PROCESSING OF FINE-CELL POLYPROPYLENE FOAMS IN COMPOUNDING-BASED ROTATIONAL FOAM MOLDING

by

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ABSTRACT

This thesis is intended to provide a scientific and engineering understanding of the technological potentials for processing fine-cell PP foams by using a compounding approach in rotational foam molding. The presented research includes a proposal for a process designed for transforming polypropylene (PP) resins into completely foamed, single-layer, single-piece useful products. The proposed process comprises dispersing a chemical blowing agent (CBA) in the PP matrix in a twin-screw compounder, pelletizing the obtained expandable composition, and using the pre-compounded pellets for foam production in one uninterrupted rotational foam molding cycle. Four types of PP resins were selected with melting flow rates (MFR) ranging from 5.5 to 35 dg/min. The PP resins and the CBA were characterized using thermal analysis instrumentation, a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA). Using different formulations, four types of pellets were compounded with a CBA from each type of PP resin for conducting rotational foam molding experiments using an uni-axial lab-scale rotational molding machine. A scanning electron microscope (SEM) was used to characterize the quality of the compounded PP pellets. The optimal processing strategies for six-fold and three-fold PP fine-cell foaming were identified via a systematic experimental parametric search. By using time-temperature profiles, recorded using a data acquisition device, the process was characterized and strategies for process improvements were established. Best foams were obtained by using the highest viscosity resins.

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%CBA = percent of chemical blowing agent (by weight) in pure resin

η = fluid viscosity (dyne-second/cm^2)

φ = volume of gas generated per unit mass of blowing agent (cm^3/g)

φ_{STP} = volume of gas generated per unit mass of blowing agent at room temperature (cm^3/g)

$\rho_{polymer}$ = density of polymer material (g/cm^3)

ΔT = temperature difference between the two pans of the DSC cell (°C)

(VER) = volume expansion ratio

D = channel width (cm)

m_{CBA} = weight of chemical blowing agent (g)

$m_{polymer}$ = weight of polymer material (g)

P = fluid density (g/cm^3)

R_D = thermal resistance of the constantan pan of the DSC cell

Re = Reynolds number

$T_{\text{CBA decomposition}}$ = decomposition temperature of the chemical blowing agent (°C)

$T_{\text{coalescence}}$ = temperature of cell coalescence (°C)

$T_{\text{polymer melting}}$ = melting temperature of the polymer (°C)

$T_{\text{processing (compounding)}}$ = processing temperature during compounding (°C)

$T_{\text{processing (foaming)}}$ = processing temperature during rotational foam molding (°C)

$T_{\text{sintering}}$ = temperature of polymer sintering (°C)

$T_{\text{thermal degradation}}$ = temperature of polymer thermal degradation (°C)

$\mathrm{T_C}$ = crystallization temperature of a polymer (°C)

$\mathrm{T_G}$ = glass transition temperature of a polymer (°C)

$\mathrm{T_M}$ = melting temperature of a polymer (°C)

T_{room} = room temperature (°C)

V = average velocity of the flow in the channel (cm/s)

V_C = volume of gas generated by CBA decomposition at polymer crystallization temperature (cm^3)

V_f = expanded foam volume (cm^3)

V_i = initial volume of the solid plastic material (cm^3)

V_m = volume of the mold (cm^3)

V_{room} = volume of gas generated by CBA decomposition at room temperature (cm^3)

CHAPTER 1

INTRODUCTION

1.1 Preamble

In the 1930s, the fascination from the optimally balanced strength and weight of some naturally occurring cellular structures, such as animal bones and wood, motivated undertakings for developing methods for converting manmade materials into foamed structures that can achieve competitive properties. Thereby, the concept of foaming plastics was established [1]. Foamed plastics were first used in the armed services during World War II [2], and since then, driven by an intensive development of a wide variety of applications, the industry of plastic foams is permanently growing.

1.1.1 Plastics Foaming Rationale

Plastics are foamed for reasons of concurrently improving the economics and enhancing the performance of plastic articles while keeping their functionality unchanged. The improved economy of foamed plastics follows from the fact that plastic foam densities can be substantially reduced, ranging from about 1.6 kg/m^3 to over 960 kg/m^3 [3], so that the resin consumption during production can be lowered. As a consequence, foamed plastic articles are lighter and less expensive than equally dimensioned non-foamed ones made of the same resin.

This is of great importance for plastic processors because the raw material costs in the production of conventional plastic articles can often reach up to 70 % [4] of the total costs.

Plastic foams comprise at least two phases, a solid polymer matrix, and a gaseous phase originating from at least one gas-generating substance such as a blowing agent [3-5]. "A foamed plastic or cellular plastic has an apparent density, which is decreased by the presence of numerous voids or cells dispersed throughout its mass", (ASTM definition D883-80C). The cellular structure of plastic foams enhances the performance of foamed plastic articles by generating unique properties, such as load bearing, cushioning, impact resistance, insulation, and buoyancy. A proportional relationship exists between the mechanical-strength properties of a foamed plastic article and the density of its foam [3, 6]. Therefore, foamed plastic articles can often be stronger than their non-foamed analogues and, because of the reduced weight, can achieve outstanding cost-to-performance and favorable strength-to-weight ratios [7].

1.1.2 Classification of Plastic Foams

The most commonly used criterion for distinguishing various plastic foam types is the combination of the average foam cell size and the cell density per unit volume. According to this criterion, plastic foams are divided into three categories that include conventional foams (cell size > 100 μm and cell density < 10^6 cells/cm^3), fine-cell foams (10 μm < cell size < 100 μm and 10^6 cells/cm^3 < cell density < 10^9 cells/cm^3), and microcellular foams (cell size < 10 μm and cell density > 10^9 cells/cm^3) [4].

However, other classification criteria for plastic foams also exist. For instance, besides being classified by the nominal dimension across the cell and the number of cells per unit volume, plastic foams can be also classified by adopting the foam surface area per unit weight as a classifying parameter. This methodology uses the BET (Brunauer, Emmett and Teller) model to measure the surface area and distinguishes between commercial foams (cell size 100-500 μm, BET surface area 0.1–1 m^2/g, cell density 10^5 cells/cm^3), fine-cell foams from cross-linked polyolefins (cell size 20-100 μm, BET surface area 10 m^2/g, cell density 10^6 cells/cm^3), microcellular foams (cell size 5-20 μm but typically < 10 μm, BET surface area 10-20 m^2/g, cell density 10^7-10^9 cells/cm^3), and ultramicrocellular foams (cell size 0.1-1 μm, BET surface area 100-400 m^2/g, cell density 10^9-10^{12} cells/cm^3) [7].

The relationship between the plastic foam glass-transition temperature and the room temperature can also be used as a classifying criterion. This kind of classification recognizes flexible, semi-flexible (or semi-rigid), and rigid foams. Flexible foams are associated with glass transition temperatures below the room temperature, semi-flexible foams are defined as an intermediate state between flexible and rigid foams, while rigid foams are associated with glass transition temperatures above the room temperature [5].

Another way of classifying plastic foams employs the fact that the cell morphology of the foam, comprising cell geometry, cell size, and cell shape, strongly affects plastic foam properties. Thus, cells may be interconnected and/or discrete and independent. This method differentiates between open-celled and closed-celled foams [5].

The foam bulk density and the void fraction can also serve as a criterion for classifying plastic foams. According to this criterion plastic cellular structures can be classified as high-density and low-density foams [7]. High-density foams assume a density of over 240 kg/m^3, while low-density foams assume a density lower than 240 kg/m^3 [3].

1.1.3 Application of Foamed Plastics

Foamed plastic articles can successfully conserve energy and natural resources. For example, foamed insulation products reduce energy consumption, while those used for protective shipping reduce product damage, and thereby contribute for lower manufacturing costs and less waste [8]. In transportation applications, the reduction of vehicle weight by replacing steel with a structural foam decreases the fuel consumption [5]. High-density foams are basically used in furniture, wires and cables [3], automotive and structural applications, while low-density foams are used for shock mitigation, insulation, and rigid packaging [7]. Rigid high-density foams are preferred for structural and load bearing applications, rigid low-density closed-cell foams are used for thermal insulation [5] and for applications where buoyancy is important [3], while rigid low-density open-cell foams are most suitable for acoustical insulation [5]. Flexible foams are used for thermal insulation, comfort cushioning, and packaging [5].

1.1.4 Recent Trends in the Industry of Foamed Plastics

The industry of plastic foams accounts for more than 10% of the entire plastic industry [8]. It is based on the use of extrusion foaming and foam injection molding as principal foam fabrication processes [3, 7]. Although dominating the industry, these processes are unable to respond to the increasing market demands for economic fabrication of very large, complex-shaped, plastic articles that can achieve improved stiffness-to-weight ratios and high surface quality without added finishing expenses [7]. Since such properties can be only achieved by creating a foam layer or a foam core in the interior of rotomolded hollow articles, in the last decade, as a response to these demands, the conventional rotomolding process has been redesigned to serve as a plastic foam fabrication process. At approximately the same time, similar reasons contributed for converting other conventional plastic processing technologies for producing hollow articles, such as twin sheet thermoforming, structural blow molding, and gas injection molding, into foam fabrication processes [7].

Conventional rotomolding is one of the oldest technologies originally designed for production of plastic hollow articles. Its most recent modification, used for production of plastic foamed articles, is commonly referred to as rotational foam molding. Unlike other processes used for producing foamed plastic articles, the rotational foam molding is capable to deliver very large products while maintaining a considerably low tooling budget. It can be effectively used for producing completely or partially foamed single-piece, plastic articles with or without a non-foamed skin surrounding the foamed core or layer [7].

1.1.5 The Importance of PP Foams

Despite PP has been discovered in 1954 [9], polyethylene (PE) is still the material of choice for rotomolding operations due to the favorable nature of its processing properties [7]. PP has not been used extensively in rotomolding, because, until recently, most PP grades had relatively poor impact properties compared to linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE) which resulted in the domination of PE-based resins in rotomolding. However, due to the nature of its end-use properties, PE failed to satisfy the market demands for providing foamed plastic articles that would simultaneously possess high performance, lightweight, and high heat resistance (beyond 120 °C). Therefore, although PE is much more favorable for foaming than PP, PP foams are preferred for applications where stiffness, chemical resistance, good heat insulation, sound deadening, and higher end-use temperatures are required. Relevant fields of PP foam applications include the automotive industry ("under-the-hood" high service temperature parts, interior, and cushioning applications), the industry for home electrical appliances (hot water and air conditioner pipes insulation), and the building industry (various insulating applications).

PP foams have recently grown in importance, especially for replacing HDPE structural foams [5]. PP was a marginal, low quality commodity, with little versatility until the early 1970s [9]. The discovery of the active $MgCl_2$-supported high yield Ziegler-Natta catalysts in 1968 dramatically expanded the property envelope of polypropylene (PP) as a consequence of which, PP has demonstrated improved economics and enhanced performance over other thermoplastic resins. PP is lighter than water (0.9 g/cm^3) and PE, its major competitor, which makes it suitable for applications that require a low-density plastic material. The permanent growth of the world market for PP from 1.5 million tons in the 1970s to over 19 million tons in 1995 is a clear confirmation of the advantages of PP over PE. Also, the price of PP has been 15% to 20% more competitive during the last decade. Predictions are that the PP production will exceed 25 million tones in 2000 [9].

1.2 Thesis Purpose Statement

Using resins that have outstanding end-use properties, such as PP, in order to produce plastic foams with improved mechanical properties is one way of achieving the goal. Another way of improving the mechanical properties of plastic foams is by decreasing the cell size and by increasing the cell-population density and uniformity of the cellular structure [3-6, 10-19]. Since rotationally foamed plastic articles with improved mechanical properties are permanently in demand, it would be highly desirable to focus on producing rotationally foam molded PP articles by yielding the smallest cell size and the highest cell-population density and uniformity possible. These were the fundamental reasons that motivated the research work that is presented in this thesis to be undertaken. Its purpose is to respond to the need of developing a technology that will be capable of processing fine-cell PP foams in rotational foam molding.

1.3 Current State of the Art

Compared to conventional rotomolding, not much work related to rotational foam molding has been published to date. Likewise, compared to PE foams, very little research has been done to date on the production of PP foams. Although many studies use terms like "polyolefin foams" or "thermoplastic foams" to claim that processes useful for foam preparation of other polyolefins (PEs) are equally applicable to the preparation of PP foams, this does not seem to be always correct. For instance, unlike PE, successful processing of fine-cell PP foams in compounding-based rotational foam molding has not been reported yet. Reasons for this probably lie in the fact that compounding PP resins with a chemical blowing agent (CBA) is difficult because of its high melt temperature. An additional reason might be the fact that PP is not favorable for foaming due to its weak melt strength, and weak melt elasticity at elevated temperatures [58].

1.4 Thesis Objective and Goals

The objective of this thesis is to develop and experimentally verify a compounding-based rotational foam molding process for producing fine-cell PP foams. In order to accomplish this objective, it is necessary to first achieve decomposition-free compounding of PP-based resins with a CBA and then develop the needed scientific and engineering basis for identifying the optimal processing window for producing PP foams having a reduced cell size structure.

1.5 Thesis Approach and Methodology

A design approach has been used to accomplish the objective of this thesis. The diagram presented in Figure 1.1 illustrates the sequence of activities that constitute the approach. Although fundamental issues relevant to the research subject and the previously established theoretical knowledge stated in the referenced literature have been carefully studied, the experimental approach in investigating the phenomena governing the processing of PP foams in rotational foam molding received principal attention in the thesis. Likewise, due to the lack of available information that would cover the behaviors of PP and a CBA during compounding, the primary source of information for the research presented in this thesis have been the results obtained from the conducted experiments.

1.6 Thesis Scope

A compounding-based, rotational foam molding process for producing fine-cell PP foams is proposed in this thesis. In order to maximize the number of independently controllable processing parameters participating in the rotational foam molding process, and thereby simplify the investigation of their effects on fine-cell PP foam production, this research mainly deals with skinless foams that occupy the mold to the full capacity. However, the concepts put forward herein are equally applicable for partially foamed, hollow, skinless, articles, and can be also used as a foundation for understanding and describing the processing of articles having a distinct unfoamed skin.

1.7 Intended Thesis Contribution

The principal objective of the present thesis is to establish processing strategies useful for producing PP-based foams that achieve desired volume expansion ratios while having a fine-celled structure in compounding–based rotational foam molding. Another objective of the thesis is to identify the relationships between the processing steps needed for producing a foamable PP-based composition by using a CBA and the mechanisms governing its foaming in rotational foam molding. A further objective of the thesis is to characterize the PP resins that are effective in yielding acceptable foams and provide formulation criteria and processing strategies for preparing useful foamable compositions thereof.

1.8 Thesis Format and Outline

The present thesis is organized in six chapters and a preliminary subdivision.

Chapter 1 presents an introductory statement about plastic foams, a statement of reasons and principles related to plastics foaming, and a summary of recent developments in the fields of plastic resins and plastics foam fabrication processes that are relevant to the proposed processing technology. It also includes an overview of the common plastic foam classification criteria, the corresponding fields of their application; and a concise statement reflecting the major problems solved in the thesis and the thesis major contributions.

Chapter 2 includes a review of previous work and the key literature recently published on rotational foam molding, PP and PP foams, and focuses on the theoretical background needed to comprehend the physical meaning of the experimental results presented in the thesis. Here, particular attention is devoted to the patent literature since it covers a substantial amount of detailed, descriptive information not available in the journal literature. The introductory section of this chapter includes a historical overview and highlights of the basic operating principles of the rotomolding process and machinery. Also, in this chapter, details are considered about the structure of PP in relation to its properties as a polymer and its ability to foam, foaming mechanisms in general and in rotational foam molding, and the relevant principles for selecting chemical blowing agents.

Chapter 3 introduces the proposed compounding-based concept for processing fine-cell PP foams in rotational foam molding. The principal issues discussed in this chapter include the production of foamable PP compositions and their subsequent processing in rotational foam molding, while the importance of the successful compounding of PP with a CBA while preventing the decomposition of the CBA is specially emphasized. This chapter proposes and thoroughly elaborates processing strategies for both decomposition-free compounding and fine-cell PP foaming.

Chapter 4 is concerned with the experimental verification of the process proposed in Chapter 3. A differential scanning calorimeter (DSC) is used to determine the transition temperatures of the four PP resins selected for experimentation. The behaviors of the CBA with and without an activator at various heating rates are characterized via thermal analysis by using a thermogravimetric analyzer (TGA). Using four different formulations for each PP resin, sixteen different foamable PP compositions are successfully compounded. These compositions are subjected to experimental parametric search over time in order to investigate the feasibility of the proposed process for producing 3-fold and 6-fold expanded PP foams. The experimental results confirmed that the proposed process is feasible for producing 6-fold and 3-fold expanded PP foams, but also indicated that it failed to deliver foams with the desired fine-cell morphologies. This indicated the need for improving the processing strategies and modifying the process.

Chapter 5 identifies the root causes for obtaining foams with poor morphologies and proposes improved processing strategies. Additional compositions without CBA are compounded from each of the four PP resins in order to conduct experimentation and comparative analysis. Scanning electronic microscope (SEM) is used to characterize the compounded foamable pellets, especially in terms of CBA particle dispersion and uniformity. The additional foaming experiments revealed the importance of sintering to decomposition timing in compounding based rotational foam molding. Based on these experiments the effects of the basic resin viscosity and the volume expansion ratio have been investigated and experimentally modeled. During the foaming experiments the in-mold temperature has been recorded via a data acquisition device with a high sampling frequency. The obtained time-temperature profiles significantly improved the process-characterization procedure in terms of identifying the differences between the desired and the actual order of events occurring in the mold during the thermal cycle. This chapter emphasizes that regardless of the basic resin viscosity, desirable fine-cell foam structures can be obtained in compound-based rotational foam molding only if pellet sintering takes place prior to the decomposition of the CBA and the processing temperature is kept under the temperature of cell coalescence. Based on the experimental results discussed in this chapter, the process has been modified and strategies for improving the cell structure of PP foams are proposed and experimentally verified. Satisfactory foam morphologies have been obtained, especially from the high–viscosity resins. As a further process modification pellet regrinding is proposed. It resulted in obtaining even better foam morphologies. By using a see-through mold and a video camera the foaming mechanisms of both foamable compounded pellets and reground pellet powders of high viscosity PP resins have been recorded and analyzed.

Chapter 6 summarizes the relevant conclusions, introduces a number of possible extensions that can be drawn from the work presented in the thesis, and identifies potential directions for future research. Recommendations for future research emphasize the need of developing practical guidelines for processing PP in compounding-based rotational foam molding. These include developing a sintering to decomposition temperature map and a map for distinguishing the theoretically calculated from the realistically required amount of CBA for a given volume expansion ratio.

CHAPTER 2

LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 Conventional Rotomolding

The conventional rotomolding (or rotational molding) is a four-step plastic processing technology designed to produce hollow, one-piece, plastic articles (toys, sporting equipment, containers, water tanks, etc.) [7, 21-26]. Figure 2.1 illustrates the fundamental principle of the rotomolding process. First, a predetermined amount of a powdered, rotomolding grade, plastic resin is charged into a vented hollow mold. In the second step, the mold is closed, and then simultaneously heated and rotated in two perpendicular axes to achieve even distribution of the melt on the internal mold surfaces. During the third step, the mold is cooled to cause the molded article to solidify. In the final, fourth step, the mold is opened and the article is removed. The mold can be then used in a new rotomolding cycle. Figure 2.2 illustrates the generalized conventional rotomolding process diagram. As shown in the diagram, if the resins are not available in a powder form, the plastic material has to be ground prior to rotomolding. If necessary, additives, such as antioxidants, may be also charged into the mold.

2.1.1 History of Rotomolding

The process used by Egyptians and Romans approximately 3000 years ago to cast hollow clay objects is considered to be the earliest application of the rotomolding concept [7, 21].

Early patents that describe methods for manufacturing hollow objects by simultaneously heating and rotating a mold charged with a heat-sensitive material in two axes go back to the 1850s. A patent search report, published by National Latex Products Co. in 1961, claims that an Englishman named Peters filed the very first patent associated with the rotomolding process in 1855 [24]. The invention is described as a rotating mechanism engaging two perpendicular axis, interconnected by a pair of bevel gears that provide bi-axial rotation to a mold for reasons of uniformly spreading the charged material into a layer over the surface of its cavity. The invention includes a separable mold design to permit charging the material (metal or other substance in a fluid or semi-fluid state) into the mold and a vent pipe to permit gas escape. External mold cooling with water is also described as being a part of this invention.

Other early patents deal more specifically with the relevant processing parameters in rotomolding. In that context, the mechanism of solidification of the molten paraffin wax in a non-porous mold while being cooled and bi-axially-rotated is considered in a 1905 patent issued to Voelke. In 1910, Baker and Perks patented an apparatus for rotational casting of chocolate eggs, while in 1920 Powell proposed the ratio between the primary and the secondary axis to be 4 to 1 intending to avoid the centrifugal force by decreasing the rotation speed [24]. This ratio is most commonly used even today.

The beginnings of the modern rotomolding process have been established in the 1940s [22-26]. From mid 1940s to the late 1950s, numerous patents related to rotomolding have been filed. This period is marked as a period of intensive development of the rotomolding equipment and handling technique [24]. During this period, the concept of rotomolding machinery went through a variety of transformations and styles such as: “rock and roll”, box oven, shuttle, and vertical-style [21, 24]. In the late 1950s or early 1960s, rotomolding machinery using the fixed-arm turret concept was introduced [21, 24]. In the early 1980s, the clamshell-style rotomolding machine was developed, while in the late 1980s a more sophisticated modification of the fixed-arm rotomolding machine named "independent-arm", or independent indexing carriage rotomolding machine, became available [21].

Currently PE accounts for more than 90% of the materials used for rotomolding [21]. In the 1980s nylon, PP and polycarbonate represented the group of non-polyethylene resins that enriched the list of materials suitable to be used in rotomolding [23]. Today, the rotomolding process is the fastest growing process in the plastic processing industry and is characterized by a typical annual growth ranging between 10% and 12% per year [25].

2.1.2 Overview of Rotomolding Machinery

Three processing parameters are essential for rotomolding, these include time, mold rotation and temperature [21]. Therefore, in order to accomplish successfully the rotomolding process, the rotomolding equipment has to be designed in such a way to provide appropriate means for bi-axial mold rotation and efficient mold heating (and subsequent cooling) during processing the plastic article for a predetermined period of time.

Time. In rotomolding, the required processing time depends on the thickness of the wall of the part, the type of plastic used and the thermal conductivity and thickness of the metal mold [21].

Mold Rotation. Bi-axial mold rotation can be achieved by using a straight arm (also called "double centerline" arm), or an offset arm (also called "cranked" arm) design, as presented in Figures 2.3 (a) and 2.3 (b), respectively. Unlike the straight arm, which is preferable for small molds, the offset arm is designed to carry large molds. In order to control independently the rotational speed of the primary (major) and the secondary (minor) axis and thereby achieve various rotation ratios, separate drives for each axis are used in both arm designs. The mold rotation along the primary axis is powered directly by the primary axis drive, while its rotation along the secondary axis is provided by using an internal shaft that transmits the power from the secondary axis drive via a set of miter gears [21, 24].

Temperature. During the rotomolding cycle, the mold is rotated and heated to the temperature needed to melt the plastic and then cooled to allow the plastic to solidify. Thereby, the charged plastic material is formed into a shape corresponding to the shape of the mold's internal wall surface. Various concepts can provide the elevated temperature for mold heating in rotomolding. The earliest mold heating concepts used in rotomolding systems were the open-flame and the hot-oil jacketed mold systems, the schematic of which is presented in Figures 2.4 and 2.5, respectively. Although the hot-oil jacketed mold system is the most efficient possible way of transferring heat to the plastic article, it is very expensive because it uses hot oil circulation in double-walled molds, and therefore is practically rendered inapplicable for industrial production. In contrast, the open-flame method possesses the lowest energy efficiency and is known to be unsafe. However, it is still used for producing very large tanks, which exceed the standard oven dimensions, and for which building a special oven is not feasible because of the low number of units ordered [21].

The most frequently used mold-heating concept in contemporary rotomolding machinery employs the hot-air recirculating oven method, which uses natural gas, oil, or electricity to generate the hot-air and circulating fans to provide the heating effectiveness by changing the air in the oven for about 25-30 times per minute [21]. The schematic of the recirculating hot-air oven is presented in Figure 2.6.

Rock and Roll-style Machines. Rotomolding machines of this type are specially designed to produce very large cumbersome parts economically. They accomplish the bi-axial mold rotation by simultaneously rotating the mold along the principal axis, (which completes the rolling mold motion), and by tilting the rotating mold sideways for a predetermined angle along the secondary axis (which completes the rocking mold motion) [21]. Figure 2.4 presents the principle of operation of the rock and roll rotomolding machine. There is also a more sophisticated version of the rock and roll machine, it is called the "rocking oven" rotomolding machine, and it is used for producing long, slender parts. It employs a recirculating hot-air system instead of the open-flame system and can therefore achieve improved mold heating efficiency [21].

Box Oven-style Machines. This type of rotomolding machine is designed for producing small articles (play balls, baby doll parts, small automotive interior parts). The machine comprises three sections: a loading/unloading platform, a cooling section with a water bath, and a heating oven. The bi-axialy rotating mold is heated in the oven, while a gas or oil burner and a recirculating fan system generate the heat. The mold cooling operation is accomplished by a simple cooling system that does not apply bi-axial rotation to the mold. A retractable air cylinder, provided in the cooling section, is used to plunge the mold in a water bath and remove it when cooling is completed [21]. The schematic of the box oven-style rotomolding machine is presented in Figure 2.7.

Shuttle-style Machines. The shuttle-style rotomolding machine is capable of producing both large and small molded parts economically. It usually employs two shuttles, both equipped with a bi-axial rotation mechanism, and a hot-air oven accessible from two opposite sides. The shuttles are interchangeably heated in the double-door oven. After the first shuttle is removed from the oven for cooling, unloading the molded article, and loading the plastic material for the next cycle, the second shuttle enters the oven to start its own rotomolding cycle [21, 24]. The principle of operation of the shuttle-style rotomolding machine is presented in Figure 2.8.

Vertical-style Machines. Unlike the previously described machines, the vertical-style rotomolding machine is designed to use the vertical plane for mold indexing in order to save floor space. This type of rotomolding machine is available in 3-arm and 6-arm versions. Each arm is provided with a bi-axial mold-rotation mechanism, so that the arms can carry the molds in a succession between the separated loading/unloading, heating and cooling stations. The 6-arm version is usually provided with three heating and two cooling chambers, thereby dividing the required mold heating/cooling time into three/two equal cycles, respectively. This is particularly useful for producing articles from vinyl plastisol, for which processing at a gradual increase of the oven temperature is required during the heating cycle [21]. The principle of operation of the 3-arm vertical rotomolding machine is presented in Figure 2.9.

Fixed-arm Turret Machines. Even today, fixed-arm turret machines are the most frequently used. This rotomolding machine provides three or four arms equally spaced on a fixed turret. The rotation of the turret causes the rotating molds, attached on the periphery of the arms, to travel around the turret and spend a portion of the cycle-time in each of the loading/unloading, heating and cooling stations on their way. Three-station fixed-arm machines are commonly used when the required heating and cooling processing times are approximately equal, while four-station fixed-arm turret machines are used where the process requires increased processing times for one of the loading, heating or cooling operation. Modern fixed-arm machines may provide various combinations of arrangements, such as two cooling stations, two loading-unloading stations, or two ovens, by which an opportunity of doubling the process times of particular segments of the cycle becomes available [21, 24]. The typical schematic of a four-fixed-arm rotomolding machine is presented in Figure 2.10.

Clamshell-style Machines. This unique rotomolding machine type is available with either straight or offset mold mounting arms, which makes it suitable for handling both small and large parts. It uses a hot-air oven chamber for both the heating and the cooling step of the rotomolding cycle. Once the heating is completed, the burners are extinguished, and the circulating fan continues to be used to initially cool the mold, after which, water spray is applied to accomplish the cooling step. This machine is characterized by a higher energy consumption because not only the mold, but also the oven, is heated from room temperature to molding temperature and then cooled back to room temperature during each rotomolding cycle [21]. The schematic of the clamshell-style rotomolding machine is presented in Figure 2.11.

Independent-arm Machines. This rotomolding machine consists of multiple, independent, self-propelled, carriages designed to move each arm around a center post and a horizontal arm mounted on each carriage to carry the mold. This arrangement transforms the machine into a set of "independent machines" using a common center post, cooling chamber and heating oven. The advantage of this type of machines is the independent design of the arms that allow the user to adjust machine settings commensurate to the processing needs [21]. Figure 2.12 illustrates the detailed principle of operation of the independent-arm machine.

2.1.3 Advantages and Disadvantages of Rotomolding

The conventional rotomolding process has unique advantages over other plastic processing technologies. The most important include the low tooling costs, the capacity to produce large-sized products that no other process can, the comfort of simultaneously running molds of different sizes and shapes on the same equipment, the convenience of almost no need for secondary operations, and the ease of molding articles with undercuts, double walls and molded inserts [21]. Tooling is relatively simple and inexpensive because rotomolding is a low-pressure process and no cooling channels and no clamping force is required, as it is the case with injection molding and blow molding [7, 23]. Trimming can be eliminated because rotationally molded parts normally have very little flash. Since the produced parts are hollow, with no core, they can be deformed inward in order to free undercuts when being removed from the mold, but the magnitude of the allowed undercut is limited by its design and the elasticity of the plastic material [21].

However, the greatest disadvantages of the rotomolding process are the long cycle times, the need to grind the materials before usage (if it is not available in powder form), the labor intensive loading/unloading operations and the relatively limited choice of rotomolding grade resins [21]. Cycle times are long because of the nature of the process which requires the temperature of the plastic and the mold during processing to be elevated from room temperature to beyond the melting temperature of the plastic, and than cooled back to room temperature.

2.2 Rotational Foam Molding

As indicated in Chapter 1, the rotational foam molding is a plastic processing technology derived from the conventional rotomolding for producing completely or partially foamed one-piece, plastic articles with or without a non-foamed skin surrounding the foamed core or layer. In order to produce plastic foams in rotational foam molding, a foamable resin must be introduced into the mold. The foamable resin is obtained by introducing a chemical blowing agent (CBA) into the polymer by means of a suitable polymer mixing technique. A CBA is a chemical or a compound that decomposes at elevated temperatures and normally, at atmospheric pressure, produces a gaseous product [7]. Accordingly, with respect to the mixing technique used, rotational foam molding methods can be based on a dry-blending or on a melt compounding approach.

Figure 2.13 illustrates the principle of operation of the rotational foam molding process and depicts the four manufacturing steps required for its accomplishment. These include mold charging, simultaneous mold heating and bi-axial rotation, mold cooling, and molded article removal. Since the rotational foam molding manufacturing steps are identical with those of the conventional rotomolding (see Figure 2.1), the currently available manufacturing equipment for conventional rotomolding can be readily used for rotational foam molding. However, due to the presence of the foamable resin in the material that is charged into the mold, the nature of the rotational foam molding process completely differs from that of the conventional rotomolding. As a consequence, there is a significant difference between the processing strategies that should be implemented in order to control each of these processes.

It should be also noted that if molds originally designed for rotomolding were to be used for rotational foam molding, a few marginal modifications would be necessary. In this context, mold-venting enhancements would be useful to allow for complete foaming of large parts [27]. Because fully foamed parts will not normally shrink as much as conventionally rotomolded parts, greater mold draft angles should be considered for easier part release [20, 27].

In order to produce articles with a distinct non-foamed skin and a foamed core or layer, two types of resins should be charged into the mold: non-foamable and foamable. Different methods of achieving a skin have been developed. Generally, these methods can be divided into two distinct groups. The first group includes methods that can function only by interrupting the molding process, while the other includes continuous methods that do not require process interruptions. Methods pertaining to the former group are usually based on a two-step operation principle. Therefore, these methods assume molds with specially designed openings that can be used to pour the foamable resin in the mold during the interruption of the rotational foam molding process, which takes place after the initially charged non-foamable resin had sintered and formed the skin inside the mold. Multiple drawbacks characterize the two-step operation principle with process interruptions. First, the mold must be made of a special construction. Second, the molding cycle is extended. Third, it is complicated.

Methods pertaining to the latter group can be based on a multi-step, a two-step, or a one-step operation principle and can produce structures with a non-foamed, solid, outer skin and a foamed layer or core in a one continuous rotational foam molding cycle. Most two-step continuous methods use a "drop-box" system comprising of a box located inside the mold that can introduce the foamable material at the time when the ufoamed skin coating is already formed by the sintering of the non-foamable material directly charged into the mold cavity prior to processing. Thereby, a foamed layer or core is formed on top of the skin. However, if a distinct skin is required to be developed on the inside surface of the foamed layer as well, a multi-step continuous operation principle must be used. In these cases, a second drop box is used to introduce the non-foamable resin on top of the already foamed structure [7].

The one-step continuous operation principle eliminates the need of drop boxes inside the mold, thereby solving the foregoing drawbacks by introducing both the foamable and the non-foamable thermoplastic resins into the mold cavity at the same time. The fundamental problem of the one-step principle is how to ensure the execution of the adhesion of the non-foamable thermoplastic resin to the surface of the mold to happen prior to the activation of the foaming resin. In some one-step rotational foam molding methods the mold is charged with blends of non-foamable powders (for the skin) and foamable pellets (for the foamed layer or core) [27]. The powder particles sinter first because of their smaller size and form the skin layer, on top of which, with the subsequent heating of the mold, the pellets form the foamed layer. Other one-step rotational foam molding methods simultaneously charge the mold with a blend of non-foamable and foamable powders (usually reground compounded pellets of a polymer with a CBA) of polymers that have significantly dissimilar melting points or significantly dissimilar particle sizes. The reason for this is to maintain the desired sequence of events in the mold, which is the skin formation to be completed prior the foamable powders start foaming [7]. Another type of one-step methods, for example, makes use of the difference of the densities of the two resins and the centrifugal force developed while rotating to distribute the resins in the mold and create the non-foamed layer first and then the foamed one. However, there is no big difference between the densities of most of the commonly used thermoplastic resins. Therefore, achieving two separate layers of cellular and non-cellular structure using this approach is unfeasible.

If skinless foam is desired, only a foamable resin should be used [7]. By decreasing the blowing agent to polymer ratio in the foamable resin, partially foamed, single-layer, skinless hollow articles can be manufactured in rotational foam molding [18-20].

2.2.1 Advantages and Disadvantages of Rotational Foam Molding

In most instances, the similarity between the rotomolding and the rotational foam molding implies agreement between their advantages and disadvantages, but some exceptions exist. For example, unlike conventional rotomolding, molding of articles with undercuts is not possible in rotational foam molding because the foamed core or layer does not allow inward article deformation.

Regarding rotational foam molding process disadvantages, it is important to note that, compared to rotomolding, the rotational foam molding process requires extended total cycle times (from 25 to 100%) [20, 27] to allow complete foaming. This is so because a greater amount of material is molded and the heat transfer is retarded by the foam structure. All other advantages and disadvantages pertaining to the conventional rotomolding process, discussed in Section 2.1.3, apply to the rotational foam molding as well.

2.2.2 Dry-blending Based Approach

Figure 2.14 illustrates the generalized dry blending-based rotational foam molding process diagram. In spite of the fact that the dry blending based rotational foam molding and the conventional rotomolding are very similar processes, they differ in the material preparation procedures (see Figure 2.2) and the processing cycle times. The plastic resins must be in a powder form if they are to be used in dry blending-based rotational foam molding [18, 19]. If the resins are not available in powder form, as is often the case with PP resins, they must be ground prior to further usage. The obtained resin powders are mixed well with a CBA and other additives to obtain a foamable blend. A hollow mold is charged with a pre-measured amount of such a blend and it is then heated and rotated in two axes until it becomes sufficiently hot to melt the powders and trigger the decomposition of the CBA, thereby initiating the polymer foaming. The mold is then cooled, opened, and the article is released.

2.2.3 Compounding-based Approach

While the conventional rotomolding and the dry-blending-based rotational foam molding use materials in a powder form, in the melt compounding-based rotational foam molding, intended for production of skinless articles, only pre-compounded pellets are charged into the mold [19]. But if the sintering behavior of the pellets is not satisfactory because of too high viscosity of the plastic resin, the pre-compounded pellets can be reground into powder before charging the mold in order to enhance the sintering behavior of the materials [7]. Also use of a reground powder is recommended for production of hollow foamed articles to better maintain a uniform thickness of the foam. A generalized process diagram of the compounding-based rotational foam molding is presented in Figure 2.15.

2.2.4 Previous Studies on Rotational Foam Molding

The surveyed patents reveal that the majority of previous studies in rotational foam molding have been concerned with developing methods capable of forming integral thermoplastic articles having a cellular layer or core and a continuous skin of a non-cellular thermoplastic material, mainly polyethylene.

Two-step Principle of Operation Studies. A two-step, dry-blending based, rotational foam molding method for manufacturing multilayered articles has been disclosed by Carrow and Rees [28]. It is based on using two types of resins, non-foamable and foamable. The non-foamable resin is molded first in order to produce a non-foamed layer. At a time after the solid particles of the non-foamable resin have melted and prior to the time when the inner surface of the outer layer become smooth and glossy the process is interrupted. The charge of the foamable resin is then added in the mold via a specially designed mold opening after which the molding operation is resumed. As a result, a foamed layer on top of the inside of the non-foamed layer is formed.

An improvement to the two-step dry-blending approach, which does not require process interruptions, has been disclosed by Duffy [29]. Both the non-foamable and foamable resins are introduced at the beginning of the operation but they are maintained separately until the non-foamable resin melts and coats the interior surface of the mold. After the outer skin is rotationally molded in the initial step, in the second step, the foamable resin is released from a specially designed two-piece container located inside the mold and held together by adhesive tape strips. Figure 2.16 (a) illustrates the container in closed position inside the mold. Due to the effect of the elevated temperature, the adhesive tape strips soften, so that the container halves cease to be held in close relationship, which causes the foamable charge to be released within the mold, while the mold is still rotating. Figure 2.16 (b) illustrates the container in open position inside the mold. An optional design, in which a flexible plastic bag is used to hold the foam charge until its rupture under certain molding thermal conditions, is also disclosed. The principle of this configuration is illustrated in Figure 2.16 (c).

Slapnik [30] also disclosed a method of rotationally molding polyethylene powder and a thermoplastic bag in which the foamable powder resin is enclosed.

One-step Principle of Operation Studies. H. Mori et al. [31] disclosed a compounding-based method of producing composite foamed shaped articles in one-step rotational foam molding. The key of this invention is the use of resins having different heat capacities. This concept uses a thermoplastic resin, containing a blowing agent, with a greater heat capacity than that of the thermoplastic resin not containing a blowing agent. Here, the heat capacity of the resin used is determined as the product of the specific heat of the particle, its density, and its volume. The specific heat is defined as the isobaric change in polymer enthalpy with temperature. Its values can be obtained from enthalpy tables or graphs, found for example in Reference [32]. Both resins are introduced into the mold at the same time. As a result, when rotomolded, the resin with the lower heat capacity will begin to melt first and thereby the inner surface of the mold will be coated before the foamable resin begins to melt. The required ratio between the melt capacity of the foaming and the non-foaming resin must be in the range of over 50 to below 1000, with a preferable value around 100. If the ratio is smaller than 50, the shaped article will have a one-layered structure where the thermoplastic resin containing a blowing agent will be in a state of intermixture with the thermoplastic resin not containing a blowing agent. If the ratio is greater than 1000, the cycle time is significantly prolonged because of the time required the foaming resin to begin to melt. An optional concept is also provided, it concerns the situation when both the foamable and the non-foamable resins are of the same class and are considered to have same heat capacities. In this case, the size of the resins can be used to set the required difference of heat capacities, because the heat capacity of the resin becomes greater as its particle size increases.

Needham [33] disclosed a compounding-based one-step method of producing hollow foamed articles by using a mixture of a CBA (sodium bicarbonate) and a nucleating agent besides the basic polyethylene in rotomolding. Since the outer skin of the molded article obtained in such a way may have a cellular foam structure and a rough surface, a method for creation of a smooth skin is also disclosed. In order to achieve a smooth skin, a polymeric additive having a melt index 1.5 to 2 times above the melt index of the basic resin (most preferably between 8 and 10 g/10 min) and a density between 0.90 to 0.94 g/cm^3 should be included in the mixture. Because the density of the additive polymer is lower than that of the basic polymer, the additive polymer will melt at a lower temperature and improve the outer skin structure. An improvement of this patent is clamed in another patent authored by the same inventor [34] where a method is disclosed that uses two resins of significantly different particle sizes for charging the mold. The principle used guarantees that the resin having the smaller particle size will form the outer skin while the powder having the greater particle size will form the inside layer or the core. If foaming of the inside core is desired the polymer having the greater particle size should be premixed with the CBA and then inserted into the mold. A direct consequence of this invention is that different resins can be used for forming the foam layer and the skin. This indicates a possibility to obtain articles with substantially different properties between the core and the skin.

Strebel [35] disclosed a compounding-based one-step method that uses two distinct thermoplastic resin components. The first component is charged into the mold in a pellet form. These pellets are obtained by mixing the ethylene polymer with a CBA in an extruder. The temperature used for mixing should be above the melting temperature of the resin but below the decomposition temperature of the CBA. The second component is charged into the mold in a powder form and is in fact a blend of ethylene polymer powders with different particle sizes and viscosities. Conventional rotomolding equipment can be used for this process. The rotational speed of the mold should be selected to permit the resin to contact the inner surface of the mold by action of gravity.

2.3 Background on Polymers

Polymers are materials that have a long-chain structure consisted of many repeating small molecules (called monomers) that are based on the element carbon [36, 37]. Plastics and elastomers are the two major polymer classes [37].

Plastic is defined as "a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or in its processing into finished articles, can be shaped by flow", (ASTM definition D883) [36]. Elastomers consist of linear polymer chains that are lightly cross-linked, these polymers possess memory and they return to their original shape after a stress is applied [37]. Plastics are classified according to their characteristics at elevated temperatures into two categories: thermoplastics and thermosets.

Thermoplastics consist of flexible linear molecular chains that are tangled together, these plastics melt and flow when heated and harden when cooled regardless of how much times the heating and cooling cycle is repeated. Thermosets consist of a highly cross-linked three-dimensional network of long chain molecules, these plastics are hardened permanently by heat and will not melt when reheated, instead they will burn [36, 37]. The structures of thermoplastics, thermosets and elastomers are illustrated in Figure 2.17.

2.3.1 Polymerization

Polymerization is the process of making long-chain polymer molecules. There are two important mechanisms for polymer synthesis: addition polymerization and condensation polymerization. Free radical polymerization is the most common type of addition polymerization. There are three significant steps that take place in free radical polymerization: initiation, propagation, and termination. A free radical is a molecule with an unpaired electron. This excess charge renders the free radical prone to join with another free radical to eliminate the surplus charge. The instability of the carbon-carbon double bonds in monomers makes them suitable for reaction with the unpaired electrons in the radical and thereby they become suitable for polymerization. In the addition polymerization process, one monomer at a time is added to the growing chain. The process is begun by an initiator that "opens up" a C=C double bond, attaches itself to one of the resulting one bonds, and leaves the second one dangling to repeat the process until its termination. Termination typically occurs in two ways: combination and disproportionation. Combination occurs when the polymers growth is stopped by free electrons from two growing chains that join and form a single chain, while disproportionation halts the propagation reaction when a free radical strips a hydrogen atom from an active chain or when the radical reacts with an impurity [36, 37].

The condensation polymerization process involves combining various chemicals in order to form a polymer. Depending on which functional groups or elements in the basic carbon chain are substituted with other functional groups or elements different polymers can be synthesized. The ends of the precursor molecules lose atoms to form water or alcohol, leaving bonds that join with each other to form bits of the final large molecules [36, 37]. The addition and condensation polymerization processes are illustrated in Figure 2.18.

2.3.2 Statistical Approach on Polymers

The basic assumption in polymer synthesis is that each chain reacts independently. Therefore, in order to generalize polymer properties, statistical methods must be used. The bulk polymer is characterized by a wide distribution of molecular weights and chain lengths. Many important polymer properties are determined primarily from the distribution of lengths and the degree of polymerization. In order to characterize the distribution of polymer lengths in a sample, two parameters are defined: number average and weight average molecular weight. The number average is just the sum of individual molecular weights divided by the number of molecules. The weight average is proportional to the square of the molecular weight. Therefore, the weight average is always larger than the number average. The degree of polymerization is related to the number of repeat units in the chain and gives a measure of the molecular weight, it strongly affects the mechanical properties of a polymer. Properties such as ductility, tensile strength, and hardness rise sharply as chain length increases. In polymer melts, the flow viscosity at a given temperature rises rapidly with increasing the degree of polymerization for all polymers [37].

2.4 Polypropylene (PP)

PP is a thermoplastic. Polymerizing propylene produces PP. Propylene, C_3H_6 ($CH_3CH{=}CH_2$), is a gas that can be derived from two main sources: co-production with ethylene and separation from gasoline cracker streams in petroleum refineries [9]. The polymerization of propylene can be conducted under broad ranges of pressures and temperatures and it results in very long polymer chains [39]. Figure 2.19 illustrates the chemistry of PP preparation.

PP is a polyolefin as well. Polyolefin is a generic term referring to the family of PE, PP, polybutylene (PB) and their derivatives. Olefins, the raw materials for polyolefins are obtained from petroleum and natural gas. Linear polymers consist of the same backbone of carbon atoms joined by one bond, but with other atoms or radicals substituted for one or more of the hydrogen. Replacing one H by a CH_3 group produces PP. The linear PE molecule is the simplest polyolefin. Ethylene C_2H_4 is a gas, which can be converted to PE [37].

2.4.1 PP Stereoregularity

PP is a polymer whose properties are significantly affected by stereoregularity [40]. Stereoregularity is the term used to describe the configuration of polymer chains. A polymer is stereoregular if its molecules can be described in terms of only one kind of a stereo-repeating unit [37].

The stereoregularity is the principal characteristic that distinguishes presently available PP from the one produced prior to the Ziegler-Natta discovery of catalysts capable of producing stereoregular PP [9]. The stereoregularity of PP is controlled by three factors. The first factor is the degree of branching. It depends on how the next monomer unit is added to the growing PP chain. Hence, the addition can be linear, as a result of adding the monomer always at the chain end, or branched, as a result of adding the monomer onto the backbone. The linear type of propylene monomer addition is illustrated in Figure 2.20 (a), while the branched type is illustrated in Figure 2.20 (b). Branched polymer is formed when there are "side chains" attached to a main chain. The schematic of a branched PP is illustrated in Figure 2.21. The second factor is the pendant methyl sequence. It depends on the manner of adding the monomer unit to the growing PP chain. Hence, the monomer unit can be inserted in a "head-to-tail" position, as depicted in Figure 2.22 (a), or in a "head-to-head" or "tail-to-tail" position, as depicted in Figure 2.22 (b). The third factor is concerned with a right or left hand monomer unit addition. It depends on the way the monomer unit is added to the growing PP chain. Hence, it can be inserted always in the same or in the opposite hand stereo arrangement. The same hand type of propylene monomer addition is presented in Figure 2.23 (a), while the opposite hand type is presented in Figure 2.23 (b) [9, 41, 42].

As a result of different combinations of the stereoregularity control factors described above, three distinct stereo arrangements of the PP chain can be obtained: isotactic (regular arrangement-all methyl groups are aligned on one side of the chain), syndiotactic (methyl groups alternating), and atactic (methyl groups randomly positioned) [41]. Schematics of these PP chain geometric forms are illustrated in Figures 2.24 (a), (b) and (c), respectively.

2.4.2 PP Copolymerization

Homopolymers incorporate only one kind of monomer into their chain. Accordingly, only propylene is used in the reaction producing PP homopolymers [39]. However, a separate kind of chain structure arises when more that one type of monomer is involved in the synthesis reaction. These polymers that incorporate more than one kind of monomer into their chain are called copolymers. There are four important types of copolymers. An alternating copolymer contains multiple monomers arranged in an alternating order along the chain. A random copolymer contains a random arrangement of the multiple monomers. A block copolymer contains blocks of monomers of the same type. Finally, a graft copolymer contains a main chain polymer consisting of one type of monomer with branches made up of other monomers [37]. Figure 2.25 displays these four different copolymer types.

Copolymerization is the process used to modify the polymer structure and morphology in order to enhance its properties or to alter them in such a way that they would match a particular application. For example, isotactic PP homopolymer has a high melting temperature, demonstrates a brittle behavior below 0 °C (because its glass transition temperature is ranging from 0 °C to –15 °C [9]), it is rigid, and have a poor transparency. In many instances, application requirements could be such that it would be desirable to lower the melting point of the homopolymer to achieve a better weldability or to lower its glass transition temperature in order to achieve a better impact resistance at low temperatures. Achieving increased flexibility and clarity is always desired. By implementing statistical (or random) and sequential copolymerization such broadening of the application field of the PP resin is attainable. For instance, the statistical copolymerization of PP with another olefin, usually ethylene or butene, results in a random copolymer resin with a lower melting point and a higher flexibility due to the introduced irregularities to the chain by the copolimerization that, as a consequence, reduce its crystallinity [9, 39].

2.4.3 PP Crystallinity

The morphology of most polymers is semi-crystalline. Polymers form mixtures of small crystals and amorphous material and therefore usually melt over a range of temperature instead of at a one melting point [37]. In general, there is a strong correlation between the polymer morphology and its structure, processing, fabrication history, and end–use properties [9, 42].

The properties of PP are directly related to its structure and morphology, which mostly depends on the fabrication history of the material. The structure of PP depends on the type of catalyst that was applied during its polymerization and the particularities related to the polymerization and compounding technologies themselves. The crystallizability of PP, which is a critical factor that governs its morphology, is related to the stereo chemistry of the PP chain - the tacticity. The tacticity strongly influences the crystallinity of a PP homopolymer. In fact, the regularity of the isotactic PP allows it to crystallize and thereby dominantly affects the degree of crystallinity. A level of tacticity of 100% is ideal and is almost never reached in practice. However, the crystallization of either isotactic or sindiotactic PP chains can result in very high degrees of crystalinity (40-70%) [9]. A high crystallinity is conditioned with a high tacticity, which further requires long, uninterrupted, stereospecific sequences along the chain. As already mentioned, any change from the correct placement of the PP molecule during polymerization causes a defect in its stereoregularity and reduces its tacticity, which results in decreased crystallinity, so that the crystallinity of the atactic PP reaches the zero level [9, 38].

The advantages of the Ziegler-Natta process include better control of the tacticity since the isolated product is mostly isotactic. Isotactic PP is prepared with various modifications of Ziegler-Natta coordination catallyst, producing polymers with varying degrees of stereoregular order, with isotacticity reaching up to 98%. Syndiotactic PP is prepared with soluble coordination catalysts and the stereoregularity attained is generally lower than that of the isotactic polymers. Atactic PP can be obtained by extraction with boiling n-heptane from isotactic PP of lower stereoregularity [40].

Despite the dominant effects of the stereoregularity on the PP morphology and the tacticity on the PP structure, these are not the only important structural properties of the PP chain that influence the PP properties. The molecular weight, the composition in blends and copolymers, and the details of the intra-chain architecture, which include the comonomer distribution in various types of copolymers, have also a significant impact. In addition, important processing parameters that affect PP properties can include the melt processing conditions, orientation, thermal history, the addition of nucleator and additives, and post-synthesis reactions relating to polymer degradation of molecular weight and polymer cross-linking [9, 38].

2.4.4 PP Melting Behavior

The melting point of a PP resin is strongly dependent on its tacticity and thermal history. Thermal history effects are generally observed in semicrystalline polymers. The melting point and nature of the melting distribution are governed by the distribution of the defects in tacticity along and between the chains. Reducing the tacticity reduces the melting point. The melting point of a semicrystalline polymer will differ from the equilibrium value due to a variety of factors, including polymer molecular weight, a distribution of noncrystallizable component along the chain, specific thermodynamic interactions in a polymer blend, diluent effects, orientation, or various morphological effects [9].

2.4.5 PP Flow Properties

Since PP resins are melted in order to be formed into shapes, the flow properties of PP are important characteristics that affect its processability and physical properties. The ASTM test method D-1238 provides a procedure to measure the amount (in grams) of material that flows through an orifice of a specified size in a specified length of time (10 minutes) using an extrusion plastometer. The values obtained are referred to as Melt Flow Rate (MFR) or Melt Flow Index (MFI). This index is inversely related to the resistance to flow (viscosity) and the average molecular weight of the material. Therefore, a higher polymer viscosity (or a higher polymer molecular weight) results in lower values of the MFR or MFI index. Also, the higher the measured MFR or MFI quantity, the easier the material flows under a given temperature and pressure [39, 43].

2.4.6 PP Rheology

The relative flow properties of PP resins can be described by the melt flow rate, but this index represents only a small part of the PP total flow properties. Therefore, it is often necessary to know the full rheological behavior of the resin in order to be able to understand and predict how a resin processes and performs in its intended use. This information is also important when products from different sources or different grades of material from the same source are compared.

Thermoplastics are non-Newtonian fluids because their viscosity changes depending on the speed (shear rate) at which the pressure or force causes them to flow. As the speed (shear rate) increases, the viscosity of non-Newtonian fluids decreases. Rheology is the science of flow, and rheometers are used to determine the flow behavior or viscosity of thermoplastic resins. Sometimes rheology testing is performed at different temperatures to determine the temperature sensitivity of a particular PP resin. Different PP resins may have different sensitivities because of the process or catalyst used to produce them. Just as important as temperature sensitivity is shear sensitivity. Like temperature sensitivity, shear sensitivity is also affected by the production process or catalyst. The differences in shear sensitivity and temperature sensitivity among PP resins (and other thermoplastic resins) exist because of another characteristic of these materials known as "molecular weight distribution" (MWD) [39, 42, 43].

The molecular weight distribution in a PP sample may be determined by high temperature gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC) [44]. GPC/SEC provides information about three important polymer characterization parameters. The first is the number average molecular weight (M_n) defined as the arithmetical mean value obtained by dividing the sum of the molecular weights by the number of molecules, as a such, it is dependent only on the number of molecules. The second is the weight average molecular weight (M_w) which is the second-power average of molecular weights and is therefore more dependent on the number of heavier molecules than is M_n. The third is the z-average molecular weight (M_z) which is the third-power average of molecular weights. The physical meaning of those parameters is defined as follows: colligative properties are related to M_n values, bulk properties associated with large deformations such as viscosity and toughness are affected by M_w values, while melt elasticity is more closely dependent on M_z values [38, 42, 44].

Since PP resins cannot be made commercially in a single molecular weight, each grade of PP resin contains polymer chains with a very wide distribution of molecular weights [39, 42]. The relative differences in the "spread" of molecular weights in PP grades separates them into the categories of "narrow MWD" (NMWD) or "broad MWD" (BMWD) products. A PP grade can also be manufactured as a NMWD or BMWD product by varying certain conditions in the production process or the catalyst used. As a result, two PP products can have the same MFR and the same average molecular weight but have significant differences in their MWD and physical properties. All things being equal, a broad MWD product is more shear sensitive than a corresponding narrow MWD product [9, 39].

2.4.7 Effect of PP Viscosity on Processing

PP resins that have a lower viscosity at processing shear rates, whether derived from a lower average molecular weight or broader MWD (more shear sensitivity), flow easier, require less pressure (and energy) to extrude and have fewer molded-in stresses. On the other hand, PP resins that have a high viscosity or broad MWD are useful in processes such as foaming, extrusion blow molding, blown film, profile extrusions, etc., because such processes require a self-supporting material before solidifying with enough melt strength to prevent collapse. A high viscosity resin at low shear rates is a definite advantage in these cases [9, 39].

Ideally, for extrusion applications, a broad MWD is advantageous so the viscosity is low in the high shear portions of the process, i.e., at the screw and die. A high molecular weight product also tends to exhibit greater toughness and chemical resistance. On the other hand, a narrow MWD is advantageous in some fiber and molding applications. Since an NMWD material contains polymer chains with more uniform molecular weights, the response of this material to internal stresses (due to flow or cooling) and external stresses (stretching) is much more uniform than with a BMWD product. This uniformity results in better drawdown characteristics for fiber production, including much higher elongation at break properties and less warpage. NMWD products also exhibit more uniform shrinkage when they are used for injection molding [9, 39].

2.4.8 PP Oxidation and Degradation

As indicated in Chapter 1, the advantages of PP include properties such as a low specific density, excellent chemical resistance, a high melting temperature, good stiffness/toughness balance, adaptability to many converting methods, great range of special purpose grades, excellent dielectric properties and a low cost. The disadvantages of PP include properties such as flammability, low-temperature brittleness, moderate stiffness, difficult printing, painting and gluing, low UV resistance, haziness and low melt strength [41]. Polymers in general, including PP, are also prone to degradation.

When PP degrades, the very long molecular chains break up into smaller lengths, decreasing the average molecular weight of the resin and affecting its viscosity. This process is called "chain scission". Since the process is very random, once it starts, there is no way to control the degree of degradation. As a result, undesirable effects, such as discoloration and loss of physical properties of the resin are manifested [39].

Unstabilized PP is extremely susceptible to air oxidation. An elevated temperature accelerates the rate of oxidation. The uncontrolled oxidation of PP is of exothermic nature and the generated heat and gases can cause unexpected melting of the polymer [9]. Moreover, the volatile polymer decomposition products contain toxic materials [45]. However, it is known that the onset of molecular weight reduction, which implies viscosity reduction as well, in PP takes place at about 230 °C and that the breakdown of volatile products is insignificant below 300 °C [38].

The oxidative processes of PP are rather complex and can include various steps such as initiation, propagation, branching, and termination. The oxidation and degradation products formed are dependant on variety of factors, including oxygen availability, impurities, residual catalyst form, physical form (molten versus solid), crystallinity, storage temperature, air pollutants, radiation exposure, metal exposure, part thickness, stress in the part, comonomer content and other additives present [9].

2.4.9 PP Stabilization

The detailed mechanism of PP stabilization is not studied well yet [9]. Most methods for polymer stabilization are based on introducing special oxidation inhibition additives into the polymer. These inhibitors (or antioxidants) provide degradation stability to the polymer by retarding the process of oxidation. Since polymer stabilization involves retardation of chemical reactions, the aging and stabilization of polymers is studied by a branch of chemical kinetics [45].

Oxidation is initiated when polymer molecules are converted to radicals by activation through ultraviolet radiation or heat [38]. Antioxidants are typically classified as primary and secondary. Primary antioxidants are defined as additives that interfere with the oxidation cycle by reacting with the formed radical and interrupting the cycle, while secondary antioxidants decompose hydroperoxides and prevent new oxidation cycles from beginning [9].

Introducing stabilizers into the polymer may be carried out with conventional extrusion equipment at high temperature at under exclusion of oxygen. Achieving a high degree of dispersion is essential to the effectiveness of the stabilizer [38]. However the cohesive properties of PP can have a detrimental effect on the degree of dispersion of additives that can be practically achieved [39].

2.5 Polyolefin Foams

PP is a polyolefin. Foams made from polyolefins inherit the properties of the basic resin they are made of [46].

Earliest patents disclosing methods for physical expansion of PE, by using volatile liquids or gas pressurized into the polymer melt and subsequently depressurized to produce a cellular polyolefin structure, go back to 1945. The gases that were used as blowing agents in these extrusion-based methods include nitrogen and a mixture of carbon dioxide and ammonia. At approximately the same time, special techniques such as cooling and radiation cross-linking have been used to produce stable PE foams [47]. Dow Chemical Company introduced the first extruded polyolefin foams to the market in 1958, crosslinked foams appeared first in Japan in the 1960s, while first polyolefin foam moldings were developed by BASF in West Germany in the 1970s [46, 48].

Four distinct principal processes for polyolefin foam preparation exist in modern practice. Of those, the most used for commercial polyolefin foam production is the expansion process, it is based on dispersing a gaseous phase throughout the fluid phase of a molten polymer. The remaining three processes include leaching out a solid or liquid that is dispersed in a plastic, sintering (welding) small resin particles together under heat and pressure, and dispersing cellular particles in a plastic [46].

2.5.1 Previous Studies on PP Foams

As already indicated in Chapter 1, compounding-based foaming of PP in rotational foam molding has not been reported yet. However, regardless of the fabrication process involved, a number of relevant previous studies on PP foaming are discussed in this section. It should be noted that a clear distinction should be made between studies on PP foams disclosed prior and after the appearance of Ziegler-Natta catalysts in 1968 which greatly improved the PP property envelope, compared to that of the PP resins available till early 1970s. Therefore, studies disclosed prior to early 1970s should be considered as an illustration of the attempts of various researches to produce PP foams.

Sneary and Pritchard [49] disclosed a method of producing PP foam by using crystalline PP, Freon 114 and isopropanol, mixing them in a closed vessel at 316 °C for 45 minutes and cooling at 135 °C, and releasing the pressure of the vessel by using a quick-opening valve. Pazinski [50] disclosed that particles of PP might be coated with a powdered blowing agent (azobisformamide), PE, and isobutylene to prepare foaming compositions. Johnstone [51] disclosed a method for producing PP foams using standard blowing agents in a presence of a azido cross-linking agent in both extrusion and blow molding. This invention claims that without the cross-linking agent the PP would neither foam nor blow mold.

Tomlinson [52] disclosed a method in which PP pellets are coated with azobisformamide as a blowing agent and a surface wetting agent. The pellets are then extruded, shopped into equally expanded pellets, and then re-coated and re-expanded by extrusion to produce foam. The invention claimed to offer big savings in the blowing agent amount by using it in a concentration of only 0.3 to 0.7% [53].

In 1984, Nojiri [54] disclosed a compounding based method of producing cross-linked PP foamed sheets by using ionizing radiation and involving a blowing agent, a cross-linking agent and PP. The invention is related to PP homopolymers and copolymers between propylene and α-olefins such as ethylene and butene. Best results have been achieved by using a random or block copolymer between propylene and 2 to 9 wt % of ethylene having a MFR between 1-20 dg/min. Both thermal decomposition type and volatile blowing agents can be used in this invention. The invention claims that when using a CBA (azodicarbonamide) for obtaining a good foam having uniform fine cells, the blowing agent should not be decomposed as much as possible in the step of kneading under heat a mixture of the polymer, the CBA and other additives. It is recommended to use a CBA that does not decompose at least 5 minutes at 185 °C.

In 1990, Alteepping [55] disclosed a method of producing a PP foamed product having a density less than 0.2 g/cm^3 by foam extrusion without the use of chemical cross-linking agents or radiation-based curing procedures. Instead, the invention is based on selection of specific components for forming the foamable composition in order to achieve a stable, low-density foam having excellent foam structure and mechanical properties. The foaming composition in this invention comprises a 70-90 wt % low-viscosity PP component having a melt viscosity (at 190 °C and a shear rate of $1000s^{-1}$) of less than 2×10^3 poise, a proportion of 10-30% of a high viscosity PP component having a melt viscosity (at 190 °C and a shear rate of $1000s^{-1}$) of greater than 2.5×10^3 poise, and a volatile blowing agent and one or more nucleating agents. The invention claims that trials revealed that omission of the high viscosity PP component results in failure to produce a stable foam, and that the usage of components with excessively large "dispersivity" results in poor foaming (e.g., foam collapse, excessive density, irregular pore size and voids). Here, the term "dispersivity" relates to the ratio between the weight average molecular weight and the number average molecular weight. Typically, isotactic PP is used for both the high and low viscosity PP resins in this invention, but it is also claimed that by including a portion of atactic PP (5-40 wt %) the uniformity of the cell size improves.

In 1992, Park [56] disclosed a tandem extrusion method for producing a thermoformable PP foam sheet having a smooth surface and a uniform cell structure which is prepared by extruding a mixture of a nucleating agent, a physical blowing agent and PP resin having a high melt strength and high melt elasticity. It is claimed in this invention that resins with melt flow rates ranging from 0.2 to 12 dg/min, measured in a melt flow instrument at 230 °C under a load of 2.16 kg, may be successfully used in the disclosed process. Also, it is emphasized that PP resins favorable for foaming may be distinguished from the ones that are not by their molecular and rheological characteristics and that the melt strength of PP is very important in foaming processes since the deformation is primarily elongational and tensile stresses are present.

2.5.2 Expansion Foaming Mechanisms

The expansion process comprises three fundamental steps: creation of small discontinuities or cells, growth of these cells to a desired volume, and stabilization and retaining of the expanded form obtained by physical or chemical means [46]. All expansion foam fabrication processes are deliberately designed to promote and control the sequential development of each of these three steps, which are shortly called: cell nucleation, cell growth, and stabilization.

Cell Nucleation. The formation of discontinuities in the molten polymer can be generated by injected gases into the fluid polymer, introduced low boiling liquids that volatilize due to increased temperature or decreased pressure, gases resulting from a chemical reaction within the fluid polymer, and chemical blowing agents which release a gas while thermally decomposing [46, 56].

In general, polyolefin foams can be produced by both physical and chemical methods [47] by using physical (volatile) or chemical (thermal decomposition type) blowing agents. The nucleation starts to occur at an initiation site within a polymer melt that has been supersaturated with a blowing agent, such a supersaturated state can be achieved either by a sudden pressure drop and a PBA or by heating a polymer containing a decomposable CBA. It is important to note that solid particles dispersed in the polymer matrix often provide the necessary nucleation sites [46].

However, in polyolefin foam technology, CBAs are most commonly used for purposes of expanding gas generation [47], while this is especially valid for the rotational foam molding process, which is low-pressure (atmospheric) by nature, and, due to the pressure insufficiency, applying physical blowing agents (PBA) would not be feasible [18]. Accordingly, only CBAs can be applied in rotational foam molding. Also, since a negligible shear motion is involved in rotomolding, the zero-shear viscosity of the polymer melt becomes an important rheological parameter in rotational foam molding [18].

Cell Growth. In general, once the cell starts growing and reaches its critical size, the ongoing diffusion of the blowing agent into it propagates its growth until it eventually stabilizes or ruptures. The rate of growth of the cells in the molten polymer can depend upon the melt strength and the melt elasticity of the surrounding molten polymer, the blowing agent pressure, the external pressure on the foam, the cell size and the permeation rate of the blowing agent through the polymer phase [46, 56].

Unlike processes that use physical expansion methods, in rotational foam molding, due to the process pressure insufficiency, the gases released from the decomposition of the CBA almost completely fail to dissolve in the polymer. As a result, almost the total available amount of gases goes into the cells and increases the cell pressure. Since the pressure of the polymer matrix remains unchanged (i.e., remains at the atmospheric level), a pressure difference is created between the cell internal pressure and the pressure of the environment, as a result of which the cell expansion and growth becomes dramatically accelerated. However, as a side effect of this pressure difference, certain amount of gas dissolves into the polymer matrix [18].

Cell Coalescence. With the continuation of cell growth, the void fraction increases, and thereby, the chances for cells meeting each other increase as well. As a result, closely located cells come into contact and, as a consequence, begin to share a common wall. Due to further cell growth and the resulting polymer drainage in the cell wall, the cell wall thickness decreases, so that it becomes highly stretched and very unstable, and therefore, prone to rupture. Such cell-wall instability causes the common wall between two neighboring cells to rupture and thereby they become transformed into one bigger cell. This transformation is referred to as cell coalescence. As a result of cell coalescence, the final cell population of the foam decreases. Since fine-celled foams are always preferred because of their better mechanical and thermal properties, the deteriorating effect of cell coalescence on the cell population density is an undesired outcome of the cell growth step in polymer foaming, and therefore, remedial measures have to be undertaken [18, 57-60].

Cell Coarsening. Unfortunately, cell coalescence is not the only cell density deterioration mechanism occurring in the foaming polymer. A distinct cell density deterioration event occurs when two adjacent cells, with different cell sizes, start to interact driven by the pressure difference between them, which is caused by their size difference. As a result of this pressure difference, the gas contained in the smaller cell diffuses to the larger cell. This causes a simultaneous tendency for a gradual size change in both cells. The smaller cell manifests such a tendency by a size decrease, i.e., over time it gets smaller and smaller, and eventually collapse, while, in contrast, the larger cell gets bigger and bigger over the same period. Finally, the former two, adjacent, differently sized, cells become one large cell. This transformation is referred to as cell coarsening. Like cell coalescence, cell coarsening deteriorates the cell population density and is therefore considered to be an undesired outcome of the cell growth stage in polymer foaming for which suppression a remedial action is required [18, 57-60]. Two principal strategies are commonly used for successful cell coarsening suppression. The first is based on nucleating the cells almost simultaneously in order to induce cell growth uniformity, while the second is based on reducing the processing time as much as possible.

Stabilization. In general, the cell stabilization strategy should be related to the stability of the cell wall and the drainage of the material from the wall that separates the cells. Increasing the viscosity of the fluid reduces the drainage effect. The viscosity increase may be caused by a chemical reaction or by a temperature reduction. The effect of the former increases the molecular weight through polymerization or cross-linking, while the effect of the latter cools the polymer below the crystallization temperature to prevent polymer flow. A recommended stabilization method for processes where the foam expansion is accomplished by heating is polymer cross-linking. This method is highly recommended if a CBA with an exothermic decomposing nature is used because the cross-linking will sharply increase the extensional viscosity of the polymer, as a consequence of which, the cell walls draining will be prevented, thereby dramatically improving the cell wall stability [46, 56].

Thermodynamically, the cell tendency to coalesce can be explained by the tendency of the overall system to lower the total free energy. In polymer foaming, such a tendency is accomplished by reducing the total surface area of two smaller cells into one smaller surface area of one bigger cell by their coalescing, as a result of which, the "surface tension" (or the surface energy) reduces as well. Since the cell-wall instability is the primary reason for cell coalescence to occur, in order to remedy the undesired outcome by suppressing cell coalescence, it would be desirable to increase the stability of the cell wall. The stability of the cell wall depends upon the polymer melt strength, since the polymer melt strength is commonly defined as the degree of resistance to the extensional flow of the cell wall during the act of polymer drainage occurring in the cell wall at the time of volume expansion. It would be therefore desirable to increase the melt strength of the polymer in order to increase the cell wall degree of resistance to extensional flow, which will, as a consequence, increase the cell wall stability. The increased cell wall stability in such a way results in cell coalescence suppression [18].

2.6 Chemical Blowing Agents

As indicated in Section 2.2, by definition, CBAs are individual compounds or mixture of compounds that liberate gas as a result of chemical reactions, including thermal decomposition or as a result of chemical reactions of CBAs or interactions of CBAs with other components of the formulation [61]. However, typically, the decomposition of nearly all CBAs is triggered by elevated temperature [7]. Most CBAs are solids [61] in a dry-powder form [7]. As such, they can be easily introduced into compositions to be foamed and can be processed by using ordinary equipment. Unlike PBAs, the use of CBAs reduces production costs because no specialized storage equipment is required [61].

2.6.1 Chemical Blowing Agent Selection Criteria

In the literature [7, 46, 47, 61, 62] various lists of general requirements that a successful, ideal, CBA should meet are provided. Actually, such lists integrate the most important criteria needed for a successful CBA selection. These include the decomposition temperature, rate of gas release, gaseous composition, ease of dispersion, storage stability, toxicity and cost [46]. Although, in reality ideal CBAs do not exist, it would be useful to take the content of such lists into account when selecting a CBA for a particular application.

During the selection of a CBA, the most important CBA properties that require special attention include the temperature at which the expanding gas is liberated, the initial temperature of decomposition, the temperature range of the maximum rate of decomposition, the gas yield (volume of gas, in cm^3, liberated by the transformation of 1 g of CBA per unit time, usually 1min, at the temperature of maximum gas liberation), the rate and kinetics of the liberation of gas, and the pressure developed by the gas [61].

2.6.2 Chemical Blowing Agent Selection Procedure

In general, plastics foaming technologies are limited by the nature of the process (PBA or CBA), the performance and the characteristics of the manufacturing equipment used, and the properties of the plastic resins, blowing agents and other additives implemented in the process. However, even the most sophisticated plastic foaming technologies are not equipped with process controls or machinery that can compensate for wrongly selected input materials, (plastic resins, blowing agents, etc.), in order to produce the desired output. Therefore, selecting the best combination of plastic resins and blowing agents for a particular foaming technology is of fundamental importance for the whole process and the quality and applicability of its output.

The present case is about processing fine-cell PP foams in compounding-based rotational foam molding. Therefore, a CBA must be used (see Section 2.5.2). Since the type of the basic plastic resin, the type of basic processing technology and the level of desired quality of the foam are already determined, the success of the present foaming process will be extremely sensitive to the type and properties of the selected CBA. The properties of the selected CBA will affect each step of the foaming process by imposing limits on the processing strategy, the quality of the foam, the economy of the foamed product and its application. Therefore, it is of crucial importance to select the best-suited CBA possible.

In order to accomplish this fundamental objective, a three-step approach is needed. The first step should include a careful and thorough assessment of the chosen foaming process, the properties of the chosen plastic resin that will be foamed by using the process, and the desired characteristics of the foam that will be produced by using the process.

The second step should provide a summary of the analysis undertaken in the previous step in a form of a list of desired properties of a well-suited, ideal CBA intended for PP compounding-based rotational foam molding application.

The third step should include a comparative analysis between the ideally required properties of the CBA for compounding-based rotational foam molding of fine-cell PP foams and the properties of commercially available CBAs.

Finally, the success of the actual selection of the CBA will depend on how similar or how different the desired (ideal) and the commercially available (real) CBA properties are.

Thus, it would be reasonable to expect that the final decision about which commercially available CBA to implement in a given process will most probably contain some compromises.

CHAPTER 3

PROCESS PROPOSAL FOR PRODUCING FINE-CELL PP FOAMS IN COMPOUNDING-BASED ROTATIONAL FOAM MOLDING

3.1 Introduction

Large-sized foamed plastic articles with complicated shapes that can satisfy severe service requirements and have improved stiffness, toughness, structural integrity, insulation ability, flotation ability, reduced weight and lower costs are increasingly in demand. As it was thoroughly elaborated in the previous two chapters, for producing such articles, the rotational foam molding is the best-suited available plastic processing technology, while PP should be the material of choice because of its outstanding properties.

The proposed rotational foam molding process is intended for manufacturing completely foamed, fine-cell, single layer, skinless, single-piece, PP articles. It is based on using extrusion melt compounding as the principal technique for preparing PP-based foamable compositions useful for producing fine-celled PP foams. Extrusion melt compounding is used in the proposed process as a means of mixing the PP resins with the CBA. The obtained molten mixture is converted into pellets that are subsequently used for charging the mold at the initiation of the rotational foam molding cycle (see Figure 2.13).

Despite the nucleation mechanisms with CBAs are not clearly described yet, there is a widely recognized belief among researches that a strong correlation exists between the achieved degree of CBA particle dispersion in the polymer matrix prior to foaming and the obtained quality of the foamed structure. This indicates that in order to obtain fine-celled PP foams that have a high cell density and a uniform cell distribution in rotational foam molding, it is important to disperse the CBA particles thoroughly into the polymer matrix of the foamable composition prior to foam production [19, 20]. Since only through intensive melt mixing a thorough and uniform dispersion of particles into a polymer matrix can be achieved [19-21], a compounding-based approach for the proposed process has been adopted.

3.2 Description of the Proposed Process

Figure 3.1 illustrates the detailed process diagram of the proposed compounding-based process for rotational foam molding of PP. It includes two distinct stages, a pellet production stage, and a foam production stage. The role of the pellet production stage is to prepare foamable PP pellets that can be used as a physical input in the foam production stage.

The pellet production stage includes three steps: grinding, dry blending and melt compounding. The first step serves for converting the selected PP resin into a powder form via a grinding operation because PP resins are rarely supplied in a powder form. Understandably, the grinding step should be ignored if the PP resin is supplied in a powder form. Either way, in the proceeding, second step, the PP powders are premixed with the selected CBA by using dry blending. If necessary, in the dry-blending step, the PP powders can also be premixed with additives other than the CBA, such as activators and antioxidants. The additives, including the CBA, are usually supplied in a powder form. In the third step, the blend of powders obtained in the dry blending step is converted into a pellet form by using extrusion melt compounding. In this step, the main task is to achieve good mixing of the PP resins and the CBA in a molten state and to provide a thorough and uniform dispersion of the CBA particles into the PP matrix. During the process of compounding, it is of crucial importance to preserve the CBA particles inactivated by adequately preventing their premature decomposition. The compounded extrudate is first cooled by passing through a cooling bath, and then pelletized in a pelletizer. Once the melt compounding stage is successfully completed, the obtained foamable PP pellets are considered to be ready for further use in the rotational foam molding process.

The foam production stage comprises the latter part of the process. In this stage, the compounded foamable PP pellets produced in the pellet production stage are used as a feed material without any intermediate intervention. The foam-production stage is initiated by pouring a predetermined shot size of foamable pellets into an open, hollow, vented, metal mold which is then closed, bi-axially rotated, and inserted into a heating chamber (usually a hot oven) to be heated while rotating. Because of the temperature gradient, the rotating mold, the foamable PP pellets, and the air inside the mold are being gradually heated and, as a consequence, a sequence of thermally driven events takes place in the mold. These include the sintering of the PP pellets and the decomposition of the embedded CBA particles in the pellets, the succession of which ultimately causes the formation of the PP foam. The mold is then cooled and the foamed product removed, which concludes the proposed compounding-based process for producing PP foams in rotational foam molding.

Since the desired output of the proposed process is a fine-celled PP foam that is characterized by a high cell density and a uniform cell distribution, each of the described processing steps should be understood as a separate processing input that can affect the quality of the final output. This indicates that the quality of the obtained PP foam will depend on how well the participating factors and processing parameters have been chosen and controlled along the whole course of the compounding-based rotational foam molding process.

3.3 Foamable PP Composition Design Issues

In compounding-based rotational foam molding, the facilities for foamable composition (pellets) and foam production do not have to be physically close and are not time-related because, as a result of the melt compounding, the CBA is conserved into the resin and will remain there until further exposure to elevated temperatures. However, in order for the foam production stage to be accomplished with a fine-celled PP foam production, the pellet production stage should deliver PP pellets with adequate properties and quality. Since the properties of the foamable pre-compounded PP pellets charged into the mold cannot be modified once the rotational foaming process is initiated, the PP pellets have to be deliberately designed to act in conformity with the changing conditions in the mold during the rotational foaming process. Thus, in order to properly design the process for pellet production, it is necessary to envision, foresee, and analyze all the process particularities pertaining to its subsequent stage, i.e., the foam production stage.

On the other hand, the accumulated effects generated by numerous factors during the course of the pellet production process eventually evolve into final pellet properties. Therefore, in order to determine an appropriate pellet processing strategy an awareness and appreciation of how these factors affect the pellet properties is highly desired. These include the influences of the selected PP carrier resin, the selected CBA, the other additives (if any), the formulation of their doses in the compound, the chosen order of their premixing, and all the further steps designed to process the mixture and convert it into a foamable composition. Thus, the final thermal and rheological behaviors of the pre-compounded pellets not only depend on the combination of the inherent properties of the basic PP resin and the additives, but also on their thermal and shear histories in respect to the grinding, dry blending and compounding steps. It is in this context that all decisions that participate in the creation of the pellet properties represent design decisions and must be clearly justified.

3.3.1 Role and Importance of the CBA

While the selected carrier PP resin usually has a major influence on the rheological and thermal properties of the pellets, the selected CBA can significantly affect the pellet affinity for being converted into fine-cell PP foams and therefore deserve a serious consideration. Thus, it is of fundamental importance to identify the most favorable CBA for fine-cell PP foaming from the outset. The CBA should be characterized in terms of its thermal behavior, particle size, and the quality and quantity of the gasses it releases while decomposing. In addition, assuming that this selection is properly completed, there are three additional, equally important conditions regarding the CBA contained in the pre-compounded PP pellets that have to be satisfied as a prerequisite for obtaining fully expanded, fine-celled, PP foams in compounding-based rotational foam molding.

First, the CBA particles dispersed throughout the pre-compounded pellets have to be in an inactivated (non-decomposed) state for reasons of using their gas-releasing ability for the subsequently needed foaming of PP. This indicates that every effort has to be undertaken for successful prevention of premature CBA decomposition during compounding.

Second, the concentration of the CBA in the pellets has to be commensurate to the desired (or required) magnitude of volumetric expansion of the material charged into the mold relative to the volume of the mold in order to achieve mold feeling with foam to the full extent.

This parameter is referred to as the volume expansion ratio (VER). This indicates that an appropriate relationship between the CBA amount and the required VER has to be developed.

Third, as already mentioned, a thorough and uniform dispersion of the CBA particles throughout the pellets is necessary for reasons of obtaining a fine-cell foam structure.

A failure to fulfill whichever of these three conditions will result in a failure to obtain fully expanded fine-cell PP foams. It is for these reasons that these three fundamental conditions represent the foundation for formulating the criteria upon which the quality of the pellets obtained in the pellet production stage should be evaluated.

3.4 Compounding Step

Compounding is defined as a continuous way of converting a pure polymer into a useful composition by adding additives in a mixing operation [63]. Mixing is usually described as the intermingling by mechanical action of two or more initially segregated components [64]. Extrusion is the most commonly used method of continuous mixing in polymer processing. In extrusion, the materials are fed through a hopper and then compressed, melted, mixed and pushed through a die by the action of one or more rotating screws located in a hot extruder barrel [64-66].

In mixing in polymer processing, a clear distinction has been made between dispersive (intensive) and distributive (extensive, laminar mixing, or blending) [63]. Dispersion is governed by the history of fluid mechanical stresses in a mixture, while distribution is determined by the history of deformation (strain) imparted to the fluid [64]. Dispersive mixing denotes reduction in size of a segregated component that has a cohesive nature, such as cohesive granular solids and liquid regions with surface tension, vapor or gas bubbles [63], it results in rupture of agglomerates and separation of closely packed particles [67]. Distributive mixing denotes deformation of the liquid by shear with some elongation, as for instance in the mixing of thermodynamically compatible melts. The objective of distributive mixing is to achieve compositional uniformity throughout the mixture [67]. All dispersive mixers must provide a good distributive mixing first in order to achieve the desired outcome [63].

Turbulent flow is the most desired mechanism of mixing, but to achieve turbulent flow in an extruder barrel (channel), the Reynolds number must exceed a value of 2000. The relationship given in Equation 3.1 for calculating the Reynolds number include the size of the

$$\mathrm{Re} = \frac{DVP}{\eta} \qquad (3.1)$$

channel D, the average velocity of the flow in the channel V, the fluid density P, and the fluid viscosity η. Since extremely high viscosities are associated with polymer melts (10^4 Pa·s) and since the viscosity η is a denominator in Equation 3.1, achieving a turbulent flow in extrusion is practically impossible because it would involve unrealistically large channel sizes and fluid velocities [64]. Thus, unfortunately, for the present case of dispersive mixing of solids into a viscous liquid matrix [68], such as the proposed dispersion of CBA particles into a molten PP matrix, the favorable randomizing effect of the turbulent flow cannot be used. As a consequence, the laminar flow remains to be the only feasible option.

3.4.1 Role and Importance of Compounding

Despite the fact that the principal motivation for introducing the melt compounding in the proposed process is its outstanding capability of dispersing solid particles in molten polymers, its contribution is primarily evaluated by its capacity to produce decomposition-free foamble pellets of a PP resin and a CBA. This is so because if there is no absolute certainty that the melt compounding technique can unconditionally provide a foamable PP composition in a form of decomposition-free PP pellets, regardless of how high the achieved degree of CBA particle dispersion would be, it would not be able to prevent the whole process of becoming meaningless and ultimately shut down. Therefore, the degree of CBA particle dispersion is not the "one and only" concern in PP melt compounding related to fine-cell PP foam production, it is rather a desired and required side-effect of a successful (decomposition-free) compounding operation. Thus, the melt compounding technique should be understood as the backbone of the proposed compounding-based rotational foam molding process for producing fine-cell PP foams. Being so fundamental and critical for the overall process performance, it is the most reasonable step from which the proposed process design should start from.

3.4.2 Temperature Constraints in Compounding

Melt mixing in polymer processes is often constrained by the sensitivity of polymers and additives to high temperature, oxidation, and shearing. In general, the processing temperature during compounding PP with a CBA has to be maintained above the melting temperature of the polymer and below the onset decomposition temperature of the CBA. The processing temperature should be higher than the melting temperature of the polymer resin for reasons of polymer flow and for achieving the finest possible dispersion of the CBA particles in the molten polymer. On the other hand, the temperature of the melt should not exceed the onset decomposition temperature of the CBA, since otherwise the CBA will decompose and instead of pellets a foamed extrudate will be obtained and all the generated blowing gases will be lost. As a consequence, no foaming will occur if such a pre-compounded product is used as a feed material in rotational foam molding. Since the presence of non-decomposed CBA particles in the foamable pellets is crucial for the foaming to occur, producing decomposition-free PP pellets should be considered as the principal issue of concern in the pellet production stage of the compounding-based rotational foam molding.

CBAs are heat-sensitive. Therefore, an adequate control of the processing temperature during compounding should maintain the processing temperature within the temperature limits favorable for decomposition-free compounding. The temperature constraints for a decomposition-free compounding of any polymer with a CBA are described by the relationship presented in Equation 3.2.

$$T_{\text{polymer melting}} < T_{\text{processing (compounding)}} < T_{\text{CBA decomposition}} \qquad (3.2)$$

To be able to use Equation 3.2 and impose actual temperature constraints on the PP compounding processing temperature, knowledge of the two critical temperatures, the melting temperature of the selected PP resin and the onset decomposition temperature of the selected CBA, is required. These data can be acquired from the corresponding material manufacturers, but due to the importance of their accuracy in the present research, it would be preferable to obtain thermal analysis spectra by conducting DSC and/or TGA experiments on specimens from the PP resins and CBA selected for use.

3.4.3 CBA Selection

Step #1. The description of the proposed process (Section 3.2), the analysis of the role of the CBA in the process (Section 3.3.1), the analysis of the role and importance of compounding (Section 3.4.1), the analysis of the temperature constrains in compounding (Section 3.4.2), as well as the criteria (Sections 2.6.1) and the established procedure for CBA selection (Section 2.6.2), are sufficient to accomplish Step #1 of the CBA selection procedure. As a result, the information acquired in Step #1 can be used for creating the list of desired properties that an ideal CBA should have to have in order to serve in fine-cell PP foam production by using the proposed compounding-based rotational foam molding process.

Step #2. *Decomposition Temperature.* Ideally, the CBA decomposition temperature for rotational foam molding applications should be 50 °C higher than the melting temperature of the polymer to minimize the amount of gas that will be lost from the polymer surface during foaming [7]. Thus, since various PP resins (homopolymers and copolymers) melt in the range of ~150-175°C [46], the ideal CBA for PP foam production in rotational foam molding should decompose in the range of ~200-225 °C. Also, the decomposition of the CBA must not be accompanied by the release of too much heat so that the polymer matrix become thermally destroyed [61].

Ideally, the CBA should be sensitive to activators, while an added CBA sensitivity to inhibitors would significantly improve the possibilities for using the CBA at a broader range of decomposition temperatures. Activators provide opportunities for reducing the decomposition temperature of CBAs, while inhibitors have an opposite effect. Typically metals in the form of oxides, salts, or organometalic complexes are used as CBA activators [46].

If using a PP foamable composition containing a CBA activator in rotational foam molding, due to the effect of the activator, the decomposition temperature of the CBA reduces, and as a result, the processing temperature can be reduced as well. A reduced processing temperature in rotational foam molding will allow maintaining higher melt strength of the molten PP resin. The higher PP melt strength will increase the stability of the cell wall (see Section 2.5.2), as a result of which, the effect of cell coalescence will be reduced significantly (if not completely suppressed), and PP foams with improved structure will be obtained.

On the other hand, since the proposed process is compounding-based, the selected CBA will have to be exposed to elevated temperatures at least two times during the course of the process, once during its compounding with the PP resin and once during the rotational foam molding process itself. In order to permit safe and efficient decomposition-free incorporation of the blowing agent into the PP resin by extrusion melt compounding, using a CBA with a higher decomposition temperature range than the one with respect to foaming would be desirable. This indicates that the desired decomposition temperature range of the ideal CBA with respect to compounding should be at least ~210-230 °C, or even higher. But, a CBA with a significantly higher decomposition temperature range then ~210-230 °C should not be used in PP foaming, because this would cause additional heating during the rotational foam molding cycle. As a result, the melt strength of the molten PP resin could be lowered to the level that it would make it useless for foaming applications [7].

However, a single CBA, even if it would be ideal, cannot have a dual decomposition temperature range during the same compounding-based rotational foam molding process, i.e., one range for the compounding operation (~210-230 °C), and another for the foaming operation (~200-225 °C). A remedial action could include using a CBA with the higher range of decomposition (~210-230 °C) in order to facilitate the compounding operation, and then using an activator to reduce the onset decomposition temperature of the same CBA during foaming, in order to preserve the melt strength of PP. But, such a proposal would prove itself unfeasible because the activator will be efficient during the foaming operation only if it is incorporated into the PP in the same way and time as the CBA, i.e., if it is compounded. Since the role of the activator is to lower the CBA decomposition temperature, nothing will stop it to achieve the same effect during the compounding operation, thereby jeopardizing the decomposition-free compounding. If employing a reversed logic, i.e., if using a CBA with the lower decomposition range (~200-225 °C), which is suited for PP foaming, while using an inhibitor to prevent the early CBA decomposition during compounding, seems to be more promising. But, ultimately, it would not improve the situation significantly, because to ensure inhibition efficiency, the incorporation of the inhibitor into the PP/CBA mixture has to be done during the compounding operation. This would suppress the unwanted early decomposition of the CBA during compounding and thereby provide good conditions for obtaining a decomposition-free foamable composition. But, the resulting permanently increased decomposition temperature of the CBA embedded in the compounded pellets, will most probably result in producing unsatisfactory cellular structures as a consequence of unsuppressed cell coalescence, due to the lower PP melt strength at elevated temperatures. Moreover, for many CBAs inhibitors are not known or do not exist. As a result of this idealized analysis, it would be reasonable to expect that a compromised solution would be the only way to overcome this problem and cope with the reality.

Rate of Gas Release. Ideally, the rate of CBA gas liberation must be adequately high and the gas must be liberated within a certain narrow temperature range [61]. Otherwise, the polymer viscosity at higher temperatures will be too low, and as a consequence, gas diffusion through the polymer will be accelerated, as a result of which gas losses during foaming will increase. Also, the gases liberated during decomposition of the ideal CBA must have a low rate of diffusion in the polymer, that is, they must stay in the mass being foamed for a rather long time [61].

Gaseous Composition. Ideally, CBAs that liberate N_2 or CO_2 are preferable [61].

Ease of Dispersion. Ideally, the CBA must readily disperse in the polymer composition [61] to facilitate the uniformity of CBA particle dispersion during compounding. Here, the role of the CBA particle size becomes important [46].

Storage Stability and Toxicity. Ideally, the gas liberated and the products of its decomposition must be noncorrosive, nontoxic, and nonflammable.

Cost. In most cases, plastics foaming is motivated by two reasons: cost and performance (see Section 1.1.1). Therefore, the cost of the ideal CBA must be reasonable enough to allow processors to achieve savings in the overall economy of the plastic foaming operations they are willing to undertake.

Step #3. CBAs can be inorganic or organic substances [62]. Three groups of CBAs are commercially available: organic nitrogen compounds, sodium bicarbonate and its mixture with citric acid, and sodium borohydride. But, only few organic nitrogen compounds are suited for polyolefin foam production. These include azodicarbonamide, N, N'-Dinitrosopentam-ethylenetetramine (DNPA), and 4,4- Oxybis (benzenesylfonylhydrazide) (OBSH). Among them, azodicarbonamide is most commonly used in commercial polyolefin foam production [46].

Table 3.1 presents the most commonly commercially available CBAs and their peak decomposition temperatures. Among those, azodicarbonamide is most often recommended for use with PP in the literature. A variety of different grades of azodicarbonamide are commercially available. Azodicarbonamide is an exothermic CBA and decomposes in a narrower temperature range ~200-210 °C [46] than the one that should be ideally suited for foaming PP (~200-225 °C).

As it can be seen from Table 3.1, other candidate CBAs for PP foaming characterized with higher decomposition temperatures than that of azodicarbonamide exist, but the negative consequences of using some of those, have been already discussed. In addition, their gas yield is much lower compared to that of azodicarbonamide.

Concluding Remarks. Finally, taking all discussed CBA selection issues into account, azodicarbonamide will be used for the proposed compounding-based rotational foam molding process for producing fine-cell PP foams.

The decomposition mechanism of azodicarbonamide is complex and not fully understood. Its decomposition rate and gas yield depend on temperature. It decomposes through two primary reactions, one yielding urea and the other hydrazodicarbonamide as an intermediate product, in addition to gaseous products. An activator not only enhances the rate of decomposition of azodicarbonamide but also alters the amount of gas yield. Known activators for azodicarbonamide include salts of transition metals (especially those of lead, cadmium, and zinc), polyols, urea, alcohol amines, and some organic acids, among which zinc oxide and zinc stearate are the most commonly used in commercial processes. Reported inhibitors for azodicarbonamide include organic acid, phenols, amines, organic anhydrides, and acid hydrazides [46].

3.4.4 Decomposition Triggering Events in PP Compounding

Even if the processing temperature is maintained within the limits given in Equation 3.2, successfully suppressing the pre-decomposition while compounding PP resins with a CBA represents a serious processing challenge. The reasons for this difficulty lie in the magnitude of the melting temperature of the PP, which is relatively high (~ 165 to 175 °C for PP homopolymers and ~ 150 to 175 °C for PP copolymers) [46], and in the magnitude of the onset decomposition temperature of the azodicarbonamide CBA suitable for PP foaming, which is relatively low (~ 200 to 210°C). As a consequence, the minimal interval between the critical temperatures that can be used for successful compounding is only about 25 °C wide. Theoretically, this processing temperature gap may look large enough, but practically it seldom provides a sufficient processing window for compounding PP resins with a CBA without provoking the pre-decomposition of the CBA. In addition, regardless of the type of compounder used, several compounding parameters can have a shrinking effect on the processing temperature gap, which makes the process of compounding a PP resin with a CBA even more difficult.

First, due to the rotating action of the plasticating screw in a compounder, the molten mixture is pumped forward relative to the barrel, which is a shearing flow that additionally heats the mixture because of the generated heat by the friction of the polymer against the barrel. If the barrel is grooved, the coefficient of friction becomes extremely large [69]. As a result, the temperature gap becomes narrower. Since the shear rate is proportional to the rotational speed of the screw, it would be necessary to minimize the screw RPMs in order to minimize the heat generated by the friction and thereby prevent the CBA pre-decomposition.

Second, CBAs are known to be thermally sensitive if exposed long enough on elevated temperatures even lower than the onset decomposition temperature. Therefore, for successfully preventing the CBA pre-decomposition due to a long residence time, it is necessary to minimize the residential time of the melted mixture in the compounder, e.g., to maximize the screw RPMs. This reasoning suggests that in order to prevent the unwanted CBA pre-decomposition, the lowest possible shear rates and the shortest possible residence times simultaneously occur during compounding. The screw rotation rate is the only parameter that can control these two variables, but since it is contradicted, an optimal range of screw RPMs capable of simultaneously satisfying both the shear rate and the residence time constraints is needed. If such an optimal number of RPMs cannot be determined, the pre-decomposition control of the compounding becomes coupled since the shear rate and the residence time cannot be controlled independently.

Third, because of the low melt strength of the PP resins at elevated temperatures [18, 19], it is often necessary to introduce additives other than a CBA during compounding the foamable PP resin, such as a CBA activator. As already mentioned, the anticipated role of the activator in the foamable composition is to lower the onset of the decomposition of the CBA during foam processing in order to lower the overall processing temperature, thereby preserving the melt strength of PP. But, the activator will tend to affect the CBA in the same way during all times. As a result, the decomposition onset of the CBA will be also lowered during compounding, thereby narrowing the compounding temperature window even further.

Fourth, the heating rate during extrusion compounding is usually higher than 100 °C/min and can easily result in CBA decomposition at lower temperatures because of the effect of thermal kinetics at high heating rates.

Fifth, local overheating may cause a few CBA particles to decompose. If using an exothermic CBA, additional heat will be released during such a local CBA particles decomposition due to the exothermic nature of the CBA. This self-heating phenomenon could cause a chain reaction and thereby trigger the premature decomposition of the complete CBA content in the compounder.

3.4.5 Proposal for a PP Compounding Strategy

The most important factor for the success of the compounding operation is the design of the extruder used for compounding. Conventional extruders for plastic processing include single-, twin-, and multiple-screw extruders. Among them, twin-screw extruders are particularly flexible in respect to the flight configuration of their screws. This flexibility is the most powerful characteristic of twin-screw extruders, it allows changing the configuration of the screws in order to modify the level of intensity of their interaction during operation, thereby making them useful for a particular purpose. Therefore, twin-screw extruders are the most appropriate for decomposition-free compounding of heat and shear sensitive materials for foamable applications. Among them, for decomposition-free compounding of mixtures such as the proposed mixture of powdered PP resin and a CBA, intermeshing co-rotating twin-screw extruders (compounders) are the most favorable [70].

There is a large theory behind the operation of intermeshing co-rotating twin screw compounders. They involve several different types of elements that are closely intermeshing. The key elements are the kneading discs that melt the polymer and disperse ingredients [69]. Normally, individual sections that slide onto a keyed or splined shaft form the screws. This allows different screw profiles to be deliberately obtained by placing different screw profiles along the shaft. Controlled shear or mixing effect can be achieved in that way [70]. Figure 3.2 presents different screw arrangements. The advantage of the intermeshing co-rotating twin-screw mixing geometry lies in the combination of kneading disc modules with screw modules that most often have self-wiping profiles [69], as shown in Figure 3.3. At the point where the two screws meet, a complete transfer of the material from one screw to the other takes place [70]. The role of the right handed screw is to transport the material while the role of the left handed screw is to control the pressure fields inside the compounder [69]. As a result, intermeshing co-rotating twin-screw compounders can incorporate and homogenize the CBA without exceeding degradation temperatures; provide a very uniform shear stress and heat history to each particle and allow precise control over the mixing process.

Considering the decomposition triggering events during PP compounding discussed in Section 3.4.4, the compromising CBA selection decision discussed in Section 3.4.3, as well as the final goal to produce satisfactory PP foams, it seems that, a proposal for foamable PP resin compounding strategy could be useful only if it includes further compromises. Namely, to prevent the decomposition, it would be necessary to run the compounding system by using the minimal conceivable, theoretically allowed, safe, processing temperature. Such a strategy would require setting the twin-screw extruder barrel heaters to the lowest melting temperature from the range of PP resins melting temperatures discussed in Section 3.4.4, which is 150 °C, and using the most "non-offensive" possible screw design, as well as a moderate screws RPM. For the present case of compounding a foamable PP composition, the screws of the intermeshing co-rotating extruder have to be specially rearranged in such a way that the generated shear field is weak and the temperature gradient is minimized. In addition, as a part of the compounding strategy, it would be necessary to introduce the grinding and dry blending steps as preparatory operations for successful pellet compounding. Since pellet compounding is the final step of the pellet production stage, all the benefits of grinding the PP resin prior to premixing it with the CBA and those of premixing the PP/CBA powders prior to compounding will be manifested in this step.

3.5 Grinding Step

3.5.1 Role of Grinding in PP Compounding

PP resins are usually supplied in a pellet form. Starting the compounding process from PP pellets would require too much local shear and local heating. As a consequence, the excessive heat would most probably trigger the decomposition of the heat-degradable CBA while still in the compounder, which is absolutely not desirable.

Even if the CBA decomposition does not occur, intensive mixing (dispersion) inside the compounder would not be possible because of the generated heat that will extremely reduce the viscosity of the polymer melt. As a result, the achieved degree of dispersion of the CBA in the polymer matrix throughout the pellets would be poor and non-uniform. Consequently, the foamed structure obtained by using such pellets will have similarly poor and non-uniform cell morphology, which is also undesirable.

Because of the above reasons, the PP resins that are supplied in a pellet form have to be mechanically ground at the initiation of the pellet production stage. The role of the mechanical grinding is to reduce the original size of the PP resin into a smaller, pre-decomposition prevention-friendly size, and thereby facilitate the CBA pre-decomposition control during compounding.

3.5.2 Proposal for a PP Grinding Strategy

A specially designed grinding head is needed for grinding PP resins supplied in a pellet or a granulated form. Otherwise, if using conventional milling or grinding machinery, the PP pellets would be ground by "shredding and tearing" [21] into sizes and shapes that would diminish the desired positive effect of the grinding operation on the efficiency of the subsequent dry-blending and compounding steps. The appropriate method for PP grinding differs from the previously described by the way how the pellet size is reduced into powder, it can be described as "pellet disintegration by a series of speed cuts" [21].

Figure 3.4 illustrates the typical design of the grinding head that should be used for grinding PP resins. It is provided with two plates, each with a series of radially arranged cutting edges, one static and the other with the ability to rotate at a high speed. The PP resins, as supplied in a pellet form, are fed in the center of the gap that separates the two plates. The key feature of this design is the gradual reduction of the gap between the cutting edges in the radial direction from the center of the plates to their periphery. As a result, during the rotation of the movable plate, each pellet is trapped between the cutting edges and thereby becomes subjected to a cutting action resulting in a gradual pellet size reduction as it travels radially, driven by the centrifugal force, to the next, narrower, gap section. Ultimately, the ground PP particles leave the gap at the periphery of the plates with a significantly reduced size [21].

During PP grinding, most of the energy input used to reduce the PP particle size is converted into heat. Since PP resins are heat sensitive and have a relatively low softening point, the success of their grinding depends on the availability of suitable refrigerants to cool the grinding chamber and/or to increase the brittleness of the resins [71].

There are two methods of using refrigerants while grinding heat sensitive polymers. The refrigerant can be fed into the grinder together with the material, or the material can be frozen prior to the grinding in order for it to shatter under impact [71]. In the former method, liquid CO_2, liquid nitrogen, or CO_2 in the form of dry ice is the most commonly used refrigerant. This method is also referred as to cryogenic grinding, while the latter method is referred to ambient grinding.

However, freezing a material before grinding is feasible only if the glass transition temperature of the material to be ground is below room temperature, but is still at a practically achievable level. For example, PP resins can very effectively be ground after freezing since their glass transition temperature ranges between - 20 °C [71] and 0 °C [9], while the glass transition temperature of unmodified PE, which is about -100 °C [71] is practically unachievable prior to and during grinding [71].

The consistence of the powder quality depends both on the immediate grinding process conditions and the rate at which the powder is cooled after grinding [72]. Wrong grinding parameters can cause powder particles to be torn and shredded resulting in irregular shapes [21]. As a consequence, small fibrils resembling as "tails" attached to the surface of the particles, can appear. These tails or hairs obstruct the freedom of flow of the particles during dry blending. Heating can reduce the presence of these fibrils, since holding the powder at a high temperature for longer allow remaining fibrils sufficient time to relax back into the particles. On the other hand, high particles cooling rates result in "freezing" the stretched fibrils in place preventing them from recoiling back into the particle [20, 21, 72]. However, the pre-mixed blend is being remelted, remixed and reshaped into pellets during compounding, so that the negative effects that might have been caused by the inconsistencies in powder quality in terms of particle size and shape will be removed. Therefore, this issue should not receive too much attention.

Taking into account the information presented in this section, the grinding strategy for the PP resins participating in this research should include freezing the resins at about - 40 °C prior to ambient grinding by using mechanical grinding equipment that is equipped with the type of grinding head described and illustrated in Figure 3.4.

3.6 Dry Blending Step

3.6.1 Role of Dry-blending in PP Compounding

As already mentioned, if uniformly dispersed, the embedded CBA particles throughout the mass of PP pellets will transform in uniformly dispersed nucleation sites during subsequent foaming. This indicates that if the degrees of dispersion and uniformity of the CBA particles in the pre-compounded PP pellets are below a certain level, fine-cell foaming will fail to occur regardless of how favorable the remaining pellet properties are. Because of these reasons, it is necessary to premix the participating materials prior to compounding. The premixing step is an intermediate step between the grinding and melt compounding steps, within the pellet production stage. Its role is to prepare a finely dry-blended mixture of PP powders and an appropriate amount of CBA, according to the prescribed formulation for the foamble composition for a desired VER, to be fed into the compounder. The benefit of the dry-blended PP/CBA powders is promoting a finer and more uniform dispersion of the CBA particles in the polymer matrix during compounding of the foamable composition. As a side effect, the premixing will also facilitate the pre-decomposition suppression during compounding.

3.6.2 Foamable Composition Formulation for a Desired VER

The volume expansion ratio (VER) of plastic foams in rotational foam molding is defined as the ratio between the expanded volume of the foam (V_f) and the initial volume of the solid unfoamed plastic material (V_i) [19]. Equation 3.3 presents this relationship.

$$(VER) = \frac{V_f}{V_i} \tag{3.3}$$

The proposed compounding-based process is intended for producing skinless PP foams in rotational foam molding that occupy the mold's volume to the full extent (see Section 1.6). Therefore, in the foam production stage, the mold will be charged only with foamable PP pellets, while the volume of the expanded foam (V_f) will be desired to be identical to the volume of the mold used (V_m). Hence, Equation 3.4 can be obtained by substituting the expanded foam volume (V_f) with the volume of the mold (V_m) in Equation 3.3.

$$(VER) = \frac{V_m}{V_i} \tag{3.4}$$

Equation 3.5 can be obtained, by substituting the initial volume of the solid unfoamed polymer material (V_i) with the ratio between its weight ($m_{polymer}$) and its density ($\rho_{polymer}$) in Equation 3.4.

$$(VER) = \frac{V_m}{m_{polymer} / \rho_{polymer}} \tag{3.5}$$

To produce PP foams with a desired VER in compounding-based rotational foam molding, the foamable PP composition must contain an appropriate amount of CBA. This amount of CBA has to be deliberately calculated and added to the PP resin intended to be compounded into a foamable PP composition. The concentration of CBA in the formulation is usually expressed in terms of the percentage of CBA by weight with reference to the amount of pure PP resin (see Equation 3.6). This amount of CBA determines the "expansion quality" of the pre-compounded foamable composition and its foaming behavior during the rotational foam molding thermal cycle.

$$\%CBA = 100\frac{m_{CBA}}{m_{polymer}} \tag{3.6}$$

In order to produce a foamable PP composition that will be characterized with certain expansion quality suitable for achieving a given value for the VER, the proportion of the CBA in the composition's formulation must correspond to its gas-generation ability (gas yield). The gas-generation ability of the total amount of CBA, contained in the foamable polymer charged into the mold has to be related to the remaining free volume of the mold. This relationship is based on the assumption that the CBA contained in the shot size is supposed to generate gas in sufficient quantities to fill the free mold's volume in order to be able to produce enough polymer foam that will ultimately fill the mold. Hence, the required gas-generation ability of the CBA, that can be expressed with the product of its weight (m_{CBA}) in grams and the gas yield (φ) in cm^3/g, has to be equal to the free volume of the mold that can be obtained by subtracting the volume of the polymer (V_i) from the total mold volume (V_m). This relationship is presented in Equation 3.7.

$$m_{CBA} \cdot \varphi = V_m - V_i \tag{3.7}$$

Equation 3.7 can be rearranged into Equation 3.8, and then (by using Equation 3.4) it can be rearranged into Equation 3.9 that expresses the appropriate weight of the CBA for achieving a given VER.

$$m_{CBA} = \frac{V_m - V_i}{\varphi} \tag{3.8}$$

$$m_{CBA} = \frac{\frac{(VER) - 1}{(VER)} \cdot V_m}{\varphi} \tag{3.9}$$

Similarly, Equation 3.5 can be rearranged into Equation 3.10 that expresses the required weight of the polymer for achieving a given VER by filling the entire volume of the mold with foam.

$$m_{polymer} = \frac{V_m}{(VER)} \rho_{polymer} \tag{3.10}$$

Equation 3.11 can be obtained by substituting the relations obtained for (m_{CBA}) and ($m_{polymer}$) from Equations 3.9 and 3.10, respectively, into Equation 3.6. Equation 3.11 expresses the percentage by weight of the selected CBA relative to the weight of the PP resin that should be introduced in the dry-blended mixture in order to obtain a given VER during subsequent foaming.

$$\%CBA = 100 \frac{(VER) - 1}{\rho_{polymer} \cdot \varphi} \tag{3.11}$$

3.6.3 Proposal for a Dry-Blending Strategy

The dry blending of powders for the proposed process requires implementation of mixers suited for a non-continuous operation. Therefore, it may be accomplished by using tumbler mixers or by mixing the powders in a high-speed mixer [21, 69, 74]. A mixer that relies on tumbling and stirring can produce considerable segregation, while high-speed mixing provides minimal segregation and superior efficiency and degree of mixing [74]. Therefore, the use of a high-speed mixer is adopted to be a part of the strategy for dry blending the PP and CBA powders. Figure 3.5 illustrates a schematic of a typical high-speed mixer that should be used for the purpose of the proposed process.

3.7 PP Foam Production Stage

3.7.1 Processing Steps in the Foam Production Stage

In the proposed process (see Figure 3.1), the foam production stage serves to convert the foamable PP composition, compounded in the pellet production stage, into a PP cellular structure, by processing it in a four-step rotational foam molding cycle (see Section 2.2 and Figure 2.13). The major objective of the proposed process is to produce fully expanded, skinless (see Section 1.6), fine-celled PP foams that have a high cell population density and a uniform distribution. The foam production stage is accomplished in four rotational foam molding processing steps.

Step #1. In the initial step, the mold is charged with a pre-measured amount of foamable PP pellets (shot size), already compounded with a view to achieving a particular pre-determined volume expansion ratio.

Step #2. Further along the rotational foam molding process, the pre-compounded foamable PP pellets, enclosed into the bi-axially rotated mold, undergo extreme thermal, rheological, and structural transformations as a result of the applied heat to the mold in a closed chamber (oven). In order to induce polymer foaming, the heating must be sufficient to penetrate the mold walls and elevate the temperature of the air inside the mold to levels exceeding the melting temperature of the PP pellets, as well as the decomposition temperature of the CBA particles embedded in the pellets.

Step#3. After the completion of the heating cycle the process immediately proceeds with the cooling cycle. As a result, the mold is cooled while it is still rotating bi-axially, in order to solidify the polymer and reach handling temperatures that allow the implementation of the final step which is concerned with unloading the produced article.

Step #4. The rotationally foam molded article is removed from the mold.

3.7.2 Process Variables in Rotational Foam Molding

Whether or not the foam production stage will be accomplished with a production of fine-cell PP foams depends on the foamable PP pellet properties and the performance of the rotational foam molding process control. Since from the initiation of the rotational foam molding process up to its last step the properties of the foamable PP pellets remain uncontrollable, the entire rotational foam molding process control relies only on three controllable process parameters to direct the process of fine-celled PP foam formation. These include the processing temperature, the processing time, and the mold rotation.

The rotational foam molding cycle includes two thermally opposed cycles; the heating and the cooling cycle. Both cycles are characterized by various processing variables.

Heating Cycle. Since the proposed compounding-based rotational foam molding process is intended for producing PP foams with a high degree of cell-distribution uniformity, the heating system, pertaining to the rotational foam molding equipment used for foam production, is required to provide a uniform mold heating at a reasonable heating rate. In general, the rate at which the material contained in the mold is heated is basically a function of the method of heating used, the temperature of the heating medium, the mold material, the thickness of the mold, the thermal conductivity of the processed material, the amount of CBA incorporated in the foamble pellets (especially if the CBA is of exothermic nature), the magnitude of the shot size, and the size of the pellets.

Usually, during the heating cycle, the oven temperature is kept at a constant level, as a result of which, the processing time becomes the principal processing parameter. Since higher oven temperatures are associated with higher heating rates and lower oven temperatures are associated with lower heating rates, establishing an appropriate control of the relationship between the oven temperature and the processing time is the key issue for a efficient rotational foam molding process control.

Cooling Cycle. As was already indicated, during the cooling cycle, the mold rotation never stops. The principal methods of cooling include mold rotation in stationary air, applying circulating cool air to the mold, applying water spray to the mold, and a combination thereof. Rotationally foamed articles are known to have virtually no "built in stresses", since the process is performed at nearly atmospheric pressure. While it is true that the heating cycle does not cause stresses in the final foamed article, the cooling cycle does. The rate of cooling especially affects the degree of article shrinkage, the final cell density of the foam, and the article brittleness. Rapid cooling results in reduced article shrinkage, lower final article density, and improved impact resistance due to the lower crystallinity developed. In conventional rotomolding, the stresses and shrinkage gradients might lower the impact resistance, so that the rate of cooling has to be controlled in order to balance article warpage against any physical property advantage gained from rapid cooling [75]. In contrast, in rotational foam molding, the warpage effect is not particularly significant due to the cellular structure of the molded article and does not require a precisely controlled cooling rate.

The molds used for rotational foam molding must be supplied with vents during both the heating and the cooling cycle. Mold venting is usually provided with Teflon tubes inserted far enough into the mold so that the material does not fill and plug the vent. Proper venting enables the full expansion of the polymer, reduces material flash from the pressure created from the released gases during CBA decomposition, and reduces warpage that may be caused by the vacuum created during rapid cooling [75].

Mold Rotation. Like in conventional rotomolding, bi-axial rotation is the most common method of mold rotation used in rotational foam molding (see Figure 2.3). Usually, the axes of rotation are perpendicularly located for achieving a simpler mechanical design of the mold-mounting assembly. The processing variables related to the mold rotation include the magnitude of rotational speeds and the rotation ratio which is obtained by varying the speed of each of the independently driven axes.

The major axis is given the higher rotational speed, while the minor axis is given the lower rotational speed [75]. The role of the mold rotation is to distribute evenly the plastic material during the heating cycle on the internal surfaces of the mold, and thereby avoid the melt continually flowing over the same path. The chosen rotation ratio determines the degree of melt distribution on the internal surfaces of the mold. For best results, this ratio has to be suitable to the shape of the particular rotationally foam molded article [21]. Often, mounting the molds off-center helps in avoiding the possible dead spots [75].

Theoretically, for each rotationally foam molded article shape, an optimum rotational speed exists for either axis of rotation [21, 75]. In general, the major to minor rotational speed ratio should be greater than 1 but should never give a whole number. Also, the rotation ratio should increase as the mold deviates from a spherical or cubical shape [75]. A rotation ratio of 4.5 to 1 is the most commonly used in practice.

3.7.3 Proposal for a Fine-cell PP Foaming Strategy

By introducing the melt compounding technique, the highest degree of dispersion of the CBA particles in the PP matrix can be achieved. But, regardless of the achieved degree of CBA particle dispersion, if adequate processing strategies are not implemented during the foaming process, the likelihood of obtaining PP foams with unsatisfactory cell morphologies will be high. Unfavorable outcomes of this type can be avoided by implementing appropriate processing strategies that will suppress the cell coalescence and promote uniform volume expansion.

As already mentioned in Section 3.7.2, the list of controllable parameters during the rotational foam molding cycle is limited only to the temperature, the heating time, the cooling time and the mold rotating speed. The process control in rotational foam molding, among the other, means dealing with both the thermal and the rheological pellet properties simultaneously. This is where the poor thermal conductivity of the pellets comes into play and results in high thermal inertia of the process, which makes it difficult to be controlled efficiently.

Decomposition-free, foamable PP pellets having a CBA particle dispersion achieving an inter-particle CBA distance in the range of 1-50 μm apart throughout the pellet mass are considered suitable for the purpose of producing fine-cell foams by the proposed process.

The sintering of the foamable PP pellets has a significant role in rotational foam molding [76]. Good sintering of the pellets should be induced in order to prevent the air from being entrapped amongst the pellets. Otherwise, the entrapped air bubbles will play a role as cell nuclei in the rotational foam processing. The dominant parameter that determines the sintering behavior of the foamable PP pellets is the viscosity of the basic PP resin. Also, the size of the pellets must be as small as possible to avoid delays in sintering. The sintering temperature of the PP pellets and their temperatures of coalescence are the characteristics of the basic resin; they cannot be controlled otherwise than by using PP resins with different viscosity/melt flow rate.

Using additives for early activation (activators) or late activation (inhibitors) the decomposition onset temperature of the CBA can be controlled in reasonable intervals. In addition, since CBAs are sensitive to the magnitude of the heating rate, by changing the heating rate the CBA activation temperature can be controlled. In fact, by selecting different oven temperatures the rate at which the mold is heated can be changed. Therefore, changing the oven temperature can also control the CBA activation.

In order to suppress cell coalescence, lowering the processing temperature as much as possible should be adopted as an overall processing strategy in rotational foam molding production. If the oven temperature is kept constant, minimizing the processing temperature indicates minimizing the processing time, which is also highly desirable for increasing the productivity of rotational foam molding. The control of the temperature of the melt can be achieved by process interruptions and introducing intermediate cooling-reheating cycles or preheating the pellets and the mold prior to processing. As a result, obtaining a fine-celled and uniform PP foam morphology becomes more attainable.

CHAPTER 4

EXPERIMENTAL VERIFICATION OF THE PROPOSED PROCESS FOR PRODUCING FINE-CELL PP FOAMS IN COMPOUNDING-BASED ROTATIONAL FOAM MOLDING

4.1 Introduction

Standard testing procedures, such as those established by the American Society for Testing Materials (ASTM), are available for determining many properties of plastics. Their importance is extended to the field of selecting materials for a new application, evaluation of the effects of modifying different resins formulations, investigating the effects of actual use on the properties of plastics, etc. However, there are many cases in which standard tests cannot be implemented, such cases are usually related to testing activities concerned with the performance evaluation of novel plastic fabrication processes or the feasibility of processing a particular plastic material in such processes.

The experimental study presented in this chapter includes both standardized and non-standardized testing procedures. It is intended to provide feedback regarding the feasibility of producing fine-cell PP foams by using the compounding-based rotational foam molding process proposed in Chapter 3. Such feedback is also needed for establishing appropriate strategies for process improvements.

4.2 Materials Used in Experimentation

4.2.1 PP Resins

Four PP resins, two branched and two non-branched, were deliberately selected to cover a large viscosity range in order to visualize the differences in their behaviors when being subjected to experimentation related to verifying the proposed process. The PP resins are described by their respective manufacturers as follows: Pro-fax PF633 of Montell Canada (PF633) is a high melt strength (HMS) PP homopolymer resin, Pro-fax SD812 of Montell Canada (SD812) is a HMS PP medium impact copolymer resin for extrusion coating, Microthene MT4390-HU of Network Polymers (MT4390) is a rotomolding-grade PP copolymer resin, while Pro-fax SD242 of Montell Canada (SD242) is a nucleated, high flow, medium impact copolymer resin [77, 39]. Among them, only MT4390 was supplied in a powder form and was therefore used as supplied, while the remaining three were subjected to grinding prior to usage. Table 4.1 presents the typical properties of the PP resins selected to be used in the present study.

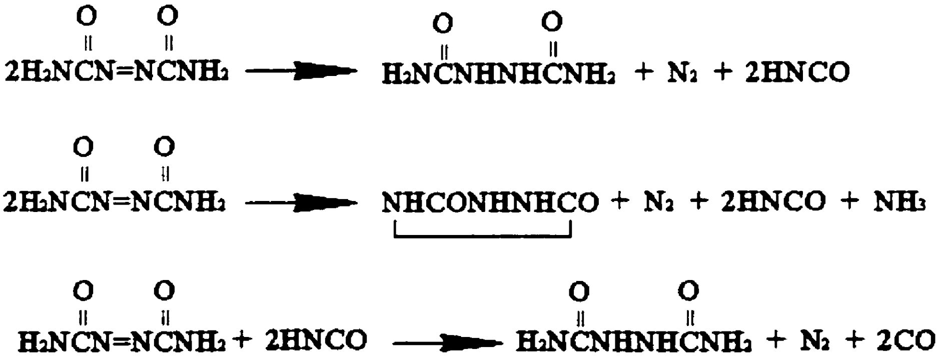
4.2.2 CBA

Based on the previous decision to use an azodicarbonamide CBA for the purpose of this research (see Section 3.4.3), the commercially available azodicarbonamides have been surveyed. During the survey, special attention has been given to issues related to the availability of the CBA candidates in a powder form and in multiple particle sizes, since the success of the intended application of the selected CBA will also depend on these properties. A pulverized CBA would allow a thorough and uniform dispersion of its particles in the polymer matrix during compounding, which is expected to result in a large density of cell-nucleation sites during the subsequent foaming operation, thereby satisfying one of the fundamental conditions for obtaining a fine-celled PP foam. In addition, a CBA available in multiple particle sizes is preferred since this would offer an additional opportunity for controlling the rate of its decomposition by varying the particle size. The relationship between the particle size of the CBA and its decomposition rate follows the principle: the finer the CBA particle size, the faster the decomposition rate [61]. As a consequence, the smaller the particle size, the more effect activators will have on the decomposition rate. Therefore, the largest particle sizes are usually recommended for those processing techniques where minimum CBA decomposition is required, such as the compounding operation pertaining to the proposed process. However, with regards to the proposed foaming operation, CBAs having a smaller particle size will ultimately have a positive effect towards reducing the cell size, improving the cell-density and cell-distribution uniformity of the of foams, because each particle would be a potential nucleation site. Thus, the presented reasons indicate that CBAs with a moderate particle size will be best suited to the present compounding-based rotational foam molding application.

After accomplishing the survey and summarizing the results of the preliminary tested CBAs originating from four different manufacturers, the pool of CBA candidates has been narrowed down to the various azodicarbonamide grades from Uniroyal Chemical, commercially available under the name "Celogen". Among those, Celogen AZ is available in two grades, as a "non-plateout" grade and as a dispersible powder. The latter is defined as "modified azodicarbonamide". It is actually a modification of Celogen AZ by chemical composition, and is therefore also referred to as Flow-treated Celogen AZ. Flow-treated Celogen AZ is available in three particle size grades: Celogen AZ-2990 (2.0 to 2.4 μm), Celogen AZ-3990 (2.4 to 3.0 μm), and Celogen AZ-5100 (4.0 to 5.0 μm) [78]. Of those, Celogen AZ-3990 is highly recommended according to its manufacturer's selection guide for rotational foam molding applications that involve PP resins which yield a fine and uniform cell structure [79].

By referring to the discussion presented in the previous paragraph, it can be concluded that the middle-sized particles of Celogen AZ-3990 would provide optimal CBA decomposition controllability and favorable nucleation behavior for the intended application. Furthermore, Celogen AZ-3990 is described as directly dispersible using most conventional mixing equipment due to the fact of being a free-flowing powder that substantially reduces agglomeration and lumping [78]. Finally, as such, Celogen AZ-3990 is considered to be appropriate for the proposed process and is therefore selected as the CBA to be used in the present experimentation.

Celogen AZ-3990. The operating temperature range of Celogen AZ-3990 is reported to be between 199 and 232 °C [78], which indicates that it is a suitable blowing agent for processing polymers at this temperature interval. Its decomposition temperature range is from 205 to 215 °C, while its gas-yield is around 220 cm^3/g [78]. The decomposition mechanism of Celogen AZ-3990 can be described by the set of chemical equations presented in Equation 4.1.



$$\begin{aligned}
&2H_2N\overset{\overset{O}{\|}}{C}N=N\overset{\overset{O}{\|}}{C}NH_2 \longrightarrow H_2N\overset{\overset{O}{\|}}{C}NHNH\overset{\overset{O}{\|}}{C}NH_2 + N_2 + 2HNCO\\
&2H_2N\overset{\overset{O}{\|}}{C}N=N\overset{\overset{O}{\|}}{C}NH_2 \longrightarrow \underbrace{NHCONHNHCO} + N_2 + 2HNCO + NH_3\\
&H_2N\overset{\overset{O}{\|}}{C}N=N\overset{\overset{O}{\|}}{C}NH_2 + 2HNCO \longrightarrow H_2N\overset{\overset{O}{\|}}{C}NHNH\overset{\overset{O}{\|}}{C}NH_2 + N_2 + 2CO
\end{aligned} \tag{4.1}$$

Table 4.2 presents the most important physical properties of Celogen AZ-3990. The gaseous product released by the decomposition of Celogen AZ-3990 comprise 65% N_2, 24% CO, 5% CO_2 and 5% NH_3, while its solid decomposition products, constituting approximately 68% of its original weight, comprise Urazol, Biurca, Cyamelide and Cyanuric Acid. The manufacturer also claims that Celogen AZ-3990 and its decomposition residue impart no odor to the finished product and that, although it is a fine, yellow powder, it may be used in white or light-colored compounds without objectionable discoloration or staining [78].

Celogen AZ-3990 is not classified as a flammable solid, its storage stability is excellent under normal conditions. Good ventilation of handling and mixing areas is recommended. Inhalation of dust, prolonged skin contact, and ingestion should be avoided [78].

Celogen AZ-3990 may be activated by metal organic salts, bases, and acids reducing its decomposition temperature to as low as 166 °C [78]. Table 4.3 provides the most recommended activators for Celogen AZ-3990 and the magnitude of their respective effects on lowering its decomposition temperature.

4.2.3 Other Additives

CBA Activator. Zinc oxide (ZnO) from Aldrich Chemical Company was the selected activator additive for Celogen AZ-3990 in the present research. The supplied ZnO was in a powder form, with a purity of 99.9% and guaranteed particle size of less than 1 μm, according to the manufacturer's data [80].

Antioxidant. Although the supplied PP resins include unknown amounts of unknown antioxidants that are incorporated during their manufacture, Irganox B215 from Ciba Specialty Chemicals was the selected antioxidant additive to be used in this study for enhancing the stability of the resins at elevated temperatures, if necessary.

4.3 Analytical Instruments

The analytical instruments used in the present experimentation segment include a differential scanning calorimeter (DSC), model TA2910, and a thermogravimetric analyzer (TGA), model TA2050. Both instruments were used for characterization of the PP resins and the CBA by means of thermal analysis testing techniques. Thermal analysis (TA) is a series of techniques that measure changes in the physical or reactive properties of a material as a function of temperature and/or time [81]. It has been widely used for the characterization and investigation of polymers [82].

4.3.1 Differential Scanning Calorimeter

The DSC measures the heat flow into or out of a sample as a function of a desired, user pre-programmed, temperature variation over time and provides a real-time plot of the relationship. The two most commonly used methods in DSC analysis include the power compensation method and the heat flux method [81, 82].

The cell of the TA 2910 DSC instrument used in this study uses the heat flow flux method. The test is conducted on a sample encapsulated in an aluminum pan that is put on a constantan thermoelectric disc together with a reference pan. After the circulation of a preheated purging gas is initiated through the cell to provide a stable environment, both pans are heated. The principle of operation of the DSC is based on the difference between the temperature of the sample pan and that of the reference pan. The instrument software uses this difference (ΔT), and the thermal resistance of the constantan disc (R_D) to calculate and plot the heat flow (dQ/dt) with respect to time or temperature by using the relationship expressed in Equation 4.2 [83].

$$\frac{dQ}{dt}=\frac{\Delta T}{R_D} \tag{4.2}$$

4.3.2 Thermogravimetric Analyzer

The TGA measures the weight change of a sample with relation to the desired, user-preprogrammed, temperature variation over time and provides a real-time plot of the relationship. The principle of operation of the TA2050 instrument used in the present study consists of recording the weight-loss during heating the sample, in presence of a purging gas. The sample is previously loaded onto a platinum sample pan and inserted into the heating chambre pertaining to the instrument. During experimentation, the sample pan is permanently hooked on an accurate balance, thereby providing data to the computer's software regarding the weight variations of the sample over time or temperature. Helium is preferred, but also Nitrogen or Argon, can be injected into the heating chamber to serve as purging gases. Another stream of the gas selected for purging runs through the balance chamber in order to provide stabile thermal conditions, and thereby protect the accuracy of the balance. The temperature of the balance chamber is also maintained by an additional water-cooling system [84].

4.4 Experimental Setup

4.4.1 Experimental Setup for Foamable PP Pellet Production

In order to put to the test the proposed processing strategy for producing foamable PP resins, and assess its applicability in a real-life industrial environment, the experimental setup for this experimentation segment comprises regular-scale industrial equipment rather than lab-scale equipment.

Accordingly, for grinding the three types of PP resins supplied in a pellet form a "Wedco" grinder (Model No. SE-12-SP) was used (see Figure 4.1), while for dry blending the PP resin powders with the additives a "Gunther Papenmaier K.G" high-speed mixer (Type: TGAHK35) was used (see Figure 4.2). The compounding operation of the dry-blended mixture obtained in such a way was carried out by using a "Werner & Pfleiderer" twin-screw intermeshing co-rotating extruder (Type: ZSK-30) presented in Figure 4.3. Figure 4.4 presents the "Automatic Apparate Machinenbau" pelletizer (Type: ASG 100) used for pelletizing the exrudate after it has been cooled in the cooling bath.

4.4.2 Experimental Setup for PP Foam Production

Unlike the experimental setup described in the previous section, the experimental setup related to the production of fine-celled PP foams comprises an uni-axial, lab-scale, rotomolding machine specially designed and built for fundamental rotomolding and rotational foam molding experiments.

In general, there are two principal reasons in favor of using a lab-scale, uni-axial, custom-build, rotomolding machine, instead of a full-scale, bi-axial, industrial rotomolding machine for fundamental rotational foam molding experimentation. First, due to the effect of the bi-axial rotating motion applied to the mold during the foaming cycle, foams produced in bi-axial rotomolding machines are rendered inappropriate for fundamental research applications because their cell morphology can often be misleading and can cause faulty conclusions to be drawn. Second, a full-scale rotomolding machine implies using full-scale molds. As a result, solving problems related to issues of little or no importance for the research work, such as resin consumption, sample storage, and sample handling, would unnecessarily diminish the efficiency of the research work. However, for rotational foam molding experiments, the results of which are intended to be used for fine adjustments of the processing parameters for producing particular products that should comply with pre-defined quality requirements, a full-scale rotomolding machine is indispensable.

In Figure 4.5, a schematic of the uni-axial, lab-scale rotomolding machine used for rotational foam molding experimentation is presented. It consists of a sliding assembly plate, an electrically heated oven, water-cooling installation, and control units for the oven temperature and the mold rotation. The sliding plate carries the uni-axial rotating arm assembly that includes a motor, gearbox, transmission, a hollow shaft, and a removable cylindrical mold. Its serves as a means for inserting the rotating mold into the oven and removing it when necessary. The rotating speed of the arm, which is driven by the motor via the gearbox and the belt-transmission pulleys, can be electronically controlled from 0-30 RPM. The water installation provides the means for mold cooling after completion of the heating cycle. A thermocouple, inserted into the oven, provides data to the oven temperature control unit. The hollow design of the shaft makes possible the insertion of another thermocouple inside the center of the mold in order to measure the in-mold temperature changes during processing. By connecting the thermocouple to a data acquisition device, the temperature changes over time occurring inside the mold can be recorded with a desired sampling frequency, and subsequently plotted.

Figure 4.6 provides a pictorial view of the already described rotational foam molding experimental setup, while Figure 4.7 provides a pictorial view of the cylindrical metal mold, used for rotational foam molding experimentation, in open position. The diameter of the mold is 1.25", while its length is 4.00". Its volume is therefore ~80 cm^3.

4.5 Materials Characterization Experiments

4.5.1 Transition Temperatures of the PP Resins

The knowledge of the transition temperatures of a plastic resin intended for use in a particular plastic fabrication process is crucial for the processor, since it provides the basics for determining the best-suited processing window to the resin properties as well as establishing the most appropriate process control. Polymer transition temperatures include the melting (T_M), the crystallization (T_C) and the glass transition (T_G) temperature. The most commonly used methodology for determining these important material-characterization parameters consists of conducting TA tests on resin specimens.

(T_M). The melting temperature of a polymer sample is determined in a heating DSC experiment. The obtained DSC plot will show a distinct endothermic peak showing the onset of melting and the maximum peak. These two points determine the melting range of the polymer. The area under the melting peak represents the heat required to melt a specific mass of the polymer. [81, 83].

(T_C). The crystallinity of semicrystalline polymers is extremely sensitive to their thermal history, it is therefore common to give the sample a known thermal history before measuring the crystallization behavior. This is accompliched in the DSC by subjecting the sample to a heat-cool-heat experiment. The first heat takes the material above its melting point, and keeps it at that elevated temperature for a certain period to erase any previous thermal history, and then the cooling segment imparts a known thermal history so that different samples can be compared using the second heat results. The sample is then heated again above the melting point and then cooled down again. The obtained DSC plot in such a way will show an distinct exothermic peak showing the onset of crystallization and the peak maximum. A polymer of higher crystallinity produces a smaller crystallization peak in the DSC experiment [81, 83].

(T_G). In a DSC experiment the glass transition temperature is manifested as a subtle change in the heat capacity of the material. It is important to note that, although it is known that traditional TA techniques, such as DSC are often not sensitive enough to detect these subtle, low energy transitions, in the present study, an attempt has been made to measure T_G of PP resins by using a DSC experiment. Since only dynamic mechanical analysis (DMA) is officially recognized as being sensitive enough to accurately measure the glass transition of a semicrystalline polypropylene sample [81], the obtained values for T_G in this study should be considered with caution.

For successfully processing the selected PP resins in the proposed compounding-based rotational foam molding process, the knowledge of the transition temperatures for each PP resin is of multiple importance. In that context, the knowledge of T_M provides the information about the lowest temperature that could be used for reducing the processing temperature during compounding in order to prevent premature CBA decomposition. Also, T_M sets the upper limits related to the allowed processing temperature increases above T_M during the foaming operation that still preserve the viscoelastic properties of the resin, suppress cell coalescence, or prevent thermal degradation. As it will be shown in section 4.6, the value of T_C is important for calculating the appropriate amount of CBA that should be pre-mixed with the resin powders prior to compounding in order to achieve a predetermined VER. The value of T_G is needed to determine how much the PP resins should be cooled prior to grinding.

Figures 4.8 to 4.11 present the resulting DSC spectra from the TA tests conducted in order to determine the transition temperatures of PF633, SD812, MT4390 and SD242, respectively. Table 4.4 provides the results obtained from these DSC experiments in a numerical form.

4.5.2 Decomposition and Activation Behaviors of the CBA

Uniformly and thoroughly dispersed CBA particles throughout the mass of the foamable PP pellets is a crucial prerequisite for obtaining fine-cell PP foams, but preventing the pre-decomposition of the CBA during their compounding is even more important because this is exactly what distinguishes these pellets from those of the unfoamable kind. This is why premature decomposition suppression strategies in compounding-based rotational foam molding are extremely important and deserve special attention.

As it was emphasized in Section 3.4.4, various factors may trigger the premature decomposition of the CBA during extrusion melt compounding of PP. Such factors include the high processing temperature, the effect of the additional heat caused by the shear action of the plasticating screw in the extruder barrel, the long residence time, the presence of CBA activators in the melt, the high heating rates and the self-heating effect of exothermic CBAs. The possible scenarios of decomposition prevention failures in compounding PP with a CBA almost always involve more than one of the decomposition triggering factors. Moreover, these factors are often interrelated, so that preventing successfully the premature CBA decomposition usually requires a strategy that is capable of dealing with multiple triggering factors at the same time. For these cases, knowing the relationship between the triggering factors would be very helpful.

The effects of the processing temperature and the rotating motion of the plasticating screw are unavoidable because these comprise the essence of extrusion. Also, there is not much more left to be done regarding the processing temperature and the rotating motion of the plasticating screw in order to diminish their role as decomposition triggering factors during compounding PP with a CBA, other than the proposed strategy for PP compounding presented in Section 3.4.5. This strategy contains two principal proposals. The first assumes using the PP resin's onset melting temperature as a processing temperature in compounding. The second assumes the existence of an optimum value for screw RPMs that would minimize the generation of additional heat due to friction between the polymer and the barrel, while simultaneously reducing the residence time of the polymer in the barrel as much as possible. But, in order to reduce the residence time of the molten PP containing CBA particles in the extruder barrel, it should be forced to move faster through the extruder. As a result, the molten PP would be exposed to a higher heating rate, which may cause unwanted pre-decomposition of the CBA particles it contains. Therefore, in order to prevent the CBA pre-decomposition, it is necessary to choose the screw RPMs with a great caution.

On the other hand, processing PP foams in rotational foam molding requires the lowest possible processing temperatures in order to suppress cell coalescence. Therefore, adding a CBA activator (ZnO in the present case) during compounding the foamable PP pellets is common practice, since it is the only solution to decrease the processing temperature during PP foaming to the acceptable level. Also, Celogen AZ-3990 is of exothermic nature, it is therefore reasonable to expect that once it reaches its decomposition onset temperature, its decomposition will be unavoidably accompanied with the self-heating effect.

Thus, in summary, the most probable scenario of a decomposition prevention failure during compounding PP can be described with the following sequence of events. If ZnO is added to the melt, the onset decomposition temperature of Celogen AZ-3990 decreases. But, such a decrease of the onset decomposition temperature of Celogen AZ-3990 occurs in the presence of high heating rates, which are caused by fulfilling the requirement of a short residence time. As a consequence, some locally overheated Celogen AZ-3990 particles will most likely start decomposing, thereby triggering a self-heating exothermic chain-reaction, which will ultimately result in unwanted PP foaming.

The above scenario of a failure to produce decomposition-free foamble PP pellets by compounding PP with Celogen AZ-3990 can be avoided only if the decomposition and the activation behaviors of Celogen AZ-3990 are known and predictable. The only way to make them known and predictable is to conduct an experimental study. Since by using a stopwatch and by performing a simple calculation one can easily prove that the magnitude of the heating rate during PP compounding usually reaches 100 °C/min and beyond, it would be desirable to analyze its effects on the decomposition and activation behaviors of Celogen AZ-3990. The best way to simulate such heating rates and acquire reliable information about the decomposition and activation behaviors of Celogen AZ-3990 at high heating rates is to conduct TA experiments on samples of various Celogen AZ-3990/ZnO combinations by using a TGA.

Therefore, samples of pure Celogen AZ-3990 and samples of mixtures between Celogen AZ-3990 and ZnO in five various concentrations, ranging from 0 to 100 phr of ZnO (phr = parts per hundred parts of CBA), were subjected to TGA experiments. In order to simulate the actual heating rates during PP compounding in a most appropriate way, three series of TGA experiments were conducted by using three different heating rates (50, 100, and 150 °C/min) Figures 4.12 to 4.14 present the obtained TGA spectra that represent the effect of ZnO on the onset decomposition temperature of Celogen AZ-3990 for each heating rate, respectively. The experimental results reveal that: (i) by increasing the concentration of ZnO in the sample the onset decomposition temperature of Celogen AZ-3990 decreases, and (ii) the onset decomposition temperature of Celogen AZ-3990 additionally decreases by increasing the heating rate. Table 4.5 provides the results obtained from these TGA experiments in a numerical form.

It is important to note that, in general, the nature of the effect of the heating rate (increasing or decreasing effect) on the onset decomposition temperature of CBAs is governed by the nature of the particular CBA itself. Figure 4.15 illustrates this relationship by using a schematic of a typical CBA decomposition weight-loss TGA plot. Namely, if an exothermic CBA is used, its self-heating effect is opposed to the kinetic effect of the high heating rate. But, because its magnitude is dominant compared to the magnitude of the kinetic effect (at least up to heating rates of 150 °C/min), the resulting effect is in fact manifested by an additional heat generation in the sample, which heat decreases the onset decomposition temperature of the CBA. By contrast, if using an endothermic CBA, its self-cooling effect is in accordance with the kinetic effect of the high heating rate, so that the resulting effect causes cooling of the sample thereby increasing the onset decomposition temperature of the CBA. This analysis indicates that endothermic CBAs could provide a better decomposition control during compounding PP at high heating rates. But, the problem with endothermic CBAs is their intrinsic much lower decomposition temperature and much lower gas generation ability compared to exothermic CBAs, which renders them inapplicable for foaming applications involving PP.

4.6 Foamable PP Pellet Production Experiments

4.6.1 CBA Gas Yield Data Correction

As indicated in Section 3.6.2, by using the derived Equation 3.11, the percentage (by weight) of the selected CBA that should be used to obtain a given VER can be calculated. Equation

3.11 involves the VER, the density of the polymer and the gas yield of the selected CBA. But, the data describing the gas yield of CBAs (φ) provided by the suppliers are referred to room temperature conditions (STP; see Table 4.2), while the decomposition of CBAs and thereby the expansion of polymeric foams occurs at elevated temperatures, that are beyond the polymer melting temperature. As a result, during the cooling cycle of the rotational foam molding process, the decreasing temperature will gradually reduce the maximum possible gas volume. Since the polymer freezing will be initiated at the onset crystallization temperature, and since the polymer will be ultimately frozen at the crystallization peak temperature, the structure of the foam will be fixed at this temperature. This indicates that the occupied gas volume at the crystallization temperature determines the void fraction of the foam [19]. Since the crystallization temperature of polymers occurs at temperatures much higher than the room temperature, the volume of the generated gas by the decomposition of the CBA at this high temperature will be significantly larger than the volume of the same gas at room temperature. Therefore, prior to introducing the gas yield data in Equation 3.11 the data for the gas yield provided by the manufacturer (at room temperature) should be corrected to their corresponding values at crystallization temperature by using the relationship provided in Equation 4.3.

$$\varphi = \varphi_{STP} \times \frac{V_c}{V_{room}} = \varphi_{STP} \times \frac{T_c}{T_{room}} \tag{4.3}$$

where V_{room}, V_C, T_{room} *and* T_C are the gas volume at the room temperature, the gas volume at the crystallization temperature, the absolute room temperature and the absolute crystallization temperature, respectively.

The room temperature is 25 °C, or 298 K. The peak crystallization temperatures of the PP resins participating in the present experimentation ranges from 111.2 °C for MT4390 up to 132.4 °C for SD242 (see Table 4.4). If using the actual T_C pertaining to each PP resin in order to calculate the necessary correction of the gas yield data (φ_{STP}), the obtained amount of CBA that should be added to the PP resins for achieving a required VER would be different for each PP resin. Such a calculation would be accurate, but the obtained foaming results would not be comparable because of the difference in the CBA concentration in the foamable resins. Therefore, to avoid such a possible drawback of the future experimental results and to make them to be comparable between themselves and with the work of other researchers, a common value of 138 °C was adopted as a crystallization temperature to be used in the calculations described above. If using 138 °C as the approximate crystallization temperature of PP resins, the absolute crystallization temperature becomes 411 K. Therefore, for the 80 cm^3 mold that is used for rotational foam molding experiments, by using Equations 4.3 and than Equation 3.11, the necessary amount of CBA for a given VER can be calculated. Since the present experimentation is intended to include 3-fold and 6-fold expansion experiments, the CBA amount needed for 3-fold expansion (VER=3) is 0.73%, while for 6-fold expansion (VER=6) it is 1.83%.

4.6.2 Compounding Foamable PP Compositions

By using the determined amounts of CBA that should be dry-blended with the PP powders prior to compounding from Section 4.6.1 for 3-fold and 6-fold expansion foams, 16 different formulations for foamable PP compositions have been prepared. The formulations included one type of pellets for 6-fold and one type for 3-fold expansion with no activator and two additional types of 6-fold expansion pellets with an activator (ZnO), out of each resin. The latter two types of 6-fold formulations contained ZnO in a concentration of 10 and 50 parts per hundred parts of CBA (phr), respectively. By using these formulations and by following the processing strategies proposed in Sections 3.4.5, 3.6.1 and 3.4.5, as well as by using the experimental setup presented in Section 4.4.1, 16 different foambable PP compositions have been compounded.

All PP resins, except MT4390, were ambient ground by using the industrial grinder (see Figure 4.1) after being frozen at –40 °C. MT4390 was already supplied in a powder form from the supplier. The obtained powders were dry-blended for 60 seconds with the prescribed amounts of Celogen AZ-3990 (with or without ZnO) according to the previously prepared formulations, in 4 kilo batches by using the industrial high-speed mixer (see Figure 4.2). For compounding the dry-blended mixtures, the screws of the industrial intermeshing co-rotating extruder (see Figure 4.3) have been specially rearranged in such a way that the generated shear field is weak and the temperature gradient is minimized. The processing temperature during compounding was kept around 150 °C by setting the controls of the six heaters along the extruder barrel at 150 °C. But, the temperature of the melt measured during compounding and displayed on the extruder's control board was fluctuating in the range of 170-175 °C, due to the additional heat generated by friction and shear. The screws were rotating at 101 RPM. The extrudate was cooled in a cooling bath and then palletized by using the industrial pelletiser (see Figure 4.4). The size of the obtained foamable PP pellets was 16 to 18 pellets per gram. Table 4.6 presents the compounded foamable PP compositions and their formulations.

4.7 Rotational Foam Molding Experiments

By using the experimental setup described in Section 4.4.2 rotational foam molding experiments have been conducted by using the foamable PP compositions the compounding of which has been described in Section 4.6.2.

Figure 4.16 presents the stages of a rotational foam molding experiment. The mold is first charged with the desired PP foaming resin and then mounted on the rotating shaft of the uni-axial lab-scale rotational molding machine. The (4"×1.25") cylindrical mold with a volume of 80cm^3, for 6-fold expansion needs a shot size of 12g, while for 3-fold expansion 24g. The mold is then inserted into the oven, usually preheated at T_{oven} = 300 °C. After the predetermined processing time, the mold is removed from the oven and the mold is cooled with tap water.

By varying the value of a particular process variable of interest, while keeping all the remaining variables participating in the process fixed, the effect of that variable on the process can be accurately identified. Therefore, experimental parametric search over time has been conducted by using the foamable PP compositions available. The parametric search over time is intended to investigate the effect of the processing time while keeping all other processing parameters fixed (e.g., type of foamable PP resin, oven temperature, mold RPMs), and eventually determine the optimal processing time for obtaining the best quality of the foam. Also, the effect of the magnitude of the shot size on PP foaming in rotational foam molding was investigated by a series of experiments using the same foamable PP resin in both 3-fold and 6-fold experiments by using a shot size of 12g and 24g, respectively.

4.8 Experimental Verification Results

The obtained experimental results of the PP foams produced in the proposed compounding-based rotational foam molding process manifested consistently coarse cell sizes (1-3mm) and uneven cell distribution. But, although the quality of the obtained foams is not satisfactory and process improvements are needed, these results have proven the feasibility of the process to produce PP foams. Figures 4.17 to 4.19 present characteristic foaming results obtained by using 6-fold foamable compositions to produce 6-fold expanded foams in a series of parametric search experiments. The obtained foams in all three cases show a lack of ability to completely fill the volume of the mold. Also, these 6-fold expanded foams are characterized with poor cell morphology, coarse cell structure, and uneven cell distribution. A reason for this may be either intensive blowing gas loss or insufficient CBA concentration in the foamable formulation. However, the foams obtained from the PF633-based resin containing 10phr ZnO (see Figure 4.17) although not completely expanded, resulted in smaller cell size and greater cell density and uniformity due to the high viscosity of the basic resin and the presence of ZnO. ZnO, as an Celogen AZ-3990 activator, lowered the onset decomposition temperature of Celogen AZ-3990 contained in the pellets, so that the complete foaming process was shifted at lower temperatures thereby maintaining higher melt strength of the material and suppressing cell coalescence. Figures 4.20 and 4.21 are characteristic examples of 3-fold expansion experiments in which 3-fold and 6-fold foamable resin have been used, respectively. The 3-fold foams obtained by using 3-fold foamable resins manifested poor cell morphology and unsatisfactory volume expansion. Using 6-fold foamable materials in 3-fold expansion experiments improved the volume expansion uniformity. Cell coalescence occurring at the part of the sample closest to the mold, which created an insulation zone to the center of the mold, characterized these experiments.

CHAPTER 5

STRATEGIES FOR IMPROVING THE PROPOSED COMPOUNDING-BASED ROTATIONAL FOAM MOLDING PROCESS FOR PRODUCING FINE-CELL PP FOAMS

5.1 Introduction

Although the proposed compounding-based rotational foam molding process proved to be feasible for producing PP foams in general, it failed to yield PP foams with the targeted fine-cell quality. As a result, a need for proposing and implementing effective processing strategies that can improve the process and thereby remedy the undesirable morphology of the produced PP foams became apparent. In such situations, according to the cyclic algorithm which was adopted from the outset to represent the overall thesis approach (see Figure 1.1), in order to address properly the present problem, it is necessary to first identify the root causes that contributed for obtaining foams with poor cell morphology. It would then become possible to propose remedial solutions, perform the necessary changes, and plan and conduct further experiments in order to verify their relevancy by evaluating the obtained experimental results.

However, in a plastic processing technology that involves many processing steps and processing parameters, such as the proposed compounding-based rotational foam molding process, any wrong processing parameter in any processing step may result in obtaining PP foams with unsatisfactory cellular structures. Also, the intrinsic properties of the PP resins and the additives affect significantly the quality of the foam. Therefore, a useful starting point in the search for understanding the probable causes due to which unacceptable PP foams have been produced, are the processing steps in which some kind of compromised design decision has been deliberately made because of their special role in the process.

5.2 Effect of Compounding

It seems to be useful to begin with hypothesizing that something went wrong in the process of compounding the PP resins. Such a hypothesis would be based on the ground that the processing temperature during compounding was deliberately lower than the peak melting temperature of the PP resins, which does not comply with the principles explained in Section 3.4.4. There are therefore reasons to believe that this may have affected the quality of the compounded pellets.

Sections 3.3.1 and 3.7.3 emphasize the requirements that the compounded foamable PP compositions have to satisfy in order to be considered useful for being processed in rotational foam molding in order to produce fine-cell PP foams. Among those, the decomposition-free status, the thoroughly dispersed and uniformly distributed CBA particles, and the appropriate CBA concentration, are the most preferred attributes that a PP pellet intended for fine-cell foaming should possess.

Although the compounded PP pellets proved their ability to foam and did not show any visible signs of CBA pre-decomposition, there still might be some pre-decomposition on the micro-scale. But, there are reasons to believe that due to the "low" processing temperature during compounding the viscosity of the "molten" polymer was too high. The effect of this, most probably, reduced the degree of the achieved dispersion and uniformity of CBA particles throughout the mass of the compounded PP pellets. The best way to check the present hypothesis and evaluate the quality of the compounded pellets is to analyze the pellet microstructure by using a scanning electron microscope (SEM).

5.2.1 Scanning Electron Microscopy

A scanning electron microscope is a surface analysis tool. It is essentially a method for particle identification, sizing and analysis that offers a significantly higher resolution than optical microscopy, so that smaller particles and the finer details of the particle surface can be observed. It also offers an increased depth of field that gives a better presentation of the topology of the sample and allows for easier particle identification. Scanning electron microscopy is an image formation system that detects the emissions from the upper surface of the sample. The principle of operation of the SEM is based on scanning an electron beam across the sample in the x and y direction. The variation of the detected signal constitutes a contrast that is utilized in the process of image formation. The resulting image reveals the surface of the sample, giving the impression of a three-dimensional view. The high resolution of an electron microscope results from the short wavelength associated with the electron beam. The electrons are produced by thermionic emission, by heating a filament to a sufficiently high temperature to induce some electrons to escape. The instrumental setup of a SEM includes an electron beam source, electron lens system, scanning or deflection coils, detectors, and signal processing and display equipment [85].

5.2.2 SEM Experimental Procedure

Plan. In order to be able to investigate the effect of compounding and properly characterize the compounded foamable PP pellets by using SEM it would be necessary to have a reference against which the microstructure of the pellets can be compared. Therefore, additional pellets consisted solely of pure PP resins have been "re-compounded" from each PP resin participating in the experimentation by using identical processing parameters as for the foamable PP compositions. Table 5.1 presents these "re-compounded" pellets from pure PP resins that will be used for reference purposes during SEM experimentation. Also, pure PP resins, as received from the suppliers, will be used for comparative analysis in order to investigate the effects of compounding on the pure resins.

Analytical Instrumentation. A scanning electronic microscope (SEM), model Hitachi S-520 was used to conduct the SEM experiments.

Sample Preparation. Both fractured and sliced sets of PP pellet samples were prepared by using a standard SEM sample-preparation procedure from each of the four PP resins. In the preparation of the fractured samples liquid nitrogen was used to freeze the samples prior to fracture in order to avoid the effects of the impact during fracture. All samples have been gold-plated before being used on the SEM.

Methodology. The microstructure of compounded 3-fold and 6-fold foamable PP compositions without ZnO will be compared with those of the "re-compounded" pellets from pure PP resins and the "non-compounded" pure PP resins. Selected microstructures will be recorded by using Polaroid imaging.

Expectations. The SEM experiments are primarily intended to characterize the foamable resins compounded by the proposed compounding-based rotational foam molding process. It is supposed to provide relevant data for evaluating the uniformity of the achieved CBA particle dispersion throughout the pellet mass and checking the pellet decomposition-free status. This will also provide a unique opportunity to observe both the effects of the viscosity of the PP resins and the effect of the amount of CBA on the compounding quality of the pellets.

5.2.3 Results and Discussion

Figures 5.1 to 5.4 present a series of SEM micrographs with systematically selected magnification that present the typical microstructures observed for each PP resin, respectively.

Figure 5.1 presents the SEM micrographs of PF633-based compositions. Unlike the micrographs of the pure PF633 resin located in the row marked with (a) in Figure 5.1, those pertaining to the "re-compounded" pure resin located in row (b) in Figure 5.1 possess a characteristic structure that can be described as a kind of closely located "parallel stripes" on all four selected magnification magnitudes. It is believed that these "parallel stripes" have been created by the action of the kneading discs during the compounding in the intermeshing co-rotating twin-screw extruder, at the moments when the material was transferred from the one screw to the other, due to their self-wiping action (see Figure 3.3). PF633 melts in the temperature range between 144.6 and 159.4 °C (see Table 4.4), while the processing temperature during compounding was kept at 150 °C. This indicates that PF633 did not melt completely during compounding, and because of its intrinsic high viscosity (MFR=5.5 dg/min; see Table 4.1) the compounding left visible "parallel stripes" that could be identified after "re-compounding" the pure resin on the fractured pellet samples. This further indicates that the degree of thoroughness and the uniformity of the dispersion of the CBA particles should be also affected by the high viscosity of the resin during the compounding operation.

The micrographs presented in the rows marked with (c) and (d) in Figure 5.1 originate from 3-fold and 6-fold PF633-based compounded pellets with Celogen AZ-3990, respectively. Unlike the 3-fold micrographs located in row (c), the microstructure of the two six-fold micrographs on the left-hand side of row (d) reveal signs of pre-decomposition, while the two on the right-hand side show clearly that the CBA particles distribution is not uniform enough although the average inter-particle distances are in the desired 1-50 μm rage. Therefore, it can be concluded that by increasing the amount of CBA from 0.73% to 1.86% Celogen AZ-3990, in the PF633-based foamable mixture, while keeping all other parameters unchanged, it becomes prone to pre-decomposition. This observation regarding the effect of the amount of CBA on the pre-decomposition during compounding is very important because it indicates that the preparation of compositions designated for higher VER may be followed by severe decomposition during compounding.

Figure 5.2 presents the SEM micrographs of SD812-based compositions. In this case, the similarities between the micrographs of the pure SD812 resin located in row (a) in Figure 5.2, and the micrographs illustrating the microstructure of the "re-compounded" pure resin located in row (b) in Figure 5.2 are much grater. Although the micrographs in row (b) are also characterized with "parallel stripes", they are much less distinguished than in the case of PF633. This can be explained by the significantly lower viscosity of SD812 (MFR=16 dg/min) although it melts in a higher temperature range than PF633 which is between 141.3 and 163.8 °C. The micrographs of SD812-based "re-compounded" pellets showed local signs of porosity. In order to present this dual microstructure of SD812 the micrographs in row (b) are branched. Since it is known that CBA residue in the extruder is not the cause for this kind of microstructure, it is believed that it can be caused by impurities in the resin or by local overheating that is manifested with creating bubbles.

Unlike PF633-based compounds containing CBA, the SD812-based 3-fold and 6-fold expansion compounds did not show signs of pre-decomposition.

Figure 5.3 presents the SEM micrographs of MT4390-based compositions. The effect of low temperature compounding can be clearly observed in the micrographs in row (a), while no signs of premature decomposition have been observed in the micrographs pertaining to 3-fold and 6-fold compositions with Celogen AZ-3990. MT4390 melts in the temperature range between 152.40 and 160.64 °C. Being compounded at 150 °C, this is the only resin among the four selected that was compounded by using a temperature that was even lower than its onset melting temperature. It is believed that this is the reason why the "parallel stripes" are so emphasized in the microstructure of the "re-compounded" resin, although its viscosity (MFR = 20 dg/min) is higher than that of SD812.

Figure 5.4 presents the SEM micrographs of SD242-based compositions. SD242 is the lowest viscosity resin (MFR=35) and it melts in the temperature range between 149.16 and 164.48 °C. The micrographs of SD242-based compositions revealed no significant signs of the low temperature compounding effect and no signs of pre decomposition.

Figure 5.5 presents isolated particles of Celogen AZ-3990 in each PP resin composition. It indicates that agglomeration and clustering of CBA particles is not present in the observed samples. This confirms the suitability of Celogen AZ-3990 in terms of particle size and dispersability (see Section 4.2.2)

Concluding Remarks. The micrographs of the PP compositions revealed that the processing temperature of 150 °C has a decreasing effect on the degree of CBA particle dispersion into the polymer matrix. The higher the viscosity of the PP resin the stronger the effect and the higher the melt temperature range of the PP resin the stronger the effect. Except in 6-fold PF633 composition with Celogen AZ-3990, no other composition manifested signs of CBA pre-decomposition during compounding. No agglomeration and clustering of CBA particles was observed. Therefore, the compounding operation, and thereby the entire pellet production stage pertaining to the proposed compounding-based rotational foam molding process, cannot be considered as being the principal reason for the poor cell morphology of the obtained PP foams, at least for the time being. Since the only possibility to successfully compound PP resins with Celogen AZ-3990 is by using a "low" processing temperature of 150 °C, no strategies for process improvement can be proposed based on the SEM experimental results.

5.3 Effect of the PP Resin Viscosity

As indicated in Section 5.2.3, the compounded foamable PP compositions that were evaluated by the results obtained from the SEM experiments contained some deficiencies but were generally classified as satisfactory. Therefore, the search for the causes of the poor cell morphology of the produced PP foams proceeded with analyzing the foam production stage, i.e., the rotational foam molding process by which the unsatisfactory foams have been produced. First of all, a thorough analysis of the existing foaming experimental results that were obtained during the initial experimental parametric search over time was conducted.

Although the quality of the obtained PP foams was unacceptable, these were obtained while conducting experiments by a series of process interruptions (cutting the processing time in the heating cycle) in predetermined time intervals in order to check the quality of the obtained PP foams with reference to the elapsed processing time. As such, especially interesting were the observed structures of the experimental results obtained by interruptions in the early stage of the process. These experimental results received special attention because they were considered as containing a significant amount of information that could be useful for understanding what is really happening inside the mold during the thermal cycle in rotational foam molding.

A further analysis of the existing experimental results indicated a significant difference in the foaming process between the PP pellets originating from low-viscosity/high MFR PP resins and the ones originating from high-viscosity/low MFR PP resins. By analyzing the experimental samples of foams obtained by deliberately interrupting the foaming process in the early stage, additional information about the differences in the sintering stages occurring in 3-fold and 6-fold PP foams produced in rotational foam molding have been acquired. It is important to note that the difference between 6-fold and 3-fold experiments is not only in the "expansion quality" (different CBA percentage), but also in the quantity (the mold is charged with double amount of pellets for obtaining 3-fold expansion) of the foamable pellets used. Here, especially useful proved to be the experimental results from the investigation of the effect of the amount of pellets charged into the mold by using 6-fold pellets for conducting 3-fold experiments, because the effect of the amount of CBA on the results was eliminated. The experimental results obtained from the pellets originating from the highest (PF633) and the lowest (SD242) viscosity PP resins regarding 3-fold and 6-fold expansion are discussed in detail in the sections that follow.

5.3.1 Effect of High-viscosity Foamable PP Pellets

The existing experimental results revealed that the foaming process of high viscosity PP foamble resins is governed by sintering. Because of the high viscosity of the basic carrier PP resin, the sintering of the pellets is slow. Consequently, both 6-fold and 3-fold rotational foam molding experiments conducted by using pre-compounded foamable compositions originating from high-viscosity PP resins indicate that the decomposition of the CBA takes place prior to the initiation of pellet sintering, which is undesirable. This order of thermal events in rotational foam molding is undesirable because when early decomposition of CBA particles in the pellets occur, a portion of the generated gas tends to escape out of the pellets while the pellets are expanding. As a consequence, the resulting decreased amount of available blowing gas for the foaming process deteriorates the final foam morphology. In addition, since the temperature of the internal mold surface is the highest, the PP pellets that are in contact with the mold are prone to early decompose their content of CBA. This is why the early decomposition is first observed among the first-row pellets, closest to the mold at the early stage of the process.

In 3-fold experiments the first-row pellets start to decompose first rather than sinter. Moreover, the experimental results indicated that the first-row pellets were not sintered even during decomposition. Here, it is important to note that, unlike the 6-fold expansion where the mold is initially poorly filled with loose pellets, for 3-fold expansion the mold is almost completely filled with loose pellets. Therefore, there are reasons to believe that during the decomposition of the CBA, they are pushed among each other because of the foaming. As a consequence, since the pellets in the first row are already soft enough, they sinter by the pushing force. The pellets in the upper rows would not sinter because they are not soft yet (although the same force pushes each of them). As the processing time increases, a foam layer is formed closer to the mold's internal surface on top of which non-sintered pellets are located. Although the foam quality is unsatisfactory, compared to 6-fold experiments, 3-fold experiments provided relatively better foam structures at optimal processing times. The described sintering stages for the 3-fold experiments are modeled in Figure 5.6, while the actual changes in the morphologies of the obtained foams are presented in Figure 5.7.

In 6-fold experiments, for identical process interruption intervals, because of the smaller amount of pellets in the mold, the early decomposition of the first-row pellets is more intensive as a result of which the amount of produced foam is greater. Unlike the 3-fold expansion experiments, the compounded pellets did not sinter well when the temperature was increased. In the case of 6-fold expansion, much less amount of pellets is charged into the mold, and consequently, the pellet to pellet contact becomes poorer. It is also believed that the higher heating rate the 6-fold expansion pellets experience in the mold due to the lower thermal inertia, i.e. a smaller amount of plastic materials causes the earlier decomposition of the CBA. Since the sintering of pellets is not as good as the three-fold expansion and the decomposition of CBA is triggered earlier, the pellets fail to form a continuous phase with isolated CBA particles. The described sintering stages for the 6-fold experiments are modeled in Figure 5.8, while the actual changes in the morphologies of the obtained foams are presented in Figure 5.9.

5.3.2 Effect of Low-viscosity Foamable PP Pellets

The rotational foam molding experimental results pertaining to the low viscosity PP pellets indicated that good sintering occurred prior to the decomposition of the CBA, which is desirable. But severe cell coalescence at long processing times was observed and it was therefore concluded that the foaming process of low viscosity PP pellets is governed by cell coalescence.

As it was discussed in Section 2.5.2, cell coalescence takes place when the melt inside the mold is heated beyond the temperature of coalescence. $T_{coalescence}$ is a property originating from the type of PP resin used for pellet compounding and cannot be directly controlled. Consequently, lowering the temperature of the melt should be the strategy of choice to suppress cell coalescence for a given PP resin. Since the sintering to decomposition timing for low viscosity PP pellets was proven to be correct it shouldn't change. But, for lowering the temperature of the melt in order to suppress cell coalescence, without disturbing the already good sintering to decomposition timing, temperature-time profiles would be needed.

5.3.3 Common Effects of High- and Low-viscosity Foamable PP Pellets

It is important to note that in both high and low viscosity PP resins foaming experimental results it was observed that the pellets were deformed like flakes and the flake-shaped pellets were oriented to the radial direction (see Figure 5.9). In the case of 3-fold experiments, the flaking of the pellets occurred at longer processing times due to the doubled shot size in 3-fold experiments in comparison with 6-fold experiments, which results in a higher thermal inertia. Therefore, the pellets in 3-fold expansion experiments were heated later. The flaking of the PP pellets is undesirable because it makes difficult the sintering to occur prior to the decomposition of the CBA and is thereby a reason for excessive blowing gas loss that results in poor morphologies of the PP foams. According to the previous experience acquired from the research work with rotationally foam molding PE-based foamable resins, their foaming did not manifest such flaking phenomena of the pellets. It would be therefore necessary to conduct experiments with "re-compounded" pellets of pure PP resins to find out if this flaking phenomena is an intrinsic characteristic of the PP resin or it is affected by the presence of Celogen AZ-3990.

5.4 Experimental

5.4.1 Experimental Investigation of the PP Pellet Flaking Phenomena

By using the experimental setup described in Section 4.4.2, and by using the sequence of experimental steps described in Section 4.7, rotational foam molding experiments have been conducted by using the "re-compounded" PP pellets the compounding of which has been described in Section 5.2.2 (see Table 5.1). The experiments were conducted by interrupting the process at each minute in the interval of 10 to 22 min processing time. The experimental results were absolutely consistent, i.e. in all cases (low-viscosity, high-viscosity, 3-fold and 6-fold) the PP pellet flaking was taking place.

Multiple hypotheses have been made regarding the possible causes for the PP pellet flaking in rotational molding. The major dilemma was between two of them. The first hypothesis was based on the possible influence of the rotation of the mold during rotational foam molding (e.g. gravity or centrifugal force). The second was based on the theory that as a consequence of the compounding, the polymer chains become oriented in the direction of the extrusion and the subsequent further stretching of the extrudate string while it passes through the cooling bath prior to pelletization. As a result of this chain orientation and the deformation memory of the material, while being exposed to a temperature gradient the pellets tend to shrink in the longitudinal axis in order to stretch in a direction perpendicular to the axis, thereby transforming their shape into a flake-like form.

In order to prove or rejected either of the hypotheses, experiments were conducted by heating the "re-compounded" pure PP resin pellets on a non-rotating flat surface. The obtained results of these experiments were again absolutely consistent, i.e., the pellets originating from each of the four participating PP resins were flake again. This result was convincing enough to reject the first hypothesis. Although, it did not prove the second hypothesis there are reasons to believe that it is correct.

Conclusive Remark. Since there was not any CBA in the PP pellets, it was therefore concluded that this pellet-flaking phenomenon is an intrinsic characteristic of the PP resins. Moreover, it was experimentally proved that PP pellet flaking is not dependent to whether the pellets are rotated or not, but it is simply manifested when exposing PP pellets at elevated temperatures. At approximately the same time, it appeared that a feasible improvement strategy would be to reduce the PP pellet size, since it would dramatically reduce the negative effect of the PP pellet flaking on the fomaing results. Therefore, by using all 16 formulations presented in Table 4.6, a new series of 16 different foamable PP compositions with decreased pellet size have been compounded. The average pellet size of the new compositions was between 31-33 pellets per gram, which is almost half of the previous PP pellet size. Table 5.2 presents these compositions.

5.4.2 Temperature Profiles

By using the foamable PP compositions with a reduced pellet size, and by using the thermocouple inserted in the center of the mold via the hollow shaft, time-temperature profiles were recorded for various foamable PP compositions. The temperature was measured at the center of the mold while processing the materials at T_{oven} = 300 °C, and it was recorded by using a special acquisition device for temperature data. The duration of the rotational foam molding heating cycle for the temperature profile data acquisition experiments was 30 min, while the mold cooling cycle was 10 min long. Since the selected sampling interval was only 0.5 seconds long, the obtained temperature profiles with respect to the elapsed processing time possess a high level of accuracy. Figures 5.10 to 5.13 illustrate the effect of the foamable PP formulation, i.e. the presence of ZnO and the desired VER (defined by the amount of Celogen AZ-3990 and the shot size) on the temperature profile in rotational foam molding, for each basic PP resin carrier, respectively. Similarly, Figures 5.14 to 5.17 illustrate the effect of the material viscosity on the temperature profiles during rotational foam molding.

The critical heating rate in rotational foam molding, is the heating rate at the internal mold surface, since it is in an intimate contact with the first-row pellets. If it is too high, it can cause premature decomposition of the CBA in respect to pellet sintering, which was observed in the foaming experimental results with high-viscosity compositions. By using the temperature profiles, it become possible to determine the heating rate inside the mold during the rotational molding experiments for each foamable PP composition, which was previously unknown. This is a sufficiently good input information in order to estimate the temperature at the mold internal surface, since its direct measurement in a continuous manner is not possible with the present experimental setup.

By carefully analyzing the time-temperature profiles, heating rates in the range of 15 to 30 °C/min have been associated with the rotational foam molding process at $T_{oven} = 300$ °C. The greatest heating rates occur during the CBA decomposition. The sudden temperature peaks, shown on the temperature profiles, represent these heating rates. These peaks are caused by the self-heating effect of the Celogen AZ-3990 during decomposition due to its exothermic nature. Another benefit of the temperature-profiles is the possibility to acquire information of the approximate time and temperature of Celogen AZ-3990 decomposition during the rotational foam molding process by analyzing the location of the temperature peaks on the plots.

For successful cell coalescence suppression in low-viscosity foamable compositions it is important to reduce the temperature of the melt while keeping the proper sequence of events (sintering prior to CBA decomposition) inside the mold unchanged. Therefore, both sintering and decomposition should be provoked to happen earlier - at lower temperatures of the melt. Since direct control of the sintering temperature of the PP pellets is impossible, increasing the content of CBA activator in the PP pellets to lower decomposition temperatures proved to be a feasible direction towards solving the cell coalescence problem and improving the cell structure of foams produced from low-viscosity resins. In Section 4.3.2, it was shown that the onset decomposition temperature of the CBA decreases with the increase of activator concentration at higher heating rates. Therefore, in order to be able to control the temperature of the melt, accurate data for the decomposition onset temperatures for the first-row pellets with various activator concentrations are needed. The temperature profiles can be a very useful tool in accomplishing this objective. Also, reducing the oven temperature in order to reduce the temperature gradient in the melt and thereby avoid unnecessary overheating of the melt near the wall seems to be useful. This is so because cell coalescence can be locally severe (near the mold wall), while the temperature of the rest of melt volume is significantly lower than $T_{coalescence}$.

5.5 Proposal for Process Modification #1

As a result of the findings presented in the previous sections, a feasible concept for a process modification proposal became available. It will be thoroughly described in the sections that follow.

5.5.1 Temperature Constraints in Fine-cell PP Foaming

Ideally, the properties of the foamable PP pellets should be designed in such a way to adequately correspond to the temperature changes during the rotational foam molding cycle. On the other hand, the process control mechanism should be capable of keeping the process parameters within the boundaries of the processing window determined by the respective temperature constraints, thereby maintaining a proper order of the sequence of thermal events inside the mold. The analysis of the previous experimental results and the conducted experiments related to the pellet flaking phenomenon and the temperature profiles clarified significantly the nature of the events occurring inside the mold during the rotational foam molding cycle. Therefore, before proposing a strategy for improving the process, it would be useful to analyze the temperature constraints that it is governed by.

In any plastic processing operation, the thermal degradation temperature of the resin is the upper heat-history limit that the resin is allowed to sustain in the course of processing. Accordingly, the processing temperature during rotational foam molding should not exceed the temperature of the PP resin's thermal degradation in any given time and in any given location throughout the mass of the foamed article. Since in rotational foam molding, the highest temperature the polymer is exposed to is the one occurring at the interface of the internal mold surface and the resin, the temperature at this location is critical with regards to polymer thermal degradation. Therefore, the time-temperature relationship must be properly balanced so that the foamed article can be obtained without resin degradation [75]. Also, a non-adequate temperature range, over which the CBA decomposes, is often the reason for reaching the thermal degradation temperature during processing resins in rotational foam molding. This is the case when the decomposition temperature range of the CBA is much higher than the processing temperature of the polymer (see Section 3.4.3). As a consequence, either the CBA will not fully decompose during processing, or the polymer temperature will have to be increased to a point where the polymer may degrade or its viscosity may become too low to allow stable bubble formation [7]. Since this general overall plastic processing temperature constraint applies to the rotational foam molding process as well, it can be expressed by the relationship presented in Equation 5.1.

$$T_{\text{processing (foaming)}} < T_{\text{thermal degradation}} \qquad (5.1)$$

On the other hand, in general, if the CBA decomposes at a temperature substantially below the melting or softening temperature of the plastic, the generated gas will be lost [7]. Accordingly, in the proposed process, if the CBA decomposition takes place earlier than the sintering of the pellets, most of the released gases will be lost through the mold vents and a very poor foam structure will be obtained.

In conventional rotomolding, sintering is commonly defined as the formation of a homogeneous melt from the coalescence of powder particles under the action of the surface tension [76]. By analogy, sintering in the proposed compounding-based rotational foam molding process can be defined as the formation of a homogenous melt from the coalescence of the pellets. The time required for the completion of pellet coalescence controls a major part of the heating time in the molding cycle.

Since the proposed process is intended for producing fine-celled PP foams, any excessive loss of the blowing gas can result in obtaining unsatisfactory cellular structures. Therefore, the pellets have to sinter before the CBA starts to decompose, and thereby prevent the unwanted gas loss. Thus, timely sintering of the foamable PP pellets is fundamental for obtaining fine-celled PP foams in compounding-based rotational foam molding.

The above reasoning clearly indicates that to ensure proper sintering timing, the CBA must have a higher onset temperature of decomposition than the sintering temperature of the pellets. Thus, the relationship between the pellet sintering temperature and the CBA decomposition temperature, presented in Equation 5.2, is a fine-cell foam processing constraint. However, the relationship presented in Equation 5.2 can be considered as a fine-cell foam CBA selection constraint.

$$T_{\text{sintering}} < T_{\text{CBA decomposition}} \tag{5.2}$$

Ideally, the CBA should start releasing gases immediately after the completion of pellet sintering. Otherwise, i.e., if the initiation of the CBA decomposition in relation to sintering is delayed, the temperature of the polymer will rise unnecessary which will decrease its viscosity, decreasing thereby its melt strength, which is not favorable for the foaming process.

To ensure the proper order of these thermal events, the CBA decomposition has to be triggered by a greater temperature than the temperature needed for completing the pellet sintering. This makes obvious the need for the processing temperature to be also greater than the decomposition temperature of the CBA. Such a relationship between the temperature of CBA decomposition and the processing temperature in rotational foam molding is, in fact, an additional fine-cell foam processing constraint. It is presented in Equation 5.3.

$$T_{\text{CBA decomposition}} < T_{\text{processing (foaming)}} \tag{5.3}$$

On the other hand, in processing fine-cell PP foams, there is also an upper temperature limit (lower than the polymer thermal degradation temperature) that determines how high the processing temperature in rotational foam molding of PP can be elevated without deteriorating the final quality of the foamed structure. The temperature of cell coalescence governs this limit. Since the low melt strength is a common characteristic applicable to PP resins, the cell structure of PP foams can be easily degraded by cell coalescence. Cell coalescence is causing formation of big bubbles and therefore is not desired in foaming (see Section 2.5.2). It is therefore strongly required the processing temperature to be kept below the temperature of coalescence at any given time. This is the reason why the prevention of cell coalescence is an extremely important issue in PP foam processing. Accordingly, the relationship between the temperature of coalescence and the processing temperature, expressed in Equation 5.4, presents another foam processing constraint.

$$T_{\text{processing (foaming)}} < T_{\text{coalescence}} \tag{5.4}$$

Equation 5.5 summarizes the relationships between all the temperature constraints in rotational foam molding discussed before, and clearly sets the boundaries in which the processing temperature should be kept by an adequate process control in order to fulfil the basic requirements for fine-cell PP foam production in rotational foam molding.

$$T_{\text{sintering}} < T_{\text{CBA decomposition}} < T_{\text{processing (foaming)}} < T_{\text{coalescence}} < T_{\text{thermal degradation}} \qquad (5.5)$$

5.5.2 Desired Sequence of Processing Steps for Fine-cell PP Foaming

As a way of achieving a fine-cell foam structure by using PP pre-compounded pellets in rotational foam molding, a special sequence of processing steps should be maintained. The ideal case, e.g., the most preferred sequence of foam processing steps is illustrated in Figure 3.6 (see also Figure 5.18).

Step #1: Mold charging. At cycle time t_0=0, a measured amount of decomposition-free pre-compounded foamable PP pellets, which include uniformly distributed CBA particles, should be charged into the mold. The mold is then closed, rotated, and heated in the oven.

Step #2: Polymer Sintering. At cycle time t_1 ($t_1 > t_0$) because of the temperature gradient, the pellets should gradually begin to sinter. If sintering was good, a continuous polymer matrix should be formed as the final sintering stage of the polymer, at cycle time t_2 ($t_2 > t_1$), shortly prior to the commencement of the decomposition of the CBA.

Step #3: CBA Decomposition. At cycle time t_3 ($t_3 > t_2$), the temperature of the melt is further increased and reaches the decomposition temperature of the CBA. This is the moment when the CBA particles dispersed in the molten polymer matrix should start to decompose and generate gases.

Step #4: Polymer Foaming. *Cell Nucleation.* Simultaneously with the decomposition of the CBA particles, at cycle time t_3, as a consequence of the generated gases in the vicinity of the CBA particles, bubbles begin to appear. This is how cell nucleation sites are created. The distribution of the cell nucleation sites follows the distribution pattern of the CBA particles. This fact shows once again that good dispersion of CBA is crucial for fine-cell foaming.

Cell Growth. At cycle time t_4 ($t_4 > t_3$), once the cell nucleation has started, cells continue to grow until the CBA gas-generation ability is exhausted. Lowering the processing temperature at this stage of the process is a common strategy to preserve and maintain higher melt strength of the foaming PP resins, and thereby suppress cell coalescence.

Step #5: Polymer Solidifying. The cooling cycle begins immediately after the heating cycle is completed. Because of the cooling action, the polymer freezes. The actual moment of freezing is always delayed for a certain period of time relative to the moment when the cooling is applied. This tardiness has been attributed to the delayed nature of thermal conductivity of the polymer.

Step #6: Molded Article Release. The mold is opened and the part is removed.

5.5.3 Process Modification #1

The process diagram presented in Figure 5.19 illustrates the proposed process modification for improving the compounding-based rotational foam molding process for producing fine-cell PP foams that was presented in Chapter 3. It basically concerns the foam production stage by introducing new processing steps under the condition of reducing the pellet size (31-33 pellets per gram) in the pellet production stage. It is based on the temperature constraints for fine-cell PP foaming presented in Section 5.5.1. The success of the modified process will depend on how well the implemented process control during rotational foam molding is capable to approximate the processing steps presented in Section 5.5.2.

5.5.4 Experimental Verification of Process Modification #1

A typical illustration of the development of the PP foam over time in rotational foam molding, obtained from the experimental parametric search by using the modified process for one foamable PP composition, is presented in Figures 5.20-5.22. Numerous series of experiments of this kind have been performed on the foamable PP resins presented in Table 5.2 by following the process diagram presented in Figure 5.19 and the temperature profiles presented in Section 5.4.2 as well as the experimental procedure presented in Section 4.7. As a result of this extensive experimentation, significant improvement of the cell morphology has been achieved. The overall best results are presented in Figure 5.23. Thereby, the modification has been experimentaly proved to be valid.

The experimental results revealed a significant advantage in achieving the desired cell size and expansion uniformity in foams obtained by processing the highest-viscosity foamable PP composition, based on PF633 (MFR = 5.5 dg/min) without the presence of ZnO when using 6-fold resins for 3-fold expansion (see Figure 5.23 for P113P). This is explained by the higher melt strength of PF633 and by the fact that when high-viscosity resins are used the foaming process is dominated by sintering, which indicates that the presence of ZnO would only induce the already early decomposition of Celogen AZ-3990 to take place even earlier. It is also important to note that by using a 6-fold resin for 3-fold expansion the amount of CBA is more than double (1.83% relative to 0.73%). This indicates that the theoretically calculated amount of CBA for 3-fold expansion is low due to the unaccounted loss of blowing gas through the mold's vent during processing. However, the results obtained by the similar foamable PP resin containing 10phr ZnO are satisfactory as well, due to the low concentration of ZnO that cannot influence dramatically the onset decomposition temperature of Celogen AZ-3990.

5.6 Process Modification #2

As a logical consequence of the significant improvement of the foams produced in the modified compounding-based rotational foam molding process by using foamable PP compositions with a reduced pellet size, came the proposal for regrinding the foamable PP pellets prior to charging the mold. The process diagram presented in Figure 5.24 illustrates this modification of the process.

The foaming mechanism of reground foamable resins in comparison to the same resins in pellet form has been investigated by using a see-through mold and by reviewing the videotaped process. The pictorial view of the experimental equipment with the see-through mold is presented in Figure 5.25. The flaking phenomena almost disappeared when using reground foamable resins. This indicated that further improvements of the cell morphology can be achieved. Therefore, a limited experimental parametric search (by using only P113P) was performed. The improved cell morphologies obtained from the experiments using reground foamable P113P are presented in Figure 5.26.

It is important to note that this modification of the compounding-based rotational molding process is with limited applicability because it is valid only for producing skinless foams. If foam with a distinct skin is needed, the foamable resin must be introduced in the mold in a pellet form.

CHAPTER 6

CONCLUDING REMARKS AND FUTURE WORK

6.1 Concluding Remarks

Since to date compounding based rotational foam molding production of PP articles has not been reported, the research presented in this thesis paves the way towards developing a new technology for rotational foam molding of PP. The presented process is also significant because it proves that acceptable PP foams can be produced without cross-linking. Another advantage of the process is the fact that, except the rotational foam molding trials, all experimentation has been conducted by using industrial full-scale equipment. This indicates that for industrial implementation of the process a minor modification of the rotational foam molding processing parameters would be necessary.

The main benefit of the melt compounding approach is the thorough and uniform dispersion of the CBA into the PP matrix, which cannot be achieved by using the dry-blending technique. Another benefit is the reduced sensitivity on powder quality inconsistencies. Since the pre-mixed blend is being remelted, remixed and reshaped into pellets during compounding, the negative effects that might have been caused by the inconsistencies in powder quality in terms of particle size and shape are being removed.

The properties of the pre-compounded pellets are constrained by the required ability to foam while being heated and to expand to a predetermined volume by forming a uniform fine-cell PP cellular structure while foaming. Therefore, the ideal pellet should be appropriately sized and should contain a sufficient amount of inactivated CBA particles commensurate with the required VER, which is thoroughly and uniformly dispersed among the other additives, if any, throughout the polymer matrix at inter-particle distances of less than 50 micrometers.

The foaming process of high-viscosity foamable PP pellets is governed by sintering. Prior to modifying the initially proposed process, it was characterized by the early decomposition of the CBA, the late sintering of the PP pellets and the big-celled foam finally obtained.

In contrast, the foaming process of lower viscosity PP pellets is governed by cell coalescence. Prior to modifying the initially proposed process, good sintering, that occurred prior to the decomposition of the CBA and severe cell coalescence at long processing times were observed from the experimental results obtained using low-viscosity PP pellets.

It has been shown in this thesis that the sintering timing in rotational foam molding of compounded foamable PP pellets directly depends on the viscosity of the basic PP resin, the size of the pellets, the VER, and the shot size.

If the foam structure is governed by sintering, the approach for obtaining the proper sintering sequence and thereby improving the foam structures in rotational foam molding of pre-compounded PP pellets include reducing the viscosity of the PP resins used, reducing the pellet size, decreasing (or eliminating) the activator amount and lowering the heating rate.

By contrast, if the foam structure is governed by cell coalescence, another approach is needed. It would be necessary then to introduce an activator, or increase its amount if already introduced, during pellet compounding in order to decrease $T_{processing}$, and thereby prevent cell coalescence. But, CBA pre-decomposition problems can be encountered during compounding such formulations if more than 50phr ZnO is used.

The first-proposed process modification, which implementation improved significantly the process and the cell morphology of the produced PP foams, was based on the above conclusions, while the second-proposed process modification was derived from it. It also improved the results, but has a limited industrial application.

6.2 Future Work

6.2.1 Alternative High-viscosity PP Resins

Since the viscosity of the resin is an advantage in PP foaming, it would be desirable to experiment with other PP resins having a higher viscosity than PF633 although sintering problems would be possible.

6.2.2 Temperature Map

Based on careful analysis of the obtained rotational foam molding experimental results and the respective time-temperature profiles, a temperature map describing the sintering to decomposition timing for a wide range of resin viscosity should be constructed. It should be expected that such a temperature map would confirm the hypothesis that using amounts of more than 10 phr of activator amount for any PP resin viscosity will not be desirable because of provoking a too early CBA decomposition in both PP compounding and PP foaming.

6.2.3 Appropriate CBA Amount

In compounding-based rotational foam molding, the gas yield of the CBA, its concentration in the pellets and the shot size determine the attainable VER. As mentioned earlier, the rotational foam molding is a low-pressure (atmospheric) process, therefore a portion of the generated gases during the decomposition of the CBA will be inevitably lost through the mold vents. Consequently, to satisfy a given volume expansion ratio and achieve foam-filling of the entire free volume of the mold, the amount of CBA introduced into the polymer should be greater than the theoretically needed in order to be able to compensate for the gas losses that will occur during foaming.

Describing the relationship between the various levels of CBA concentration in the pellets and the practically achieved volume expansion ratio is not a trivial task. In order to be able to predict by how much the theoretically needed concentration of CBA in the pellets should be increased to account for the gas losses and achieve a predetermined VER an experimental approach would be needed.

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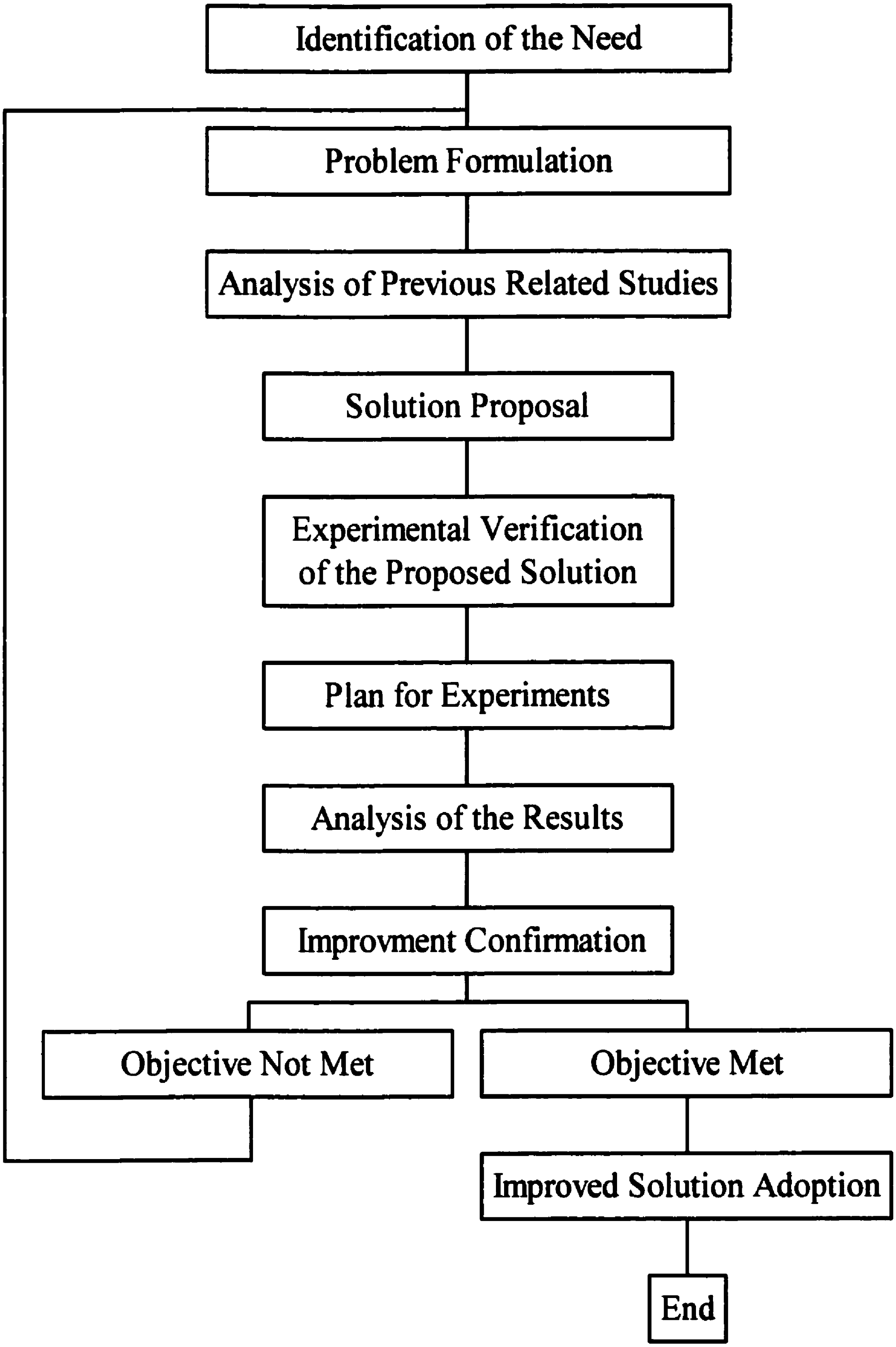
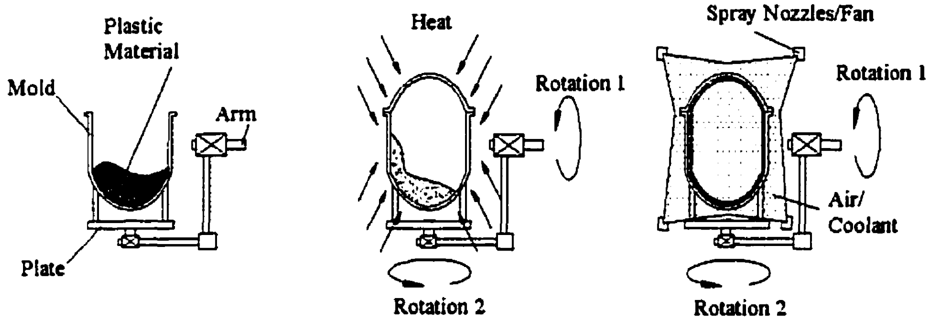


Figure 1.1: Thesis Approach Algorithm



(a) Mold Charging (t_1 = Cycle Start)

(b) Mold Rotation and Heating ($t_2 > t_1$)

(c) Mold Rotation and Cooling ($t_3 > t_2$)

(d) Molded Article Removal (t_4 = Cycle End)

Figure 2.1: Conventional Rotomolding Process Principle of Operation

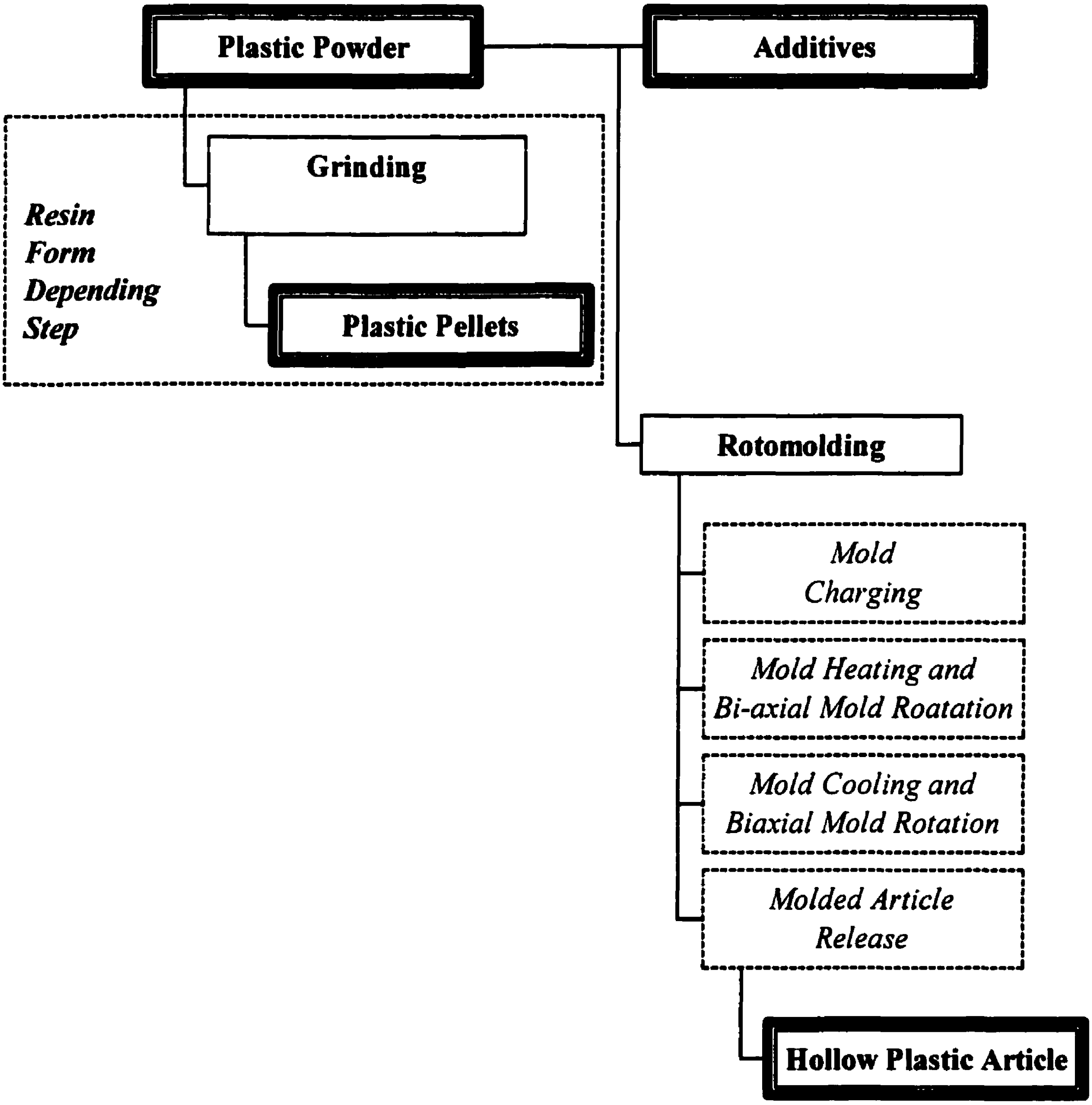


Figure 2.2: Generalized Conventional Rotomolding Process Diagram

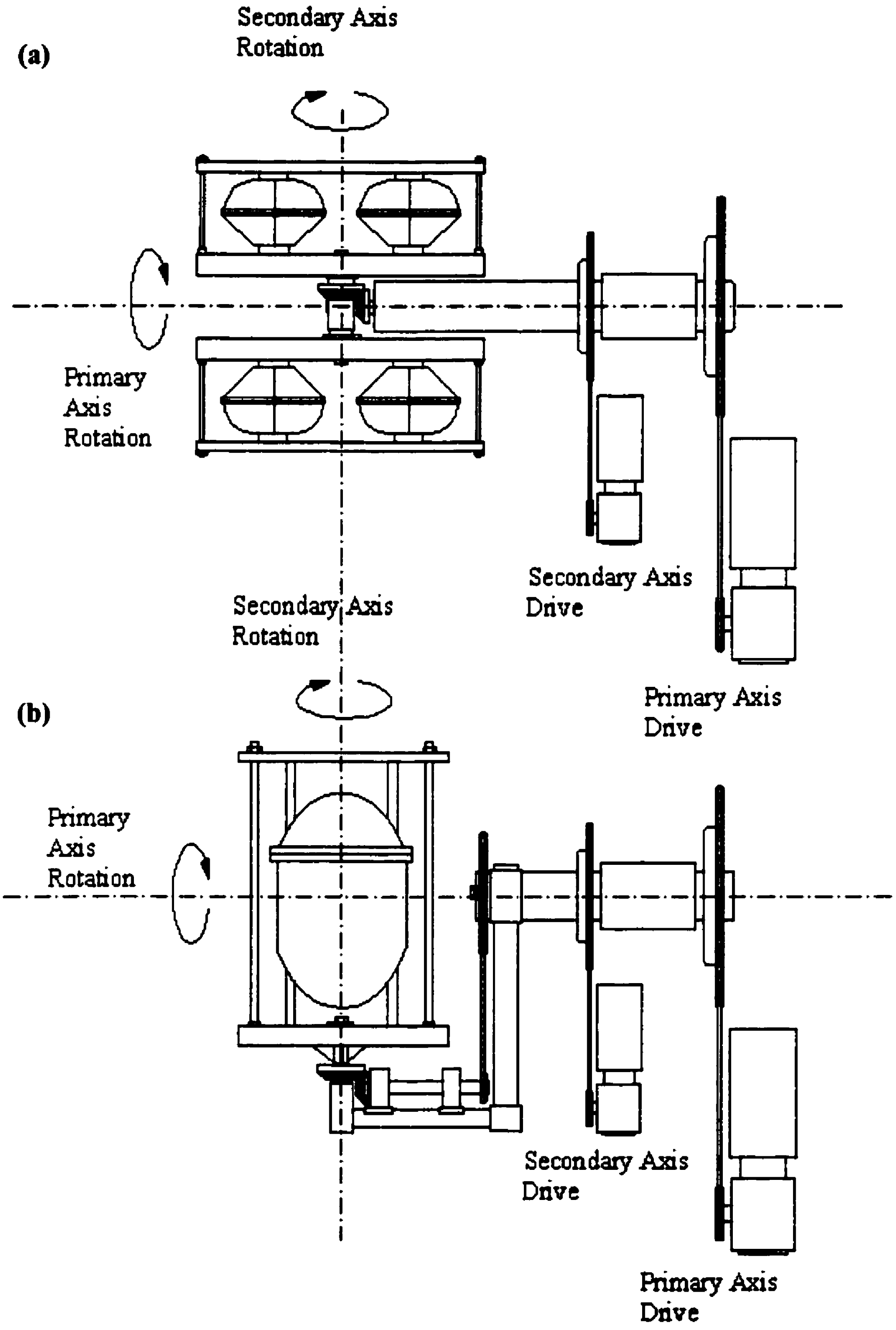


Figure 2.3: Typical Mold-mounting Assembly Configurations
(a) Straight arm (or double centerline) mounting
(b) Offset arm (or cranked arm) mounting

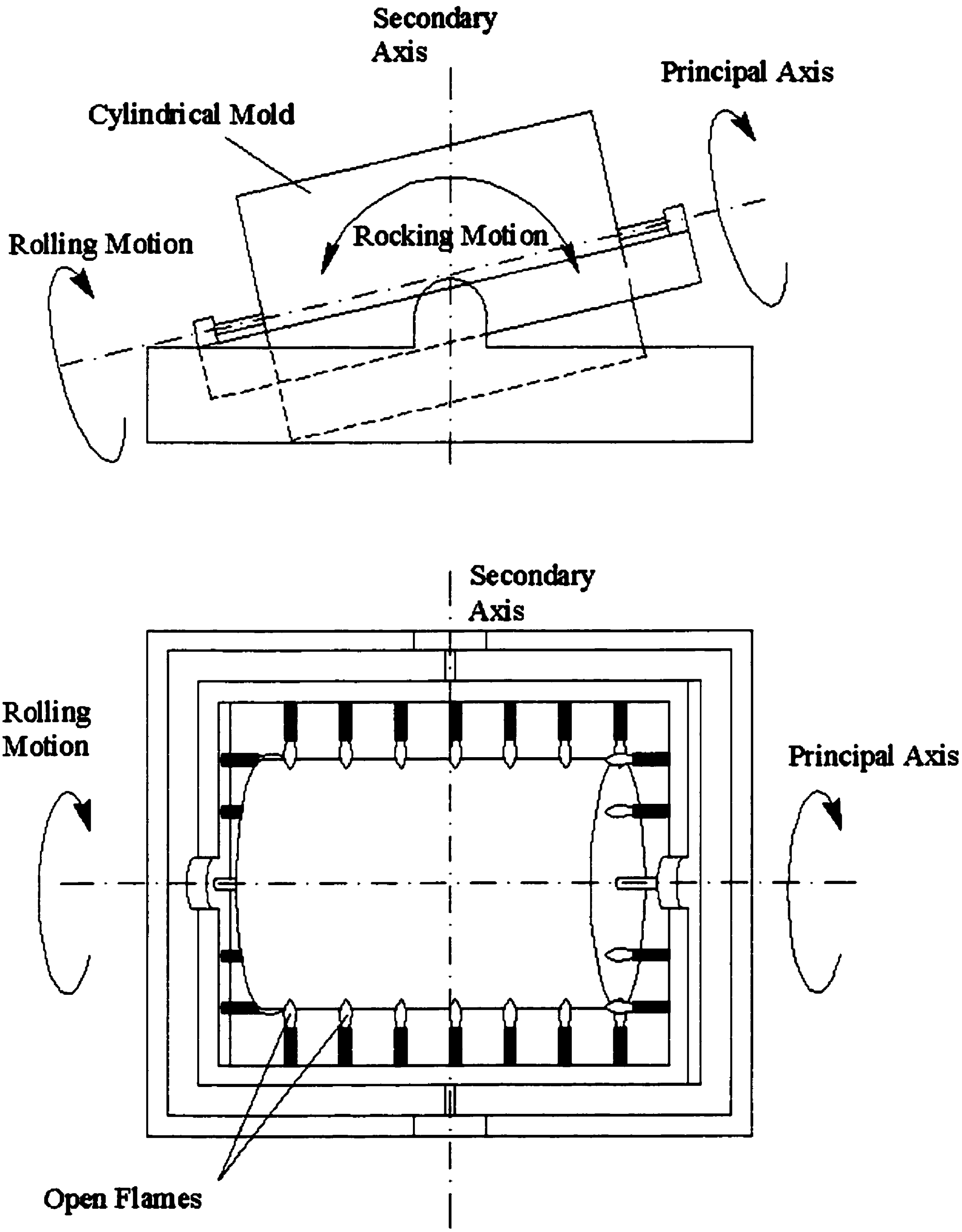


Figure 2.4: Schematic of the Open-flame Mold Heating Concept Applied on a Rock and Roll Rotomolding Machine

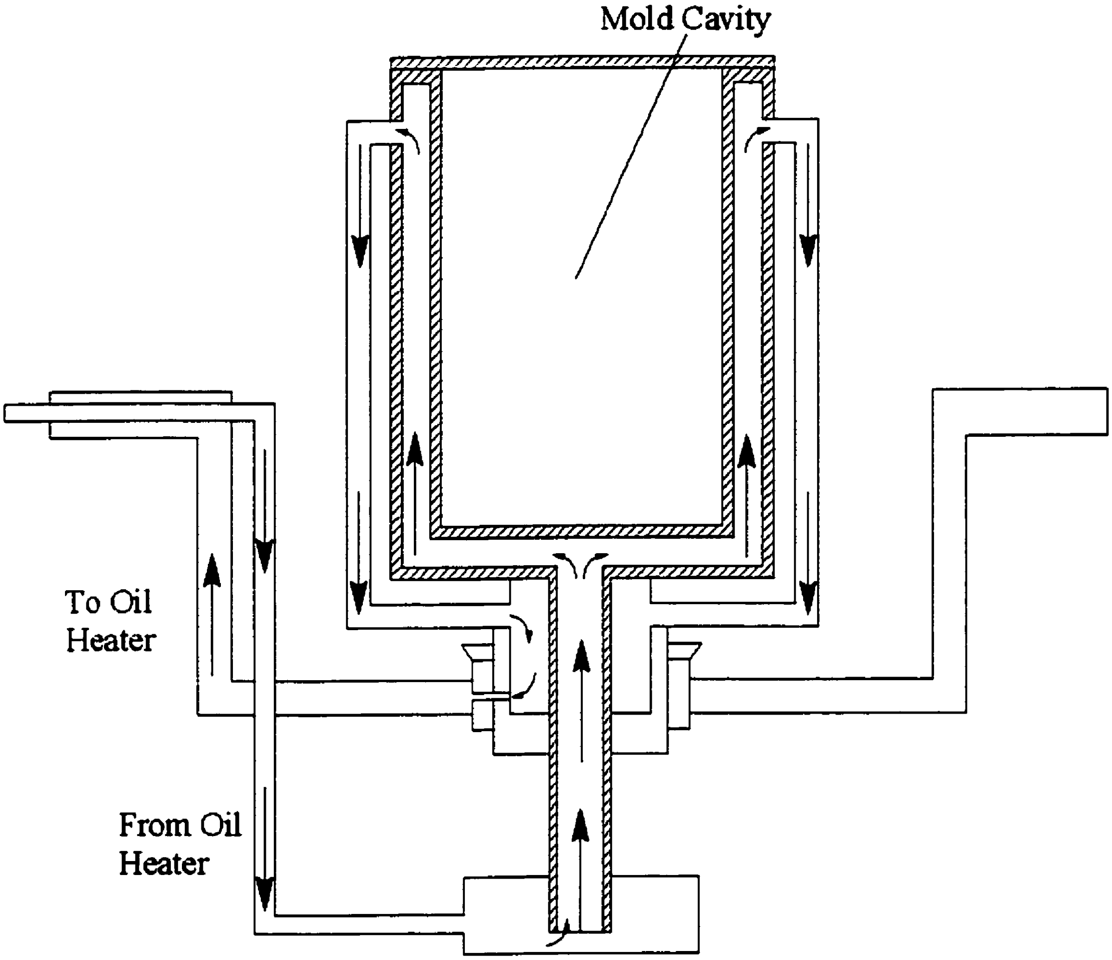


Figure 2.5: Schematic of a Hot-oil Jacketed Mold Heating System

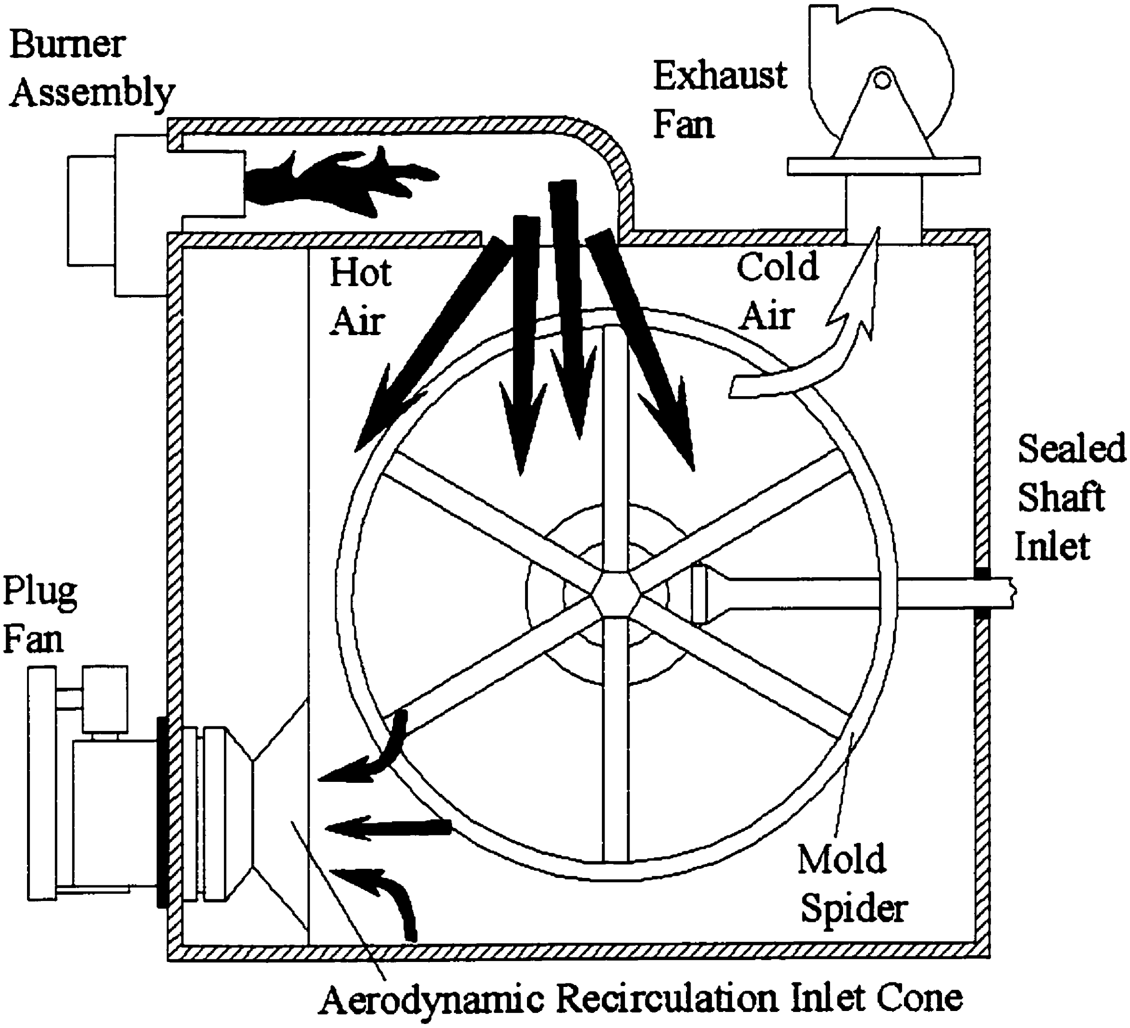


Figure 2.6: Schematic of a Hot-air Recirculating Oven

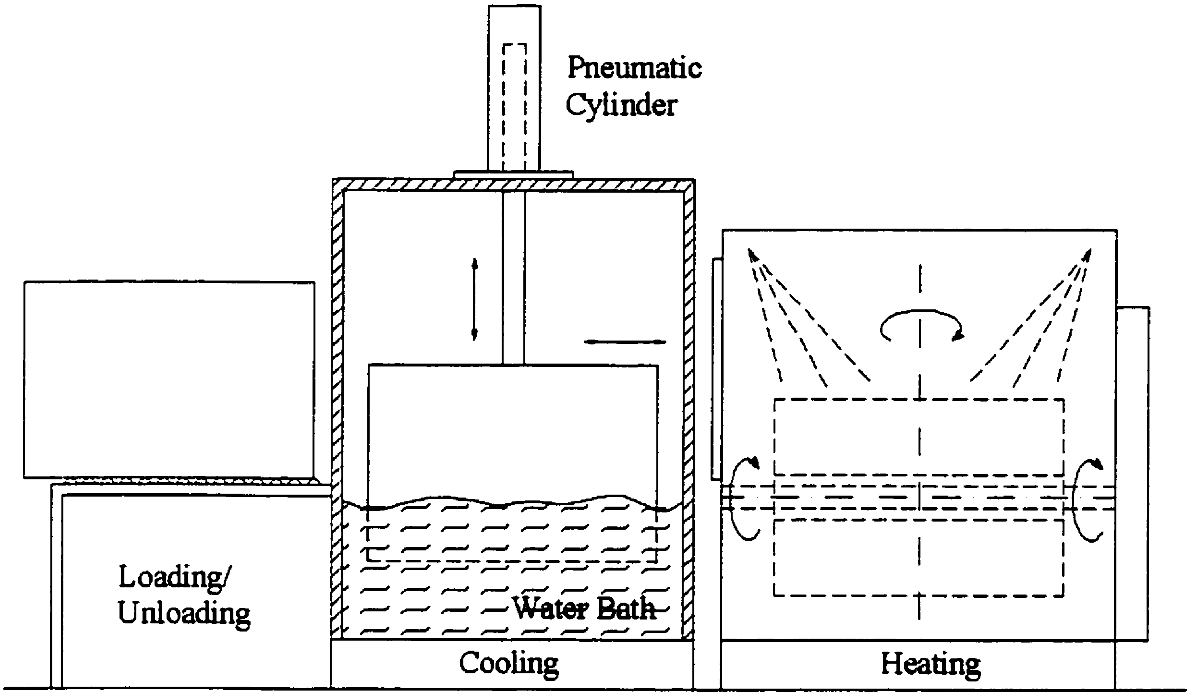


Figure 2.7: Schematic of a Box Oven Rotomolding Machine

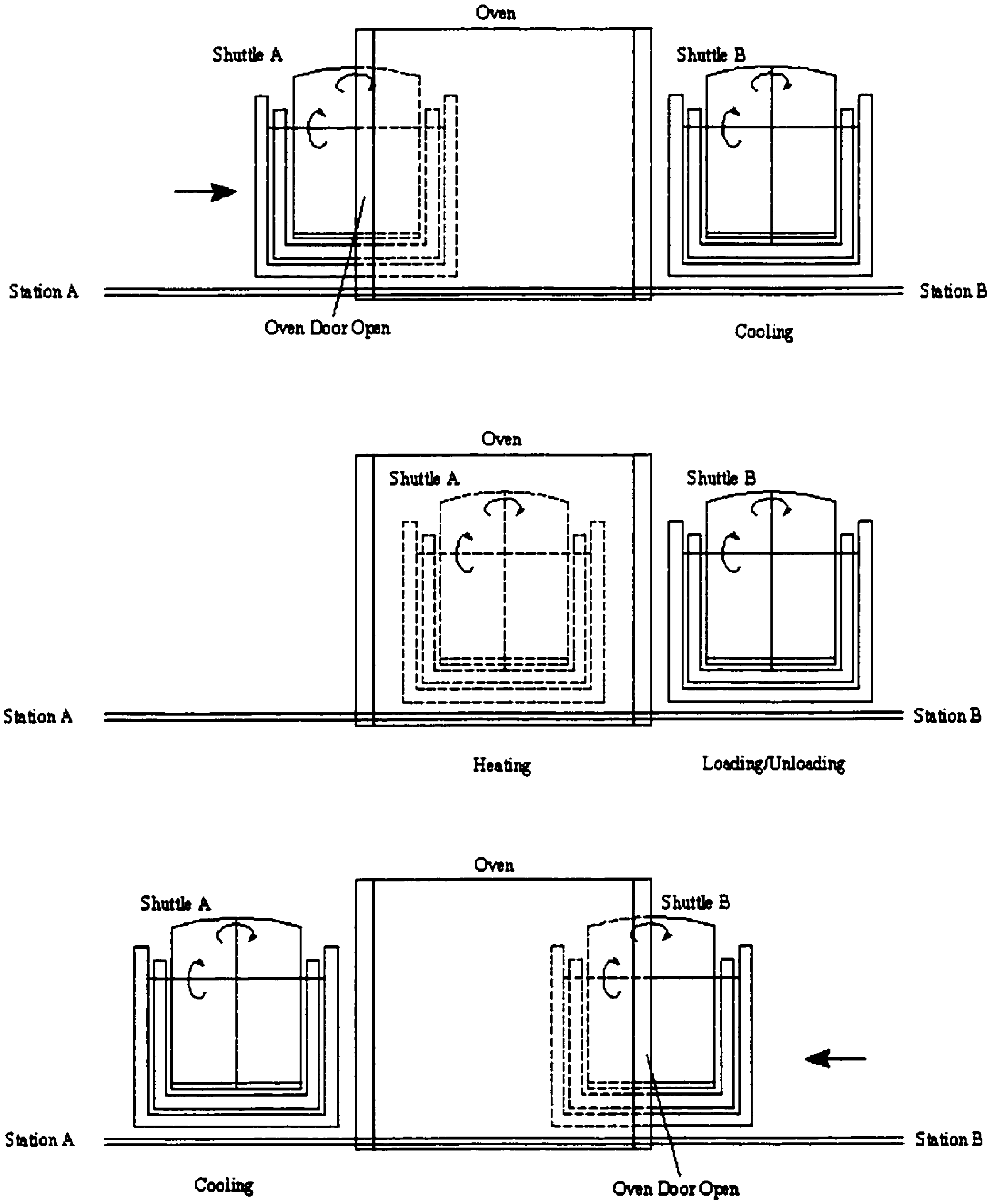


Figure 2.8: Shuttle-style Rotomolding Machine Principle of Operation

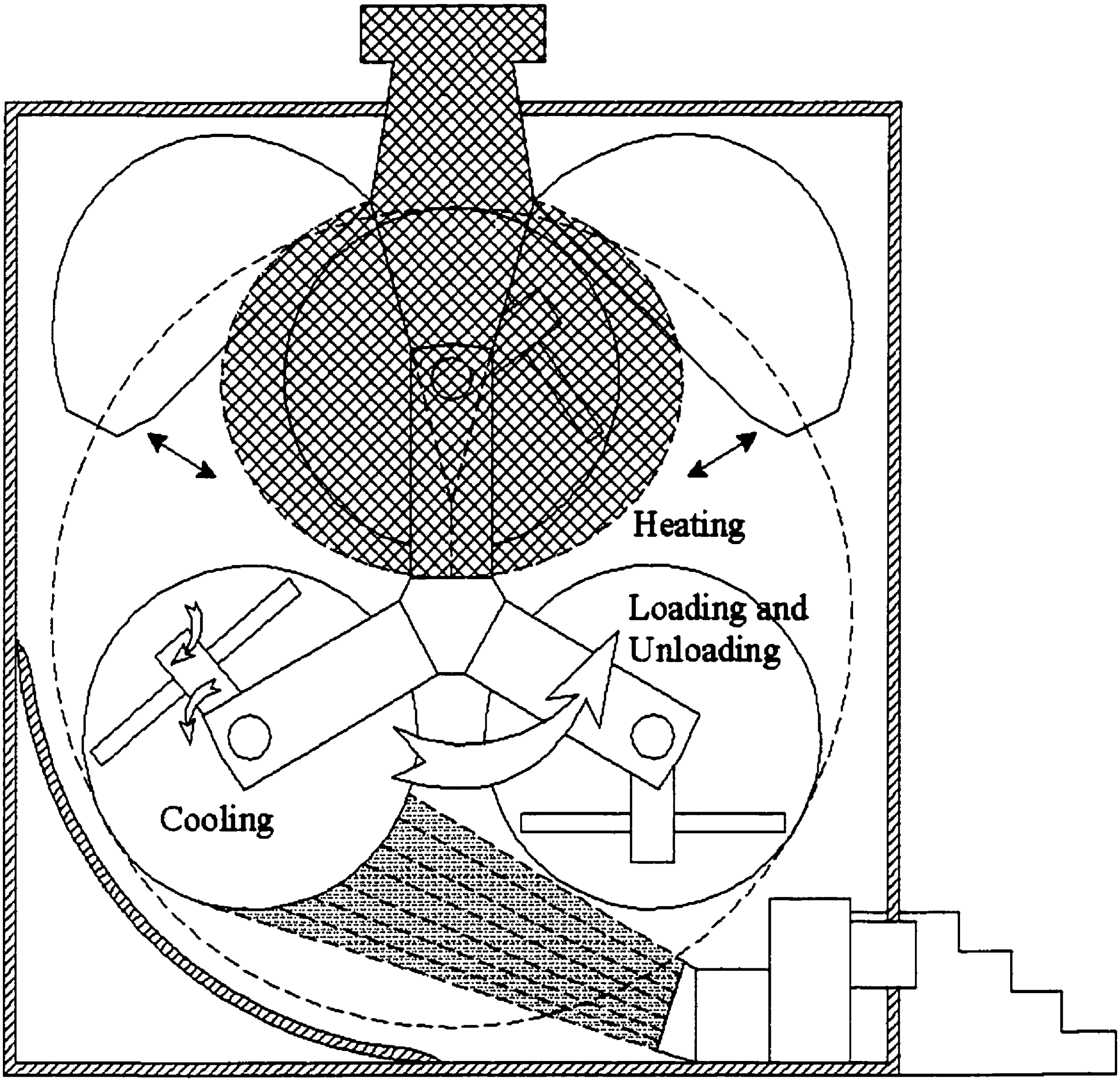


Figure 2.9: 3-arm Vertical-style Rotomolding Machine Principle of Operation

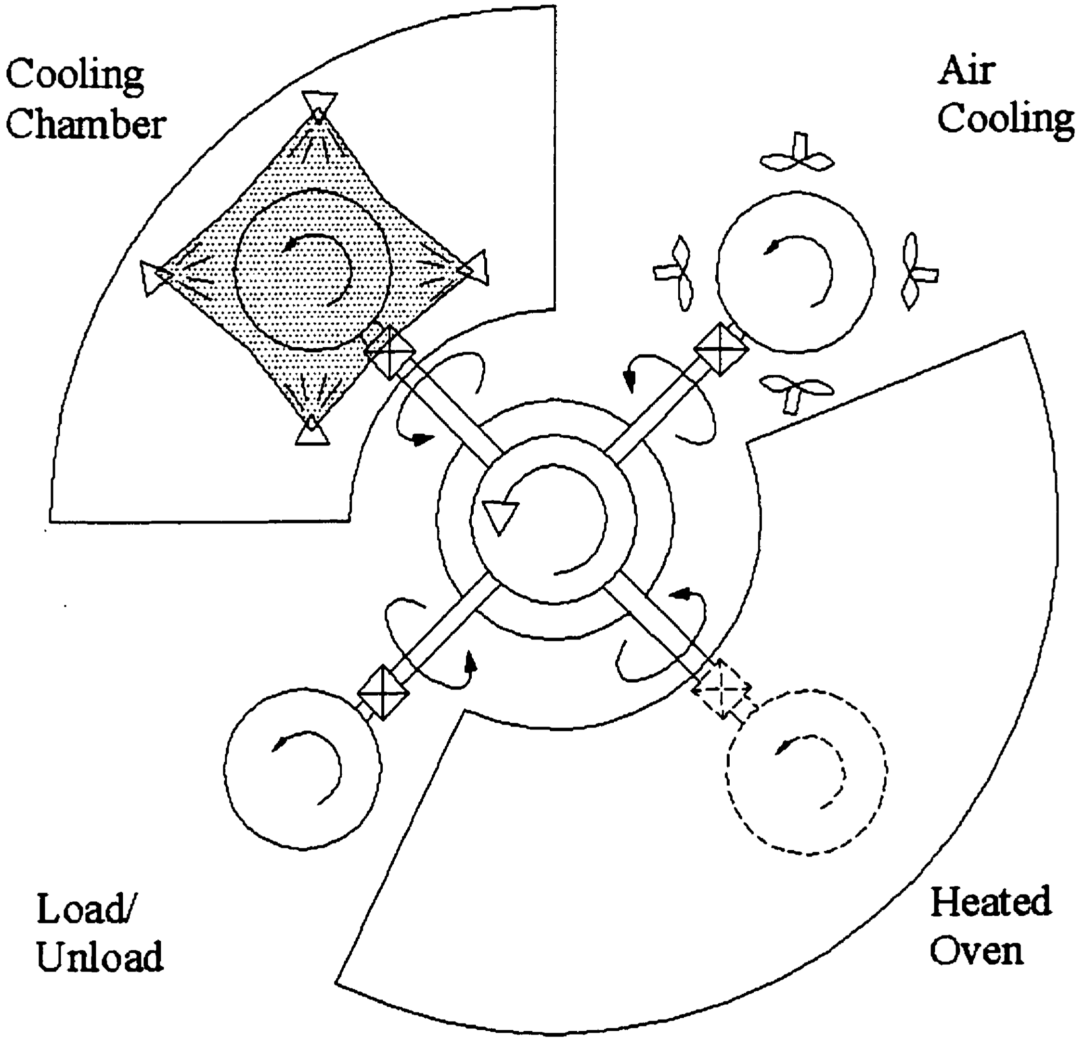
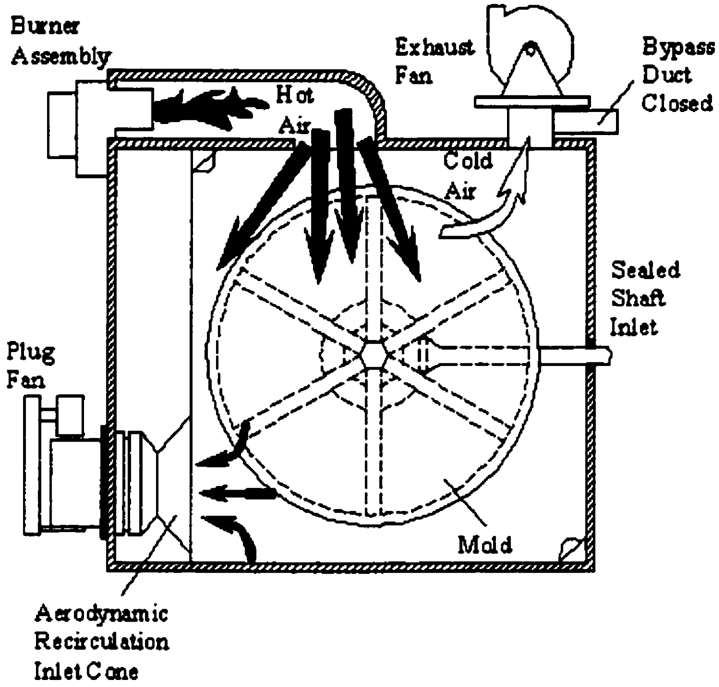
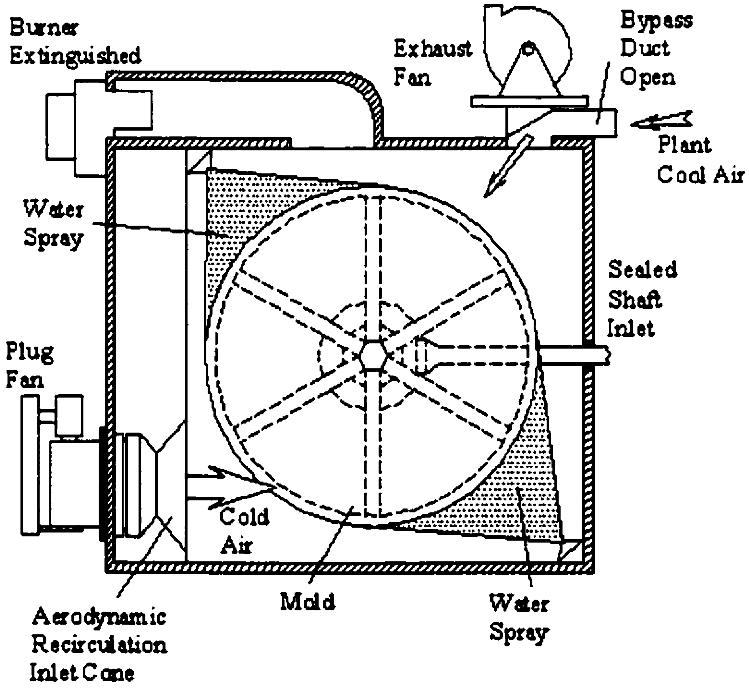


Figure 2.10: Typical Schematic of a Four-fixed-arm Rotomolding Machine



(a) Heating Cycle



(b) Cooling Cycle

Figure 2.11: Clamshell-style Rotomolding Machine Principle of Operation
(a) Heating cycle
(b) Cooling cycle

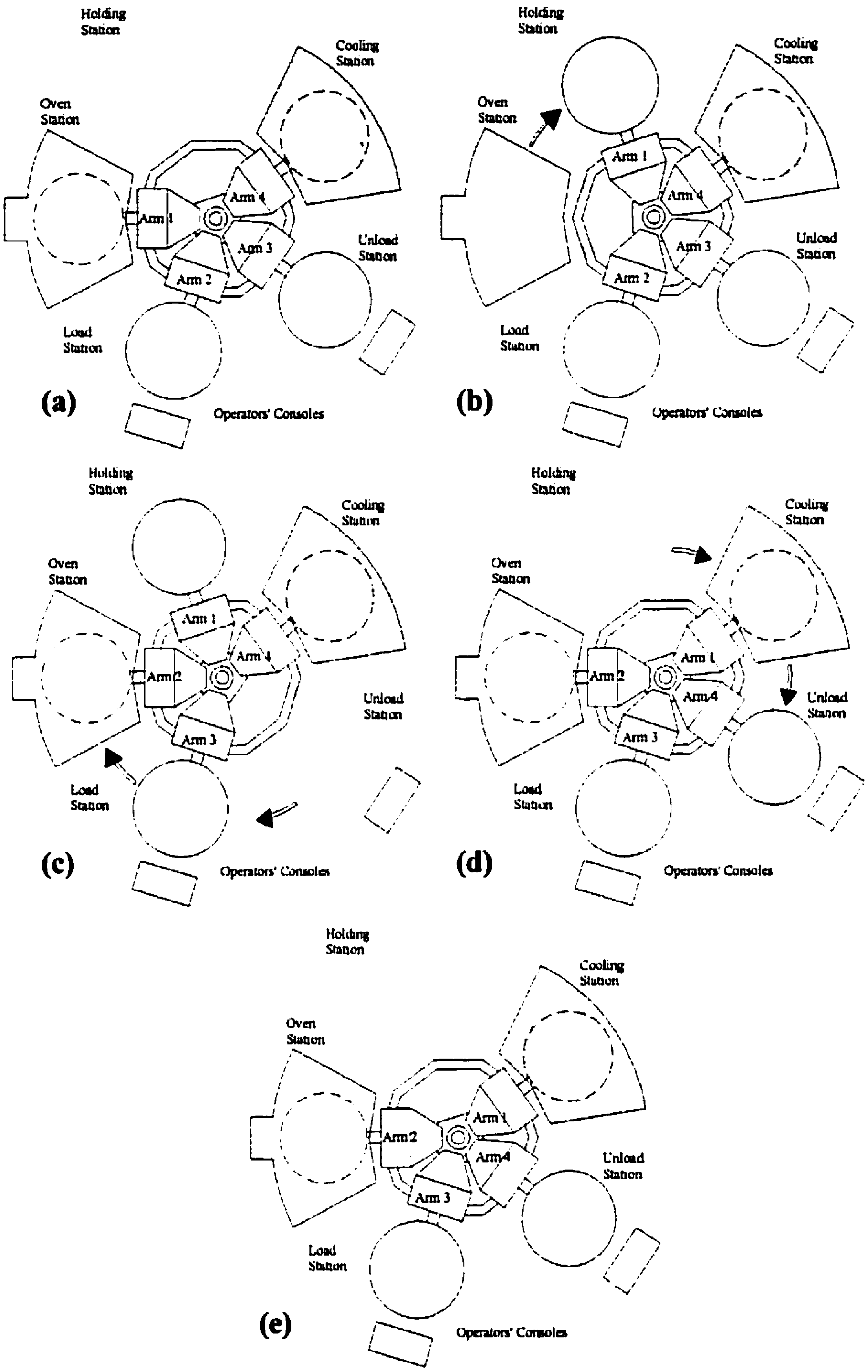


Figure 2.12:Detailed Independent-arm Rotational Molding Machine Principle of Operation

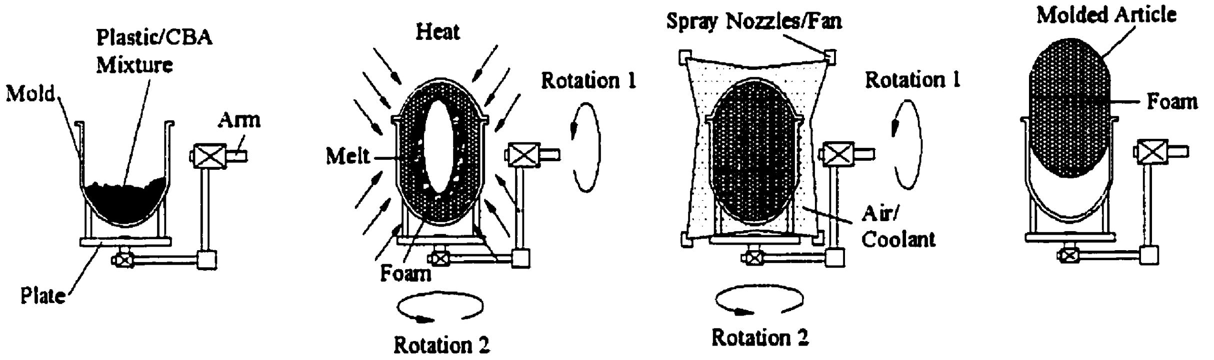
(a) Arm 1 completed the oven cycle, while arm 2 loading operation is not completed yet.

(b) Arm 1 exits the oven and begins the cooling in the holding station.

(c) If loading completed, arm 2 enters oven and starts cycle. If ready, arm 3 moves to loading station.

(d) If cooling completed, arm 4 moves to unloading station. Arm 1 enters cooling station.

(e) Machine is ready to repeat automatic sequence.



(a) Mold Charging (t_1 = Cycle Start)

(b) Mold Rotation and Heating ($t_2 > t_1$)

(c) Mold Rotation and Cooling ($t_3 > t_2$)

(d) Molded Article Removal (t_4 = Cycle End)

Figure 2.13: Rotational Foam Molding Process Principle of Operation

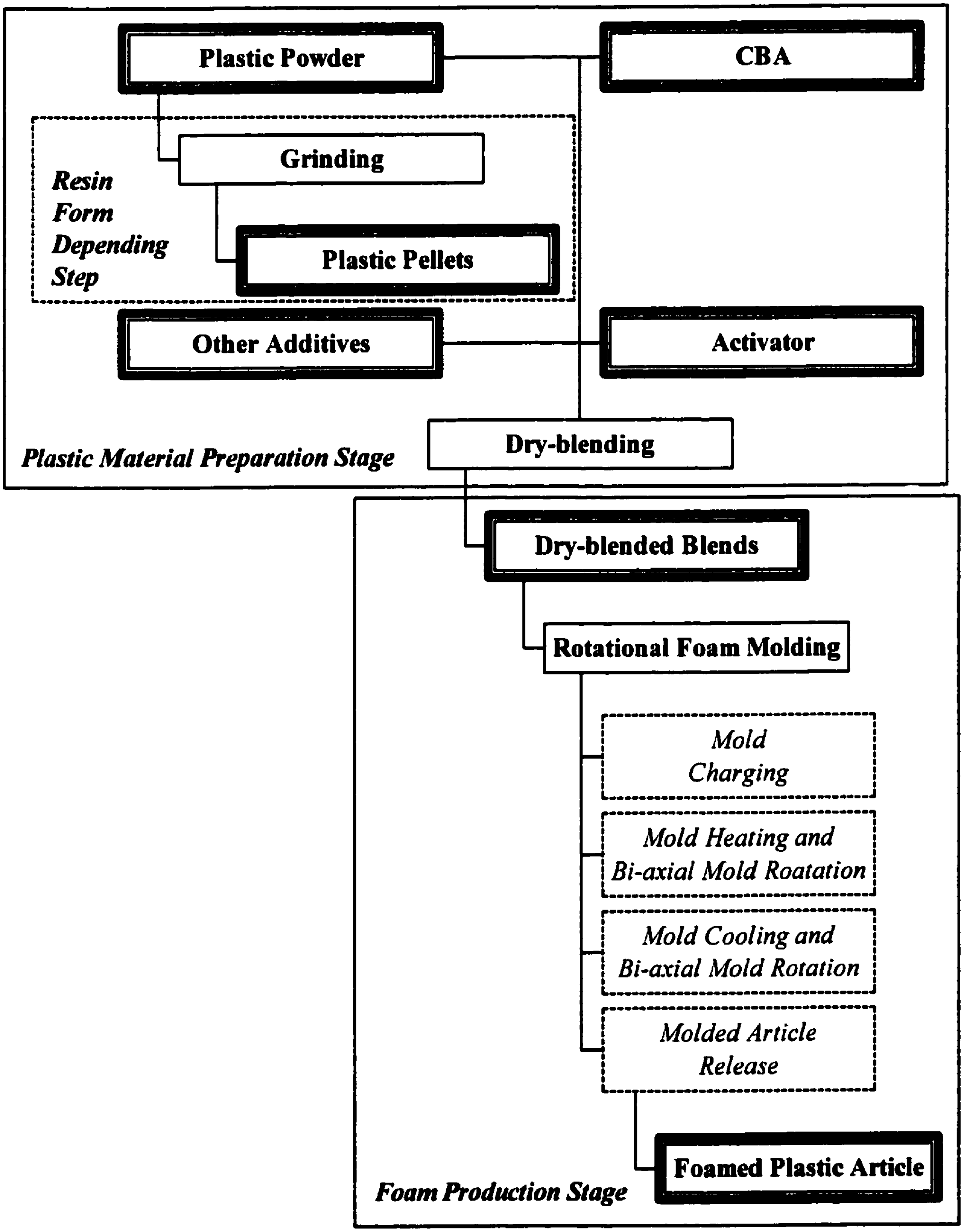


Figure 2.14: Generalized Dry-blending Based Rotational Foam Molding Process Diagram

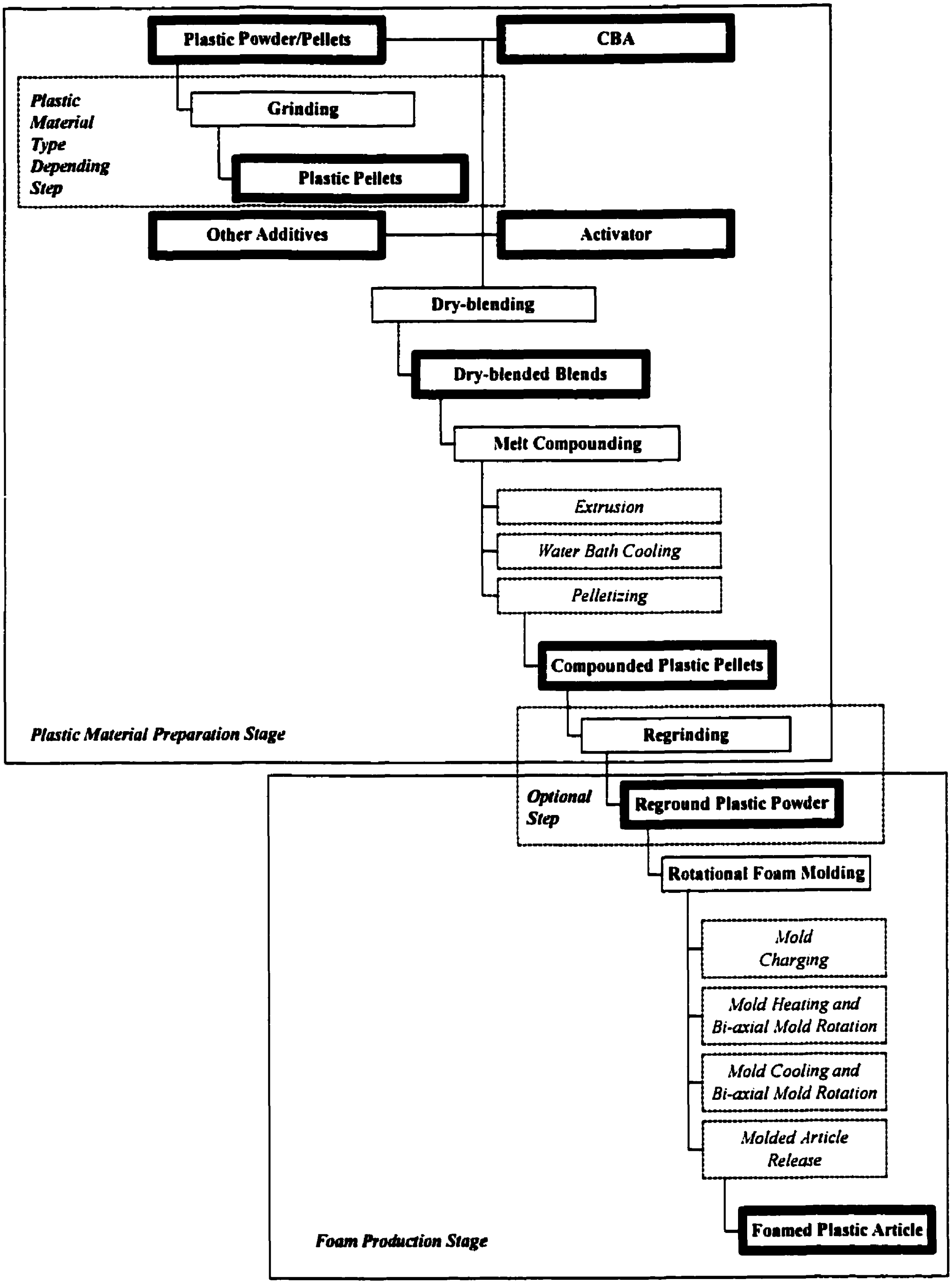


Figure 2.15: Generalized Compounding-based Rotational Foam Molding Process Diagram

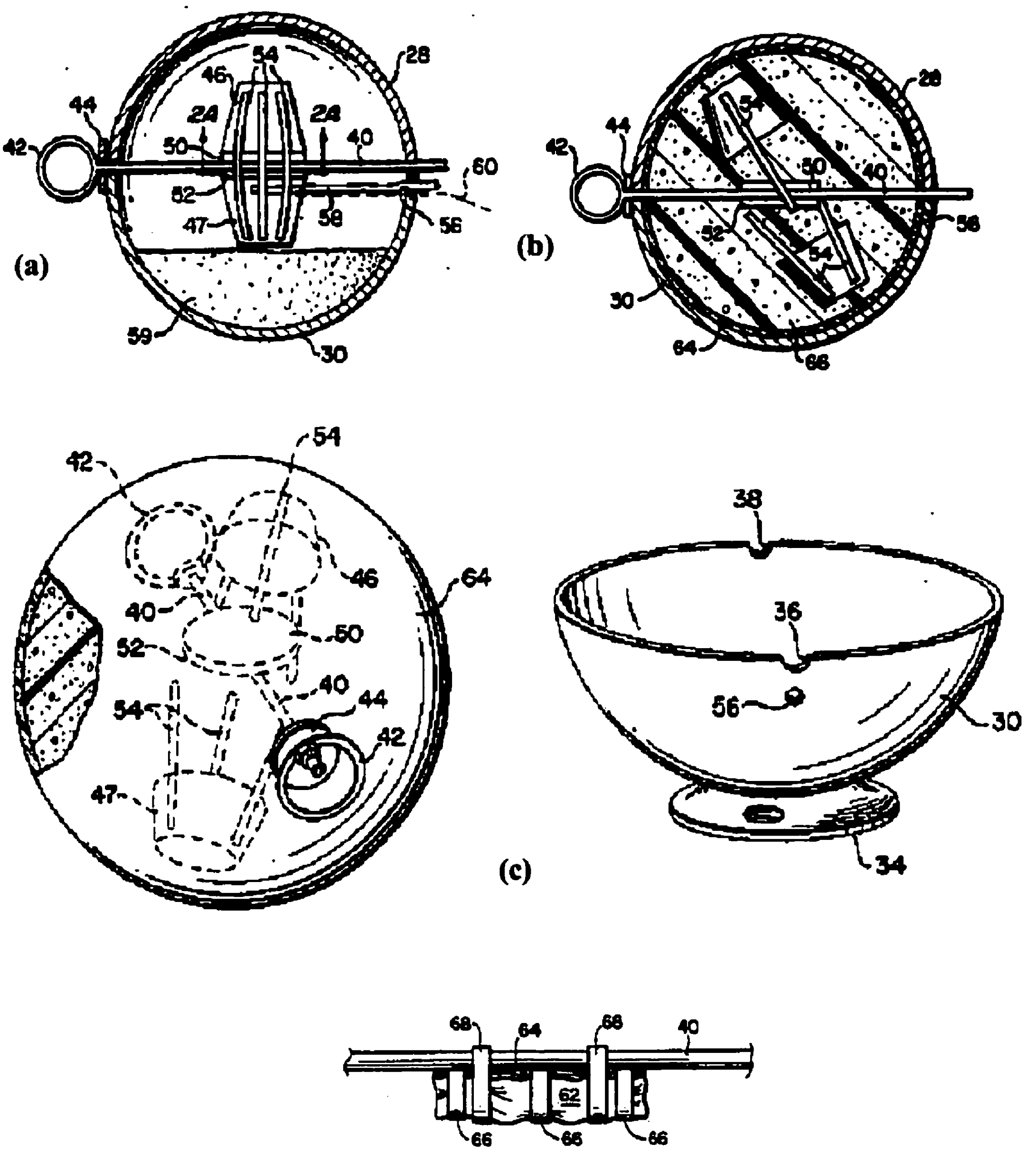


Figure 2.16: Illustration of U.S. Pat. No. 4,952,350 (8/1990)

(a) The container for the foamable resins in closed position inside the mold held together by adhesive tape strips.

(b) The container in open position after the adhesive stripes have softened and the foamable charge has been released inside the mold.

(c) Optional design. A plastic bag that releases its foamable content after being ruptured by the elevated temperature during the rotational molding cycle.

(Source: IBM Patent Server)

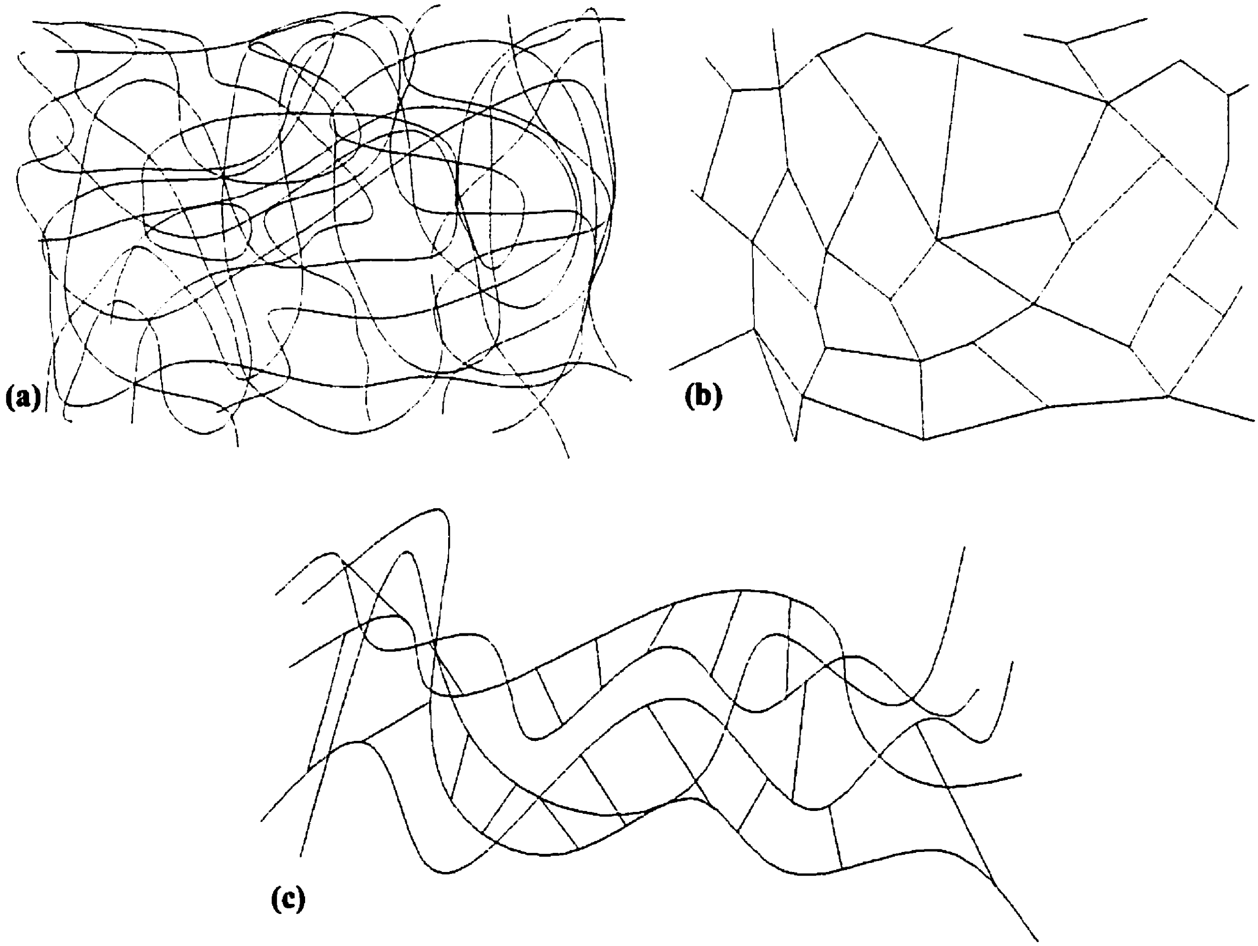
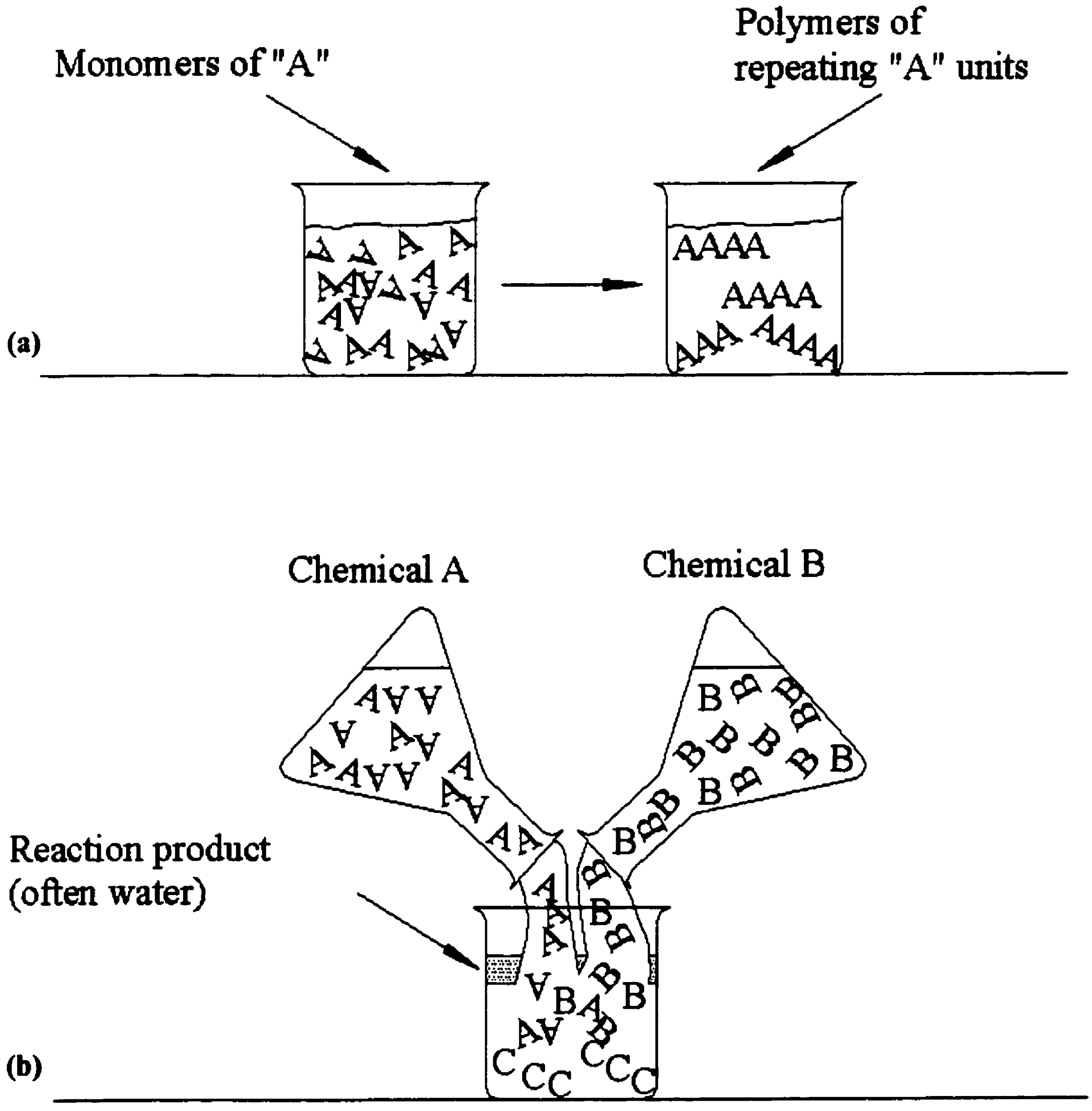


Figure 2.17: Types of Polymer Structures
(a) Thermoplastics
(b) Thermosets
(c) Elastomers



A and B react to form polymer C-C-C-C-C-..........

Figure 2.18: Polymerization Reactions

(a) Addition polymerization
(b) Condensation polymerization

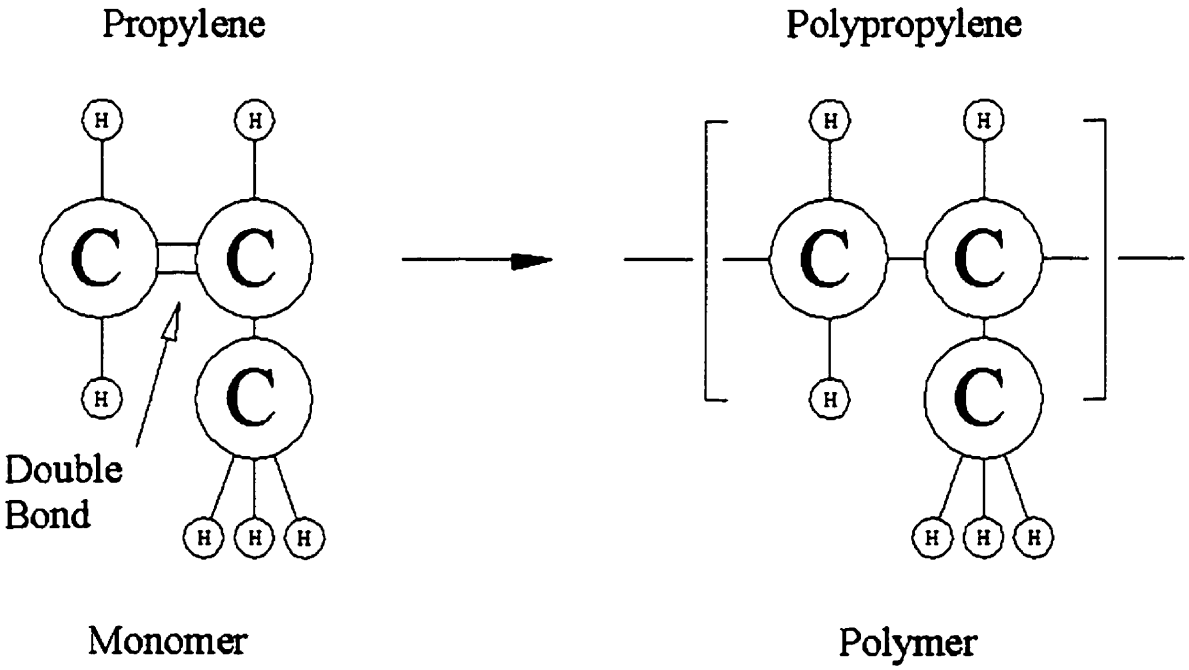


Figure 2.19: Schematic of the Chemistry of Polypropylene Preparation

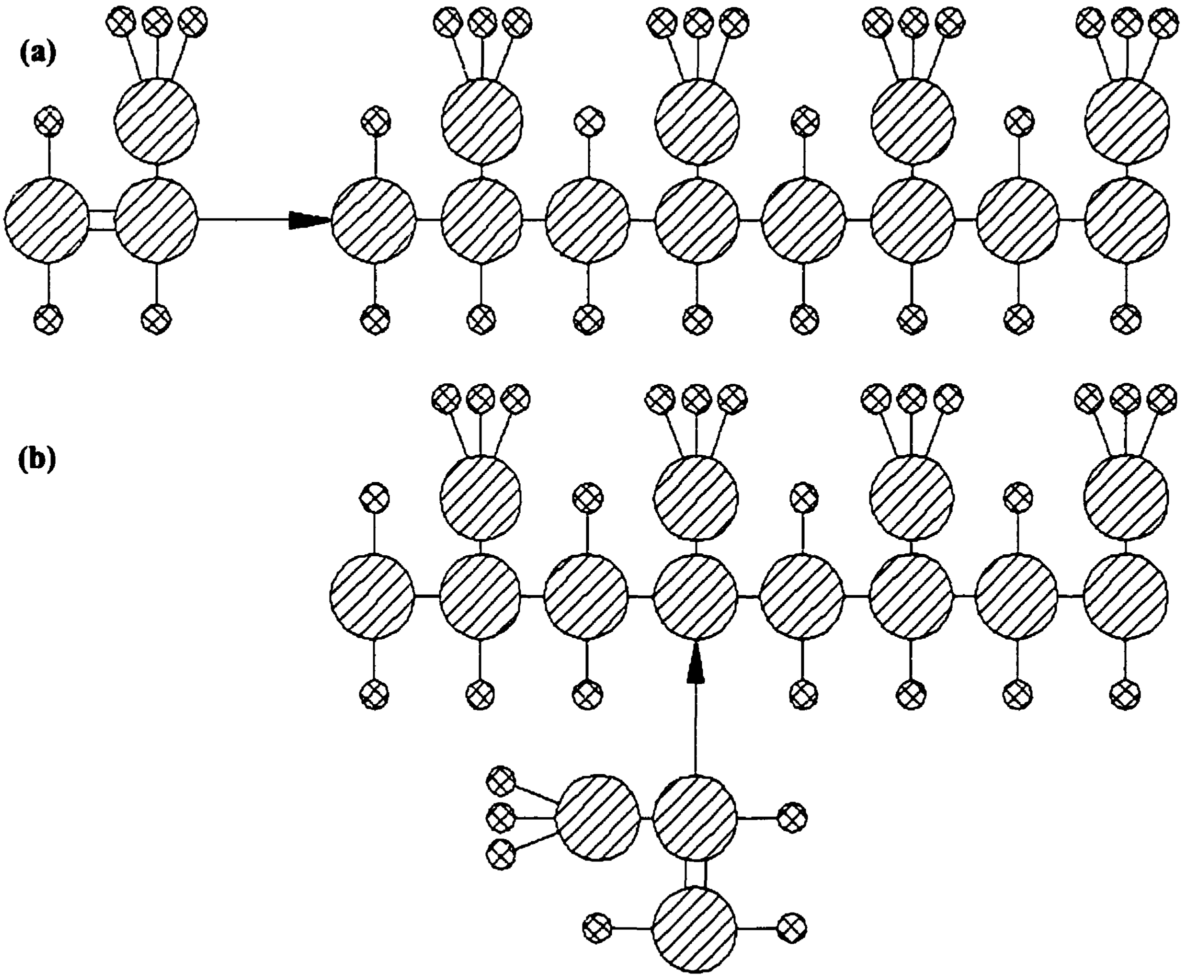


Figure 2.20: Schematic of Linear and Branched Types of Addition of the Propylene Monomer to the Growing PP Chain
(a) Linear
(b) Branched

(Symbols: Big Circle = Carbon Atom; Small Circle = Hydrogen Atom)

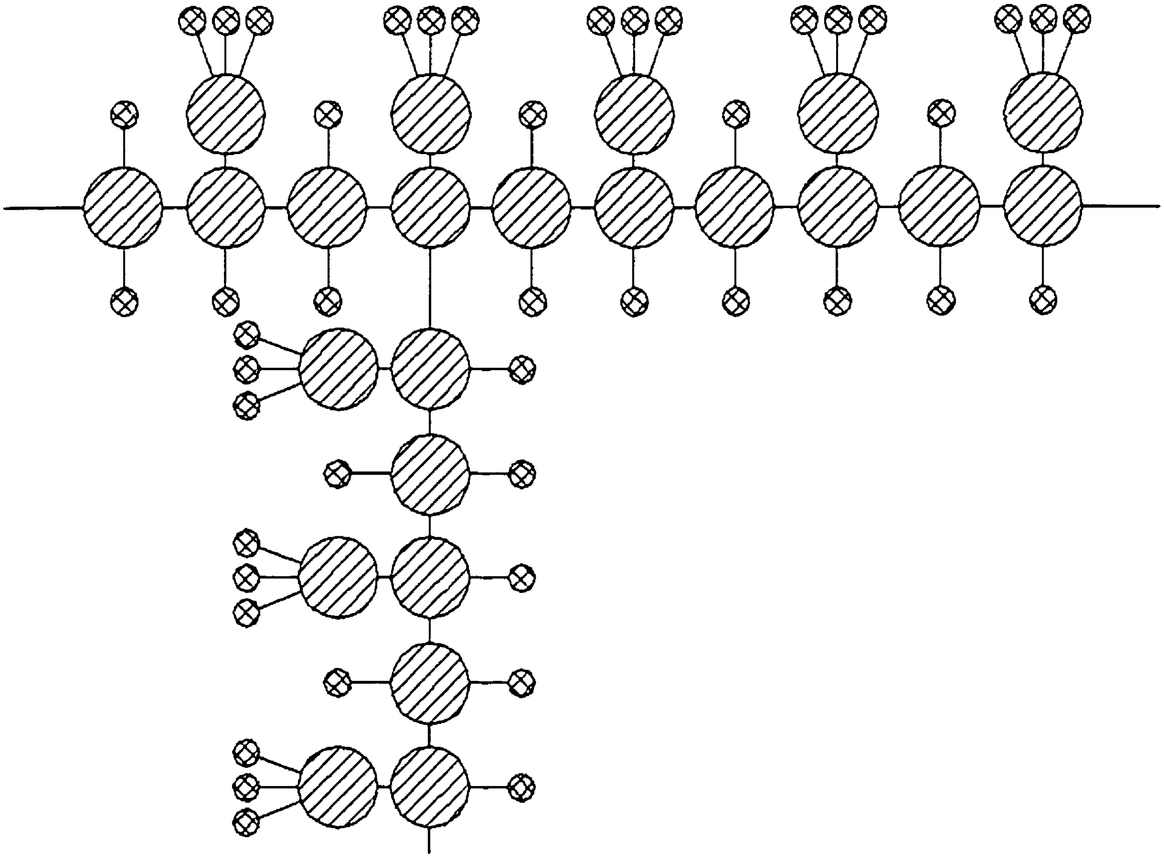


Figure 2.21: Branched PP

(Symbols: Big Circle = Carbon Atom; Small Circle = Hydrogen Atom)

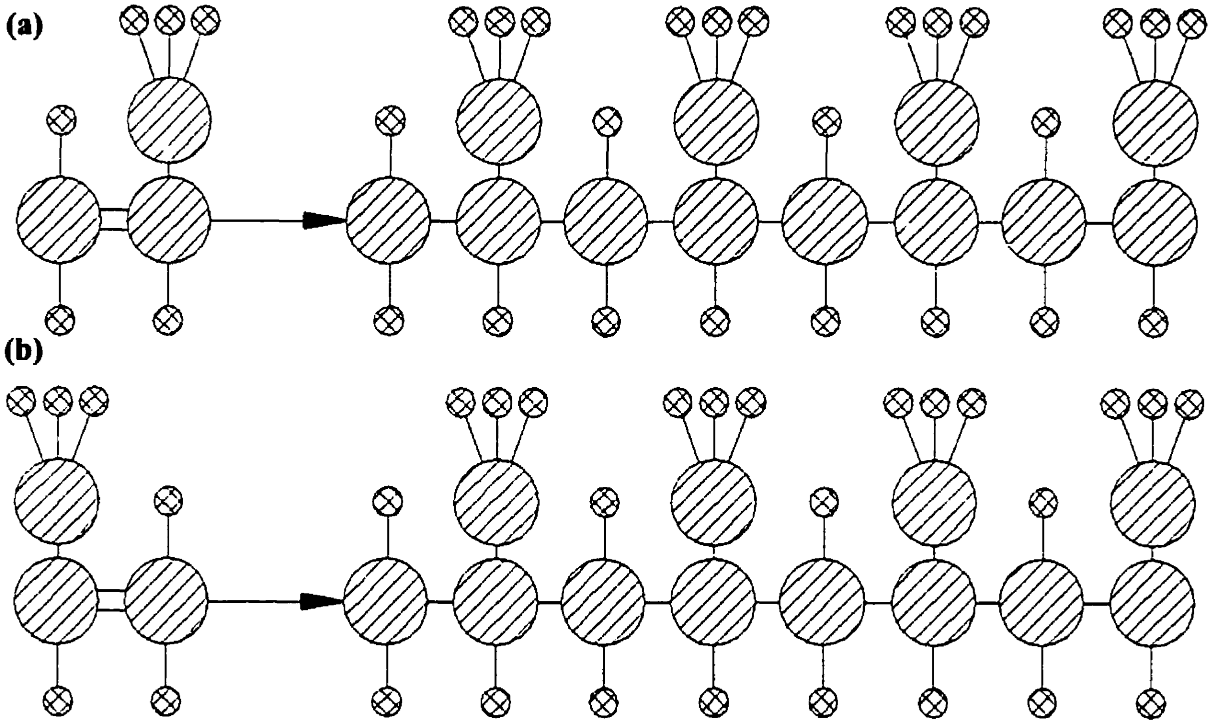


Figure 2.22: Schematic of Head-to-tail and Tail-to-tail Types of Addition of the Propylene Monomer to the Growing PP Chain

(a) Head-to-tail

(b) Tail-to-tail

(Symbols: Big Circle = Carbon Atom; Small Circle = Hydrogen Atom)

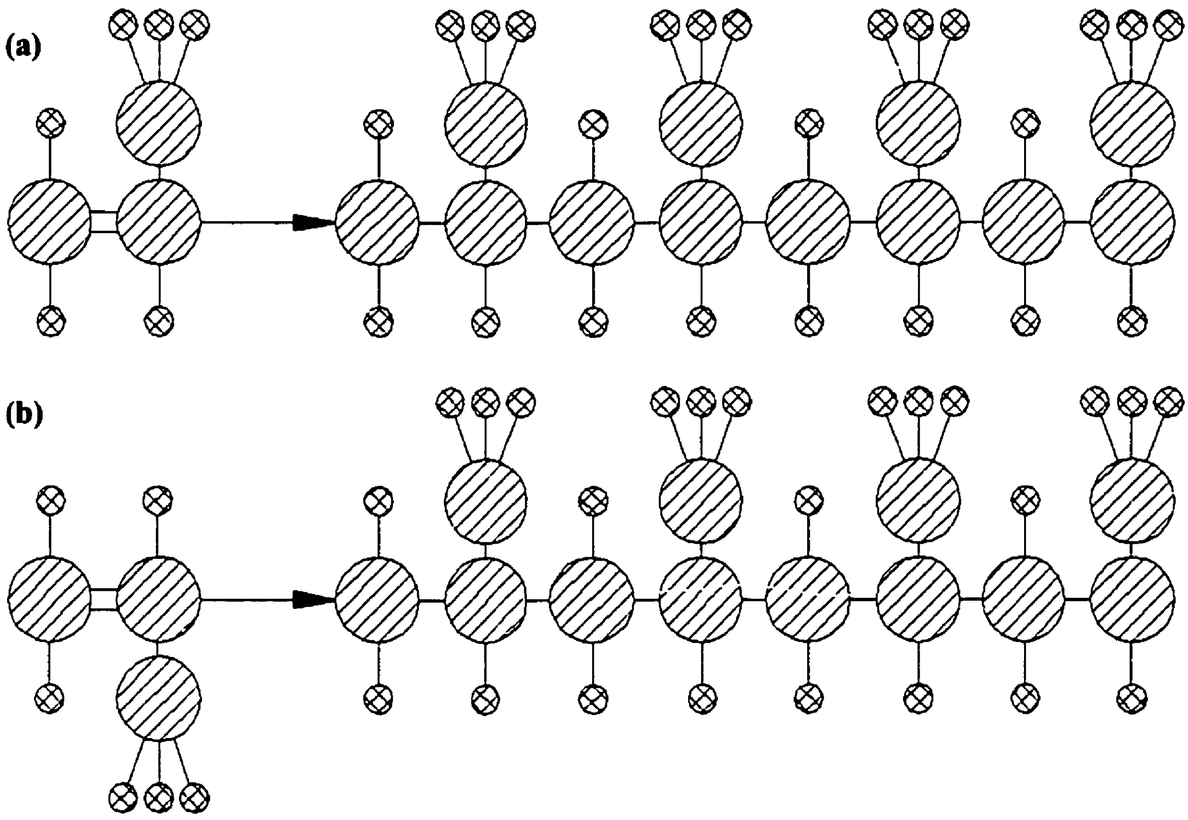


Figure 2.23: Schematic of Same Hand and Opposite Hand Side Types of Addition of the Propylene Monomer to the Growing PP Chain

(a) Same hand
(b) Opposite hand

(Symbols: Big Circle = Carbon Atom; Small Circle = Hydrogen Atom)

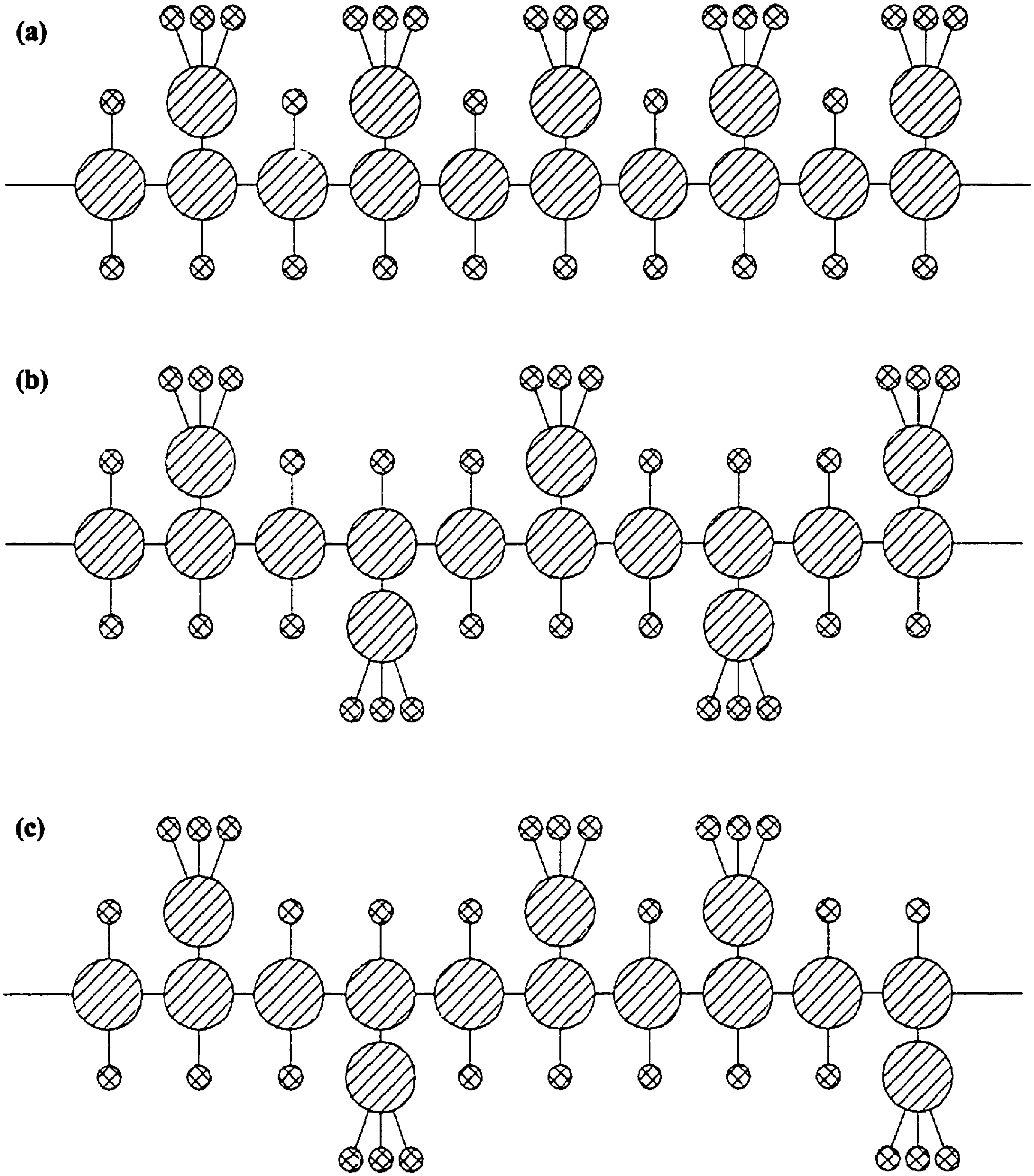
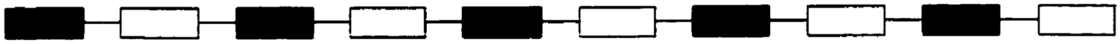
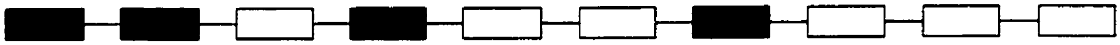


Figure 2.24: Schematics of Various PP Chain Geometric Forms
(a) Isotactic PP
(b) Syndiotactic PP
(c) Atactic PP

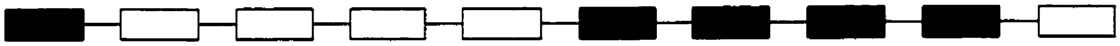
(Symbols: Big Circle = Carbon Atom; Small Circle = Hydrogen Atom)



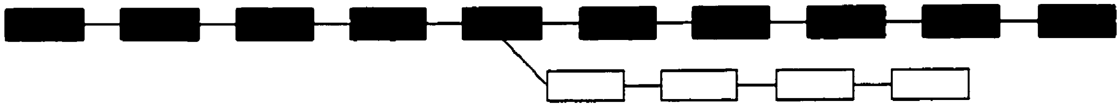
(a) Alternating Copolymer



(b) Random Copolymer



(c) Block Copolymer



(d) Grafted Copolymer

Figure 2.25: Important Copolymer Formulations

(Symbols: Black Rectangle = Monomer A; White Rectangle = Monomer B)

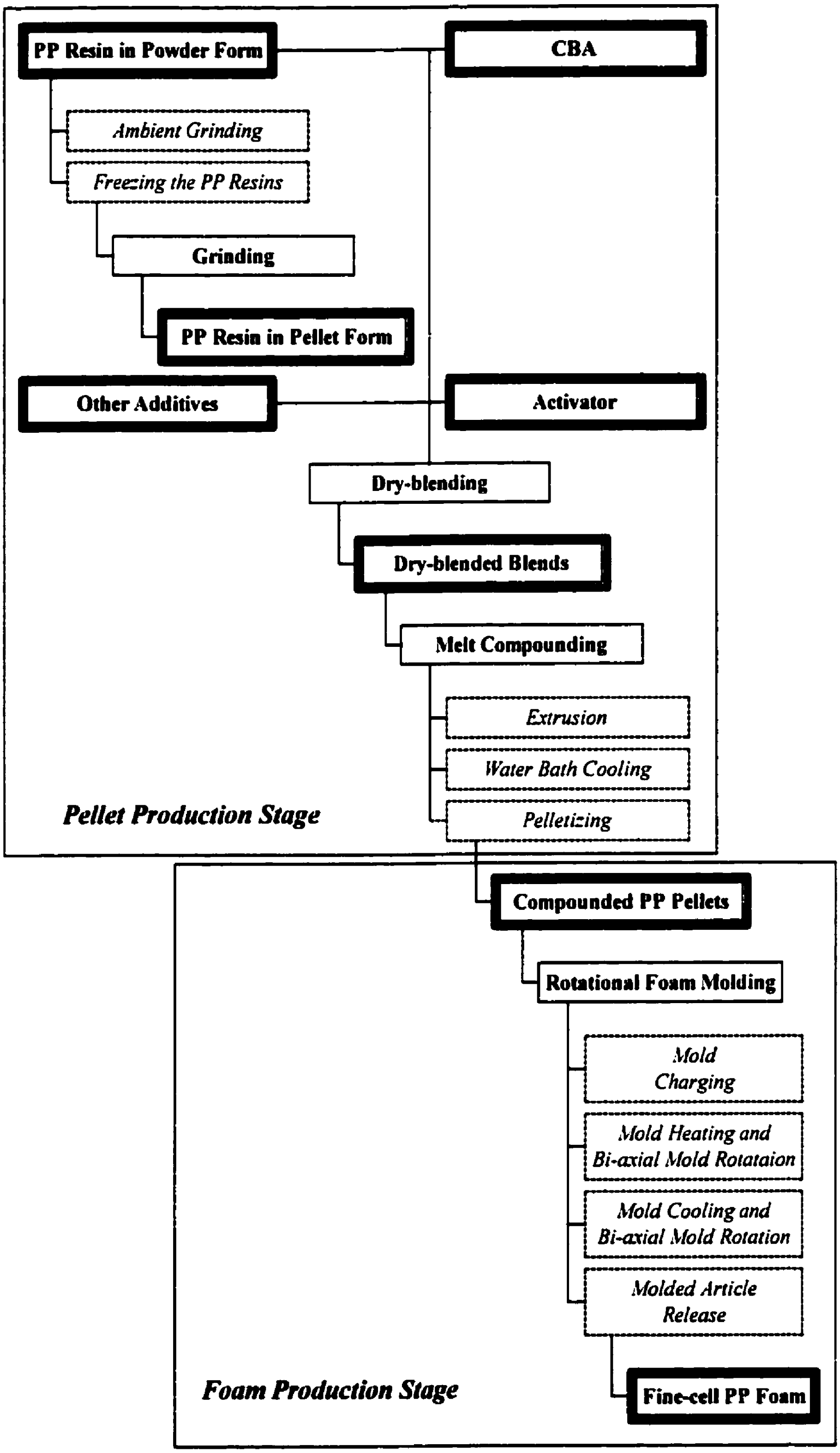


Figure 3.1: Detailed Process Diagram of the Proposed Compounding-based Rotational Foam Molding Process for Producing Fine-cell PP Foams

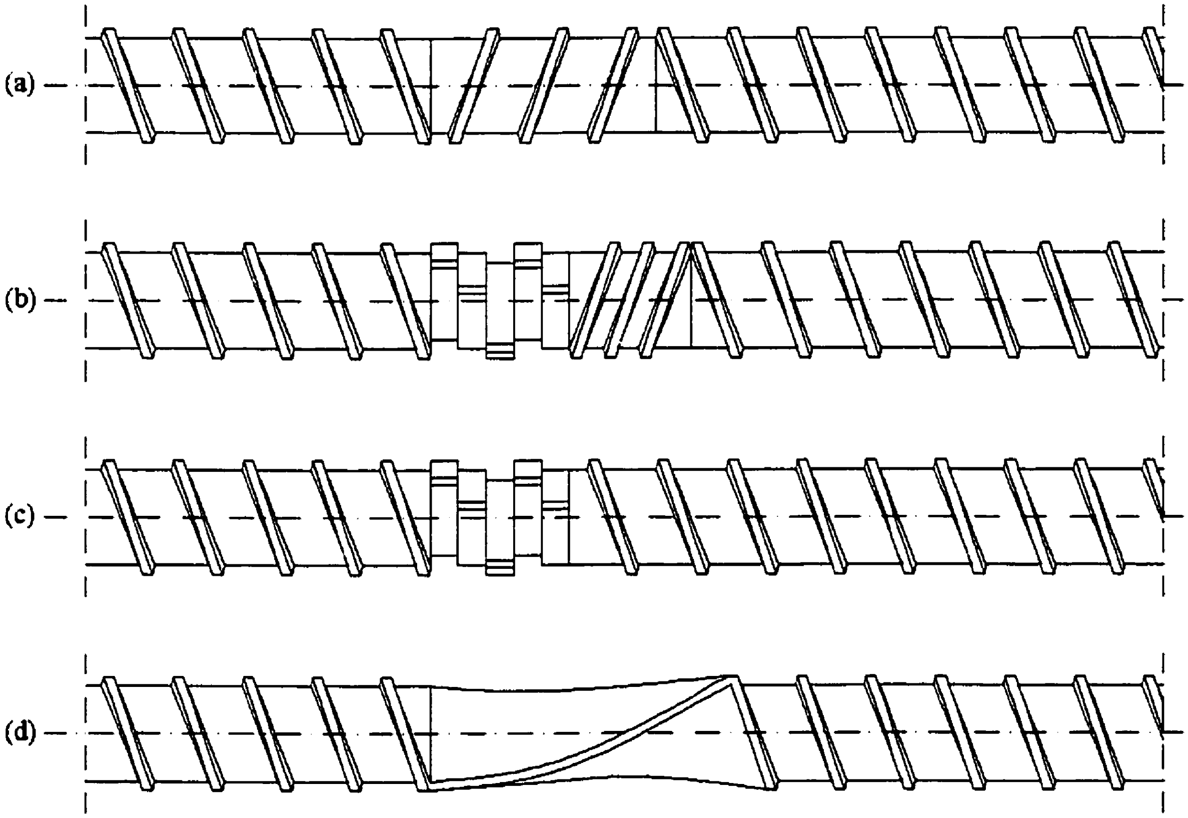


Figure 3.2: Typical Screw Arrangements in the Plasticating Zone of a Twin-screw Co-rotating Compounder

(a) Left-hand screw
(b) Right-hand kneading block, left-hand screw
(c) Right-hand kneading block
(d) Large-pitch left-hand screw

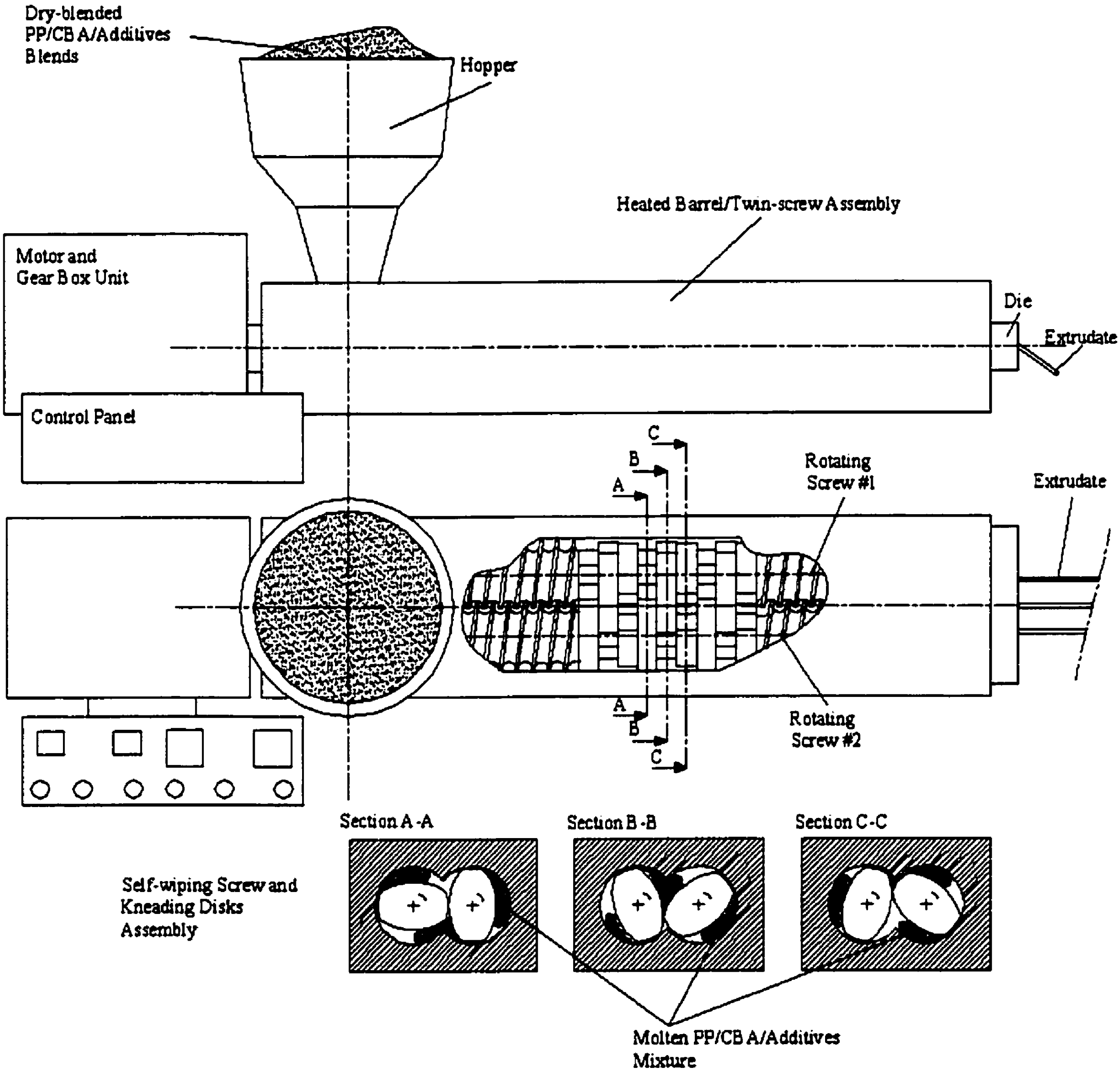


Figure 3.3: Typical Schematic of an Intermeshing Co-rotating Twin-screw Extruder

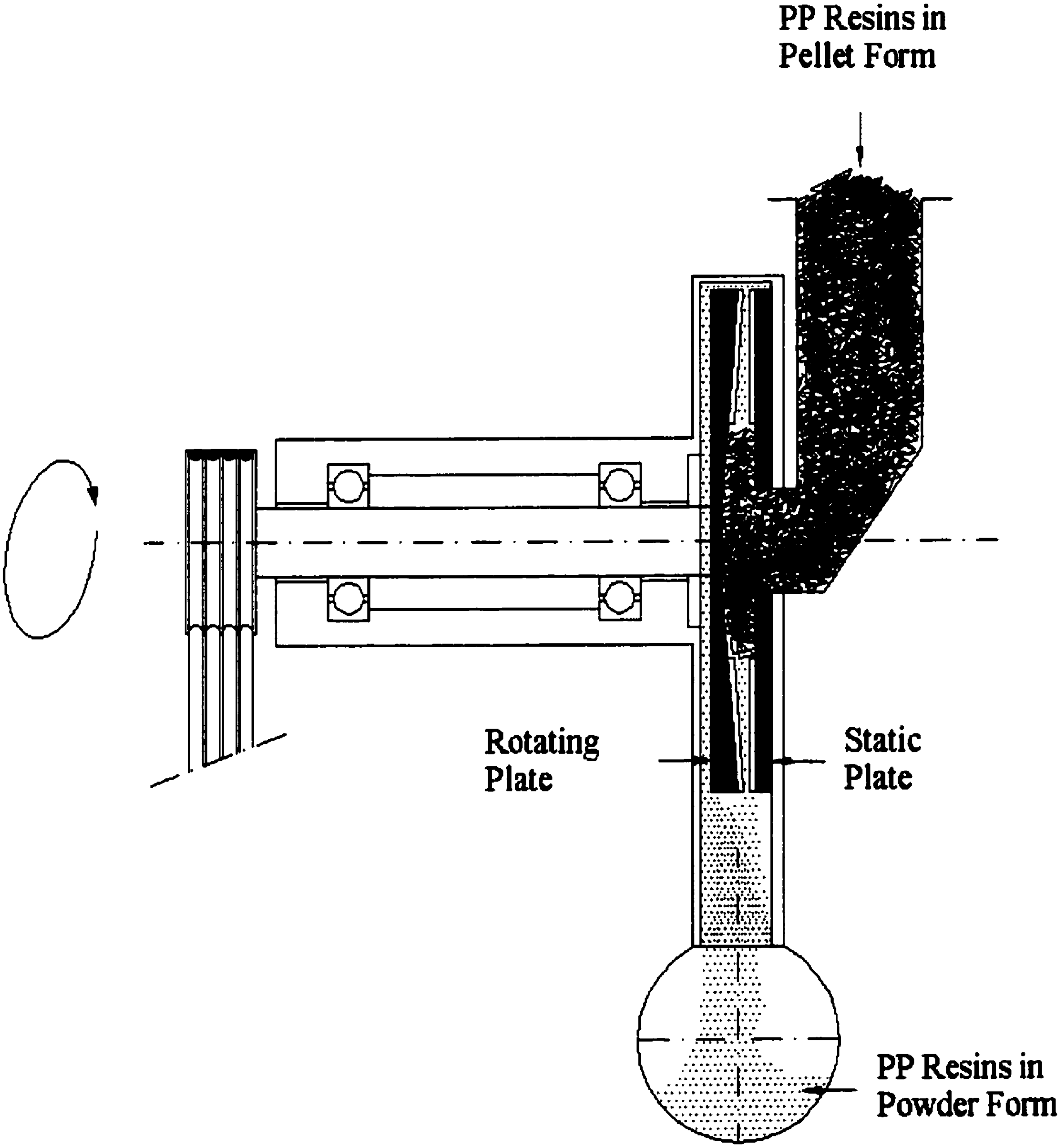


Figure 3.4: Typical Schematic of a Grinding Head

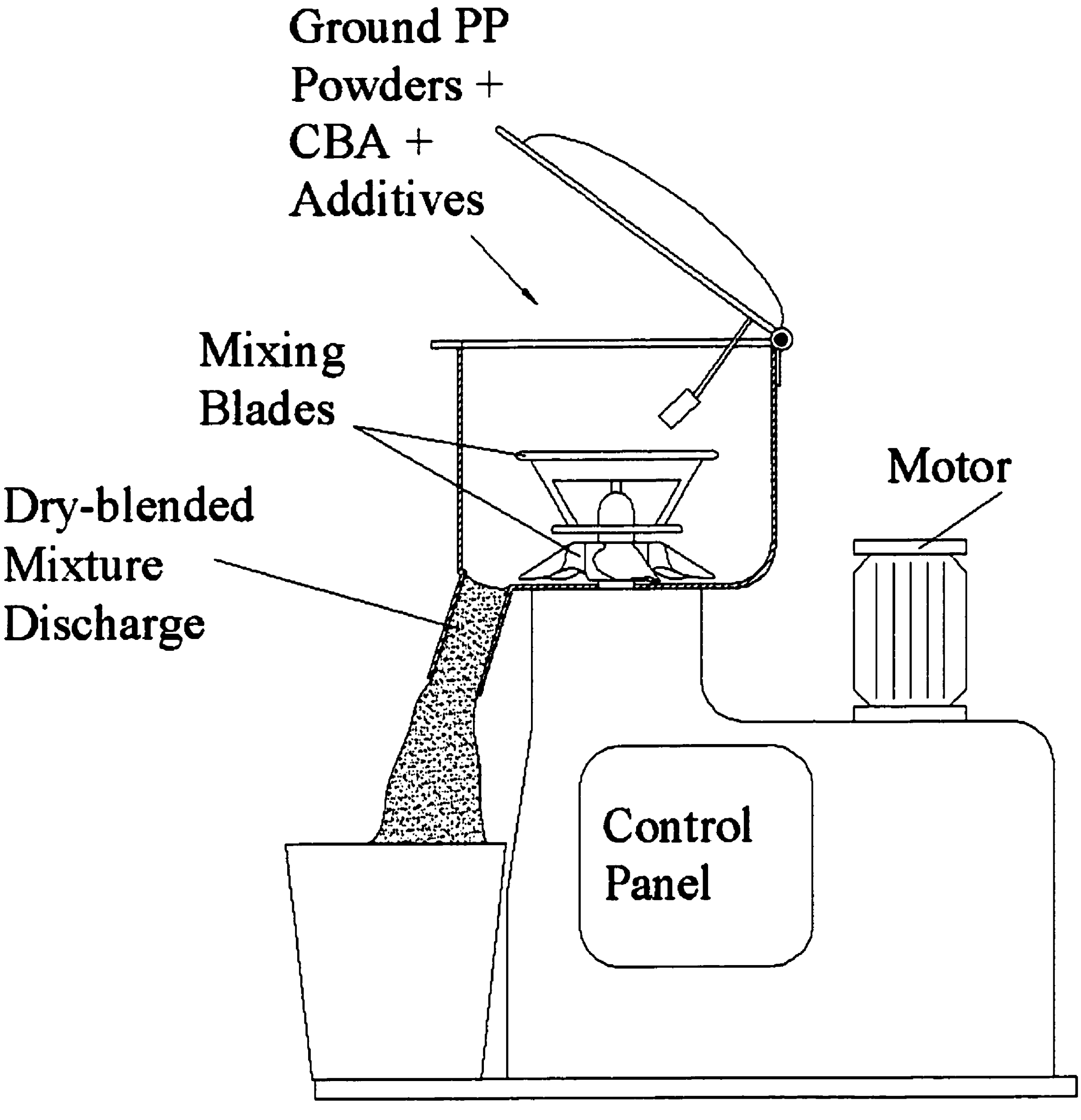


Figure 3.5: Typical Schematic of a High Speed Mixer

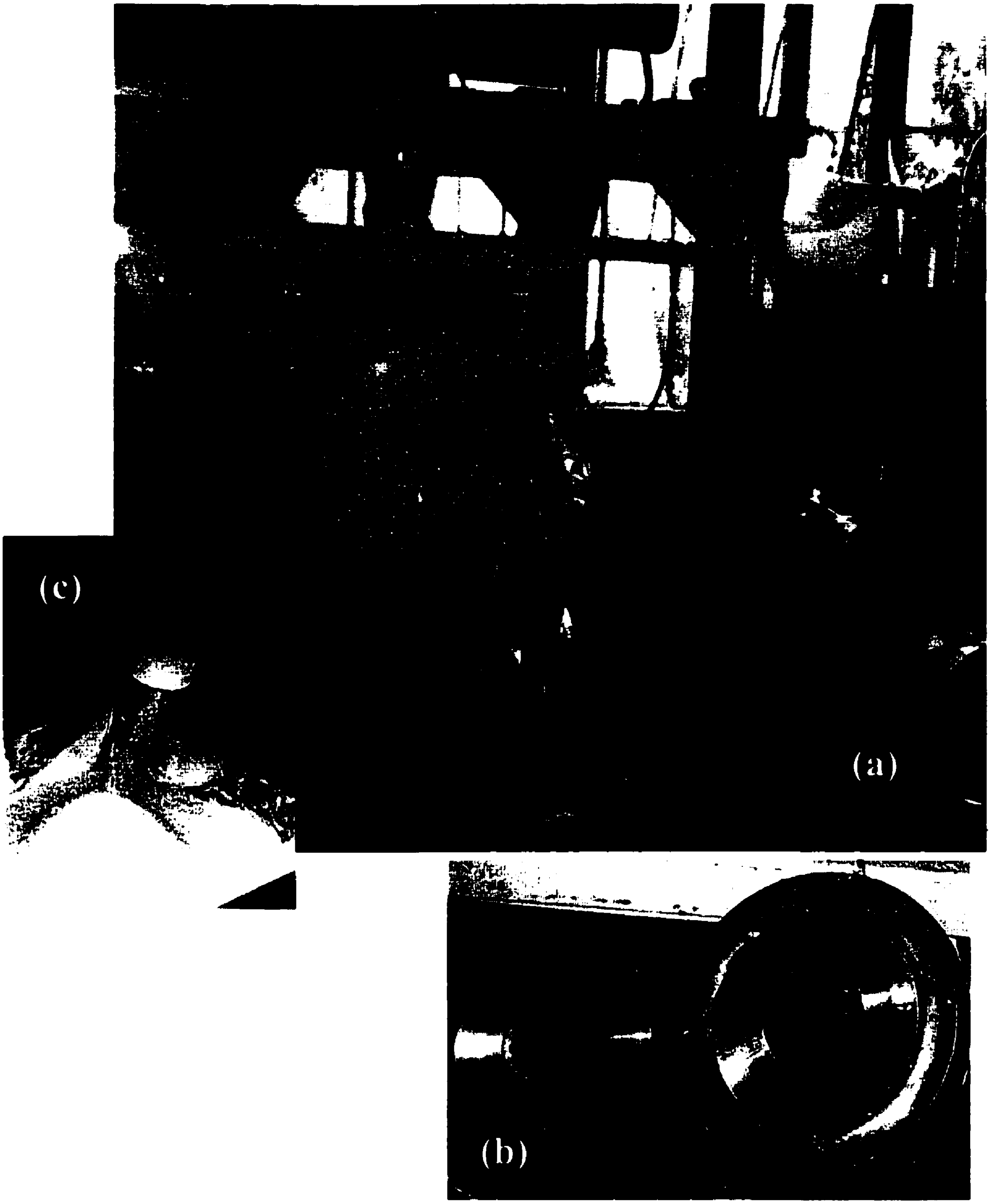


Figure 4.1: The Grinding Equipment Used To Pulverize the PP Resins
(a) Grinder: "Wedco", Model No. SE-12 SP
(b) The static and the rotating grinding plates
(c) The obtained PP powder

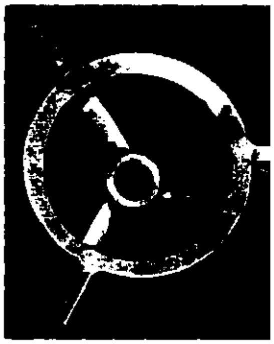


Figure 4.2: The Hi
(a) Hig
(b) The

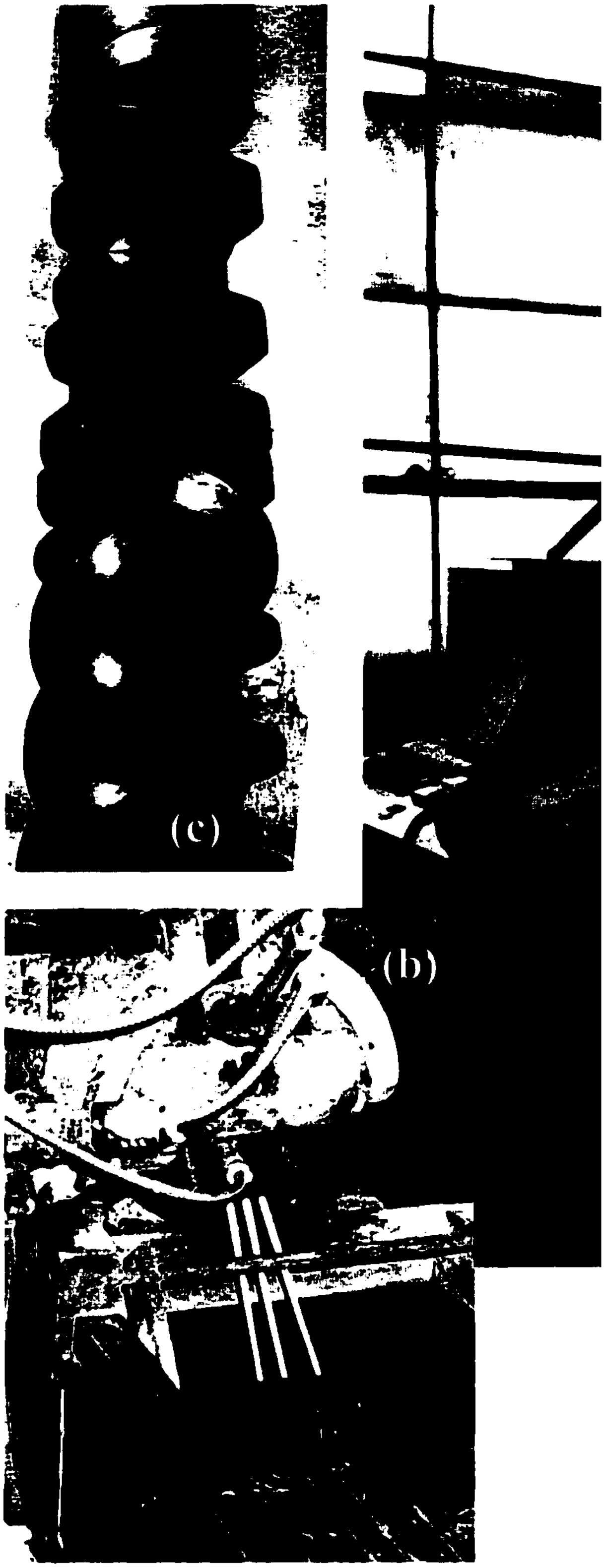


Figure 4.3: The Intermeshing Co-rotating T

(a) Intermeshing co-rotating twi
Type: ZSK-30
(b) The extrudate exiting the ext
(c) Typical twin-screw extruder

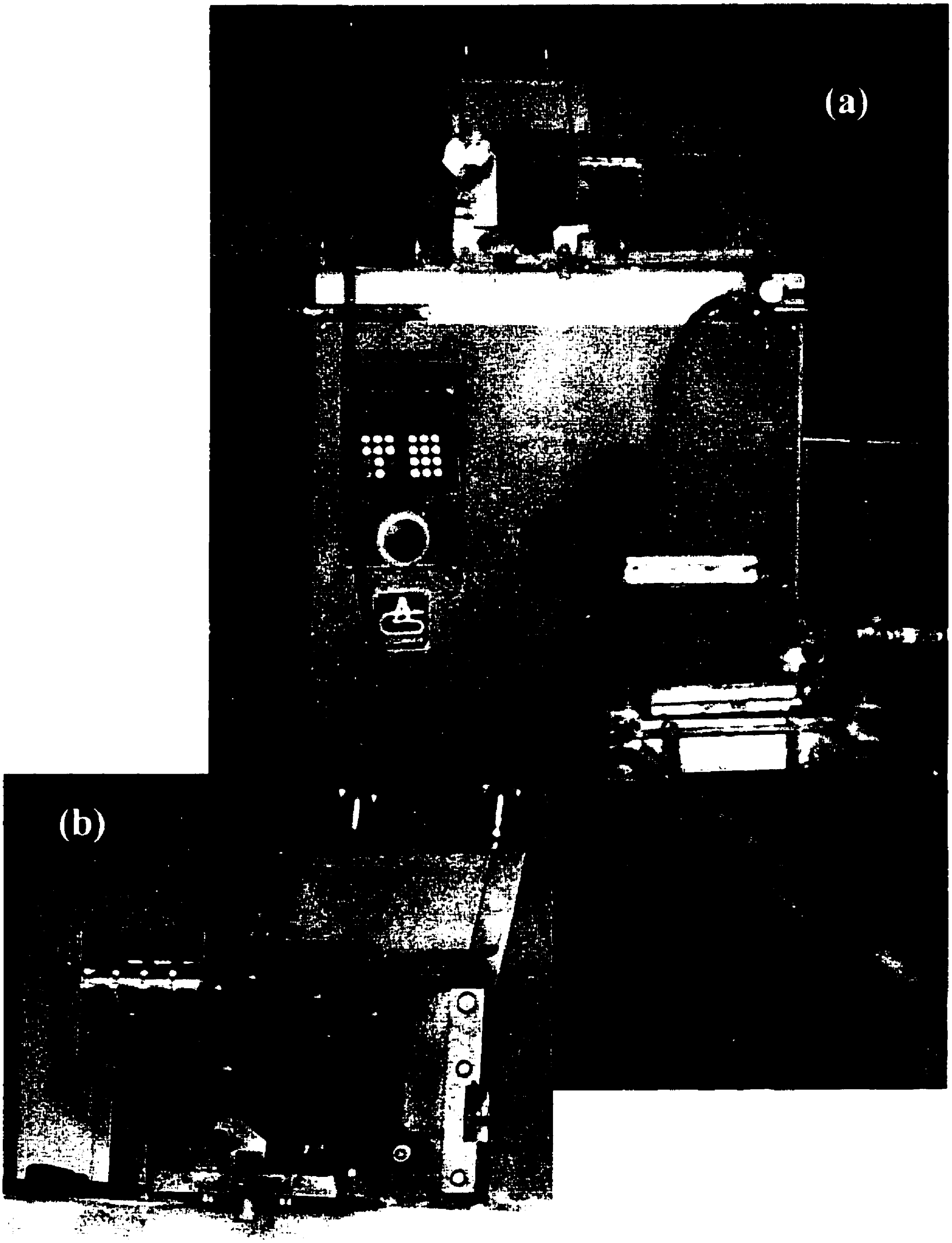
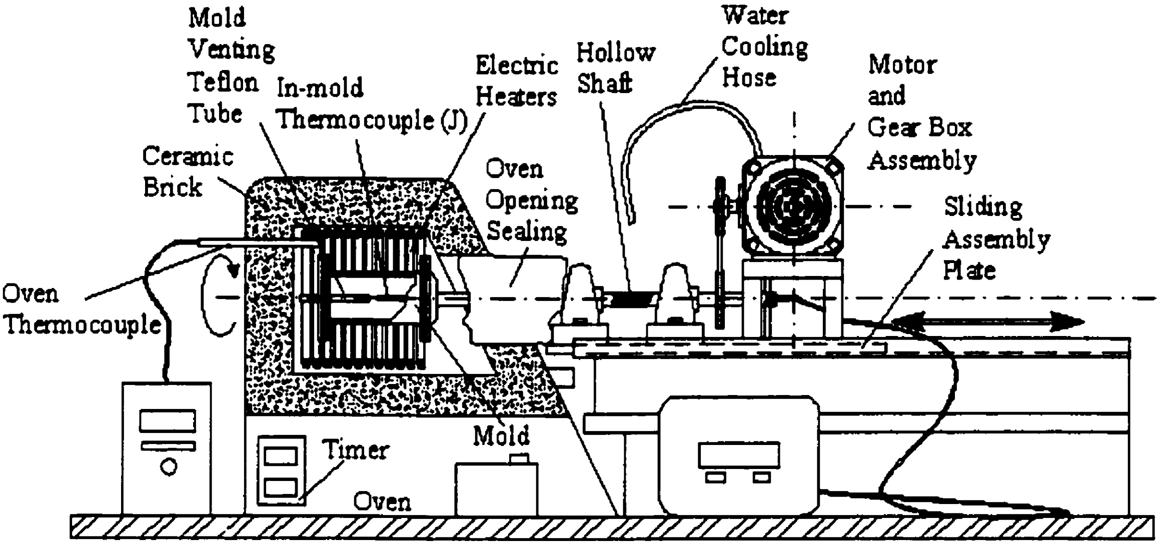


Figure 4.4: The Pelletizer Used

(a) Pelletizer: "Automatic Apparate Machinenebau", Type: ASG 100
(b) View of the pelletizer's cutting head entrance

(a) Mold Heating Step



(b) Mold Cooling Step

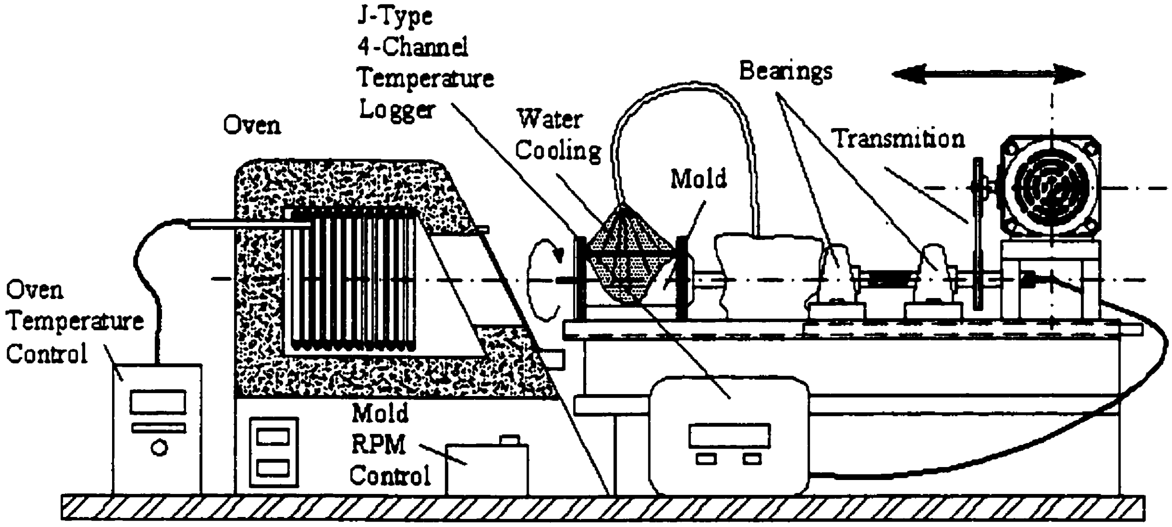


Figure 4.5: Schematic of the Uni-axial Lab-scale Rotational Foam Molding Machine Used for Rotational Foam Molding Experimentation

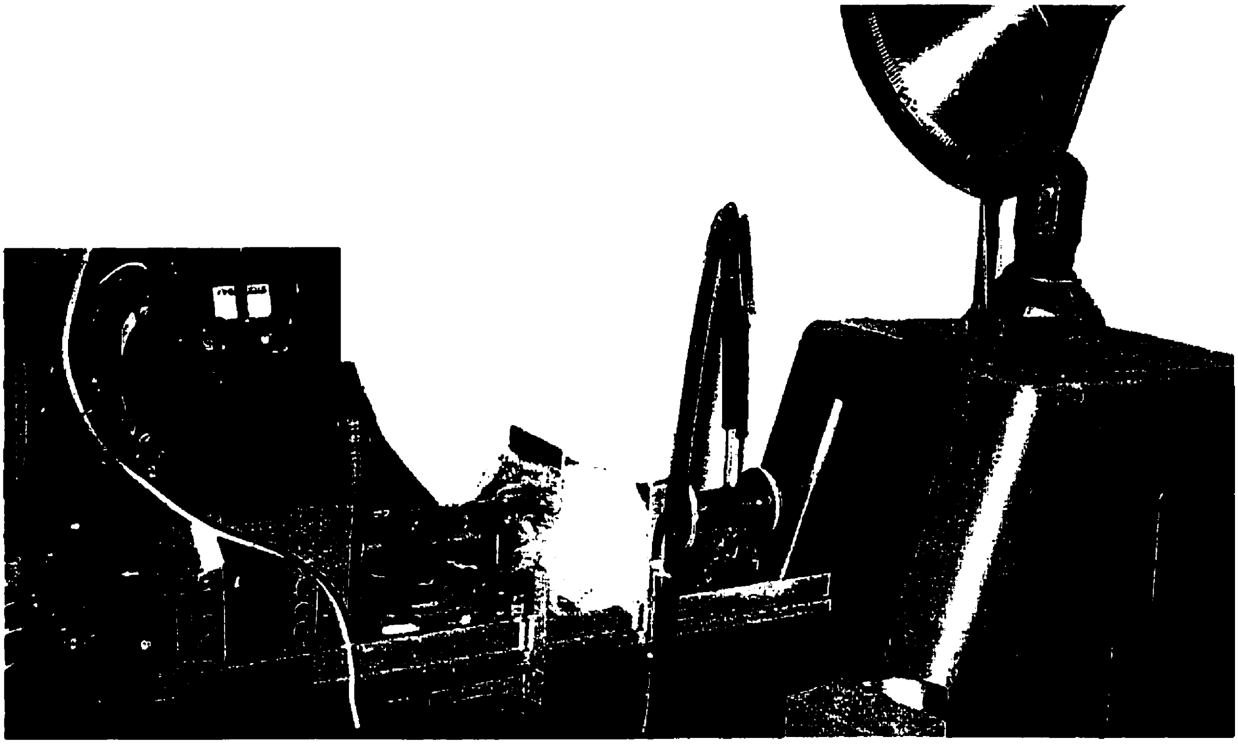


Figure 4.6: The Lab-scale Uni-axial Rotational Molding Machine Used for Rotational Foam Molding Experimentation

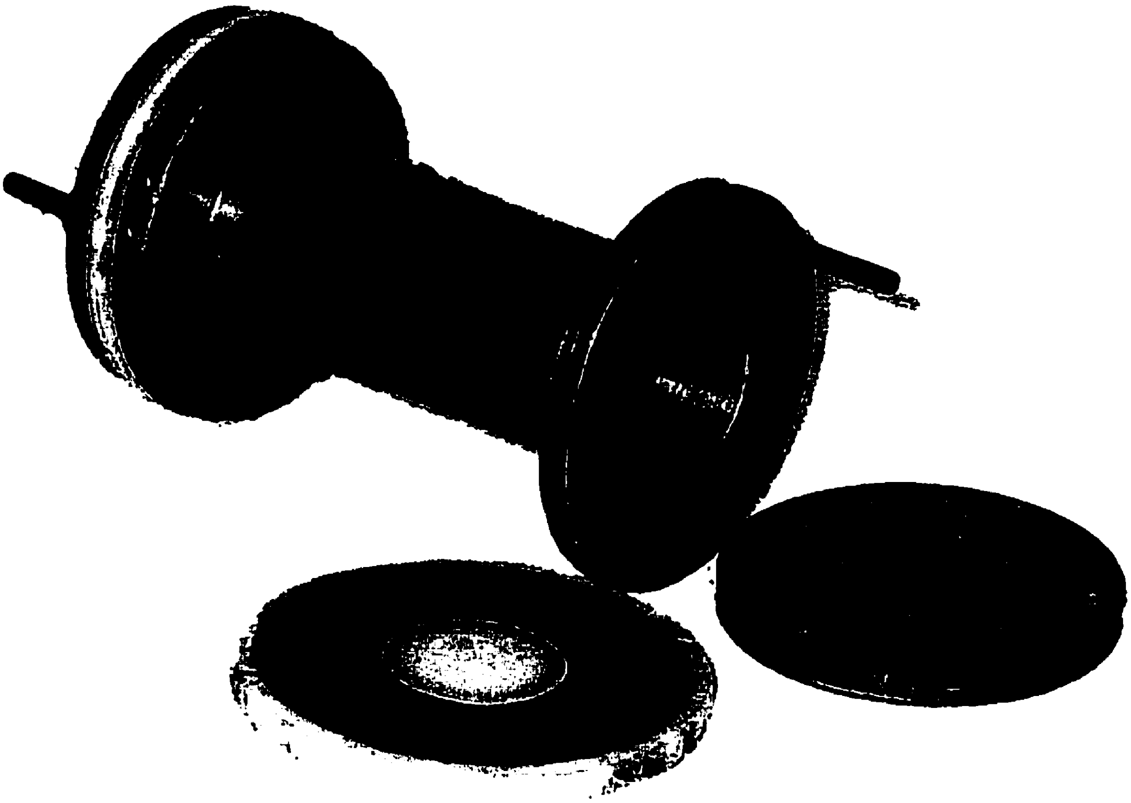


Figure 4.7: The Cylindrical (4" × 1.25") Mold
Used for Rotational Foam Molding Experimentation in Open Position

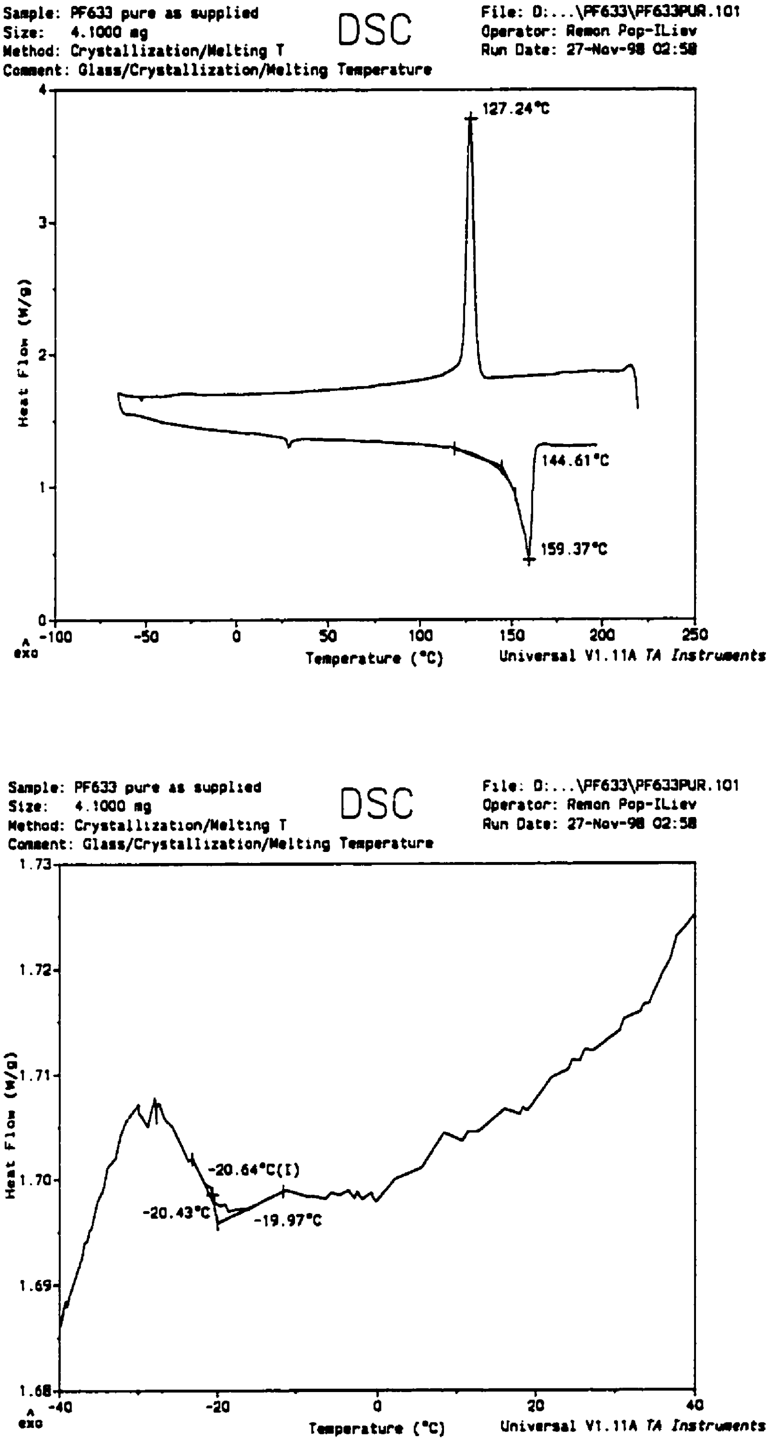


Figure 4.8: Transition Temperatures of PF633 (pure as supplied) at 10 °C/min by DSC Thermal Analysis: T_M = 159.4 °C, T_C = 127.2 °C and T_G = -20.4 °C

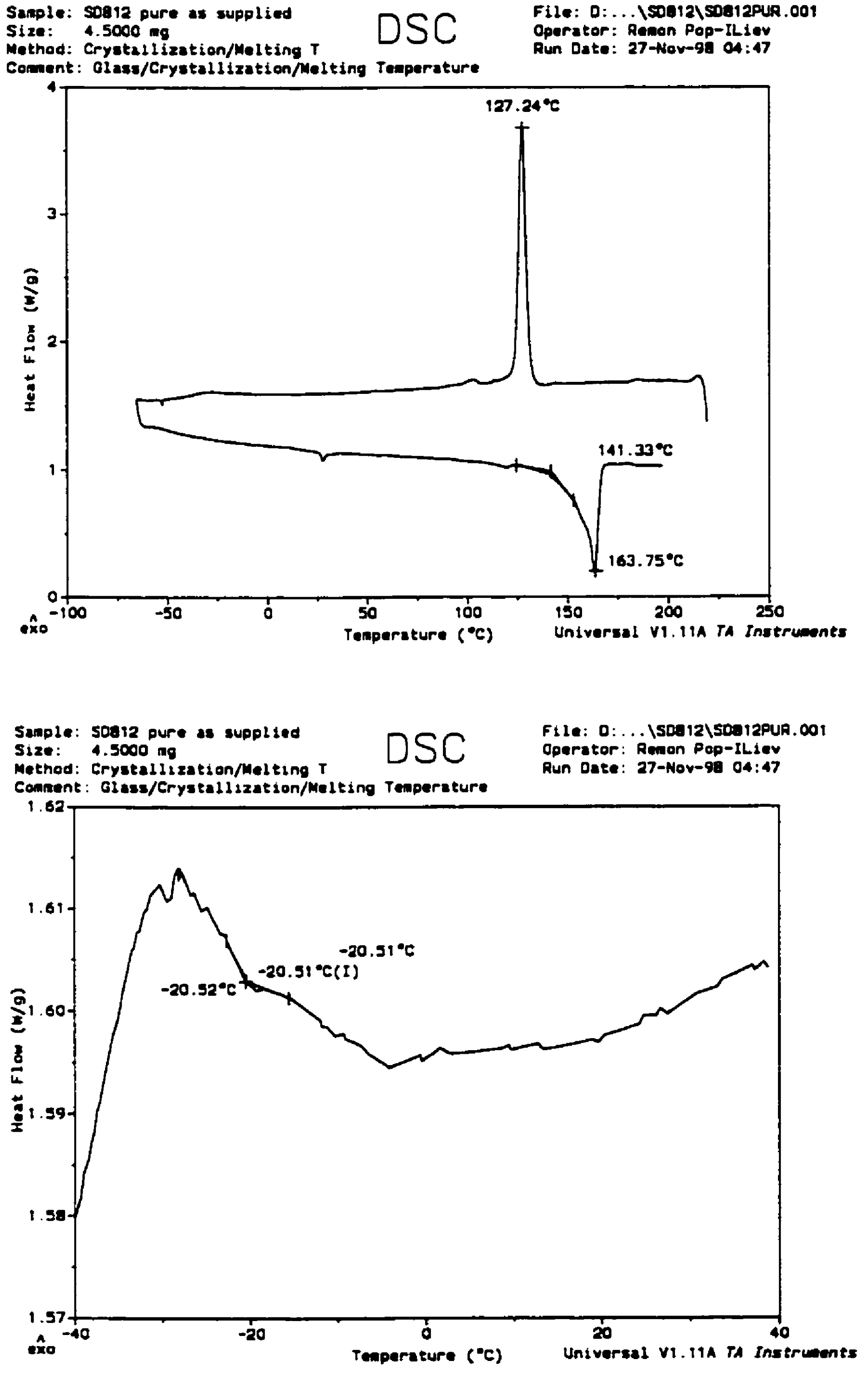


Figure 4.9: Transition Temperatures of SD812 (pure as supplied) at 10 °C/min by DSC Thermal Analysis: T = 163.8 °C, T_C = 127.2 °C and T_G = -20.5 °C

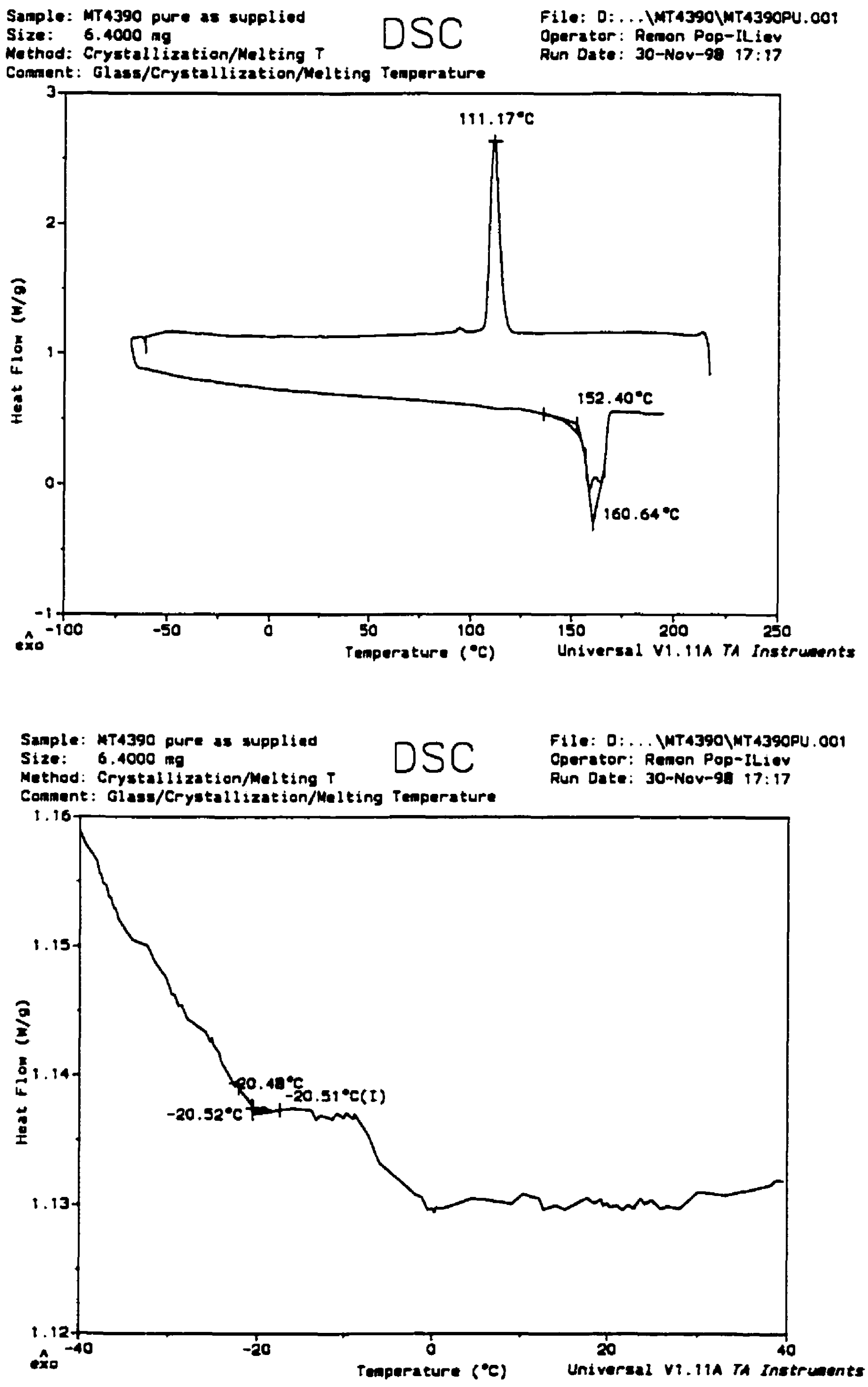


Figure 4.10: Transition Temperatures of MT4390 (pure as supplied) at 10 °C/min by DSC Thermal Analysis: T_M = 160.6 °C, T_C = 111.2 °C and T_G = -20.5 °C

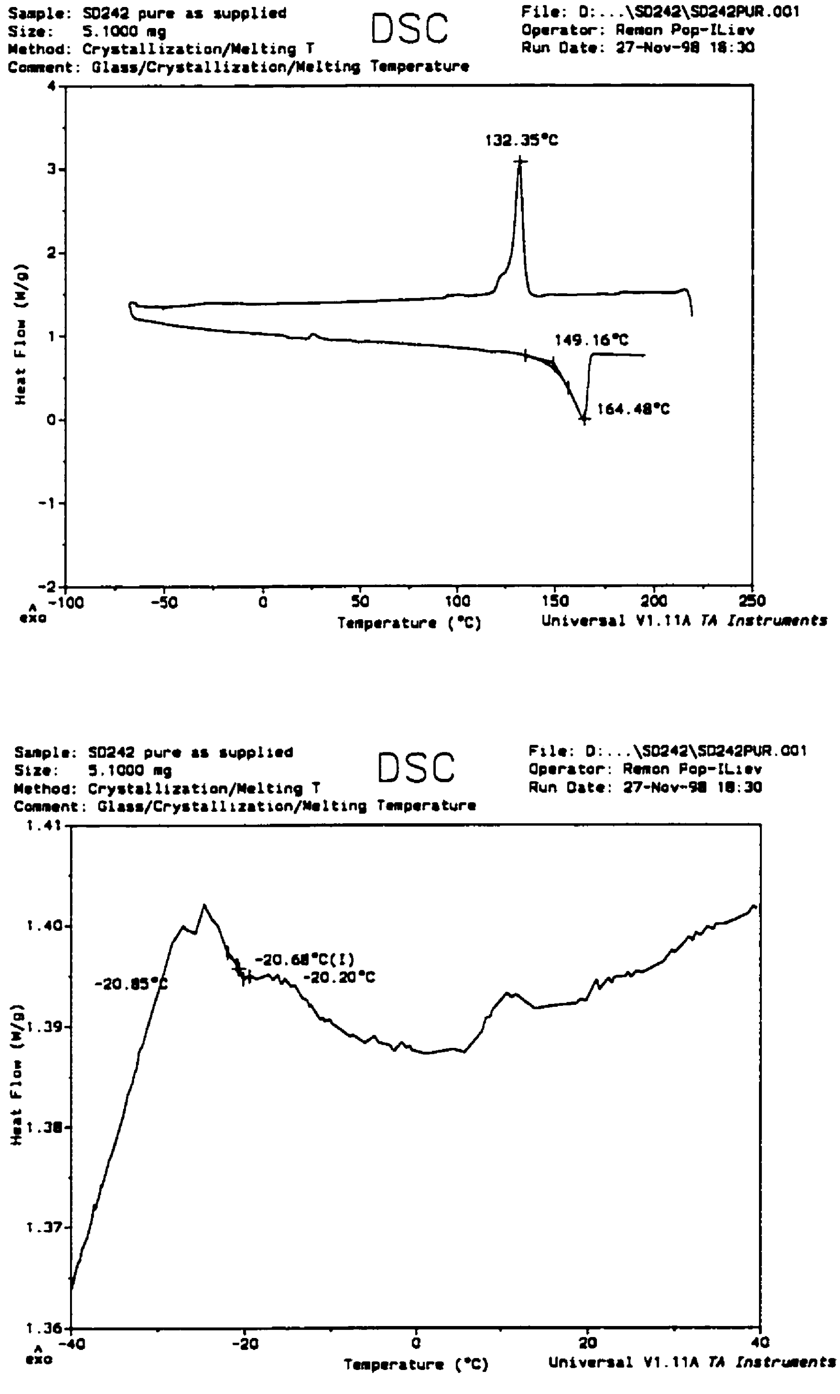


Figure 4.11: Transition Temperatures of SD242 (pure as supplied) at 10 °C/min by DSC Thermal Analysis: T_M = 164.5 °C, T_C = 132.4 °C and T_G = -20.7 °C

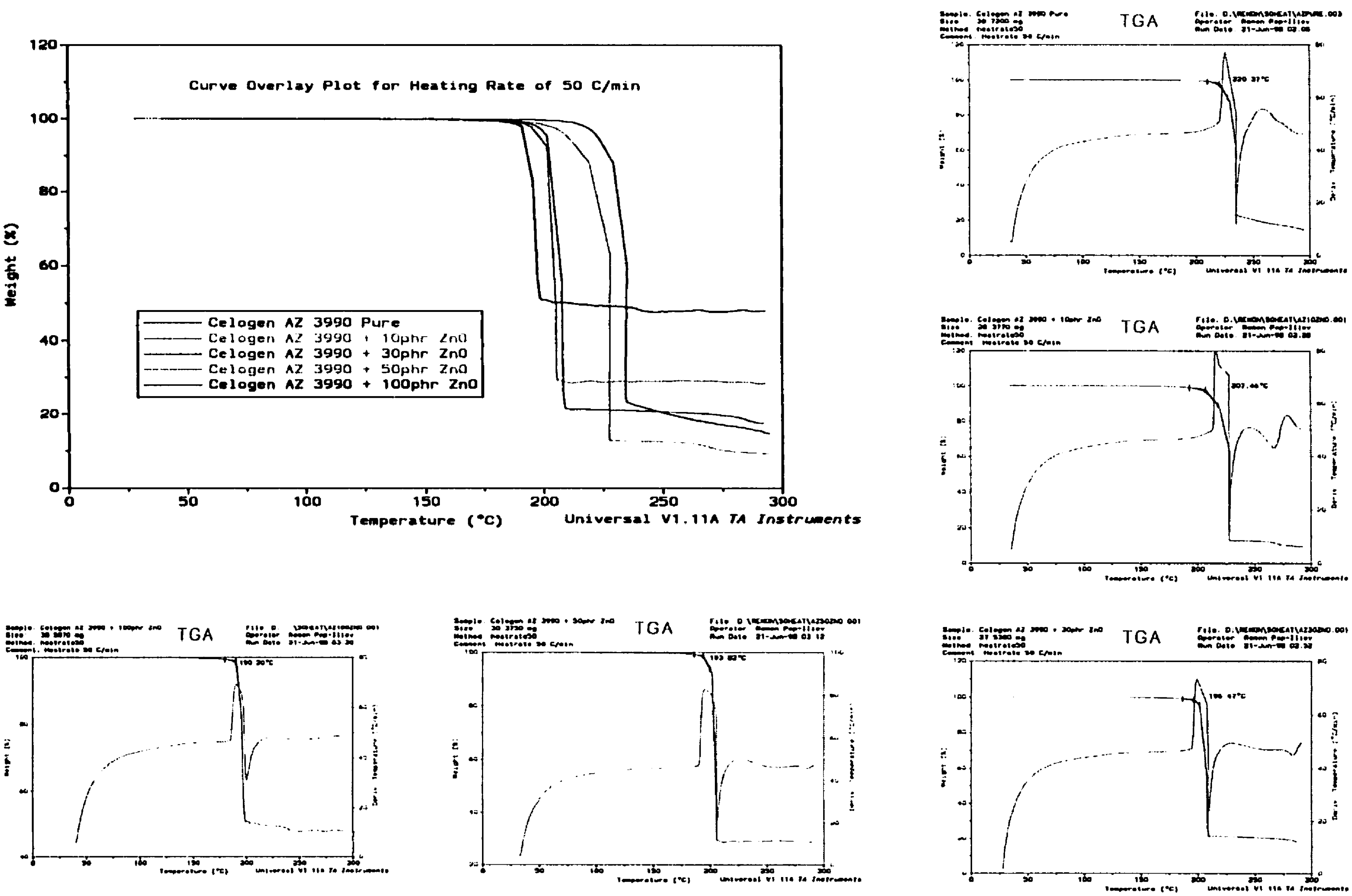


Figure 4.12: Effect of ZnO on the Decomposition Temperature of Celogen AZ-3990 at a Heating Rate of 50 °C/min

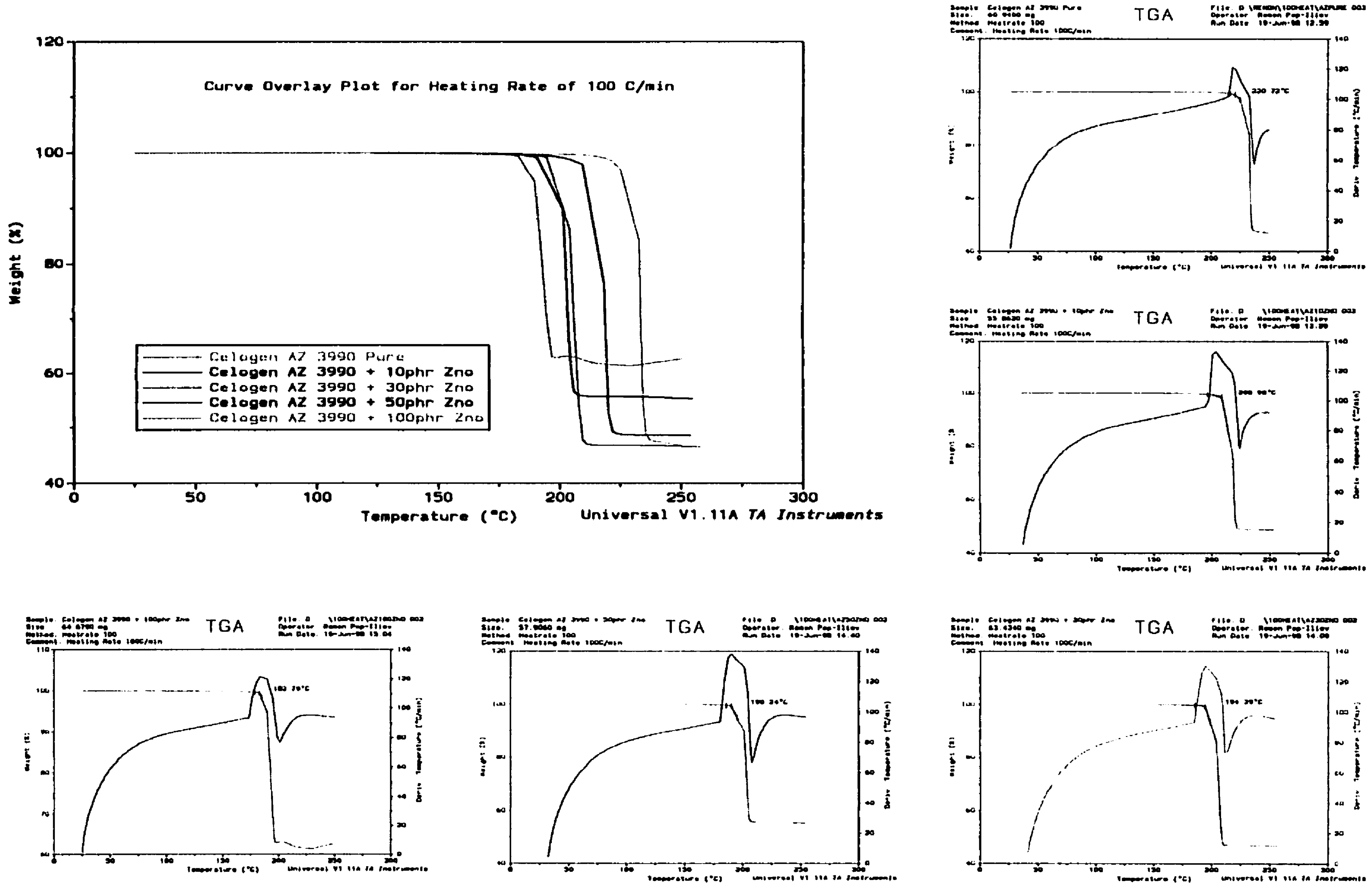


Figure 4.13: Effect of ZnO on the Decomposition Temperature of Celogen AZ-3990 at a Heating Rate of 100 °C/min

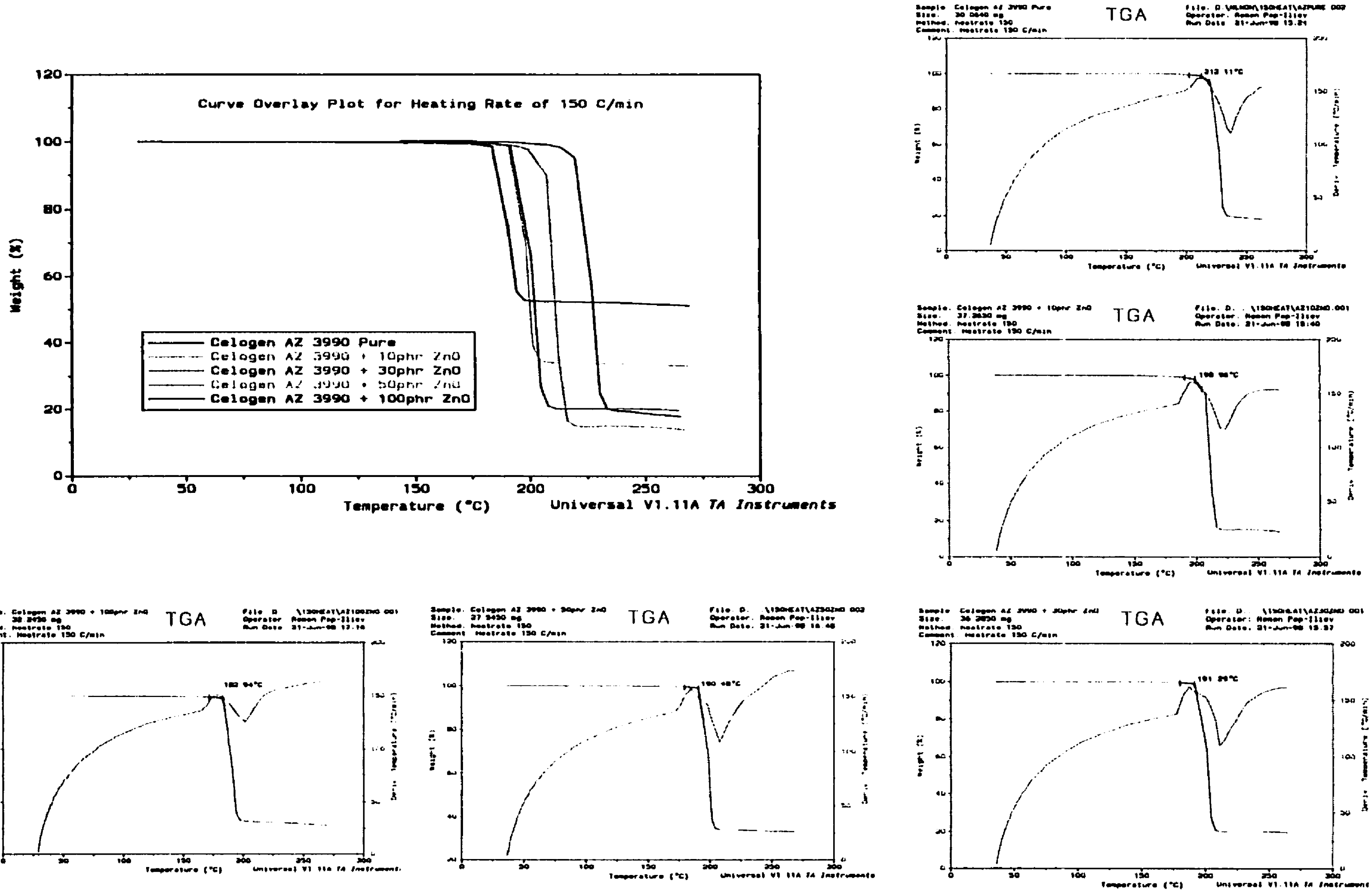


Figure 4.14: Effect of ZnO on the Decomposition Temperature of Celogen AZ-3990 at a Heating Rate of 150 °C/min

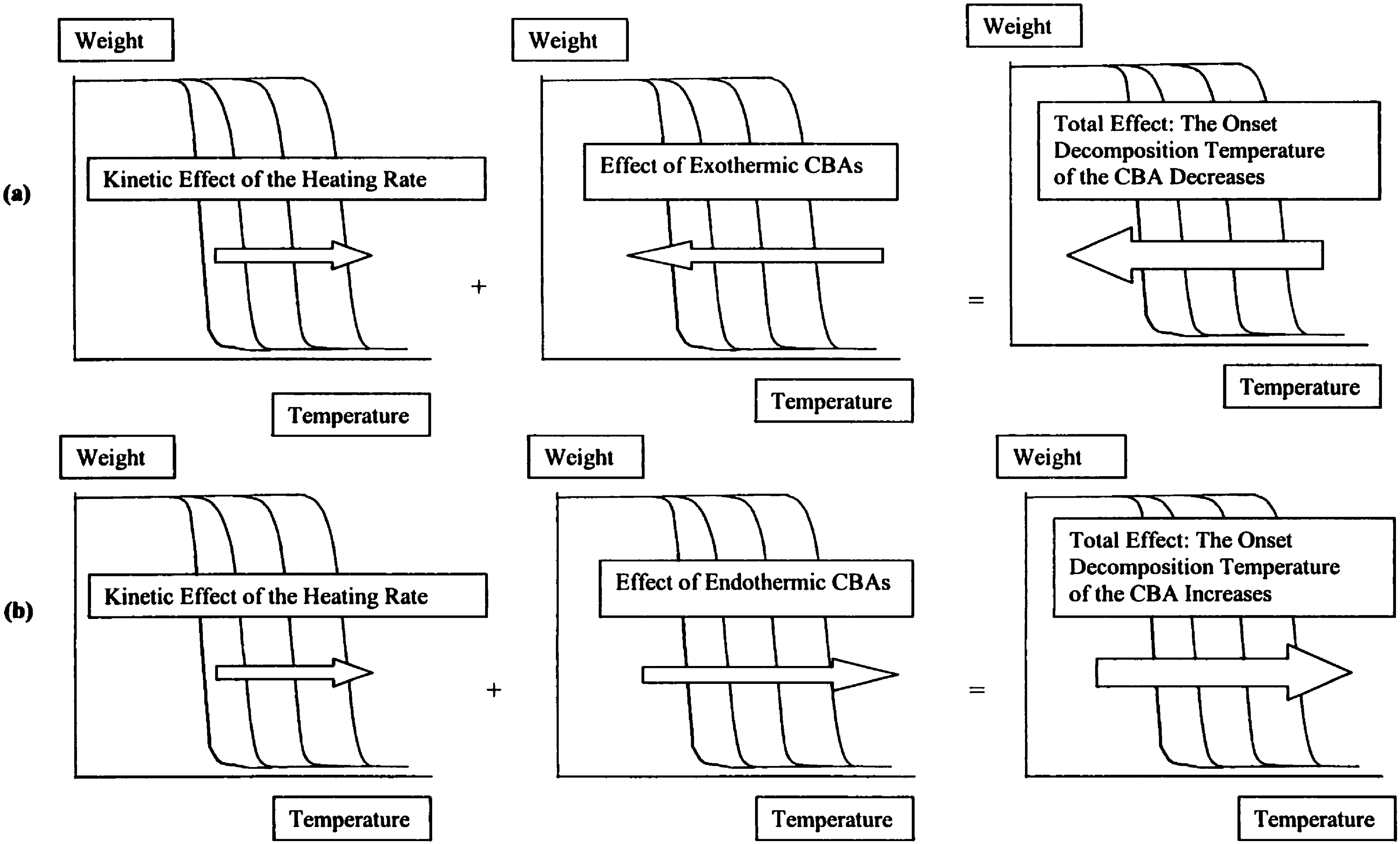


Figure 4.15: Effect of the Heating Rate on the CBA Onset Decomposition Temperature

(a) Exothermic CBA (Celogen AZ-3990)
(b) Endothermic CBA

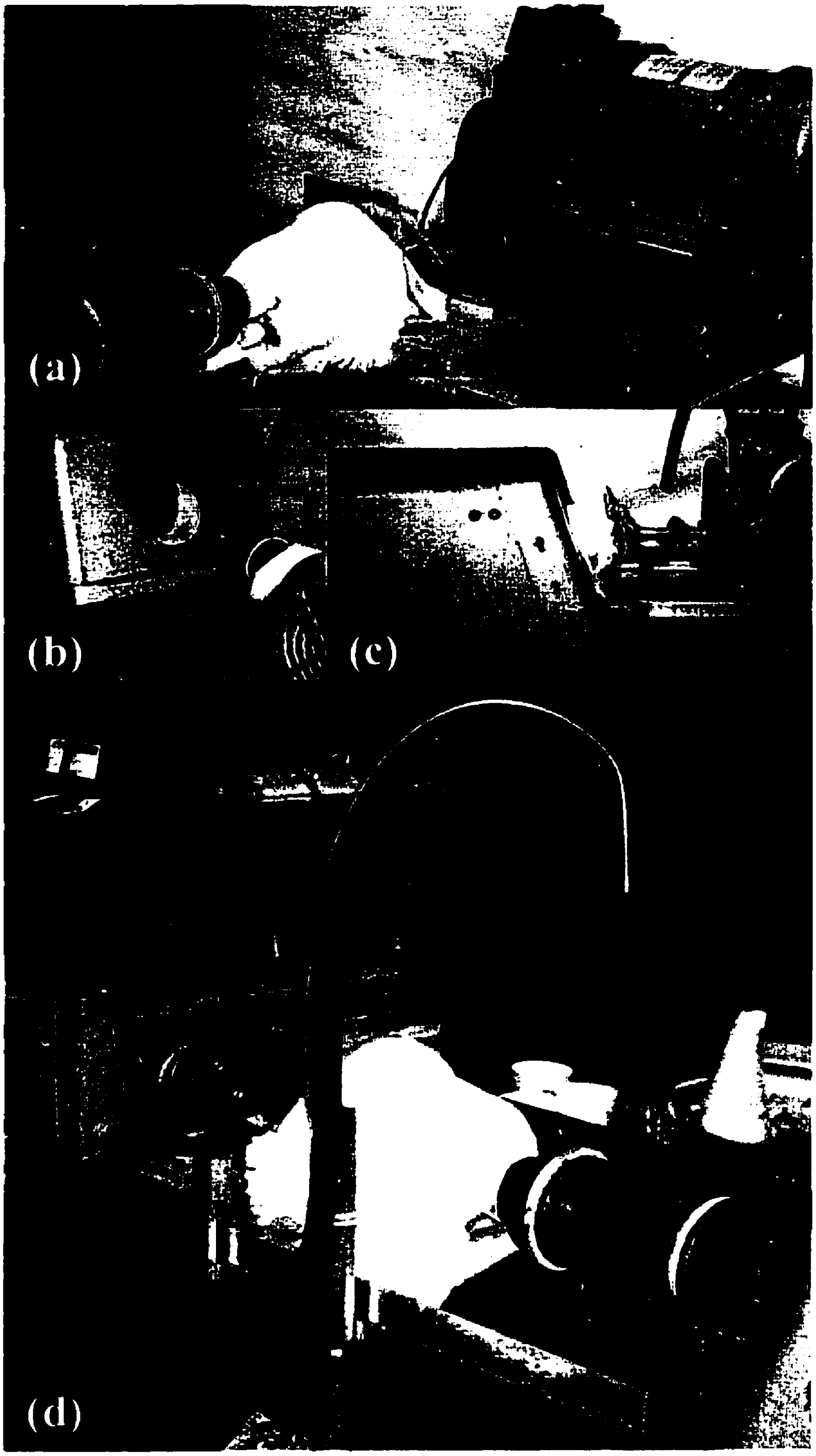
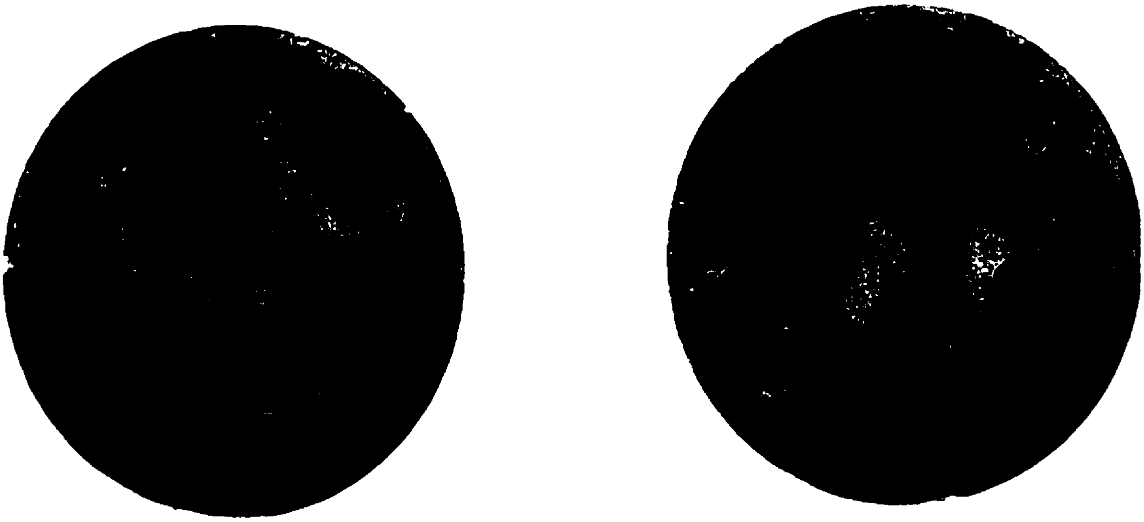


Figure 4.16: Various Stages of a Rotational Foam Molding Experiment

(a) Charged mold mounted on the rotating shaft
(b) Mold insertion into oven
(c) Rotational foam molding
(d) Mold cooling

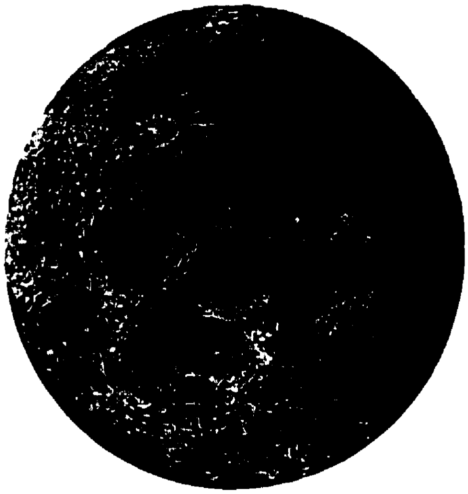
(P101P) t_{proc} = 11 min

(P101P) t_{proc} = 12 min



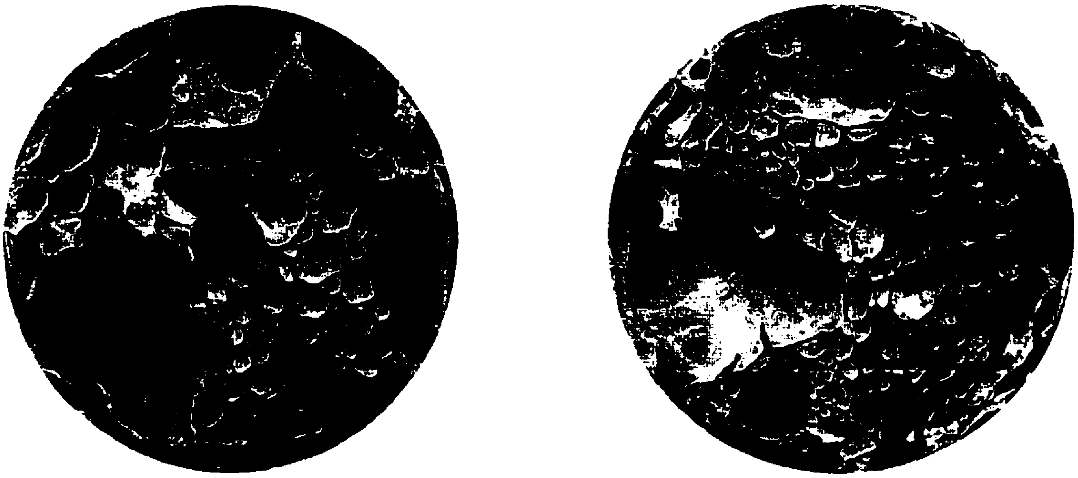
(P101P) t_{proc} = 13 min

(P101P) t_{proc} = 14 min



(P101P) t_{proc} = 15 min

Figure 4.17: Foam Morphologies of P101P (6x6; Toven = 300 °C) Magnification = 200%



(P303P) t_{proc} = 12 min

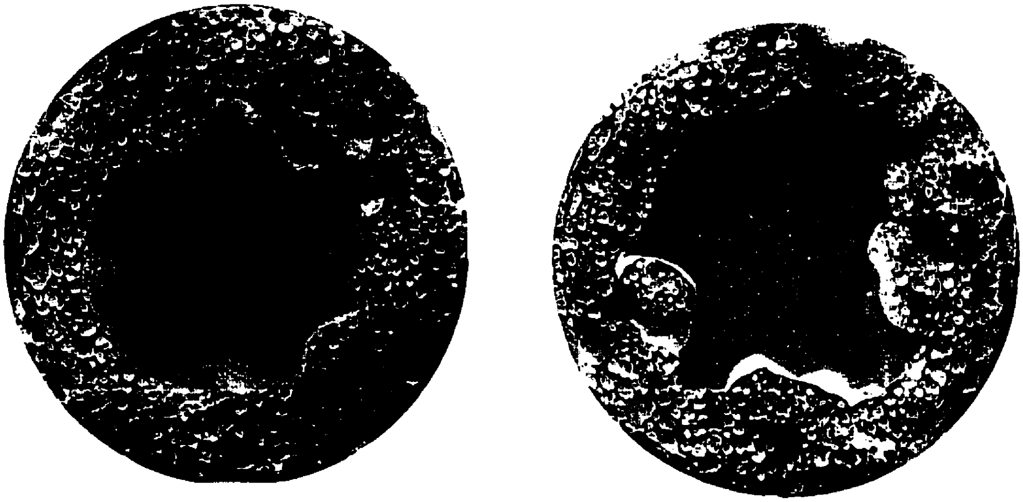
(P303P) t_{proc} = 12.5 min

(P303P) t_{proc} = 13 min

(P303P) t_{proc} = 13.5 min

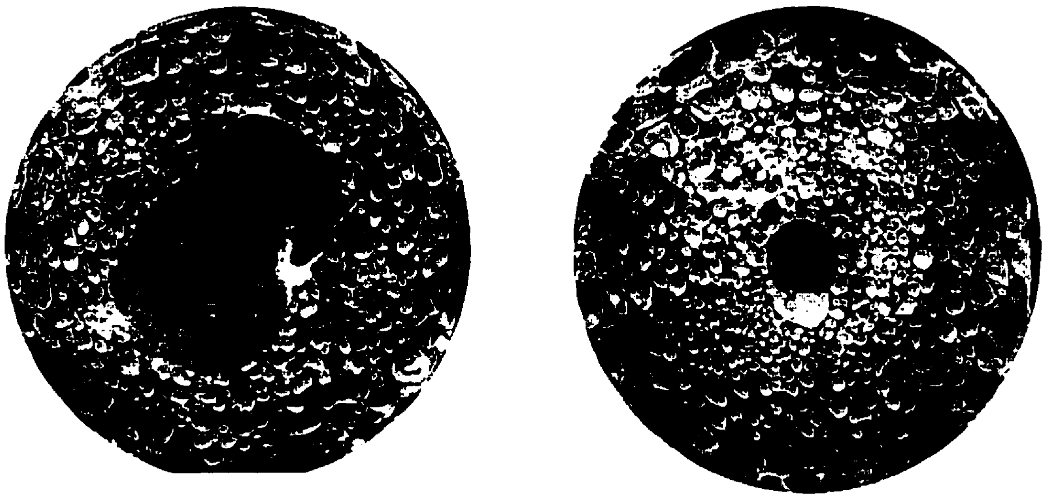
(P303P) t_{proc} = 14 min

Figure 4.18: Foam Morphologies of P303P (6x6; Toven = 300 °C) Magnification = 200%



(P401P) $t_{proc} = 9$ min

(P401P) $t_{proc} = 9.5$ min



(P401P) $t_{proc} = 10$ min

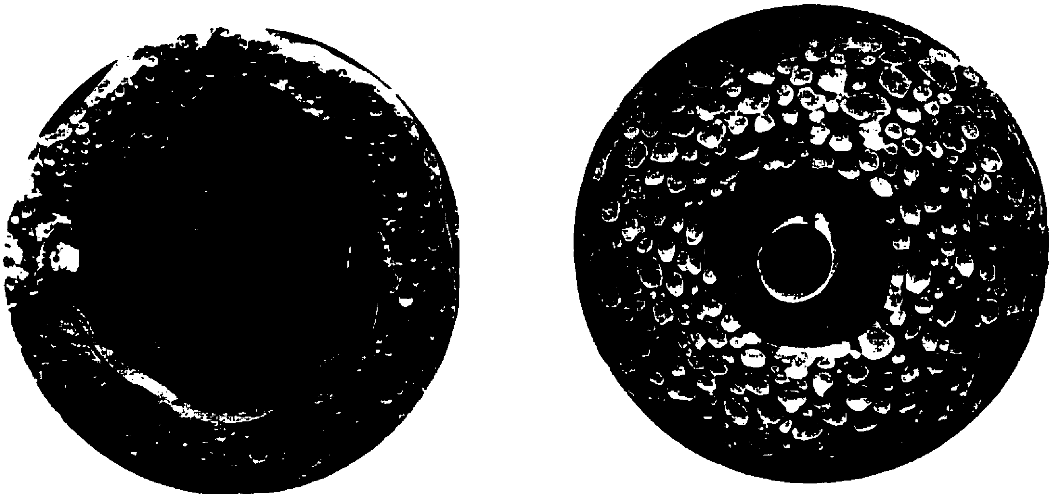
(P401P) $t_{proc} = 10.5$ min

(P401P) $t_{proc} = 11$ min

Figure 4.19: Foam Morphologies of P401P (6x6; Toven = 300 °C) Magnification = 200%

(P404P) t_{proc} = 12 min

(P404P) t_{proc} = 13 min

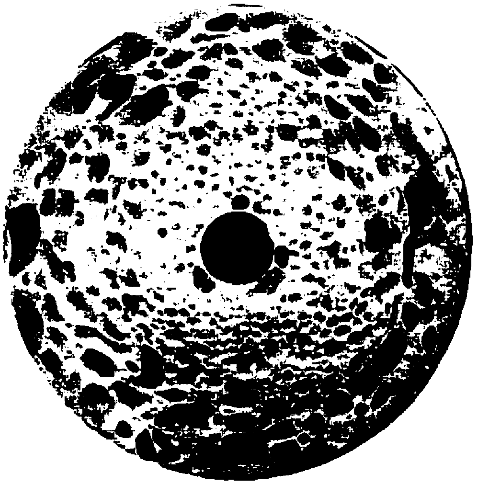


(P404P) t_{proc} = 14 min

(P404P) t_{proc} = 14.5 min

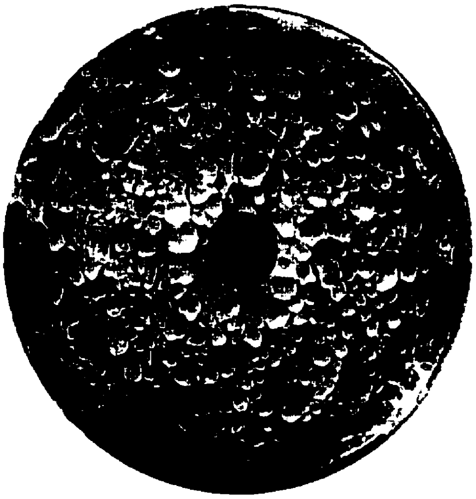
(P404P) t_{proc} = 16 min

**Figure 4.20: Foam Morphologies of P404P (3x3; Toven = 300 °C)
Magnification = 200%**

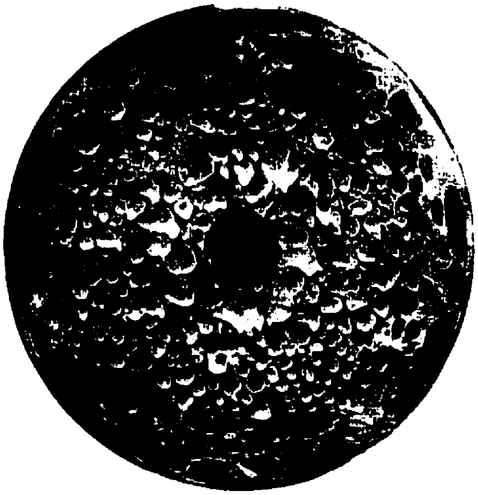


(P403P) t_{proc} = 14 min

(P403P) t_{proc} = 15min



(P403P) t_{proc} = 16 min



(P403P) t_{proc} = 17min

(P403P) t_{proc} = 18min

**Figure 4.21: Foam Morphologies of P403P (6x3; Toven = 300 °C)
Magnification = 200%**

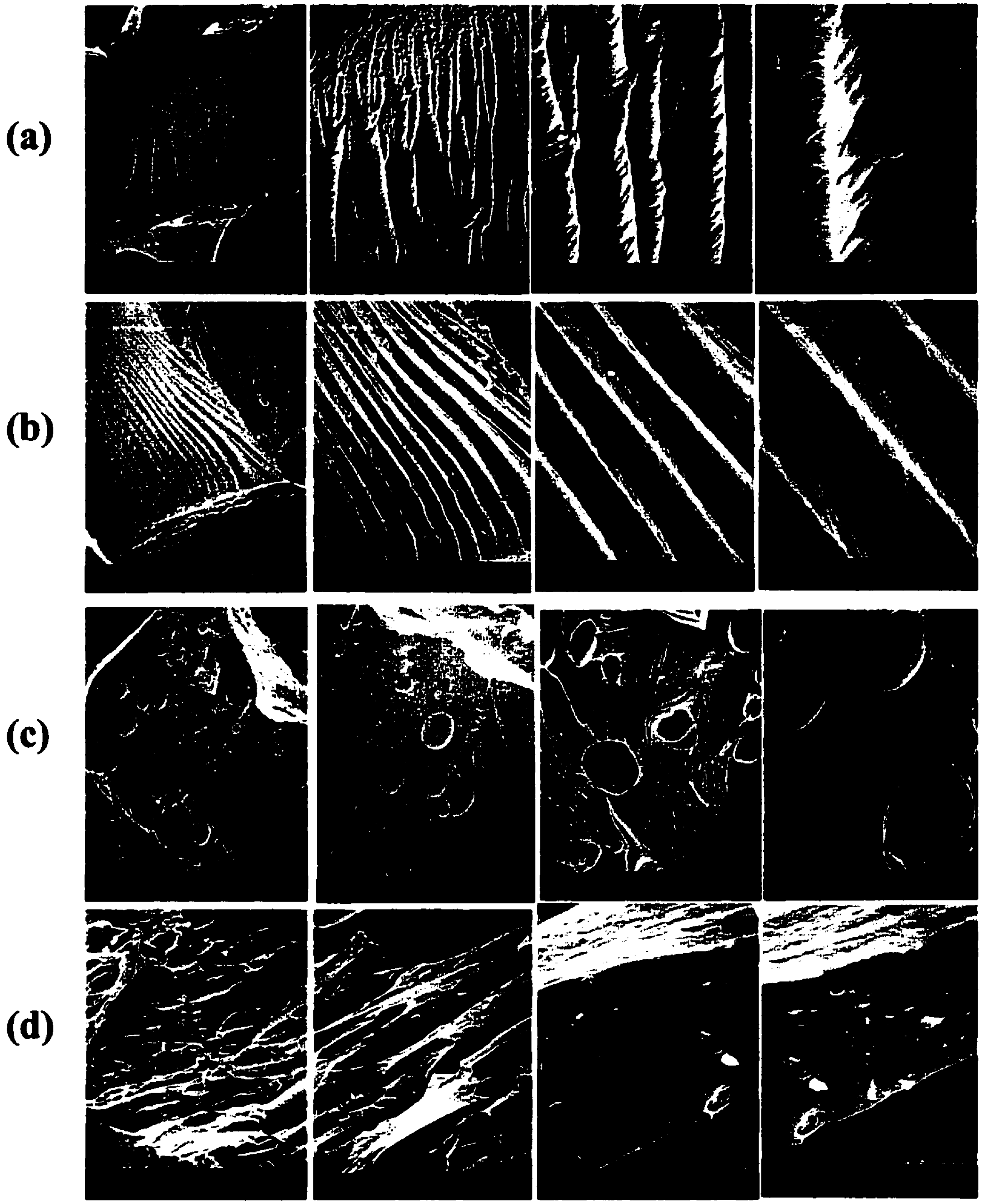


Figure 5.1: SEM Micrographs of Fractured Samples of PF633-based Compositions

(a) Pure PF633 resin as supplied
(b) Compounded pure PF633
(c) PF633+0.73% Celogen AZ-3990
(d) PF633+1.83% Celogen AZ-3990

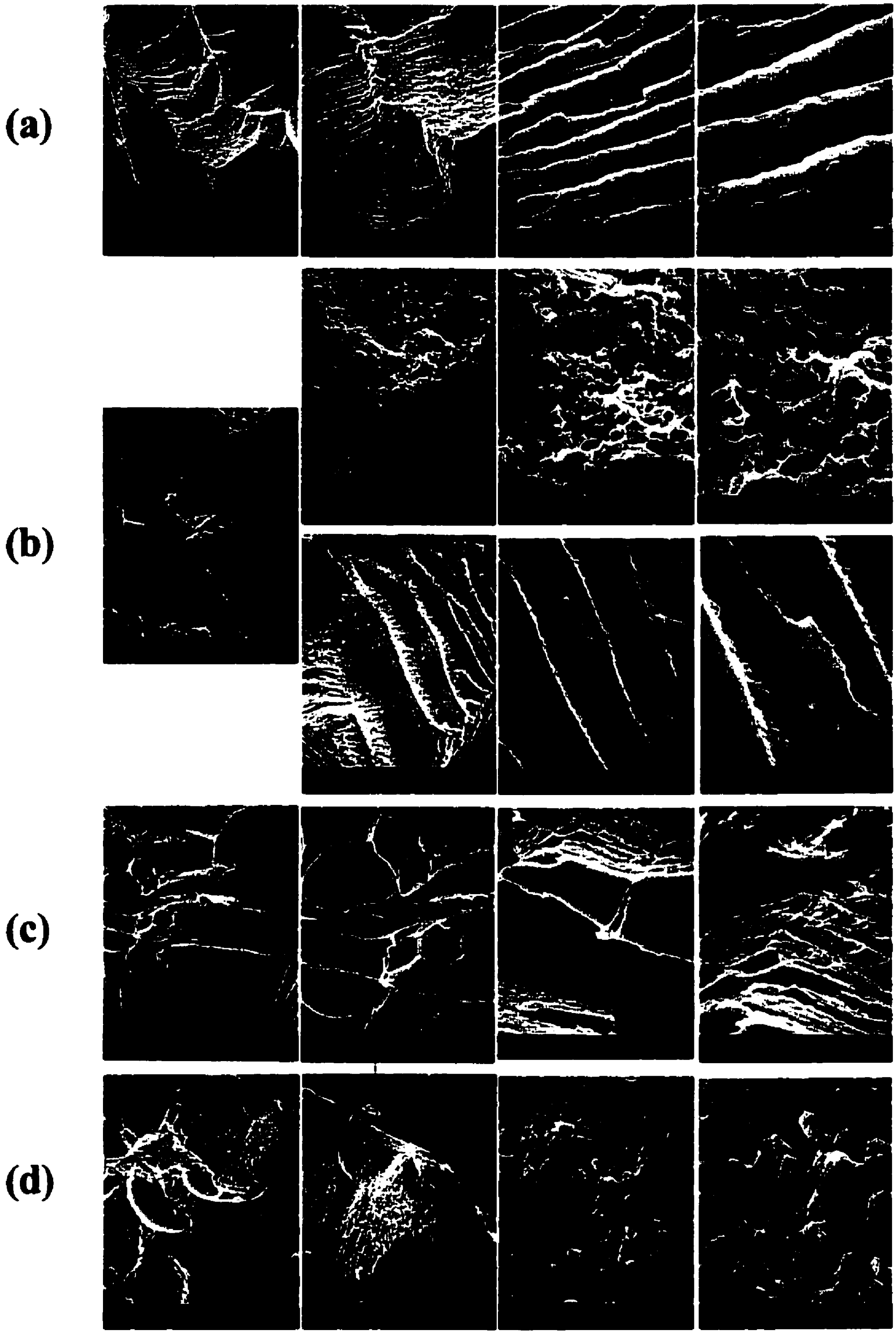


Figure 5.2: SEM Micrographs of Fractured Samples of SD812-based Compositions

(a) Pure SD812 resin as supplied
(b) Compounded pure SD812
(c) SD812+0.73% Celogen AZ-3990
(d) SD812+1.83% Celogen AZ-3990

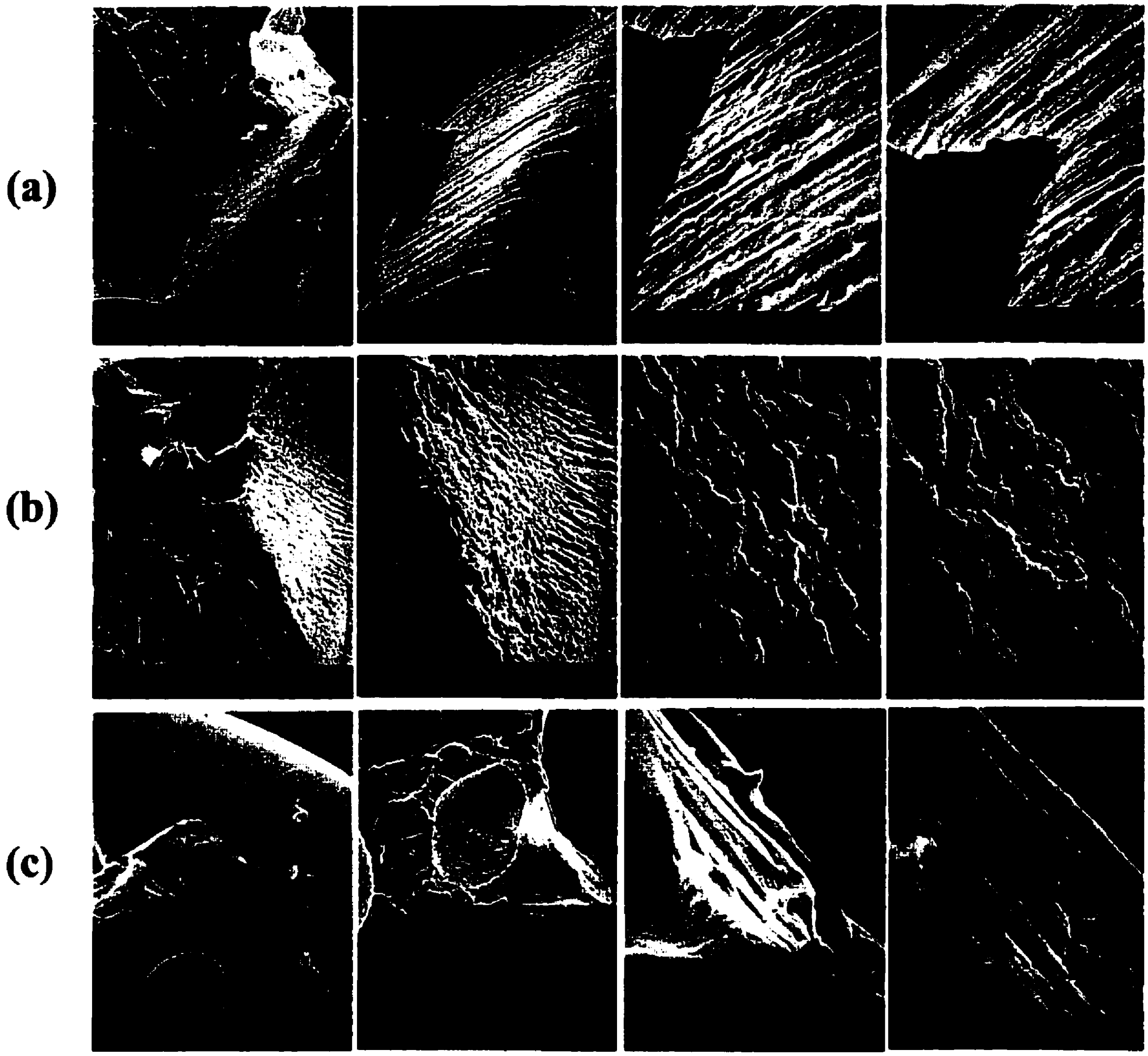


Figure 5.3: SEM Micrographs of Fractured Samples of MT4390-based Compositions
(a) Compounded MT4390
(b) MT4390+0.73% Celogen AZ-3990
(c) MT4390+1.83% Celogen AZ-3990

(Note: MT4390 was supplied in a powder form. Therefore, SEM images of the pure resin are not available.)

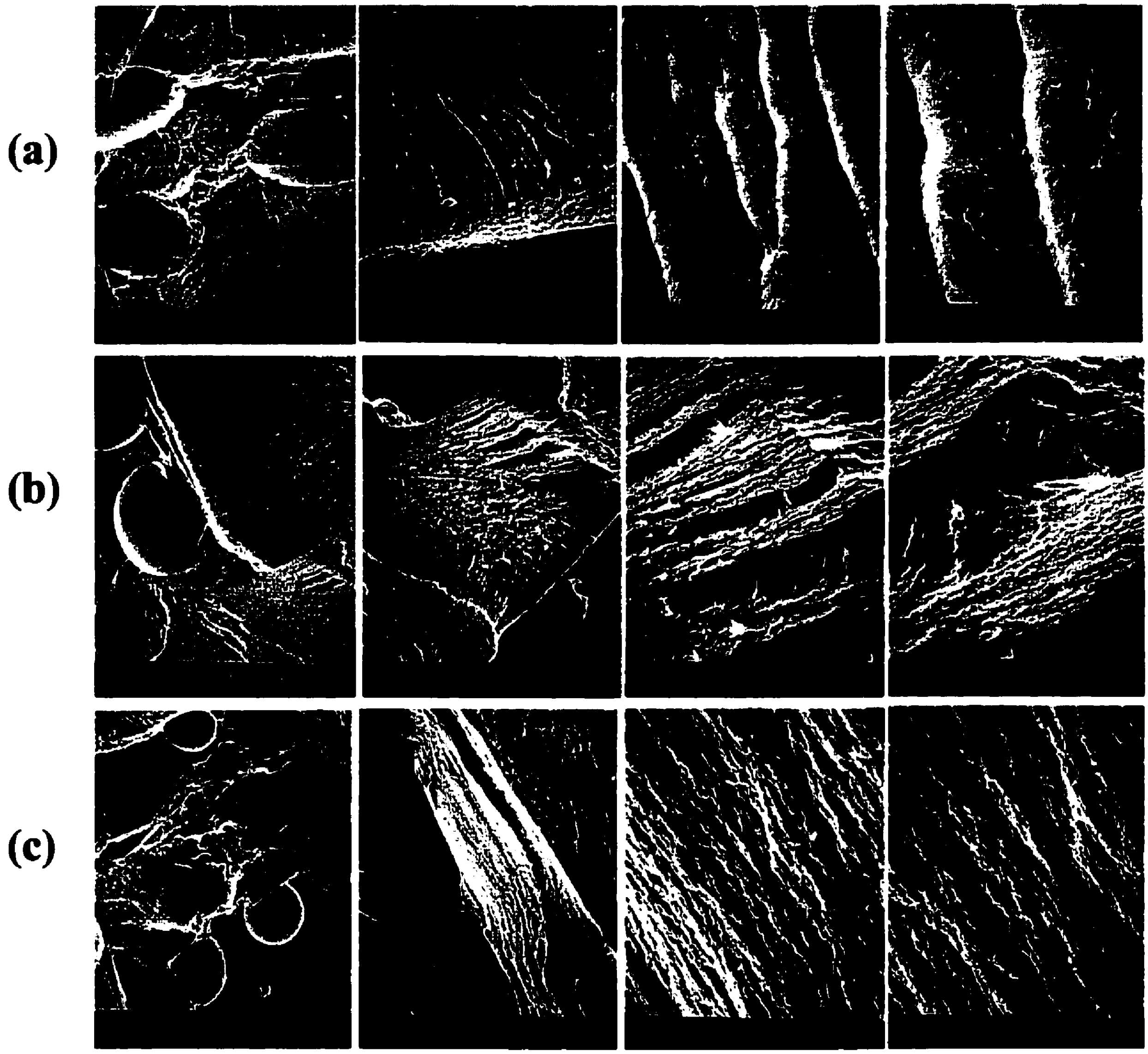


Figure 5.4: SEM Microgrphs of Fractured Samples of SD242-based Compositions
(a) Compounded SD242
(b) SD242+0.73% Celogen AZ-3990
(c) SD242+1.83% Celogen AZ-3990

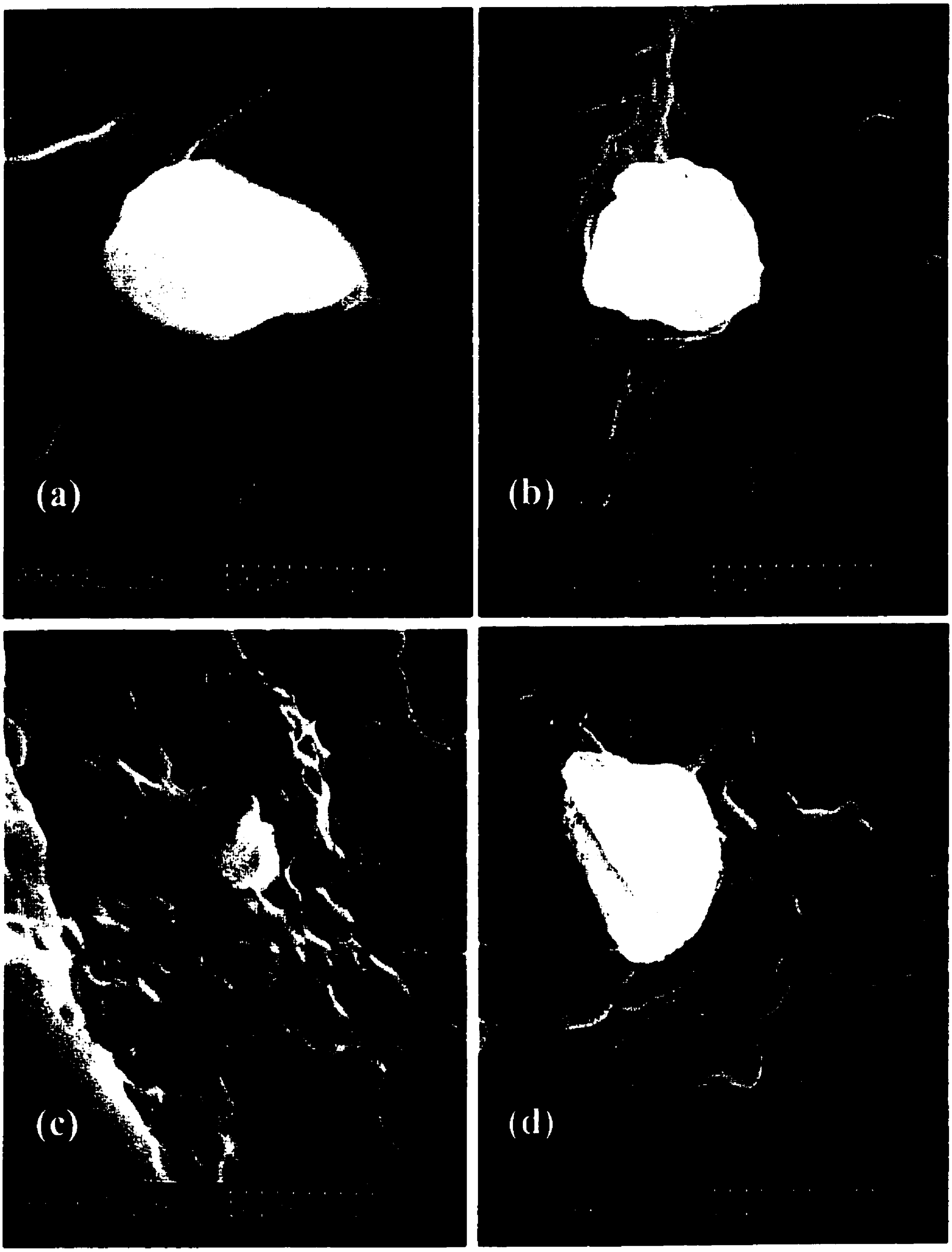


Figure 5.5: Isolated Particles of Celogen AZ-3990 in Various PP Compositions

(a) PF633
(b) SD812
(c) MT4390
(d) SD242

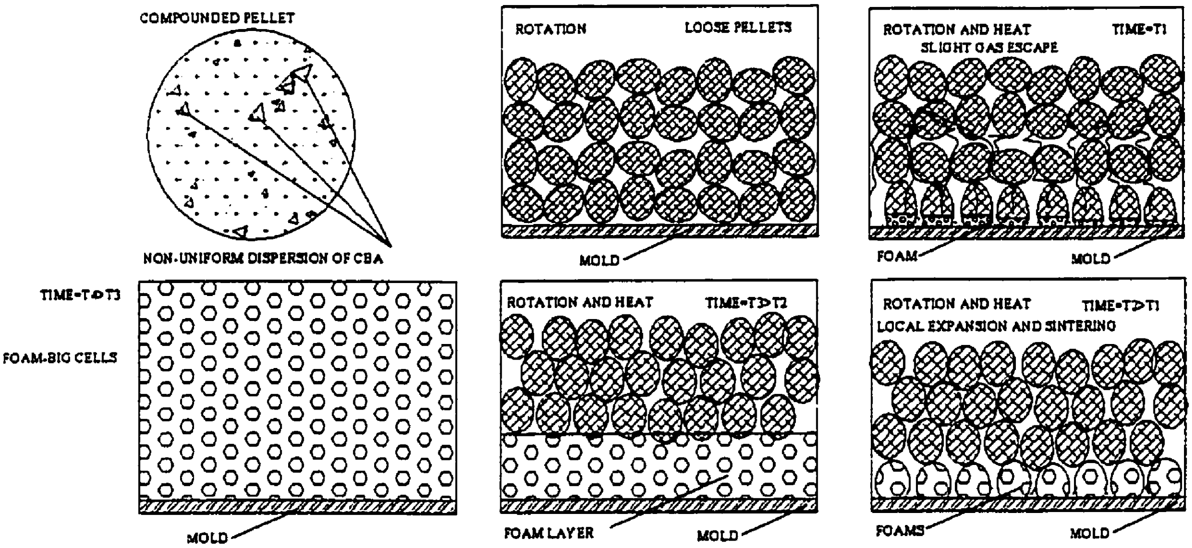
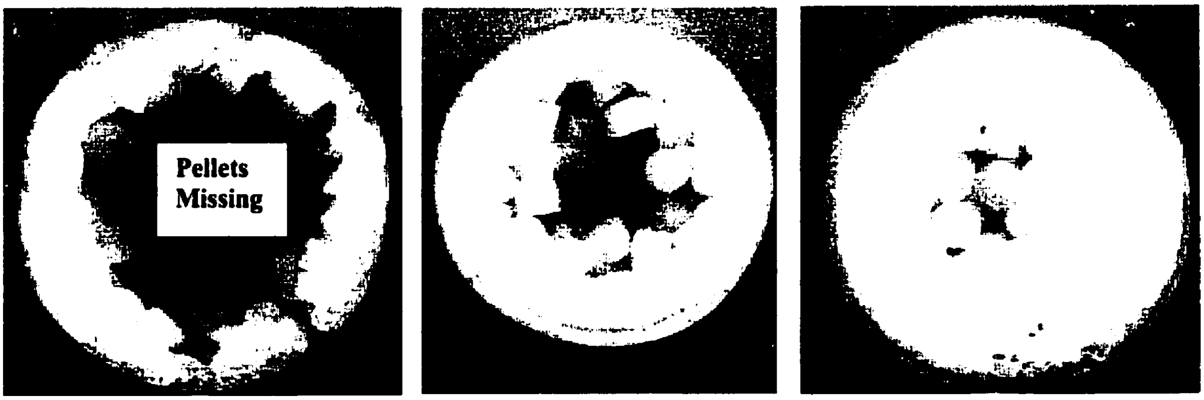


Figure 5.6: Morphology Change in Rotational Foam Molding of 3-fold Expanded Foams Using 6-fold Pellets (P101P=PF633+1.83%Celogen AZ-3990+10phr ZnO)



(t_{proc}=11 min) (t_{proc}=12 min) (t_{proc}=13 min)

**Figure 5.7: Sintering Stages in a 3-fold Experiment (T_{oven} = 300 °C)
[3-fold Experiment Using 6-fold Pellets (P101P)]**

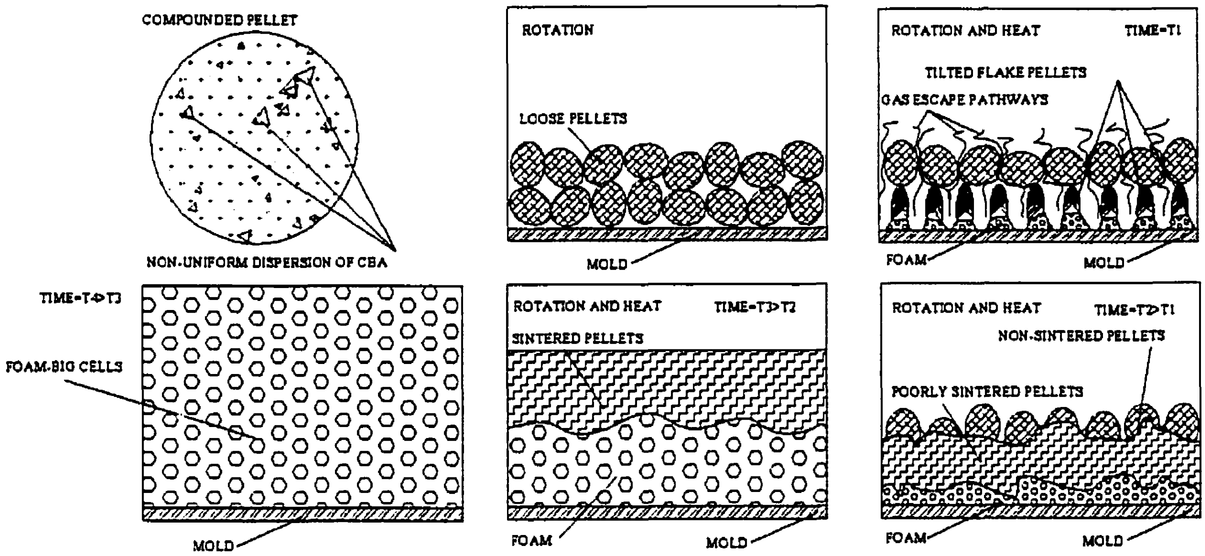
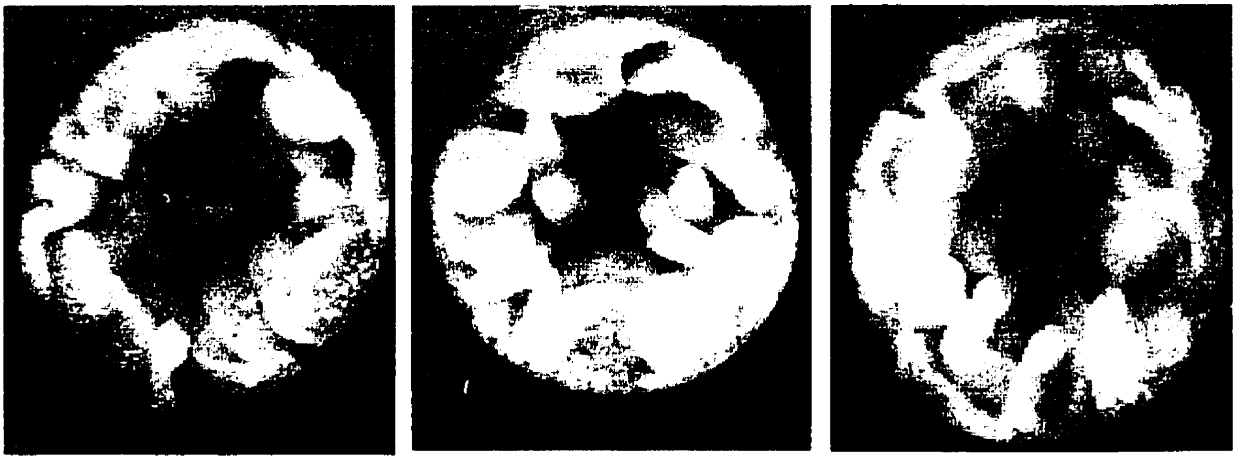


Figure 5.8: Morphology Change in Rotational Foam Molding of 6-fold Expanded Foams Using 6-fold Pellets (P101P=PF633+1.83%Celogen AZ-3990+10phr ZnO)



(t_{proc}=11 min) (t_{proc}=12 min) (t_{proc}=13 min)

Figure 5.9: Sintering Stages in a 6-fold Experiment (T_{oven} = 300 °C)
[6-fold Experiment Using 6-fold Pellets (P101P)]

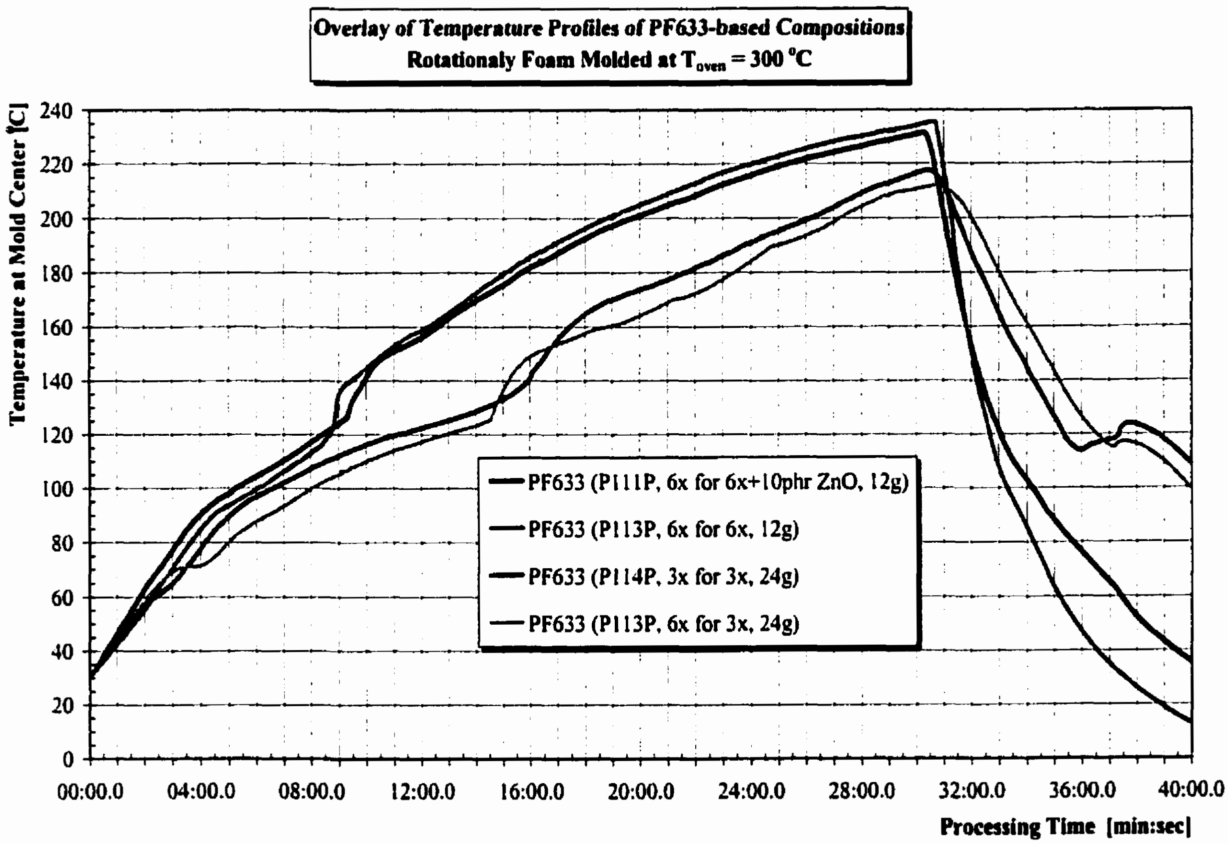


Figure 5.10: Effect of ZnO and VER (Celogen AZ-3990 amount and shot size) on the Temperature Profile of PF633-based Compositions During Rotational Foam Molding

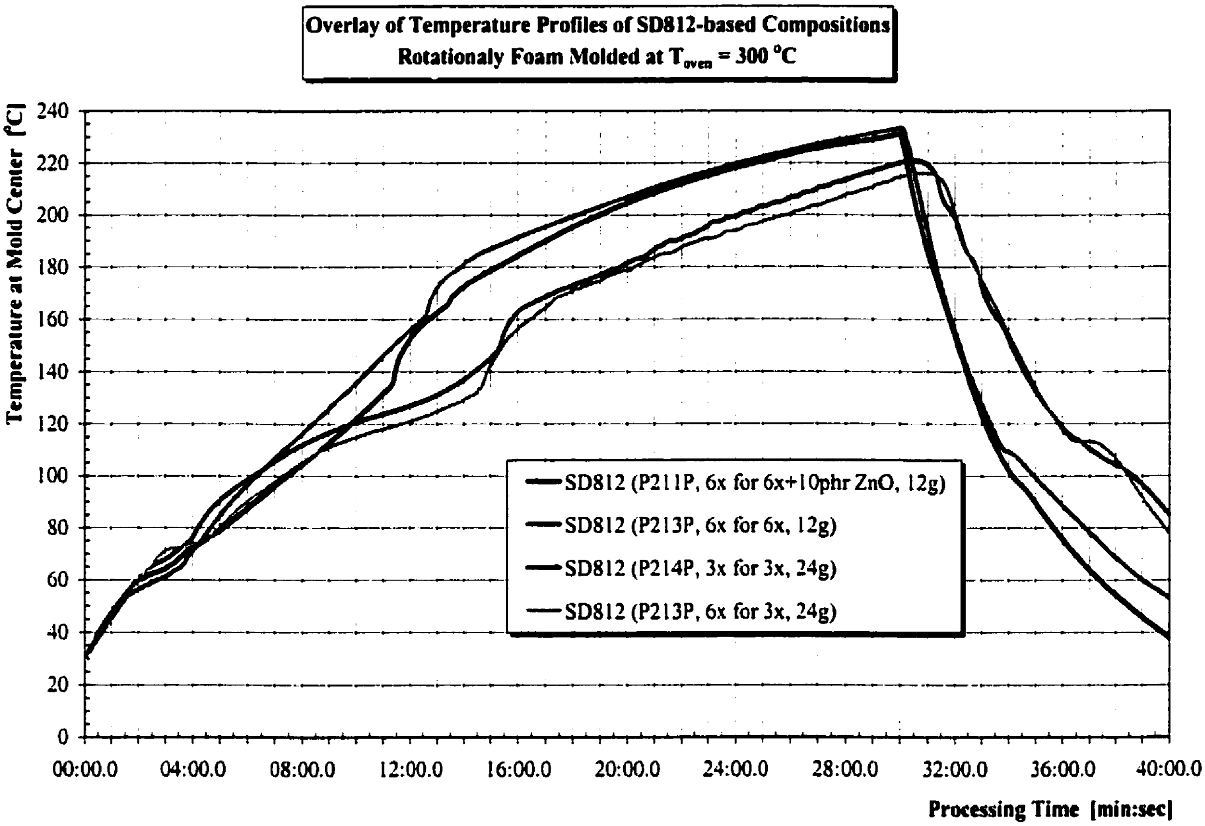


Figure 5.11: Effect of ZnO and VER (Celogen AZ-3990 amount and shot size) on the Temperature Profile of SD812-based Compositions During Rotational Foam Molding

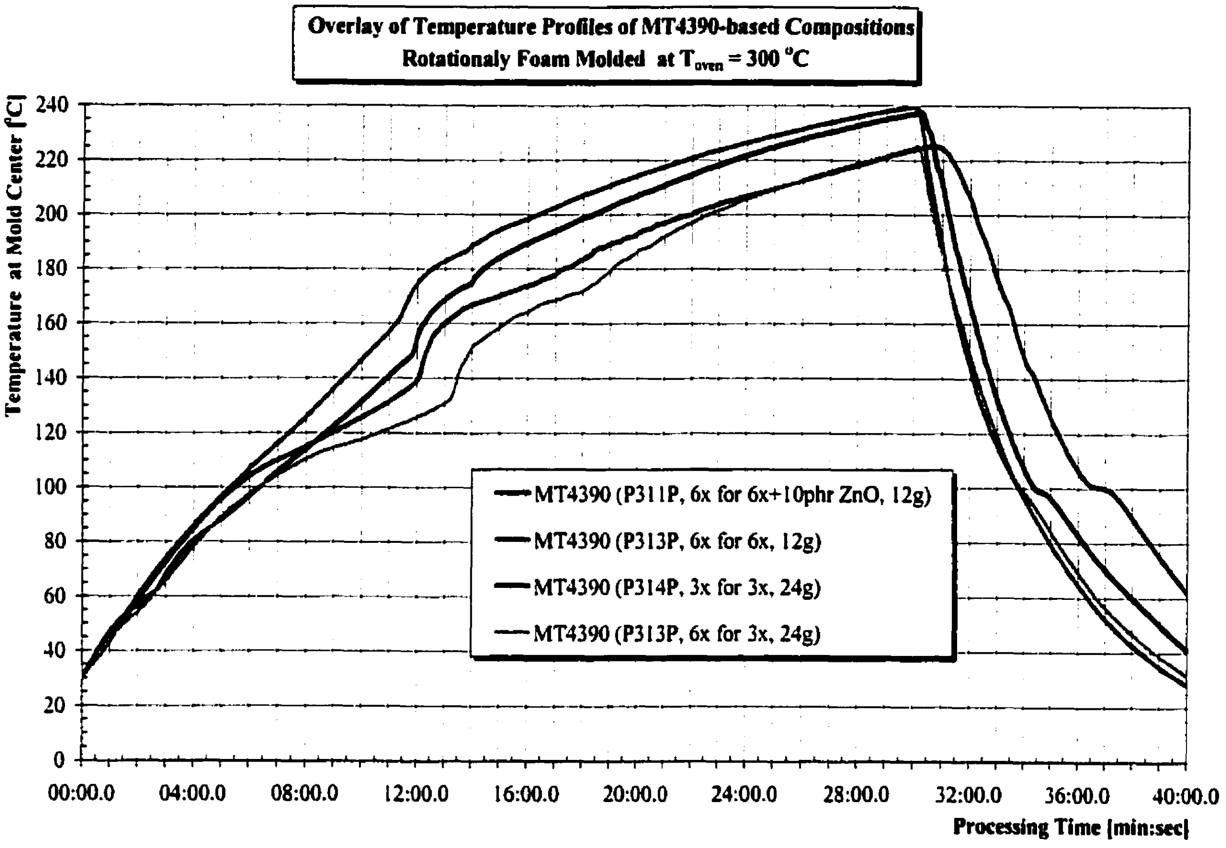


Figure 5.12: Effect of ZnO and VER (Celogen AZ-3990 amount and shot size) on the Temperature Profile of MT4390-based Compositions During Rotational Foam Molding

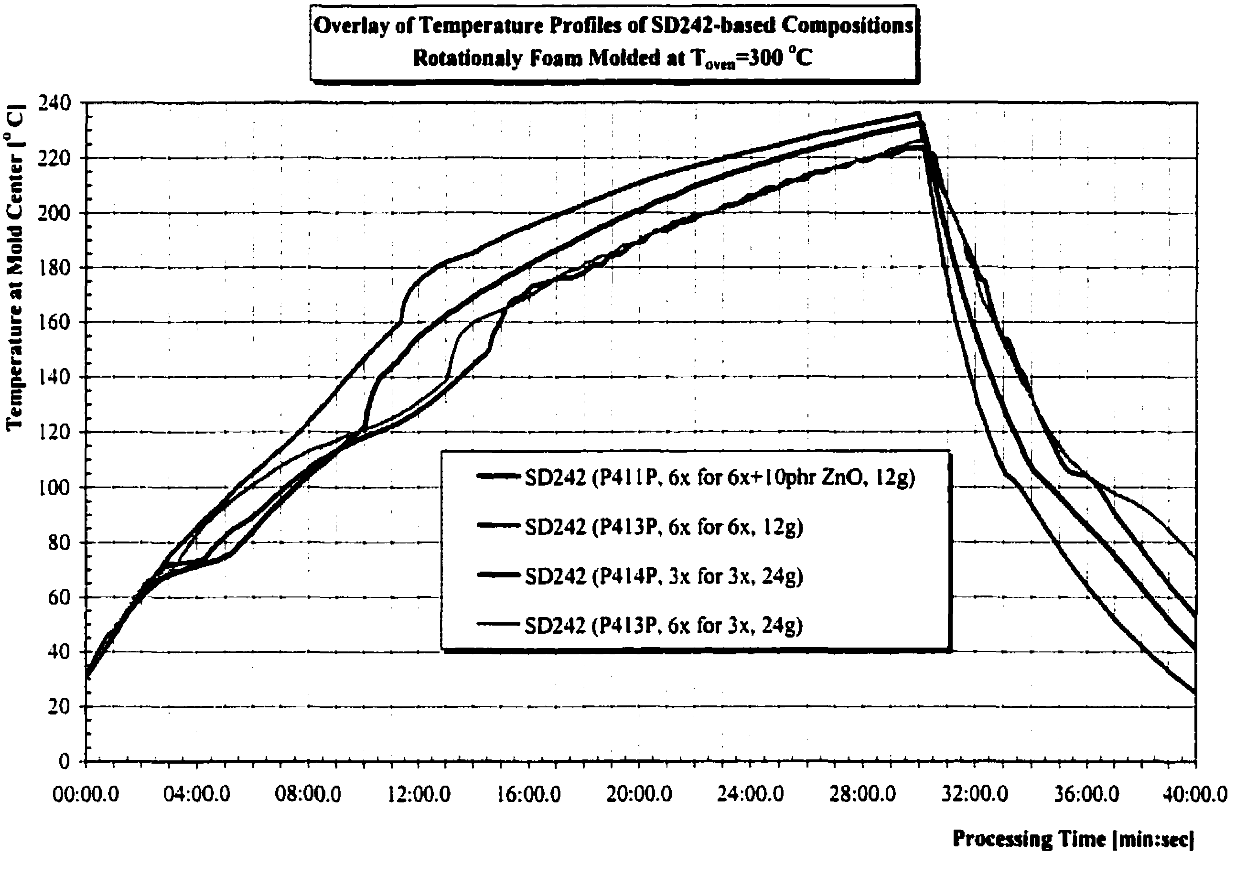


Figure 5.13: Effect of ZnO and VER (Celogen AZ-3990 amount and shot size) on the Temperature Profile of SD242-based Compositions During Rotational Foam Molding

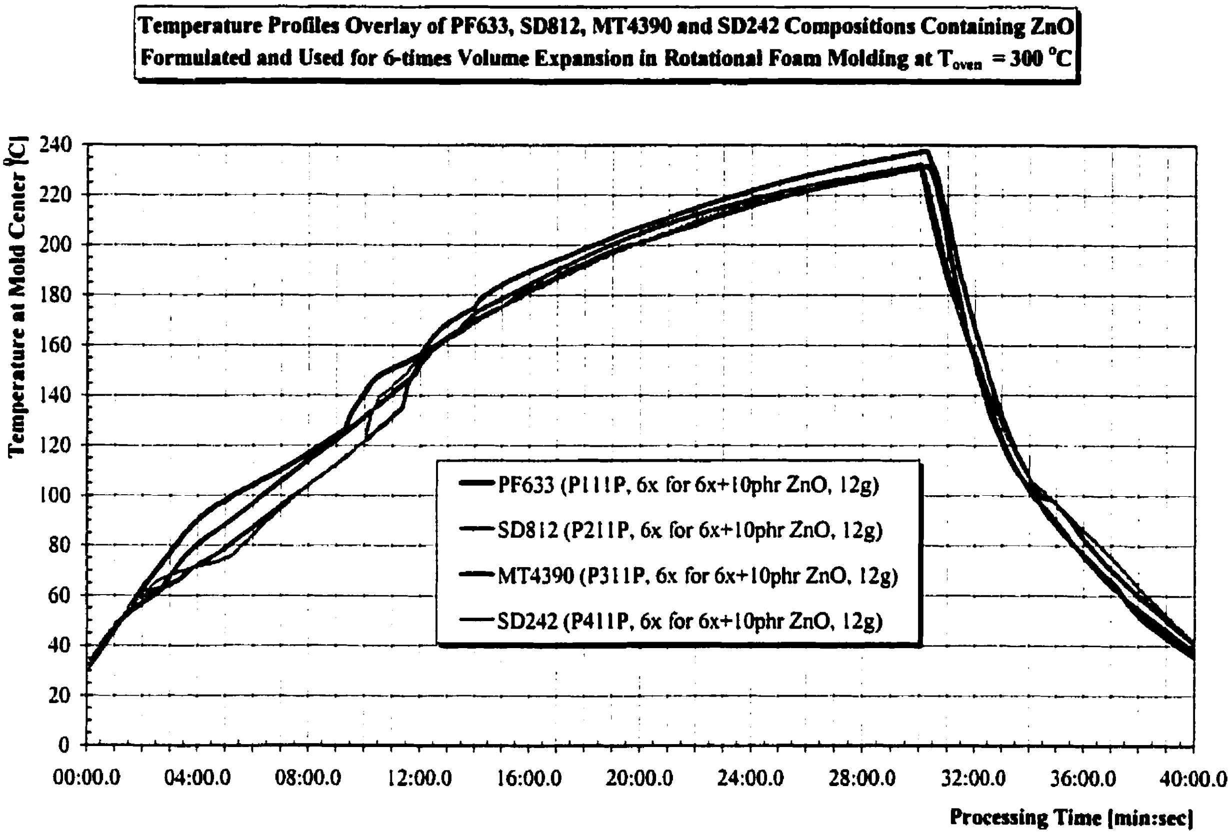


Figure 5.14: Effect of PP Composition Carrier (material viscosity) on Temperature Profiles of Compositions Containing ZnO, Formulated and Used for 6-fold Expansion in Rotational Foam Molding at T_{oven} = 300 °C

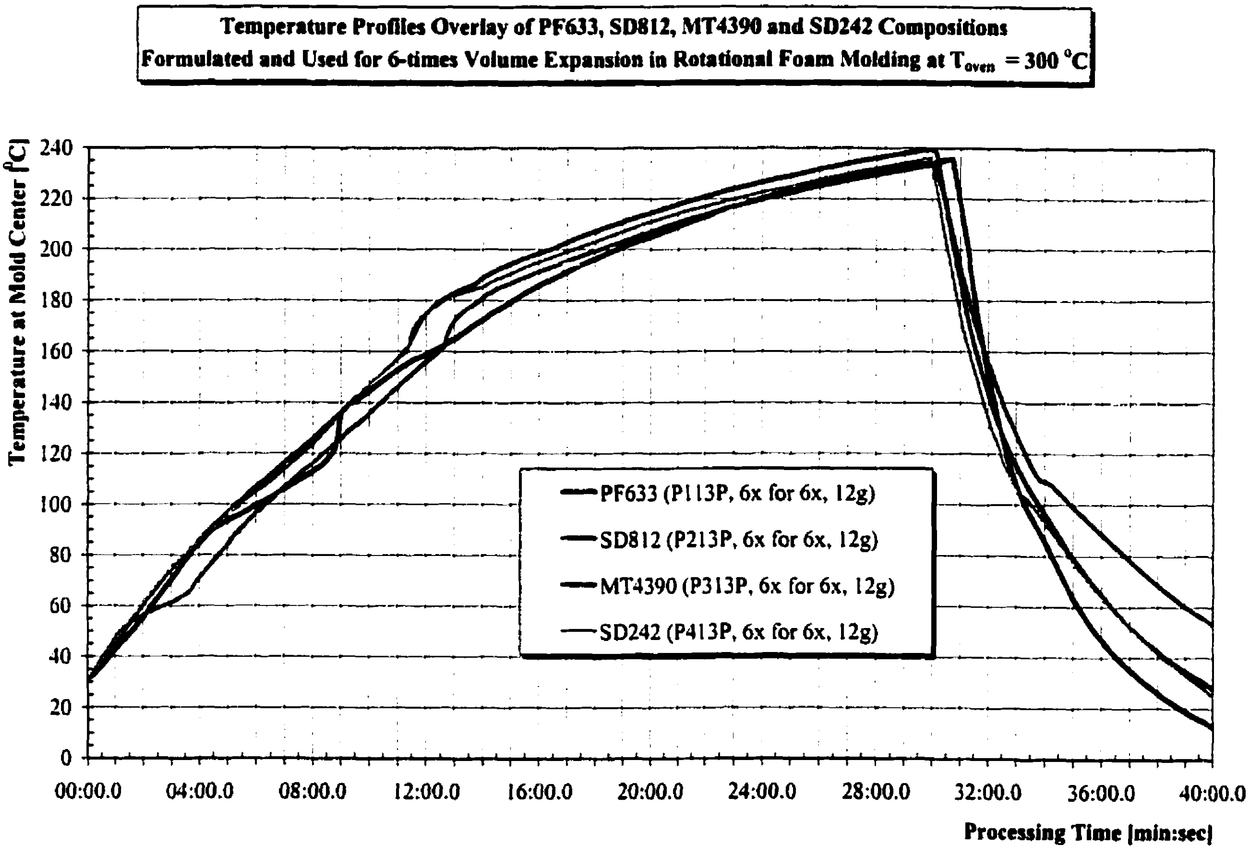


Figure 5.15: Effect of PP Composition Carrier (material viscosity) on Temperature Profiles of Compositions Formulated and Used for 6-fold Expansion in Rotational Foam Molding at T_{oven} = 300 °C

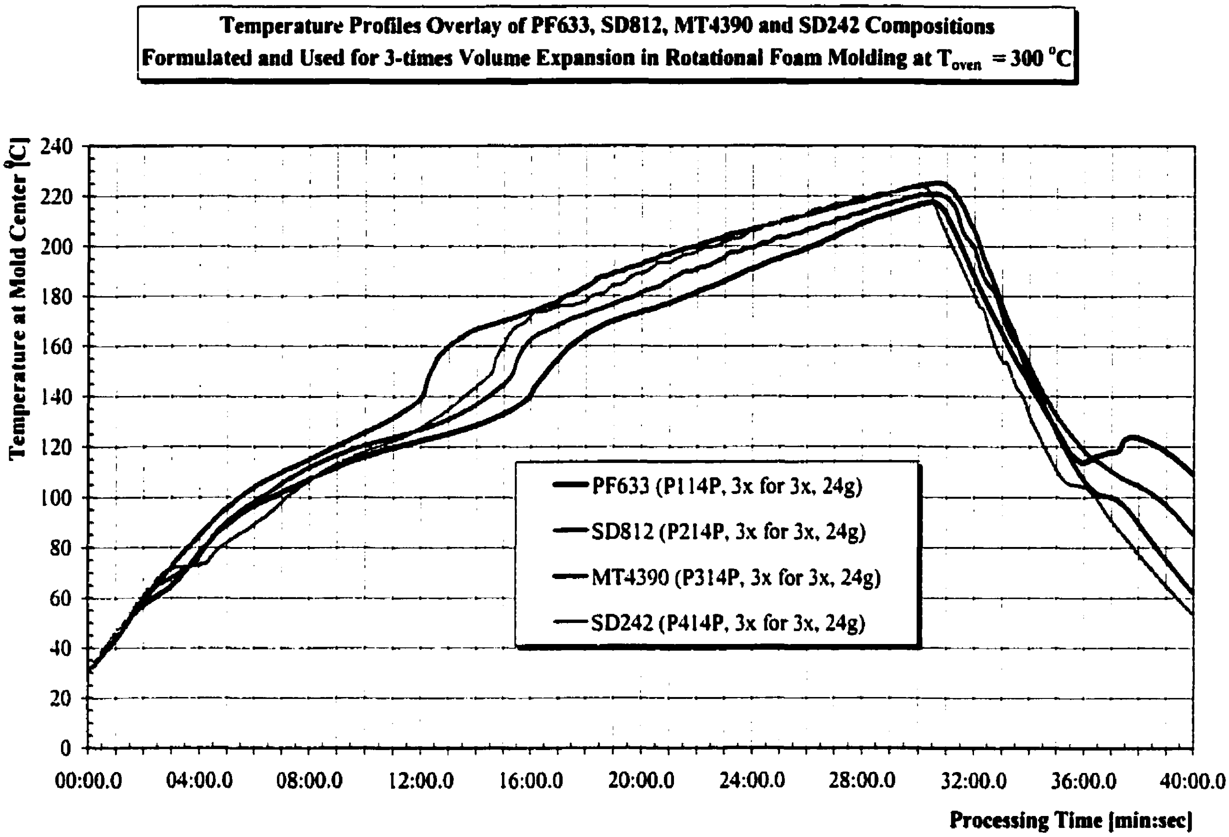


Figure 5.16: Effect of PP Composition Carrier (material viscosity) on Temperature Profiles of Compositions Formulated and Used for 3-fold Expansion in Rotational Foam Molding at T_{oven} = 300 °C

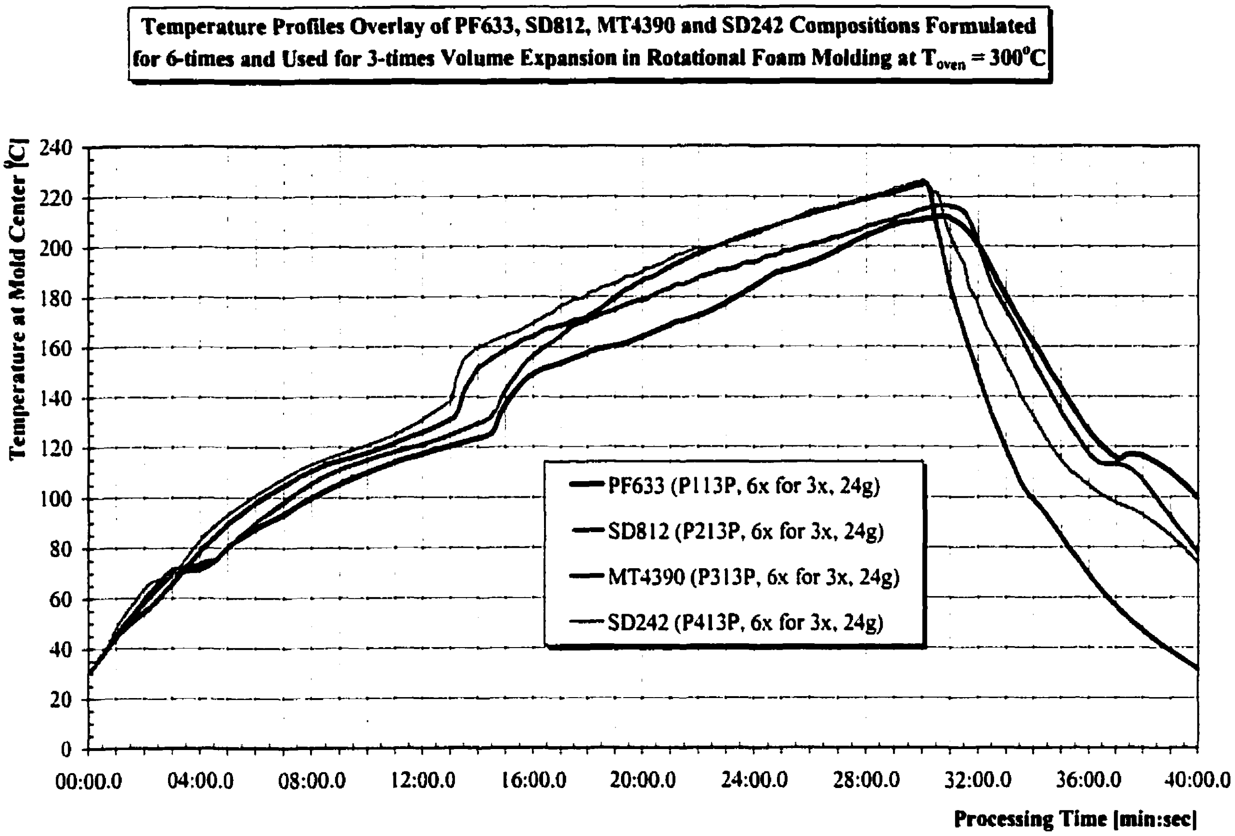


Figure 5.17: Effect of PP Composition Carrier (Material Viscosity) on Temperature Profiles of Compositions Formulated for 6-fold and Used for 3-fold Expansion in Rotational Foam Molding at T_{oven} = 300 °C

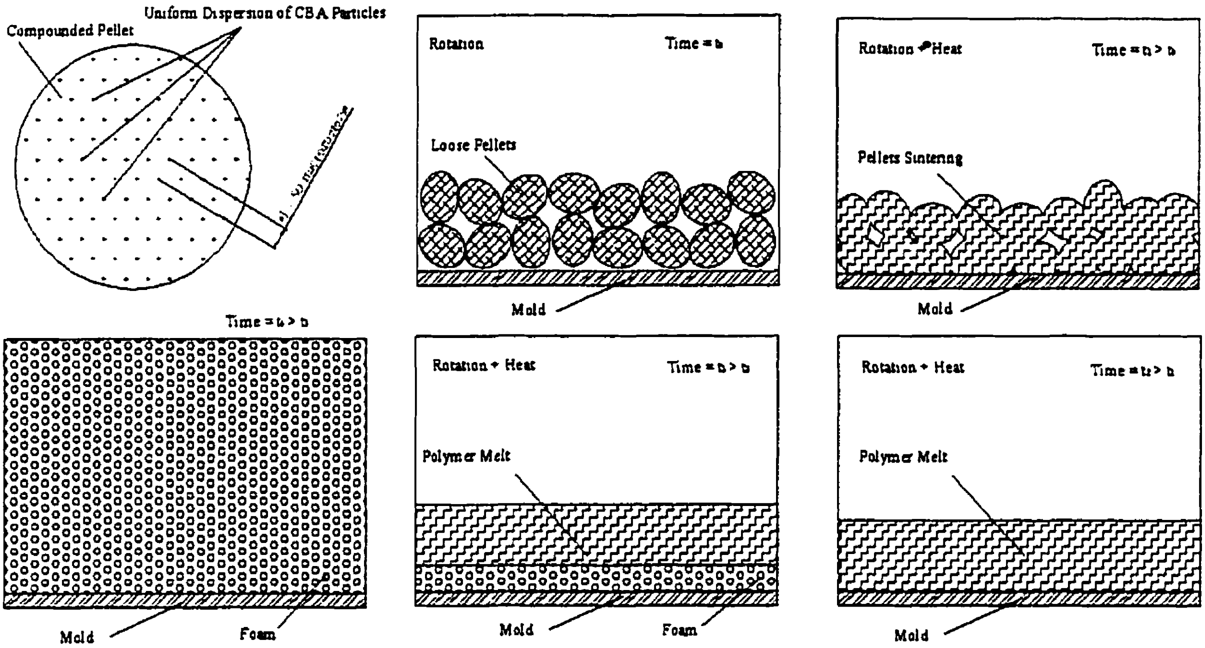


Figure 5.18: Desired Sequence of Events in Processing Fine-cell PP Foams in Compounding-based Rotational Foam Molding (Ideal Case)

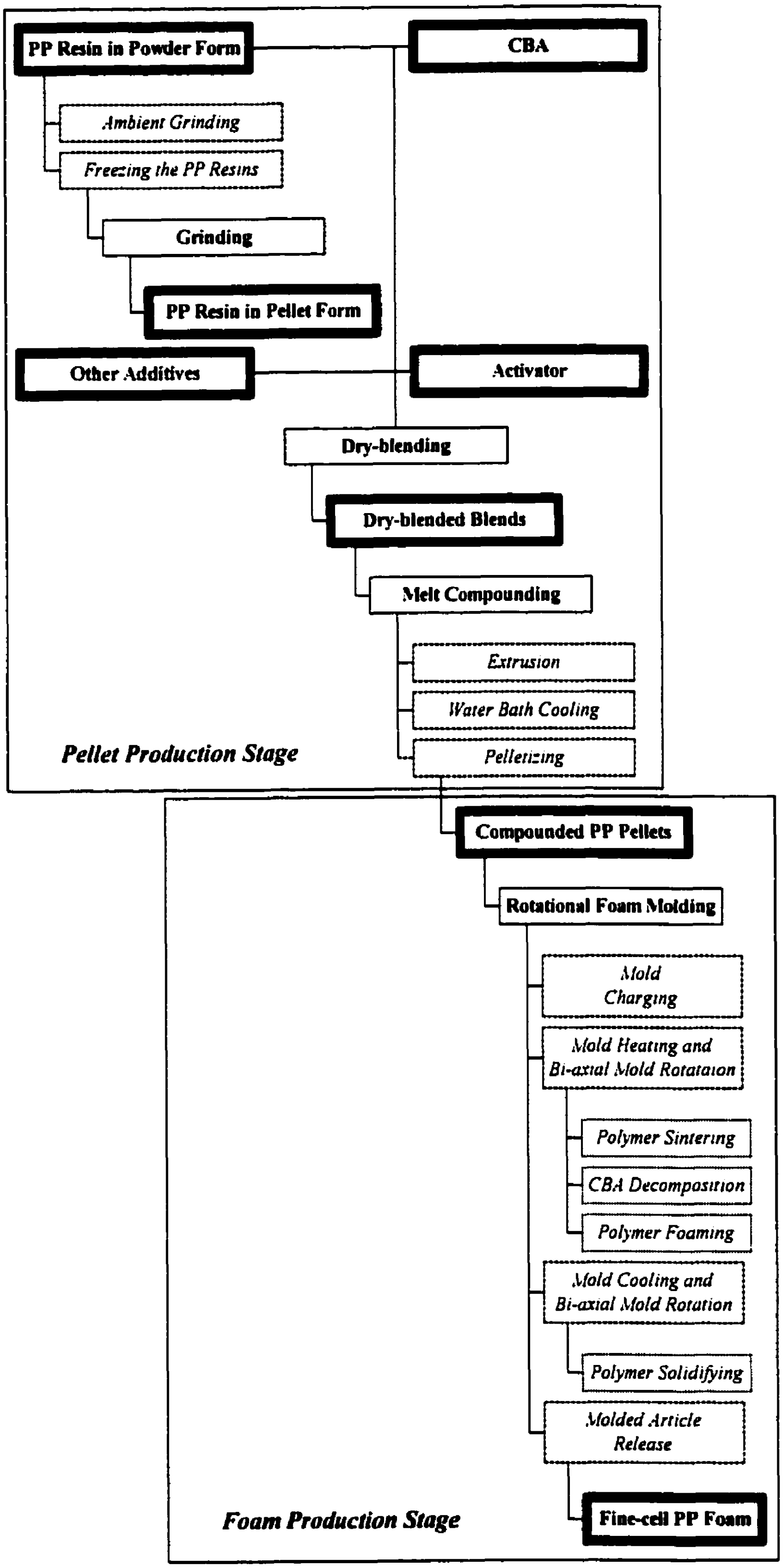
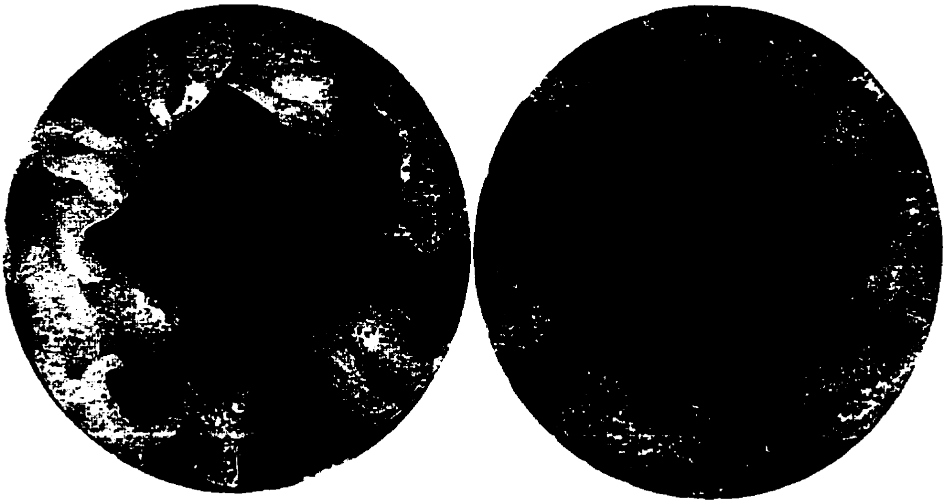
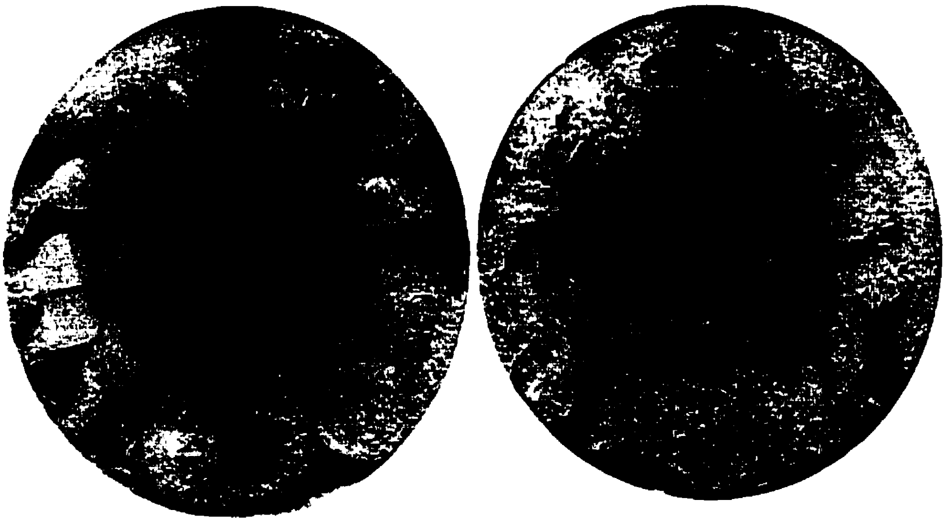


Figure 5.19: Detailed Process Diagram of the Modified Compounding-based Rotational Foam Molding Process for Producing Fine-cell PP Foams (Modification #1)



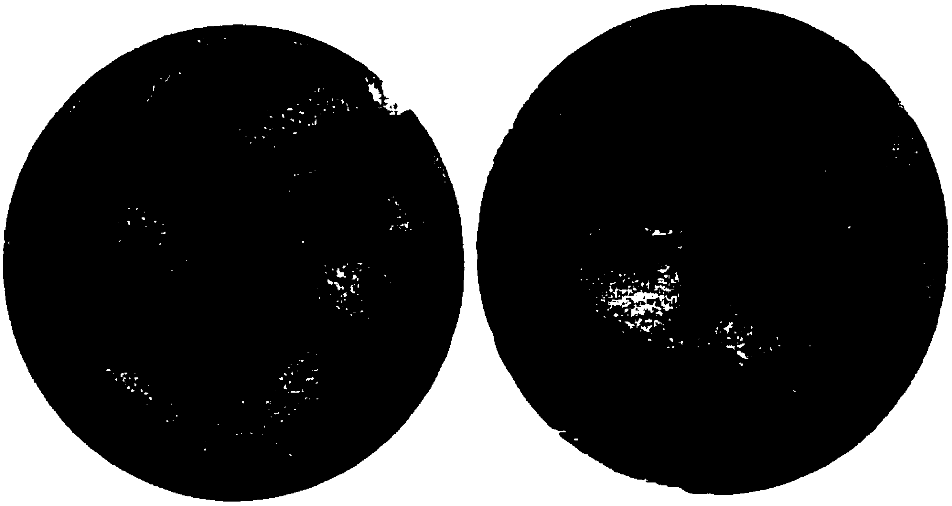
(P111P) t = 9min

(P111P) t = 9.5 min



(P111P) t = 10 min

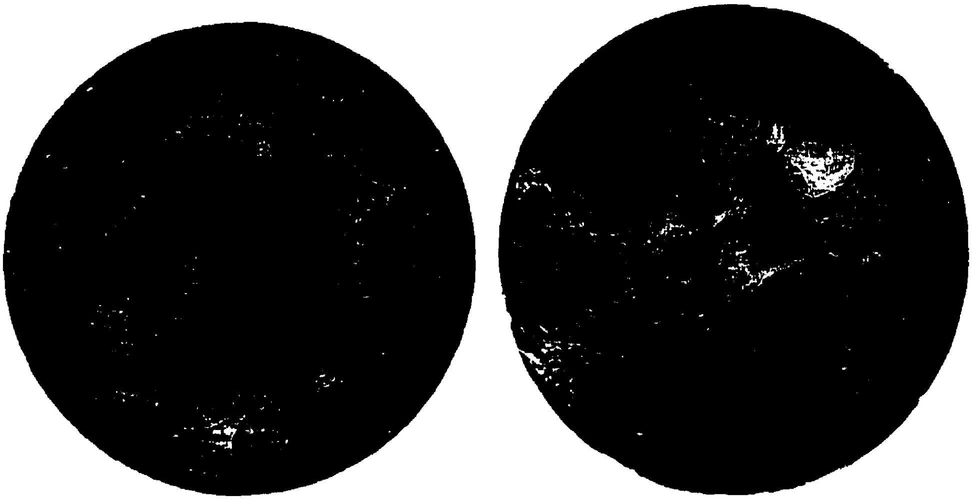
(P111P) t = 10.5 min



(P111P) t = 11min

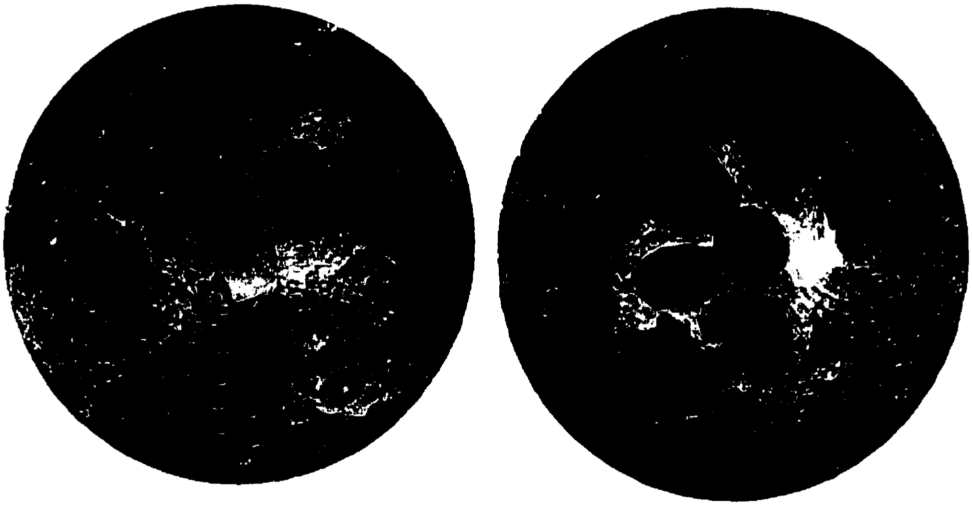
(P111P) t = 12min

Figure 5.20: P111P Parametric Search (9-12 min)
W=12g; Toven=300 °C; Mold RPM=17.5
(Composition Formulated for 6-fold and Used for 6-fold Expansion)
Magnification : 200%



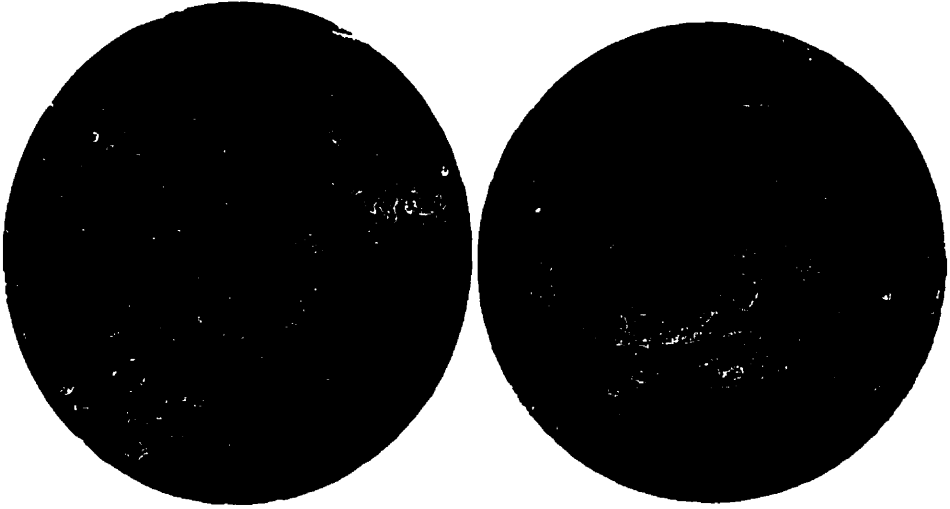
(P111P) t = 13 min

(P111P) t = 14 min



(P111P) t = 15 min

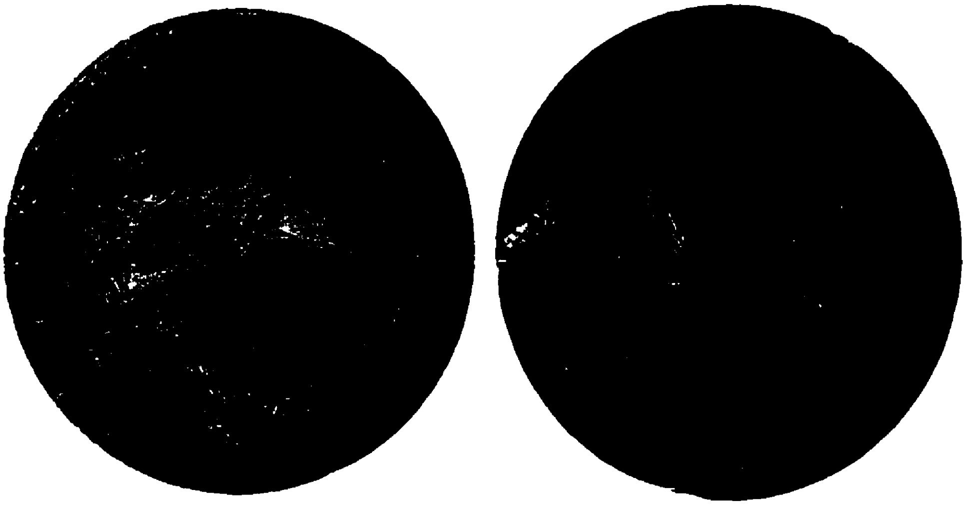
(P111P) t = 16 min



(P111P) t = 17 min

(P111P) t = 18 min

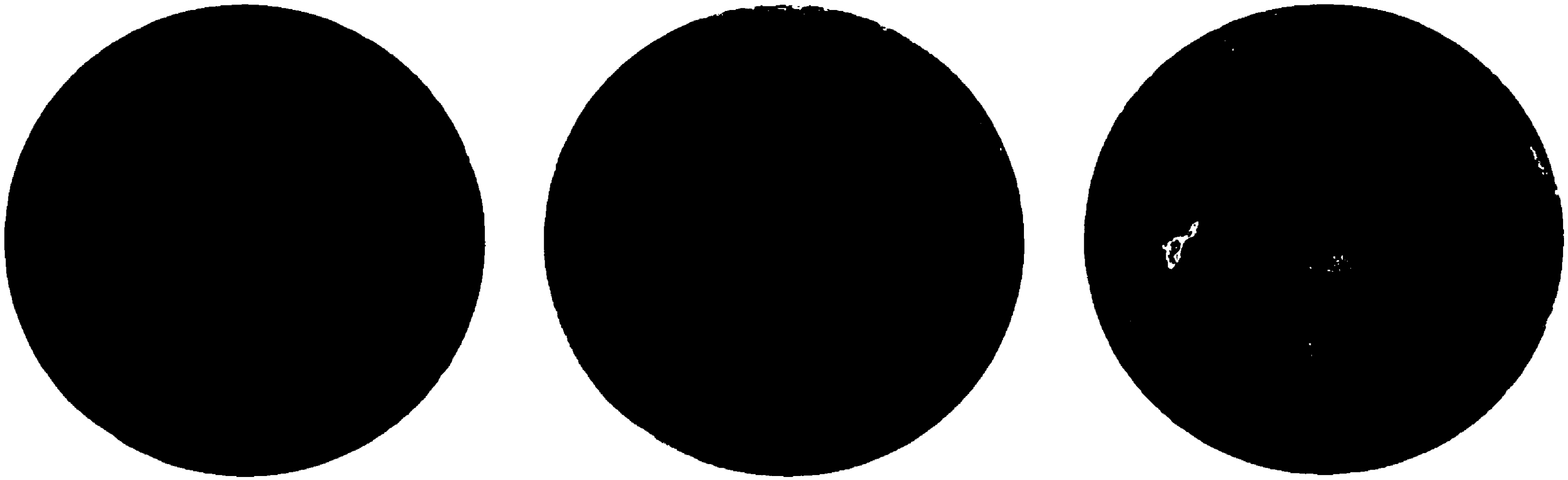
Figure 5.21: P111P Parametric Search (13-18 min)
W=12g; Toven=300 °C; Mold RPM=17.5
(Composition Formulated for 6-fold and Used for 6-fold Expansion)
Magnification : 200%



(P111P) t = 19 min

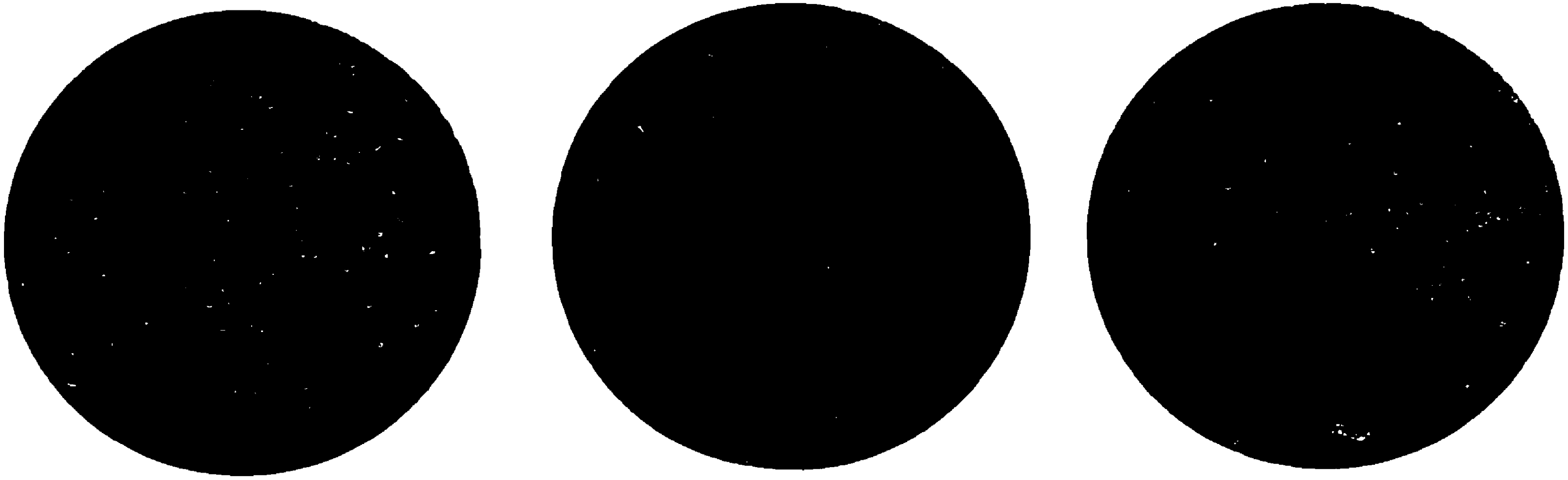
(P111P) t = 20 min

Figure 5.22: P111P Parametric Search (19-20 min)
W=12g; Toven=300 °C; Mold RPM=17.5
(Composition Formulated for 6-fold and Used for 6-fold Expansion)
Magnification : 200%



(P113P) t = 19 min (6x6) (P113P) t = 22 min (6x3) (P111P) t = 19 min (6x3)

(a) Cell Morphology of High-viscosity PP Foams in Compounding-based Rotational Foam Molding (T_{oven} = 300 °C)



(P214P) t = 22 min (3x3) (P314P) t = 20 min (3x3) (P414P) t = 18 min (3x3)

(b) Cell Morphology of Low-viscosity PP Foams in Compounding-based Rotational Foam Molding (T_{oven} = 300 °C)

Figure 5.23: Cell Morphologies of PP Foams Produced by Process Modification #1; Magnification = 200%

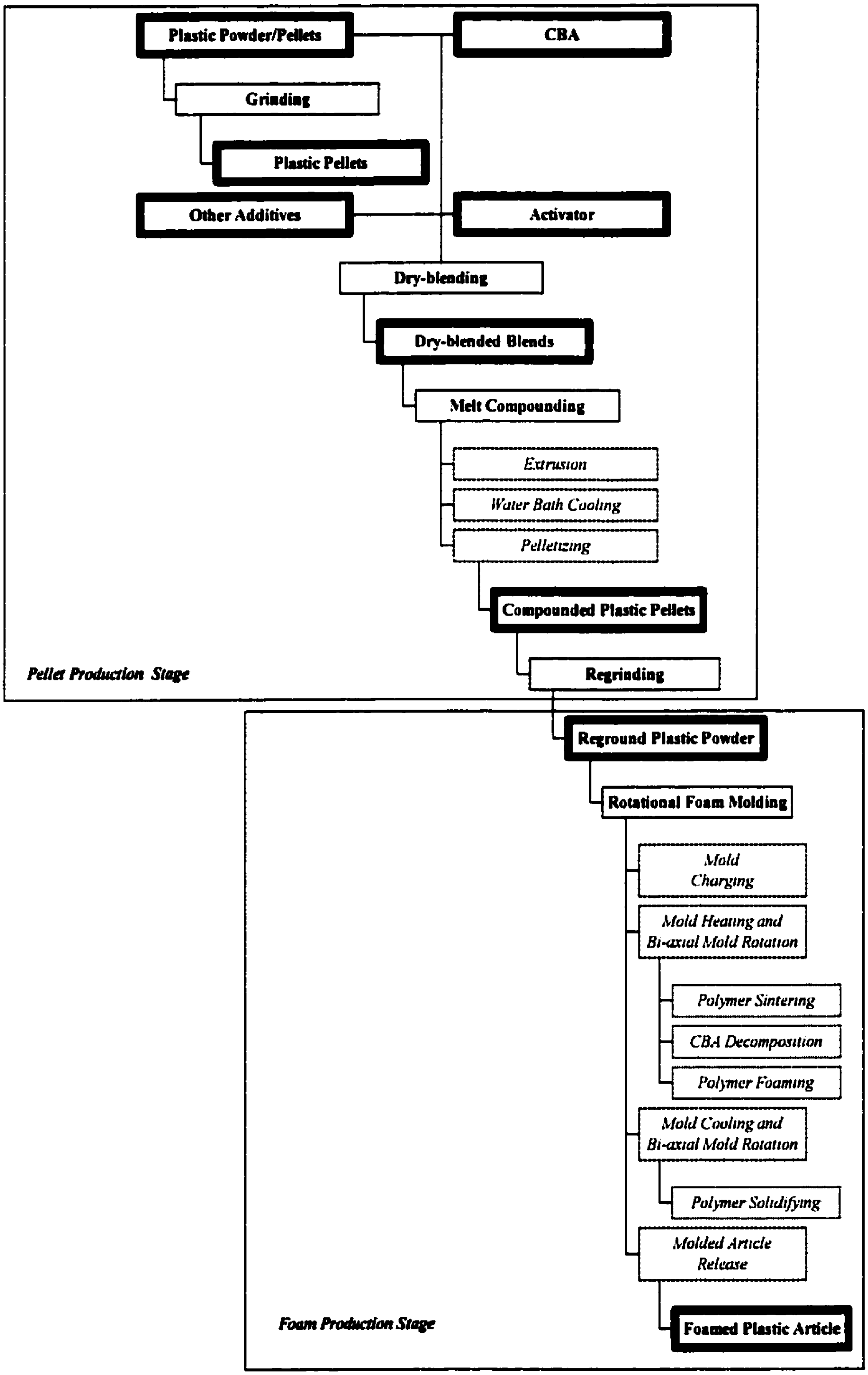


Figure 5.24: Detailed Process Diagram of the Modified Compounding-based Rotational Foam Molding Process for Producing Fine-cell PP Foams (Modification #2)

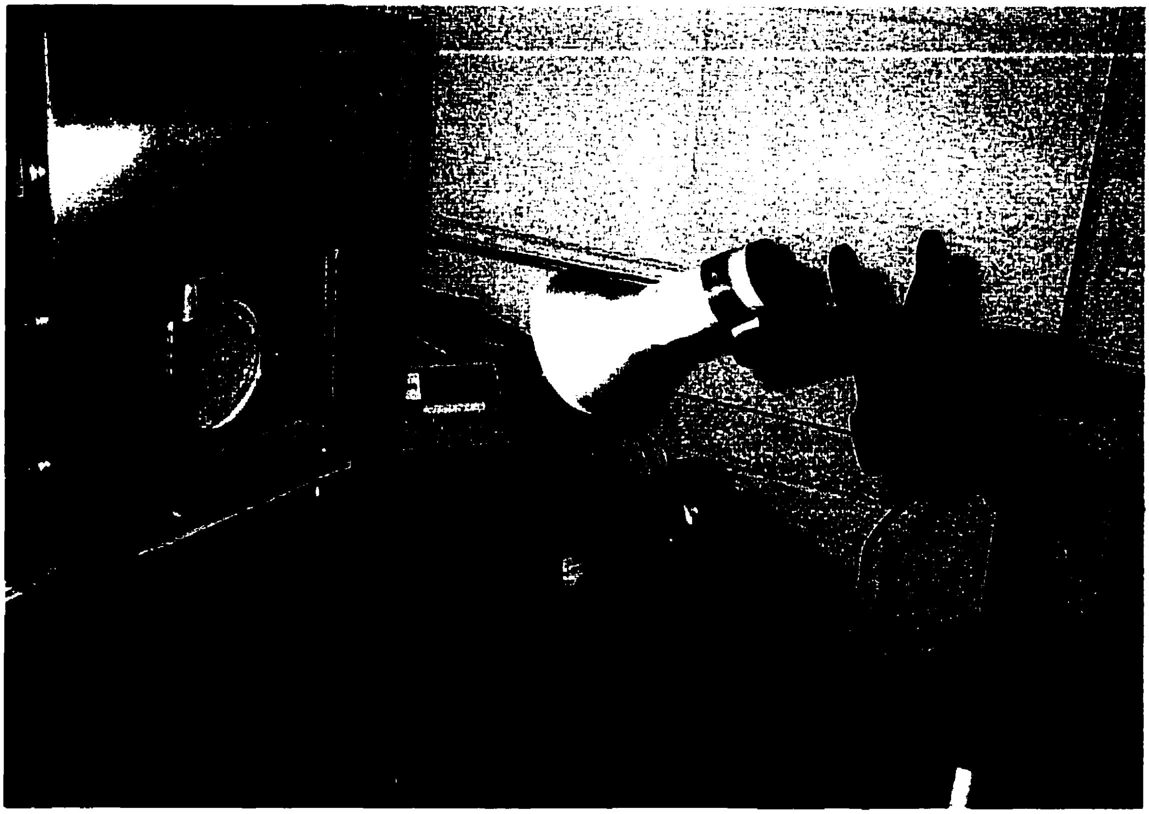


Figure 5.25: Pictorial View of the Experimental Setup Using a See-through Mold

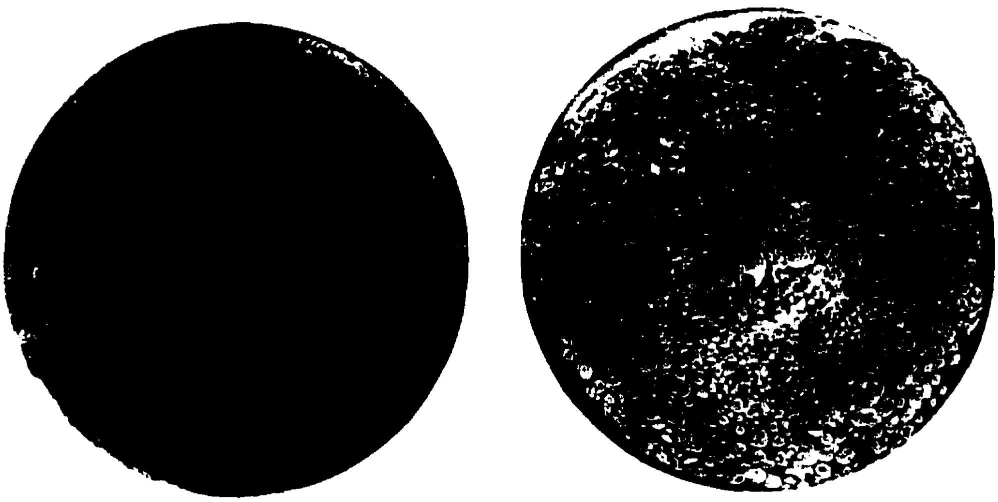


Figure 5.26: Cell Morphologies of Foams Produced by Process Modification #2 (P113P Reground) t = 22 min (6x3)
T_{oven} = 300 °C; Magnification = 200%

Table 3.1: Chemical Blowing Agents and Typical Peak Decomposition Temperatures

#	Blowing Agent	Typical Peak $T_{decomposition}$ ^{0}C	Ref.
1	Diazoaminobenzene	100	[7]
2	Benzene sulfonic acid hydrazide	104	[7]
3	N,N'-dimethyl-N,N'-dinitrocerephchalamide	105	[7]
4	Azobisisobutyronitrile	115	[7]
5	Tetramethylene dinitrosodimethylurethane	125	[7]
6	p,p-Oxybis (N--aitroso-N-methyl) benzenesulfonamide	130	[7]
7	Urea-biuret (33:67)	135	[7]
8	beta-Naphthalene sulfonic acid hydrazide	138	[7]
9	Sodium bicarbonate-citric acid (4:3)	140	[7]
10	Sodium bicarbonate-melamine (95:5)	140	[7]
11	Benzene-l,3-dlsulfonic acid dihydrazide	145	[7]
12	1,6-Di-n-decyl azobisformamide	145	[7]
13	Diphenyl-4,4'-di(sulfonyl azide)	145	[7]
14	Benzene sulfonic acid N-phenyl hydrazide	146	[7]
15	Diphenyl sulfone-3,3'-dlsulfonyl hydrazide	150	[7]
16	p,p'-Oxybis (benzenesulfonyl hydrazide)	150	[7]
17	1,6-Di-phenyl Azobisformamide	176	[7]
18	Dinitrosopentamethylene tetramine	185	[7]
19	Azodicarbonamide	200	[7]
20	p,p'-Oxybis (benzenesulfonyl semicarbazide)	210	[7]
21	Trihydrazino-sym-triazine	230	[47]
22	Bisbenzene sulfonylhydrazide	240	[47]
23	Barium azodicarboxylate	245/250	[7]/[47]

Table 4.1: Typical Properties of the PP Resins Used for Experimentation

Typical Resin Properties	ASTM Method	PF633	SD812	MT4390	SD242
Melt flow rate, 230/2.16, dg/min	D1238	5.5	16	20	35
Density at 23 °C, g/cm^3	D792B	0.90	0.90		0.90
Density g/cm^3	D1505			0.90	
Tensile Stress at Yield, psi (Mpa)	D638	5,100 (36)	3,800 (26)		4,000 (280
Tensile Strength at Yield, at 2"/min psi	D638			2,600	
Tensile Elongation at Yield, %	D638	9	6		5
Flexural Modulus, 1% Secant at 0.05 in/min, psi (Mpa)	D790A	200,000 (1,400)	190,000 (1,300)		210,000 (1,400)
Flexural Modulus, 1% Secant psi	D790			120,000.00	
Hardness, Rockwell R	D785A	92	72		
Deflection Temperature at 66 psi/455 kPa, °C	D648	111	104	75	114
Heat Distorsion Temperature at 264 psi °C	D648			48	
Notched Izod Impact Strength at 23 °C, ft-lbs/in (J/m)	D256A		2.7 (150)		1.3 (70)
Room Temperature Impact 1/8" Specimen	ARMSTD			20	
Drop weight Impact strength at -29 °C, ft-lbs (J)	Montell		18 (24)		15 (20)
Homopolymer/Copolymer		H	C	C	C
Branched/Non-branched		B	B	NB	NB
Reference		[77]	[77]	[39]	[77]

Table 4.2: Physical Properties of Celogen AZ-3990

Physical Properties	Celogen AZ-3990
Chemical Composition	Modified Azodicarbonamide
Gas Composition	65% N_2; 24% CO; 5% CO_2; 5% NH_3
Gas Yield/Gram	220 cc's @ STP
Decomposition Range	205-215°C
Physical Form	Fine, yellow powder
Molecular Weight	-
Specific Gravity	1.65 @ 25°C
Bulk Density	25 lbs./cu. ft.
Solubility	Somewhat soluble in polyalkylene glycols and dimethylformamide. Relatively insoluble in benzene, ethylene dichloride, acetone, and water.
Average Particle Size	2.4-3.0 micrometers

Table 4.3: Activators Recommended for Celogen AZ-3990 and Their Effect on $T_{decomposition}$

Activator	$T_{decomposition}$ of activated Celogen AZ-3990
Dinitrosopentamethylene tetramine	155
Zinc Oxide	165
Silica and zinc oxide	190
Urea	197

Table 4.4: Transition Temperatures of the PP Resins Used for Experimentation (DSC)

PP Resin	Onset Melting Temperature °C	Peak Melting Temperature °C	Peak Crystallization Temperature °C	Glass Transition Temperature °C
PF633	144.6	159.4	127.2	-20.4
SD812	141.3	163.8	127.2	-20.5
MT4390	152.4	160.6	111.2	-20.5
SD242	149.2	164.5	132.4	-20.7

Table 4.5: Effect of ZnO on the Onset Decomposition Temperature of Celogen AZ-3990 at Various Heating Rates

	Heating Rate		
TGA Sample Content	50 °C/min	100 °C/min	150 °C/min
Celogen AZ-3990 Pure	220.37	220.72	212.11
Celogen AZ-3990 + 10phr ZnO	207.46	208.98	198.96
Celogen AZ-3990 + 30phr ZnO	196.47	194.39	191.29
Celogen AZ-3990 + 50phr ZnO	193.82	190.24	190.48
Celogen AZ-3990 + 100phr ZnO	190.20	182.79	182.94

Table 4.6: Compounded PP Pellets (Average pellet size: 16-18 pellets per gram)

#	CODE	PP Pellet Formulation	VER
1	P101P	PF633+1.83%AZ+10phr ZnO	6
2	P102P	PF633+1.83%AZ+50phr ZnO	6
3	P103P	PF633+1.83%AZ	6
4	P104P	PF633+0.73%AZ	3
5	P201P	SD812+1.83%AZ+10phr ZnO	6
6	P202P	SD812+1.83%AZ+50phr ZnO	6
7	P203P	SD812+1.83%AZ	6
8	P204P	SD812+0.73%AZ	3
9	P301P	MT4390+1.83%AZ+10phr ZnO	6
10	P302P	MT4390+1.83%AZ+50phr ZnO	6
11	P303P	MT4390+1.83%AZ	6
12	P304P	MT4390+0.73%AZ	3
13	P401P	SD242+1.83%AZ+10phr ZnO	6
14	P402P	SD242+1.83%AZ+50phr ZnO	6
15	P403P	SD242+1.83%AZ	6
16	P404P	SD242+0.73%AZ	3

Table 5.1: PP Pellets Compounded for Reference Purposes by Using Pure PP Resins

#	CODE	PP Pellet Formulation
1	P105P	PF633 Pure Compounded
2	P205P	SD812 Pure Compounded
3	P305P	MT4390 Pure Compounded
4	P405P	SD242 Pure Compounded

Table 5.2: Compounded PP Pellets (Average pellet size: 31-33 pellets per gram)

#	CODE	PP Pellet Formulation	VER
1	P111P	PF633+1.83%AZ+10phr ZnO	6
2	P112P	PF633+1.83%AZ+50phr ZnO	6
3	P113P	PF633+1.83%AZ	6
4	P114P	PF633+0.73%AZ	3
5	P211P	SD812+1.83%AZ+10phr ZnO	6
6	P212P	SD812+1.83%AZ+50phr ZnO	6
7	P213P	SD812+1.83%AZ	6
8	P214P	SD812+0.73%AZ	3
9	P311P	MT4390+1.83%AZ+10phr ZnO	6
10	P312P	MT4390+1.83%AZ+50phr ZnO	6
11	P313P	MT4390+1.83%AZ	6
12	P314P	MT4390+0.73%AZ	3
13	P411P	SD242+1.83%AZ+10phr ZnO	6
14	P412P	SD242+1.83%AZ+50phr ZnO	6
15	P413P	SD242+1.83%AZ	6
16	P414P	SD242+0.73%AZ	3