literature review on foaming in rotational molding. Chapter 3 summarizes the experimental methods and materials used in this study. A comparative study of the characteristics of various chemical blowing agents in rotational foam molding is presented in Chapter 4. Chapter 4 also deals with the screening of a versatile blowing agent for the foaming process. A detailed experimental study on the effect of rheological properties on the process of foaming and final properties of the foamed parts has been undertaken in Chapter 5. Chapter 6 presents the experimental results on the effect of surface tension and its role in the foaming process. Concluding remarks and suggestions for future work are offered in Chapter 7.

Chapter 2

Literature Review

This chapter presents an overview of literature on the process of rotational molding and foaming in rotational molding. Previous studies in processing, materials, blowing agents and foaming mechanism are discussed.

2.1 The Rotational Molding Process

The rotational molding process and the properties of the rotomolded parts are significantly affected by processing parameters, such as oven temperature, oven time, cooling rate, rotation speed and the ratio of rotational speed between the primary and secondary axes [Kontopoulou, 1999]. The impact strength of the rotomolded part is directly correlated with the inside air temperature in the mold [Crawford, 1992]. Measurements of the internal air temperature provide a means of characterization of the

rotational molding cycle. Based on this finding, the ROTOLOGTM system was developed which uses temperature measurements taken from inside the mold as it rotates. A typical internal air temperature profile during a rotational molding cycle is shown in Figure 2.1. The different stages of heating and cooling can be described as follows [Kontopoulou, 1999]:

Induction: In the beginning of the cycle, the polymer is present in powder form only and powder flows freely. The thermal energy passes directly to the powder pool through the mold wall and the temperature rises steadily up to point A.

Adhesion: From point A to B, the powder particles begin to adhere to the mold and each other and the first layer of plastic is created. The inside air temperature rise slows down as the melt absorbs the heat being inputted to the system and a great deal of thermal energy is consumed during phase change.

Sintering: The particles, after point B, have reached their melting temperature and begin to coalesce and form a porous network. Sintering lasts until point C, at which particles lose their individual identities and take on the form of a melt pool. Air pockets are trapped during this stage and form bubbles.

Bubble Dissolution: Between points C and D the density of the melt pool increases and the bubbles that formed in the previous stage decrease in size. Heating continues up to a desired maximum temperature. It is this peak temperature that Crawford and Nugent [Crawford, 1992] determined was directly related to the final properties of the final product and was crucial for deciding the optimum processing conditions.

Cooling: At point D, the mold is removed from the oven to the cooling area and the melt temperature decreases steadily until reaching point E. Solidification begins to occur after point E which represents the crystallization temperature of the polymer. In foaming, the



Figure 2.1: Typical inside mold air temperature profile during a rotational molding cycle

bubble dissolution and cell growth will continue up to point E and it will be terminated after this point

The initial size of the bubbles in the melt is generally affected by the particle size and shape of the resin. The diameter of the bubbles affects the rate of bubble dissolution. Also, increasing the oven temperature and the initial powder temperature has a beneficial effect on the bubble dissolution rate, as well as the overall heating cycle and the overall uniformity of melt density [Tiang, 2001].

It is clear that obtaining optimal processing conditions is critical in the production of high quality rotationally molded parts. Processing conditions may vary with resin types as

each material exhibit its own unique melting behavior characterized by its sintering rate and rheological properties.

2.2 Materials

Rotational molding is a materials-dependent process. In order for a material to be appropriate for rotational molding, it must possess sufficient melt flow properties enabling the melt to coat the surface of the mold evenly. Also, rotomolding process is limited to those polymers that are capable of being efficiently pulverized into fine powders. In addition, due to elevated temperatures and long cycle times, the plastic must have a degree of thermal stability to prevent thermal degradation, and must have suitable powder heat transfer characteristics [Beall, 1998; Crawford, 1996].

A large percentage (over 85%) of the materials currently used in the rotational molding industry is polyethylene materials [Moony, 1995]. Polyethylene gained a strong presence in the rotational molding industry in the 1960s with the introduction of LLDPE. This polymer material provides a good balance between cost, processability and performance [Maziers, 2003].

2.2.1 Metallocene Catalyzed Polyethylene

A number of studies have been conducted investigating the advantages of metallocene catalyzed polyethylene in rotational molding industry. Metallocene polyethylene materials have the ability to control the molecular weight distribution more narrowly than resins produced using conventional Ziegler-Natta catalysts [Keating, 1999]. Metallocene polyethylenes possess rheological and physical properties that are desirable in rotomolding [Fatnes, 2000] and offer some significant process advantages [Annechini, 2001].

The unique feature of the rotational molding process is that the polymer is subjected to low shear forces. Due to this fact, polymers with a narrow molecular weight distribution give a good combination between ease of melt flow at low shear forces and mechanical strength of the final product [Fatnes, 2000].

It was found by Takacs *et al.* [2000] that metallocene resins used in their work had lower elasticity and showed lower zero-shear viscosity and melting temperature compared to the Ziegler-Natta materials. The low zero-shear viscosity at lower shear rates is an advantage for processing by rotational molding as it makes the flow of the metallocene polyethylene much easier than for a comparable Ziegler-Natta based LLDPE [Fatnes, 2000].

Fatnes [2000] noted that due to improved flow, a metallocene resin has a higher sintering rate in the rotomolding process, which provides a potential for reduced cycle time.

However, Kontopoulou [1999] found the cycle time required to completely remove bubbles from a metallocene polyethylene was comparable to that for a conventional Ziegler-Natta polyethylene with the same viscosity. Even though the results of sintering experiments confirmed the faster sintering process for the metallocene polyethylene.

Work by Wang [2000] reported on the results of an experimental investigation in which processing conditions were related to the microstructure and mechanical properties of metallocene polyethylene. It was noted that metallocene polyethylene exhibited excellent resistance to impact at both high and low temperatures and always produced a ductile failure mode. The author mentioned by using metallocene polyethylene in rotational molding, it was possible to reduce cycle time, reduce energy consumption and get a wider processing window. The broader operating window was shown by the optimum mechanical properties being reached.

Annechini [2001] observed that the impact properties of rotationally molded parts could be improved by using metallocene polyethylene. It was also confirmed that the metallocene LLDPE materials offered a wider processing window which allowed reducing cycle times without loss of impact strength. Though the author noticed an increase in warpage of the metallocene polyethylene parts which was attributed to increased crystallinity.

Fatness [2000] summarized the advantages of metallocene polyethylene resins in rotational molding, stating that they promise improved mechanical properties even at higher MFI, reduced cycle time, wider processing window and good flow properties.

2.2.2 Material Properties and Foaming

In rotational foam molding, the air pockets between plastic particles behave as nucleating sites for foaming and prevent the formation of small cells by the cell coarsening mechanism. It is important to minimize the size of entrapped air pockets before the activation of the blowing agent [Liu, 1998]. Liu *et al.* [1998] concluded that it was the characteristics of the polyethylene powder that governed nucleation rather than the blowing agent. They also found that an optimum zero-shear viscosity was required for the rotational foam molding. A low zero-shear viscosity was desired for the air bubble removal in the early stages. However, at low zero-shear viscosity, cell coalescence may be a problem, as the lower shear viscosity implies lower melt strength. Behravesh [1998] found that by increasing the melt strength and controlling the temperature, coalescence could be limited. Liu *et al.* [1998] agreed with these findings.

In rotational molding, the formation of gas bubbles is affected by different parameters. It was observed that the size and shape of the particle play a role during the stage of the gas bubble formation [Crawford, 1995; Bellehumeur, 2000]. Crawford [1995] noted that powder with fine particles tend to have a greater void content. The author also indicated

that the bubbles were dependent on the melt flow index of the material as well as the particle size distribution. Findings of Bellehumeur [2000] are generally in agreement with this; however, it was stated that the polymer rheological properties seem to dominate the bubble formation process.

By using appropriate processing conditions, metallocene catalyzed polyethylene could be used in rotational foam molding to produce a foam that would perform as well as a Ziegler-Natta catalyzed foam. Metallocene polyethylene provided better impact resistance than conventional polyethylene and experienced its peak value at lower processing temperatures [Archer, 2004].

2.3 Blowing Agents

2.3.1 Physical Blowing agents

The physical blowing agents are gases or volatile liquids which are directly injected into the melt polymer and pressurized during the foaming process. The gas type physical blowing agents are typically atmospheric gases, such as nitrogen and carbon dioxide. The volatile liquids used as physical blowing agents include hydrocarbons, chlorocarbons and chlorofluorohydrocarbons [Throne, 1996].

Due to some limitations such as explosion and flammability risks, ageing problems and environmental emission controls, chemical blowing agents have been received greater attention for the foaming process [Archer, 2004]. In order to keep the blowing agent dissolved in the polymer melt, the system pressure must consistently exceed the equilibrium vapor pressure of the blowing agent [Klempner, 2004]. Physical blowing agents are not typically used in rotational molding because the rotational molding process normally operates at pressures very near atmospheric, therefore the pressure is not high enough to enable gas dissolution within the polymer melt. Also due to the high cost of incorporating a pressure vessel into the mold of rotomolding machines, chemical blowing agents are better suited for use in rotational molding [Archer, 2004].

2.3.2 Chemical Blowing Agents

Chemical blowing agents are compounds that release gas as a result of chemical reactions, including thermal decomposition or interactions with other components of the formulation. The reaction can produce some solid residues that remain in the polymer after foaming process. The residues are more stable than the reactants in most cases [Klempner, 2004].

The final foam structure largely depends on the properties of the blowing agent and using compatible blowing agent and polymer can offer a unique performance or economic advantage. The properties that require special attention while selecting a chemical blowing agent include: onset decomposition temperature, rate of decomposition, gas yield and type of evolved gases [Klempner, 2004].

An appropriate chemical blowing agent should fulfill the following criteria [Reedy, 1999]:

- To reach complete decomposition, the decomposition temperature of the blowing agent should correspond to the process temperature.
- The developed gas should be easily dispersed in the matrix.
- The developed gas should not have a strong smell or be corrosive, and should be nontoxic and environmentally safe.
- The developed gas and decomposition by-products should have no damaging effects on the processing equipment or the polymer matrix.

Chemical blowing agents can be exothermic or endothermic. Exothermic blowing agents generate heat during the decomposition process and evolve mainly nitrogen gas. Once decomposition begins, it continues spontaneously and is difficult to stop before it reaches full decomposition. This results in faster decomposition over a narrow temperature range. Endothermic blowing agents absorb heat during the process of decomposition and in general mainly generate carbon dioxide. Consequently they have a broader decomposition time and temperature range [Throne, 1996]. For both kinds of chemical blowing agents, the decomposition reaction releases more than one kind of gas. However, the percentages of the other gases are small and their effect on the foaming process is not as important as the effect of the main gases evolved. In general, endothermic blowing agents produce smaller cell size due to the lower pressure exerted by carbon dioxide than that exerted by nitrogen [Pontiff, 2000].

Chemical blowing agents were selected from three categories for this research work:

1. Azodicarbonamide (Organic blowing agent)

Azodicarbonamide is one of the most commonly used exothermic chemical blowing agents [Heck, 1998]. This compound is the most efficient of exothermic species in terms of gas yield, relatively inexpensive foaming agent that can be used for foaming of polyolefins. It is an organic chemical in the form of yellow to orange, odorless, crystalline powder [Cary, 1999]. Throne [1996] gives the reaction of decomposition for the Azodicarbonamide as follows:

$$H_2N(C=O)N=N(C=O)NH_2 \rightarrow NH_3 + CO + N_2 + HNCO$$

The gaseous products of the reaction represent 33% of the total products and the percentages of gases evolved by decomposition are 62% N_2 , 35% CO, and 3% NH_3 and CO_2 [Throne, 1996].

Using Azodicarbonamide may have several disadvantages [Klempner, 2004]:

- Ammonia can cause rusting and staining of the molds.
- By-products of the reaction with certain polymers can give a yellow color the molded part.
- Ammonia can cause polymer degradation.
- The generation of CO may cause headaches and nausea for the workers when molding with the blowing agent.

2. 4,4'-oxy-bis(benzenesulfonylhydrazide) (Organic blowing agent)

4,4'-oxy-bis(benzenesulfonylhydrazide), sometimes known as OBSH, is a chemical blowing agent of considerable interest in the sulfonylhydrazide category of exothermic blowing agents. This material is a white powder with a decomposition temperature of 160°C which evolves 125cc/g of nitrogen gas and a small amount of water [Throne, 1996].

Because the decomposition products are nonvolatile and nontoxic, this blowing agent gives no color and no smell to plastic articles. It is possible to obtain foams with small, uniform cells by using OBSH because of the absence of the stepwise changes during decomposition [Klempner, 2004]. This material should not be subjected to temperatures in excess of 177°C as darkening of its polymeric decomposition residue will result [Heck, 1998]

3. Sodium bicarbonate (Inorganic blowing agent)

Sodium bicarbonate is an endothermic blowing agent. Sodium bicarbonate decomposes at a temperature of approximately 140°C. The products of its decomposition are carbon dioxide and water. Sodium bicarbonate is commonly used with citric acid. The ratio of
the blend can be varied in order to modify the decomposition temperature range [Pontiff, 2000]. The components and the resultant products are considered as safe, because most of the components of the blend are food additives and the products are non-toxic [Heck, 1998]. The chemical reaction of this blend (sodium bicarbonate and citric acid) is as follows:

$$C_6H_8O_7 + 3 \text{ NaHCO}_3 \rightarrow (C_6H_5Na_3O_7).2(H_2O) + 3 \text{ CO}_2 + H_2O$$

The blend of sodium bicarbonate and citric acid is the most popular endothermic blowing agent used as a cell nucleator because it helps to produce fine cells on the foam products [Pontifff, 2000]. The foaming activity and rate of decomposition of sodium bicarbonate is relatively low. Therefore, there are no danger of rapid gas escaping from the mold or large cells and pores forming [Klempner, 2004].

Understanding the mechanism of gas migration through foam membranes would be important. The solubility of gas in polymer depends on the molecular characteristics of both the gas and polymer. In an unpressurized system, the solubility of the liberated gas from a blowing agent is so low that it is immediately available as free gas [Throne, 2000]. In general, the solubility increases with increasing temperature indicating a positive energy of activation [Throne, 1996]. According to Throne [1996], the permeability (a measure of the movement of the small molecules through solids and liquids) of polyethylene to a species is determined by kinetic and thermodynamic factors:

$$P=D\times S \tag{2.1}$$

Permeability of nitrogen is less than that of carbon dioxide in polyethylene. The value of permeability for nitrogen is 2.7cm³ mm/s mm² cmHg, while this value is 35 cm³ mm/s mm² cmHg [Archer, 2004].

Diffusivity represents the time-dependant mobility or mass transfer of molecules through a system. The diffusivity of a gas is a function of its molecular weight and shape [Michaels, 1961]. According to kinetic theory, the diffusion coefficient of an ideal gas is inversely proportional to the square of the molecular diameter (at 760 mmHg and 270K):

$$D = \frac{10}{d_g^2} \sqrt{1/M_w}$$
(2.2)

To achieve low density foam, gases must have a reasonably high solubility and very low diffusivity in the polymer [Throne, 1996]. Heck [1998] stated that nitrogen is a more efficient expanding gas because of its lower rate of diffusion through polymers compared to carbon dioxide. Also blowing agents generating carbon dioxide gave poor foaming performance and much broader cell size distribution. These results were attributed to the higher diffusion rate of carbon dioxide. As nitrogen is an inert gas, it may also help to protect the part against oxidation and thermal degradation.

2.4 Foaming in Rotational Molding

Over the past few decades much research has been undertaken in the area of polymer foam products. This trend has had a strong impact on the rotational molding industry, where the production of foamed polymers has become progressively more important, particularly polyolefin foams. Polyolefin foams can have a density very close to the unfoamed polymer or they can have a density of 250 times less than the neat polymer [Throne, 1996]. The conditions of the foaming process dictate the structural characteristics of the foam.

Throne [1996] suggested the following method of classification for foams:

• According to the physical form, they can be flexible, semi-rigid or rigid.

- According to the material used as a precursor, it can be liquid, prepolymer or polymer.
- According to the cell structure, they can be open, reticulated or closed.
- Also, it is indicated the use of adducts: filled with solids, filled with liquids, no adducts, fiber reinforced or syntactic.

The foaming process can be broken down into three major steps:

- Cell Nucleation
- Cell growth
- Cell Termination and Stabilization

2.4.1 Cell Nucleation

Nucleation is a thermodynamic phenomenon where the formation of bubbles begins. This phenomenon is produced as a result of an induced thermodynamic change in the system. The externally induced thermodynamic change produces a supersaturated state; as a result, the system follows a process to re-establish the stable state by some internal adjustments. One way in that the system can respond is bubbling [Lee, 2000].

There are two types of nucleation: homogeneous and heterogeneous. Homogeneous nucleation can occur in an initially homogeneous liquid, and then the bubbles form by a self-nucleation process [Saunders, 2004]. Homogeneous nucleation should produce foams with smaller cell sizes and more uniform cell size distribution [Throne, 1996].

For most foaming processes, bubbles begin to grow on heterogeneous surfaces. Heterogeneous nucleation can occur anywhere an inhomogeneity exists. In rotational molding, catalyst particles, pigments, fillers, unmelted crystallites, solid residue from decomposed chemical blowing agents and minor impurities such as dust and debris can be heterogeneous sources [Throne, 2000].

The cell nucleation mechanism in rotational molding of foamed plastic is unique [Liu, 1998]. Cell nucleation in processes such as extrusion and injection molding depends greatly on the characteristics of the chemical blowing agent; while it depends mostly on entrapped air packets between polymer particles in rotational molding.

In all foaming technologies, the primary objective is to form as fine bubbles as possible. Large bubbles deplete gases from the polymer surrounding fine bubbles; therefore, an initial mixture of large and small bubbles results in a few even larger bubbles [Throne, 2000].

The differential pressure needed to begin bubble growth is dependent on the surface tension of the liquid, σ , and the initial radius of the bubble, R_o :

$$\Delta \mathbf{P} = \mathbf{P}_{i} - \mathbf{P}_{0} = \sigma/\mathbf{R}_{0} \tag{2.3}$$

where P_i is the pressure of the gas inside the bubble and P_o is that in the surrounding liquid. The typical initial bubble radius is around 0.1 micron [Throne, 2002].

2.4.2 Cell Growth

Once a bubble has been nucleated, it begins to grow [Throne, 2000]. The rate of cell growth depends on the rate of gas generation from the blowing agents, the rate of gas diffusion to the polymer matrix and the viscoelastic nature of the polymer phase [Klempner, 2004].

There are three stages of bubble growth [Throne, 2000]:

- Inertial bubble growth
- Diffusional bubble growth
- Membrane formation

Inertial bubble growth is the first stage. Bubbles grow by pushing the surrounding polymer melt outward. The inertial bubble growth rate is inversely dependent on the polymer viscosity. However, it is still not clear which viscosity dominants the bubble growth. Extensional viscosity might be used since the gas/polymer interface is being biaxially stretched. In addition, the region removed from the growing bubbles is undergoing local shear and therefore shear viscosity might be considered. The zero-shear viscosity has also been considered; however, expansion rates of 10,000 s⁻¹ have been proposed during the very early stages of bubble growth and this brings the use of zero-shear viscosity into question. Regardless of which viscosity dominates, polymer viscosity decreases significantly with increasing temperature. Therefore bubbles grow more rapidly at higher melt temperatures [Throne, 2002].

Diffusional bubble growth occurs when the bubbles have depleted the gas from the polymer melt surrounding the bubbles. This stage of growth depends on diffusion of gas through the polymer melt to the growing bubble site. The parameters that affect the diffusivity of gas are initial gas concentration, size of the gas molecule, free volume of the polymer and melt temperature. Typically, diffusional bubble growth is dramatically slower than inertial bubble growth [Throne, 2002].

Membrane formation is the final stage of bubble growth. The polymer melt viscosity is no longer the dominant characteristic of the foam. Membrane formation depends strongly on the melt elasticity of the polymer. The bubbles that were spherical begin to stretch the polymer into a film between the bubbles. Stretching continues until the polymer forms a biaxially oriented membrane between each bubble [Throne, 2000].

2.4.3 Cell Termination and Stabilization

Termination is the final step of foaming. This is generally achieved by cooling, which freezes the cellular structure in place. The bubble growth stops due to the balance between internal gas pressure and the forces resisting further expansion. Cell stabilization is also affected by blowing agent type and concentration as well as a number of matrix polymer properties, including viscosity, elasticity and surface tension [Throne, 2002].

The density of the foamed polymer is an important parameter. It determines the relative contents of the solid and gas phase in a material and is a fundamental morphological parameter of foamed polymers. The density can be related to many relevant physical properties of foamed plastics, such as mechanical, thermophysical and electrical properties [Klempner, 2004].

Deanin [1974] realized that density was probably the most important factor in terms of its effect on properties. In his study, the foam density correlated directly with tensile modulus. Ramsteiner [2001] studied the deformation behavior of polymer foams and concluded that the density of the foam was the dominating factor in determining mechanical properties such as tensile and compressive modulus and strength. Ramsteiner's results fit well with the Gibson and Ashby model. The Gibson and Ashby [1997] model is a simple mechanical model that treats the foam structure as an array of cubic cells. Lin [1997] also examined the structure and property relationships of the foamed plastic and found that the relative density was the most important structural characteristic of foam.

Archer [2004] investigated the effect of foam density on flexural and compressive properties. It was found that foam density was by far the most influential parameter over flexural properties of foam and there was a linear relationship between both flexural and compressive strength with foam density. D'Agostino [2004] also stated that a reduction in foam density led to a proportional decrease in stiffness when working on foaming with polymer microspheres in rotational molding.

2.5 Factors Affecting Foaming

During the foaming process in rotational molding, the matrix polymer is deformed and displaced as cells form and grow. The speed and ease of bubble growth is determined by the melt properties of the matrix polymer. When cells expand, the surrounding material is required to stretch, introducing extensional forces in the surrounding melt. It has been shown that the melt elasticity and melt viscosity affect cell growth dynamics in viscoelastic polymer melts [Street, 1968; Suh, 1985]. However, the cell growth stage of the foaming process is controlled by extensional viscosity and melt strength, due to the stretching actions. A higher extensional viscosity provides greater resistance to deformation, which may slow the cell growth [Takacs, 2002].

Generally, zero-shear viscosity is considered as an important parameter in rotational foam molding. Liu [1998] stated that zero-shear viscosity is one of the key material parameters as it contributes in sintering and removal of trapped air bubbles. It was concluded that low viscosity may lead to an increase in undesired cell coalescence, as the material may have low melt strength.

The melt elasticity in the foaming process acts as a resistance to deformation. Higher melt elasticity indicates that as polymer chains are stretched apart, they will work harder to return to their original orientation. It was shown by Takacs [2002] that resin with higher melt elasticity produce foams with a larger number of expanded cells. Takacs

[2002] also found that a Ziegler-Natta catalyzed polyethylene produced a larger cell size than a metallocene catalyzed grade of similar melt index. Zhang [2002] also noted the molecular weight affects foaming. It was observed that the cell sizes of high density polyethylene decreases as the molecular weight increases.

Surface tension also has impact on the foaming process. Throne [2000] noted that during the bubble nucleation in the foaming process, the differential pressure needed to begin bubble growth is dependent on the surface tension of the melted polymer. Tinson [2004] found that when comparing the differences in sintering materials of polymer particles with similar rheological properties, surface tension becomes the key parameter in rotational molding. Xu [2005] also observed that the bubble life span in the foaming process increased by decreasing the surface tension. Xu [2005] concluded that with a decrease of surface tension, the gas pressure inside a bubble would decrease; therefore, the bubble dissolution rate is retarded due to a slow gas loss.

Cell morphology and growth is not only dependent on the polymer properties, but also on processing conditions and powder properties [Klempner, 2004]. It has been observed that the density reduction due to blowing agent addition improves the impact strength of rotationally molded parts. However, Liu [1999] found this was counteracted by longer cycle time. Archer [2004] observed that by increasing the oven removal temperature, the average cell size generally increases. Liu [2001] investigated the effect of particle size on foaming. It was found that the foaming rate of powder is higher than that of pellets, and under certain conditions, the impact strength of pellet-foamed parts was better than that of powder-foamed parts. However, pellet-foamed parts were shown to have about the same tensile properties as parts produced using powder.

Chapter 3

Experimental

This chapter describes the materials and experimental procedures used in this study. Procedures for material and structural characterization are discussed.

3.1 Resin Characterization

Several varieties of rotational molding grade polyethylenes were selected for this study: One metallocene catalyzed linear low density polyethylene (LLDPE) and five metallocene catalyzed medium density polyethylenes (mMDPE) representing a broad range of rheological properties; and five metallocene catalyzed medium density polyethylenes (mMDPE) for the study of effect of surface tension properties. All materials were supplied in powder form by Total Petrochemicals. The physical properties and general information of the resins used in this study are reported in Table 3.1.

Material	Туре	Comonomer Type	MFI (g/10min)	Density (g/cm ³)	Melting Point (°C)	Mw
mPE-RA	LMDPE	hexene	7	0.935	116	62,852
mPE-RB1	MDPE	hexene	8	0.934	123	54,972
mPE-RB2	MDPE	hexene	4	0.940	126	62,433
mPE-RB3	MDPE	hexene	3.5	0.941	123	62,729
mPE-RB4	MDPE	hexene	2.7	0.934	123	70,297
mPE-RB5	MDPE	hexene	2	0.932	123	72,945
mPE-SB1	MDPE	hexene	4	0.940	126	64,272
mPE-SB2	MDPE	hexene	4	0.940	126	64,517
mPE-SB3	MDPE	hexene	4	0.940	126	64,156
mPE-SB4	MDPE	hexene	4	0.940	126	62,255
mPE-SB5	MDPE	hexene	4	0.940	126	62,465

Table 3.1: Material properties. Data provided by resin manufacturers.

Each material is identified with a code indicating the type of resin (mPE for metallocene polyethylene), followed by a letter representing the property that the resin is studied on (R for rheological properties and S for surface tension), then a code for the manufacturer (A for Borealis and B for Total Petrochemicals) and finally a number to put them in order.

3.1.1 Rheological Properties

Rheological properties of the polymer resins including dynamic viscosity (η^*), storage modulus (G') and loss modulus (G'') were provided by Total Petrochemicals and measurements of extensional viscosity were made at 190°C using a Rosand twin bore capillary rheometer (Bohlin Instruments, Ltd.).

Dynamic measurements are useful for the study of the viscoelasticity of the materials. The storage modulus provides good indication of the elastic behavior of the polymer melt, whereas the loss modulus is representative of the viscous behavior of the material. Zero-shear viscosity values for the resins were extrapolated from the dynamic viscosity data using the Cross Model [Macosko, 1994].

$$\eta = \frac{\eta_0}{1 + (\lambda \dot{\gamma})^{(1-n)}}$$
(3.1)

Extensional viscosity was measured using the Rosand capillary viscometer over the range of shear rate of 10s⁻¹ to 5000s⁻¹. The extensional viscosity was calculated by using the Cogswell method [Cogswell, 1996]. This method relates the elongational viscosity to the entrance pressure drop at the capillary die.

$$\eta_e = \frac{9(n+1)^2 \Delta P_e^2}{32\eta \dot{\gamma}^2}$$
(3.2)

$$\dot{\gamma} = 4Q/(\pi r^3) \tag{3.3}$$

$$\dot{\varepsilon} = 4\eta \dot{\gamma}^2 / [3(n+1)\Delta P_a] \tag{3.4}$$

3.1.2 Molecular Weight Distribution

Molecular weight distribution (MWD) of the resins was provided by Total Petrochemicals. MWD tests were performed using gas permeation chromatography (GPC). This parameter is thought to have an effect on processing and final properties of foams [Crawford, 1996].

3.1.3 Surface Tension

The measurements of surface tension were performed by a researcher at McMaster University, using the pendant drop method at 190°C.

3.2 Blowing Agent Characterization

The most important criteria for blowing agent selection include its decomposition temperature, rate of gas release, gas composition, ease of dispersion, storage stability and cost [Throne, 1996]. Several types of chemical blowing agents (CBA) were used in this study in order to identify efficient and multipurpose blowing agents for rotational foam molding. Exothermic and endothermic blowing agents with different decomposition behavior and gas yield capability were selected from three categories of blowing agents: Azodicarbonamide, 4,4'-oxy-bis(benzenesulfonylhydrazide) and Sodium bicarbonate. Structures can be found in Figure 3.1.

Nine blowing agents were chosen including: Genitron OB and EPC (supplied by Lanxess Inc.), Hydrocerol BIH, BIF and CF (supplied by The Queens University of Belfast,

Clariant), Celogen OT and AZ (supplied by Chemtura Corporation), Tracel AZ^{*} and OBSH (supplied by ROWA Group USA, LLC). All materials were provided in powder form. Physical and thermal properties of chemical blowing agents and suppliers are reported in Table 3.2.

A code is assigned for each blowing agent indicating the chemical name (AZ for Azodicarbonamide, OB for 4,4'-oxy-bis(benzenesulfonylhydrazide) and SB for Sodium bicarbonate), followed by the type of reaction that it makes (Ex for exothermic and En for endothermic), and finally an abbreviation for the blowing agent trade name.

These blowing agents covered a wide range of properties. In order to study their decomposition behavior and verify the provided technical data, Thermogravimetric Analysis (TGA) performed to give a more in-depth understanding of how the agents would react at any given temperature.



Figure 3.1: Structure of three categories blowing agents used in this study

^{*} Tracel AZ is an experimental blowing agent.

Table 3.2: H	Properties of	chemical	blowing	agents.	Data	provided by	v the suppliers.
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СВА	Blowing Agent Trade Name	Chemical Name	Color (Powder)	Type of Reaction	Decomp. Temp. (°C)	Gas Yield (ml/g)	Gas Evolved
AZ/Ex/G-EPC	Genitron EPC	Azodicarbonamide	Yellow	Exo	160 -190	190	N ₂ /CO/CO ₂ /NH ₃
AZ/Ex/C-AZ	Celogen AZ130	Azodicarbonamide	Yellow	Exo	206 - 213	210 - 220	N ₂ /CO/CO ₂ /NH ₃
AZ/Ex/T-AZ	Tracel DB 120 (AZ)	Azodicarbonamide	Yellow	Exo	130		N ₂ /CO/CO ₂ /NH ₃
OB/Ex/G-OB	Genitron OB	4,4'-oxy-bis(benzene sulfonylhydrazide)	White	Exo	140 - 160	125	N ₂ /H ₂ O
OB/Ex/C-OT	Celogen OT	p,p'-oxy-bis(benzene sulfonylhydrazide)	White	Exo	160	120 - 125	N ₂ /H ₂ O
OB/Ex/T-OB	Tracel OBSH	4,4'-oxy-bis(benzene sulfonylhydrazide)	White	Exo	160		N ₂ /H ₂ O
SB/En/BIH	Hydrocerol BIH	Sodium bicarbonate	White	Endo	140 - 160	190 - 230	CO ₂
SB/En/BIF	Hydrocerol BIF	Sodium bicarbonate	White	Endo	140 - 160	240 - 280	CO ₂
SB/En/CF	Hydrocerol CF	Sodium bicarbonate	White	Endo	150 - 170	90 - 120	CO ₂

3.2.1 Thermogravimetric analysis (TGA)

The decomposition behavior of the blowing agents was studied by thermogravimetric analysis (TGA) under atmospheric air. Thermogravimetric analysis is an analytical technique in which the mass of a substance is measured as a function of temperature or time, while the substance is subjected to a controlled temperature program in a controlled atmosphere. The TGA determines thermal stability of a sample by monitoring the weight change that occurs as the sample is heated to the desired conditions and provides a realtime plot.

The thermogravimetrical experiments were performed using a Netzsch STA 409 PC/PG. An Al203 crucible was used to place the sample inside the heating chamber. Experiments in non-isothermal conditions were performed over a temperature range from room temperature to 250°C, with a heating rate of 5°C/min. This temperature range well simulated the rotomolding process. The atmosphere used was air and the flow rate 30ml/min, according to the specifications of the standard method. The mass of the sample ranged between 30-70 mg.

3.3 Sample Preparation

Dry blended PE/CBAs were prepared for rotational foam molding process using various concentrations of blowing agents. Blowing agents were added at a concentration of 0.5, 1.5 and 2.5 wt% for monolayer foams and 2.5 wt% for skin-foam sandwiches.

All mixtures were dry blended using a blender at high speeds for 5 minutes. It is essential to have the blowing agent thoroughly dispersed in the polymer powder prior to charging the mold since the dispersion of the blowing agent in the polymer matrix has a strong impact on the quality of foamed structure.

Chemical Blowing Agent Concentration

In order to measure the efficiency of blowing agent concentration on the volumetric expansion of the material charged into mold, PE/CBA blends were prepared in different weight ratios. The parameter is referred to as volume expansion ratio (VER). By definition, the VER of plastic foams in rotational foam molding is defined as the ratio between the expanded volume of the foam (V_{foam}) and the initial volume of the solid unfoamed plastic material (V_i) as given in Equation (3.5):

$$VER = \frac{V_{foam}}{V_i}$$
(3.5)

Equation (3.6) provides the formula for calculating the weight percentage of the blowing agent to the weight of the polymer resin that should be used in the blend in order to obtain the VER during the foaming process.

$$\% CBA = 100 \frac{VER - 1}{\rho_{\text{Resin}} \phi}$$
(3.6)

The data describing the gas yield, ϕ , of blowing agents provided by the suppliers are referred to room temperature conditions, while the decomposition of blowing agents and the expansion of polymeric foams occurs at elevated temperature. Therefore, before introducing the gas yield data in Equation (3.6), the data provided by the manufacturer for the gas yield should be corrected by using Equation (3.7):

$$\phi = \phi_{STP} \times \frac{V_C}{V_{room}} = \phi_{STP} \times \frac{T_C}{T_{room}}$$
(3.7)

3.4 Uniaxial Rotational Molding

Rotational molding experiments of monolayer foams were performed in a laboratory scale uniaxial rotomolding machine. The machine consisted an electrically heated oven, a square Teflon coated steel mold and a control panel (Figure 3.2).

The steel mold was approximately $9.5 \text{cm} \times 9.5 \text{cm} \times 10 \text{cm}$ cube shaped mold made of 1.6 mm thick steel. The front of the mold was covered with Pyrex glass to allow visual observation of the process. A silicone based mold release, Dura Kote (Chemtrend), was applied to the mold surfaces to prevent sticking. Cooling was provided by a table fan.

The oven temperature was set at a panel temperature at 407 °C. A shot weight of 100g was used in all experiments which produces unfoamed part wall thickness of 3 mm. The mold rotation speed was 4 RPM. Conditions for all experiments were kept identical, except the maximum inside air temperature of molding, at which the mold was removed from the oven. A broad range of temperature was used in order to study the effect of maximum air temperature inside the mold on the final properties of the rotomolded foams. Inside air temperature was recorded every 30 seconds during the rotomolding experiments and was plotted as a function of time. The rotomolded part was removed from the mold at 50 °C.

3.5 Biaxial Rotational Molding

Rotational molding experiments of skin-foam runs were carried out using a Caccia 1400R shuttle type machine at the Queen's University of Belfast. The machine consisted of three major components: a heating chamber, a cooling chamber and a steel cube-shaped mold. The heating unit was powered by a LPG burner with a capacity of 7700 Kcal/hr.



Figure 3.2: Schematic of the lab-scale uniaxial rotational molding machine and the mold

The dimension of steel mold was approximately 33cm ×33cm× 33cm, made of 2mm mild steel sheet. The mold was mounted on the arm of machine and coated with the mold release agent (Dexter Frekote 770-NC). A tapered PTFE vent pipe was inserted on the lid of the mold through a circular hole, providing adequate venting and avoiding pressure build up inside the mold. A thermocouple was passed in the vent pipe and into the mold to measure the internal air temperature. The thermocouple was secured in place by a wire wool bung to avoid any escape of resin powder down the vent tube.



Figure 3.3: Datapaq temperature-measuring device

The first shot of 900g of skin material was placed in the mold before the lid was clamped in place. The heating cycle was started when the oven temperature reached 300°C and the mold was moved into the oven under biaxial rotation. The mold rotation ratio of 4:1 was used. When the inside air temperature was reached 160°C, the mold was removed from the oven. The second shot of 900g polymer/CBA mix was added and the mold was put back in the oven until it reached the required inside air temperature. Then the mold moved to the cooling area. During the cooling cycle, mold was cooled by airflow under biaxial rotation. The rotomolded part was removed from the mold at 90°C.

A Datapaq temperature-measuring device (Figure 3.3) was used to record inside mold air temperature and oven temperature. The device consists of data logger/transmitter, a thermal barrier, antenna/receiver, mineral insulated thermocouples and Insight Software. The transmitter was placed inside the thermal barrier for heat protection of the oven during heating cycle. The barrier was placed on the top of the mold. Thermocouples were attached to the transmitter. The information was transmitted, viewed and analyzed in real time on the computer screen and stored on the logger for verification.

3.6 Density

The density of the rotomolded parts was determined using a Mirage MD-200S electronic densimeter. Specimens with dimensions of $2\text{cm} \times 1\text{cm}$ were cut from the center of the same side of molded parts. This instrument operates using the Archimedes principle. The determination of the density value is based on the density of water at 4°C (1g/cm³). The measurements were repeated four times in order to determine their reproducibility and the average values have been reported.

3.7 Wall Thickness

The wall thickness of the foamed rotomolded parts was measured by using a Mitutoyo horseshoe-shaped digital micrometer. Mean wall thickness was determined by taking measurements at twenty positions on the same side of the molded wall of each sample. Figure 3.4 shows the positions of the points taken on the mold wall.

×	×	×	×
>	ĸ	>	<
×	×	×	×
×	×	×	×
	×)	×
×	×	×	×
-		•	\rightarrow
	× , × × ×	× × × × × × × × × ×	× × × × × × × × × × × × × × × × × × ×

Figure 3.4: Positions for the wall thickness measurements on rotomolded part

	SHAFT SIDE						
	1	2	3	4	5	6	
1	×		×	×		×	
2		×			×		
3	Max		×	×		×	
4	×		×	×		×	
5		×			×		
6	×		×	×		Min	
			WINDO	W SIDE			

Figure 3.5: Maximum and minimum wall thickness positions

Almost in all samples of monolayer foams the maximum and minimum thicknesses were observed at the same positions, maximum thickness at position [1, 3] and minimum thickness at position [6, 6] (Figure 3.5). This was due to the mold design and geometry.

3.8 Cell Morphology and Cell Size Distribution

The cross sections of molded parts were observed under an optical microscope and cell size distribution, average cell size and cell density of the foamed parts were determined. For each part, three cross-sectional samples were cut from the same side of the molded part. To ensure the cross-sectional samples were representative of the entire part, each sample was taken from a different region of the part wall. Samples were placed on microscope slides and studied using Olympus SZ 4045 optical microscope equipped with a video camera. Microscope images were captured using a personal computer with a frame grabber board where the images were stored. Cell properties of each sample images were measured using the image analysis software SigmaScan Pro 3.0 [Jandel Scientific Software, 1996]. A total distribution was determined by adding the individual cell distribution per sample area. The total distribution was then scaled in order to report the total number of cells per 100mm² (cell density).

Chapter 4

CBA Screening

The final foam properties depend largely on the properties of the blowing agents. The purpose of this chapter is to assess the suitability of different chemical blowing agents, study the effect of the decomposition behavior on the production of cellular rotationally molded parts of metallocene polyethylene and characterize appropriate blowing agent for rotationally molded foam applications. This section examines the differences in foam structure and physical properties observed between foamed parts produced with different chemical blowing agents.

4.1 Material

Foaming experiments were performed using mPE-RB1 as the reference metallocene resin. Blowing agents were added at a concentration of 0.5%, by weight. Properties of this resin are presented in Table 4.1.

Property	Method	Value
Density	ISO 1183	0.934 g/cm^3
Melt Index, 2.16 kg	ISO 1133	8 g/10 min
Melting Point	ISO 11357-3	123°C
Zero Shear Viscosity		1052 Pa.s

Table 4.1: Properties of mPE-RB1- metallocene polyethylene

Table 4.2: Thermal properties of the blowing agents from TGA analysis

Blowing Agent	Stages of Decomposition	Onset Temp. (°C)	Peak Decom. Temp. (°C)	Mass Change (%)
AZ/Ex/G-EPC	1	175	176	47.1
AZ/Ex/C-AZ	1	215	215	66.0
AZ/Ex/T-AZ	1	146	147	21.3
OB/Ex/G-OB	1	166	166	44.7
OB/Ex/C-OT	1	165	165	41.2
OB/Ex/T-OB	1	166	166	54.5
	1	138	149	30.5
SB/En/BIH	2	179	191	3.9
SB/En/BIF	1	138	153	36.1
	1	142	147	14.3
SB/En/CF	2	181	190	8.0
	3	219	222	9.9

4.2 CBA Characterization

The decomposition behavior of the blowing agents was studied by thermogravimetric analysis. Results are presented in Figures 4.1 to 4.9. The onset decomposition temperatures, the temperatures at the maximum decomposition rate and mass changes after decomposition are summarized in Table 4.2.

Thermal decomposition of the SB/En/BIH and SB/En/BIF took place at the lowest temperature, 138°C. Since the onset decomposition temperature of these two blowing agents was very close to the melting temperature of the resin (123°C), it was expected that the blowing agents start to decompose while the melting and sintering process of the resin occurs. The gas generated from these early decomposed blowing agents may not be used entirely for blowing because the polymer matrix is not completely melted to form a continuous phase. However, since the temperatures at the maximum decomposition rates are 149°C and 153°C for SB/En/BIH and SB/En/BIF respectively, most decomposition must occur after the formation of a continuous phase of the polymer matrix. Therefore, SB/En/BIH and SB/En/BIF can be potential candidates as blowing agents for the rotational foam molding. A second minor decomposition reaction observed for SB/En/BIH from the DTG curve.

The DTG curve for SB/En/CF indicates that three main weight-loss stages occurred during the decomposition of this blowing agent, which resulted in a long activation range. SB/En/CF exhibited a complicated decomposition behavior.

AZ/Ex/G-EPC and AZ/Ex/C-AZ with onset decomposition temperatures of 175°C and 215°C, showed the highest onset decomposition temperatures and exhibited the maximum gas yield. Using theses high activation temperature blowing agents resulted in cavities in the final foamed part. This was related to the low melt viscosity and strength of the resin at high temperatures, preventing the formation of stable bubbles.

Consequently, high activation temperature and/or high gas yield were considered as a non-appropriate property for the blowing agents that are candidates for rotational foam molding. AZ/Ex/T-AZ (experimental blowing agent) provided the minimum weight loss. The rate of weight loss began to increase gradually from 146°C which is the onset temperature and led to a long activation range.

Decomposition of OB/Ex/G-OB, OB/Ex/C-OT and OB/Ex/T-OB occurred at the similar temperature, 166°C. These blowing agents followed very similar patterns of decomposition behavior. One notable characteristic was that the decomposition rate is very high. This implies that bubbles can be nucleated almost simultaneously, because most blowing agent particles will be decomposed almost at the same time. It should be emphasized that the decomposition rate of endothermic blowing agents (SB) are very low, and therefore, bubble nucleation will not occur simultaneously.

Summary of the results are presented in Figures 4.10 to 4.12.



Figure 4.1: TGA plot, decomposition behavior of AZ/Ex/G-EPC at a heating rate of 5°C/min



Figure 4.2: TGA plot, decomposition behavior of AZ/Ex/C-AZ at a heating rate of 5°C/min



Figure 4.3: TGA plot, decomposition behavior of AZ/Ex/T-AZ at a heating rate of 5°C/min



Figure 4.4: TGA plot, decomposition behavior of OB/Ex/G-OB at a heating rate of 5°C/min



Figure 4.5: TGA plot, decomposition behavior of OB/Ex/C-OT at a heating rate of 5°C/min



Figure 4.6: TGA plot, decomposition behavior of OB/Ex/T-OB at a heating rate of 5°C/min



Figure 4.7: TGA plot, decomposition behavior of SB/En/BIH at a heating rate of 5°C/min



Figure 4.8: TGA plot, decomposition behavior of SB/En/BIF at a heating rate of 5°C/min



Figure 4.9: TGA plot, decomposition behavior of SB/En/CF at a heating rate of 5°C/min



Figure 4.10: Decomposition behavior of all chemical blowing agents



Figure 4.11: Onset and peak decomposition temperature of chemical blowing agents



Figure 4.12: Mass change percentage of chemical blowing agents

4.3 Rotomolding Cycles

The rotomolding experiments were performed in the uniaxial rotational molding machine at different inside air temperatures in order to compare the performance of the blowing agents. The maximum inside air temperatures are presented in Table 4.3. In the first experiment for each material, the heating cycle interrupted when the inside air temperature in the mold reached the decomposition temperature of the blowing agent. It is important to maintain the processing temperature as low as possible to minimize the negative effects of cell coalescence and/or coarsening on the foam structure.

Figure 4.13 shows the inside air temperature profile of the rotational molding cycles at maximum inside air temperature (IAT) of 180°C. A comparison of the temperature profiles for the rest of IATs are presented in Appendix A. (Lines between points are provided for clarity and have no physical meaning.)

Blowing Agent (0.5%)	Maximum Inside Air Temperature (°C)					
Virgin Resin	210	220	230			
AZ/Ex/G-EPC	180	190	200	210	220	
AZ/Ex/C-AZ	180	190	200	210	220	
AZ/Ex/T-AZ	140	150	160	170	180	
OB/Ex/G-OB	170	180	190	200	210	
OB/Ex/-OT	160	170	180	190	200	
OB/Ex/T-OB	160	170	180	190	200	
SB/En/BIH	150	160	170	180	190	
SB/En/BIF	150	160	170	180	190	
SB/En/CF	160	170	180	190	200	

Table 4.3: Maximum inside air temperatures during rotational foam molding



Figure 4.13: Rotomolding profile for the blends of 0.5% CBA- Maximum IAT = 180°C

The shape of the temperature profiles was similar and all blends followed the same trend during heating and cooling cycles. In all graphs, four distinct stages can be seen during the heating cycle: induction, adherence, sintering and densification. However, temperature profiles showed different rates of sintering and densification for different blowing agents which is due to the different thermal insulation behavior of the foams being produced. Longer processing time was required for the cycles with lower rate of sintering and densification in order to reach the maximum inside air temperature. Also because of the thermal insulating properties of the foam, the inside air temperature overshot the removal temperature by up to 10°C.

After removal from the oven, the cooling stage started. The inside air temperature decreased steadily, until melt crystallization took place. It can be seen that the rate of heating in the sintering and densification stages of heating cycle and rate of cooling in the cooling cycle for the blends were considerably lower than the unfoamed part.

Due to the yellow color of the AZ blowing agent, it imparted a yellowish color to the final foamed part. Also the AZ blowing agents produced foams hard to de-mold.

4.4 Density

Figure 4.14 shows the effect of maximum inside air temperature on the foam density. The lowest foam densities were obtained with AZ (exothermic) blowing agents, AZ/Ex/C-AZ and AZ/Ex/G-EPC. There was an exception for AZ/Ex/T-AZ. Since the decomposition rate of AZ/Ex/T-AZ is very small and it has a very long activation range, its decomposition behavior is different (AZ/Ex/T-AZ is an experimental blowing agent). The density experienced a slight reduction with increasing maximum inside air temperature.



Figure 4.14: Density of the rotomolded foam parts as a function of maximum inside air temperature. Lines between points are provided for clarity and have no physical meaning.

OB (exothermic) blowing agents showed a slight increase in densities (OB/Ex/-OT, OB/Ex/G-OB and OB/Ex/T-OB) compared to AZ blowing agents. Foams containing OB blowing agents showed the least sensitivity in density to the changes of the inside air temperature and it is almost independent of the mold removal temperature. It was also noted that with OB blowing agents, there is less than 1.5% difference between the lowest and highest foam density and this can show a broad processing window for OB agents in rotational foam molding.

There is a distinct difference between densities of foams produced using SB (endothermic) blowing agents (SB/En/BIH, SB/En/BIF and SB/En/CF) and the exothermic blowing agents. SB blowing agents have the lowest activation temperature which is close to the melting point of the resin. The evolved gas from the early stages of decomposition may not be used totally for the foaming since the polymer matrix is not melted completely. Also at lower temperature, polymer melt shows higher melt viscosity. The lower density of the foams containing SB agents would seem to be in agreement with the theories that a higher melt viscosity will produce foam with higher density. SB/En/BIH and SB/En/BIF gave a density of 0.570 g/cm³ to 0.660 g/cm³, indicating that density did not vary much with inside air temperature.

Generally, exothermic blowing agents produced lower density foams. Although there is a difference in blowing agent activation temperatures, it can be seen that this trend is reproducible for a range of activation temperatures.

4.5 Wall Thickness

Figure 4.15 presents the average wall thickness of the molded foams as a function of inside air temperature of the mold. It was observed that wall thickness was inversely related to the density. Foams with a lower density gave a larger wall thickness. This is in agreement with the findings of Archer [2004] and Shutov in Klempner's book


Figure 4.15: Average wall thickness of the rotomolded foam parts as a function of maximum inside air temperature. Lines between points are provided for clarity and have no physical meaning.



Figure 4.16: Average wall thickness as a function of density

[Klempner, 2004] which state that the wall thickness is a linear function of foam density within a broad range of density (Figure 4.16).

Similar trend was observed for the wall thicknesses as obtained for densities. The AZ blowing agents, AZ/Ex/C-AZ and AZ/Ex/G-EPC (with exception of AZ/Ex/T-AZ) resulted in larger wall thicknesses than the rest of blowing agents. AZ/Ex/C-AZ showed the highest thickness, about 2.5 times higher than the unfoamed polymer. The wall thickness of the unfoamed part is approximately 3 mm.

OB blowing agents resulted in a slight decrease in wall thickness. For this category, it was found that the wall thickness values remained unchanged with the changes of mold removal temperature. This would be expected since density did not vary much with inside air temperature.

Foams containing SB blowing agents showed the lowest wall thickness and there was a significant difference between wall thicknesses of the foams produced using SB blowing

agents and foams containing exothermic agents. Similar to the densities, wall thickness of SB foams did not experience large variations with changes in the inside air temperature.

4.6 Volume Expansion Ratio

The volume expansion ratio (VER) for all samples has been calculated by implementing Equation (3.6) and then Equation (3.7) for the 100 g shot size of polyethylene used for rotational foam molding experiments. The room temperature is 25°C (298 K). If assuming an average value of 114°C for the crystallization temperature of polyethylene resin, the absolute crystallization temperature would be 387 K.

Figures 4.17 and 4.18 show the effect of the maximum inside air temperature on the volume expansion ratio for the blowing agents in comparison with other agents and with the expected value, respectively. Variations in the volume expansion ratio with inside air temperature followed the trend of changes in wall thickness. The highest volume expansion ratio was obtained with AZ/Ex/C-AZ and the lowest with SB/En/CF. Generally, endothermic agents gave lower expansion ratio than exothermic agents.

AZ blowing agents showed that a direct relationship exits between VER and the inside air temperature. At lower temperatures, they gave lower expansion ratio than expected value and at higher temperatures they reached or passed the expected value.

OB blowing agents exhibited a different trend. It was observed that over the range of inside air temperature tested, the volume expansion ratio did not change and almost were independent of the mold removal temperature. They showed almost the same value as expected. Also the volume expansion ratio of the foams produced by SB blowing agents did not vary very much with the inside air temperature. For all SB foams, the volume expansion ratio obtained was significantly lower than expected. There was an increase in the VER for SB/En/CF at 190°C which is related to the third stage of decomposition.



Figure 4.17: Volume expansion ratio of the rotomolded foam parts as a function of maximum inside air temperature. Lines between points are provided for clarity and have no physical meaning.



Figure 4.18: Volume expansion ratio vs. expected value



Figure 4.18: Volume expansion ratio vs. expected value

4.7 Cell Morphology

The cell size distribution has been shown to be a very important parameter when studying foams. The size and number of cells produced have a significant impact on the foam density and final properties of the foamed part. The average cell density and cell size of the foamed parts are shown in Figures 4.19 and 4.20. It was noted that there is a general downward trend between the cell density and inside air temperature. AZ blowing agents (with the exception of AZ/Ex/T-AZ) produced foams with a lower cell density and larger cell structure than two other categories of blowing agents. It can also be seen that the cell size of AZ foams were the most sensitive to changes in processing temperature and showed a significant change in the cell size as the inside air temperature increased while cell sizes in OB and SB foams did not vary very much with the mold removal temperature.

It is believed that the combination effect of the cell size and cell density should be in accordance with the foam density reduction trend with increasing temperature. It was observed earlier that the lowest foam density was obtained with AZ blowing agents and it seems that larger cell size in the AZ foams compensates the converse effect of the lower



Figures 4.19: Cell density as a function of maximum inside air temperature



cell density. OB foams showed lower foam density than SB foams, due to their higher cell density, although both categories showed very similar cell sizes. However, as foam density for OB foams was not observed to vary over the temperature range tested and the cell density decreased with temperature, it is logical to assume that average cell size has stronger impact on the foam density.

The cell size distributions obtained using 0.5% blowing agent are shown in Figures 4.21 to 4.23. In general, all samples followed a similar trend to that with higher inside air temperature, the peak of the cell distribution moved to the larger cell sizes, it resulted in broader distribution and showed less uniformity. Variance in the cell size distribution for the foamed parts is presented in Table 4.4. Variance shows the distribution around the weighted average; in other words it is a way to demonstrate the degree of being spread out. It can be seen from this table that AZ blowing agents showed the highest nonuniformity for the range of inside air temperature tested and OB agents exhibited the least. This confirms that OB blowing agents can provide wider processing window for rotational foam molding than the rest of the blowing agents. It can be concluded that in rotational foam molding a balance between decomposition rate, decomposition temperature and gas yield should be found to produce a uniform cell size distribution.

CBA	PIAT	140	150	160	170	180	190	200	210	220
AZ/Ex/G-EPC						3.300	5.947	5.932	15.016	20.709
AZ/Ex/C-AZ						3.896	5.852	11.054	22.250	20.370
AZ/Ex/T-AZ 0		0.519	0.789	0.882	1.424	1.763				
OB/Ex/G-OB					1.260	1.547	1.417	1.669	1.940	
OB/Ex/C-OT			1.486	1.259	1.219	1.461	1.488			
OB/Ex/T-OB			1.468	1.276	1.859	2.175	1.918			
SB/En/BIH		0.983	1.211	0.996	1.529	2.082				
SB/En/BIF		1.574	1.695	2.146	2.241	2.342				
SB/En/CF			0.785	0.742	0.828	1.405	1.615			

Table 4.4: Variances of cell size distribution of foamed parts



Figure 4.21: Cell size distribution of foamed parts- AZ blowing agents



Figure 4.22: Cell size distribution of foamed parts- OB blowing agents



Figure 4.23: Cell size distribution of foamed parts- SB blowing agents

Figures 4.24 to 4.32 show optical images of the cross-sectioned samples of the foamed parts. It is clearly seen that AZ blowing agents (with exception of AZ/Ex/T-AZ) gave a much larger cell sizes and lower cell density than OB and SB blowing agents, especially in higher temperatures. OB and SB blowing agents resulted in similar cell sizes. It can be seen that for the AZ foams there was a dramatic change in the cell size and shape, and cell density as the inside air temperature increased. At higher temperature the cell structure developed was destroyed and a coarse foam structure was obtained. Because of the lower melt viscosity and melt strength at higher temperatures, the high gas yield of AZ blowing agents resulted in cell coarsening,

It was also observed that the inner surface of the foam (close to the inside of the mold cavity) has smaller cell size and lower cell density, while cell size and cell density for the outer surface was similar to the centre of foam. This pattern was more obvious for the SB foams. The reason which may explain this is that the rotational molding process involves heat transfer from the oven into the polymer through the mold wall. When foaming begins, cells near to the wall produce an insulating effect. Therefore, the melt will be colder towards the inside of the mold cavity and this means higher viscosity and later nucleation and cell growth. Different diffusion behavior of N_2 and CO_2 towards the melt surface may also explain the different cell size and cell density at the inner surface of SB and AZ and OB foams. The escape rate of CO_2 is faster than that of N_2 in melted polymer.

Shape of the cells for all foams is mostly circular (spherical), however elliptical cells with varied degree of elongation also can be seen. All blowing agents gave a closed cell structure. In higher temperatures, it can be seen that two or more adjacent cells tend to get connected to each other and this is believed to be due to the cell coalescence and/or coarsening. When cell coalescence or coarsening occurs, the cell density deteriorates and consequently, the mechanical properties also deteriorate. Effective strategies for minimizing these two phenomena need to be established.



Figures 4.24: Cross-sectional images of foamed parts containing 0.5% AZ/Ex/G-EPC

Figures 4.25: Cross-sectional images of foamed parts containing 0.5% AZ/Ex/C-AZ





Figures 4.26: Cross-sectional images of foamed parts containing 0.5% AZ/Ex/T-AZ

Figures 4.27: Cross-sectional images of foamed parts containing 0.5% OB/Ex/G-OB





Figures 4.28: Cross-sectional images of foamed parts containing 0.5% OB/Ex/C-OT

Figures 4.29: Cross-sectional images of foamed parts containing 0.5% OB/Ex/T-OB





Figures 4.30: Cross-sectional images of foamed parts containing 0.5% SB/En/BIH

Figures 4.31: Cross-sectional images of foamed parts containing 0.5% SB/En/BIF





Figures 4.32: Cross-sectional images of foamed parts containing 0.5% SB/En/CF

4.8 Summary

The objective of this chapter is to obtain initial information on processing parameters and blowing agent selection by comparing the performance of different blowing agents over a wide range of processing temperatures. Chemical blowing agents from three different categories were investigated, AZ (exothermic), OB (exothermic) and SB (endothermic); and physical and morphological properties of the foamed parts were examined. Examined exothermic blowing agents release N₂ and endothermic blowing agents generate CO_2 . Exothermic blowing agents showed very high decomposition rate, while decomposition rate of endothermic blowing agents is low. It was found that because of low melt viscosity and strength of resin at high temperature, high activation temperature could be considered as a non-appropriate property for the blowing agent. Also low gas yield and long activation range may lead to a problematic foaming performance. Exothermic blowing agents produced lower density foams than endothermic blowing agents and OB blowing agents showed a wider processing window. OB blowing agents also provided the same volume expansion ratio as expected.

Cell size of AZ foams were the most sensitive to changes in processing temperature and showed a significant change in the cell size as the inside air temperature increased; while cell sizes in OB and SB foams did not vary very much with mold removal temperature. AZ blowing agents showed the highest nonuniformity of cell size distribution for the range of inside air temperature tested and OB agents exhibited the least. It was found that in rotational foam molding a balance between decomposition rate, decomposition temperature and gas yield should be found to produce a uniform cell size distribution.

It was concluded that OB blowing agents, followed by SB blowing agents offer the broadest operating window and the best foaming performance and were selected as the most suitable blowing agent for producing metallocene foams by rotational molding.

The optimum maximum inside air temperature at which the mold was removed from the oven, was found to be in the range of 180°C-190°C.

Chapter 5

Effect of Rheology

Rheological properties of the polymer material will impact the quality of the foam being produced. During the foaming process in rotational molding, the matrix polymer is deformed and displaced as cells form and grow. The speed and ease of bubble growth are determined by the melt properties of the matrix polymer. When cells expand, the surrounding material is required to stretch, introducing extensional forces in the surrounding melt. It has been shown that the melt elasticity and melt viscosity affect cell growth dynamics in viscoelastic polymer melts. However, the cell growth stage of the foaming process is controlled mainly by extensional viscosity and melt strength, due to the stretching actions. The objective of this chapter is to study the effect of rheological properties on the foaming process for rotational molding applications and examine morphology and physical properties of the molded foams.

5.1 Material Characterization

5.1.1 Rheological Properties

Table 5.1 shows the zero-shear of the six tested materials for the examination of the rheological properties, sorted from the lowest to highest zero-shear viscosity. Zero-shear viscosity has an important influence on the first steps of cell growth [Throne, 1996]. During initial growth, the cells require a low shear viscosity in order to reach their desired size and structure [Klempner, 2004]. Also lower zero-shear viscosity can be translated to better flow properties and faster sintering time. However, a very low zero-shear viscosity may not be beneficial for the foaming process as the associated reduction in melt strength (the degree of resistance to extensional flow) may lead to cell coalescence.

Material	Zero-Shear Viscosity (Pa.s)				
mPE-RA	966				
mPE-RB1	1052				
mPE-RB2	2672				
mPE-RB3	3199				
mPE-RB4	4948				
mPE-RB5	7271				

Table 5.1: Zero-shear viscosity of material resins (190°C)

Figure 5.1 shows the extensional viscosity as a function of extensional rate at 190°C. Measurements were made using the method of Cogswell [1996]. The extensional viscosity is an important property in foaming process which influences the cell growth, since during this stage the gas/polymer interface is being biaxially stretched [Throne, 2002]. mPE-RB3 showed the highest extensional viscosity for the range of extension rate



Figure 5.1: Extensional viscosity for tested material resins at 190°C



Figure 5.2: Storage modulus for tested material resins at 190°C

higher than 10 s⁻¹. A higher extensional viscosity will translate to greater resistance to deformation, which may slow cell growth. In addition, higher extensional viscosity can stabilize and terminate cell growth easier [Throne, 2002]. At the last stages of the cell growth, as the cells expand, the walls become thinner. In this case, the polymeric matrix with higher melt strength prevents cell rupture or coalescence. According to the values of the extensional viscosities, mPE-RB3 would exhibit more capacity to withstand the stretching forces during the last stages of the cell growth. It was observed that low extensional viscosity and low melt elasticity of mPE-RA and mPE-RB1 were not able to stabilize the growth of large cells and experienced rupture at higher blowing agent concentrations.

The melt elasticity also acts as a resistance force to deformation. As polymer chains are stretched, they will try harder to return to their original orientation. The storage modulus of the molded materials is presented in Figure 5.2. mPE-RA and mPE-RB1 exhibited considerably lower melt elasticities than the rest of resins. It can be seen from the graph that the storage modulus increases with increasing zero-shear viscosity. The storage modulus represents the elasticity of the melt and plays a significant role in sintering (coalescence) and cell growth dynamics. This should be an early indication that mPE-RB4 and mPE-RB5 might not be ideal resins for foaming application because of very high melt elasticity. The strong elastic forces will be difficult to overcome in foaming.

The loss modulus versus frequency is plotted in Figure 5.3. The loss modulus represents a material's viscous flow behavior. Comparing the loss modulus plot to storage modulus measurements, it can be seen that the trends are almost similar; however, the loss modulus exhibited larger values and a lower slope. mPE-RA and mPE-RB1 have very close loss modulus, but deviate as frequency increases. As a measure of the viscous property of the polymer melt, the loss modulus is important for both the early stage of cell growth and the terminal cell stabilization stage. While a higher loss modulus causes



Figure 5.3: Loss modulus for tested material resins at 190°C



Figure 5.4: Dynamic viscosity for tested material resins at 190°C

difficulties through the initial cell growth, it is favorable for achieving the desired final cell size during the cell stabilization stage.

The dynamic viscosity of polymer materials at 190°C is presented in Figure 5.4. Rotational molding is a temperature and time dependent process, in addition to its low shear character. However shear viscosity might be considered in the foaming process, because in the early stages of cell growth, shear forces can be introduced in foaming where expansion is very fast.

5.1.2 Molecular Weight Distribution (MWD)

The molecular weight distributions of all tested material resins are presented in Figure 5.5. As expected, mPE-RA showed the narrowest distribution. mPE-RB1, mPE-RB2, mPE-RB4 and mPE-RB5 had virtually identical distributions, followed by mPE-RB3 which showed the broadest distribution.



Figure 5.5: Molecular weight distribution of tested material resins

5.2 Monolayer Foam Moldings

5.2.1 Rotomolding Cycles

The first set of experiments was intended to use the information obtained from CBA screening experiments and study the behavior of polymer materials by using a concentration of 0.5% of two chemical blowing agents, OB/Ex/G-OB and SB/En/BIF.

A comparison of the inside air temperature profiles of material resins recorded in the uniaxial rotational molding machine can be seen in Figure 5.6 and 5.7. The heating cycle was interrupted when the inside air temperature in the mold reached 190°C which were found to be optimum in the Chapter 4.

The temperature profiles reflect the different melting behaviors of the polymers. The cycle times and shape of the temperature profiles for mPE-RA and mPE-RB1 were almost identical. Powder particles of these two resins started to melt and adhere on the mold earlier than the other. These resins have very close zero-shear viscosities.

The rest of polymer materials followed similar trend during the induction and adhesion stages. As the zero-shear viscosity increased, the rate of foaming and densification increased and shorter processing time was required in order to reach the maximum inside air temperature. It is due to the fact that by increasing zero-shear viscosity, materials produced lower foam thickness and consequently provided lower thermal insulation. Because of thermal insulating properties of the foam, the inside air temperature overshot the removal temperature by up to 6° C.

Polymer materials with high zero-shear viscosity and melt elasticity produced foams with bumpy surfaces. It was observed that powder particles tend to keep their identities. Similar observations have been made for both blowing agents. For further study, the next set of experiments was performed to produce foams with lower density by increasing the blowing agent concentration. The experiments performed using a concentration of 1.5% of OB/Ex/G-OB. SB/En/BIF was eliminated from further experiments as it was observed that endothermic blowing agents created a relatively small density reduction. This is due to the limiting heat flow parameters and diffusing behavior of carbon dioxide. This will be discussed in the next section.

Figure 5.8 shows the inside air temperature profile of the rotomolding cycles recorded in the uniaxial rotational molding machine with maximum inside air temperature of 180°C. By increasing zero-shear viscosity, significant reduction in the processing time was observed and the rate of foaming and densification was considerably increased. A shorter processing time was required due to the different thermal insulating properties of the foams; resins with lower zero-shear viscosity produced thicker foams which provided more thermal insulation to the heat flow during heating and cooling cycles. The cycle time required to complete the rotomolding process of mPE-RA and mPE-RB1 was comparable and the shape of the temperature profiles is almost identical.

The next set of experiments examines the use of higher concentration of OB/Ex/G-OB to reduce the density of the foam to the possible minimum value. Foam moldings were performed using polymer materials with 2.5% OB/Ex/G-OB. mPE-RA, mPE-RB1 and mPE-RB2 produced foams with very large voids and severe deformations with the addition of 2.5% blowing agent (Figure 5.10), therefore these three resins were eliminated from further experiments. This is related to the fact that mPE-RA, mPE-RB1 and mPE-RB2 have low melt strength and low zero-shear viscosity that could not provide enough resistance during the cell growth for the amount of expansion caused by 2.5% of blowing agent. When cells expand, the surrounding polymer shell is required to stretch and cells collapse if the melt properties of the matrix polymer do not support the extension.



Figure 5.6: Rotomolding profile for the blends of 0.5% OB/Ex/G-OB- Max IAT = 190°C



Figure 5.7: Rotomolding profile for the blends of 0.5% SB/En/BIF- Max IAT = 190°C







Figure 5.9: Rotomolding profile for the blends of 2.5% OB/Ex/G-OB- Max IAT = 180°C



Figure 5.10: mPE-RB1 + 2.5% OB/Ex/G-OB

A comparison of the inside air temperature profiles of material resins recorded in the uniaxial rotational molding machine can be seen in Figure 5.9. The heating cycle was interrupted when the inside air temperature in the mold reached 180°C. As the zero-shear viscosity increased, the rate of foaming and densification increased significantly and considerable shorter processing time was required in order to reach the maximum inside air temperature. It is due to the fact that resins with lower zero-shear viscosity produced higher thickness foams which provided more thermal insulation to the heat flow during heating and cooling cycles.

5.2.2 Density

Figure 5.11 shows density measurements of the parts produced using 0.5% blowing agent. Results are presented for two chemical blowing agents, OB/Ex/G-OB and SB/En/BIF. As expected, density is reduced in all cases when blowing agents were added (Density of unfoamed part $\approx 1 \text{gr/cm}^3$). It can be seen that greater density reductions were



Figure 5.11: Foam density of the parts containing 0.5% chemical blowing agent





obtained using OB/Ex/G-OB rather than SB/En/BIF, the density was reduced approximately 19% more while using this blowing agent.

The mPE-RA foamed parts had the lowest densities. As zero-shear viscosity and storage modulus increase, foams showed higher densities. Density values followed similar trends for the foamed parts produced by both blowing agents. There is a distinct difference between densities of foams produced using OB/Ex/G-OB (exothermic) and SB/En/BIF (endothermic). This is in good agreement with the results found in earlier experiments. The differences in the foam densities can be explained by the following scenarios or some combination of them:

- 1- This can be due to the differences in exothermic and endothermic reactions. Exothermic blowing agents release more energy during process of decomposition than needed for the reaction. Once decomposition has started, it continues spontaneously and goes on even when the energy supply has been stopped. Endothermic blowing agents need energy for decomposition. The gas release stops quickly after termination of heat supply and the initial layer of foam will cut the heat flow and terminate the foaming process.
- 2- According to Liu [Liu, 1998], exothermic blowing agents cause more reduction in foam density due to their higher decomposition rate. Higher decomposition rate leads to the higher cell size and/or cell density.
- 3- It also may be explained by the difference in permeability of the evolved gases. Exothermic blowing agents produce N₂ and endothermic blowing agents generate CO₂. Difference in the permeability of the gases may be the cause of the greater density reduction in foams containing OB/Ex/G-OB. The permeability of N₂ (2.7 cm³ mm/s cm² cmHg) is less than the permeability of CO₂ (35 cm³ mm/s cm² cmHg) [Throne, 1996].

4- Different behavior in terms of diffusion of N₂ and CO₂ towards the melt surface under concentration gradient may explain the differences in density reduction. CO₂ will diffuse, while N₂ will not [Throne, 1996].

For further investigation, foaming experiments performed using higher concentrations of OB/Ex/G-OB. Figure 5.12 shows density measurements for parts produced using 1.5% and 2.5% blowing agent. All materials were molded using 1.5% OB/Ex/G-OB; however three materials were selected for higher concentration of 2.5% OB/Ex/G-OB as was explained in previous section. By increasing blowing agent from 0.5% to 1.5%, foams experienced a significant density reduction of approximately 67%. The density was reduced approximately 76% using 2.5% blowing agent, compared to the 0.5% OB/Ex/G-OB.

Materials with lower zero-shear viscosity and storage modulus produced lower foam density. mPE-RB5 with the highest melt elasticity showed greatest resistance to cell growth and exhibited the lowest density. The same trend was observed for all concentrations of OB/Ex/G-OB.

mPE-RA, mPE-RB1 and mPE-RB2 showed very bad performance using 2.5% blowing agent. Besides lower viscosity and melt elasticity, it can be explained by their lower loss modulus. Higher loss modulus can help in the cell stabilization process to prevent cell collapse before recrystallization.

5.2.3 Wall Thickness

Figures 5.13 and 5.14 present average wall thickness of foamed parts produced by 0.5% OB/Ex/G-OB & SB/En/BIF, 1.5% and 2.5% OB/Ex/G-OB, respectively. It was observed that wall thickness was related inversely to the foam density; foams with lower density gave larger wall thickness.









Similar trend can be seen for the wall thicknesses as obtained for densities. OB/Ex/G-OB resulted in higher wall thickness than SB/En/BIF. At lower zero-shear viscosity and storage modulus, foams showed lower thickness. By increasing concentration of OB/Ex/G-OB from 0.5% to 1.5% and 2.5%, foams exhibited significant increase in wall thickness. (Thickness of unfoamed part \approx 3mm)

5.2.4 Cell Morphology

The observations of cell morphology from cross-sectional areas provided evidence of the effect of process parameters on foaming.

The average cell size and cell density obtained using 0.5% blowing agent are shown in Figures 5.15 and 5.16. There is a general downward trend for the cell size as zero-shear viscosity and storage modulus increased for both blowing agents. Lower viscosity and melt elasticity allow cell nucleation at early stages and formed cells continue to grow and produce large cells. The largest cell size observed with mPE-RA. This is because of the lower zero-shear viscosity of mPE-RA which led to the faster initial cell growth. The higher zero-shear viscosity of mPE-RA5 in comparison with the rest of resins caused considerable limitation in the cell inflation.

Foams containing SB/En/BIF showed more sensitivity in cell size to the changes in zeroshear viscosity, a significant reduction of 60% can be seen in cell sizes from mPE-RA to mPE-RB5, while this amount is 45% for the foams using OB/Ex/G-OB.

The number of cells for the foams containing OB/Ex/G-OB increased slightly by increasing zero-shear viscosity. However, this increase was offset by the considerable reduction in the cell sizes. Thus, it was the decrease in the cell size that caused the foam density to increase, despite the increase in cell densities.








A similar trend for cell density was observed for the foams produced by SB/En/BIF for mPE-RA, mPE-RB1, mPE-RB2 and mPE-RB3, higher viscosity led to increased number of cells. A different behavior was noticed for mPE-RB4 and mPE-RB5 as the number of cells decreased by increasing zero-shear viscosity.

As discussed in the previous chapter, it was assumed that the combined effect of the cell size and cell density should be in accordance with the foam density reduction trend and average cell size has a stronger impact on the foam density. The results totally support these assumptions.

It can be seen that OB/Ex/G-OB resulted in much higher cell density and smaller cell size than SB/En/BIF for the same polymer materials. This may be explained by differences in the decomposition rate of blowing agents. Blowing agents that evolve all their gas during a short period of time and over a narrow range of temperature may produce finer cell structures; all the cells will be nucleated approximately at the same time, the pressure in all the cells will be almost the same and coarsening will not take place. For slow decomposing blowing agents, the cells formed at early stages will continue to grow and produce a coarse cell population. The lower cell density for foams containing SB/En/BIF may alternatively be explained by the fact that the escape rate of carbon dioxide is faster than that of nitrogen in foamed parts.

Examples of some of the cross-sectional images used in this analysis are shown in Figure 5.17 to aid in visualizing changes. Higher blowing agent concentrations (1.5 and 2.5%) were also used in this study, however their cell morphology could not be analyzed using this two-dimensional image analysis technique as many cells overlapped one another.



Figures 5.17: Cross-sectional images of the foamed parts containing 0.5% chemical blowing agent

5.3 Two Shot Skin-Foam Moldings

In order to examine the foaming performance of the tested polymer materials under industrial processing conditions, skin-foam rotomolding experiments were performed using a pilot scale, biaxial rotational molding machine. mPE-RB1, mPE-RB2 and mPE-RB3 were selected for performing the skin-foam experiments. Due to the high melt elasticity, mPE-RB4 and mPE-RB5 were eliminated from further examination. Also mPE-RA was not used in the skin-foam study as it showed very similar results to mPE-RB1 in monolayer foam experiments. Skin-foam moldings were conducted using 2.5% and 3.5% OB/Ex/G-OB. In monolayer experiments, the concentration of 2.5% of blowing agent led to low quality foams, however because of industrial quality machinery in biaxial rotomolding machine, it was possible to use higher concentrations of blowing agents.

5.3.1 Rotomolding Cycles and Thickness Measurements

All skin-foam experiments were completed using following conditions:

- Skin: 450 g mPE-RB1+ 450 g mPE-RB3
- Foam: Resin + (2.5 or 3.5)% OB/Ex/G-OB
- 2nd shot added at 180°C

The first set of experiments was intended to study the effect of oven removal temperature on the molded foams. The rotomolding experiments were performed using 900 g shot weight of selected polymer materials and 2.5% OB/Ex/G-OB at two different maximum inside air temperatures, 160°C and 180°C. The inside air temperature profiles of rotomolding cycles are presented in Figure 5.18. All the moldings provided good foaming performance and produced foams with uniform and nice finished surface.

Figure 5.19 shows the average thickness measurements of the foams produced. It can be seen that the highest thickness were obtained using mPE-RB1, followed by mPE-RB2 and mPE-RB3. This is in agreement with results found from earlier experiments. Higher zero-shear viscosity and storage modulus led to foams with lower thickness. They showed approximately 3 times higher thickness than the unfoamed polymer (Thickness of unfoamed part \approx 3mm). It was noted that by increasing the inside air temperature, foams experienced a slight decrease in average thickness.

The next set of experiments were conducted using a higher amount of polymer materials for the foam layer (1800 g shot weight) and 2.5% OB/Ex/G-OB in order to study the effect of longer cycle time. Figure 5.20 shows the inside air temperature profile of the rotational molding cycles recorded in the biaxial rotational molding machine. The moldings were removed from the oven at 160°C; however, due to thermal inertia and the insulating effect of the foam, the inside air temperature reached 190°C. mPE-RB1 produced foam with severe deformations and extensive structural failure. The inner surface was extremely bumpy and very large voids can be seen in the skin-foam boundary. mPE- RB2 and mPE-RB3 performed well, however, early evidence of separation at the interface of the foam layer and skin layer for mPE- RB2 was observed. Examples of the cross-sectional and inner surface images are shown in Figure 5.20.

This may be explained by the differences in the melt strength. mPE-RB3 showed the highest extensional viscosity, followed by mPE- RB2 and mPE- RB1. Extensional viscosity acted as a resistance to deformation and facilitated the stabilization and termination of the cell growth. At the last stage of cell growth, as the cells expand, the walls become thinner. In this case, the polymeric matrixes with higher melt strength prevented cell rupture or coalescence. mPE-RB3 with higher melt strength exhibited more capacity to withstand the stretching forces during the last stages of the cell growth. Low extensional viscosity in addition to low melt elasticity of mPE-RB1 was not able to stabilize the growth of large cells.

The average thickness of the foamed parts is shown in Table 5.2. Surprisingly, mPE-RB3 showed much higher thickness than mPE-RB2. mPE-RB2 and mPE-RB3 provided approximately 4 times higher thickness than the unfoamed part (Thickness of unfoamed part \approx 6mm).

The next set of experiments examines the use of higher concentration of OB/Ex/G-OB to reduce the density of the foam to the possible minimum value under extreme processing conditions. Foam moldings were performed using 1800 g shot weight of polymer materials with 3.5% OB/Ex/G-OB. mPE-RB1 was eliminated from further examinations due to the poor performance in the last set of experiments. mPE-RB2 produced a very deformed foam with bumpy surfaces and long cracks along the interface of the foam layer and skin. mPE-RB3 exhibited very nice performance and showed about 6.5 times higher thickness than unfoamed part. Due to the very long processing cycle, some thermal degradation had occurred in the foam-skin boundary (Figure 21).

The poor performance of mPE-RB2 compared to the mPE-RB3 could be explained again by the lower extensional viscosity. At the extreme processing conditions and with higher blowing agent concentrations, large cells were not able to stabilize and experienced rupture.



Figure 5.18: Rotomolding profiles for skin-foam experiments- 2.5% OB/Ex/G-OB



Figure 5.19: Average thickness of foam in skin-foam moldings

Table 5.2:	Average thickness of foam in skin-foam moldings	
	Skin: 450 g mPE-RA+ 450 g mPE-RB3	
	Foam: 1800 g RESIN+ OB/Ex/G-OB	

	2.5% OB/Ex/G-OB	3.5% OB/Ex/G-OB
mPE-RB1	NA	NA
mPE-RB2	20 mm	NA
mPE-RB3	27 mm	40 mm



Figure 5.20: Rotomolding profiles for skin-foam experiments- 2.5% OB/Ex/G-OB





5.4 Summary

In this chapter the effect of rheological properties of the resins on the foaming process and final foam properties was studied and morphological and physical properties of the molded foams were examined. Also the influence of processing parameters and blowing agent concentration on monolayer and multilayer foams were investigated.

Experiments on the foaming behavior of several rotational molding grade metallocene polyethylenes revealed that the foaming process and final foam properties are profoundly influenced by the rheological properties of the polymer materials. Generally, resins with lower zero-shear viscosity and melt elasticity resulted in lower foam density. This trend is applicable for all the tested concentrations of blowing agent in this study. It was concluded that a very low zero-shear viscosity may not be desirable for the foaming process as the associated reduction in melt strength could not support the extension.

The extensional viscosity was observed to affect significantly the rotational foam molding process. A higher extensional viscosity will translate to greater resistance to deformation, which may slow cell growth. In addition, higher extensional viscosity can stabilize and terminate cell growth easier.

mPE-RB3 due to the high extensional viscosity, exhibited more capacity to withstand the stretching forces during the stage of cell growth. It was observed that low extensional viscosity and low melt elasticity of mPE-RA and mPE-RB1 were not able to stabilize the growth of large cells and experienced rupture at higher blowing agent concentrations.

The melt elasticity of the polymeric matrix was showed to be an influencing factor during the foaming process. The strong elastic forces of mPE-RB4 and mPE-RB5 were difficult to overcome during the foaming process and the powder particles of these two resins tended to keep their identities.

The cell distributions were measured for the foamed parts. Attempts were made to correlate differences in cell sizes with the rheological properties of different resins. There is a general downward trend for the cell size as zero-shear viscosity and storage modulus increased for both blowing agents. The largest cell size observed with mPE-RA. This is because of the lower zero-shear viscosity of mPE-RA which led to the faster initial cell growth. The higher zero-shear viscosity of mPE-RA5 in comparison with the rest of resins caused considerable limitation in the cell expansion.

Experiments on two shot skin-foam moldings of metallocene polyethylene showed that there is a good correlation between the foam produced in monolayer moldings and skinfoam moldings. Similar to monolayer foaming, higher zero-shear viscosity and storage modulus led to foams with lower thickness. It was found that the maximum inside air temperature has no significant effect on the foam thickness, and resins with low zeroshear viscosity and melt elasticity exhibited poor performance with long processing time.

The effect of extensional viscosity is more pronounced in foaming with high concentrations of blowing agent and extreme processing conditions.

Chapter 6

Effect of Surface Tension

The interfacial properties of polymer melts are important in rotational molding and surface tension has been recognized as a driving force for particle coalescence in sintering [Tinson, 2004]. However, surface tension is expected to retard cell growth during foaming process by providing an additional resistance to the cell boundary [Han, 1981]. The objective of this chapter is to examine the role of surface tension of polymer materials in the foaming process for rotational molding applications and study morphology and physical properties of the foamed parts being produced.

6.1 Material Characterization

6.1.1 Surface Tension

The surface tensions of five tested polymer materials are presented in Figure 6.1. Surface tension measurements have been performed using the pendant drop method at 190°C.



Figure 6.1: Surface tension of tested material resins

According to literature [Tinson, 2004] surface tension is a decreasing linear function of temperature. It can be seen that mPE-SB5 showed the highest value of surface tension, followed by mPE-SB4, mPE-SB3, mPE-SB2 and mPE-SB1. Difference in surface tensions corresponds to different additives (thermoplastic elastomers) that have been added to a metallocene rotational molding grade polyethylene. It is believed that higher surface tension decreases the rate of cell growth during the foaming process, especially

when the cell size is small [Han, 1981].

6.1.2 Rheological Properties

The rheological properties of the polymer materials were obtained through dynamic mechanical rheological tests. The storage modulus, loss modulus and dynamic viscosity of polymer materials at 190°C are presented in Figures 6.2, 6.3 and 6.4, respectively. It can be clearly seen that all the materials showed very similar rheological properties for the tested range of shear rate. It was found by Tinson [2004] that rheological properties are dominant parameters in the sintering of polymer particles. However, when comparing the differences in sintering of two or more materials with similar rheological properties, the surface tension becomes the key parameter. This is based on the fact that the rheological properties exponentially decrease with temperature while surface tension only decreases linearly.



Figure 6.2: Storage modulus for tested material resins at 190°C



Figure 6.3: Loss modulus for tested material resins at 190°C



Figure 6.4: Dynamic viscosity for tested material resins at 190°C

6.2 Rotomolding Cycles

Rotomolding experiments were performed a using uniaxial rotational molding machine with a concentration of 0.5% of two chemical blowing agents, OB/Ex/G-OB and SB/En/BIF. Figures 6.5 and 6.6 show the inside air temperature profiles of the rotational molding cycles. The heating cycle was interrupted when the inside air temperature in the mold reached 190°C. It was observed that cycle times and the shape of the temperature profiles for the experiments using OB/Ex/G-OB are virtually identical. The temperature profiles of the experiments using SB/En/BIF showed a slight difference during the stage of sintering, mPE-SB4 and mPE-SB5 exhibited higher rate of sintering than the rest of materials. Comparing the rotomolding cycles of two blowing agents, a higher rate of densification and cooling was observed for the OB/Ex/G-OB experiments and longer processing time was required in order to reach the maximum inside air temperature. This is due to the fact that OB/Ex/G-OB produced lower foam density and consequently provided higher thermal insulation. Because of thermal insulating properties of the foam, the inside air temperature overshot the removal temperature by up to 5°C.

6.3 Density

Figure 6.7 shows density measurements of the parts produced using 0.5% blowing agents, OB/Ex/G-OB and SB/En/BIF. It can be seen that greater density reductions were obtained using OB/Ex/G-OB rather than SB/En/BIF, the density was reduced by approximately 25% more while using this blowing agent (Density of unfoamed part \approx 1gr/cm³). This is in agreement with results found from earlier experiments.

It was found that the density of foam produced by OB/Ex/G-OB did not vary very much with surface tension; the density showed a very slight increase as surface tension increased. However, foams containing SB/En/BIF showed more sensitivity in density to







Figure 6.6: Rotomolding profile for the blends of 0.5% SB/En/BIF- Max IAT = 190°C







Figure 6.8: Wall thickness of the foamed parts containing 0.5% chemical blowing agent

the changes in surface tension. mPE-SB1 foamed parts had the lowest density and by increasing surface tension, foams exhibited higher density values.

Foams produced by exothermic and endothermic blowing agents behaved differently upon changes in surface tension. In the case of SB/En/BIF (endothermic), the trend of changing density corresponds to the changes in surface tension, where higher surface tension led to an increase in foam density. It was found by Han [1981] that higher surface tension decreases the rate of cell growth by providing resistance for the cell boundary; this is of greater importance for smaller cell sizes. The small size of the cells produced by SB/En/BIF may explain the sensitivity the foams to the variation of surface tension.

It can be seen that rheology has a stronger effects on the foams produced by OB/Ex/G-OB (exothermic) than surface tension. This could be due to the larger size of the cells that exothermic blowing agent created during the foaming process and made the cell growth less sensitive to the value of surface tension.

6.4 Wall Thickness

Figure 6.8 presents average wall thickness of foamed parts produced by 0.5% OB/Ex/G-OB and SB/En/BIF. The trend of changes of wall thickness with surface tension is related inversely to the changes of the foam density. The wall thickness of the foams containing OB/Ex/G-OB did not show much variation over the changes of surface tension; while by increasing surface tension, the wall thickness of foams produced by SB/En/BIF decreased. Generally, OB/Ex/G-OB resulted in higher wall thickness than SB/En/BIF.

6.5 Cell Morphology

The average cell size and cell density obtained using 0.5% blowing agent are shown in Figures 6.9 and 6.10. A portion of the cross-sectional images are also shown to aid in visualizing changes (Figure 6.11). The results provide some explanations for the changes in foam density. It can be seen that OB/Ex/G-OB resulted in higher cell size and cell density than SB/En/BIF for the same polymer materials. The results are in good agreement with findings in Chapter 4, since the rheological properties of the resins are similar to those of mPE-RB3.

The cell size and cell density of the foams containing OB/Ex/G-OB are almost independent of the changes in surface tension and explains the behavior of the foam density. This indicates that while using an exothermic blowing agent, rheological properties of the resins are dominant parameters in the foaming process. This may be explained by the high decomposition rate of exothermic blowing agent. It is believed that gas release during a short period of time and over a narrow range of temperature can overcome the resistance of higher surface tension.

There is a downward trend for the cell size and cell density of the foams containing SB/En/BIF as surface tension increases. Similar to the foam densities, size and number of cells are sensitive to the changes in surface tension. It could be due to the low decomposition rate of endothermic blowing agent. The slow evolution of blowing agents caused the nucleation of small cells at early stages. It is believed that for the range of viscosity tested in this work, the gas pressure inside a small cell would not be sufficient to overcome the resistance provided by surface tension. At higher surface tension, the pressure difference between the cell and the surrounding polymer melt will increase which leads to smaller cell size and lower cell density.











Figures 6.11: Cross-sectional images of the foamed parts containing 0.5% chemical blowing agent

6.6 Summary

In this chapter the role of surface tension in the foaming process for rotational molding applications was studied and physical and morphological properties of the foamed parts were examined. Five polymer materials with similar rheological properties and different surface tension were selected. An exothermic (OB/Ex/G-OB) and an endothermic (SB/En/BIF) blowing agent were used to conduct the foaming experiments. By examining and comparing the foamed part properties of materials with similar rheological properties, it can be concluded that type of reaction of the blowing agent (exothermic and endothermic) determines the resin property (surface tension or rheology) that contributes to the trend of changes in foam properties.

For foams containing exothermic blowing agent, rheological property is the key parameter and foamed part properties are independent of the changes in surface tension. All the resins resulted in similar physical and morphological properties. This is due the high decomposition rate of exothermic blowing agent; fast gas release over a narrow range of temperature can offset the changes in surface tension. Also, larger cell size created by exothermic blowing agent makes the cell growth less sensitive to the value of surface tension.

For foams containing endothermic blowing agent, it was found that the surface tension becomes the key factor in the foaming process. The foam properties correlated well with the trend of changes in surface tension and higher surface tension led to an increase in foam density. The small size of the cells produced by endothermic blowing agent may explain the sensitivity to the variation of surface tension. The low decomposition rate of endothermic blowing agent results in small cells and it is believed that the gas pressure inside the cell would not be adequate to overcome the resistance provided by surface tension. Measuring surface tension with rheological properties can help to further understand the foaming process in the rotational molding of different materials.

Chapter 7

Concluding Remarks and Recommendations

7.1 Conclusions

An experimental study of the rotational foam molding of metallocene catalyzed polyethylenes revealed that through the use of suitable chemical blowing agents, metallocene polyethylenes provide good weight reduction and lead to a unique foaming performance.

7.1.1 CBA Screening and Processing Parameters

The investigations of the foaming performance of three different categories of chemical blowing agents over a wide range of processing temperatures demonstrated that selecting an appropriate chemical blowing agent is very crucial as the final foam structure depends greatly on the properties of the blowing agent. This study leads to the following conclusions:

- It was observed that endothermic blowing agents resulted in smaller density reduction than exothermic blowing agents. This is due to the limiting heat flow parameters, higher permeability and diffusing behavior of CO₂ compared to N₂. It was concluded that producing low density foams using an endothermic blowing agent would be difficult.
- Decomposition temperature, decomposition rate and the amount of gas generated are the critical parameters of blowing agents. It was observed that a balance between these three parameters should be found in order to achieve control over the foam structure. The high activation temperature could be considered as a non-appropriate property for the blowing agent leading to a poor foam structure and a warped, overcooked molding. Also low gas yield and long activation range may provide a problematic foaming performance.
- The processing conditions were also seen to affect the final properties of the foams. Under the experimental procedures, by increasing the maximum inside air temperature, the average cell size increased and consequently resulted in higher density reduction. Cell sizes of the Azodicarbonamide (AZ) foams were the most sensitive to changes in processing temperature, while cell sizes in the foams containing 4,4'-oxy-bis(benzene sulfonylhydrazide) (OB) and Sodium bicarbonate (SB) did not vary much with mold removal temperature. The optimum maximum inside air temperature at which the mold was removed from the oven, was determined to be in the range of 180°C-190°C.

It was concluded that OB blowing agent offers the broadest operating window and the best foaming performance and in particular, Genitron OB was selected as the most suitable blowing agent for producing metallocene foams by rotational molding.

7.1.2 Foam Properties

Rotational foam molding experiments were performed in monolayer and skin-foam moldings and morphology and physical properties of the foamed parts were examined.

Monolayer Moldings

The addition of 0.5% of Genitron OB led to an average density reduction of 40% in monolayer experiments, while it was 25% for 0.5% of Hyrocerol BIF. Therefore greater density reductions were obtained using exothermic blowing agent. Increasing the amount of Genitron OB concentration resulted in significant reduction in foam density. The density was reduced approximately 67% using 1.5% blowing agent and approximately 76% using 2.5% blowing agent.

The cell size distributions were also measured for the foamed parts. In general, all samples followed a similar trend and with higher inside air temperature, the peak of cell distribution moved to the larger cell sizes and resulted in broader distribution.

It was assumed that the combination effect of the cell size and cell density should be in accordance with the foam density reduction trend. The results totally support these assumptions. The observations of the variation in the cell density and cell size corresponded well with the variations of the foam density, wall thickness and volume expansion ratio. It was observed that the average cell size has stronger impact on the foam density than cell density. It was also demonstrated that the wall thickness is inversely a linear function of the foam density.

Attempts were made to correlate differences in cell sizes with the rheological properties of different resins. There is a general downward trend for the cell size as zero-shear viscosity and storage modulus increased for both blowing agents. The largest cell size observed with mPE-RA. This is because of the lower zero-shear viscosity of mPE-RA which led to the faster initial cell growth. The higher zero-shear viscosity of mPE-RA5 in comparison with the rest of resins caused considerable limitation in the cell expansion.

• Skin-Foam Moldings

Experiments on two shot skin-foam moldings of metallocene polyethylene demonstrated that there is a good correlation between the foam properties produced in monolayer moldings and skin-foam moldings. Similar to monolayer foaming, higher zero-shear viscosity and storage modulus led to foams with lower thickness. The processing conditions were also seen to affect the foaming process. Resins with low zero-shear viscosity and melt elasticity exhibited poor performance with long processing time. However, the maximum inside air temperature was shown to have no significant effect on the foam thickness. In terms of rheology, it was concluded that polymer materials with high extensional viscosity could provide a promising foaming performance at different processing conditions.

7.1.3 Effect of Rheology

Experiments on the foaming behavior of several rotational molding grade metallocene polyethylenes showed that the foaming process and final foam properties are profoundly influenced by the rheological properties of the polymer materials. Based on the experimental results, the following conclusions may be drawn:

• Resins with lower zero-shear viscosity resulted in lower foam density. Due to higher thermal inertia and the insulating effect of the foams produced by low zero-shear viscosity, longer processing time was required in order to reach the maximum inside air temperature. This trend is applicable for all the tested concentrations of blowing agent in this study. It was concluded that a very low zero-shear viscosity may not be

desirable for the foaming process as the associated reduction in melt strength could not support extension.

- The extensional viscosity was observed to significantly affect the rotational foam molding process. Polymeric matrix with higher melt strength provided higher resistance to the cell rupture. Although mPE-RB3 has considerably lower zero-shear viscosity and melt elasticity compared to mPE-RB4 and mPE-RB5, mPE-RB3 provided a promising foaming performance at different processing conditions due to the higher extensional viscosity and exhibited more capacity to withstand the stretching forces during the stage of cell growth. The effect of extensional viscosity is more pronounced in foaming with high concentrations of blowing agent and extreme processing conditions. Resins with low melt strength could not offer enough resistance for the expansion caused by high concentration of the blowing agent.
- The storage modulus, representing the melt elasticity, was shown to be an influencing factor during the foaming process. In general, resins with lower melt elasticity resulted in lower foam density. Also polymer materials with high melt elasticity produced foams with rough surfaces. This is due to the fact that the powder particles of the resins with high storage modulus tend to keep their identities during the process. Endothermic blowing agents could not overcome the high amount of melt elasticity, therefore they provided very small density reduction.

In general, properties of the foams containing endothermic blowing agents showed more sensitivity to the changes in rheological properties compared to the foams produced by exothermic blowing agents.

7.1.4 Effect of Surface Tension

The effect of surface tension on the foaming process and foam properties was examined. By examining and comparing the foamed part properties of materials with similar rheological properties, it can be concluded that type of reaction of the blowing agent (exothermic/endothermic) determines whether the surface tension of the resin contributes to the trend of changes in foam properties.

For foams containing exothermic blowing agent, it was found that rheology is the dominant parameter and foamed part properties are independent of the differences in surface tension. However, it was found that the surface tension becomes the key factor in the foaming process of the foams produced using endothermic blowing agents. The foam properties correlated well with the trend of changes in surface tension and higher surface tension led to an increase in foam density. Measuring surface tension with rheological properties can help to further understand the foaming process in the rotational molding of different materials.

7.2 Recommendations for Future Work

In order to observe the cell nucleation process and cell growth under various processing conditions, a hot stage microscopy is proposed. In this technique, the samples are heated up to the desired temperatures on a hot stage and foam development can be observed and recorded using a microscope and camera. By using the information provided by this technique, the effect of the viscous and elastic properties of the polymer material, as well as the importance of the melt strength during the foaming process could be studied. A balance between different parameters involved in the cell growth process could be found by developing a mathematical model.

The two dimensional bubble analysis technique used in this study is not acceptable for studying low density foams with high cell counts because of excessive cell-overlap. A new method should be developed which can analyze samples in three dimensional.

A comparison of the mechanical properties of the foamed parts can provide valuable information regarding the possible commercial applications for the final products.

An extensive investigation on the multilayer moldings is needed in order to study the foaming behavior of the polymer materials under various operating conditions.

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Appendix A

Rotomolding Profiles for blends of mPE-RB1 + 0.5% CBA



Figure A.1: Rotomolding profile for mPE-RB1 + 0.5% AZ/Ex/G-EPC



Figure A.2: Rotomolding profile for mPE- RB1 + 0.5% AZ/Ex/C-AZ



Figure A.3: Rotomolding profile for mPE- RB1 + 0.5% AZ/Ex/T-AZ



Figure A.4: Rotomolding profile for mPE- RB1 + 0.5% OB/Ex/G-OB



Figure A.5: Rotomolding profile for mPE- RB1 + 0.5% OB/Ex/C-OT



Figure A.6: Rotomolding profile for mPE- RB1 + 0.5% OB/Ex/T-OB



Figure A.7: Rotomolding profile for mPE- RB1 + 0.5% SB/En/BIH



Figure A.8: Rotomolding profile for mPE- RB1 + 0.5% SB/En/BIF



Figure A.9: Rotomolding profile for mPE- RB1 + 0.5% SB/En/CF



Figure A.10: Rotomolding profile for unfoamed mPE-RB1