

AN ABSTRACT OF THE THESIS OF

Juergen H. Lenz for the degree of Master of Science in Industrial Engineering presented on March 16, 2012.

Title: Materials and Process Design for Powder Injection Molding of Silicon Nitride for the Fabrication of Engine Components

Abstract approved: _____

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A new material system was developed for fabricating the combustion engine of an unmanned aerial vehicle. The material system consisted of a mixture of nanoscale and microscale particles of silicon nitride. Magnesia and yttria were used as sintering additives. The powders were mixed with a paraffin binder system. The binder-powder was analyzed for its properties and molding attributes. The study involved several steps of the development and processing. These steps include torque rheometry analysis, mixing scale-up, property measurements of binder-powder, injection molding, binder removal, sintering, scanning electron microscopy analysis and mechanical properties measurements. Simulations of the injection molding process were conducted to assess the feasibility of manufacturing a ceramic engine and to determine its optimal process parameters. The model building required for the simulation was based on flow and solidification behavior data compiled for the binder-powder mixture. The simulations were performed using the Moldflow software package. A design of experiments approach was set up in order to gain an understanding of critical process parameters as well as identifying a feasible process window. Quality criteria were then analyzed in order to determine the optimal production parameters. The study resulted in the successful development of design parameters that will enable fabrication of silicon nitride engine components by powder injection molding.

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Materials and Process Design for Powder Injection Molding of Silicon Nitride for the
Fabrication of Engine Components

by

Juergen H. Lenz

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Juergen H. Lenz, Author

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**MATERIALS AND PROCESS DESIGN FOR POWDER INJECTION
MOLDING OF SILICON NITRIDE FOR THE FABRICATION OF
ENGINE COMPONENTS**

1. INTRODUCTION

1.1. Statement of the Problem

An unmanned aerial vehicle (UAV), often referred to as a drone, is a flying machine, which is either self-controlled or remote controlled by a navigator on the ground. It has a big variety of usage, such as remote sensing, surveillance, exploration, transport, armed attacks or search and rescue. UAVs are not limited to physiological restrictions of human pilots. Therefore, they can achieve longer endurance. A long endurance enables the UAV to fulfill missions with high overall flight time and therefore also missions with longer distance to the target. The critical constraint is only set by the fuel-range. Also UAVs are lacking in-flight refueling capability. By 2012 no successful UAV in-flight refueling has been achieved. This is why a very light and energy efficient powertrain is of high demand. Also maintenance can't be performed in remote mission locations. Therefore the powertrain has to have very low maintenance requirements.

An engine, which is made out of ceramic, instead of metal, would be much lighter due to the low density of ceramic materials. Less mass on an airplane means higher endurance. A combustion engine made out of a metal alloy has a big weakness. It's main cause for maintenance and malfunction is wear. With every stroke of a piston tiny chips of metal are broken lose on the cylinder running surface and are flushed away in the lubricating oil. However, a ceramic material has better wear resistance, higher service temperature and low thermal expansion. Due to the low thermal expansion the gap between the piston and the cylinder surface doesn't expand as much as a similar design with a metal alloy. All this would result in less maintenance. However, to date only a few prototypes have been built [4],[49] and mass production has never been achieved since manufacturing costs of such engines are higher. In summary, a combustion engine for an unmanned aerial vehicle

(UAV) demands a material with high strength, low density, high hardness and low thermal expansion. Figure 1.1 shows an engine design for UAVs by Northwest UAV Propulsion Systems Inc.



FIGURE 1.1: Light Weight NWUAV 34cc Engine Design [36]

Silicon nitride (Si_3N_4) fulfills all of these requirements and also has outstanding wear resistance, chemical stability and good thermal shock resistance [1]. These properties make silicon nitride a good candidate material for a ceramic engine. Silicon nitride already plays a significant role in aerospace, defense and automotive sector applications. Especially, products like bearings and cutting tools out of silicon nitride are nowadays very common. Most application nowadays have a simple shape. Powder injection molding has the ability to manufacture ceramic powders into complex shaped parts.

Powder injection molding can process pelleted powder-binder mixtures in complex shapes. The process is similar to plastic injection molding. The mold cavity is filled with the meted material under pressure and cooled down until it solidified.

The molded part is then subjected to debinding. There are various debinding routes reported until date, there are three different categories of debinding. Solvent debinding, thermal debinding and catalytic debinding. Either one or a combination of these technique can be used.

The debound part is then sintered under controlled time, temperature and atmospheric conditions to get the final part of desired dimensions, density, microstructure and thus properties. Controlling the sintering atmosphere is vital to avoid any oxidation at high temperature [14]. Additionally, many ceramics cannot be sintered by themselves. The process generally involves sintering aids, which densify the ceramic part. Thus, selection and optimization of sintering aids turns out to be one more important step in the PIM process. It is very important to note that the chemistry, size and the composition of the sintering aids affect the solids loading and thus possibly the microstructure [32] [7].

1.2. Objectives of this Thesis

Figure 1.2 shows details some of the specific issues that could be explored in the current work on fabricating silicon nitride parts by powder injection molding (PIM). The optimal solids loading of a feedstock is dependent on the particle characteristics. For a feedstock with a given binder system, the rheological and thermal properties are dependent on the solids loading. The powder and feedstock material characteristics help us in designing the process conditions. The sintering conditions and characteristics of sintering aids affect the microstructure of the sintered part, which in turn controls the final properties.

The major research challenges thus involve:

1. Determining the effect of powder characteristics on the material properties of the feedstock (rheological and thermal properties)
2. Designing the process conditions (process design, mold design and part design) from the material properties of the powder-polymer mixtures
3. Determining the effect of powder characteristics (chemistry, particle size and sintering aids) on the microstructure of the sintered parts
4. Determining the effect of sintering conditions (time and temperature combinations) on the microstructure of the sintered parts
5. Determining the effect of microstructure of the sintered parts on its properties.

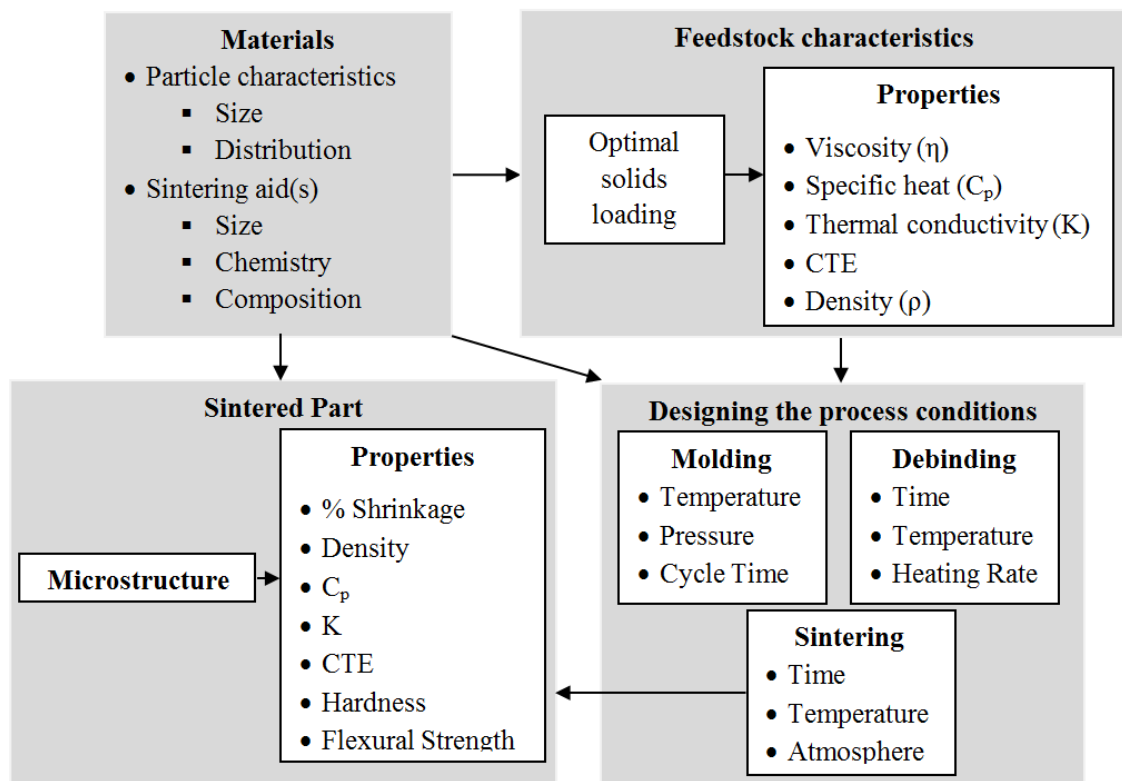


FIGURE 1.2: Factors affecting the PIM Design

The present thesis will focus on the first two issues involving the development of design tools for identifying materials and process conditions for successfully applying silicon nitride to the PIM of engine components for UAV. These two challenges can be broken down in sub-objectives. The sub-objectives for the characteristics on the material properties of powder-polymer mixtures are:

1. Determining the properties of the raw powders used (average particle size, shape)
2. Determining the maximum volume fraction of powder in the binder (solids loading)
3. Determining the feedstock properties (viscosity, thermal conductivity, specific heat capacity, no-flow temperature, eject temperature and transition temperature, pressure volume temperature behavior and density)

The sub-objectives for the process conditions are:

1. Determining the simulated flow characteristics (fill time, pressure at injection location, maximal shear stress at wall)
2. Analyze predicted defects (air traps, short shots)
3. Determining the response for a quality criteria in the feasible process window (DOE)
4. Determining one set of PIM process parameter as a trade of (optimization)

1.3. Structure of this Thesis

In Chapter 2 the scientific background is explained as a foundation for this project. The material section outlines the reasoning behind the question why Si_3N_4 was chosen. Followed by that Si_3N_4 is described. Its historical development, crystal structure, synthesis methods and properties summarized. The applications of Si_3N_4 and research done towards future applications like the ceramic engine. Those applications come with the question of how they are manufactured. This is explained in the processing section along with some processing requirements like binder component and sintering additives. The chapter is ended by showing how there is a gap of knowledge where a new material system is needed.

Chapter 3 presents the materials and methods used in this project. All the powders used are listed and the material characterization methods are defined. These material properties measurements are particle size analysis, torque rheometry, Vickers hardness, fracture toughness, scanning electron microscopy, weight and dimension measurements. Next the methods used to analyze the pelleted powder-binder-mixture. This mixture is called feedstock. The techniques how to get the feedstock properties are described. These properties are viscosity, thermal conductivity, specific heat capacity, no-flow temperature, ejection temperature and transition temperature, pressure volume temperature behavior and density. In addition, details of the material processing methods such as mixing, scale-up, molding, debinding and sintering are presented. There were two different parts used in this project, both are described either via technical drafts and 3D rendered pictures. The exact simulation settings and DOE techniques and their setup are explained and the optimization software mentioned.

Chapter 4 presents the results from the study. The first step was to analyze the powder properties. Then the rheological behavior was measured. The torque rheometry was plotted. Subsequently the material system composition for scale up was determined. The feedstock properties were obtained. These properties were viscosity, thermal conductivity, specific heat capacity, no-flow temperature, ejection temperature and transition temperature, pressure volume temperature behavior and density. The scanning electron microscopy images were acquired and structural patterns identified. The weight and dimensions were taken of the molded part as well as from the sintered part, but the hardness and the fracture toughness were measured for the sintered part. The simulation results showed that the validation part could be successfully molded and the results from the engine part simulation showed a production feasibility in a certain process window. The process window is defined as the feasible ranges for the three process parameters mold temperature, melt temperature and injection time. This window was then analyzed in a DOE study. For the ceramic engine part the DOE results were given for each quality criteria in form of 3D and 2D plots. These quality criteria were bulk temperature, clamp force, injection pressure, shear stress, sink mark depth, temperature at flow front, cooling time, volumetric shrinkage, time at end of packing and part weight. Subsequently an optimization was performed using a NLP-model to identify the best combination of process parameters.

Chapter 6 summarizes the major conclusions, presents the achieved objectives and identifies the future research.

Appendix A contains the paper "Powder Injection Molding of Ceramic Engine Components for Transportation" published in *JOM Journal of the Minerals, Metals and Materials Society* (Volume 64) with data based on the work from this thesis. The other appendices give the raw data and log files from the simulations and optimization.

2. BACKGROUND

2.1. Material Selection

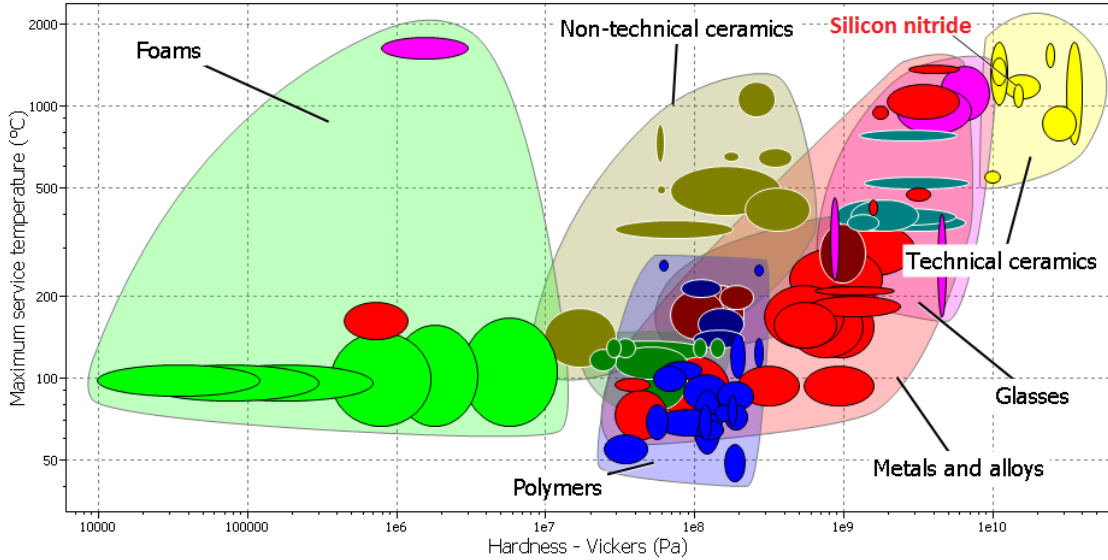


FIGURE 2.1: Ashby Plot of Service Temperature versus Hardness

For the application of a combustion engine a material with high hardness, high service temperature, good strength and low thermal conductivity are required. In Figure 2.1 the maximum service temperature was plotted as function of the Vickers hardness. The Ashby plot in this figure was created using the CES EduPack 2011 by Granta Design. High hardness is crucial for the intended application. The maximum service temperature is needed to withstand the temperature use during combustion. This plot showed the material family of the technical ceramics in the right top corner. It was found that technical ceramics had a superior combination of these properties compared to other materials. Silicon nitride was found centered in the group of technical ceramics in this case.

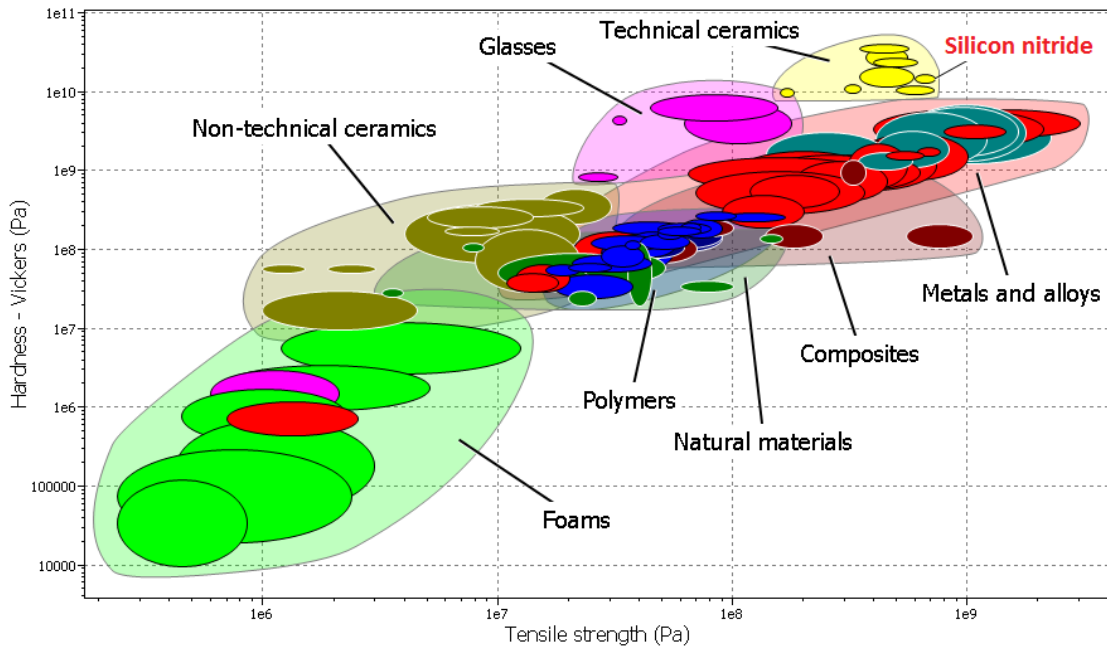


FIGURE 2.2: Ashby Plot of Hardness versus Tensile Strength

In the second Ashby plot, the Vickers hardness was plotted against the tensile strength (Figure 2.2). Tensile strength is crucial for the intended application, because of the resulting shock loading coming from the motion of the piston. In Figure 2.2 technical ceramics were found in the right upper corner. In case of the tensile strength there was some overlapping with the composites, metal and alloys materials families, but silicon nitride still showed good standing relative to most of the materials from these groups. It was also found that silicon nitride is the best candidate within the technical ceramics group.

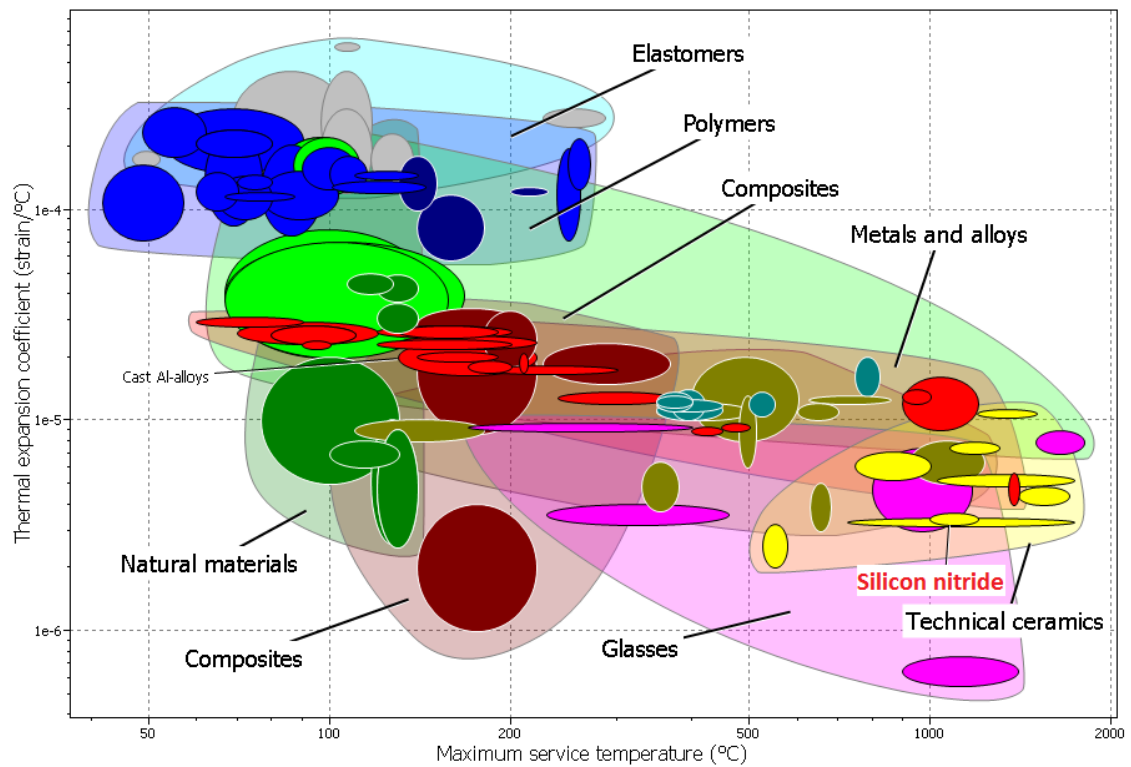


FIGURE 2.3: Ashby Plot of Thermal Expansion versus Service Temperature

In the third Ashby Plot, the thermal expansion coefficient of the materials is plotted as a function of the maximum service temperature (Figure 2.3). A small thermal expansion coefficient is good, because the engine can be assembled with smaller gaps to compensate expansion during operation. This also helps the overall endurance of the whole system. Silicon nitride was found in the lower right corner, it has better expansion attributes than all materials from the metals and alloys family, which are currently used to manufacture engines.

2.2. Silicon Nitride

2.2.1 History of Silicon Nitride

The earliest known reference regarding silicon nitride was made by Deville and Wohler in 1857 [5]. The first patent involving silicon nitride was issued in 1896 by H. Mehner [31]. However, significant commercial use didn't start until the late 1940s [42]. During the last 50 years, silicon nitride has been studied extensively [12]. Processes were developed and a lot of progress has been made with identifying useful sintering additives [30]. The understanding of sintering additives has made silicon nitride more competitive due to lowered costs [20]. Improvements in processing were made in the 70s. Pressureless sintering and high gas pressure sintering techniques became common methods used in the industry [42]. Recently, it has been shown that the synthesis of silicon nitride particles can be done on a large scale [40]. It has also been shown that mechanical properties increase with increasing nano scale powder content [51].

2.2.2 Crystal Structure of Silicon Nitride

Silicon nitride exists in 3 different crystallographic structures, the α , β and γ phase. The α and β phases are the most common forms and can be achieved under atmospheric pressure. The third phase, γ , is metastable and has only been discovered recently [55]. This phase can only be created under very high pressure. The raw material for industrial usage is α -silicon nitride. This can be transformed during sintering into the β structure if a liquid phase is present [57].

2.2.3 Synthesis of Silicon Nitride Powder

TABLE 2.1: Silicon Nitride Synthesis Methods

Method	Chemical process
direct nitridation	$3 \text{ Si} + 2 \text{ N}_2 \rightarrow \text{Si}_3\text{N}_4$
carbothermal nitridation	$3 \text{ SiO}_2 + 6 \text{ C} + 2 \text{ N}_2 \rightarrow \text{Si}_3\text{N}_4 + 6 \text{ CO}$
diimide synthesis	$\text{SiCl}_4 + 6 \text{ NH}_3 \rightarrow \text{Si}(\text{NH})_2 + 4 \text{ NH}_4\text{Cl}$ $3 \text{ Si}(\text{NH})_2 \rightarrow \text{Si}_3\text{N}_4 + 2 \text{ NH}_3$
vapor phase synthesis	$3 \text{ SiCl}_4 + 4 \text{ NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12 \text{ HCl}$

Silicon nitride does not occur naturally. The major production routes are shown in Table 2.1. Direct nitridation is commonly used for micro sized powder. The direct nitridation of silicon is performed in an atmosphere of N_2 , N_2/H_2 or NH_3 at temperatures above 1100°C but below the melting point of silicon nitride (1410°C)[43]. On the other hand, vapor phase synthesis has been used for nano sized powder[40]. The vapor phase synthesis takes place between different gaseous species in the temperature range from 800°C up to 1400°C . Usually, the starting materials are SiCl_4 and ammonia which react to form amorphous silicon nitride. In particular ammonolysis of silicon monoxide (SiO) vapor was expected to be effective to produce nano sized silicon nitride powder [21].

2.2.4 Mechanical and Thermal Properties

TABLE 2.2: Properties of Pressureless Sintered Silicon Nitride [1]

Property	Value and Unit
Density	3.27 g/cm ³
Hardness	1450 kg/mm ²
Thermal conductivity	29 W/m-K
Coefficient of thermal expansion	3.3 * 10 ⁻⁶ °C
Temperature stability	1000 °C
Toughness-K _{IC}	5.7 MPa-m ^{-0.5}

Table 2.2 shows typical values for pressureless sintered silicon nitride at room temperature. In comparison hot-pressed silicon nitride has higher values in terms of density (3.3 g/cm³), hardness (1580 kg/mm²) and toughness-K_{IC} (6.1 MPa-m^{-0.5}). Additionally, silicon nitride has excellent wear resistance, good oxidation and creep resistance and good thermal shock resistance. Silicon melts at 1410 °C[42], which sets the upper bound for temperature exposure. Due to the low self-diffusion coefficient of the nitrogen atoms of 6.3×10^{-20} cm²/s at 1400 °C sintering without sintering additives is almost impossible [22]. All the attributes vary depending on the sintering parameters used and the sintering additives in the mixture.

2.2.5 Applications of Silicon Nitride

The silicon nitride market share is growing continuously since the 70s [37]. The mechanical and thermal properties make silicon nitride a useful material for applications, such as bearings, cutting tools, valves, turbocharger rotors, turbine blades, molten metal handling, thermocouple sheaths, welding jigs and fixtures and welding nozzles. In foundries all the equipment exposed to liquid metal can be manufactured from silicon nitride. Other industries, where silicon nitride can be used include electronics, aerospace, defense and automotive sector. In the automotive sector, ceramics are desired for wear-resistant applications, for instance in a break disk or engine block. If these parts are made out of silicon nitride they could last longer and therefore increases the overall lifespan of a car. Silicon nitride is useful in cutting tools for titanium machining. In the electronic industry silicon nitride is used as a dielectric and for photolysis.

2.2.6 Previous Ceramic Engine Development

Silicon nitride has good thermal shock resistance (in case of a combustion engine ΔT of 600 °C) and good creep resistance, therefore is a desirable material for the design of a complete engine. One of the early studies on silicon nitride in the automobile industry was in 1971 by the Ford Motor Company [42]. After that General Motors filed a patent in 1981 concerning ceramic insulated pistons [48]. In 1991 Isuzu Motor Company from Japan made a whole functioning ceramic engine prototype [49]. Additionally a British research group at Cambridge University built a fully functioning engine [4].

2.3. Ceramic Fabrication

The different stages of the ceramic fabrication process are illustrated in Figure 2.4.

1. Feedstock preparation: The powder and binder system are selected and powder ratios defined. Both are fed into an extruder to produce a homogeneous feedstock. The continuous string coming from the mixing extruder is then pelletized. This is also called “scale-up”.
2. Injection molding: The pellets are fed into the feeder of the injection machine. Once the process parameters are set the mold gets filled with the molten material.
3. Debinding: Binder removal is either done by solvent debinding or thermal debinding or one after another.
4. Sintering: The part is heated up under a controlled atmosphere with a defined heating slope and holding time to promote micro-structural change.
5. Finished Part: The part has the final net shape, however finishing operations may be necessary, for instance breaking edges and removal of the runners.

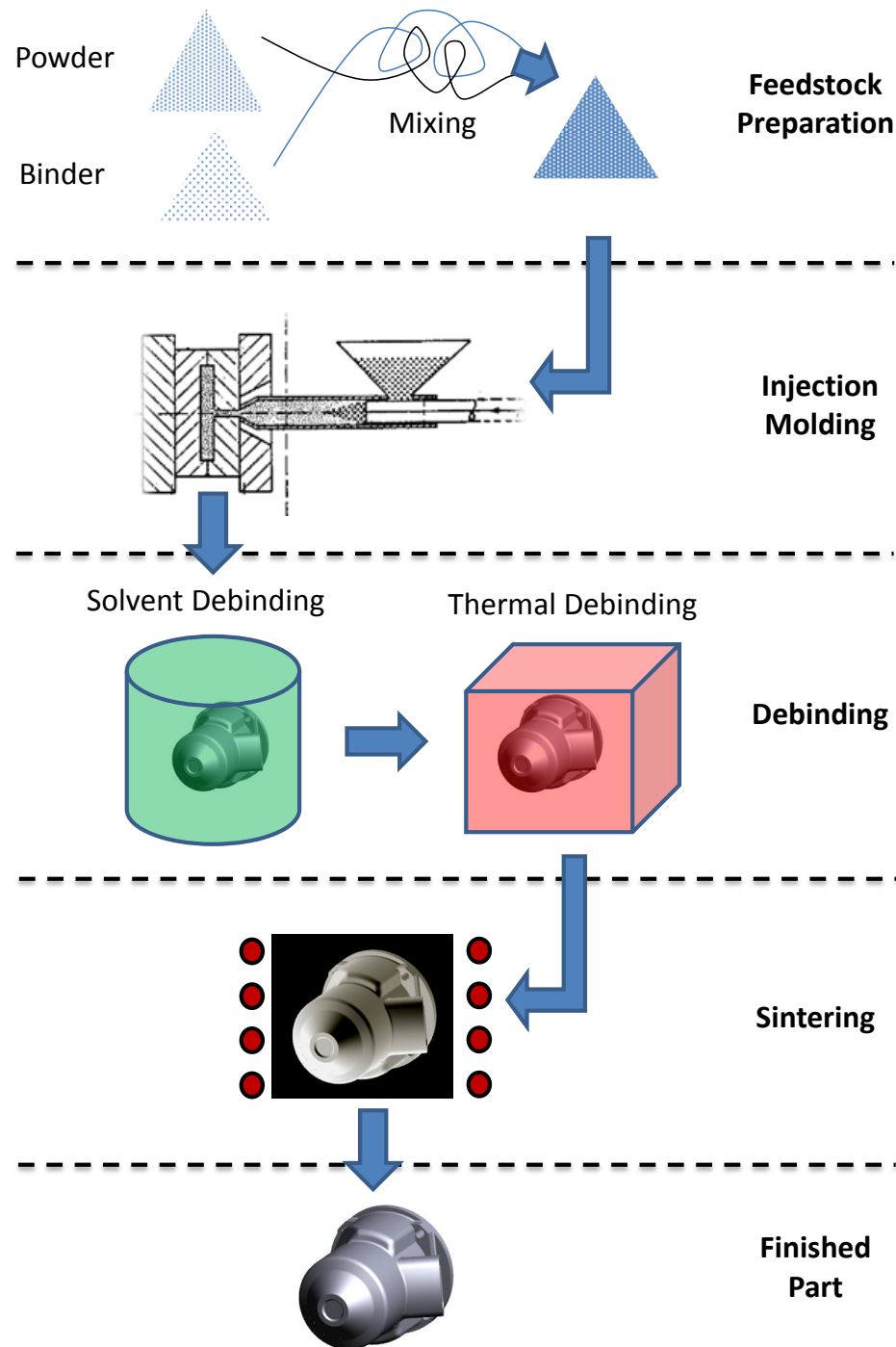


FIGURE 2.4: Stages of the Ceramic Fabrication Process

2.4. Powder Injection Molding

Powder injection molding (PIM) is a well established sub-category of injection molding, which has the ability to fabricate ceramics. It has the ability of near-net-shape fabrication of complex shapes. In PIM, ceramic powder is mixed with a polymer binder (and wax/additives) and used to mold parts in an injection molding machine in a manner analogous to the processing of conventional thermoplastics [35] [15] [15] [17]. A common problem with PIM is that the final component dimensions do not match with those specified for the component as it undergoes shrinkage. Hence, the percent shrinkage should be calculated so as to design the mold before injection molding of the part [19]. Although, the PIM process is well known, various research challenges have to be addressed and optimized for the successful application of the PIM process for new materials and applications. The steps involved in the powder injection molding process is given in the Figure 2.5. Molding conditions should be optimized to avoid any defects in injection molded parts, also called green parts.

2.4.1 Applications of PIM

There are many applications of PIM products in the end-consumer market as well as the industry products. Over the last two decades the market size of PIM products has been steadily growing. Some examples of such products for some selected industry sectors are electronics (printed circuits, heat sinks), mechanical (welding nozzles, foundry equipment, bearings), tools (machining tools, drill bits, casting core), automotive (valves, transmission parts, turbocharger rotor blades) and end-consumer (jewelry, kitchen knives, coffee cups).

2.4.2 Defects

The five main defects, which can occur during injection molding, are air traps, short shots, jetting, flashing, weld lines. Air traps occur when flow fronts coming from different

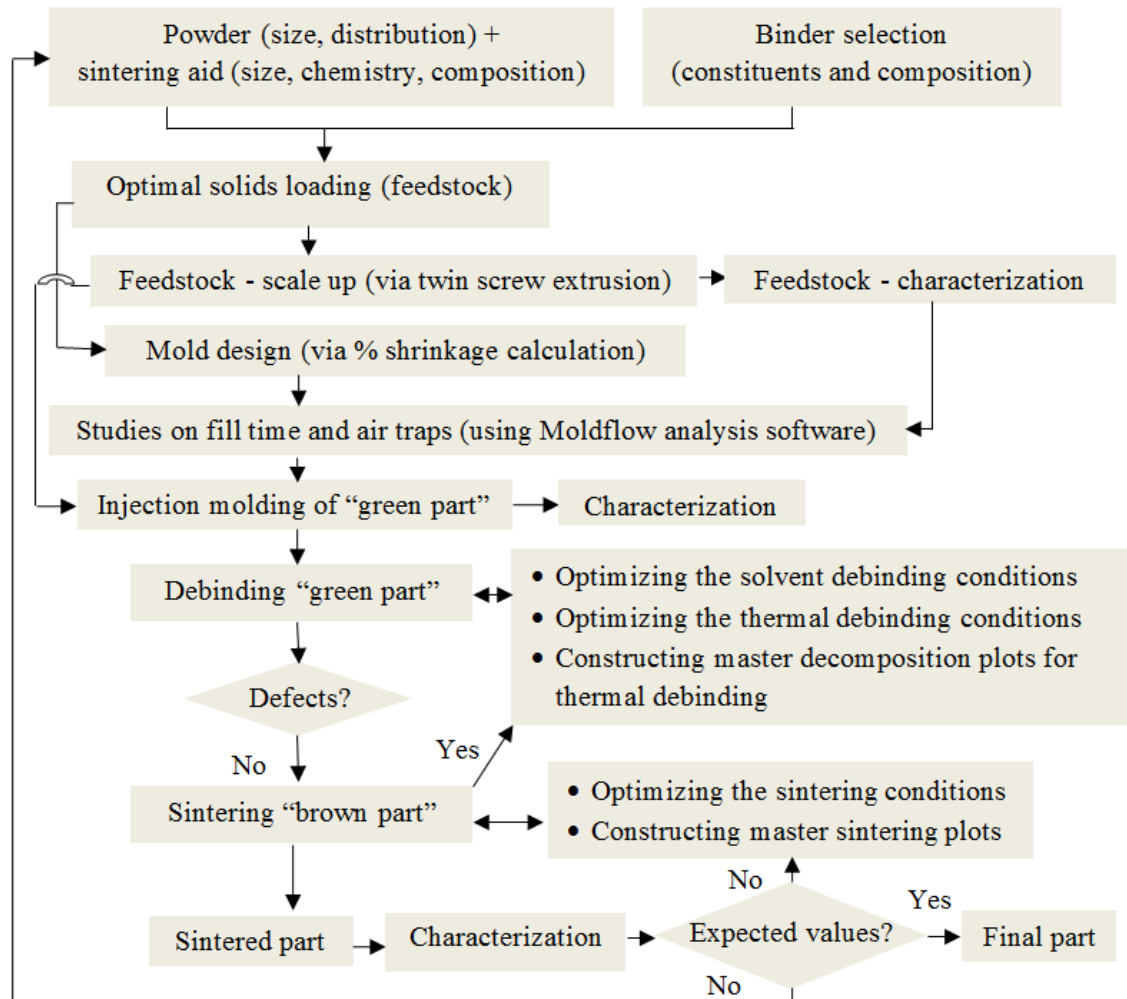


FIGURE 2.5: Flowchart Describing the Steps Involved in the Powder Injection Molding Process

directions surround and trap a bubble of air in a mold corner. Short shots are incomplete filling of a mold cavity, because the flow freezes before it reaches all mold areas. Jetting occurs when polymer melt is pushed at a high velocity through restrictive areas without forming contact with the mold wall. Flashing occurs when a thin layer of material is forced out of the mold cavity at the parting line. Weld lines are created when two independent flow fronts travelling in different directions meet. When they bond, the result can be some permanent residuals which can be seen after ejection.

2.5. Binder

2.5.1 Role of the Binder

Binders play a very crucial role in processing of components by powder injection molding. Binders are multi component mixtures of several polymers. A binder typically consists of primary component to which various additives like dispersants, stabilizers, and plasticizers are added. The basic purpose of binders hold the powder together after molding and to sustain the parts shape. The binders are mixed with ceramic powders to make feedstocks which are afterwards used as starting materials for powder injection molding. Binders are removed after molding prior to sintering of the component. The binder powder mixture (feedstock) should satisfy various rheological requirements for successful molding of the components without formation of any defects. The viscosity of the feedstock should be in an ideal range for successful molding. A very low viscosity during the molding process will result in separation of powders and binders. On the other hand, too high a viscosity will impair the mixing and molding process. Apart from the requirement of ideal viscosity range during molding process, the feedstock should also have the characteristic of large increase in viscosity on cooling. The large increase in viscosity will assist in preserving the shape while cooling. The binder should possess the characteristic of faster removal

during debinding without forming defects in the injection molded component. The binder which provides strength is removed gradually increasing the susceptibility of the green part for formation of defects. The binder should also possess the characteristic of burning out completely without leaving any residual carbon. It is very hard for a single binder to fulfill all the characteristics of feedstock. The binder system used in injection molding process typically contains multiple components each performing a specialized task. In the case of silicon nitride paraffin wax and stearic acid have been proven to be very effective [53] also poly ethylene glycol (PEG) is used widely [33].

2.5.2 Mixing Technologies

The main objective of mixing is to obtain a uniform coating of binder on the ceramic particle surface. Other objectives are to mix all the components of binder system uniformly, breaking down powder agglomerates and to process a uniform feedstock. Various factors like particle size, shape, size distribution, binder properties affect the mixing behavior of the feedstock. The presence of air in the feedstock can result in formation of defects during injection molding. The feedstock after mixing is discharged from the equipment and precautions should be taken to prevent segregation of the feedstock during this process. It is preferable to solidify the feedstock in the homogeneous condition. Continuous mixing of the feedstock during cooling can also result in obtaining homogeneous feedstock. The temperature of mixing has to be chosen appropriately in case of thermoplastic binders. The temperature of mixing is carried out at intermediate temperatures. Mixing at low temperatures at which the mixtures still possess high yield strength will cause cavitation defects in the injection molded parts. Mixing at too high a temperature can result in binder degradation resulting in lowering of viscosity and separation of powder from the binder. The inhomogeneities in the feedstock occur due to either the binder separating away from the ceramic particles or due to segregation of ceramic particles in the binder. During agitation the smaller particles fill the interstitial pores between large particles

resulting in segregation of powders. The torque required for mixing decreases as the agglomerates are broken and liquid due to melting of binder is released in the feedstock. The torque continues to decrease as more amount of liquid is released with continuous mixing. The torque reaches a steady state where the rate of mixing equals to the rate of demixing. A homogenous mixture will show a steady torque with mixing time. The viscosities of the feedstocks vary with the shear rate. Some of the mixtures are single screw extruder, twin screw extruder, twin cam, double planetary, Z-blade mixtures, etc. Out of all the available mixtures the twin screw extruder is most successful as it combines high shear rate and short dwell time at high temperature. The equipment consists of twin screws that counter rotate and move the feedstock through the heated extruder barrel. The discharge from the equipment is in the form of uniform cylindrical product.

2.5.3 Binder Systems

Table 2.3 shows exemplary binder systems, which are used throughout the industry and on a lab scale.

2.5.4 Debinding

There are three basic categories of binder removal methods. The first one is solvent debinding, where a liquid acid is used to discompose the binder in the part [25] [54] [8] [56]. The second method thermal debinding [29] [23] [26]. Here the part is heated to produce polymer degradation. It has to be done very carefully in order not to cause any defects. The third binder removal method is catalytic debinding [9] [2] [10]. Here a gas nitric acid is used. A special reactor has to be used. One or more debinding techniques are selected and their conditions are optimized, so as to retain the part shape without the formation of defects [13]. These debound samples are generally called brown parts.

TABLE 2.3: Examples of Binder Composition used in Injection Molding

Binder Composition	Metal Powder	Source
30 % Paraffin Wax 10 % Carnauba Wax 10 % Bees Wax 45 % Polypropylene 5 % Stearic Acid	316L Stainless Steel	[46]
85 % Paraffin Wax 15 % Ethylene Vinyl Acetate	316L Stainless Steel	[47]
45 wt. % Low Density Polyethylene 45 wt. % Paraffin Wax 10 wt. % Stearic Acid	316L Stainless Steel	[45]
64 % Paraffin Wax 16 % Microcrystalline Paraffin Wax 15 % Ethylene Vinyl 5 % High Density Polyethylene	17-4 PH Stainless Steel	[52]
50 % High Density Polyethylene 50 % Paraffin Wax	HS12-1-5-5 High-Speed Steel	[6]
65 % Paraffin Wax 30 % Polyethylene 5 % Stearic Acid	Copper	[34]
79 % Paraffin Wax 20 % High Density Polyethylene 1 % Stearic Acid	Iron-Nickel	[24]
55 % Paraffin Wax 25 % Polypropylene 5 % Stearic Acid 15 % Carnauba.	Fe-Ni	[27]

2.6. Sintering

The main sintering methods used in the industry are reaction bonding, hot pressing, hot-isostatic pressing, gas-pressure sintering and pressureless sintering. During the sintering $\alpha\text{-Si}_3\text{N}_4$ transforms into $\beta\text{-Si}_3\text{N}_4$ [22].

2.6.1 Pressureless Sintering

The pressureless sintering method is basically a chamber where the material is heated up under atmospheric pressure. To avoid unwanted reactions a inert gas, usually nitrogen is used. Since the pressure is the same from every direction density variation in the final part will be minimal. It was first observed in 1974 [42] that dense silicon nitride can be achieved via pressureless sintering. Figure 2.6 shows three different phases of liquid phase sintering. These phases are explained in Section 2.6.2.

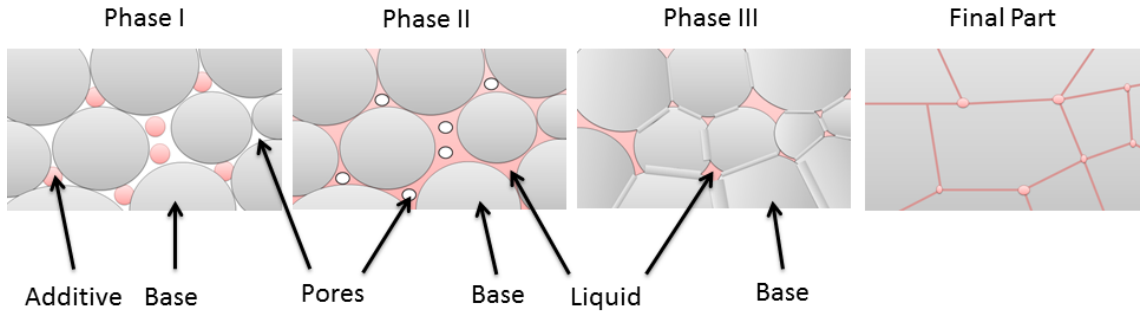


FIGURE 2.6: Stages of the Sintering Process

2.6.2 Liquid Phase Sintering (LPS)

Liquid phase sintering (LPS) is independent from the sintering method. The basic concept is that additives added to the material get into a liquid state to promote densification. The basic mechanism is divided into three stages: partial rearrangement, solution precipitation and final densification. Partial rearrangement happens first. After the additives melted the liquid capillary forces lead to movement of the solid particles to a state of

higher packing. This stage happens rather quickly, because actual particle movement takes place. The other two stages depend on diffusion through the liquid and solid. The next phase is solution precipitation. In this stage Ostwald ripening takes place [41]. That means particles will go into solution preferentially and precipitate on larger particles. Also particles will chose positions with lower chemical potential. The last stage is final densification also known as solid-state or skeleton sintering. Here a structure is formed and last pores are filled [30]. Figure 2.7 shows the relative densification of the different stages. In this figure base reefers to the ceramic powder and the additives to the sintering additives. Section 2.6.3 explains the need and types of sintering additives.

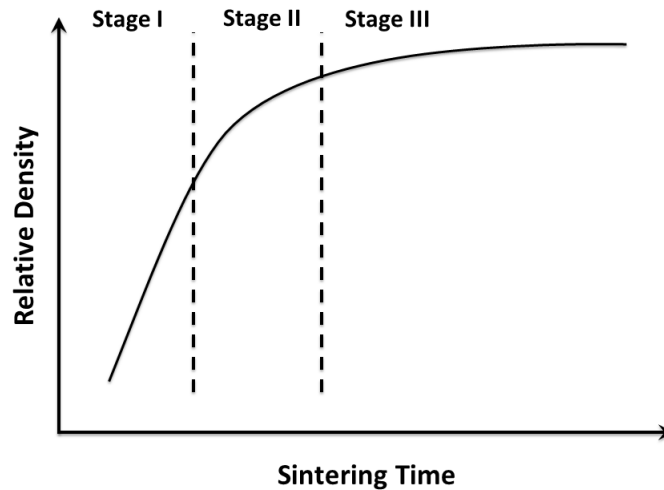


FIGURE 2.7: Schematic of the Stages of Liquid Phase Sintering

2.6.3 Sintering Additives for LPS

The main task for the sintering additives is to promote densification. This is achieved by creating a liquid phase before the actual powder begins to melt [3]. Since higher densification results in higher strength and toughness a content of 5% yttria and 5% magnesia are very good sintering additives [11]. But this is just one example. Other additives which provide enough densification are Y_2O_3 [43] and $LiYO_2$ [3]. In general the higher the density is the higher the strength will be and longer sintering time will burn off the additive and result in weight loss. Also additives will lower the necessary temperature and decrease the necessary holding time and also prevent abnormal grain growth [28].

2.7. Simulation of PIM

The problem of simulating the PIM process is a combined finite-element-method (FEM) and computational-fluid-dynamics (CFD) problem due to the nature of the material. The material is a non-Newtonian fluid, the viscosity varies with temperature and with shear rate. There are different commercial software packages to perform such simulations. One of the most sophisticated packets is Moldflow Insight by Autodesk. It has been continuously improved over the last 25 years. It is also capable of dealing with the different phases of injection molding. There are two main phases, the filling phase and the packing phase. The filling phase deals with the flow front traveling through the tool and forms a frozen layer due to heat loss where it faces the tool directly. The packing phase deals increased pressure once the tool is filled. There is also a compression of the plastic binder components of the material. The plastics are very compressible and will compress up to 15 % [44]. The Moldflow software can perform a finite element analysis with its non-Newtonian, non-isothermal solver, which uses the governing model of the Hele-Shaw flow.

2.7.1 Hele-Shaw Model

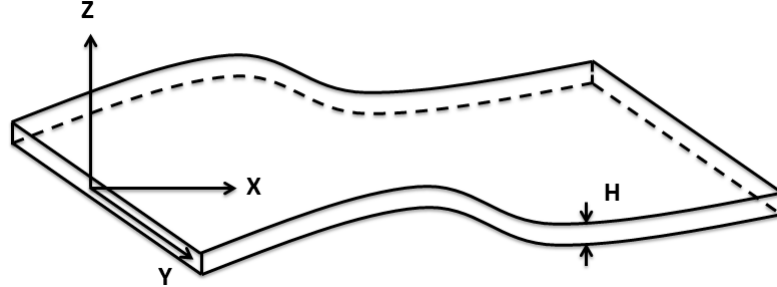


FIGURE 2.8: Sketch of a Hele-Shaw Cell

The model used in Moldflow to describe the flow behavior is the Hele-Shaw flow. Here the assumptions are made that there is only laminar flow, inertia and gravity are neglected and with the partition into small cells (Figure 2.8) the velocity profile becomes parabolic in case of a decreasing height of the cell ($H \rightarrow 0$).

Equation 2.1 states the relationship between that parabolic velocity (u) profile at the current pressure $p(x,y,t)$ with viscosity (μ). H stands for the height of the cell.

$$u = \nabla p \frac{z^2 - H^2}{2\mu} \quad (2.1)$$

After integrating the velocity with respect to z and substituting this equation into the continuity equation, the velocity field is only depending on the two dimensions x and y . (see Equation 2.2).

$$\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} = 0 \quad (2.2)$$

Equation 2.3 demands that the gradient pressure perpendicular to the wall of the cell is 0. $\hat{n}$ is the normal vector to the wall. This is also called the no-penetration boundary condition.

$$\nabla p * \hat{n} = 0 \quad (2.3)$$

2.7.2 Dual Domain Mesh

The dual domain model creates a mesh only consisting of triangles. First the thickness of the part is determined by calculating the distance between the elements on opposite sides of the part. Then, ideally, there would be a one-to-one correspondence between the elements. Usually that is not the case, since there are differences in geometry or curvature from one side compared to the other. The mesh can be generated with the built-in mesh generator “Fusion type-Dual Domain”. The mesh can be evaluated by the aspect ratio (Equation 2.4), and by the match percentage is the percentage of elements for which a matching element on the other side of the part was found. The reciprocal match percentage is the percentage of the matched elements that match back to the same element.

$$aspect\ ratio = \frac{4 * \sqrt{3} * Area\ of\ triangle}{sum\ of\ squares\ of\ edge\ lengths} \quad (2.4)$$

2.8. Potential Gaps in Knowledge

There is a lack of data published regarding silicon nitride with measured properties and design nano sized powders. There is a potential for improvement of the understanding of the behavior of this material system with powder ratio variation. The PIM process is widely used in the industry for the fabrication of silicon nitride parts, but the design protocols for powder injection molding for silicon nitride are not available. If such a database of material properties exists, the potential will be improved for design of better parts, reducing cost of trial and error runs and expand the opportunities to decide in favor of silicon nitride. Also, completely new applications can emerge with the information for design for manufacturing.

2.9. Rationale for this Thesis

The present thesis will focus on identifying material properties and process conditions for successfully applying silicon nitride to powder injection molding and to enable the simulation of powder injection molding with the silicon nitride material system. To achieve this, the material characteristics of powder-polymer mixtures have to be measured. These properties include raw powders characteristics (average particle size, shape), maximum volume fraction of powder in the binder (solids loading) and the feedstock properties (viscosity, thermal conductivity, specific heat capacity, no-flow temperature, eject temperature and transition temperature, pressure volume temperature behavior and density). The second rationale is to explore the process conditions. This is done by obtaining the simulated flow characteristics (fill time, pressure at injection location, maximal shear stress at wall), analyze predicted defects (air traps, short shots) and determine the response for a quality criteria. This is done in the entire feasible process window. Based on the obtained data one set of PIM process parameter will be identified to be the best trade off.

3. MATERIALS AND METHODS

3.1. Materials

Four different ceramic powders and four different binder components were used in this project. The two main ceramic powders were silicon nitride powders with two different particle sizes. They were both provided by Northwest UAV Propulsion Systems Inc. The two other ceramic powders were the sintering additives, yttria and magnesia. They were both acquired from Inframat Advanced Materials LLC. The product number for yttria was 39N-0802 and the product number for magnesia was 12N-0801. The four binder components were paraffin wax, polypropylene (Proflow 3000), Fusabond E226 and stearic acid.

3.2. Material Analysis

3.2.1 Particle Size Analysis

In order to measure the mean particle size and its distribution a multiple-angle laser diffraction instrument by the Brookhaven Instruments Corporation was used (Figure 3.1). The instrument had a BI-APD High Sensitivity Detector and was powered with a CVI Melles Griot Helium Neon Laser. The software package to analyze the data was also provided by Brookhaven Instruments.

3.2.2 Torque Rheometry

Torque rheometry was performed to identify the critical solids loading of the ceramic powder in the four component binder. The critical solids loading is the maximum amount of powder, which can be mixed with the binder present. It is expressed in wt.%. The torque rheometry was done with a CW Intelli-Torque Plasticorder (Brabender) with a

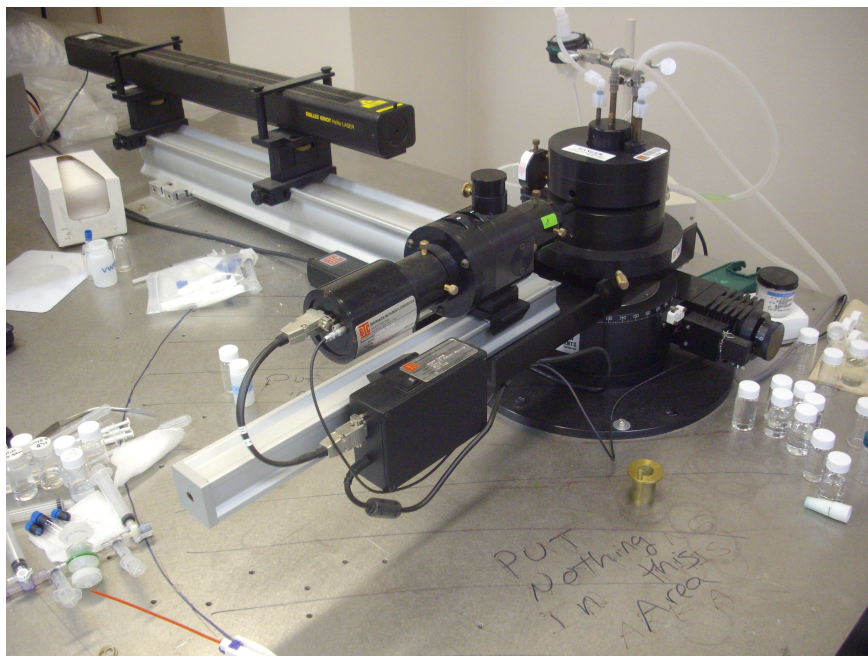


FIGURE 3.1: CVI Melles Griot Helium Neon Laser

maximum chamber volume of 46 inch³ (753.80 cm³). Figure 3.2 shows the used machine. It had three heat zones, which were heated to 150 °C. The machine was equipped with Z-blades, which are named after the shape they have. The powder-binder mixture was mixing at a constant speed of 50 rpm. 10 g of the four component binder mixture was initially added to the chamber, which melted shortly after. The pre-mixed powder was added to have an initial solids loading of 72 wt.%. Subsequently the powder addition was increased at a rate of 1 wt.% and processed until the torque was stabilized, to ensure uniform mixing of the powder and binder.

3.2.3 Vickers Hardness

The Vickers hardness measurement was performed at the materials characterization lab in Dearborn 201 at Oregon State University. A LECO M400A Hardness Tester with a test load of 9.80 N (1 kilopond) was used to make the indentation and a Leica DMRM digital camera in combination with the Qimaging Micropublisher 3.3 and the QCapture



FIGURE 3.2: Brabender CW Intelli-Torque Plasticorder

Pro software package were used to collect the images. The test was done according to ASTM C132708.

3.2.4 Weight and Dimensions

The parts were weighted on a ACCULAB Sartourious VICON scale and the dimensions were measured with a precision caliper.

3.2.5 Scanning Electron Microscopy (SEM)

All SEM images were collected on a FEI Quanta 600 FEG SEM dual beam scanning electron microscope. For the captured pictures a voltage range from 5 kV to 30 kV and a spot from 1 to 6 was used. Since all samples for SEM imaging must be electrically conductive the specimens were sputtered with gold to get a very thin conductive coat.

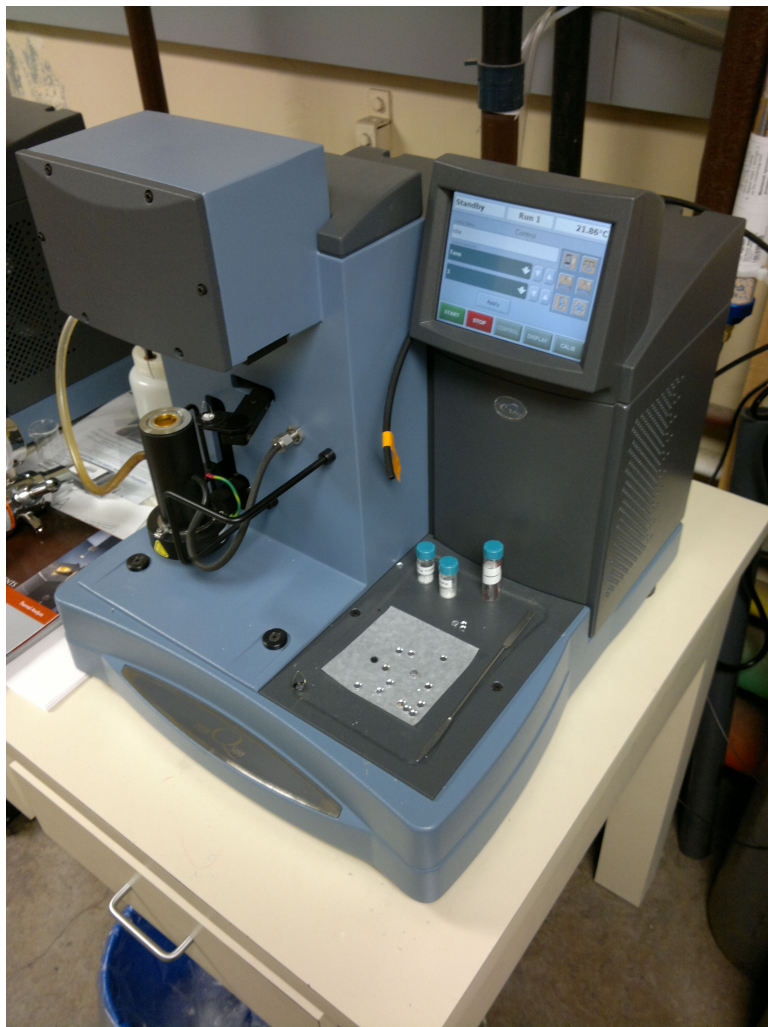


FIGURE 3.3: Thermogravimetric Analyzer - TA Instruments Q500

3.2.6 Thermogravimetric Analysis (TGA)

In order to determine the actual powder content in the powder-polymer mixture thermogravimetric analysis was performed. The instrument used was the TA Instruments Q500 as seen in Figure 3.3. The data collection was done via the Thermal Advantage Software Release Package. Nitrogen was set to a flow rate of 40 mL / min and oxygen to 60 mL / min. The heating rate was 20 °C / min. The experiment was conducted in the range from 20 °C to 600 °C.

3.3. Feedstock Analysis

Feedstock pellets were sent to Datapoints Lab in Ithaca, NY to measure several flow and thermal properties.

3.3.1 Capillary Rheometry - Viscosity

In general polymer viscosity depends on shear rate and temperature. The liquid viscosity tends to decrease as its temperature increases. The Williams-Landel-Ferry model (WLF) mathematically describes the temperature dependency. A Goettfert Rheograph 2003 capillary rheometer was used to determine the viscosity data. It covers a shear rate range of 10 - 10 000 $\dot{\gamma}$. The pressure drop across the die was measured for each flow rate and the viscosity-shear rate data was calculated using a Weissenberg-Rabinowitsch correction. The test was done according to the ASTM D3835.

3.3.2 Thermal Conductivity

Thermal conductivity was measured using a transient line-source technique, which is standardized in ASTM D5930. Several points were measured starting in the molten state and cooling through transition to solid state and a static load was applied to ensure contact between the probe and the material. In this specific case, the experiment was conducted on an Instron 8872 Servohydraulic UTM machine.

3.3.3 Specific Heat Capacity

Heat capacity is the measurable physical quantity of heat required to change a substance's temperature and the specific heat capacity, which is the heat capacity per unit mass of a material. A Perkin Elmer DSC7 differential scanning calorimeter (DSC) was used to heat and cool the material over a temperature range, and simultaneous heat flow measurements were made. This was done according to ISO 11357-4 and the ASTM E1269 standards from 2005. The material was heated to its molten state and data measured in the cooling phase,

which was a controlled cooling to 40 °C at a rate of 20 °C per minute. The specific heat was expressed as a function of temperature.

3.3.4 No-Flow Temperature

The no-flow temperature is the solidification temperature of the melted material. The material was heated until molten and then cooled slowly under pressure. The no flow temperature is defined as the temperature, where the flow rate is less than 2 mm per min at a pressure of 130 bar. The test was performed with a Goettfert capillary rheometer.

3.3.5 Ejection Temperature and Transition Temperature

The transition temperature is the onset of crystallization transition, whereas the ejection temperature is the end of crystallization, which is also called glass transition temperature. Similar to the determination of the specific heat capacity, a differential scanning calorimeter was used and the material was heated to its molten state and data was measured in the cooling phase. It was cooled down to 40 °C at a rate of 20 °C per minute. While cooling down the transition and ejection temperature were recorded. This test was done with a Perkin Elmer DSC7 differential scanning calorimetry according to the ASTM D3418 and ISO 11357-2 standards.

3.3.6 Pressure-Volume-Temperature Behavior (PVT)

The pressure-volume-temperature behavior is essential for post filling injection molding simulation. The data was gathered by putting a sample piece of the material of about 1 g in the PVT apparatus. The apparatus was set to one temperature and the isothermal data acquisition was done by readings the volume for the specified temperature while the pressures was varied from 0-200 MPa. Then the machine was set to a higher temperature and the process was repeated.

3.3.7 Density Measurements

Density was determined using the displacement method. Using a high precision analytical balance, the sample was weighed in air, then in water. This was repeated twice and the average taken. The test was done according to ASTM D792 and ISO 1183-1. Melt density is essential for calculating thermal diffusivity and estimating flow rates and volume. The pellets were loaded into the capillary rheometer and heated up until they melted. Then the material was extruded at a constant volumetric flow rate for a certain time span. A defined specimen was extruded and its mass measured. This was done three times. Now that the volumetric flow rate and the time is known the volume can be calculated and therefore its melt density. All this was done according to the ASTM D3835 standard.

3.4. Material Processing

3.4.1 Mixing and Scale-Up

The material mix has been scaled-up at Entek Manufacturing, Inc. located in Lebanon, OR. The extruder had co-rotating twin-screw with a diameter of 27 mm. It was manufactured by Entek Extruders and had a L/D ratio of 40 and 10 heat zones. These heat zones were heated up to 160 °C and the screws were rotating with 200 rpm. The extruder and the two feeders can be seen in Figure 3.4. The feeder on the left was the binder feeder and the feeder on the right was the powder feeder. After the extrusion, continuous strings of material were air cooled on a conveyor belt system and chopped into pellets (Figure 3.5).

3.4.2 Molding

The part were molded at Kinetics Climax Inc., a company specialized in powder injection molding and located in Wilsonville, OR.



FIGURE 3.4: Entek Twin Screw Extruder



FIGURE 3.5: Entek Pellet Chopper

3.4.3 Thermal Debinding and Sintering

Thermal debinding and sintering were performed at Kyocera Industrial Ceramics Corporation in Vancouver, WA. The sintering temperature was 1850°C and the furnace was filled with nitrogen and pressurized at 100psi.

3.5. 3D-Models and Drafts

Two different PIM components were used in this thesis. A small mutli-channel part was used for material process validation, based on a moldable mold. The second part was a hollow cylinder from the engine design development by NWUAV Propulsion Systems (McMinnville, OR). This part was explored for its manufacture ability using the Moldflow software.

3.5.1 Validation Part

The part has a rectangle shape with multiple channels. A schematic can be seen in Figure 3.6. With this test specimen molding, sintering, shrinkage and weight loss was analyzed for this particular for material system. All SEM image recordings were taken with this part.

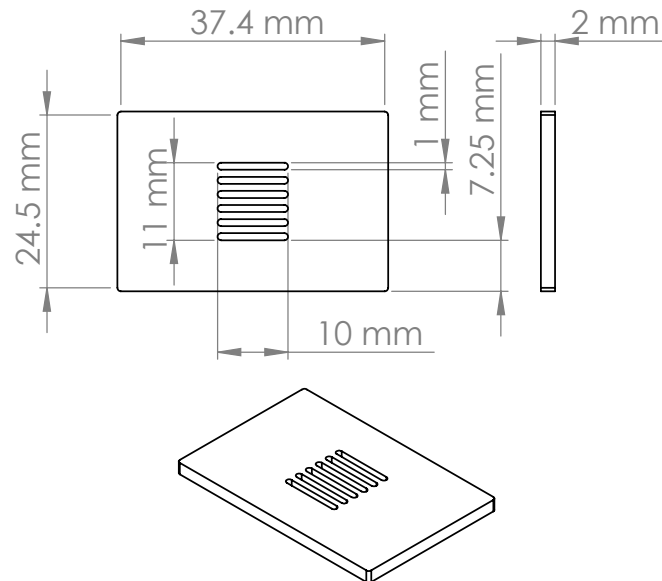


FIGURE 3.6: Multi-Channel Validation Part

3.5.2 Cylinder for Ceramic Engine

The second selected part for simulation is from an engine design development by NWUAV Propulsion Systems. The top, side and isomeric view of the part can be seen in Figure 3.7. A simulation of the powder injection molding process was carried out and the optimal process parameters for the quality criteria predicted by the simulation were calculated.

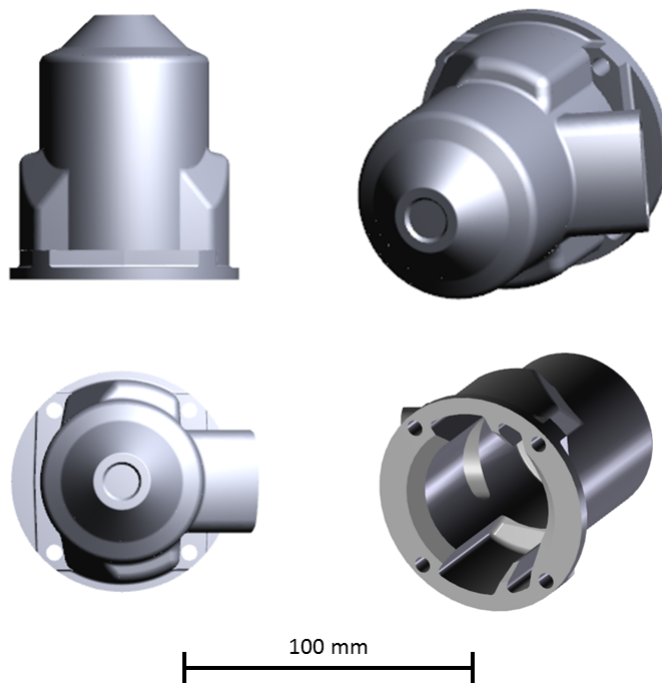


FIGURE 3.7: Cylinder for Ceramic Engine

3.6. PIM Simulation

The Moldflow software was setup in order to perform the simulation with a fill phase and a pack phase. The necessary steps to perform the simulation run were importing the 3D model, generating and selecting the material database and setting the process parameter.

3.6.1 PIM-Process Input Parameters

The powder injection molding process parts quality is determined by the settings of the three main process parameters. These three process parameters are:

1. **Melt temperature:** At this temperature the material is ejected from the extruder into the mold. During the filling this temperature remains constant. The temperature has to be above the transition temperature, so the material is molten while injecting.
2. **Mold temperature:** The mold is preheated to this temperature. If this temperature is too low the flow freezes before the mold is filled. If it is too high the cooling time required, until the mold can be opened, will take very long.
3. **Injection time:** The injection time is the time it takes for the mold to fill completely. If it is set too low too much pressure is applied and too much shear in the material created. If it is set too high the flow will cool down too much.

Other process parameters were ambient temperature, which was assumed to be 25 °C and velocity/pressure switch-over was initialized at 99 %.

3.6.2 PIM-Process Output Parameters

The powder injection molding process can be evaluated by certain measurands. These indicators are used to evaluate the process quality. The main physical quantifiers were the following:

1. Injection Pressure (P_i): This is the pressure the machine is applying to the material over the extruder screw. The pressure increases during filling and reaches its peak at the point when the mold is filled and switch -over occurs. The unit of injection pressure is mega pascal (MPa).
2. Clamp Force (f_c): The clamp force is the force required to hold the two mold section together during the filling. This force is the area perpendicular to the mold dividing section times the pressure. It is expressed in kilo newton (kN)
3. Shear Stress (τ): The shear stress is the force within the material in two imaginary layers. It can cause frictional heat with heats the material up. Its unit is mega pascal (MPa).
4. Bulk Temperature at End of Fill (T_b): This is the variation in the temperature at the end of the fill. The unit is either kelvin or celsius. It doesn't matter since it is a spread.
5. Sink Mark Depth (D_s): The sink marks are the difference in the volume after filling and pressure dropping and after freezing completely solid. The unit is millimeter (mm).
6. Temperature at Flow Front(T_{ff}): The temperature at flow front is the temperature which the flow has when it passes this position for the first time. This is also a measurement variation, not a absolute temperature measurement.
7. Cooling Time (t_C): The cooling time is the time required after packing until the part is solid enough so it can be ejected. The unit is seconds (s).
8. Volumetric Shrinkage at Ejection (V_S): The volumetric shrinkage is the percentage increase in local density from the end of the packing phase to the density at room

temperature. This is the percent measurement compared to before. Therefore it is dimensionless (%).

9. Time at End of Packing (t_{ep}): The time at the end of packing is the sum of the fill time, the packing time and the holding time after pressure release for cooling. This is expressed in seconds (s).

10. Part weight (W): It's the estimated weight based on the material injected. The weight is express in gramm (g).

3.6.3 Import 3D Model

The part which was sought to be simulated has to be of a closed 3D shape. It was imported as a IGS file.

3.6.4 Material Database

A custom material database was developed based on the properties measured in Section 4.3. was made in Moldflow Simulation.

3.6.5 Mold Material

Material used for the mold in the simulation is P-20 tool steel. The thermal properties (Table 3.1) are important to calculate the heat exchange between the heated mold and the injected material.

TABLE 3.1: Thermal Properties of Mold Material

Property	Value
Density	7.8 g/cm ³
Specific Heat	460 J/kg-C
Thermal Conductivity	29 W/m-C
Coefficient of Thermal Expansion	$1.2 \cdot 10^{-5}$ 1/°C

Its mechanical properties (Table 3.2) are needed to estimate potential deformation.

TABLE 3.2: Mechanical Properties of Mold Material

Property	Value
Elastic Modulus (E)	200000 MPa
Poissons ratio (ν)	0.33

3.6.6 Machine simulation

The Moldflow software emulates a real injection molding machine. This generic machine is set to a maximum injection pressure of 180 MPa and a maximum clamp force of 5000 kN. These values are representing a typical injection molding machine. Different machine setup, for instance different screw diameter were not taken into account.

3.7. Design of Experiments

In order to get information on the whole possible process window of PIM a series of simulations were conducted while varying three process parameters (mold temperature, melt temperature and injection time). Two different DOE setups were used in this thesis.

3.7.1 Taguchi Method

The Taguchi method of conducting design of experiments was used in the present structure. It is an estimation of the sensitivity of one process parameter relative to an other. The ranks of the most influencing factors and the percentage of the influence is based on the signal-to-noise ratio. The Taguchi orthogonal array design with two levels, three factors $L_4(2^3)$ results in four runs. Each run is only done a single time. The factor combination for each run is given in Table 3.3.

TABLE 3.3: Taguchi Orthogonal Array Design

Run	Factors		
	A	B	C
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

3.7.2 Box-Behnken - Face Centered Cubic Design

The Box-Behnken design is a design method with the goal of getting a response surface model. The design which was used in this thesis consists of 3 factors, 3 center points and gets 10 coefficients for the quadratic model. The 15 necessary runs to get the coefficients for the quadratic model are displayed in Table 3.4.

3.8. Optimization

In order to solve the NLP-model LINGO 13.0 was used. It is a comprehensive modeling language with a solver for non-linear programming by LINDO Systems inc. Chicago, IL.

TABLE 3.4: Box-Behnken Design

Run	Factors		
	A	B	C
1	-1	-1	-1
2	-1	-1	1
3	-1	1	-1
4	-1	1	1
5	1	-1	-1
6	1	-1	1
7	1	1	-1
8	1	1	1
9	-1	0	0
10	1	0	0
11	0	-1	0
12	0	1	0
13	0	0	-1
14	0	0	1
15	0	0	0

4. RESULTS AND DISCUSSION

4.1. Powder Properties

There were four different ceramic powders used in this project. Two different silicon nitride (Si_3N_4) powders were used. These two Si_3N_4 powder had different particle sizes, a larger one and a smaller one forming a bimodal powder. The two other ceramic powder were sintering additives, yttria (Y_2O_3) and magnesia (MgO). The particle size analysis gave the distribution of the small silicon nitride powder, which detected a majority of the particles having a median diameter of 20 nm. Figure 4.1 shows the distribution of the small Si_3N_4 powder.

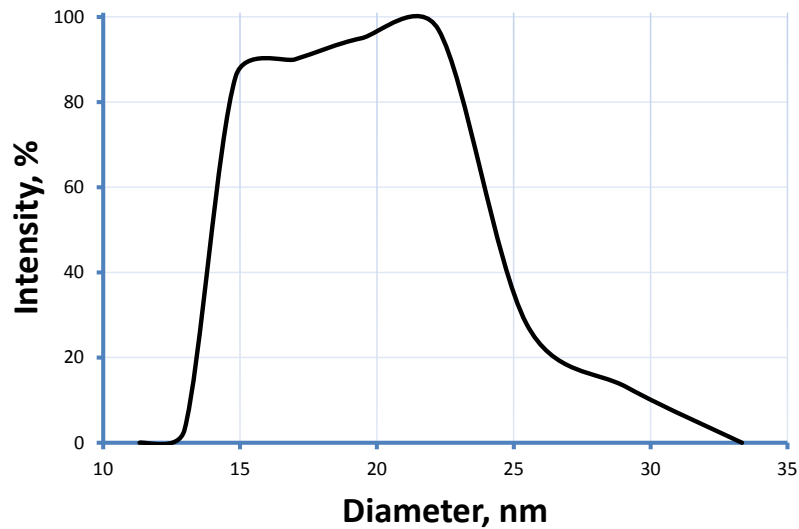


FIGURE 4.1: Silicon Nitride Powder Particle Size Distribution (small)

The second silicon nitride powder was a large sized powder. The particle size analysis revealed a median size distribution of 130 nm. The distribution is given in Figure 4.2.

Yttria and magnesia were obtained from Inframat Advanced Materials LLC. The particle size distribution of the yttria powder is given in Figure 4.3. The median diameter was 70 nm. The vendors specifications (Product No.: 39N-0802) claimed an average particle size

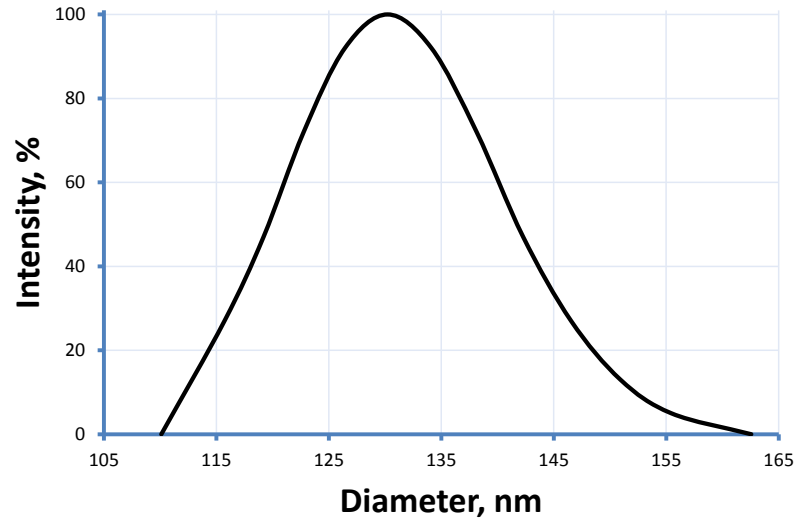


FIGURE 4.2: Silicon Nitride Powder Particle Size Distribution (large)

between 30-50 nm. The result indicates either agglomeration or slightly larger particles.

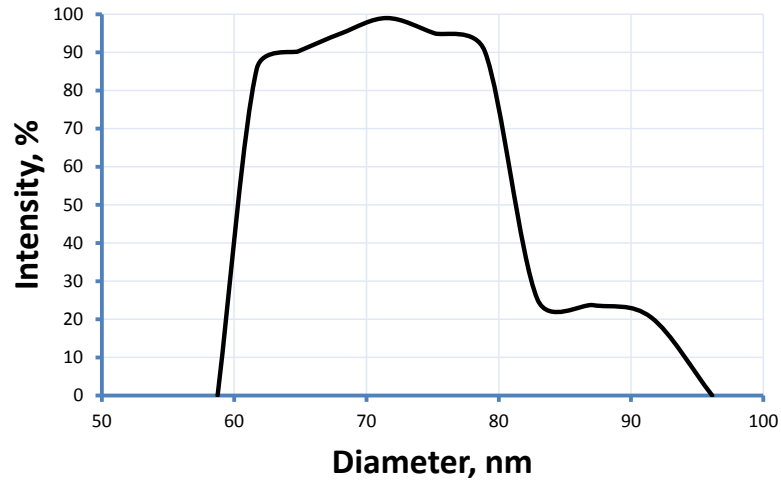


FIGURE 4.3: Yttria Powder Particle Size Distribution

The second sintering additive used was magnesia. The vendor (Product No.: 12N-0801) specified the median around 30 nm. The particle size analysis found a median diameter of 50 nm and a distribution (Figure 4.4) which showed a range of 45 nm to 60 nm, where particles with the same quantity were found. This leads to the assumption of either powder agglomeration or slightly bigger average particles than specified.

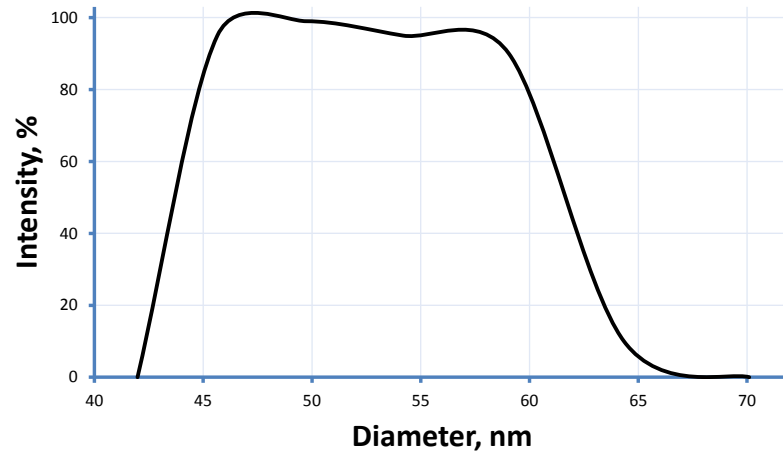


FIGURE 4.4: Magnesia Powder Particle Size Distribution

A summary of all powders used and the median diameter for each powder found by the particle size measurements is stated in Table 4.1.

TABLE 4.1: Summary of Particle Size Measurements

Ceramic Powder	Median Diameter
Si_3N_4 (small)	20 nm
Si_3N_4 (large)	130 nm
Y_2O_3	70 nm
MgO	50 nm

4.2. Material System Parameters

The material system consists of the main ceramic powder (bimodal silicon nitride mixture), the sintering additives and the binder.

4.2.1 Silicon Nitride Powders

The idea behind adding smaller powder particles is that it would fill the gaps between larger powder particles. This way the material mix is denser and has less pores. Because of the higher packing density the effort to sinter the material would decrease. This results in a lower sintering temperature and shorter sintering duration. Table 4.2 shows the ratio of the two different silicon nitride powders. This ratio is based on previous test trials, which indicated higher maximum for the packing density of mixtures with higher ratio of small powder.

TABLE 4.2: Silicon Nitride Powder Composition

Material	Weight Percentage
large Si_3N_4 powder	95 %
small Si_3N_4 powder	5 %

4.2.2 Sintering Additive Powders

Yttria and magnesia were used to enable liquid phase sintering. The composition was based on a literature study and approved for pressureless sintering and high pressure sintering. Table 4.3 shows these compositions. A 100 g sample of this powder composition has been used for the torque rheometry.

4.2.3 Binder Components

Table 4.4 shows the four different components of the binder system and their ratio used. This binder-mix is widely used for ceramics.

TABLE 4.3: Ceramic Powder and Sintering Additives Composition

Material	Weight Percentage
bimodal Si_3N_4	91 %
Y_2O_3	5 %
MgO	4 %

TABLE 4.4: Binder Composition

Material	Weight Percentage
Paraffin Wax	50 %
Polypropylene (Proflow 3000)	35 %
Fusabond E226	10 %
Stearic Acid	5 %

4.2.4 Torque Rheometry Outcome

Figure 4.5 shows the mixing torque as a function of time. Solids loading (ϕ) is the main ceramic powder and sintering additives content in the powder-binder mixture. This was increased during the experiment as a function of time. Solid loading is the fraction of the weight in percent of the powder in regard to the powder binder mixture. The figure shows the initial solids loading of 73 wt. % and the one wt. % steps until no further addition was possible. at 86 wt. %. At 86 wt. %, critical solids loading (ϕ_c) was reached. Unmixed loose powder was observed. With this material system 86 wt. % is equivalent to 60 vol. %. The material appearance was dry and loose which indicated non-uniform mixing of the powder and binder, at that time the mixing torque did not stabilize.

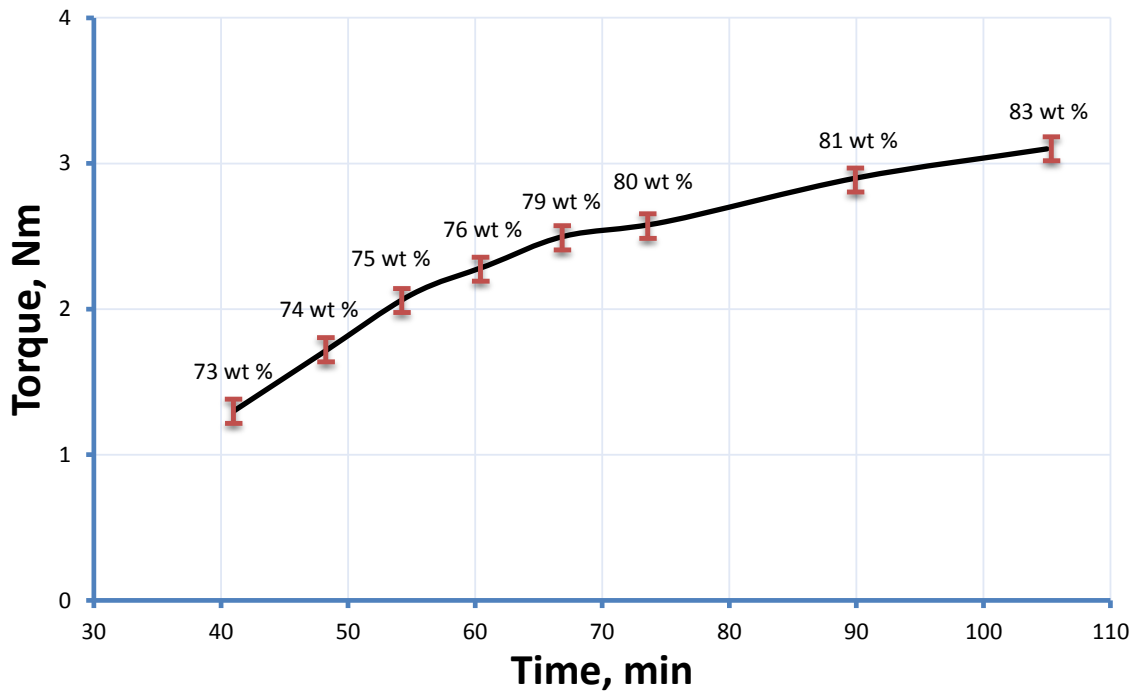


FIGURE 4.5: Torque Rheometry Data

4.2.5 Binder-Powder Ratio

As result form the torque rheometry 80 wt. % was chosen to be used for the scale-up which was conducted as described in Section 3.4.1. About 15 kg of powder-binder-mixture was extruded and pelletized. After pelletizing a sample was used to perform thermogravimetric analysis. The resulting weight loss over temperature is shown in Figure 4.6. The residual had a weight ratio of 80.07 %. The ratio of the pelleted feedstock is listed in Table 4.5. The density of the pellets was 2.304 g/cm^3

TABLE 4.5: Binder-Powder Ratio

Material	Weight Percentage
Ceramic Powders	80.07 wt. %
4-Component-Binder	19.93 wt. %

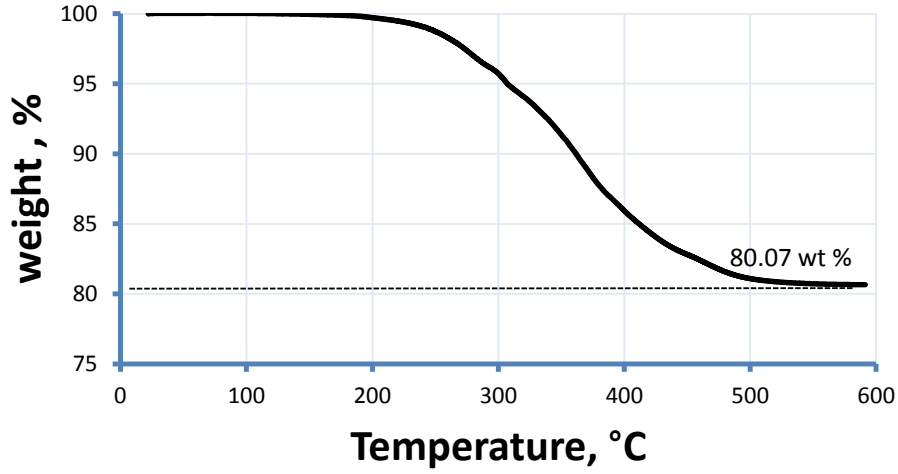


FIGURE 4.6: Thermogravimetric Analysis of the Powder-Binder-Mixture

4.3. Feedstock Properties

Several feedstock properties are necessary to create a custom database in order to conduct a PIM simulation. These properties are viscosity, thermal conductivity, specific heat capacity, no-flow-temperature, the pressure-volume-temperature behavior and the solid and melt density.

4.3.1 Viscosity

Figure 4.7 shows the shear rate ($\dot{\gamma}$) and the viscosity (η) for different temperatures on a logarithmic scale. The test was conducted between 150 °C and 180 °C since this range is covering from melting to degradation. The symbols are the experimental measurements for each shear rate and temperature. The lines are calculated fits for each temperature. The Cross -Williams-Landel-Ferry models was used to express the temperature and shear rate dependence of the suspension viscosity respectably.

$$\eta(T, \dot{\gamma}) = \frac{\eta_o(T)}{1 + \left(\frac{\eta_o \dot{\gamma}}{\tau^*}\right)^{1-n}} \quad (4.1)$$

, with

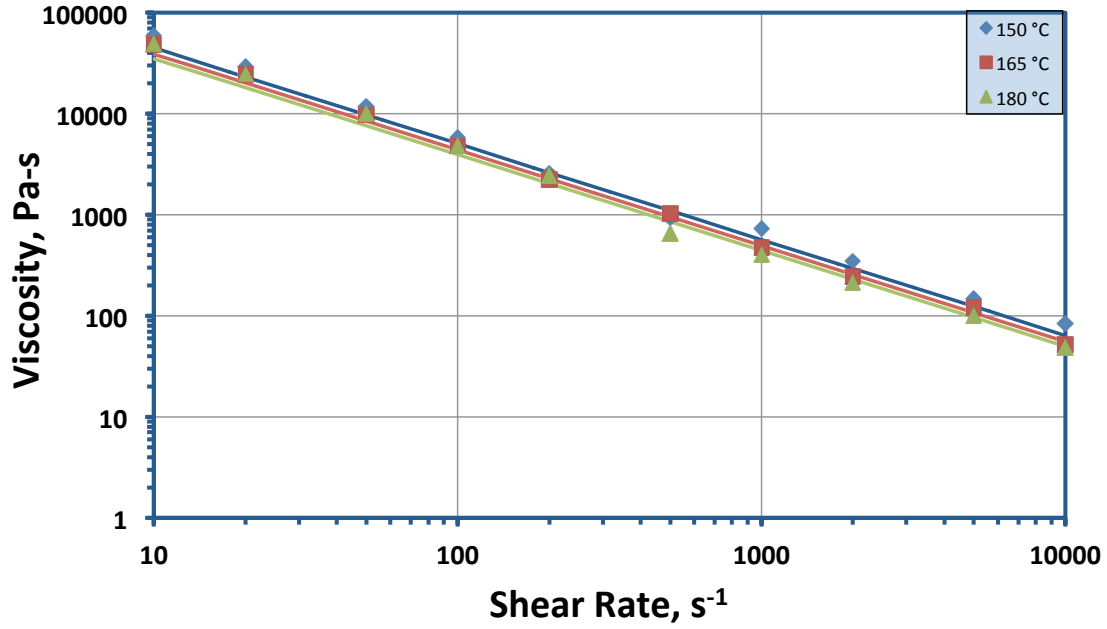


FIGURE 4.7: Viscosity as a Function of Shear Rate and Temperature

$$\eta_o(T) = D_1 * e^{\left(-\frac{A_1(T-D_2)}{A_2+(T-D_2)}\right)} \quad (4.2)$$

Equation 4.2 shows the WLF model, which is used to express the specific viscosity at the current temperature. To extend that model to also include the effect of the shear rate the Cross model Equation 4.1 is added. This Cross model gives the viscosity at any given shear rate and temperature condition. In the simulation this is calculated for each cell. The coefficients to fit the model on the measured points are given in Table 4.6. For the simulation the viscosity is important to calculate flow front velocity.

TABLE 4.6: Rheological Constants

Coefficient	Definition	Si ₃ N ₄ Feedstock
n	Slope of the shear-thinning curve	0.0508
τ^* (KPa)	Weissenberg-Rabinowitsch correction constant	130.12
D_1 (Pa-s)	Scale factor for viscosity	1.0 E+23
A_1	WLF temperature shift factor	42.28
D_2 (K)	Glass transition temperature (zero gauge pressure)	373
A_2 (K)	WLF temperature shift factor	51.6

4.3.2 Thermal Conductivity

The thermal conductivity is essential to calculate the heat loss and therefor the cooling process of the molted part. The measurement points are listed in Table 4.7 and plotted in Figure 4.8.

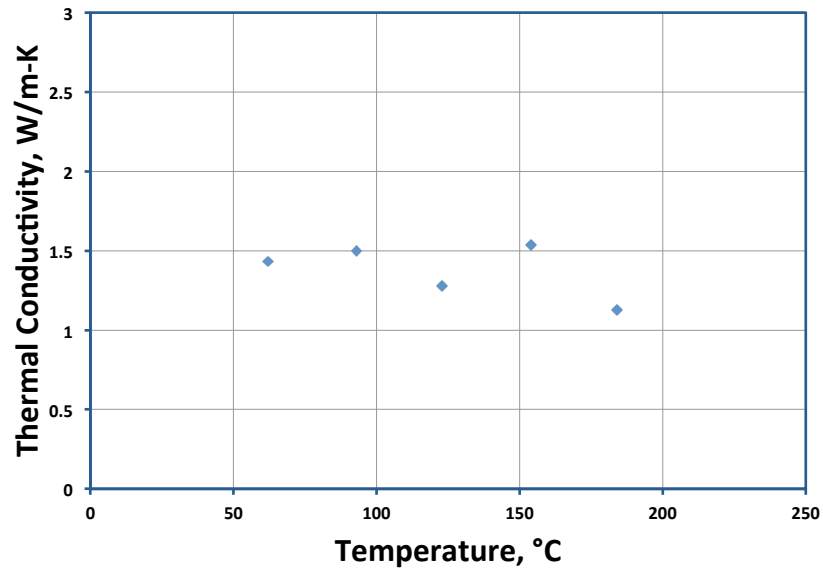


FIGURE 4.8: Thermal Conductivity as Function of Temperature

TABLE 4.7: Thermal Conductivity Data

Temperature in °C	k in W/m-K
184	1.125
154	1.534
123	1.275
93	1.498
62	1.432

4.3.3 Specific Heat Capacity

The specific heat capacity is also crucial to calculate cooling process and the increasing in injection pressure due to colder flow. The measurements are listed in Table 4.8. The melt specific heat is 1160 J/kg-K (at 53 °C). The plot of the measurement point with a fit is shown in Figure 4.9. There the peak was found at 47 °C and an additional peak was observed in the 60 °C to 90 °C range.

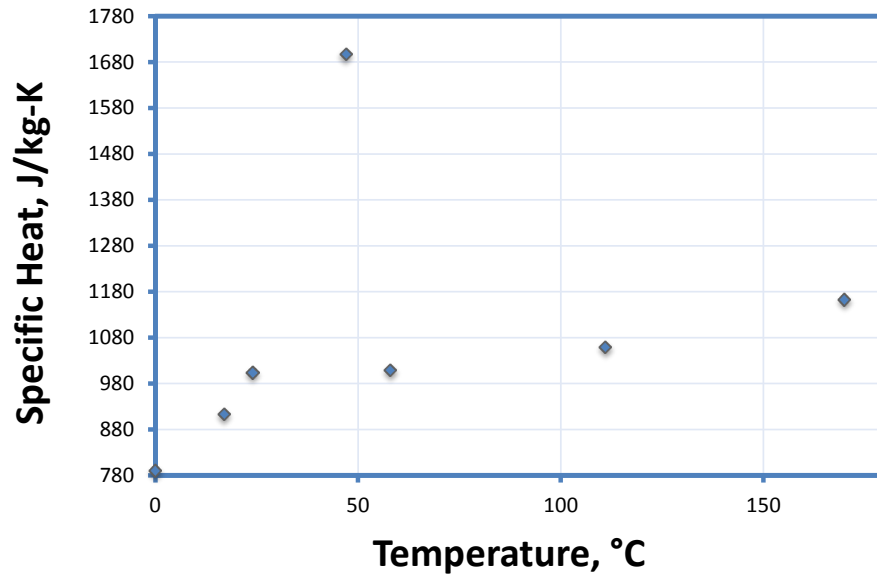


FIGURE 4.9: Specific Heat

TABLE 4.8: Specific Heat Data

Temperature in $^{\circ}C$	C_p in J/kg-K
170	1163
111	1059
58	1009
47	1698
24	1004
17	913
0	791

4.3.4 No-Flow Temperature

The no-flow temperature measured was $150^{\circ}C$. This properties is relevant for the simulation to describe solidification behavior.

4.3.5 Density

The initial solid density measurement took place at $23^{\circ}C$ and resulted in $2300 \text{ kg/m}^3 = 2.3 \text{ g/cm}^3$. The melt density was $2110 \text{ kg/m}^3 = 2.11 \text{ g/cm}^3$.

4.3.6 Pressure-Volume-Temperature Behavior (PVT)

Figure 4.10 shows the variation in specific volume as function of the pressure and temperature. This relationship is important to calculate shrinkage during the cooling phase. The measurement points shown as markers in the figure were used to build a Tait two-domain model to express the volume as function of temperature and pressure. The two domains are the melt domain, which is above the transition temperature (T_f) and the solid domain, which is below the transition temperature.

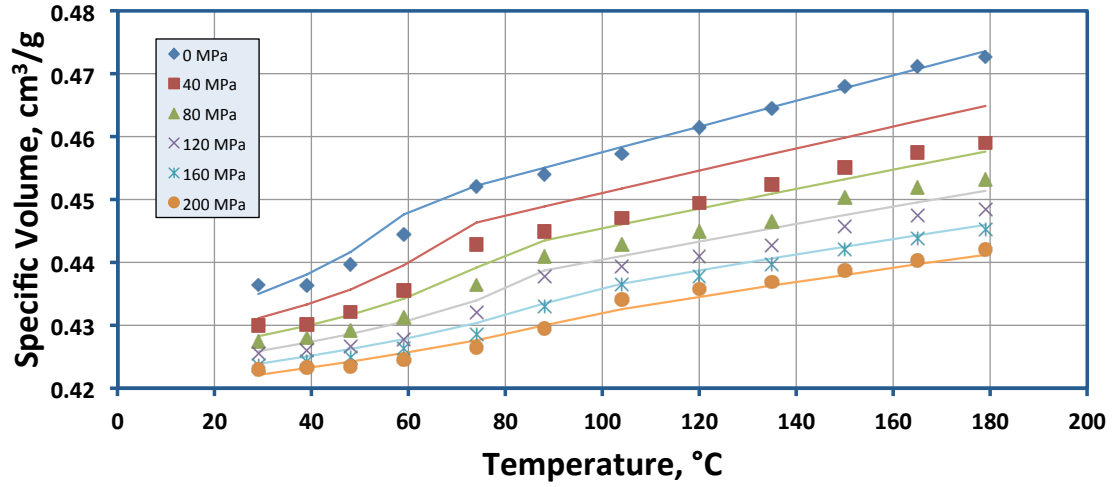


FIGURE 4.10: Specific Volume versus Temperature and Pressure

$$v(T, P) = v_0(T) \left[1 - 0.0894 * \ln \left(1 + \frac{P}{B(T)} \right) \right] + v_f(T, P) \quad (4.3)$$

The Equation 4.3 shows the volume model valid for both domains. v is the specific volume in cm^3/g , P is the pressure in MPa, $B(T)$ is a temperature dependent parameter also in MPa, v_0 is the specific volume at room temperature, v_f is the specific volume above the transition temperature. All temperatures are in $^{\circ}\text{C}$.

$$T_f(P) = b_5 + b_6 * p \quad (4.4)$$

The first domain described is the molten state. This is the case when $T \geq T_f$. Where T_f is depended on the pressure. See Equation 4.4.

$$v_0(T) = b_{1m} + b_{2m} * \bar{T} \quad (4.5)$$

$\bar{T}$ is any temperature above the transition temperature. The transition temperature at atmospheric pressure for this material was 53°C .

$$B(T) = b_{3m} * e^{-b_{4m} * \bar{T}} \quad (4.6)$$

$B(T)$ is expressed as shown in Equation 4.6. For the molten state the v_f component is always zero.

$$v_f(T, P) = 0 \quad (4.7)$$

The second domain is the solid state (and semi-solid state). This is the case if $T < T_f$.

$$v_0(T) = b_{1s} + b_{2s} * \bar{T} \quad (4.8)$$

For v_0 the solid coefficients are now used, see Equation 4.8.

$$B(T) = b_{3s} * e^{-b_{4s} * \bar{T}} \quad (4.9)$$

with the solid coefficients $B(T)$ can now be expressed according to Equation 4.9. But in this case the $\bar{T}$ values now stand for temperatures below the transition temperature.

$$v_f(T, P) = b_7 * e^{(b_8 * \bar{T} - b_9 * P)} \quad (4.10)$$

All subscripts with m and s are suffering to the melt and solid states. The coefficients for the PVT model are shown in Table 4.9.

TABLE 4.9: PVT Coefficients

Coefficient	Definition	Si ₃ N ₄ Feedstock
b ₅ (K)	Crystallization Temperature	336.1500 K
b ₆ (K/Pa)	Pressure Sensitivity of b ₅	1.7250 E-07
b _{1m} (m ³ /kg)	Tait Constant for melt	0.0005
b _{2m} (m ³ /kg-K)		2.0440 E-07
b _{3m} (Pa)		2.6346 E+08
b _{4m} (1/K)		0.0036
b _{1s} (m ³ /kg)	Tait Constant for solid	0.0004
b _{2s} (m ³ /kg-K)		1.0430 E-07
b _{3s} (Pa)		7.7033 E+08
b _{4s} (1/K)		0.0005
b ₇ (m ³ /kg)	Transition of Specific Volume from Solid to Molten	1.6100 E-05
b ₈ (1/K)		0.0383
b ₉ (1/Pa)		1.4410 E-08

4.4. Green Properties of Validation Part

After the net shape process, in this case after the PIM, the part is called green part. The green part can be seen in the left of Figure 4.11.

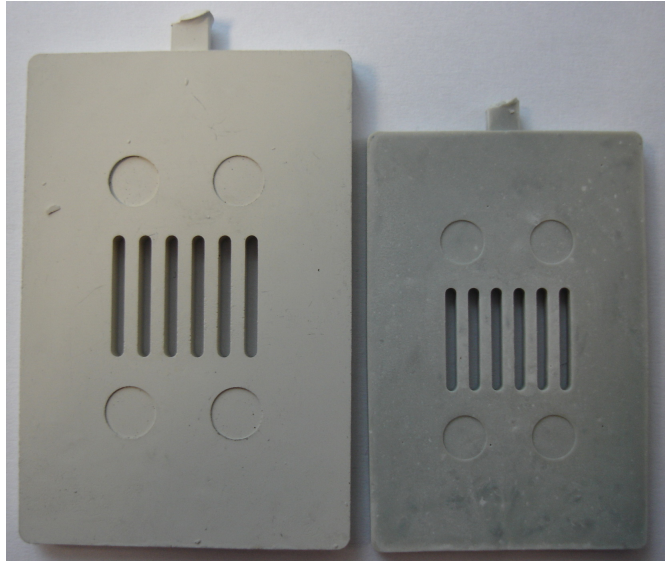


FIGURE 4.11: Validation Part - Molded Part (left) and Sintered Part (right)

4.4.1 Scanning Electron Microscopy (SEM)

A SEM image of the green part can be seen in Figure 4.12. The image shows the approximately rounded α -silicon nitride particles properly mixed with the binder.

4.4.2 Weight and Dimensions

The green parts weighted on average 4.05 ± 0.01 g. The solid green density was 2.304 g/cm^3 . Its volume was 1.759 cm^3 . The measured values can be seen in Table 4.10. Seven different specimens measured and the average was calculated. The values are referring to Figure 4.13.

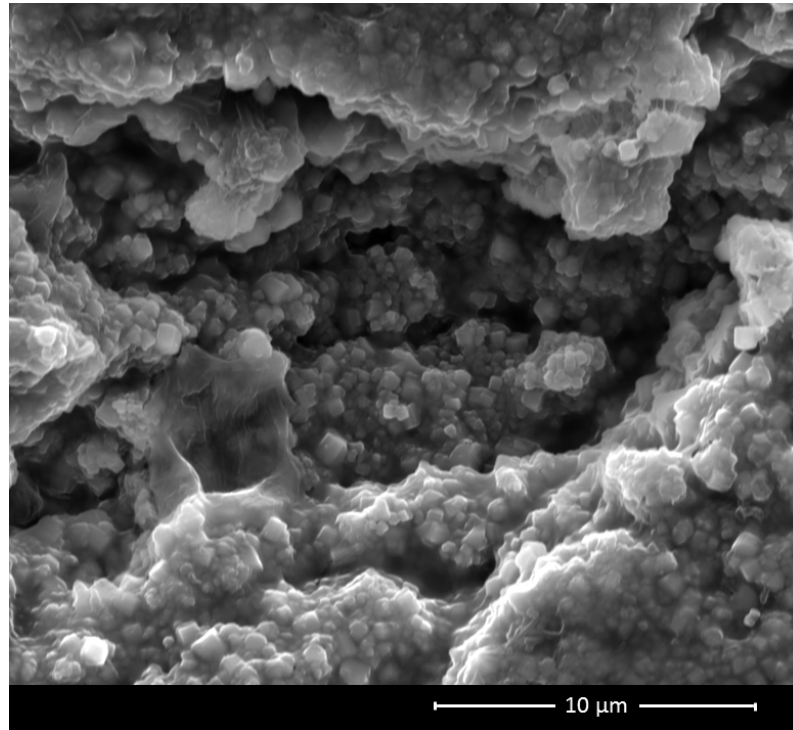


FIGURE 4.12: SEM of Green Validation Part

4.5. Sintered Properties of Validation Part

The part after it has been sintered can be seen in the right of Figure 4.11.

4.5.1 Scanning Electron Microscopy (SEM)

A SEM image of the sintered part can be seen in Figure 4.14. No binder or powder residuals were found. The grain growth on orientation indicate a complete transformation to β -phase silicon nitride.

TABLE 4.10: Molded Part Dimensions

Attribute	Value
Height	25.4 ± 0.1 mm
Length	38.1 ± 0.1 mm
Width	2.0 ± 0.1 mm
Channel Width	0.9 ± 0.1 mm
Channel Length	9.1 ± 0.1 mm

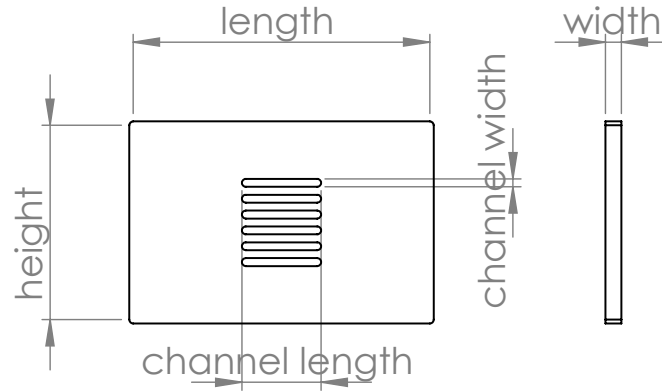


FIGURE 4.13: Validation Part - Shrinkage Measurement

4.5.2 Weight and Dimensions

The sintered specimen parts weighted on average 3.09 ± 0.01 g. The measured dimension characteristics are shown in Table 4.11. The attributes are referring to Figure 4.13.

From the new dimensions a volume of 1.122 cm^3 was estimated. With the given weight and the new volume a sintered density was calculated. The new density is 2.75 g/cm^3 .

4.5.3 Shrinkage and Weight Loss

The sintered part had 63.81 % of its original volume. This was also observed in the measurements. The length shrank 16.2 %, the height about 15 % and the width 14.58 %. The green part average weight was 4.05 ± 0.01 g and the sintered parts mass was $3.09 \pm$

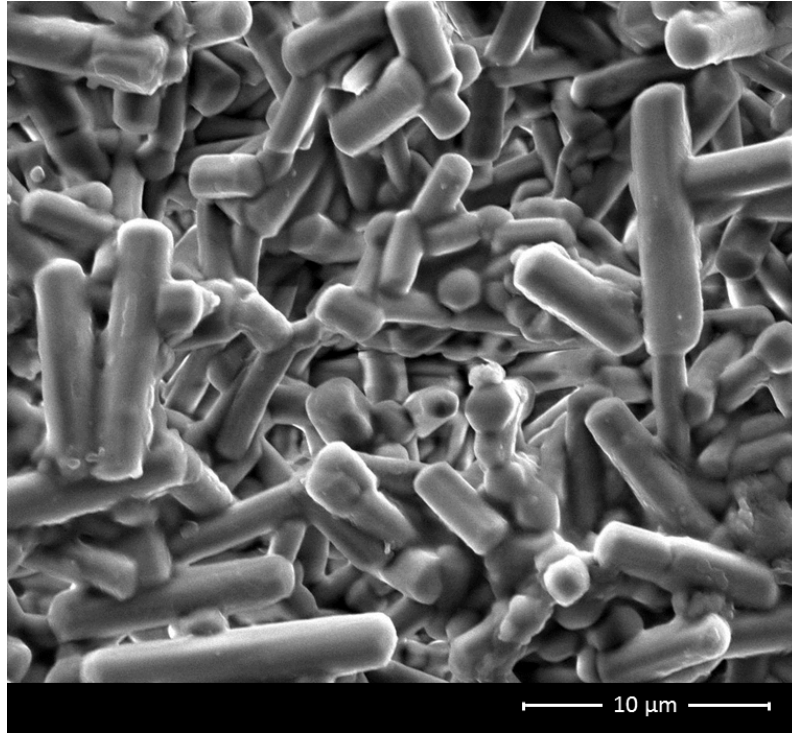


FIGURE 4.14: SEM of Sintered Validation Part

0.01 g. Therefore a weight loss of 23.63 % occurred. The 23.63 % are greater than the 19.97 % binder content measured with by the thermogravimetric analysis. This indicated slight loss of weight due to decomposition of powder.

4.5.4 Hardness

Vickers hardness measurement was performed with a loading force of 1 kp. The two mean diagonal length were :

$$d_1 = 39.94\mu\text{m} \text{ and } d_2 = 36.63\mu\text{m}$$

The imprint by the diamond shaped test head can be seen in Figure 4.15.

The average diameter was: $d_{avg} = \frac{36.63+39.94}{2}\mu\text{m} = 38.285\mu\text{m}$.

$$HV = \frac{(2 * F * \sin(\frac{136^\circ}{2}))}{d^2} \quad (4.11)$$

TABLE 4.11: Sintered Part Dimensions

Attribute	Value
Height	21.4 ± 0.1 mm
Length	31.9 ± 0.1 mm
Width	1.7 ± 0.1 mm
Channel Width	0.9 ± 0.1 mm
Channel Length	7.5 ± 0.1 mm

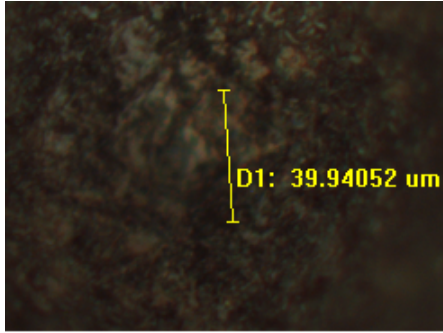


FIGURE 4.15: Vickers Hardness Measurement

$$HV = \frac{1.854 * F}{d^2} \quad (4.12)$$

Using the measured imprint diameters in Equation 4.11 and 4.12 resulted in a hardness value of 1200 ± 50 HV1. This is 13 % lower than the ideal value of 1450 HV (Source: International Syalons).

4.6. Building the Custom Material Database

In order to perform a Moldflow simulation of the silicon nitride material system, a customized materials database had to be created. The space of such a material system was udb. The four main characteristics of a material system in regard to the PIM simulation are process parameters, rheological behavior, thermal properties (specific heat capacity

and thermal conductivity) and the pressure-volume-temperature behavior. In order to create a new blank database *Thermoplastics material* category was selected. In the *Description* tab name and the category were stated. Figure 4.16 shows the *Recommended Processing* tab of the material database editor. Here preferred mold and melt temperature setting were entered. Also the ejection temperature was added here. In order to calculate the time required until were part can be ejected. Figure 4.17 shows the *Rheological Properties* tab. The transition temperature and the viscosity model are filled in here. After selecting the WLF model the constants from Section 4.3.1 were added. Figure 4.18 shows the *Thermal Properties* tab. There the specific heat and thermal conductivity data measured was added. Figure 4.19 shows the 'pvT Properties' tab. Here the melt and sold density as well as the coefficients of the two domain Tait model from Section 4.3.6 were added.

Thermoplastics material

Shrinkage Properties		Filler Properties		MuCell [®] Material Properties		Optical Properties		Environmental Impact		Quality Indicators	
Description	Recommended Processing	Rheological Properties		Thermal Properties		pVT Properties		Mechanical Properties			
Mold surface temperature	23			C							
Melt temperature	150			C							
Mold temperature range (recommended)											
Minimum	23			C							
Maximum	33			C							
Melt temperature range (recommended)											
Minimum	150			C							
Maximum	180			C							
Absolute maximum melt temperature	300			C							
Ejection temperature	34			C							
View test information for ejection temperature...											
Maximum shear stress	0.25			MPa							
Maximum shear rate	100000			1/s							
Name Nano Silicon Nitride - Jürgen Lenz											
										OK	
										Help	

FIGURE 4.16: Material Database Editor - Processing

Thermoplastics material

Shrinkage Properties Filler Properties MuCell[®] Material Properties Optical Properties Environmental Impact Quality Indicators

Description Recommended Processing Rheological Properties Thermal Properties pvT Properties Mechanical Properties

Viscosity

Default viscosity model: Cross-WLF View viscosity model coefficients... Plot Viscosity

Juncture loss method coefficients

c1 Pa^{1-c2}

c2

Transition temperature

Trans: 53 C View test information...

Moldflow Viscosity Index: VI(63)320926

Melt mass-flow rate (MFR)

Temperature: C

Load: Kg

Measured MFR: g/10min

☐ Extension viscosity

Name: Nano Silicon Nitride - Jürgen Lenz

OK Help

Cross WLF Viscosity Model Coefficients

Cross-WLF viscosity model

n: 0.05081

Tau*: 130124 Pa

D1: 1e+023 Pa-s

D2: 373 K

D3: 0 K/Pa

A1: 42.28

A2~: 51.6 K

Plot Viscosity

View test information...

OK Help

FIGURE 4.17: Material Database Editor - Rheological Behavior

Thermoplastics material

Shrinkage Properties Filler Properties MuCell[®] Material Properties Optical Properties Environmental Impact Quality Indicators

Description Recommended Processing Rheological Properties Thermal Properties pvT Properties Mechanical Properties

Specific heat data

	Temperature (T) C	Specific heat (Cp) J/kg-C	Heating/cooling rate C/s
1	170	1163	0
2	111	1059	0
3	58	1009	0
4	47	1698	0
5	24	1004	0
6	17	913	0
7	0	791	0

Plot specific heat data...

View specific heat test information...

Thermal conductivity data

	Temperature (T) C	Thermal conductivity (k) W/m-C	Heating/cooling rate C/s
1	184	1.125	0
2	154	1.534	0
3	123	1.275	0
4	93	1.498	0
5	62	1.432	0

Plot thermal conductivity data...

View thermal conductivity test information...

Name Nano Silicon Nitride - Jürgen Lenz

OK Help

FIGURE 4.18: Material Database Editor - Thermal Properties

Thermoplastics material

Shrinkage Properties	Filler Properties	MuCell [®] Material Properties	Optical Properties	Environmental Impact	Quality Indicators
Description	Recommended Processing	Rheological Properties	Thermal Properties	pvT Properties	Mechanical Properties
Melt density	2.1365	g/cm ³			
Solid density	2.3244	g/cm ³			
2-domain modified Tait pvT model coefficients					
b5	336.15	K			
b6	1.725e-007	K/Pa			
b1m	0.0004503	m ³ /kg			
b2m	2.044e-007	m ³ /kg-K			
b3m	2.63458e+008	Pa			
b4m	0.003566	1/K			
b1s	0.0004342	m ³ /kg			
b2s	1.043e-007	m ³ /kg-K			
b3s	7.70331e+008	Pa			
b4s	0.0004824	1/K			
b7	1.61e-005	m ³ /kg			
b8	0.03829	1/K			
b9	1.441e-008	1/Pa			
Plot pvT data...					
View test information...					
Name: Nano Silicon Nitride - Jürgen Lenz					
OK Help					

FIGURE 4.19: Material Database Editor - Pressure-Volume-Temperature

4.7. Simulation Results of Validation Part

The purpose of the simulation of the validation part was to see if the material, which was developed, sintered. It was necessary to see if the feedstock properties that were measured and simulated a part were in agreement with molding experiments.

4.7.1 Mesh for the Validation Part

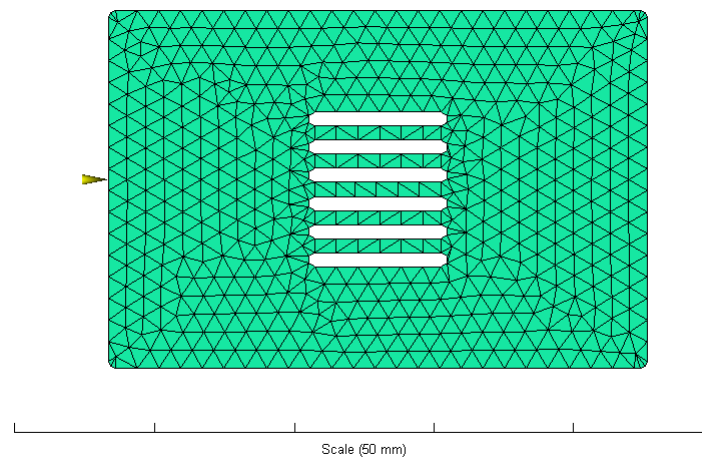


FIGURE 4.20: Validation Part Mesh

The mesh created for the validation part is shown in Figure 4.20.

TABLE 4.12: Mesh Parameters for the Validation Part

Attribute	Value
Mesh Type	Fusion
Triangles	2954
Connected Nodes	1467
Surface Area	23.481 cm ²
Volume	1.842 cm ³
Maximum Aspect Ratio	9.0
Average Aspect Ratio	1.57
Minimum Aspect Ratio	1.16
Manifold Edges	4431
Reciprocal Percentage	99.7 %
Match Percentage	99.3 %

Table 4.12 summarizes the mesh parameters. For fill and pack analysis, the recommended minimum match percentage is 85 %. That is why the mesh showed a high enough accuracy in order to be used for the simulation. The average aspect ratio was 1.57. This is significantly below the recommended average aspect ratio of 6, while the maximum individual value was 9 and the recommendation maximum individual value less than 20. The match percentage was 99.3 %. The match percentage is the percentage of elements for which a matching element on the other side of the part was found.

4.7.2 Process Parameters

For the simulation the arithmetic middle of the recommended process window was chosen. These parameters were:

1. Mold surface temperature 28 °C

2. Melt temperature 165 °C

3. Injection time 0.2 s

It was clear that these parameters were not the absolute optimal settings, but a good chose in regard to check the feasibility.

4.7.3 Injection Pressure

Figure 4.21 shows the distribution of the pressure in the part. The biggest pressure was 27.97 MPa and it was reached at 0.233 s fill time. The predicted pressure peak is significantly smaller than the maximum pressure of an average injection molding machine. The default injection machine used in Moldflow was capable of 180 MPa, maximal injection pressure.

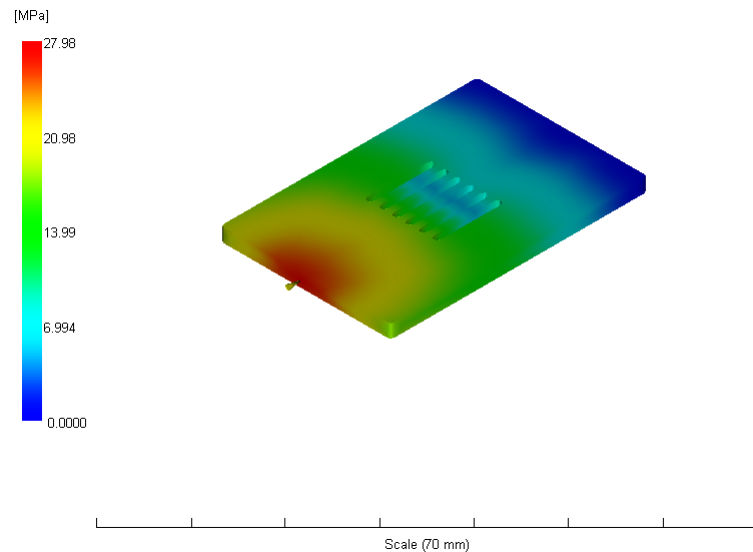


FIGURE 4.21: Validation Part - Pressure

4.7.4 Clamp Force

The maximum estimated clamp force was 2.3 kN (0.2343 tonnes force) and it occurred at 0.237 s. Most injection molding machines can hold the clamp together with around 150 tonnes. Therefore this is also no a criterion for exclusion.

4.7.5 Filling

Figure 4.22 shows the filling time and the behavior. The percent numbers given in this figure are percent of the filling time elapsed. The simulation showed a smooth uniform flow until the area with the multi-channels was reached. Here, due to increased friction and faster cooling rate the flow front inside the channels was slower compared to the rest of the part. At the 75 % filling stage the backwards movement of the bypassed flow, can be seen. This is called the hesitation effect. This effect was described by Sheomaker ([44] on page 37) in detail. The danger of weld lines exists here, due to the two different flow fronts which collide. If the flow is warm enough, they will unite, but if one flow front has cooled down to the transition temperature already there will be weld lines. In this case the two flow fronts merged completely.

4.7.6 Summary of Validation Part Simulation

For the validation part an adequate mesh was generated. Its features satisfied the criteria in order to have an accurate simulation. The clamp force didn't show high spikes and was low overall compared to average machine capabilities. The filling analysis showed complete filling with a minor hesitation effect present. The simulation demonstrated that the properties of the silicon nitride material system are predicting molding feasibility of the silicon nitride - polymer mixture. This was applied into design for manufacturing of the engine component for the UAV.

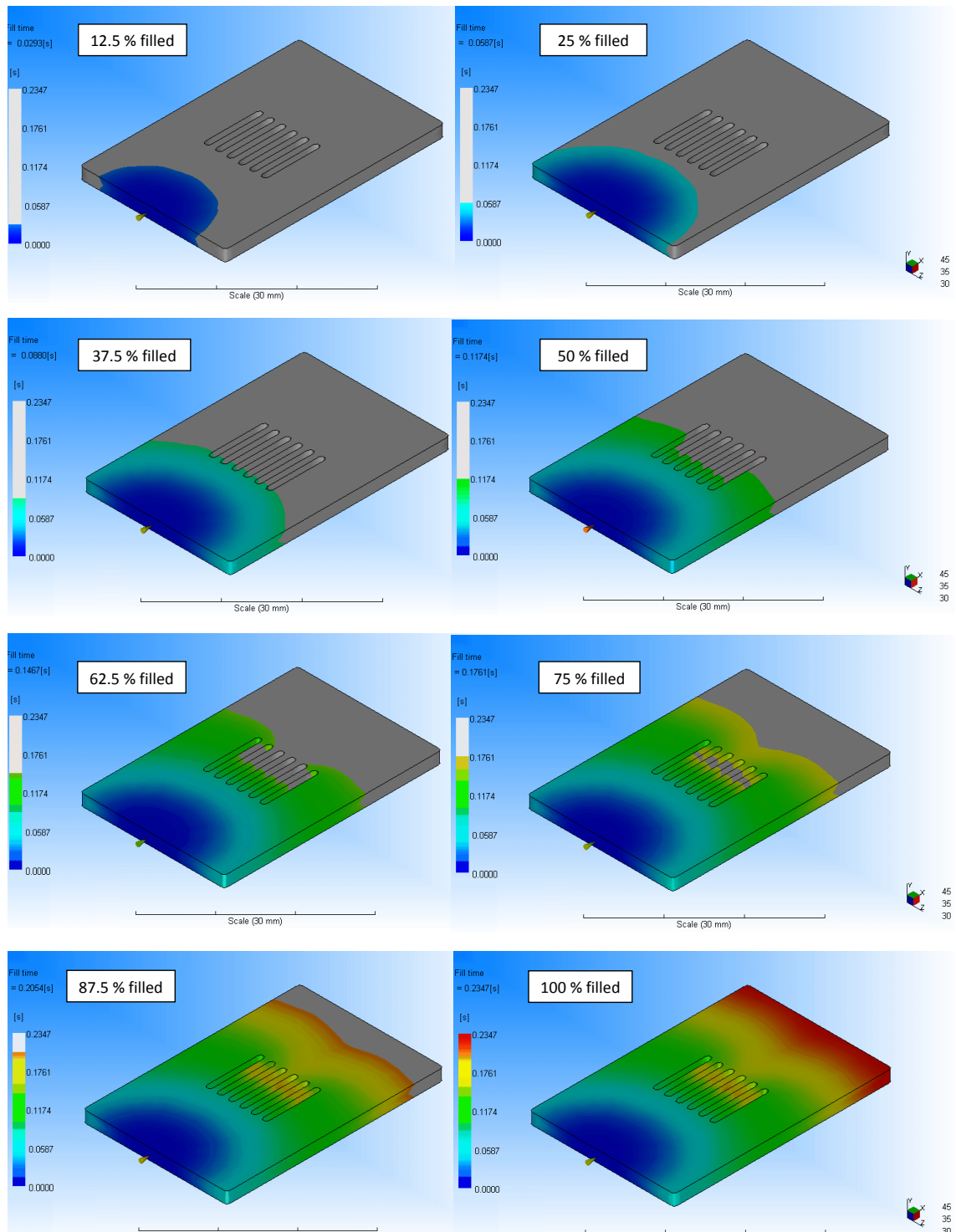


FIGURE 4.22: Validation Part - Fill Time and Fill Behavior

4.7.7 Validation of Simulation Model

The simulation and the actual molding were conducted with similar process settings. The simulation predicted a weld line in the channels and at about 75 % of the length of the channels, measured from the direction of the injection location. The formation of this weld line is shown in Figure 4.22. The actual molded part showed a weld line at the predicted position. This indicated an accurate model for the simulation of the injection of this material system.

4.8. Simulation Results of Engine Part

4.8.1 Mesh for the Engine Part

The mesh created for the engine part can be seen in Figure 4.23. Table 4.13 shows the features of this mesh.

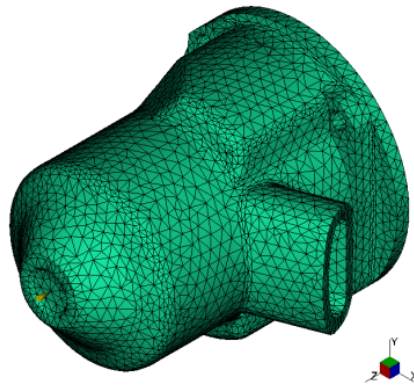


FIGURE 4.23: Engine Part Mesh

The features of the mesh indicated that the mesh had an accuracy, which was high enough, in order to use the mesh in the simulation. The average aspect ratio was 2.14 which is below the recommended average aspect ratio of 6, while the maximum individual value was 20, which is the upper limit in terms of recommendations for that parameter. The match percentage was 81.0 %. This is slightly lower than the recommended 85 % minimal

TABLE 4.13: Mesh Parameters for the Engine Part

Attribute	Value
Mesh Type	Fusion
Triangles	12732
Connected Nodes	6358
Surface Area	315.037 cm ²
Volume	61.459 cm ³
Maximum Aspect Ratio	20.6
Average Aspect Ratio	2.14
Minimum Aspect Ratio	1.16
Manifold Edges	19098
Reciprocal Percentage	79.5 %
Match Percentage	81.0 %

match. The present percentage was not in the recommended zone, but the Moldflow software defines the critical match percentage as 50 %. Below this value the simulation will not carry out the run simulations.

4.8.2 Process Parameters

For the initial simulation of the engine part the arithmetic middle of the recommended process window was chosen. These parameters were:

1. Mold surface temperature 28 °C
2. Melt temperature 165 °C
3. Injection time 0.2 s

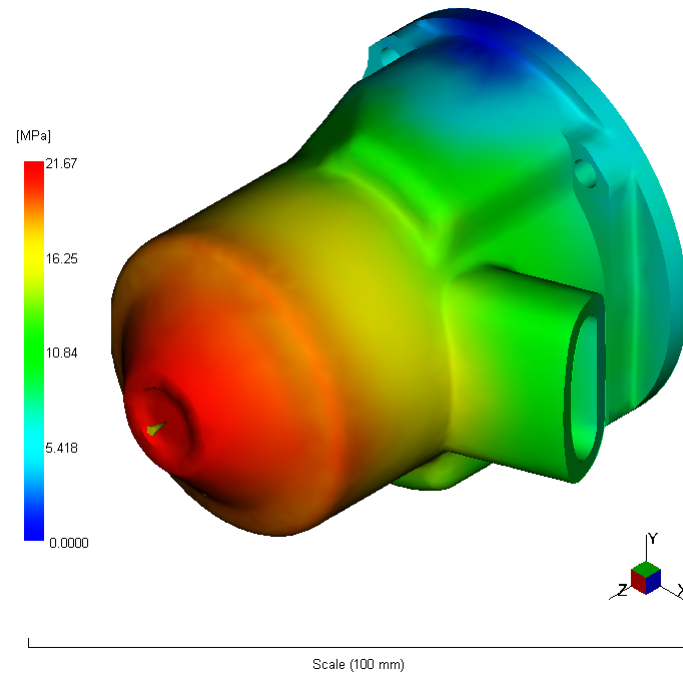


FIGURE 4.24: Injection Pressure at Cubically Centered Process Parameter Settings

4.8.3 Injection Pressure

The maximum pressure estimated in the simulation was 21.67 MPa and occurred at 0.204 sec. This peak was observed near the injection location. The full pressure distribution throughout the part is shown in Figure 4.24. The pressure has to be smaller than the maximal injection pressure provided by the injection machine. Also pressure estimation needed to fill one single part is needed to estimate how many parts can be filled simultaneously in case of mass production. Table 4.14 shows some common molding machines and the maximum pressure they can apply. Also the number how many of these engine parts can be made simultaneously by these machines. These estimations were based on just the pressure needed for the mold. This number might be smaller due to the pressure needed for the runner and gate system, which was not included. The first machine in Table 4.14 is just a virtual machine, but the 180 MPa pressure was used to have an estimate of an typical machine type.

TABLE 4.14: Number of Mold Cavity Based on Max. Pressure of Various Machines

Manufacturer	Model Name	Pressure	Mold Cavities
Moldflow	Default Injection Machine	180 MPa	8 units
Battenfeld	4500/1900 BK	177.7 MPa	8 units
Cincinnati Milacron	VS33-C28	125 MPa	5 units
Arburg	Allrounder 1500T 45mm	250 MPa	11 units
Netstal	1200H-460 50mm	141 MPa	6 units
Welltec Machinery Ltd.	250F (55mm)	174 MPa	8 units
Krauss Maffei	KM 800 60	242 MPa	11 units

4.8.4 Clamp Force

The clamp force is defined as the force required to hold the two mold sections together during the filling stage. This force is the product of area perpendicular to the mold dividing section and the pressure. Therefore the pressure has a linear correlation to the clamp force. The simulation estimated a clamp force of 60.1 kN (6.12 tonnes-force) at 0.204 seconds. The whole force level during the filling can be seen as a function of time in Figure 4.25.

The clamp force is usually not the limiting factor when it comes to simultaneous mold filling. Table 4.15 shows an overview of common injection molding machines and the maximum clamp force they can apply and also the resulting feasible simultaneously filled mold cavities. Only the Cincinnati Milacron VS33-C28 could produce a smaller amount of parts because it exceeds the maximal clamp force with the settings near the pressure limitation. The virtual Moldflow machine doesn't give a standard recommended maximum, basically every maximum clamp force value could be simulated.

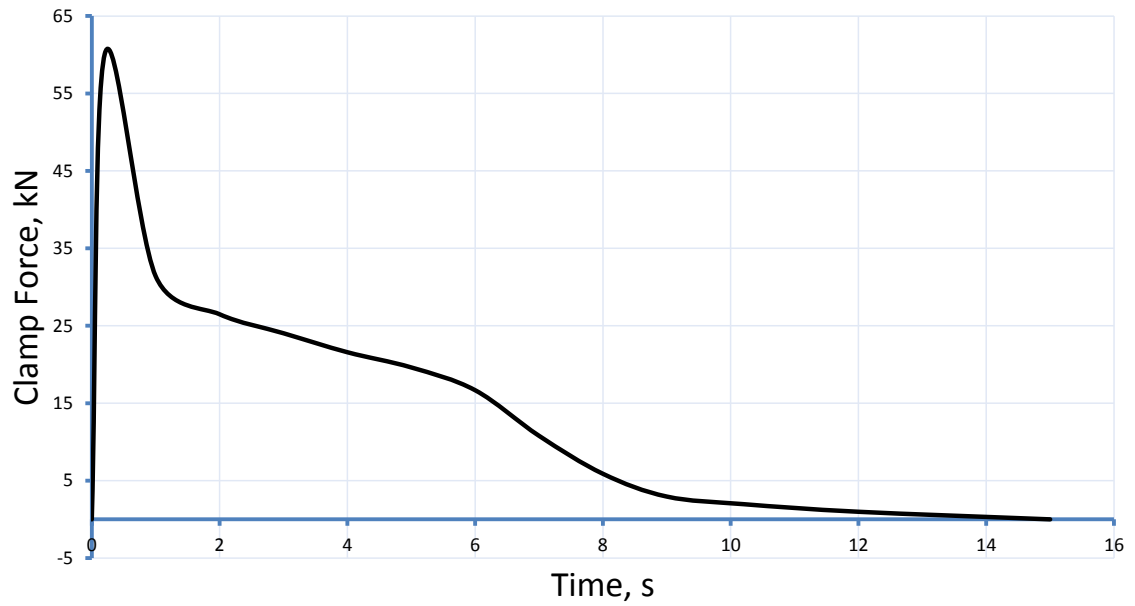


FIGURE 4.25: Clamp Force at Cubically Centered Process Parameter Settings

TABLE 4.15: Number of Mold Cavity Based on Max. Clamp Force of Various Machines

Manufacturer	Model Name	Clamp Force	Mold Cavities
Moldflow	Default Injection Machine	NA	NA
Battenfeld	4500/1900 BK	4491 kN	73 units
Cincinnati Milacron	VS33-C28	294 kN	4 units
Arburg	Allrounder 1500T 45mm	1951 kN	32 units
Netstal	1200H-460 50mm	1196 kN	19 units
Welltec Machinery Ltd.	250F (55mm)	2608 kN	43 units
Krauss Maffei	KM 800 60	892 kN	14 units

4.8.5 Filling

Figure 4.26 shows the fill behavior and the required time to fill the cavity. No significant flow front velocity differences were observed. The part was filled smoothly with no hesitation or racetrack effects. A racetrack effect would mean that parts of the mold which

are easier to fill will be flushed with a melt of a high flow front velocity. This is not the case. A uniform distribution of the material and smooth filling with a lot of parallel flow paths was observed.

4.8.6 Temperature at Flow Front

Figure 4.27 shows the temperature of the flow front while passing that point in the part. As a general guideline the flow front temperature should not drop more than 2 °C to 5 °C during the filling phase. If the flow temperature drops more than that, the risk to have a short shot or hesitation is high. In the case of the engine part, the temperature dropped about 0.5 °C from 164.5 °C to 165 °C. Also no hot spots or cold spots were found.

4.8.7 Ramp Speed

The injection velocity can be regulated during filling. With this injection profile the flow front velocity can be kept constant even though the area of the flow front changes all the time because of the shape of the part. It usually can be set up with up to 10 different points at a common molding machine control. The optimal profile of the flow rate as a function of the shot volume is shown in Figure 4.28.

4.8.8 Weld Lines

Weld lines are created when two independent flow fronts traveling in different directions meet. When they bond, the result can be some permanent residuals which can be seen after ejection. In case the two melt fronts were hot enough they merge completely. But if not, two different cases may occur. Either there will be just visual remains like a notch or color change on the surface of the part, or they might be structural problems as well. This means that the part may be more likely to fracture at this line, especially if the weld line has poor quality. The potential danger of a fracture is only a real concern if the area is subjected to stress. Figure 4.29 shows where weld lines are likely to occur in the part

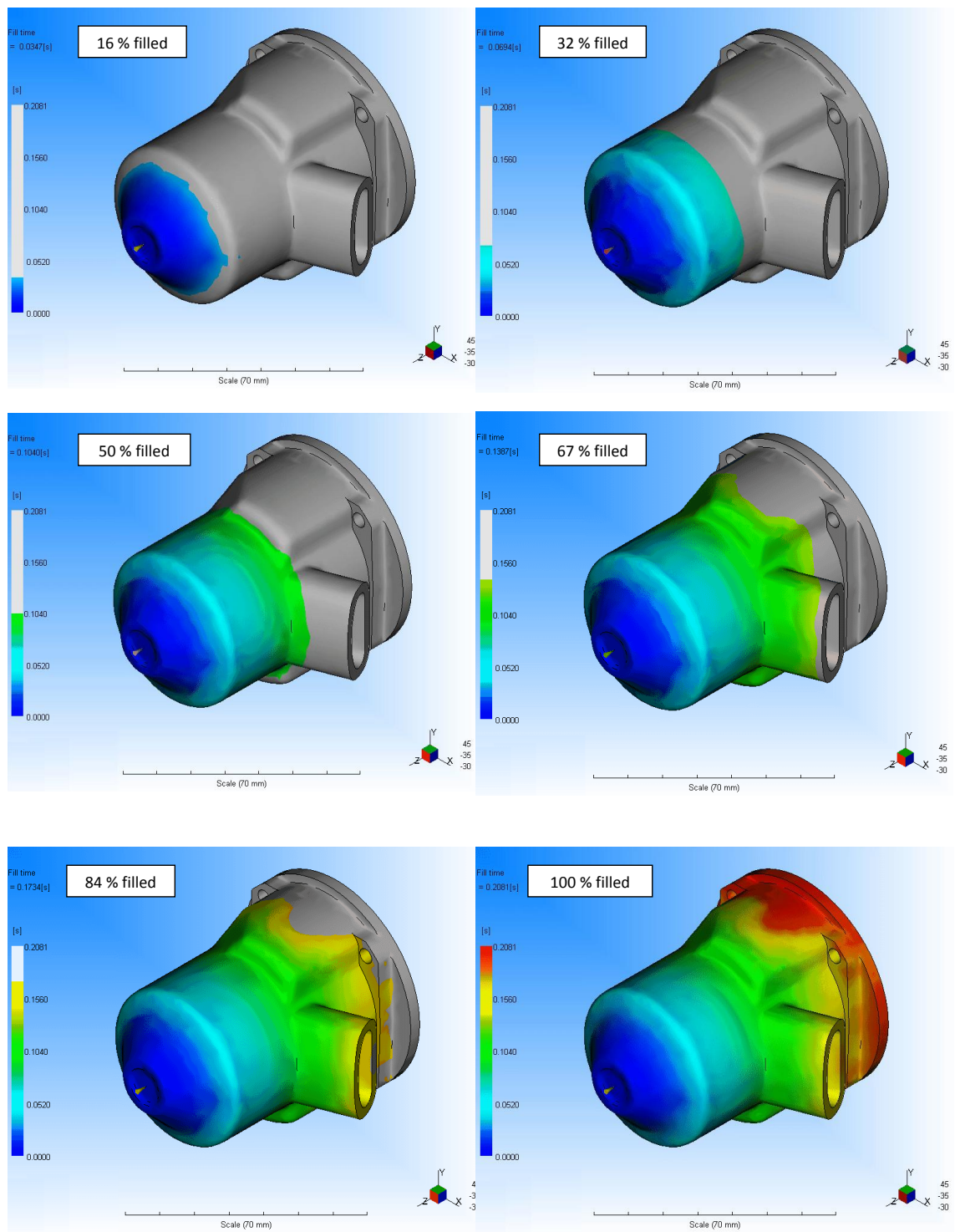


FIGURE 4.26: Engine Part - Fill Time and Fill Behavior

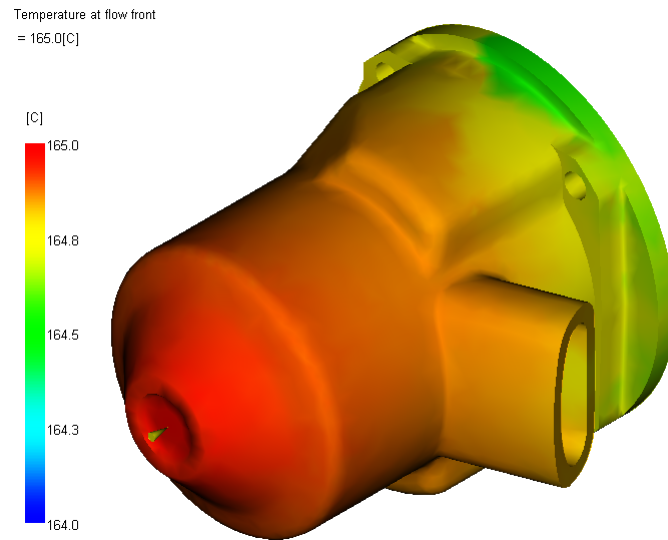


FIGURE 4.27: Temperature at Flow Front after Filling at Cubically Centered Process Parameter Settings

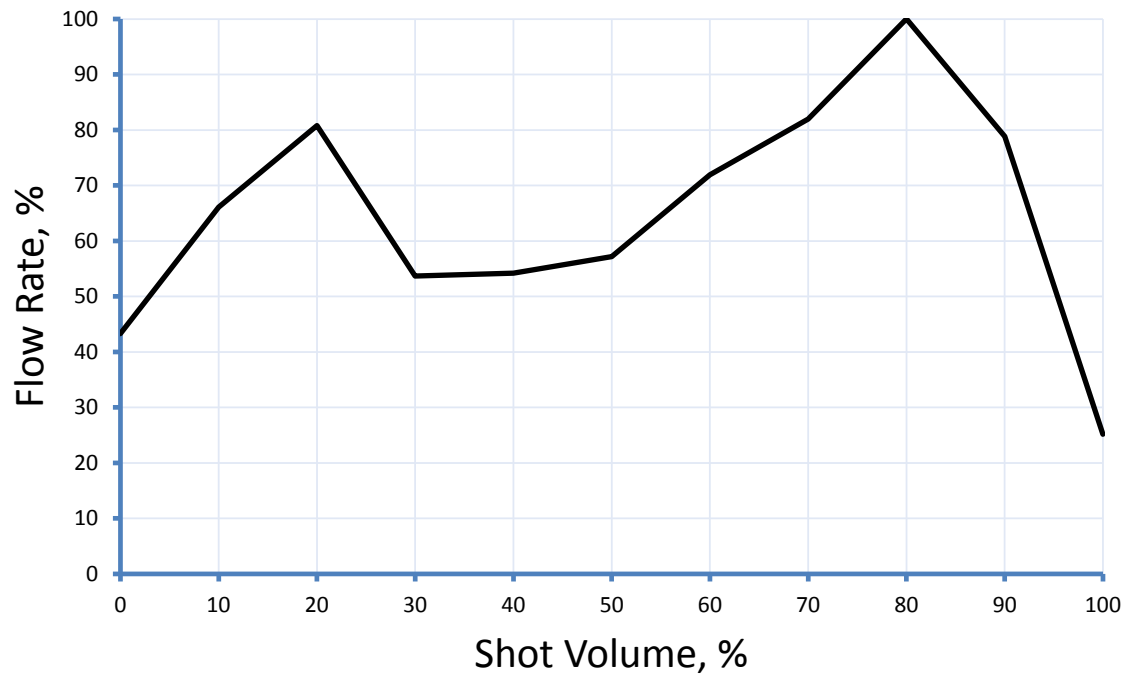


FIGURE 4.28: Ramp Speed Recommended for the Engine Part

and also the orientation at which the two flow fronts meet. Most of the weld lines are not in areas of high applied stress and the visual defects are not critical for the purpose.

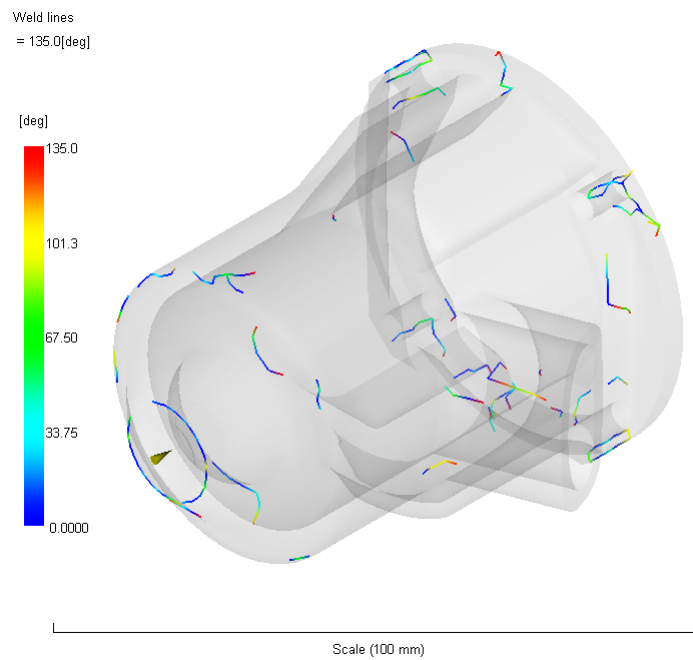


FIGURE 4.29: Weld Lines of the Engine Part at Cubically Centered Process Parameter Settings

4.8.9 Air Traps

An air trap occurs when air is caught inside the mold cavity. Usually they are found in the areas which fill at the very last. The result can be a small hole. Figure 4.30 shows the spots where the risks of air traps are located on the engine part.

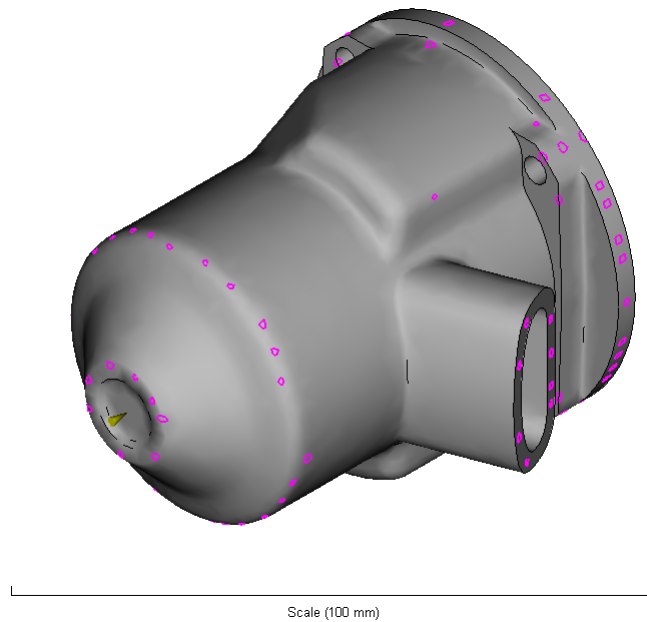


FIGURE 4.30: Air Traps at Cubically Centered Process Parameter Settings

4.8.10 Time Distribution

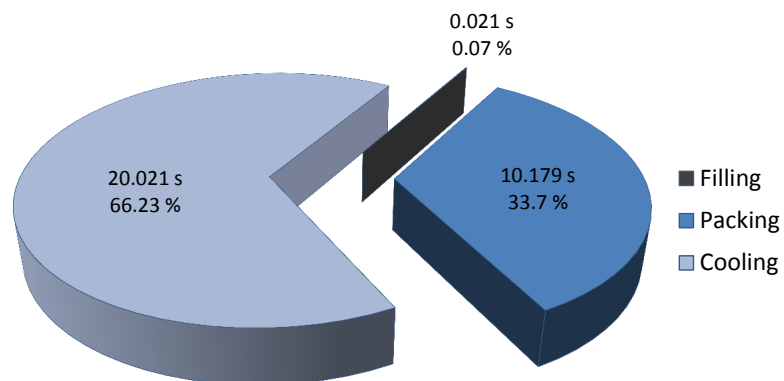


FIGURE 4.31: Fill, Pack and Cooling Time

Figure 4.31 shows the time distribution of the 3 phases of the powder injection molding process. The mold was filled in 0.02 s. It took another 10.17 s to pack the part and release the pressure. The cooling is the longest segment in the molding cycle with 20.02 s.

4.8.11 Summary of Engine Part Simulation

The simulation demonstrated that it was feasible to mold the specific engine part with the newly developed silicon nitride material system. The pressure needed was equivalent to one eighth of the capabilities of a typical injection molding machine, which means multiple parts could be manufactured simultaneously. The calculated clamp force was 60.1 kN. This also means that multiple parts can be fabricated simultaneously. The fill behavior was smooth and no large flow front velocity differences were found. This also shows in the temperature at the flow front. The temperature dropped 0.5°C from the injection of the material to the coldest point at the end of the filling phase. This small difference between the highest and lowest temperature in the mold indicated that there were no hot spots or cold spots. In order to get this smooth filling the ramp speed which controls the flow rate was adapted to the shape of the part. The time at the end of packing was 30.2 s. After packing the part must be cooled until it reaches ejection temperature. In terms of the risk of potential defects, weld lines may occur at the molded state. But these will most likely not hinder densification and grain growth during sintering and therefore maybe be present at the final stage. The air traps visualization helps to find spots, which need a close inspection look after molding and can be used as recommendations for local air vents in the mold to let the trapped air escape.

4.9. DOE Results

The part's properties highly depend on the molding parameters. Two parts molded from the same material and molded with the same tool, but under different conditions will have different completely different properties. In order to get a better understanding of how the process parameters influence the different quality criteria and to find the optimal values for those process parameters, a DOE analysis was performed. A full factorial design in the case of a 3 level 3 factor setup results in 27 runs. In order to reduce this number a smart approach with the Taguchi Method and the Box-Behnken Design was chosen.

4.9.1 Quality Criteria used for DOE-Analysis

Ten different quality criteria which were analyzed and are listed in Table 4.16. They were grouped in four different categories, Pressure-Related, Temperature-Related, Velocity-Related and Dimension and Scale.

TABLE 4.16: Quality Criteria of PIM used for DOE

Category	Quality Criteria
Pressure-Related	Injection Pressure
	Clamp Force
	Shear Stress
Temperature-Related	Cooling Time
	Temperature at Flow Front
	Bulk Temperature
	Time at the End of Packing
Dimension and Scale	Part Weight
	Volumetric Shrinkage at Ejection
	Depth of Sink Mark

TABLE 4.17: Process Window Used for PIM Simulations

Influencing Factor	Unit
Mold Temperature	23 °C to 33 °C
Melt Temperature	150 °C to 180 °C
Injection Time	0.16 s to 0.24 s

4.9.2 Process Window

To get an initial process window, the lower bound of the mold temperature was explored with several simulation runs until a temperature was found where no short shots occurred anymore. Short shot are the case when the materials solidifies before the part is filled completely. Afterward the procedure was repeated with the mold temperature. The upper bonds where chosen from the process recommendation by Datapoints Labs. This initial process window is shown in Figure 4.32. The preferred parameters were yet to be determined at this stage.

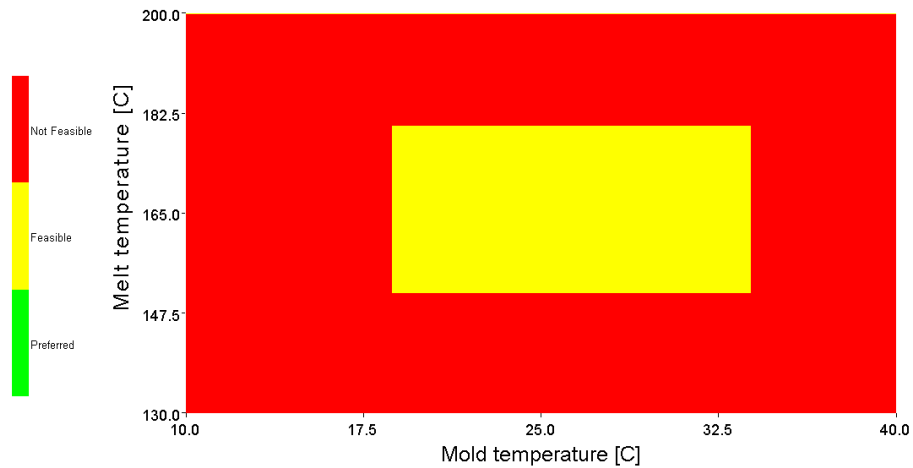


FIGURE 4.32: Initial Process Window

The injection time was also narrowed down in several iterations until a reasonable range was found. The process window, which was used for the DOE analysis is shown in Table 4.17.

TABLE 4.18: Taguchi Analysis Parameter Settings

Run	Factors		
	Mold Temperature	Melt Temperature	Injection time
1	23 °C	150 °C	0.16s
2	23 °C	180 °C	0.24s
3	33 °C	150 °C	0.24s
4	33 °C	180 °C	0.16s

4.9.3 DOE Setup for Taguchi Design

The two level three factor Taguchi analysis always has 4 runs as seen in Table 3.3. These low and high states are applied to the process window. The process setting for the 4 Taguchi runs can be seen in Table 4.18.

4.9.4 Exemplary Calculation

Cooling time was picked to show how the percentage of the factor influence was calculated. First all means were calculated. One mean value was calculated for each level of each factor. According to the design run one and two had a low factor A (mold temperature) setting. the mean for factor A low was $(11.1807 + 12.0259) / 2 = 11.6$. The mean for factor A high (third and fourth run) was $(26.5858 + 27.2281) / 2 = 22.91$. Table 4.19 shows all means for the cooling time. The deltas are the differences between the two means for each factor.

The percentages were calculated by taking the ratios of the mean delta for the factor and the sum of all deltas. For factor A the ratio was $15.3 / (15.3 + 0.74 + 0.10) = 0.9476$. The ratio times hundred is the percentage influence of the factor. In the case of cooling time factor A had a percentage influence of $0.9476 * 100 = 94.76$ %.

TABLE 4.19: Response Table for Means for Cooling Time

Level	A	B	C
1	11.60	18.88	19.20
2	26.91	19.63	19.31
Delta	15.30	0.74	0.10
Rank	1	2	3

4.9.5 Factor Influences for All Quality Criteria

After conducting the four simulation runs the percentage of influence for each factor were calculated for each quality criteria. As an intermediate step the signal-to-noise ratios were calculated. Based on these ratios, the relative influences % can be obtained. These influences are shown in Table 4.20.

4.9.6 DOE Setup for Box-Behnken Design

The setup for the three level three factorial Box-Behnken design (Table 3.4) was applied to the entire process window. 15 different simulation runs with the individual process settings are shown in Table 4.21.

4.9.7 Bulk Temperature at End of Fill

Bulk temperature indicates the variation weighted average temperature across the thickness. The unit is Kelvin, because it only expresses the variation not the absolute temperature. A high variation may cause non-uniform shrinkage. It is therefore better to have a low bulk temperature. The Taguchi calculations show that the result is influenced by 11.92% by the mold temperature, by 4.17% by the melt temperature and by 83.90% by the injection time. Figure 4.33 shows the bulk temperature results for 3 different injection times. We pick the lowest plane because we want to minimize it.

The bulk temperature is now plotted for just the lowest injection time (Figure 4.34). Here

TABLE 4.20: Factor Influences According to Taguchi Analysis

Qualities	Percentage Influences		
	Mold Temperature	Melt Temperature	Injection Time
Bulk Temperature	11.92%	4.17%	83.90%
Clamp Force	1.97%	73.51%	24.52%
Injection Pressure	2.5%	95.83%	1.67%
Shear Stress	30.09%	48.77%	21.14%
Sink Mark Depth	5.28%	89.64%	5.08%
Temperature at Flow Front	6.88%	55.89%	37.23%
Cooling Time	94.76%	4.61%	0.63%
Volumetric Shrinkage	16.75%	79.37%	3.88%
Time at End of Packing	0.16%	0.02%	99.82%
Part Weight	13.72%	85.23%	1.05%

TABLE 4.21: Box-Behnken Parameter Settings

Run	Factors		
	Mold Temperature	Melt Temperature	Injection Time
1	150 °C	23 °C	0.16s
2	150 °C	33 °C	0.16s
3	150 °C	23 °C	0.24s
4	150 °C	33 °C	0.24s
5	180 °C	23 °C	0.16s
6	180 °C	33 °C	0.16s
7	180 °C	23 °C	0.24s
8	180 °C	33 °C	0.24s
9	150 °C	28 °C	0.20s
10	180 °C	28 °C	0.20s
11	165 °C	28 °C	0.16s
12	165 °C	28 °C	0.24s
13	165 °C	23 °C	0.20s
14	165 °C	33 °C	0.20s
15	165 °C	28 °C	0.20s

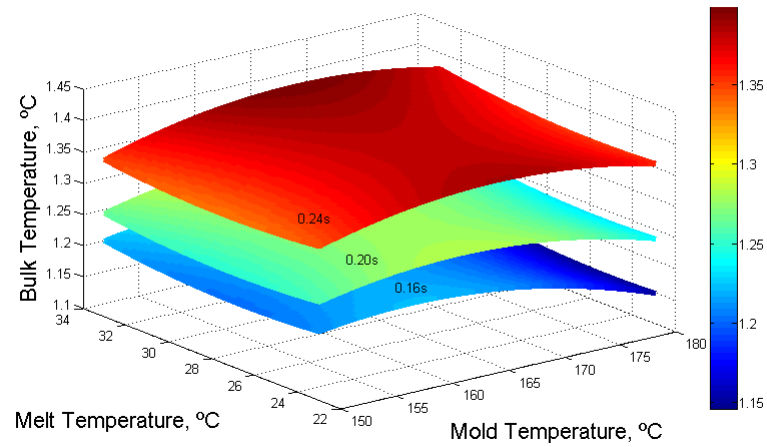


FIGURE 4.33: Bulk Temperature

we can easily spot the minimum at 180 °C melt temperature and a mold temperature between 23 and 29 °C. As predicted by the Taguchi analysis the melt temperature has a very low contribution. In fact we can choose within a range and the result remains the same.

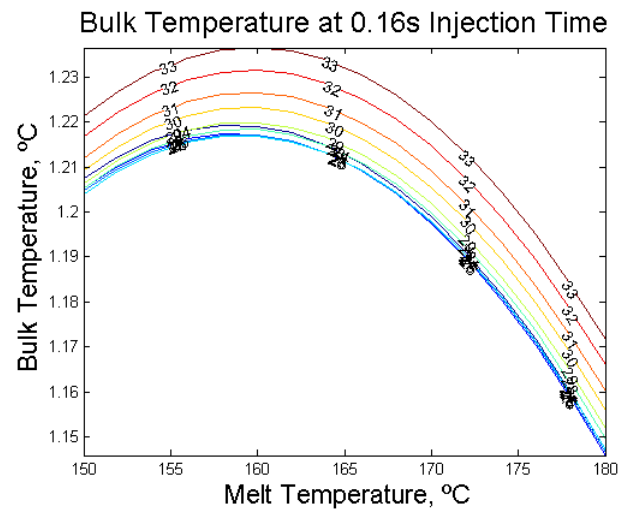


FIGURE 4.34: Bulk Temperature at 0.16 s Injection Time

4.9.8 Clamp Force

The clamp force is the force required to hold the two mold pieces together during the injection phase. The goal is to minimize the required force in order to produce as much parts as possible simultaneously. The Taguchi analysis showed that the melt temperature had the biggest influence with 73.51%. The other parameter were of lower significance (mold temperature had 1.97% and the injection time 24.52%). Figure 4.35 shows three different planes of melt temperature plotted against the injection time and mold temperature. Here it can be seen that the plane with 180 °C melt temperature is the lowest.

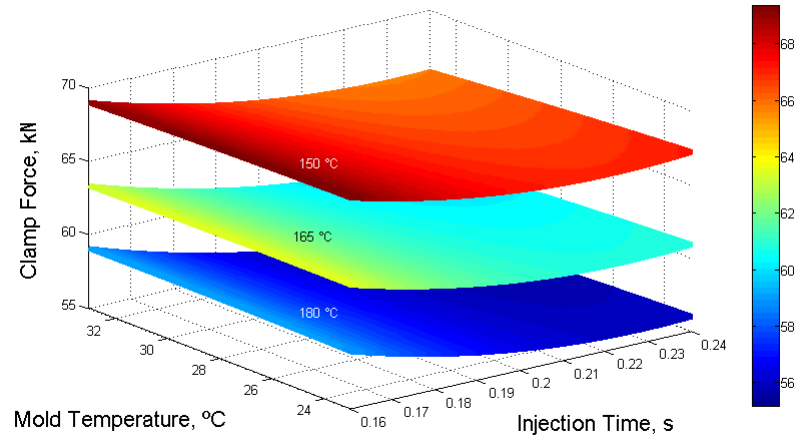


FIGURE 4.35: Clamp Force

In Figure 4.36 only 180 °C melt temperature was used to generate a 2-dimensional plot. Here it can be seen that a high melt temperature and a high injection time will result in the lowest clamp force.

4.9.9 Injection Pressure

The injection pressure is the required pressure to squeeze the material into the cavity. It is better if a low pressure is required, because multiple parts can be molded with one stroke. Taguchi analysis showed that the biggest influence on the result has a change in melt temperature (95.83%). The two other parameters were not significant (mold temperature

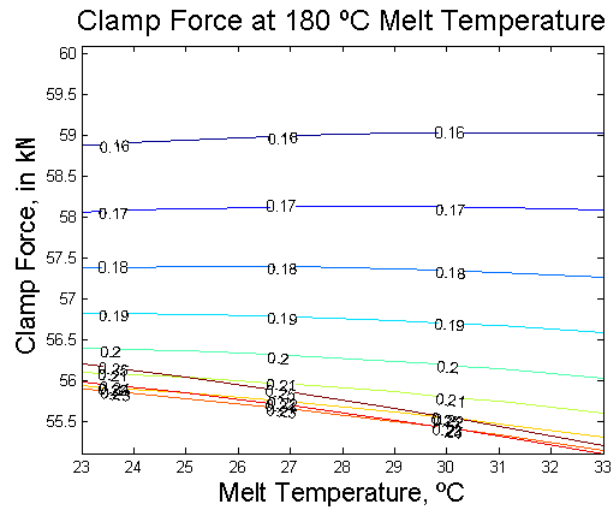


FIGURE 4.36: Clamp Force at 180 °C Melt Temperature

2.5% and injection time 1.67% contribution). Figure 4.37 shows three different melt temperature planes and the lowest one was the highest temperature.

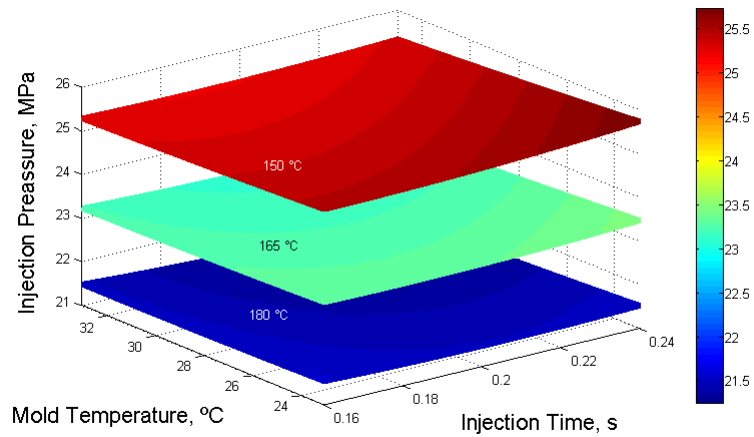


FIGURE 4.37: Injection Pressure

Figure 4.38 shows the two remaining process parameters and the resulting injection pressure. A local minimum can be observed with a 33 °C mold temperature and an injection slightly higher than 0.23 s.

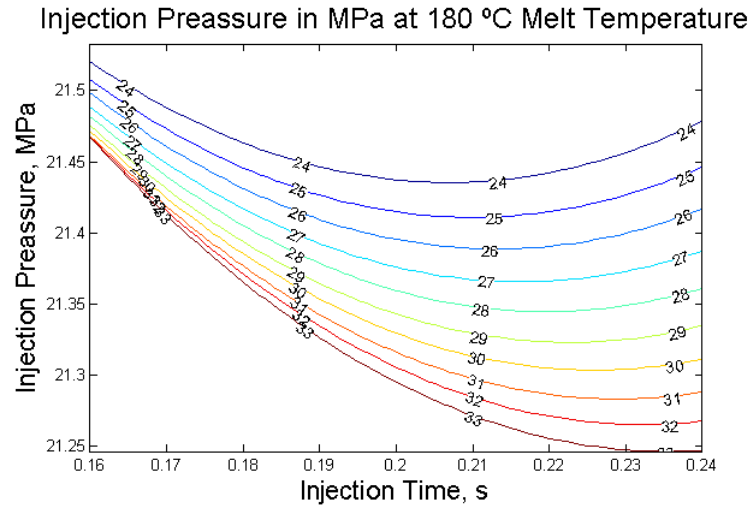


FIGURE 4.38: Injection Pressure at 180 °C Melt Temperature

4.9.10 Shear Stress

Shear stress during injection molding should be minimized, because the risk of powder binder separation is lower with lower shear stress. Taguchi analysis revealed that all three process parameters have a big influence on the result. The mold temperature had 30.09%, the melt temperature had 48.77% and the injection time had 21.14%. Figure 4.39 shows three different planes for the injection time plotted in a mold and melt temperature space. The lowest values were found in the 0.16 second plane. The 2D-plot with just the 0.16 s injection time values showed a local minimum around 174 °C melt temperature and 26 °C mold temperature.

4.9.11 Sink Mark Depth

The sink marks are an indicator for potential shrinkage due to a hot core. For each element it is calculated after the pressure has come down to zero. At this point it is important to know how much material is still melt, subsequently the part's shape is going to be calculated for the case when all material solidifies. It is desired to minimize sink mark depths. The Taguchi analysis showed that melt temperature was the main influence on the sink marks with 89.64% relative influence. The other parameters were mold temperature

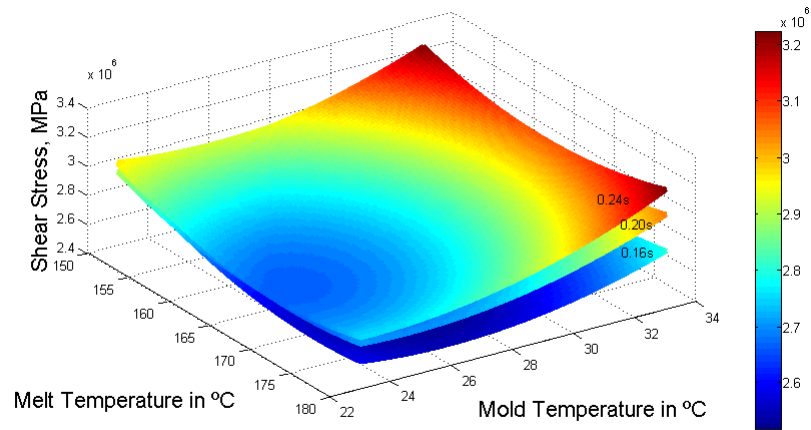


FIGURE 4.39: Shear Stress

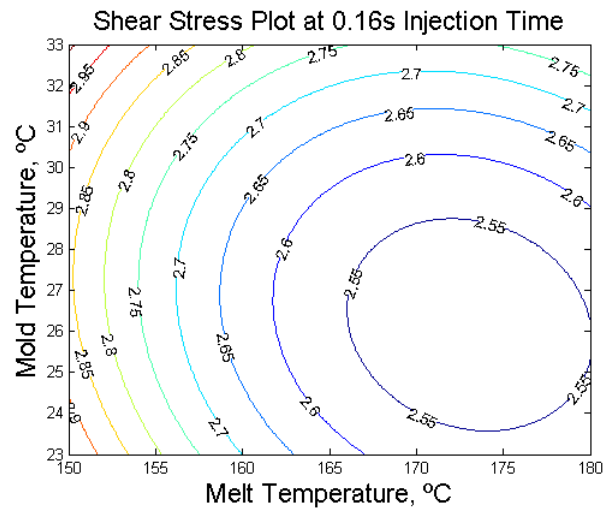


FIGURE 4.40: Shear Stress at 0.16 s Injection Time

with 5.28% and injection time with 5.08%.

Figure 4.41 shows the predicted sink mark depths for the entire process window. It was found that the lowest sink mark depths are in the lowest mold temperature plane. Figure 4.42 shows the values with 150 °C melt temperature. The figure shows that a high injection time and a low mold temperature results in the lowest sink mark depths.

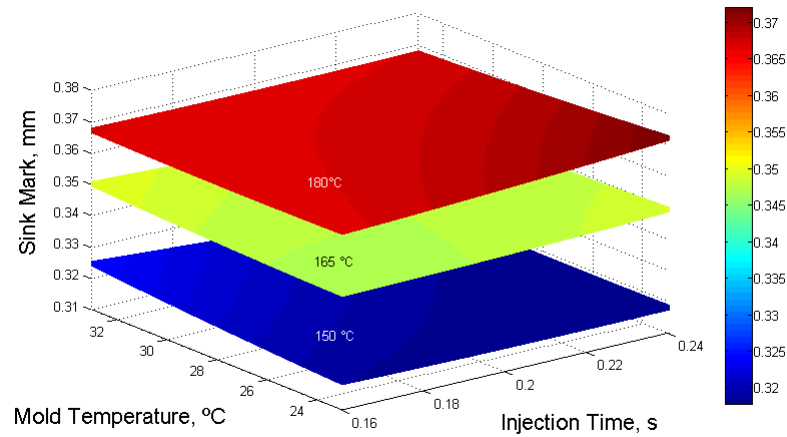


FIGURE 4.41: Sink Mark Depth

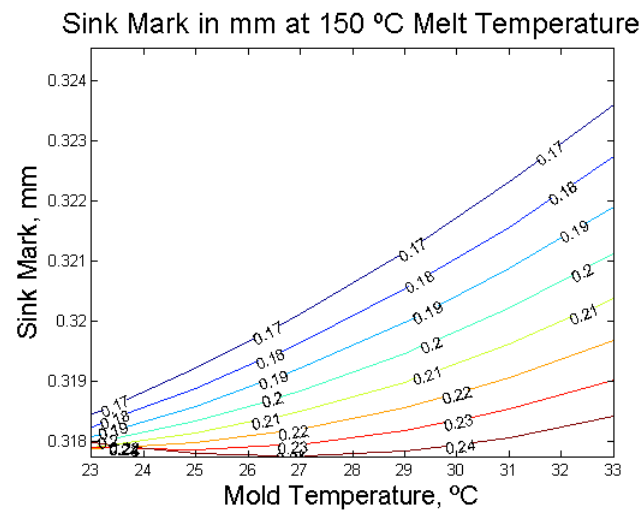


FIGURE 4.42: Sink Mark Depth at 150 °C Melt Temperature

4.9.12 Temperature at Flow Front

The temperature at flow front is the temperature which the flow has when it passes this position for the first time. Looking at the whole path, it was possible to see how the flow front loses its temperature over the distance. The drop of the temperature should ideally be as small as possible. The Taguchi analysis identified melt temperature as the highest impact with 55.89% relative influence. Mold temperature had 6.88% and injection time had 37.23%.

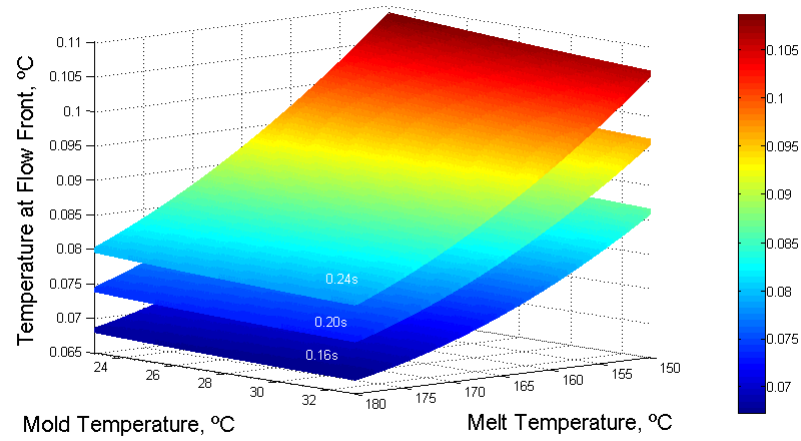


FIGURE 4.43: Temperature at Flow Front

Figure 4.43 shows the temperature distribution for the entire process window. It was found that a short injection time led to the smallest flow front variation.

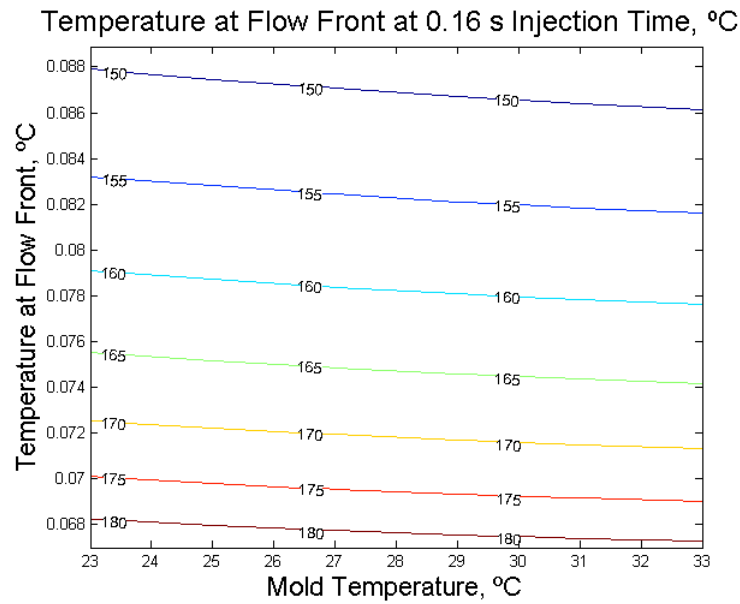


FIGURE 4.44: Temperature at Flow Front at 0.16 s Injection Time

Figure 4.44 shows the resulting flow front for 0.16 s injection time. A high melt temperature is referred. It leads to the smallest flow front variation (0.1085 °C).

4.9.13 Cooling Time

The cooling time is the time required after packing until the part is solid enough so it can be ejected. The part doesn't have to be completely frozen. If the core is still molten, but the outer shell is strong enough so the part doesn't break, it can already be ejected. Moldflow simulated the cooling automatically until a thick enough frozen layer is present. The cooling time should be minimized to achieve a higher cycle time. The Taguchi analysis showed that the mold temperature is the parameter with the highest influence (94.76%). Melt temperature had 4.61% and injection time had 0.63% relative influence. Figure 4.45 shows the cooling time for the entire process window. As predicted, a low mold temperature led to a low cooling time.

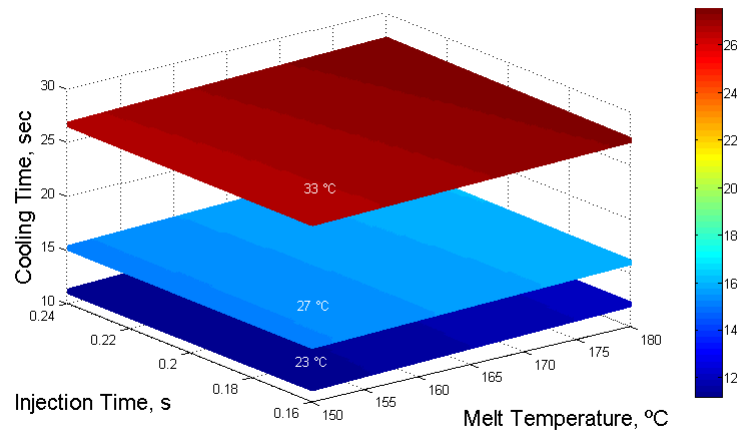


FIGURE 4.45: Cooling Time

Figure 4.46 shows the cooling time for the lowest mold temperature. It also showed that a low melt temperature and a high injection time led to the lowest cooling time.

4.9.14 Volumetric Shrinkage

The volumetric shrinkage is the percentage increase in local density from the end of the packing phase to the density at room temperature. The volumetric shrinkage should be minimized. The Taguchi analysis showed that the melt temperature had the biggest influ-

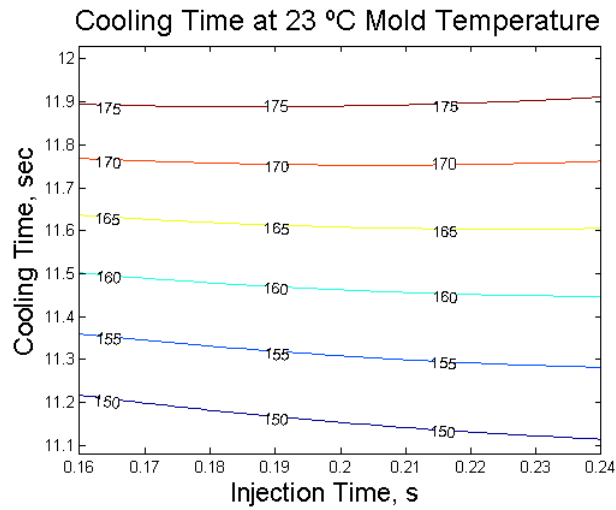


FIGURE 4.46: Cooling Time at 23 °C Mold Temperature

ence with 79.37%. Mold temperature had 16.75% and injection time had 3.88% relative influence. Figure 4.47 shows the volumetric shrinkage for the entire process window. Here the lowest melt temperature values had the lowest volumetric shrinkage.

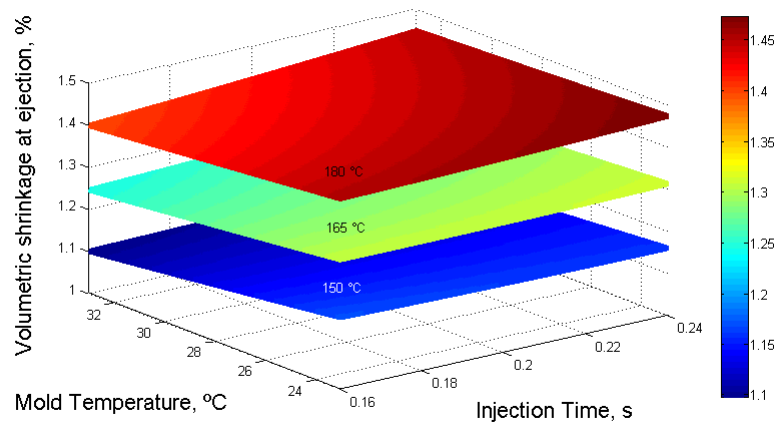


FIGURE 4.47: Volumetric Shrinkage

Figure 4.48 shows the volumetric shrinkage for the highest melt temperature. The figure shows that a short injection time and a high mold temperature were preferable.

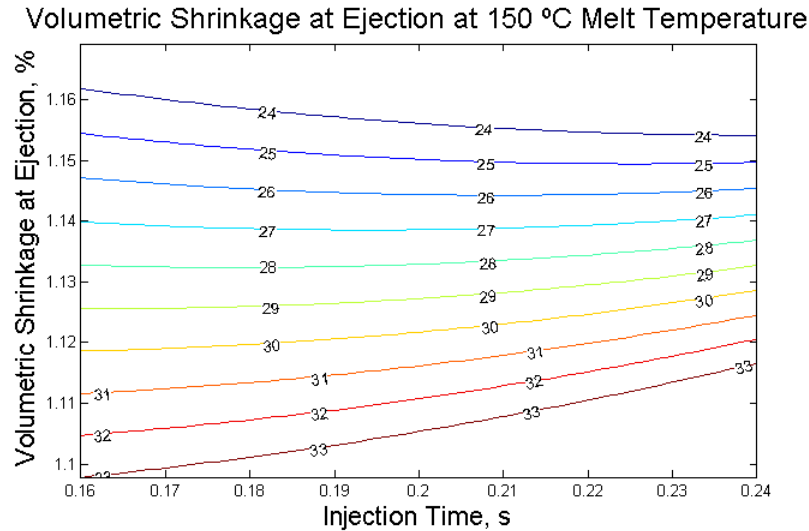


FIGURE 4.48: Volumetric Shrinkage at 150 °C Melt Temperature

4.9.15 Time at End of Packing

The time at the end of packing is the sum of the fill time, the packing time and the holding time after pressure release for cooling. The time required should be minimized. The Taguchi analysis revealed that injection time has an influence near to 100 % (99.82%). This means that varying the other two parameters, mold temperature and melt temperature, won't change the resulting time at the end of packing significantly. Figure 4.49 shows the resulting time at the end of packing for the entire process window.

The results for the shortest injection time are shown in Figure 4.50. The other two parameters with the predicted little influence affect the on a not significant magnitude.

4.9.16 Part Weight

The part weight should be minimized. The melt temperature had the biggest influence (85.23%). Mold temperature was second (13.72%) and injection time third (1.05%). Figure 4.51 shows the resulting part weight for the entire process window. A high melt temperature and a low mold temperature is favorable.

Figure 4.52 shows the part weight result with the lowest mold temperature. Here it was

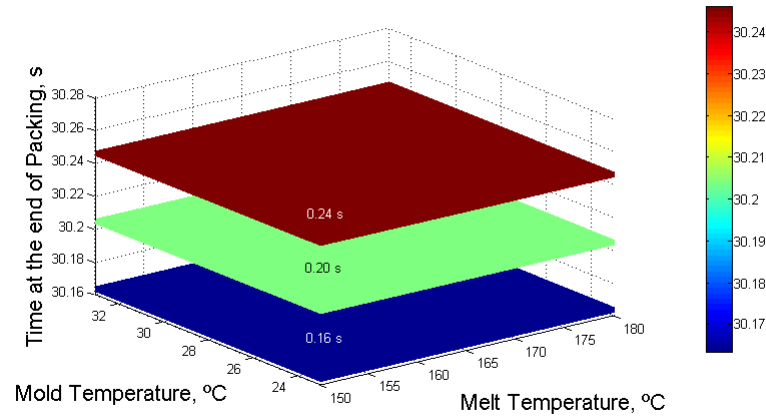


FIGURE 4.49: Time at End of Packing

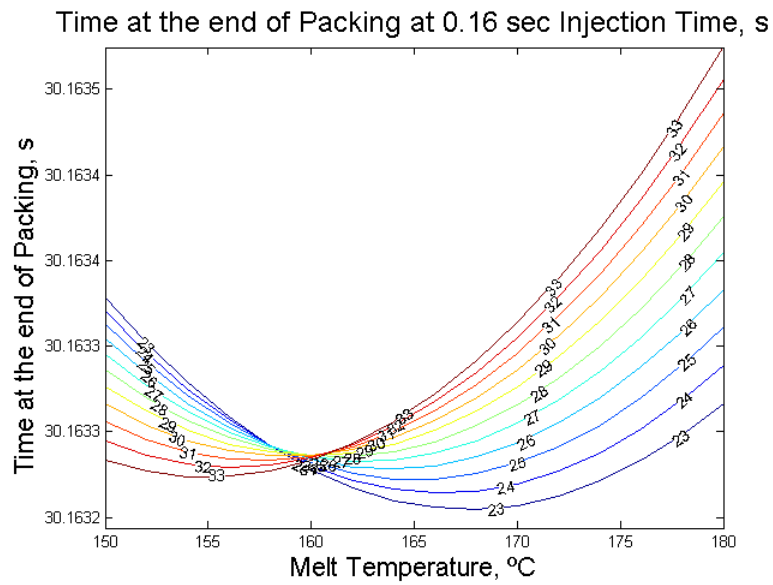


FIGURE 4.50: Time at End of Packing at 0.16 s Injection Time

found that the injection time setting is not relevant for this quality criteria.

4.9.17 Summary of DOE-Analysis

A summary of the minimal and maximal result and their difference percentage for each criteria is shown in Table 4.22. The process conditions to obtain the minimum for each criteria is shown in Table 4.23. In this table it can be seen that the process parameters are

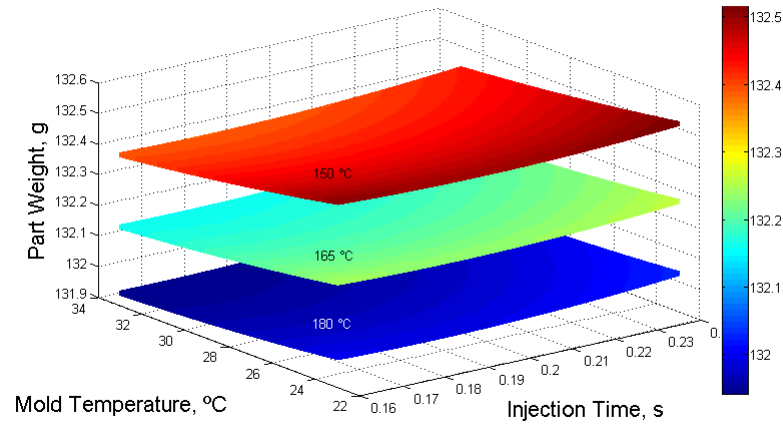


FIGURE 4.51: Part Weight

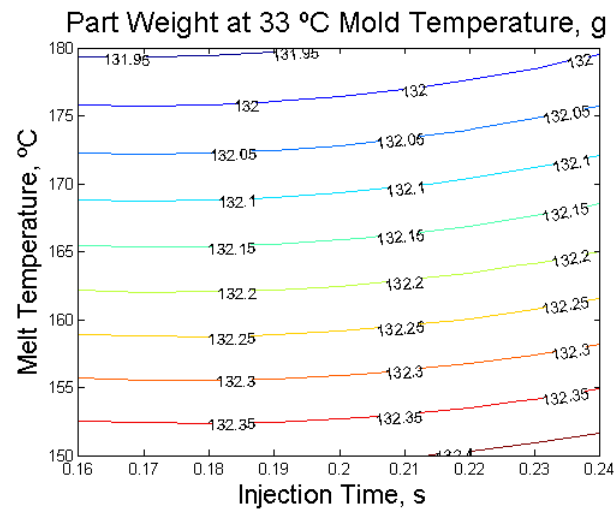


FIGURE 4.52: Part Weight at 33 °C Mold Temperature

contradictory. A single set of process parameters cannot be chosen to get the minimal for each quality criteria. The mold temperature was the dominant influence on the cooling time. The melt temperature was the dominant influence on the clamp force, injection pressure, shear stress, sink mark depth, temperature at flow front, volumetric shrinkage and part weight. The injection time was dominant on the bulk temperature and the time at the end of packing.

TABLE 4.22: Range for Each Criteria

Quality	Bulk Temp.	Clamp F.	Pressure	Stress	Sink Mark	Flow Front	Cool Time	Shrink.	End of Pack.	Weight
Units	K(d)	N	MPa	MPa	mm	K(d)	s	%	s	kg
Min.	1.1458	55117.1	21.3	2.52	0.317	0.0672	11.115	1.0978	30.163	0.1319
Ma.x	1.4310	69311.2	25.7	3.22	0.371	0.1085	27.472	1.4721	30.246	0.1325
% Diff.	19.93	20.48	17.36	21.82	14.57	38.03	59.54	25.42	0.27	0.43

TABLE 4.23: Best Process Parameter Settings for Each Criteria

Quality	Bulk Temp.	Clamp F.	Pressure	Stress	Sink Mark	Flow Front	Cool Time	Shrink.	End of Pack.	Weight
Melt Temp.	180 °C	180 °C	180 °C	173.067 °C	150 °C	180 °C	150 °C	150 °C	168 °C	180 °C
Mold Temp.	25.26 °C	33 °C	33 °C	26.162 °C	27 °C	33 °C	23 °C	33 °C	23 °C	33 °C
Injection Time	0.16 s	0.24 s	0.24 s	0.16 s	0.24 s	0.16 s	0.24 s	0.16 s	0.16 s	0.16 s

4.10. Optimization

4.10.1 Optimization Approach

The idea behind the optimization is to reduce the differences between the absolute minimum and the current result of each quality criteria. This is done by minimizing the sum of all the differences where each difference is weighted the same. This will cause that quality criteria with small amount of change in general, for instance quality criteria with a small percent of change over the range of the whole process window is weighted less. Also if a result of a quality criteria doesn't change at all if one process parameter is changed then the process parameter will be changed that is best for the other quality criteria.

4.10.2 Nonlinear Programming - Model (NLP)

A NLP-model was built. It had an objective function, 27 variables and 20 non-linear constraints. These constraints contained all 10 surface responses. It was solved with Lingo 13.0.

Objective Function: $Min \sum_{i=1}^{10} \Delta(Y_{Best}), Y(x_1, x_2, x_3)_i$

Δ is the difference in percent between the result under optimal process parameters (x_1, x_2, x_3) for that quality criteria and the result with process parameters which are chosen in respect to other quality criteria as well.

Constraints:

$$Y_i = q_{i1} + q_{i2} * c_1 + q_{i3} * c_2 + q_{i4} * c_3 + q_{i5} * c_1^2 + q_{i6} * c_1 * c_2 + q_{i7} * c_1 * c_3 + q_{i8} * c_2^2 + q_{i9} * c_2 * c_3 + q_{i10} * c_3^2$$

$$\Delta_i = (1 - Y_{Best}/Y_i) * 100, c_1 = (\frac{1}{15} * x_1) - 11, c_2 = (25 * x_2) - 5, c_3 = (\frac{1}{5} * x_3) - 5.6$$

Nomenclature: Index i (from 1 to 10) : Quality criteria, x_1 : Melt Temperature, x_2 : Injection Time, x_3 : Mold Temperature, q_{ij} : quadratic RSM coefficient, c_k : conversion coefficient

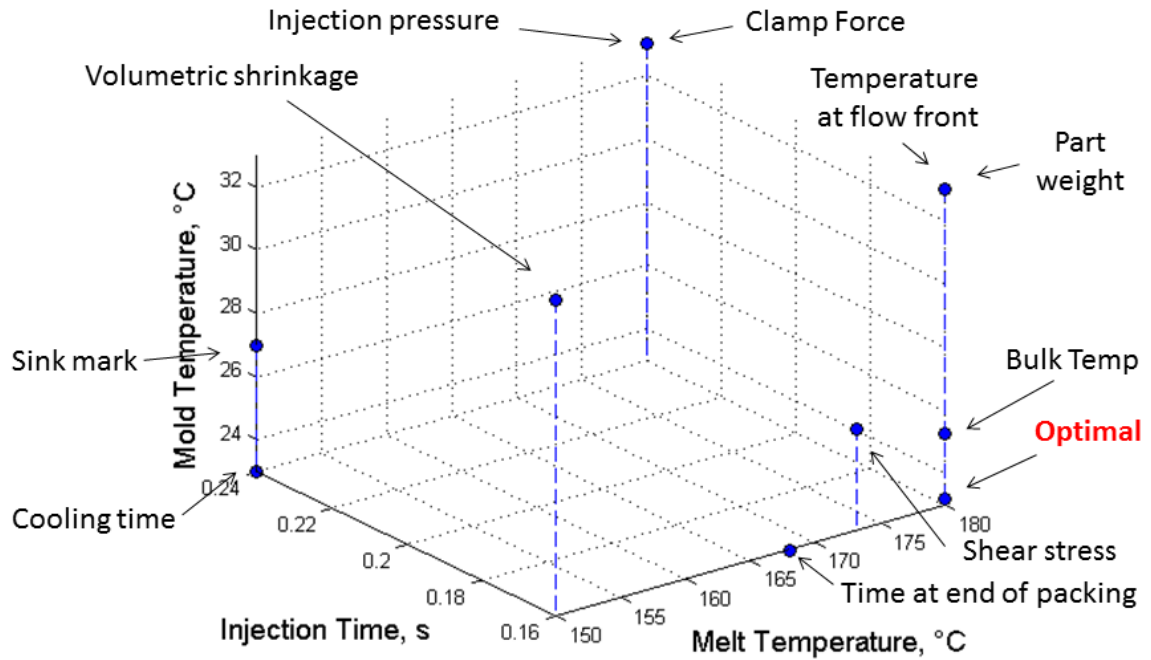


FIGURE 4.53: Optimal Process Conditions

4.10.3 Optimization Result

The result of the model was a melt temperature of 180 °C, an injection time of 0.16 seconds and a mold temperature of 23.19 °C. Where this point described by the process parameters as coordinates is located relative to the optimal process conditions of the quality criteria is shown in Figure 4.53. The minimal sum of all differences found was 55.84.

The results of each quality criteria, the minimum and their difference is shown in Table 4.24.

TABLE 4.24: Results at Optimized Process Parameters

Quality	Bulk Temp.	Clamp F.	Pressure	Stress	Sink Mark	Flow Front	Cool Time	Shrink.	End of Pack.	Weight
Units	K(d)	N	MPa	MPa	mm	K(d)	s	%	s	kg
Min.	1.145	55110	21.3	2.52	0.317	0.06728	11.11	1.0978	30.16	0.1319
Opt.	1.147	58890	21.55	2.57	0.366	0.06815	12.08	1.45	30.16	0.1319
% Diff.	0.11	6.42	1.29	1.95	13.33	1.282	8.03	24.19	0	0

5. CONCLUSIONS AND FUTURE WORK

5.1. Present Thesis

In this present thesis, a composition of powder and binder ratios has been identified. a mixture of bimodal Si_3N_4 powder with Y_2O_3 and MgO as a sintering aids. It molded successfully. Debinding and pressureless liquid phase sintering were also achieved under acceptable parameter settings.

1. After identifying the intended composition powder ratios the material was scaled up to a quantity of about 20 kg. With the TGA analysis a content of 80.07 % ceramic powder was shown.
2. The collected data on the feedstock analysis a custom material database has been built. This database was successfully loaded into the Moldflow software and their values read by the simulation solver.
3. After sintering the material properties were measured for this specific Si_3N_4 composition. The values were in the expected range. A densification to around 99 % of the theoretical density was achieved. The parts shrank on average 17.2 %. Linear shrinkage was found. High hardness of around 1300 HV was measured.
4. The validation part was successfully simulated and by analyzing various result metrics the feasibility was proven. These findings were backed up by molding of the actual part and validate properties with the simulation software.

5. The engine component was simulated and successful filling was shown. An analysis for potential molding defects was performed and only minor superficial defects may occur. The prediction of various mold process factors was related to machine requirements. This showed that many parts can be made simultaneously and therefore keep manufacturing costs at a reasonable level. Complete filling was predicted. The pressure needed to mold the part was 21 MPa, the calculated clamp force was 60.1 kN. The flow front temperature drop was very small (0.5 C). This small The time at the end of packing was 30.2 s. Minor superficial defect may occur.
6. The Taguchi analysis identified the influences of each process parameter on each quality criteria. From this data the parameter with the biggest influence was identified for each quality criteria. The Box-Behnken Analysis was performed and for each quality criteria the result was expressed as a function of the three process parameters. This helped to visualize the response of the result to a change in process parameter. Also the minimum for each quality criteria was identified. These local minimums were the points in the process window with the optimal process parameter settings for the specific quality criteria. The findings showed that these optimal settings were different for each quality criteria. The main findings were the high influence of injection time on bulk temperature and the high influence of melt temperature pressure and stress and clamp force. A NLP-Model of the responses for all criteria was built. This model iterated the perfect trade of between the different settings. The process parameter settings with the best compromise were identified.

5.2. Future work

5.2.1 Material System

The binder system and sintering additive ratios can be optimized. This work used built on empirical studies, but they were incomplete due to the vast possibilities of binder component and additive materials and ratio combinations. Varying the sintering conditions may result in lower feasible sintering temperature Sintering in this study was not done at the lowest possible sintering temperature and time for this material system. Improving these settings will lower manufacturing cost. The mechanical properties after sintering can also be further improved by varying different process settings. The machinability of this material system can be looked into more deeply. Process steps after sintering may include burring, trimming or finishing.

5.2.2 Part Manufacturing

To injection mold the engine part the manufacturing of the mold, is necessary. After the mold is available and the machine is set up mold can be conducted. The next steps after molding would be debinding, sintering and finalizing.

5.2.3 Engine System

Once the engine part is produced it can be assembled with the other engine components of the engine design into a fully functional engine. The system-level performance can be evaluated and compared to a metal engine. After the engine is evaluated and sufficiently tested it can be built into the UAV.

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APPENDICES

A Publication in Journal of the Minerals, Metals and Materials Society

Appendix A contains the publication in the Journal of the Minerals, Metals and Materials Society from 3/2/2012. The papers title is “Powder Injection Molding of Ceramic Engine Components for Transportation”. Some results presented in this thesis have been published beforehand in the paper attached.

Powder Injection Molding of Ceramic Engine Components for Transportation

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Silicon nitride has been the favored material for manufacturing high-efficiency engine components for transportation due to its high temperature stability, good wear resistance, excellent corrosion resistance, thermal shock resistance, and low density. The use of silicon nitride in engine components greatly depends on the ability to fabricate near net-shape components economically. The absence of a material database for design and simulation has further restricted the engineering community in developing parts from silicon nitride. In this paper, the design and manufacturability of silicon nitride engine rotors for unmanned aerial vehicles by the injection molding process are discussed. The feedstock material property data obtained from experiments were used to simulate the flow of the material during injection molding. The areas susceptible to the formation of defects during the injection molding process of the engine component were identified from the simulations. A test sample was successfully injection molded using the feedstock and sintered to 99% density without formation of significant observable defects.

INTRODUCTION

Transportation is the second largest energy-consuming sector, accounting for 30% of the world's total delivered energy and 60% of world oil demand.¹ The energy efficiency in typical diesel engines used in transportation is less than 40%.² Thus, major emphasis has been focused during the last 50 years on improving the efficiency of engines used for transportation. The rising cost of fuels has further accelerated these research efforts. Use of components made from or coated with ceramics enables engines to operate at higher temperature with reduced heat loss relative to metal components, resulting in increased fuel efficiency. In several research studies an increase in efficiency of 7–12% has been reported by coating engine components with ceramics.^{3,4} Small gas turbines made from ceramics with 40% electrical efficiency have been identified as a future engine for transportation.⁵

Some applications where engines made of ceramic components have increasing potential are in

unmanned aerial vehicle (UAV) propulsion and portable power generation.^{6,7} Silicon nitride, due to its high temperature stability (up to approximately 1400°C), good wear resistance, excellent corrosion resistance, and low weight has been the favored material for manufacturing high-efficiency advanced heat engine components for transportation^{8–10} and for rotors in UAVs. However, silicon nitride exhibits high hardness, which prohibits extensive machining of fabricated components. Thus, use of silicon nitride heat engine components greatly depends on the ability to fabricate near net-shape components economically. Various techniques such as slip casting,¹¹ gel casting,¹² injection molding,^{13–15} and robocasting¹⁶ have been explored to manufacture near net-shape silicon nitride engine components. Among these techniques, due to its inherent ability to manufacture high-volume complex near net-shape parts economically, injection molding has evolved as the primary process to manufacture engine components from silicon nitride.

Various studies dealing with injection molding of engine components from silicon nitride are reported

in the literature.^{10–12} Several prototype engine components were successfully fabricated using injection molding and tested at different laboratories in the world.^{8,10,15} However, component size and performance constraints have severely limited widespread applicability in conventional aerospace and automotive applications. Further, the lack of material property data for component and process design has also negatively impacted the awareness of these material and process options among the engineering community. The current paper discusses the design and manufacturability of the injection molding process to fabricate engine components for UAV applications. The material property data obtained from experimental results were used to simulate the flow of the material during the injection molding process. Both binder and feedstock properties were measured to allow for interpolation of properties for feedstock compositions different from the measured value for design considerations. The areas susceptible to formation of defects during the injection molding process of the rotors were identified from the simulations. These results indicate that UAV and portable power generation applications may potentially be a suitable fit with ceramic injection molding technologies.

EXPERIMENTAL PROCEDURES

Commercially available Si_3N_4 , and a multicomponent polymer system based on paraffin wax, polypropylene, was chosen as the binder to facilitate a multistep debinding process. Twin screw extrusion of the Si_3N_4 feedstock with 60 vol.% solids loading (ϕ) was performed with a co-rotating 27-mm twin screw extruder (Entek). The extruded feedstocks were pelletized for further characterization. Thermogravimetric analysis (TGA) was performed on the extruded feedstocks using a TA-Q500 (TA Instruments) thermal system operated under nitrogen flow in the temperature range of 50–600°C at heating rate of 20°C/min. Calorimetric measurements were carried out using a TA-Q1000 unit (TA Instruments) over a temperature range of 20–200°C. The samples were heated at the rate of 20°C/min under nitrogen atmosphere.

The rheological characteristics of the feedstock were examined using a Gottfert Rheograph 2003 capillary rheometer at different shear rates and temperatures. The testing was carried out in accordance with ASTM D 3835. The temperatures were between the highest melting temperature and the lowest degradation temperature of the binder system. A Gnomix pressure–volume–temperature (PVT) apparatus was used to find the PVT relationships of the feedstock materials. The test was carried out in accordance with ASTM D 792. Moldflow software developed by Autodesk Inc. was used for simulating the injection conditions. Confirmation injection molding cycles were performed on the feedstocks with an Arburg 221M injection molding machine. Debinding and sintering was

performed on a custom-built production furnace at Kyocera.

RESULTS AND DISCUSSION

Thermal Properties

The thermal properties of the extruded feedstocks provide basic guidelines for selecting various process parameters during fabrication of components by injection molding. The information provided by TGA–DSC analysis can be used to design thermal debinding profiles and select the appropriate temperature for injection molding. The TGA analysis of the feedstock used in the present study showed a two-stage degradation corresponding to burnout of the filler phase from 175°C to 400°C and backbone polymers from 400°C to 550°C. DSC analysis of the feedstock showed two endothermic peaks representing the melting of filler phase (paraffin wax) and backbone polymers. The specific heat values ranged from 790 J/kg K at 0°C to 1160 J/kg K at 170°C. Based on the DSC analysis, the melt temperature of the feedstock during injection molding was targeted between 135°C and 180°C. The thermal conductivity data of the feedstock and the binder mixture are shown in Fig. 1. An increase in thermal conductivity of the binder is observed with the addition of silicon nitride powder.

Rheological Properties

To evaluate the dependence of feedstock viscosity on temperature, apparent viscosity–shear rate curves of the Si_3N_4 feedstock and binder mixture were measured at different temperatures. The temperatures were between the highest melting temperature (135°C) and lowest degradation temperature (180°C) of the feedstocks. Figure 2 shows the change in viscosity with shear rate at various temperatures for the feedstock and binder mixture. The viscosity of the feedstock decreased with increasing shear rate, indicating pseudoplastic behavior. The viscosity of the feedstock was found to be higher than that of the binder mixture at any given shear rate–temperature conditions.

PVT Measurements

The PVT behavior of the silicon nitride feedstock and binder mixture is shown in Fig. 3. The PVT analysis estimates the specific volume of the melt in a cavity as a function of the cavity pressure and temperature. These plots help to understand the compressibility and temperature effects during a typical injection molding cycle. The hold pressure should be chosen after appropriately referring to the PVT diagram so that the residual cavity pressure is near atmospheric pressure before mold opening. This in turn ensures avoidance of any part ejection and/or relaxation issues. From Fig. 3, it is clear that the binder mixture has a higher slope value, meaning more thermal expansion than that of the

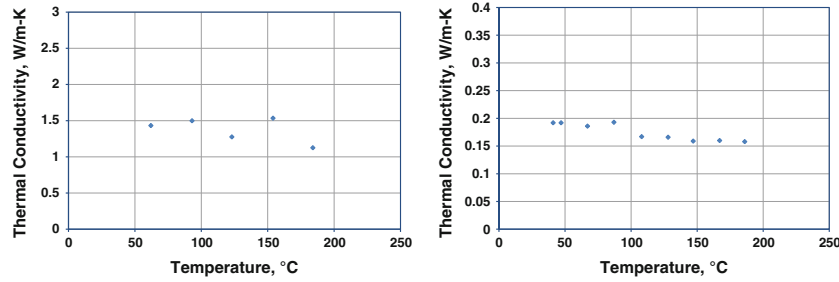


Fig. 1. Thermal conductivity of the Si_3N_4 feedstock (left) and binder mixture (right).

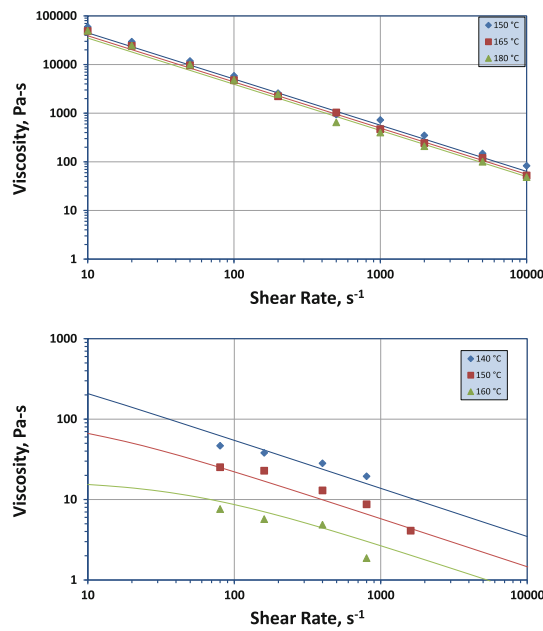


Fig. 2. Viscosity of the Si_3N_4 feedstock (top) and binder mixture (bottom) at different shear rate and temperature combinations, indicating pseudoplastic behavior.

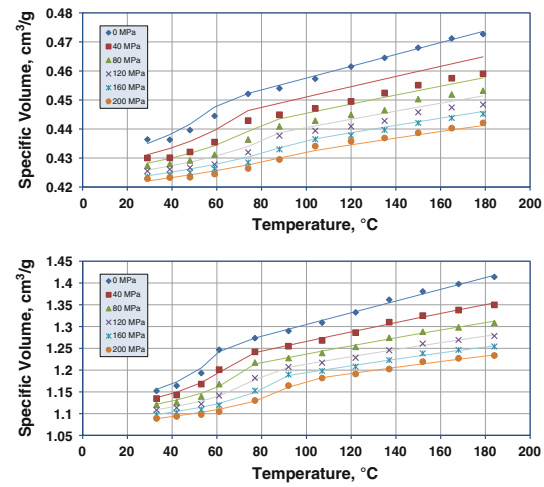


Fig. 3. PVT relationships for Si_3N_4 feedstock (top) and binder mixture (bottom).

feedstock. Thus, the increased powder content reduces the thermal expansion of the feedstock, indicating lower tendency for shrinkage in the final part.

Injection Molding Simulations

The primary goal of the present study is to use the information obtained from the feedstock characterization techniques to simulate the injection molding of silicon nitride components. Such simulations will enable engineers to understand the feasibility of the injection molding process to manufacture a selected part. These simulations will also assist in reducing lead times and costs to develop material and process parameters as well as part designs. In the present

study, the engine part geometry considered for fabrication from silicon nitride using powder injection molding (PIM) is shown in Fig. 4. The feedstock material properties discussed in “[Thermal Properties](#)”, “[Rheological Properties](#)” and “[PVT Measurements](#)” sections were used to study the mold filling behavior of these target geometries to assess changes to be made in the feedstock material composition, part geometry, mold geometry (including gate location and size), and process conditions to develop optimized design of the target component. Figure 5 shows the simulated progressive filling pattern during injection molding of the silicon nitride feedstocks in terms of the pressure distribution in the path. The results indicate that complete filling of the part cavity is possible with the developed feedstock. Additional simulations were carried out to identify the susceptibility to defect formation during injection molding. The simulation results, showing the variation in bulk temperature which can result in warpage of the component due to thermal stresses, are presented in Fig. 6. The simulation results

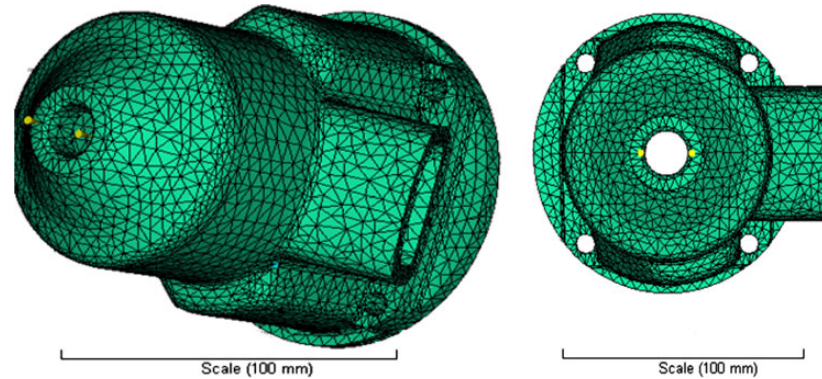


Fig. 4. Meshed geometry of the engine part.

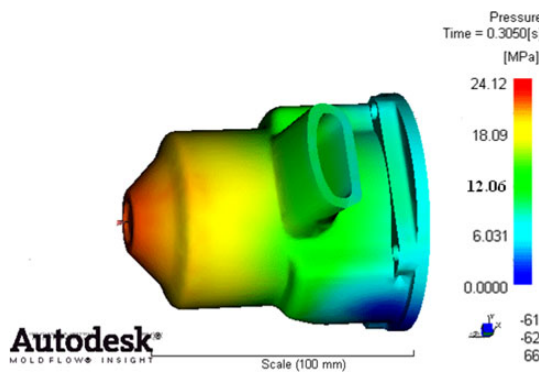


Fig. 5. Pressure distribution in the part during mold filling, illustrating the flow path.

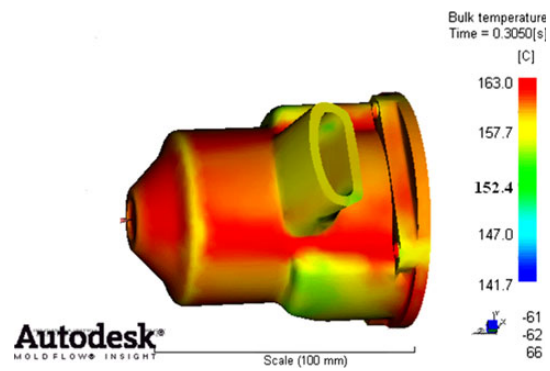


Fig. 6. Bulk temperature distribution in the UAV engine part to assess thermal stresses.

identifying the critical locations for air traps and weld lines are shown in Fig. 7.

In addition to the above simulations of the targeted UAV engine geometry, a series of injection molding cycles were performed with the silicon nitride feedstock to mold test samples. Injection molding of the test samples was carried out with the aim of evaluating the debinding and sintering characteristics of the feedstock. The test samples were successfully injection molded, debound, and sintered. The sintered part showed linear shrinkage of 17.2% in all directions, corresponding to 99% of theoretical density. The parts had hardness of 90 HRA. Detailed sensitivity studies will be conducted in future work to understand material–geometry–process combinations that eliminate these defects. It is expected that these simulations will enable efficient incorporation of changes to the feedstock material formulation, as well as part geometry and mold design, and avoid time-consuming and expensive trial-and-error troubleshooting of defects.

CONCLUSIONS

This research study shows the applicability of the injection molding process to the manufacture Si_3N_4 engine components for UAV and portable power applications. The material property data of the feedstocks and binders were used as critical inputs to simulate the injection molding of Si_3N_4 engine components. The simulation studies identified the defect-prone areas of the rotors during injection molding. The simulation techniques can be used in the engineering community to evaluate the feasibility of manufacturing various engine components from Si_3N_4 by injection molding. A prototype part was successfully injection molded, debound, and sintered to 99% density without formation of any defects, demonstrating the viability of the feedstock composition.

ACKNOWLEDGEMENTS

The authors thank NWUAV Propulsion Systems (application development) Entek Manufacturing (feedstock mixing), Kinetics Inc. (injection molding),

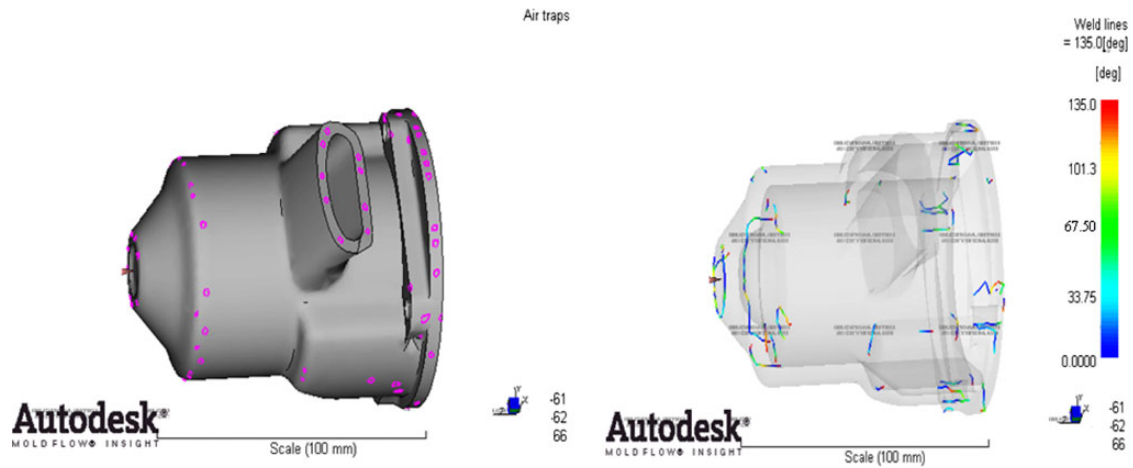


Fig. 7. Simulations showing critical areas for air traps (left) and weld line (right) distributions.

and Kyocera (debinding and sintering) for their technical support, and ONR for financial support.

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B Simulation Logs

Validation Part Appendix B1 gives the log output from the Moldflow simulation for the simulation of the validation part.

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Flow Analysis

Version: ami2012-barium_main_sp2 (Build 11271-001) 64-bit build

Analysis running on host: JHLenz-PC Operating System: Windows 7

Processor type: GenuineIntel Intel64 Family 6 Model 37 Stepping 5 ~2660 MHz Number of Processors: 4

Total Physical Memory: 3956 MBytes

No mesh for the cores was found. Core shift analysis switched OFF
Date : FEB14-12 Time : 04:36:18 File name : multi_channel_study~1

Summary of analysis inputs :

Solver parameters :

```

No. of laminae across thickness           =    12
Intermediate output options for filling phase
  No. of results at constant intervals     =    20
  No. of profiled results at constant intervals =    0
Intermediate output options for packing phase
  No. of results at constant intervals     =    20
  No. of profiled results at constant intervals =    0
Flow rate convergence tolerance           =    0.5000 %
Melt temperature convergence tolerance     =    0.0200 C
Mold-melt heat transfer coefficient
  Filling                                 = 5000.0000 W/m^2-C
  Packing                                 = 2500.0000 W/m^2-C
  Detached, cavity side                   = 1250.0000 W/m^2-C
  Detached, core side                     = 1250.0000 W/m^2-C
Maximum no. of flow rate iterations       =    125
Maximum no. of melt temperature iterations =    200
Nodal growth mechanism                   = Multiple
Pressure work option                     =    1

```

Material data :

Polymer : Nano Silicon Nitride - Jürgen Lenz

```

pvT Model: 2-domain modified Tait
coefficients: b5 = 336.1500 K
b6 = 1.7250E-07 K/Pa
Liquid phase      Solid phase
-----
b1m = 0.0005 b1s = 0.0004 m^3/kg
b2m = 2.0440E-07 b2s = 1.0430E-07 m^3/kg-K
b3m = 2.6346E+08 b3s = 7.7033E+08 Pa
b4m = 0.0036 b4s = 0.0005 1/K
      b7 = 1.6100E-05 m^3/kg
      b8 = 0.0383 1/K
      b9 = 1.4410E-08 1/Pa

```

Specific heat: Tabulated data:

Temperature T (K)	Specific Heat Cp (J/kg-K)
273.1500	791.0000
290.1500	913.0000
297.1500	1004.0000

320.1500	1698.0000
331.1500	1009.0000
384.1500	1059.0000
443.1500	1163.0000

Thermal conductivity: Tabulated data:

Temperature T (K)	Thermal Conductivity K (W/m-K)
335.1500	1.4320
366.1500	1.4980
396.1500	1.2750
427.1500	1.5340
457.1500	1.1250

Viscosity model:

Cross-WLF
 coefficients: n = 0.0508
 TAUS = 1.3012E+05 Pa
 D1 = 1.0000E+23 Pa-s
 D2 = 373.0000 K
 D3 = 0.0000 K/Pa
 A1 = 42.2800
 A2T = 51.6000 K

Transition temperature = 53.0000 C

Mechanical properties data:

E1 = 2449.9999 MPa
 E2 = 2449.9999 MPa
 v12 = 0.3800
 v23 = 0.3800
 G12 = 887.7000 MPa

Transversely isotropic coefficient of
 thermal expansion (CTE) data:

Alpha1 = 0.0002 1/C
 Alpha2 = 0.0002 1/C

Residual stress model without CRIMS

Process settings :

Machine parameters :

Maximum machine clamp force = 7.0002E+03 tonne
 Maximum injection pressure = 1.8000E+02 MPa
 Maximum machine injection rate = 5.0000E+03 cm³/s
 Machine hydraulic response time = 1.0000E-02 s

Process parameters :

Fill time = 0.2000 s
 Stroke volume determination = Automatic
 Cooling time = 20.0000 s

Velocity/pressure switch-over by = Automatic
 Packing/holding time = 10.0000 s

Ram speed profile (rel):

% shot volume % ram speed

0.0000 100.0000
 100.0000 100.0000

Pack/hold pressure profile (rel):
 duration % filling pressure

0.0000 s	80.0000	
10.0000 s	80.0000	
20.0000 s	0.0000	
Ambient temperature		= 25.0000 C
Melt temperature		= 165.0000 C
Ideal cavity-side mold temperature		= 28.0000 C
Ideal core-side mold temperature		= 28.0000 C

NOTE: Mold wall temperature data from Cool analysis not available

Model details :

Mesh Type		= Dual Domain
Mesh match percentage		= 99.3 %
Reciprocal mesh match percentage		= 99.7 %
Total number of nodes		= 1467
Total number of injection location nodes		= 1
The injection location node labels are:		
	26	
Total number of elements		= 2954
Number of part elements		= 2954
Number of sprue/runner/gate elements		= 0
Number of channel elements		= 0
Number of connector elements		= 0
Average aspect ratio of triangle elements		= 1.5696
Maximum aspect ratio of triangle elements		= 8.9978
Minimum aspect ratio of triangle elements		= 1.1558
Total volume		= 1.8417 cm ³
Volume filled initially		= 0.0000 cm ³
Volume to be filled		= 1.8417 cm ³
Sprue/runner/gate volume to be filled		= 0.0000 cm ³
Total projected area		= 1.9593 cm ²

Filling phase results summary :

Maximum injection pressure (at 0.2328 s) = 27.9758 MPa

End of filling phase results summary :

Time at the end of filling		= 0.2350 s
Total weight (part + runners)		= 3.9824 g
Maximum Clamp force - during filling		= 0.2215 tonne
Recommended ram speed profile (rel):		
%Shot volume	%Flow rate	

0.0000	28.2382
10.0000	61.5292
20.0000	83.9170
30.0000	79.1843
40.0000	63.3169
50.0000	59.2526
60.0000	76.5640
70.0000	100.0000
80.0000	74.5724
90.0000	63.5541
100.0000	49.6269

Melt front is entirely in the cavity at % fill = 0.0000 %

Packing phase results summary :

Peak pressure
 - minimum among cavity nodes (at 0.248 s) = 3.2919 MPa
 Clamp force - maximum (at 0.237 s) = 0.2343 tonne
 Total weight - maximum (at 2.145 s) = 4.0143 g

End of packing phase results summary :

Time at the end of packing = 30.2329 s
 Total weight (part + runners) = 4.0143 g

Packing phase results summary for the part :

Bulk temperature - maximum (at 0.248 s) = 166.3610 C
 Bulk temperature - 95th percentile (at 0.248 s) = 164.6878 C
 Bulk temperature - 5th percentile (at 30.233 s) = 28.4350 C
 Bulk temperature - minimum (at 30.233 s) = 28.3545 C

 Wall shear stress - maximum (at 2.145 s) = 16.7855 MPa
 Wall shear stress - 95th percentile (at 1.145 s) = 1.9029 MPa

 Volumetric shrinkage - maximum (at 0.248 s) = 7.6196 %
 Volumetric shrinkage - 95th %ile (at 0.248 s) = 7.3492 %
 Volumetric shrinkage - 5th %ile (at 6.145 s) = 4.5300 %
 Volumetric shrinkage - minimum (at 10.233 s) = 0.1620 %

 Total part weight - maximum (at 2.145 s) = 4.0143 g

End of packing phase results summary for the part :

Total part weight (excluding runners) = 4.0143 g

 Bulk temperature - maximum = 29.0370 C
 Bulk temperature - 95th percentile = 29.0254 C
 Bulk temperature - 5th percentile = 28.4350 C
 Bulk temperature - minimum = 28.3545 C
 Bulk temperature - average = 28.8826 C
 Bulk temperature - root-mean-square deviation = 0.1765 C

 Frozen layer fraction - maximum = 1.0000
 Frozen layer fraction - 95th percentile = 1.0000
 Frozen layer fraction - 5th percentile = 1.0000
 Frozen layer fraction - minimum = 1.0000
 Frozen layer fraction - average = 1.0000
 Frozen layer fraction - root-mean-square deviation = 0.0000

 Volumetric shrinkage - maximum = 7.5241 %
 Volumetric shrinkage - 95th percentile = 7.3213 %
 Volumetric shrinkage - 5th percentile = 4.5310 %
 Volumetric shrinkage - minimum = 0.2713 %
 Volumetric shrinkage - average = 5.9669 %
 Volumetric shrinkage - root-mean-square deviation = 0.9569 %

 Sink index - maximum = 4.0497 %
 Sink index - 95th percentile = 3.8398 %
 Sink index - minimum = 2.4402 %
 Sink index - root-mean-square deviation = 0.9675 %

Sink Mark Analysis

Execution time
 Analysis commenced at Tue Feb 14 04:36:17 2012
 Analysis completed at Tue Feb 14 04:37:27 2012
 CPU time used 67.52 s

Appendix B2 gives the log output from the Moldflow simulation for the simulation of the engine part.

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Flow Analysis

Version: ami2012-barium_main_sp2 (Build 11271-001) 64-bit build

Analysis running on host: JHLenz-PC Operating System: Windows 7

Processor type: GenuineIntel Intel64 Family 6 Model 37 Stepping 5 ~2660 MHz Number of Processors: 4

Total Physical Memory: 3956 MBytes

No mesh for the cores was found. Core shift analysis switched OFF

Date : JAN27-12 Time : 17:33:31 File name : all_small-2

Summary of analysis inputs :

Solver parameters :

```

No. of laminae across thickness          = 12
Intermediate output options for filling phase
  No. of results at constant intervals    = 20
  No. of profiled results at constant intervals = 0
Intermediate output options for packing phase
  No. of results at constant intervals    = 20
  No. of profiled results at constant intervals = 0
Flow rate convergence tolerance          = 0.5000 %
Melt temperature convergence tolerance    = 0.0200 C
Mold-melt heat transfer coefficient
  Filling                                = 5000.0000 W/m^2-C
  Packing                                = 2500.0000 W/m^2-C
  Detached, cavity side                  = 1250.0000 W/m^2-C
  Detached, core side                    = 1250.0000 W/m^2-C
Maximum no. of flow rate iterations      = 125
Maximum no. of melt temperature iterations = 200
Nodal growth mechanism                   = Multiple
Pressure work option                     = 1

```

Material data :

Polymer : Nano Silicon Nitride - Jürgen Lenz

pvT Model:2-domain modified Tait

coefficients: b5 = 336.1500 K

b6 = 1.7250E-07 K/Pa

Liquid phase Solid phase

```

b1m = 0.0005 b1s = 0.0004 m^3/kg
b2m = 2.0440E-07 b2s = 1.0430E-07 m^3/kg-K
b3m = 2.6346E+08 b3s = 7.7033E+08 Pa
b4m = 0.0036 b4s = 0.0005 1/K
      b7 = 1.6100E-05 m^3/kg
      b8 = 0.0383 1/K
      b9 = 1.4410E-08 1/Pa

```

Specific heat: Tabulated data:

Temperature T (K)	Specific Heat Cp (J/kg-K)
273.1500	791.0000
290.1500	913.0000
297.1500	1004.0000

320.1500	1698.0000
331.1500	1009.0000
384.1500	1059.0000
443.1500	1163.0000

Thermal conductivity: Tabulated data:

Temperature T (K)	Thermal Conductivity K (W/m-K)
335.1500	1.4320
366.1500	1.4980
396.1500	1.2750
427.1500	1.5340
457.1500	1.1250

Viscosity model:

Cross-WLF
 coefficients: n = 0.0508
 TAUS = 1.3012E+05 Pa
 D1 = 1.0000E+23 Pa-s
 D2 = 373.0000 K
 D3 = 0.0000 K/Pa
 A1 = 42.2800
 A2T = 51.6000 K

Transition temperature = 53.0000 C

Mechanical properties data:

E1 = 2449.9999 MPa
 E2 = 2449.9999 MPa
 v12 = 0.3800
 v23 = 0.3800
 G12 = 887.7000 MPa

Transversely isotropic coefficient of
 thermal expansion (CTE) data:

Alpha1 = 0.0002 1/C
 Alpha2 = 0.0002 1/C

Residual stress model without CRIMS

Process settings :

Machine parameters :

Maximum machine clamp force = 7.0002E+03 tonne
 Maximum injection pressure = 1.8000E+02 MPa
 Maximum machine injection rate = 5.0000E+03 cm³/s
 Machine hydraulic response time = 1.0000E-02 s

Process parameters :

Fill time = 0.2000 s
 Stroke volume determination = Automatic
 Cooling time = 20.0000 s

Velocity/pressure switch-over by = Automatic
 Packing/holding time = 10.0000 s

Ram speed profile (rel):

% shot volume % ram speed

0.0000	100.0000
100.0000	100.0000

Pack/hold pressure profile (rel):

duration % filling pressure

0.0000 s	80.0000	
10.0000 s	80.0000	
20.0000 s	0.0000	

Ambient temperature = 25.0000 C
 Melt temperature = 165.0000 C
 Ideal cavity-side mold temperature = 28.0000 C
 Ideal core-side mold temperature = 28.0000 C

NOTE: Mold wall temperature data from Cool analysis not available

Model details :

Mesh Type	= Dual Domain
Mesh match percentage	= 81.0 %
Reciprocal mesh match percentage	= 79.5 %
Total number of nodes	= 6358
Total number of injection location nodes	= 1
The injection location node labels are:	
	3029
Total number of elements	= 12732
Number of part elements	= 12732
Number of sprue/runner/gate elements	= 0
Number of channel elements	= 0
Number of connector elements	= 0
Average aspect ratio of triangle elements	= 2.1371
Maximum aspect ratio of triangle elements	= 20.6324
Minimum aspect ratio of triangle elements	= 1.1590
Total volume	= 61.4588 cm ³
Volume filled initially	= 0.0000 cm ³
Volume to be filled	= 61.4588 cm ³
Sprue/runner/gate volume to be filled	= 0.0000 cm ³
Total projected area	= 46.6984 cm ²

Filling phase results summary :

Maximum injection pressure (at 0.2041 s) = 23.1305 MPa

End of filling phase results summary :

Time at the end of filling	= 0.2081 s
Total weight (part + runners)	= 129.8459 g
Maximum Clamp force - during filling	= 6.1296 tonne

Recommended ram speed profile (rel):

%Shot volume	%Flow rate
--------------	------------

0.0000	43.2824
10.0000	66.1073
20.0000	80.7883
30.0000	53.6740
40.0000	54.2052
50.0000	57.1848
60.0000	71.9095
70.0000	81.9492
80.0000	100.0000
90.0000	78.8352
100.0000	25.1804

Melt front is entirely in the cavity at % fill = 0.0000 %

Packing phase results summary :

Peak pressure
 - minimum among cavity nodes (at 0.214 s) = 3.5181 MPa
 Clamp force - maximum (at 0.204 s) = 6.1324 tonne
 Total weight - maximum (at 12.114 s) = 132.1879 g

End of packing phase results summary :

Time at the end of packing = 30.2042 s
 Total weight (part + runners) = 132.1879 g

Packing phase results summary for the part :

Bulk temperature - maximum (at 0.214 s) = 168.2600 C
 Bulk temperature - 95th percentile (at 0.214 s) = 167.0830 C
 Bulk temperature - 5th percentile (at 30.204 s) = 28.1549 C
 Bulk temperature - minimum (at 30.204 s) = 28.0478 C

 Wall shear stress - maximum (at 10.204 s) = 10.4963 MPa
 Wall shear stress - 95th percentile (at 6.368 s) = 2.6159 MPa

 Volumetric shrinkage - maximum (at 0.214 s) = 7.7410 %
 Volumetric shrinkage - 95th %ile (at 0.214 s) = 7.5561 %
 Volumetric shrinkage - 5th %ile (at 9.368 s) = 3.4582 %
 Volumetric shrinkage - minimum (at 7.368 s) = 3.1064 %

 Total part weight - maximum (at 12.114 s) = 132.1879 g

End of packing phase results summary for the part :

Total part weight (excluding runners) = 132.1879 g

 Bulk temperature - maximum = 56.4156 C
 Bulk temperature - 95th percentile = 43.5012 C
 Bulk temperature - 5th percentile = 28.1549 C
 Bulk temperature - minimum = 28.0478 C
 Bulk temperature - average = 32.8376 C
 Bulk temperature - root-mean-square deviation = 5.0842 C

 Frozen layer fraction - maximum = 1.0000
 Frozen layer fraction - 95th percentile = 1.0000
 Frozen layer fraction - 5th percentile = 1.0000
 Frozen layer fraction - minimum = 0.3207
 Frozen layer fraction - average = 0.9969
 Frozen layer fraction - root-mean-square deviation = 0.0387

 Volumetric shrinkage - maximum = 7.6987 %
 Volumetric shrinkage - 95th percentile = 7.3873 %
 Volumetric shrinkage - 5th percentile = 3.4582 %
 Volumetric shrinkage - minimum = 3.1064 %
 Volumetric shrinkage - average = 5.5278 %
 Volumetric shrinkage - root-mean-square deviation = 1.3208 %

 Sink index - maximum = 4.2308 %
 Sink index - 95th percentile = 3.9081 %
 Sink index - minimum = 2.0736 %
 Sink index - root-mean-square deviation = 1.2538 %

Sink Mark Analysis

Execution time
 Analysis commenced at Fri Jan 27 17:33:30 2012
 Analysis completed at Fri Jan 27 17:43:01 2012
 CPU time used 560.98 s

Appendix B3 gives the log output from the Moldflow simulation for the design of experiment runs of the engine part.

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Design of Experiments

Version: ami2012-barium_main_sp2 (Build 11271-001)
 64-bit build

Analysis running on host: JHLenz-PC Operating System: Windows 7
 Processor type: GenuineIntel Intel64 Family 6 Model 37 Stepping 5 ~2660 MHz Number of Processors: 4
 Total Physical Memory: 3956 MBytes

Analysis commenced at Fri Jan 27 17:43:04 2012

Loading original study ...

Loading study model ...

Analysis is using stored mesh match and thickness data
 Match data was computed using the maximal-sphere algorithm

Loading general parameters ...
 Formatting first study duplicate ...

Analysis mode = DOUBLE ANALYSIS

First analysis ...

Analysis type = INFLUENCES
 Number of variables = 3
 Number of qualities = 10

Variable information ...

Mold surface temperature
 Range = [23 : 33] C

Melt temperature
 Range = [150 : 180] C

Injection time
 Range = [0.16 : 0.24] s

Quality information ...

Bulk temperature at end of fill Weight = 1.00

Clamp Force Weight = 1.00

Injection pressure Weight = 1.00

Shear stress Weight = 1.00

Sink mark depth Weight = 1.00

Temperature at flow front Weight = 1.00

Cooling time Weight = 1.00

Volumetric shrinkage at ejection Weight = 1.00

Time at end of packing Weight = 1.00

Part weight Weight = 1.00

Create Design of Experiments ...

Design of Experiments = TAGUCHI

Number of experiments = 4

Build set of studies...

Run studies ...

Failed	Waiting	Running	Completed
0	3	1	0
0	3	1	0
0	3	1	0
0	3	1	0
0	3	1	0
0	3	0	1
0	2	1	1
0	1	2	1
0	1	2	1
0	1	1	2
0	1	1	2
0	1	0	3
0	0	1	3
0	0	1	3
0	0	0	4

Analyze results ...

Ranking of variable influences ...

Influences on quality #1, Bulk temperature at end of fill

Calculate = Standard deviation

11.92% Mold surface temperature

4.17% Melt temperature

83.91% Injection time

Influences on quality #2, Clamp Force

Calculate = Single value

1.97% Mold surface temperature

73.51% Melt temperature

24.52% Injection time

Influences on quality #3, Injection pressure

Calculate = Single value

2.50% Mold surface temperature

95.83% Melt temperature

1.67% Injection time

Influences on quality #4, Shear stress

Calculate = Single value

30.09% Mold surface temperature

48.77% Melt temperature

21.14% Injection time

Influences on quality #5, Sink mark depth

Calculate = Maximum

5.28% Mold surface temperature

89.64% Melt temperature

5.07% Injection time

Influences on quality #6, Temperature at flow front

Calculate = Standard deviation
 6.88% Mold surface temperature
 55.89% Melt temperature
 37.23% Injection time

Influences on quality #7, Cooling time

Calculate = Standard deviation
 94.77% Mold surface temperature
 4.61% Melt temperature
 0.63% Injection time

Influences on quality #8, Volumetric shrinkage at ejection

Calculate = Standard deviation
 16.75% Mold surface temperature
 79.37% Melt temperature
 3.88% Injection time

Influences on quality #9, Time at end of packing

Calculate = Single value
 0.16% Mold surface temperature
 0.02% Melt temperature
 99.82% Injection time

Influences on quality #10, Part weight

Calculate = Single value
 13.72% Mold surface temperature
 85.23% Melt temperature
 1.05% Injection time

Set parameters for the second analysis ...

Second analysis ...

Analysis type = RESPONSES
 Number of variables = 3
 Number of qualities = 10

Variable information ...

Melt temperature Range = [150 : 180] C

Injection time Range = [0.16 : 0.24] s

Mold surface temperature Range = [23 : 33] C

Create Design of Experiments ...

Design of Experiments = FACE CENTERED CUBIC
 Number of experiments = 15

Build set of studies...

Run studies ...

Failed	Waiting	Running	Completed
0	11	0	4
0	11	0	4
0	11	0	4
0	11	0	4
0	10	1	4
0	10	1	4
0	10	1	4
0	10	1	4
0	10	1	4
0	10	1	4

0	10	1	4
0	10	1	4
0	10	1	4
0	10	1	4
0	9	2	4
0	9	1	5
0	9	1	5
0	8	2	5
0	8	1	6
0	8	1	6
0	8	0	7
0	7	1	7
0	7	1	7
0	7	0	8
0	6	1	8
0	6	1	8
0	5	2	8
0	5	1	9
0	4	2	9
0	4	2	9
0	4	1	10
0	4	1	10
0	3	2	10
0	3	1	11
0	2	2	11
0	2	2	11
0	2	1	12
0	1	2	12
0	1	2	12
0	1	1	13
0	1	1	13
0	1	0	14
0	0	1	14
0	0	1	14
0	0	0	15

Analyze results ...

Optimization of variables for each quality ...

Optimum on quality #1, Bulk temperature at end of fill

Calculate = Standard deviation
 Range = [1.14583 : 1.43102] C
 Minimum value = 1.14583 C
 with 180 C as Melt temperature
 with 0.16 s as Injection time
 with 25.2609 C as Mold surface temperature

Optimum on quality #2, Clamp Force

Calculate = Single value
 Range = [5.61864 : 7.06558] tonne
 Minimum value = 5.61864 tonne
 with 180 C as Melt temperature
 with 0.24 s as Injection time
 with 33 C as Mold surface temperature

Optimum on quality #3, Injection pressure

Calculate = Single value
 Range = [21.2644 : 25.7302] MPa
 Minimum value = 21.2644 MPa
 with 180 C as Melt temperature
 with 0.24 s as Injection time
 with 33 C as Mold surface temperature

Optimum on quality #4, Shear stress
 Calculate = Single value
 Range = [2.51904 : 3.22224] MPa
 Minimum value = 2.51904 MPa
 with 173.067 C as Melt temperature
 with 0.16 s as Injection time
 with 26.1617 C as Mold surface temperature

Optimum on quality #5, Sink mark depth
 Calculate = Maximum
 Range = [0.317745 : 0.371949] mm
 Minimum value = 0.317745 mm
 with 150 C as Melt temperature
 with 0.24 s as Injection time
 with 27 C as Mold surface temperature

Optimum on quality #6, Temperature at flow front
 Calculate = Standard deviation
 Range = [0.0672811 : 0.108568] C
 Minimum value = 0.0672811 C
 with 180 C as Melt temperature
 with 0.16 s as Injection time
 with 33 C as Mold surface temperature

Optimum on quality #7, Cooling time
 Calculate = Standard deviation
 Range = [11.1152 : 27.472] s
 Minimum value = 11.1152 s
 with 150 C as Melt temperature
 with 0.24 s as Injection time
 with 23 C as Mold surface temperature

Optimum on quality #8, Volumetric shrinkage at ejection
 Calculate = Standard deviation
 Range = [1.09789 : 1.47213] %
 Minimum value = 1.09789 %
 with 150 C as Melt temperature
 with 0.16 s as Injection time
 with 33 C as Mold surface temperature

Optimum on quality #9, Time at end of packing
 Calculate = Single value
 Range = [30.1633 : 30.246] s
 Minimum value = 30.1633 s
 with 168 C as Melt temperature
 with 0.16 s as Injection time
 with 23 C as Mold surface temperature

Optimum on quality #10, Part weight
 Calculate = Single value
 Range = [131.941 : 132.514] g
 Minimum value = 131.941 g
 with 180 C as Melt temperature
 with 0.16 s as Injection time
 with 33 C as Mold surface temperature

Write quality results to file ...
 Write contour results to file ...

Execution time
 Analysis commenced at Fri Jan 27 17:43:04 2012
 Analysis completed at Fri Jan 27 20:08:57 2012
 CPU time used 33.94 s

Appendix B4 gives the results of all Taguchi and all Box-Behnken simulation runs.

Taguchi Responses

Variables:		Mold temperature		Injection time		Bulk temperature		Clamp force		Injection pressure		Shear stress		Sink mark depth		Temperature (flow front)		Cooling time		Volumetric shrinkage		Time at end of packing		Part weight	
Runs:	K	K	s	K(d)	N	Pa	Pa	m	K(d)	s	%	s	kg												
0	296.2	423.2	0.16	1.20676	69276.9	2.55E+07	2.83E+06	0.00032	0.087786	11.1807	1.15967	30.1634	0.132484												
1	296.2	453.2	0.24	1.38909	55919.2	2.15E+07	2.68E+06	0.000374	0.080033	12.0259	1.46776	30.2454	0.132016												
2	306.2	423.2	0.24	1.37137	65667.1	2.53E+07	3.11E+06	0.00032	0.106108	26.5858	1.11202	30.2455	0.132414												
3	306.2	453.2	0.16	1.16996	58992.3	2.15E+07	2.73E+06	0.000368	0.067425	27.2281	1.3914	30.1636	0.131933												

Box Benken Responses

Variables:		Melt temperature		Injection time		Mold temperature		Bulk temperature		Clamp force		Injection pressure		Shear stress		Sink mark depth		Temperature (flow front)		Cooling time		Volumetric shrinkage		Time at end of packing		Part weight	
		Runs: K	K	s	K	K(d)	N	Pa	Pa	Pa	m	K(d)	s	%	s	kg											
0	423.2	0.16	296.2	1.20676	69276.9	2.55E+07	2.83E+06	0.00032	0.087786	11.1807	1.15967	30.1634	0.132484														
1	423.2	0.16	306.2	1.22533	68913.5	2.53E+07	3.07E+06	0.000322	0.085951	26.5762	1.10284	30.1634	0.132401														
2	423.2	0.24	296.2	1.37756	67116.1	2.57E+07	2.96E+06	0.000317	0.108461	11.1569	1.16435	30.2459	0.132521														
3	423.2	0.24	306.2	1.37137	65667.1	2.53E+07	3.11E+06	0.00032	0.106108	26.5858	1.11202	30.2455	0.132414														
4	453.2	0.16	296.2	1.15644	58878.5	2.16E+07	2.68E+06	0.000365	0.068271	12.0362	1.45661	30.1634	0.132009														
5	453.2	0.16	306.2	1.16996	58992.3	2.15E+07	2.73E+06	0.000368	0.067425	27.2281	1.3914	30.1636	0.131933														
6	453.2	0.24	296.2	1.38909	55919.2	2.15E+07	2.68E+06	0.000374	0.080033	12.0259	1.46776	30.2454	0.132016														
7	453.2	0.24	306.2	1.41256	55064.6	2.13E+07	3.34E+06	0.000366	0.07827	27.51	1.45679	30.2453	0.132011														
8	423.2	0.2	301.2	1.25425	67005.1	2.54E+07	3.04E+06	0.00032	0.097542	15.1068	1.13628	30.2045	0.132448														
9	453.2	0.2	301.2	1.22696	56441.4	2.14E+07	2.70E+06	0.000366	0.072798	15.9856	1.4333	30.2044	0.131953														
10	438.2	0.16	301.2	1.20505	63474.4	2.33E+07	2.61E+06	0.000349	0.074839	15.5803	1.27864	30.1632	0.132196														
11	438.2	0.24	301.2	1.41772	60641.1	2.33E+07	2.76E+06	0.000346	0.090239	15.5766	1.28706	30.2457	0.132219														
12	438.2	0.2	296.2	1.2772	61268.4	2.34E+07	2.73E+06	0.000347	0.083645	11.6215	1.30993	30.2044	0.132245														
13	438.2	0.2	306.2	1.2971	60661.6	2.31E+07	2.96E+06	0.000349	0.081898	26.9621	1.2536	30.2043	0.132153														
14	438.2	0.2	301.2	1.28495	60156.6	2.31E+07	2.62E+06	0.000348	0.083015	15.5803	1.28679	30.2042	0.132188														

Appendix B5 contains the table with the coefficients used to generate the response surface for each quality criteria.

Response surface equations

Terms:\Factors:	Injection time													
	Mold surface temperature													
	Clamp force													
	Bulk temperature at end of fill													
	Injection pressure													
	Shear stress													
	Sink mark depth													
	Temperature at flow front													
	Cooling time													
	Volumetric shrinkage at ejection													
Time at end of packing														
Part weight														
0	0	0	0	0	1.27805	60851.5	2.32E+07	2.70E+06	0.000347	0.082717	15.569	1.28213	30.2043	0.132191
1	1	0	0	0	-0.00803	-5268.28	-2.00E+06	-88767.3	2.41E-05	-0.01191	0.417939	0.153072	-6.83E-05	-0.00023
2	0	1	0	0	0.100474	-1512.74	8918.8	91670.1	-1.81E-07	0.007884	0.025377	0.009882	0.041086	1.57E-05
3	0	0	1	0	0.006927	-315.989	-117214	132161	2.11E-07	-0.00085	7.68409	-0.02417	-4.86E-05	-3.62E-05
4	2	0	0	0	-0.03572	698.053	158751	146674	-4.20E-06	0.002527	-0.02004	0.003825	9.02E-05	9.34E-06
5	1	1	0	0	0.019802	-184.98	-69444.3	54700.5	1.53E-06	-0.00228	0.035701	0.007836	-0.00011	4.40E-06
6	1	0	1	0	0.003078	133.94	34894.8	38870.7	-1.36E-06	0.000197	-0.01856	0.004123	7.58E-05	1.39E-05
7	0	2	0	0	0.035052	1032.59	62161.1	-39006.8	3.58E-07	-0.0001	0.012222	0.001881	7.67E-05	1.62E-05
8	0	1	1	1	-0.00185	-256.745	-49442.7	64027.6	-1.35E-06	-0.00018	0.040688	0.00734	-7.68E-05	5.91E-06
9	0	0	2	0	0.010821	-60.1928	18609.1	121090	4.15E-07	0.000129	3.72555	0.000802	-5.33E-06	7.63E-06

C Optimization Source and Output

Appendix C1 gives the raw code of the model in syntax and keywords compatible with Lingo.

```

MODEL:
!Objective Function: Minimize the differences in Percent from Best to current;
MIN = d1+d2+d3+d4+d5+d6+d7+d8+d9+d10;

!Constraints for Bulk temperature at end of fill;
q1 = 1.27805;@BND(-1,q2,1); q2 = - 0.00802559;q3 = 0.100474;q4 =
0.00692696;@BND(-1,q5,1);
q5 = - 0.0357225;q6 = 0.0198017;q7 = 0.00307791;q8 = 0.0350522;@BND(-1,q9,1);
q9 = - 0.00185097;q10 = 0.0108211;
y1 = q1 + q2 * a1 + q3 * a2 + q4 * a3 + q5 * a1 * a1 + q6 * a1 * a2
+ q7 * a1 * a3 + q8 * a2 * a2 + q9 * a2 * a3 + q10 * a3 * a3;
d1 = ( 1 - 1.14583 / y1 ) * 100;

!Constraints for Clamp Force;
w1 = 60851.5;@BND(-10000,w2,1); w2 = -5268.28;@BND(-1600,w3,1);w3 = -1512.74;
@BND(-1000,w4,1); w4 = -315.989;
w5 = 698.053;@BND(-200,w6,1); w6 =-184.98;w7 = 133.94;w8 =
1032.59;@BND(-1000,w9,1);
w9 = -256.745;@BND(-100,w10,1);w10 = -60.1928;
y2 = w1 + w2 * a1 + w3 * a2 + w4 * a3 + w5 * a1 * a1 + w6 * a1 * a2
+ w7 * a1 * a3 + w8 * a2 * a2 + w9 * a2 * a3 + w10 * a3 * a3;
d2 = ( 1 - 55117.1 / y2 ) * 100;

!Constraints for Injection pressure;
r1 = 23214000;@BND(-10000000,r2,1); r2 = -1996770;r3 =
8918.8;@BND(-200000,r4,1);r4 = -117214;
r5 = 158751;@BND(-100000,r6,1) ; r6 = -69444.3 ; r7 = 34894.8 ;r8 = 62161.1
;@BND(-100000,r9,1);
r9 =-49442.7 ;r10 = 18609.1;
y3 = r1 + r2 * a1 + r3 * a2 + r4 * a3 + r5 * a1 * a1 + r6 * a1 * a2
+ r7 * a1 * a3 + r8 * a2 * a2 + r9 * a2 * a3 + r10 * a3 * a3;
d3 = ( 1 - 21264400 / y3 ) * 100;

!Constraints for Shear stress;
t1 = 2700820;@BND(-100000,t2,1); t2 = -88767.3;t3 = 91670.1;t4 = 132161;
t5 = 14667; t6 = 54700.5; t7 = 38870.7 ;@BND(-50000,t8,1);t8 = -39006.8;
t9 = 64027.6 ;t10 = 121090;
y4 = t1 + t2 * a1 + t3 * a2 + t4 * a3 + t5 * a1 * a1 + t6 * a1 * a2
+ t7 * a1 * a3 + t8 * a2 * a2 + t9 * a2 * a3 + t10 * a3 * a3;
y4_small = y4 / 100;
d4 = ( 1 - 24144 / y4_small ) * 100;

!Constraints for Sink mark depth;
u1 = 0.000347429000; u2 = 0.000024107100;@BND(-1,u3,1);
u3 = -0.000000180671;u4 = 0.000000210511;@BND(-1,u5,1);
u5 = -0.000004199860; u6 = 0.000001525490;@BND(-1,u7,1); u7 = -0.000001360600;
u8 = 0.000000357615;@BND(-1,u9,1);u9 = -0.000001345330;u10 = 0.000000414731;
y5 = u1 + u2 * a1 + u3 * a2 + u4 * a3 + u5 * a1 * a1 + u6 * a1 * a2
+ u7 * a1 * a3 + u8 * a2 * a2 + u9 * a2 * a3 + u10 * a3 * a3;
d5 = ( 1 - 0.00031765/ y5 ) * 100;

!Constraints for Temperature at flow front;
i1 = 0.0827173;@BND(-1,i2,1); i2 = -0.0119051;i3 = 0.00788401;@BND(-1,i4,1);i4
= -0.000854393;
i5 = 0.00252682;@BND(-1,i6,1);i6 =-0.00227827;i7 = 0.000197439;@BND(-1,i8,1);i8
= -0.000103763;
@BND(-1,i9,1);i9 = -0.000179469;i10 =0.000129018;

```

```

y6 = i1 + i2 * a1 + i3 * a2 + i4 * a3 + i5 * a1 * a1 + i6 * a1 * a2
    + i7 * a1 * a3 + i8 * a2 * a2 + i9 * a2 * a3 + i10 * a3 * a3;
d6 = ( 1 - 0.0672811/ y6 ) * 100;

!Constraints for Cooling time;
o1 = 15.569; o2 = 0.417939; o3 = 0.0253773; o4 = 7.68409; @BND(-1,o5,1);
o5 = -0.0200442; o6 = 0.0357009; @BND(-1,o7,1); o7 = -0.0185573; o8 = 0.0122224;
o9 = 0.0406883; o10 = 3.72555;
y7 = o1 + o2 * a1 + o3 * a2 + o4 * a3 + o5 * a1 * a1 + o6 * a1 * a2
    + o7 * a1 * a3 + o8 * a2 * a2 + o9 * a2 * a3 + o10 * a3 * a3;
d7 = ( 1 - 11.1152 / y7 ) * 100;

!Constraints for Volumetric shrinkage at ejection;
p1 = 1.28213; p2 = 0.153072; p3 = 0.00988157; @BND(-1,p4,1); p4 = -0.0241659;
p5 = 0.00382536; p6 = 0.00783592; p7 = 0.00412275 ; p8 = 0.00188077;
p9 = 0.0073402; p10 = 0.000801706;
y8 = p1 + p2 * a1 + p3 * a2 + p4 * a3 + p5 * a1 * a1 + p6 * a1 * a2
    + p7 * a1 * a3 + p8 * a2 * a2 + p9 * a2 * a3 + p10 * a3 * a3;
d8 = ( 1 - 1.09789/ y8 ) * 100;

!Constraints for Time at end of packing;
@bnd(-1,f2,1); @bnd(-1,f4,1); @bnd(-1,f6,1); @bnd(-1,f9,1); @bnd(-1,f10,1);
f1 = 30.204300000000; f2 = -0.000068300000; f3 = 0.041085800000; f4
=-0.000048600000;
f5 = 0.000090166700; f6 = -0.000113000000; f7 = 0.000075750000; f8 = 0.000076666700;
f9 = -0.000076750000; f10 = -0.00005333330;
y9 = f1 + f2 * a1 + f3 * a2 + f4 * a3 + f5 * a1 * a1 + f6 * a1 * a2
    + f7 * a1 * a3 + f8 * a2 * a2 + f9 * a2 * a3 + f10 * a3 * a3;
d9 = ( 1 - 30.1633 / y9 ) * 100;

!Constraints for Part weight;
@BND(-1,j2,1); @BND(-1,j4,1);
j1 = 0.132191000000; j2 = -0.000234494000; j3 = 0.000015718000; j4
=-0.000036202000;
j5 = 0.000009342220; j6 = 0.000004400000; j7 = 0.000013915000; j8 = 0.000016182200;
j9 = 0.000005907500; j10 = 0.000007632220;
y10 = j1 + j2 * a1 + j3 * a2 + j4 * a3 + j5 * a1 * a1 + j6 * a1 * a2
    + j7 * a1 * a3 + j8 * a2 * a2 + j9 * a2 * a3 + j10 * a3 * a3;
d10 = ( 1 - 0.1319 / y10 ) * 100;

!Transformation form normalized values to process window;
@BND(-1,a1,1); @BND(-1,a2,1); @BND(-1,a3,1);
a1 = ( 0.06666666666 * x1 ) - 11;
a2 = ( 25 * x2 ) - 5;
a3 = ( 0.2 * x3 ) - 5.6;
END

```

Appendix C2 gives the output from the Lingo software after solving the model.

Model_output.txt
 Local optimal solution found.
 Objective value: 55.83490
 Infeasibilities: 0.1117587E-07
 Total solver iterations: 85

Model Class: NLP

Total variables: 27
 Nonlinear variables: 13
 Integer variables: 0

Total constraints: 25
 Nonlinear constraints: 20

Total nonzeros: 78
 Nonlinear nonzeros: 40

Variable	Value	Reduced Cost
D1	0.1088132	0.000000
D2	6.419269	0.000000
D3	1.290889	0.000000
D4	1.119354	0.000000
D5	13.32933	0.000000
D6	1.281882	0.000000
D7	8.029750	0.000000
D8	24.18510	0.000000
D9	0.9728455E-04	0.000000
D10	0.7041146E-01	0.000000
Q1	1.278050	0.000000
Q2	-0.8025590E-02	0.000000
Q3	0.1004740	0.000000
Q4	0.6926960E-02	0.000000
Q5	-0.3572250E-01	0.000000
Q6	0.1980170E-01	0.000000
Q7	0.3077910E-02	0.000000
Q8	0.3505220E-01	0.000000
Q9	-0.1850970E-02	0.000000
Q10	0.1082110E-01	0.000000
Y1	1.147078	0.000000
A1	1.000000	-21.33922
A2	-1.000000	14.63342
A3	-0.8872977	0.000000
W1	60851.50	0.000000
W2	-5268.280	0.000000
W3	-1512.740	0.000000
W4	-315.9890	0.000000
W5	698.0530	0.000000
W6	-184.9800	0.000000
W7	133.9400	0.000000
W8	1032.590	0.000000
W9	-256.7450	0.000000
W10	-60.19280	0.000000
Y2	58897.92	0.000000
R1	0.2321400E+08	0.000000
R2	-1996770.	0.000000
R3	8918.800	0.000000
R4	-117214.0	0.000000
R5	158751.0	0.000000
R6	-69444.30	0.000000
R7	34894.80	0.000000
R8	62161.10	0.000000
R9	-49442.70	0.000000

```

Model_output.txt
R10      18609.10      0.000000
Y3       0.2154249E+08 0.000000
T1       2700820.      0.000000
T2      -88767.30      0.000000
T3       91670.10      0.000000
T4       132161.0      0.000000
T5       14667.00      0.000000
T6       54700.50      0.000000
T7       38870.70      0.000000
T8      -39006.80      0.000000
T9       64027.60      0.000000
T10      121090.0      0.000000
Y4       2441732.      0.000000
Y4_SMALL 24417.32      0.000000
U1       0.3474290E-03  0.000000
U2       0.2410710E-04  0.000000
U3      -0.1806710E-06  0.000000
U4       0.2105110E-06  0.000000
U5      -0.4199860E-05  0.000000
U6       0.1525490E-05  0.000000
U7      -0.1360600E-05  0.000000
U8       0.3576150E-06  0.000000
U9      -0.1345330E-05  0.000000
U10      0.4147310E-06  0.000000
Y5       0.3665023E-03  0.000000
I1       0.8271730E-01  0.000000
I2      -0.1190510E-01  0.000000
I3       0.7884010E-02  0.000000
I4      -0.8543930E-03  0.000000
I5       0.2526820E-02  0.000000
I6      -0.2278270E-02  0.000000
I7       0.1974390E-03  0.000000
I8      -0.1037630E-03  0.000000
I9      -0.1794690E-03  0.000000
I10      0.1290180E-03  0.000000
Y6       0.6815476E-01  0.000000
O1       15.56900      0.000000
O2       0.4179390      0.000000
O3       0.2537730E-01  0.000000
O4       7.684090      0.000000
O5      -0.2004420E-01  0.000000
O6       0.3570090E-01  0.000000
O7      -0.1855730E-01  0.000000
O8       0.1222240E-01  0.000000
O9       0.4068830E-01  0.000000
O10      3.725550      0.000000
Y7       12.08565      0.000000
P1       1.282130      0.000000
P2       0.1530720      0.000000
P3       0.9881570E-02  0.000000
P4      -0.2416590E-01  0.000000
P5       0.3825360E-02  0.000000
P6       0.7835920E-02  0.000000
P7       0.4122750E-02  0.000000
P8       0.1880770E-02  0.000000
P9       0.7340200E-02  0.000000
P10      0.8017060E-03  0.000000
Y8       1.448119      0.000000
F2      -0.6830000E-04  0.000000
F4      -0.4860000E-04  0.000000
F6      -0.1130000E-03  0.000000
F9      -0.7675000E-04  0.000000
F10     -0.5333330E-05  0.000000

```

Model_output.txt

F1	30.20430	0.000000
F3	0.4108580E-01	0.000000
F5	0.9016670E-04	0.000000
F7	0.7575000E-04	0.000000
F8	0.7666670E-04	0.000000
Y9	30.16333	0.000000
J2	-0.2344940E-03	0.000000
J4	-0.3620200E-04	0.000000
J1	0.1321910	0.000000
J3	0.1571800E-04	0.000000
J5	0.9342220E-05	0.000000
J6	0.4400000E-05	0.000000
J7	0.1391500E-04	0.000000
J8	0.1618220E-04	0.000000
J9	0.5907500E-05	0.000000
J10	0.7632220E-05	0.000000
Y10	0.1319929	0.000000
X1	180.0000	0.000000
X2	0.1600000	0.000000
X3	23.56351	0.000000

Row	Slack or Surplus	Dual Price
1	55.83490	-1.000000
2	0.000000	-87.08316
3	0.000000	-87.08316
4	0.000000	87.08316
5	0.000000	77.26868
6	0.000000	-87.08316
7	0.000000	87.08316
8	0.000000	77.26868
9	0.000000	-87.08316
10	0.000000	-77.26868
11	0.000000	-68.56032
12	0.000000	-87.08316
13	0.000000	-1.000000
14	0.000000	-0.1588863E-02
15	0.000000	-0.1588863E-02
16	0.000000	0.1588863E-02
17	0.000000	0.1409795E-02
18	0.000000	-0.1588863E-02
19	0.000000	0.1588863E-02
20	0.000000	0.1409795E-02
21	0.000000	-0.1588863E-02
22	0.000000	-0.1409795E-02
23	0.000000	-0.1250907E-02
24	0.000000	-0.1588863E-02
25	0.000000	-1.000000
26	0.000000	-0.4581647E-05
27	0.000000	-0.4581647E-05
28	0.000000	0.4582486E-05
29	0.000000	0.4066080E-05
30	0.000000	-0.4581647E-05
31	0.000000	0.4582486E-05
32	0.000000	0.4066080E-05
33	0.000000	-0.4581647E-05
34	0.000000	-0.4065241E-05
35	0.000000	-0.3607077E-05
36	-0.1117587E-07	-0.4582066E-05
37	0.000000	-1.000000
38	0.000000	-0.4049612E-04
39	0.000000	-0.4049612E-04
40	0.000000	0.4049612E-04
41	0.000000	0.3593215E-04

Model_output.txt

42	0.000000	-0.4049612E-04
43	0.000000	0.4049612E-04
44	0.000000	0.3593215E-04
45	0.000000	-0.4049612E-04
46	0.000000	-0.3593215E-04
47	0.000000	-0.3188252E-04
48	0.000000	-0.4049612E-04
49	0.000000	-0.4049612E-02
50	0.000000	-1.000000
51	0.000000	-236480.5
52	0.000000	-236480.5
53	0.000000	236480.5
54	0.000000	209828.6
55	0.000000	-236480.5
56	0.000000	236480.5
57	0.000000	209828.6
58	0.000000	-236480.5
59	0.000000	-209828.6
60	0.000000	-186180.5
61	0.000000	-236480.5
62	0.000000	-1.000000
63	0.000000	-1448.440
64	0.000000	-1448.440
65	0.000000	1448.440
66	0.000000	1285.198
67	0.000000	-1448.440
68	0.000000	1448.440
69	0.000000	1285.198
70	0.000000	-1448.440
71	0.000000	-1285.198
72	0.000000	-1140.353
73	0.000000	-1448.440
74	0.000000	-1.000000
75	0.000000	-7.609874
76	0.000000	-7.609874
77	0.000000	7.609874
78	0.000000	6.752223
79	0.000000	-7.609874
80	0.000000	7.609874
81	0.000000	6.752223
82	0.000000	-7.609874
83	0.000000	-6.752223
84	0.000000	-5.991232
85	0.000000	-7.609874
86	0.000000	-1.000000
87	0.000000	-52.35405
88	0.000000	-52.35405
89	0.000000	52.35405
90	0.000000	46.45363
91	0.000000	-52.35405
92	0.000000	52.35405
93	0.000000	46.45363
94	0.000000	-52.35405
95	0.000000	-46.45363
96	0.000000	-41.21820
97	0.000000	-52.35405
98	0.000000	-1.000000
99	0.000000	-3.315281
100	0.000000	-3.315281
101	0.000000	3.315281
102	0.000000	2.941641
103	0.000000	-3.315281
104	0.000000	3.315281

Model_output.txt

105	0.000000	2.941641
106	0.000000	-3.315281
107	0.000000	-2.941641
108	0.000000	-2.610111
109	0.000000	-3.315281
110	0.000000	-1.000000
111	0.000000	-757.0828
112	0.000000	-757.0828
113	0.000000	757.0828
114	0.000000	671.7578
115	0.000000	-757.0828
116	0.000000	757.0828
117	0.000000	671.7578
118	0.000000	-757.0828
119	0.000000	-671.7578
120	0.000000	-596.0491
121	0.000000	-757.0828
122	0.000000	-1.000000
123	0.000000	0.000000
124	0.000000	0.000000
125	0.000000	0.000000

D Matlab Scripts

Appendix D1 shows one exemplary Matlab script used to generate the 3D plots for each of the 10 quality criteria.

```

Injection_Preassure.m

%Injection Preassure

x2 = linspace (0.16 , 0.24);
x3 = linspace (23,33);

[x2 x3] = meshgrid(x2,x3);

x1 = 150;

a1 = ( 0.0666666 * x1 ) - 11;
a2 = ( 25 * x2 ) - 5;
a3 = (0.2 * x3 ) - 5.6;

q1 = 23200000;
q2 = -2000000;
q3 = 8918.8;
q4 = -117214;
q5 = 158751;
q6 = -69444.3;
q7 = 34894.8;
q8 = 62161.1;
q9 = -49442.7;
q10 = 18609.1;

y1 = q1 + q2 .* a1 + q3 .* a2 + q4 .* a3 + q5 .* a1 .* a1 + q6 .* a1 .* a2 ...
      + q7 .* a1 .* a3 + q8 .* a2 .* a2 + q9 .* a2 .* a3 + q10 .* a3 .* a3;
y1small = y1 /1000000;
mesh(x2,x3,y1small);

hold on

x1 = 165;

a1 = ( 0.0666666 * x1 ) - 11;
a2 = ( 25 * x2 ) - 5;
a3 = (0.2 * x3 ) - 5.6;

y2 = q1 + q2 .* a1 + q3 .* a2 + q4 .* a3 + q5 .* a1 .* a1 + q6 .* a1 .* a2 ...
      + q7 .* a1 .* a3 + q8 .* a2 .* a2 + q9 .* a2 .* a3 + q10 .* a3 .* a3;
y2small = y2 /1000000;
mesh(x2,x3,y2small);

hold on

x1 = 180;

a1 = ( 0.0666666 * x1 ) - 11;
a2 = ( 25 * x2 ) - 5;
a3 = (0.2 * x3 ) - 5.6;

y3 = q1 + q2 .* a1 + q3 .* a2 + q4 .* a3 + q5 .* a1 .* a1 + q6 .* a1 .* a2 ...
      + q7 .* a1 .* a3 + q8 .* a2 .* a2 + q9 .* a2 .* a3 + q10 .* a3 .* a3;
y3small = y3 /1000000;
mesh(x2,x3,y3small);

xlabel('Injection Time, sec', 'FontSize',16);
ylabel('Mold Temperature, °C', 'FontSize',16);
zlabel('Injection Preassure, MPa', 'FontSize',16);

```

Appendix D2 shows one exemplary Matlab script used to generate the 2D plots for each of the 10 quality criteria.

```

Injection_Preassure_2D.m

%Injection Preassure 2D

x2min = 0.16;
x2max = 0.24;
stepx2 = 0.001;

x3min = 23;
x3max = 33;
stepx3 = 2;

[x2 x3] = meshgrid(x2min:stepx2:x2max, x3min:stepx3:x3max);

x1 = 180;

a1 = ( 0.0666666 * x1 ) - 11;
a2 = ( 25 * x2 ) - 5;
a3 = (0.2 * x3 ) - 5.6;

q1 = 23200000;
q2 = -2000000;
q3 = 8918.8;
q4 = -117214;
q5 = 158751;
q6 = -69444.3;
q7 = 34894.8;
q8 = 62161.1;
q9 = -49442.7;
q10 = 18609.1;
y1small = y1 / 1000000;
y1 = q1 + q2 .* a1 + q3 .* a2 + q4 .* a3 + q5 .* a1 .* a1 + q6 .* a1 .* a2 ...
      + q7 .* a1 .* a3 + q8 .* a2 .* a2 + q9 .* a2 .* a3 + q10 .* a3 .* a3;

[C,h] = contour(x2,y1small,x3);
clabel(C,h);

xlabel('Injection Time, sec', 'FontSize',16);
ylabel('Injection Preassure, MPa', 'FontSize',16);
title('Injection Preassure in MPa at 180 °C Melt Temperature', 'FontSize' ,18)

```

Appendix D3 shows the Matlab script used to generate the plot of the entire process window and the optimal conditions for each quality criteria.

```

                                Process_window.m
%Process Window Overview

length = 11;
data = [180 0.16 25.26; 180 0.24 33; 180 0.24 33; ...
        173.1 0.16 26.2; 150 0.24 27; 180 0.16 33; ...
        150 0.24 23; 150 0.16 33; 168 0.16 23; ...
        180 0.16 33; 180 0.16 23.2]';

for i = 1:length
    line = [data(1,i) data(2,i) 23;
            data(1,i) data(2,i) data(3,i)];
    plot3(line(:,1), line(:,2), line(:,3), '--');
    hold on
    %plot3(data(1,i),data(2,i), data(3,i), 'x')
    scatter3(data(1,i),data(2,i), data(3,i), 'filled', ...
             'MarkerEdgeColor','k','MarkerFaceColor','b');
end

grid on

axis([150 180 0.16 0.24 23 33])
xlabel('Melt Temperature, °C')
ylabel('Injection Time, s')
zlabel('Mold Temperature, °C')

```


E Datapoints Lab Reports on Silicon Nitride and Binder

Appendix E1 gives the report on the analysis conducted by Datapoints Lab.

Test Report

OSU-85wt%

Client	Juergen Lenz
Company	Oregon State University
Address	State Corvallis, Oregon United States
Sample Received	2/1/2011
Sample Source	Oregon State University
Report Prepared	2/7/2011
Prepared By	
Title	Engineer
Issued By	
Title	Operations Manager

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Toll-Free (U.S.): 1-888-328-2422

This data is available in True Digital format



C-MOLD/Moldflow *TestPak*™ Results

18023.21000.udb

Analysis	Property & T-CODE	Value	Units
Filling & Cooling	Cross/WLF Model (01313):		
	n	0.05081	
	τ^*	1.428E+05	Pa
	D1	1.000E+23	Pa•s
	D2	373	K
	D3	0	K/Pa
	A1	42.28	
	A2	51.60	K
	Juncture Loss Constants (01360):		
	C1		Pa^(1-C2)
	C2		
	Melt Density (01000)	2110	kg/m ³
	Melt Specific Heat (01100)	1158	J/kg•K
	Melt Thermal Conductivity (01200)	1.311	W/m•K
	Transition Temperature (01500)	326	K
	Specific Heat Table (01101)	See Page 7	
	Thermal Conductivity Table (01201)	See Page 8	
Post-Filling	Two-Domain Tait PVT Model (01004):		
	b5	3.360E+02	K
	b6	1.700E-07	K/Pa
	b1m	4.503E-04	m ³ /kg
	b2m	2.036E-07	m ³ /kg•K
	b3m	2.656E+08	Pa
	b4m	3.647E-03	1/K
	b1s	4.339E-04	m ³ /kg
	b2s	1.001E-07	m ³ /kg•K
	b3s	7.907E+08	Pa
	b4s	1.000E-04	1/K
	b7	1.641E-05	m ³ /kg
	b8	3.812E-02	1/K
	b9	1.430E-08	1/Pa
Shrink / Warp - Uncorrected Stress	Anisotropic Mechanical Properties (01602)		
	Modulus E ₁ (flow direction)		MPa
	Modulus E ₂ (transverse direction)		MPa
	Poisson's ratio ν_{12}		
	Poisson's ratio ν_{23}		
	Shear Modulus G		MPa
	Anisotropic Thermal Expansion (01702)		
	CLTE α_1 (flow direction)		x 10E-6/°C
	CLTE α_2 (transverse direction)		x 10E-6/°C

TestPaks™ is a trademark of DatapointLabs. C-MOLD and Moldflow are trademarks of Moldflow Corporation.

Viscosity



Method	ASTM D 3835: 2008 Determination of Properties of Polymeric Materials by Means of a Capillary Rheometer	
Instrument	Goettfert Rheograph 2003 Capillary Rheometer	
Specimen	type	pellets
	drying	none
	other preparation	none
Parameters	initial pressure	0 MPa
	barrel diameter	12 mm
	die entry angle	180 °C
	die inner diameter	1 mm
	die length	20 mm
	preheating time	6 min
Data Correction		
Precision	temperature	+/- 0.1 °C
	die inner diameter	+/- 0.0069 mm
	die length	+/- 0.025 mm
Uncertainty	per standard	

Polymer rheology characterizes the complex flow behavior of plastics. A capillary rheometer measures viscosity as a function of temperature and shear rate. The Goettfert rheometer utilizes direct measurement of melt pressures through a side mounted pressure transducer.

Viscosity Data

150 °C		165 °C		180 °C	
Shear Rate s ⁻¹	Viscosity Pa·s	Shear Rate s ⁻¹	Viscosity Pa·s	Shear Rate s ⁻¹	Viscosity Pa·s
10	59283.40	10	48681.90	10	49534.90
20	29458.90	20	24158.10	20	24706.50
50	11786.30	50	9636.67	50	9978.66
100	5838.19	100	4763.37	100	4848.87
200	2574.05	200	2232.07	200	2470.24
500	934.35	500	1030.84	500	650.99
1000	724.19	1000	468.96	1000	401.79
2000	349.29	2000	243.35	2000	210.37
5000	148.27	5000	119.81	5000	100.88
10000	82.93	10000	52.39	10000	48.67

Viscosity Continued

Cross/WLF Model (C-MOLD, Moldflow)

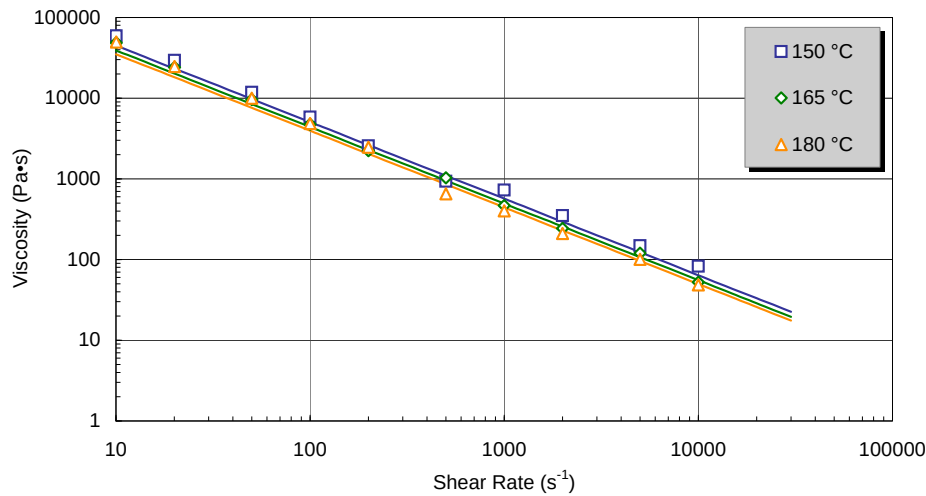
$$\eta(T, \dot{\gamma}) = \frac{\eta_0(T)}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*}\right)^{1-n}}, \text{ where}$$

$$\eta_0(T) = D_1 \exp\left[-\frac{A_1(T - D_2)}{A_2 + (T - D_2)}\right]$$

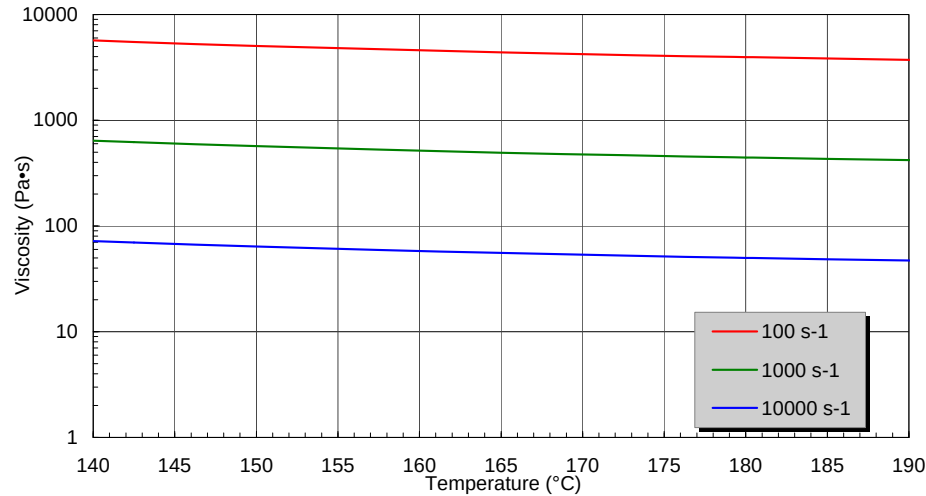
Coefficients (SI units)

n	0.05081
τ*	142790.32
D1	1E+23
D2	373
A1	42.28
A2	51.6

Viscosity vs Shear Rate



Viscosity vs Temperature



Specific Heat



Method	Based on ASTM E1269: 2005 Determining Specific Heat Capacity by Differential Scanning Calorimetry	
Instrument	Perkin Elmer DSC7	
Specimen	type	pellets
	drying	none
	other preparation	cut from pellet
Parameters	purge gas	N2
	purge gas purity	99.99 %
	purge gas rate	25 ml/min
	cooling rate	20 °C/min
	initial temperature	180 °C
	final temperature	-20 °C
	equilibration times	4 min
	sample weight	9.12 mg
Calibration Standards	sample pans	Al, volatile
	temperature	In, Zn
	heat flow	In
	specific heat	sapphire

Heat capacity is a thermodynamic quantity and is a measure of the amount of heat retained by the material. The DSC can measure this property over a range of temperatures and in both solid and melt states.

Transition Analysis

extrapolated onset	53 °C
peak	47 °C
extrapolated end	34 °C

Notes: An additional peak was observed in the 60° to 90°C range.



Digital Data at www.matereality.com

Specific heat measurements are not included in our current scope of accreditation.

Tested By: WL

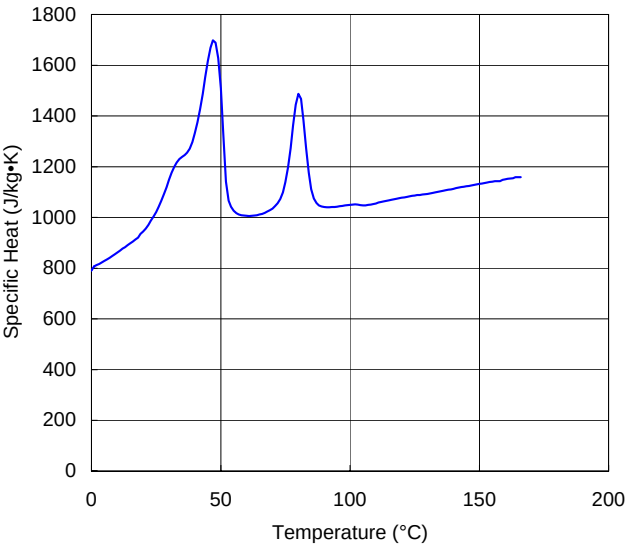
Certified By: PC

Test Date: 2/2/2011

Specific Heat Continued

Specific Heat Data

Temp °C	Cp J/kg·K
170	1163
111	1059
58	1009
47	1698
24	1004
17	913
0	791



Thermal Conductivity

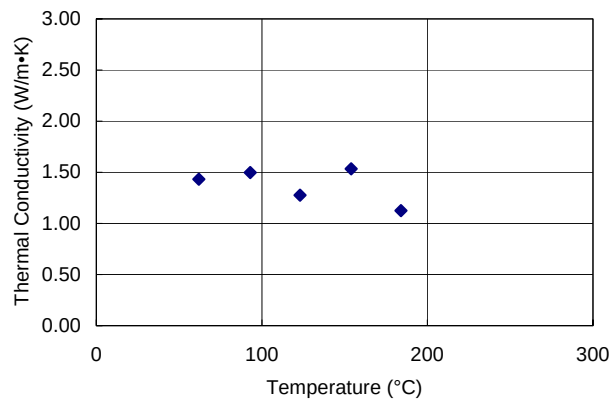


Method	ASTM D 5930: 2001 Thermal Conductivity of Plastics by Means of a Transient Line-Source Technique	
Instrument	Instron 8872 Servohydraulic UTM	
Specimen	type	pellets
	drying	none
	other preparation	none
Parameters	calibration material	60,000 cstk PDMS
	probe constant	0.805
	probe length	50 mm
	loading temperature	200 °C
	initial temperature	180 °C
	final temperature	30 °C
	probe voltage	3.5 V
	acquisition time	45 s
Uncertainty	per standard	

Thermal conductivity is a measure of the rate of heat conduction of the material. It is a critical property for heat transfer calculations. The line-source method measures thermal conductivity in both melt and solid state.

Thermal Conductivity Data

Temp °C	k W/m•K
184	1.125
154	1.534
123	1.275
93	1.498
62	1.432



PVT



	Method	Non-standard. Pressure-specific volume-temperature measurements using high-pressure dilatometry	
	Instrument	Gnomix PVT apparatus	
	Specimen	type	pellets
		drying	none
		other preparation	cut from pellets
Parameters	solid density method	ASTM D792	
	immersion liquid	water	
	PVT confining fluid	Mercury	
	max temperature	180 °C	
	measurement type	isothermal heating scan	
	heating rate	approx. 3 °C/min	

PVT data are equation-of-state thermodynamic properties that describe the compressibility and volumetric expansion of the material. Dilatometry measures the change in volume of a specimen subjected to different temperatures and pressures.

Initial Solid Density

Density 23°C	2304 kg/m3
--------------	------------

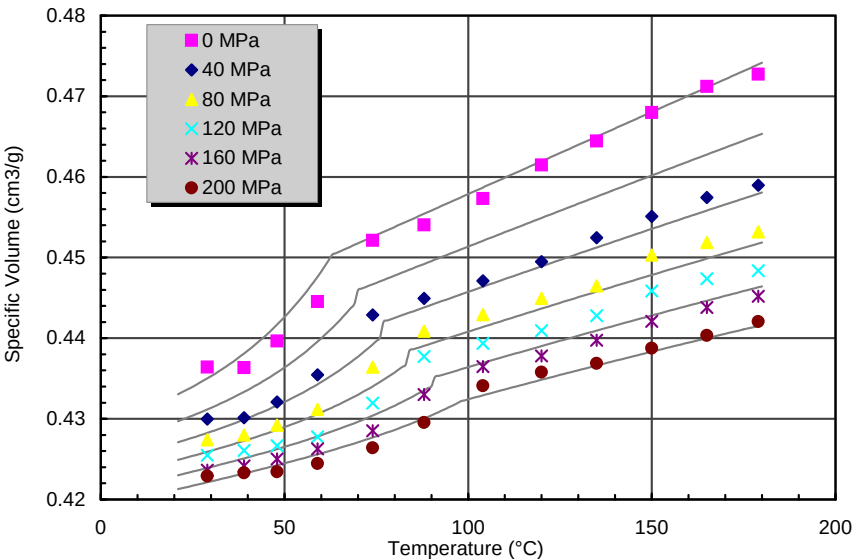
 Digital data at www.matereality.com
PVT measurements are not included in our current scope of accreditation.

Tested By: WL
Certified By: PC
Test Date: 2/3/2011

Pressure-Volume-Temperature Data

Specific Volume cm3/g						
Temp °C	Pressure MPa					
	0	40	80	120	160	200
29	0.4364	0.4300	0.4274	0.4255	0.4236	0.4229
39	0.4363	0.4301	0.4280	0.4261	0.4242	0.4233
48	0.4396	0.4321	0.4292	0.4267	0.4250	0.4234
59	0.4445	0.4355	0.4312	0.4278	0.4263	0.4245
74	0.4521	0.4429	0.4364	0.4320	0.4285	0.4264
88	0.4540	0.4449	0.4409	0.4377	0.4330	0.4295
104	0.4573	0.4471	0.4429	0.4394	0.4365	0.4341
120	0.4615	0.4495	0.4449	0.4409	0.4378	0.4358
135	0.4645	0.4524	0.4465	0.4428	0.4397	0.4369
150	0.4680	0.4551	0.4503	0.4458	0.4421	0.4387
165	0.4712	0.4575	0.4519	0.4474	0.4438	0.4403
179	0.4727	0.4590	0.4532	0.4484	0.4452	0.4421

Modified Two-Domain Tait Model (C-MOLD, Moldflow)



Coefficients	
b5	6.30E+01
b6	1.70E-01
b1m	4.503E-01
b2m	2.036E-04
b3m	2.656E+02
b4m	3.647E-03
b1s	4.339E-01
b2s	1.001E-04
b3s	7.907E+02
b4s	1.000E-04
b7	1.64E-02
b8	3.812E-02
b9	1.430E-02

Modified Two-Domain Tait Equation

$$v(T, p) = v_0(T) \left(1 - C \ln \left(1 + \frac{p}{B(T)} \right) \right) + v_t(T, p), T_t(p) = b_5 + b_6 p$$

$$\text{for } T > T_t(p): v_0(T) = b_{1m} + b_{2m}(T - b_5), B(T) = b_{3m} \exp(-b_{4m}(T - b_5)), v_t(T, p) = 0$$

$$\text{for } T < T_t(p): v_0(T) = b_{1s} + b_{2s}(T - b_5), B(T) = b_{3s} \exp(-b_{4s}(T - b_5)), v_t(T, p) = b_7 \exp(b_8(T - b_5) - b_9 p)$$

Model Terms	Units
specific volume, v	cm³/g
pressure, P	MPa
temperature, T	°C

Appendix E2 gives the analysis of the four component binder. This analysis contains the viscosity, thermal conductivity and pressure-volume-temperature behavior.

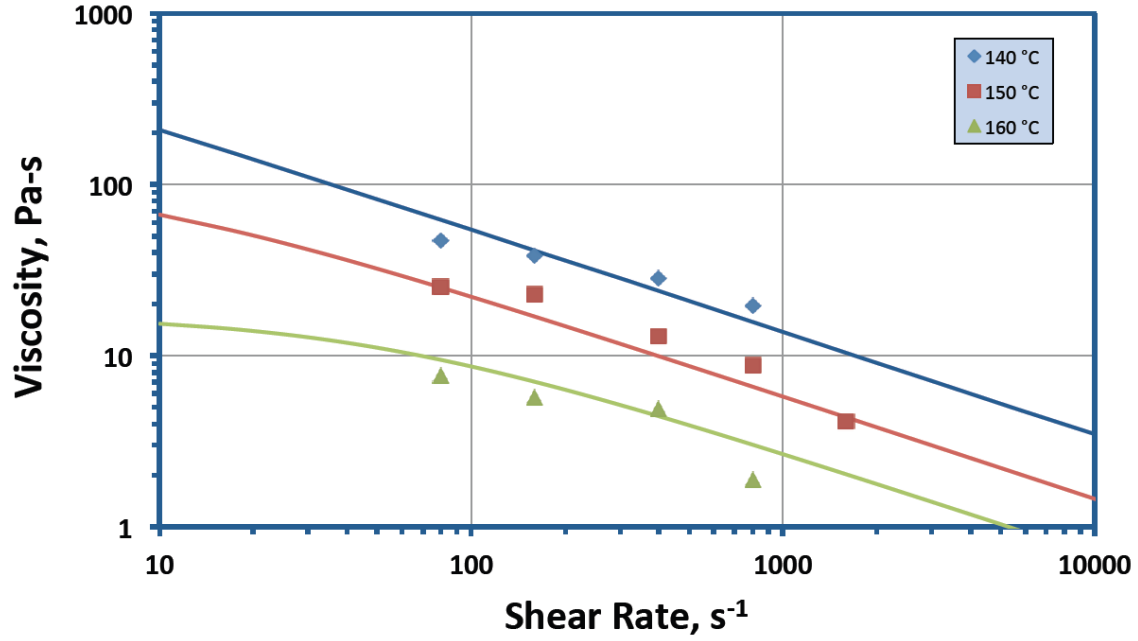


FIGURE 0.1: Binder Viscosity Measurements and WLF-Model

TABLE 0.1: Values of Rheological Constants for Binder WLF-Model

Coefficient	Definition	Binder Feedstock
n	slope of the shear-thinning curve	0.4012
τ^* (KPa)	Weissenberg-Rabinowitsch correction constant	793.461
D_1 (Pa-s)	Scale factor for viscosity	$4.29 * 10^{23}$
A_1	WLF temperature shift factor	78.13
D_2 (K)	Glass transition temperature (zero gauge pressure)	333
A_2 (K)	WLF temperature shift factor	51.6

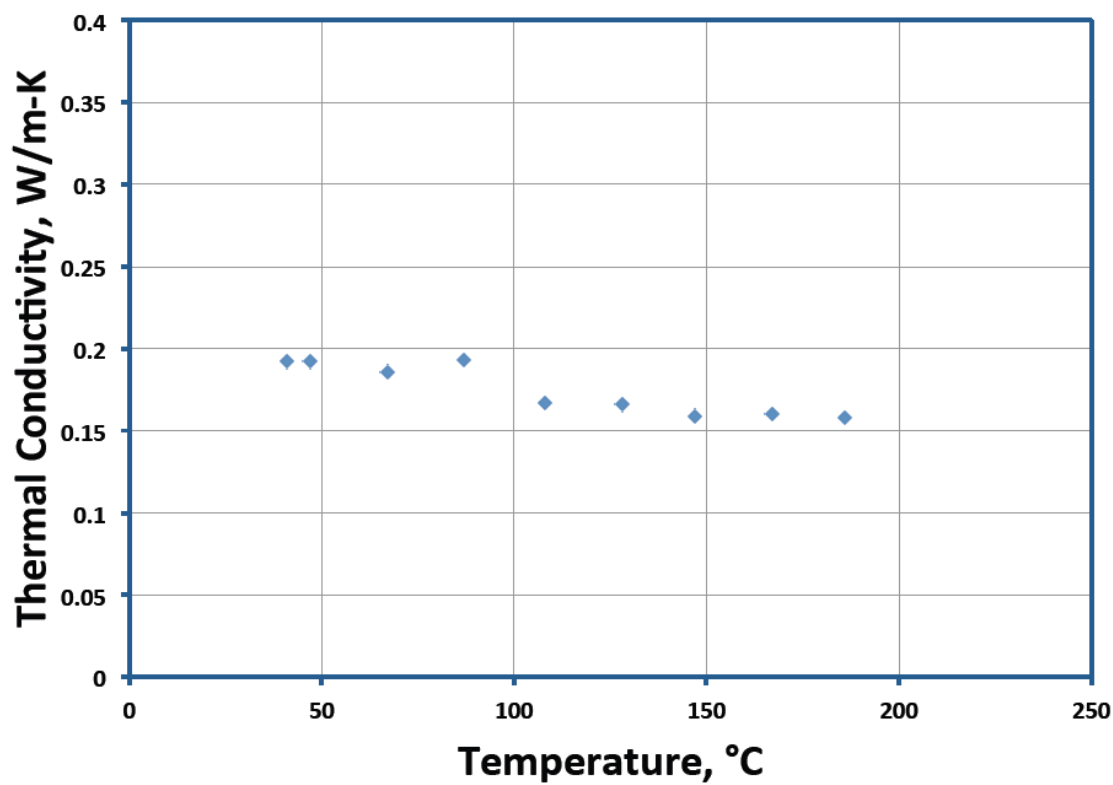


FIGURE 0.2: Binder Thermal Conductivity

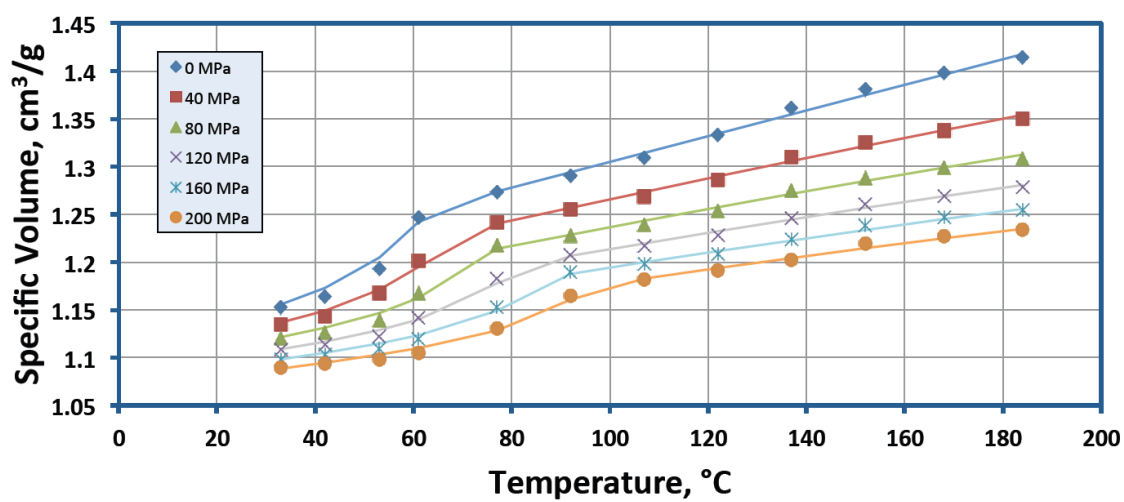


FIGURE 0.3: Binder PVT Measurements and PVT-Model

TABLE 0.2: Thermal Conductivity Measurement for Binder

Temperature in $^{\circ}C$	k in W/m $^{\circ}K$
186	0.158
167	0.16
147	0.159
128	0.166
108	0.167
87	0.193
67	0.186
47	0.192
41	0.192

TABLE 0.3: PVT Coefficients for Binder

Coefficient	Definition	Binder Feedstock
b5 (K)	Crystallization Temperature	63 K
b6 (K/Pa)	Pressure Sensitivity of b5	0.147
b1m (m^3/kg)	Tait Constant for melt	1.255
b2m ($m^3/kg - K$)		$1.344 * 10^{-3}$
b3m (Pa)		125.6
b4m (1/K)		$=5.867 * 10^{-3}$
b1s (m^3/kg)	Tait Constant for solid	1.17
b2s ($m^3/kg - K$)		$8.568 * 10^{-4}$
b3s (Pa)		239.6
b4s (1/K)		$4.155 * 10^{-3}$
b7 (m^3/kg)	Transition of	0.0846
b8 (1/K)	Specific Volume	0.06688
b9 (1/Pa)	from Solid to Molten	0.01387

