Characterization and prediction of SLS processability of polymer powders with respect to powder flow and part warpage

Author(s): Amado Becker, Antonio F.

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Characterization and prediction of SLS processability of polymer powders with respect to powder flow and part warpage

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DOCTOR OF SCIENCES

of

ETH ZURICH

(Dr. sc. ETH Zurich)

presented by

ANTONIO FELIPE AMADO BECKER

MSc. Pontificia Universidad Católica de Chile

born on 06.04.1981

citizen of

CHILE

accepted on the recommendation of

Prof. Dr.-Ing. K. Wegener / Examiner

Prof. D.Sc. MSc. Gideon N. Levy / Co-Examiner

2016
The present work was developed during my position as Research Assistant at Inspire AG from 2009 to 2015, specifically at the facilities of the Innovation Center for Additive Manufacturing Switzerland ICAMS located in St. Gallen.

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A. Felipe Amado Becker

St. Gallen, 15.10.2015
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<th>Description</th>
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<tr>
<td>( \alpha )</td>
<td>[/]</td>
<td>Degree of crystallization</td>
</tr>
<tr>
<td>( t )</td>
<td>[s]</td>
<td>Time</td>
</tr>
<tr>
<td>( t_{1/2} )</td>
<td>[s]</td>
<td>Half crystallization time</td>
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<tr>
<td>( n )</td>
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<td>Avrami crystallization exponent</td>
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<tr>
<td>( k )</td>
<td>[1/s]</td>
<td>Avrami crystallization rate constant</td>
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<tr>
<td>( K_O )</td>
<td>[mm]</td>
<td>Hoffmann-Lauritzen growth constant</td>
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<td>( K_G )</td>
<td>[1/K²]</td>
<td>Hoffmann-Lauritzen crystallization constant</td>
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<tr>
<td>( T )</td>
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<td>Temperature</td>
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<td>[K]</td>
<td>Glass transition temperature</td>
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<tr>
<td>( T_o )</td>
<td>[K]</td>
<td>Equilibrium melting temperature</td>
</tr>
<tr>
<td>( T_\infty )</td>
<td>[K]</td>
<td>Temperature at which molecular diffusion in negligible</td>
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<tr>
<td>( G' )</td>
<td>[Pa]</td>
<td>Dynamic storage shear modulus</td>
</tr>
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<td>Time dependent shear modulus</td>
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<tr>
<td>( G_\infty )</td>
<td>[Pa]</td>
<td>Fully relaxed shear modulus (time independent)</td>
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<td>[s]</td>
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<td>[/]</td>
<td>Relative fraction of transient shear modulus of branch ( i )</td>
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<td>Activation energy of the crystallization transport</td>
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<td>Universal gas constant</td>
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<tr>
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<td>[kJ/kg/K]</td>
<td>Heat capacity molten state (constant pressure)</td>
</tr>
<tr>
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<td>Unit</td>
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<td>$C_{p_{\text{eff}}}$</td>
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<td>Effective heat capacity (constant pressure)</td>
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<td>[kJ/kg/K]</td>
<td>Nitrogen (gas) heat capacity</td>
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<td>Thermal conductivity molten state</td>
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<td>Bulk density molten state</td>
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<td>Effective bulk density</td>
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<tr>
<td>$x_{nm}$</td>
<td>[%]</td>
<td>Relative volume fraction for molten domain</td>
</tr>
<tr>
<td>$x_{rp}$</td>
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<td>Relative volume fraction not sintered domain</td>
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<td>Melting enthalpy</td>
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<td>[J/g]</td>
<td>Crystallization enthalpy</td>
</tr>
<tr>
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<td>[mm]</td>
<td>Effective layer thickness</td>
</tr>
<tr>
<td>$t_d$</td>
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<td>[K]</td>
<td>Part bed surface temperature</td>
</tr>
<tr>
<td>$T_b$</td>
<td>[K]</td>
<td>Piston temperature</td>
</tr>
<tr>
<td>$T_f$</td>
<td>[K]</td>
<td>Powder feed temperature</td>
</tr>
<tr>
<td>$t_l$</td>
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<tr>
<td>$v_r$</td>
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<td>Roller rotational speed</td>
</tr>
<tr>
<td>$v_t$</td>
<td>[mm/s]</td>
<td>Roller translational speed</td>
</tr>
<tr>
<td>$\Delta V_{sh}$</td>
<td>[/]</td>
<td>Bulk volume contraction coefficient</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>[/]</td>
<td>Strain tensor</td>
</tr>
<tr>
<td>$\sigma$</td>
<td></td>
<td>Stress tensor</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>AM</td>
<td>Additive Manufacturing</td>
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<tr>
<td>BioDM</td>
<td>Bio Deposition Manufacturing</td>
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</tr>
<tr>
<td>BPM</td>
<td>Ballistic Particle Manufacturing</td>
<td></td>
</tr>
<tr>
<td>CLOM</td>
<td>Curve Laminated Object Manufacturing</td>
<td></td>
</tr>
<tr>
<td>DLP</td>
<td>Digital Light Processing</td>
<td></td>
</tr>
<tr>
<td>DOD</td>
<td>3D Printing Drop on Demand</td>
<td></td>
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<tr>
<td>EDM</td>
<td>Electron Beam Melting</td>
<td></td>
</tr>
<tr>
<td>FDM</td>
<td>Fused Deposition Modeling</td>
<td></td>
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<tr>
<td>HSS</td>
<td>High Speed Sintering</td>
<td></td>
</tr>
<tr>
<td>LENS</td>
<td>Laser Engineered Net Shaping</td>
<td></td>
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<tr>
<td>LOM</td>
<td>Laminated Object Manufacturing</td>
<td></td>
</tr>
<tr>
<td>MLS</td>
<td>Micro Light Switch</td>
<td></td>
</tr>
<tr>
<td>MPSL</td>
<td>Mask Projection Stereolithography</td>
<td></td>
</tr>
<tr>
<td>PLOM</td>
<td>Polymeric Laminated Object Manufacturing</td>
<td></td>
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<tr>
<td>SGC</td>
<td>Solid Ground Curing</td>
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<tr>
<td>SHS</td>
<td>Selective Heat Sintering</td>
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<tr>
<td>SIS</td>
<td>Selective Inhibition Sintering</td>
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<tr>
<td>SLA</td>
<td>Stereolithography</td>
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<tr>
<td>SLM</td>
<td>Selective Laser Melting</td>
<td></td>
</tr>
<tr>
<td>SLS</td>
<td>Selective Laser Sintering</td>
<td></td>
</tr>
<tr>
<td>SMS</td>
<td>Selective Mask Sintering</td>
<td></td>
</tr>
<tr>
<td>UC</td>
<td>Ultrasonic Consolidation</td>
<td></td>
</tr>
<tr>
<td>3DP</td>
<td>3 Dimensional Printing</td>
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Kurzfassung


Abstract

Among the current Additive Manufacturing technologies, Selective Laser Sintering (SLS) constitutes nowadays the most promising technique to become a widespread manufacturing process that can complement, and eventually replace, traditional manufacturing methods. However, the current lack of deep understanding of the process due to its complexity has hindered a faster adoption by the industry for the production of end-use products. The main reasons are the reduced reliability of the sintered parts and the small spectrum of materials that can be currently processed.

In this context, the following work addressed two main aspects not previously investigated in the SLS field. On the first hand, the flowability of SLS powders was examined employing a rotational drum that emulates the handling condition of the raw powdered material during the process. An existing powder characterization technique was modified and adapted in order to be able to characterize the flowability of powders at elevated temperature. This system allowed for the first time the evaluation of micron sized powders under close handling conditions and temperature as those that are found in the SLS chamber. Additionally, a new characterization index was proposed based in the combined analysis of dynamic volume expansion and powder rearrangement, which was empirically validated and can successfully predict the packing density of materials suitable for the SLS process. Thus, the development cycle for new powders can be improved, while the cost and time to market can also be reduced.

On the second hand, a transient multiphysics model of the SLS process was developed in order to better understand the coupled phase change and viscoelastic behavior from the molten state during the crystallization stage under the thermal environment of the process. In particular, the effect of the machine process parameters was investigated, including the layer thickness, base powder height, part bed, feeders and piston heater temperatures. It was found out that the process does not follow an isothermal crystallization during the first sintered structures and that a ‘step-wise’ phase change takes place in the first stack of layers, being responsible for the development of the undesired warpage phenomenon due to the non-continuous stress state development along the build axis when a proper build set up is not selected. This result helps to better understand the SLS process and gives additional insights where the R&D efforts need to be concentrated in the future in order to improve the technology towards an established industrial manufacturing process.
1 Introduction

1.1 Additive Manufacturing Overview

Historically, manufacturing has been during centuries a key driver of the economic growth and of the social welfare development of countries. The permanent technological innovation constitutes one of the main characteristic of this activity, which leads to the continuous improvement and creation of new products associated to the introduction of novel production methods. Among these novel processes Additive Manufacturing (AM) constitutes nowadays a revolutionary technique. In general, Gebhardt [1] defines AM as a layer-based automated fabrication process for making 3-dimensional physical objects directly from 3D-CAD data without using part-depending tools. These processes are unique in the sense that they differentiate from the classical “subtractive” methods such as turning, milling or drilling were raw material is removed from a predefined solid volume. According to Bourell et al. [2] AM covers a broad collection of process that, depending on the specific application considered, can be classified in several other subsets such as Rapid Prototyping, Rapid Manufacturing, Automated Fabrication, Solid Freeform Fabrication and/or more recently as 3D Printing. These general names refer in principle to a common layer wise production concept and the differences arise from a combination of a historical background, particularities of each process and the final destination and performance of the produced parts.

The early stages of AM originated from the fusion of a topography technique proposed by Branthier [3] who suggested a layered process for making a mold for topographical relief maps by stacking wax plates, and a photo sculpture method developed by Willem [4] as an attempt to create exact three-dimensional replicas of any object, including human forms, by placing cameras equally distributed along a circumference around the object, followed by a manual carving of a block of raw material. Swainson [5] combined the advantages of both techniques and proposed a process to form a three dimensional figure in a medium having two active components by causing two radiation beams to intersect in the media and to initiate a photopolymerization process at a defined point within a layer. Afterwards, Housholder [6] suggested a method to deposit planar layers of material sequentially and prior to the deposition of the next layer, a portion of its area is solidified to define the portion of the article in that layer
whereby the article is formed layer wise. The unsolidified material is removed to obtain the desired object and the selective solidification of each layer may be accomplished by using heat and a selected mask or by using a controlled heat scanning process.

The first ideas of Swainson [5] and Housholder [6] constitute the precursors of what nowadays is known as Stereolithography (SLA) and Selective Laser Sintering (SLS), which will be described in more detail in section 1.2. The concepts patented by each author are depicted in Figure 1.1.

![Figure 1.1](image)

Figure 1.1: Swainson [5] two active components combined with laser interferometry method (left) and Housholder [6] molding process for forming a three-dimensional object in layers (right).

Initially, the first processes developed during the decade of 1980 were capable of producing parts with reduced structural stability, lower dimensional accuracy and surface characteristics not useful for functional parts. They were mostly used for visual inspection and test purposes with lower requirements. Nevertheless, as AM technologies are characterized by the integration of several components, the continuous improvement of computers, electric heaters and motors, digital controllers and lasers has enabled the production of parts with increasing overall quality and performance, leading not only to the substitution of conventional manufacturing processes in specific applications, but also the development of new products not feasible before.

From a historical perspective and taking into account the investigations performed during the past, it was not until the decade of 1980 that the research efforts were intensified and the publication of patents increased considerably [7]. The higher research interests in this field led to the first commercial AM systems that come up into the market. According to Wholers [8], in late 1987, the company 3DSystems founded by Chuck Hull shipped its first SLA unit to customers within United States followed by production systems in April 1988.
Despite the broad spectrum of technologies currently available and their different functional concepts or approaches, the main common features of an AM process can be, in general, described as follows:

- Objects can be made with almost any degree of geometric intricacy without a compromise in the complexity of the process. These techniques can even generate "unusual geometries" that are not feasible to be achieved by traditional manufacturing methods [9]. Even combinations of several parts or assemblies can be produced in one single build step.

- AM systems reduce the manufacturing time for complex-shape short production runs significantly not only because of the geometric flexibility, but also due to the decrease of the associated steps of the entire production chain. The rate of adding material is not faster in comparison to high speed subtracting or material injection methods, but several related production steps or resources required by traditional techniques are not necessary (e.g., the design and manufacture of molds for injection methods or the programming of tooling sequences of CNC machines).

- The materials spectrum for AM processing covers metals, ceramic, polymers and their combinations or composites. However, suitable materials must fulfill several previous requirements to be processable in comparison to raw materials used in the traditional manufacturing industry and thus must be specifically produced or adapted for a particular AM application. These requirements reduce the materials available and increase the production costs.

- Some AM technologies enable the combination of multiple materials that can even be varied in a controlled manner at almost any location within an object. However, due to the complexity of the materials deposition mechanisms and the compatibility between different materials coupled to their dissimilar processability this feature is still restricted and most AM equipments are considered as mono-material processing units.

- Part properties obtained by AM are in general not spatially homogeneous and anisotropy is an inherent condition of the objects due to the layer-wise deposition sequence. However, inhomogeneity within a layer is less significant and AM parts depict a transversely isotropic behavior, where the maximum property difference is observable between a direction contained within a layer and the perpendicular orientation to the build plane.

- Despite the high automation of AM processes post processing steps are required, either to manually remove parts from the supporting medium or to perform additional surface or
thermal treatments. It is still not technically possible to obtain parts ready to be used directly out from the build chamber and to be integrated in its final function.

- Design for AM is still in its early stage of development. The geometric flexibility has been widely used by artists and prototyping applications since the beginnings of AM, but new ways of conceiving functional parts are just being investigated. In this direction, for instance, topology optimization methods used in lightweight construction have found a strong synergy with this technology.

The main ideas described can be visually combined and summarized in Figure 1.2 in relation to the associated manufacturing cost [10, 11]. Figure 1.2a depicts the impact of the geometric intricacy per unit employing conventional production processes in comparison to AM. In general, for very simple product shapes AM is not competitive in relation to traditional manufacturing. However, the cost for AM remains almost constant as the geometric complexity increases while for traditional production techniques it rises at a higher marginal rate. Above the break-even where the cost is the same independent of the kind of technology used the term “complexity for free” is used to refer the higher degree of shape modifications that can be included at almost no additional cost. This concept enables the development of new design methods that take advantage of the synergy between shape and functionality expanding the limits of conventional manufacturing. However, due to the constant marginal cost of AM, above a certain number of units, traditional production is still competitive hindering the use of AM technologies for massification purposes as depicted in Fig 1.2b.

![Figure 1.2](image-url)
As many technologies under development, AM presents several technical limitations that still need a strong fundamental research to be overcome. However, despite the evident drawbacks, AM offers unique features not addressed by traditional manufacturing technologies, positioning AM as a revolutionary concept. This statement is supported by the results presented in the Hype Cycle curve for the most emerging technologies in 2013 depicted in Figure 1.3.

![Emerging Technologies Hype Cycle 2013](image)

Figure 1.3: Emerging Technologies Hype Cycle 2013 [12].

According to Gartner [12] this diagram provides a graphic representation of the maturity and adoption of technologies and applications. In principle it describes the current development phase of a technology in terms of the industry or users expectations and the particular state within its life cycle. In this diagram AM technologies can be recognized under the term 3D Printing. This term is currently used in many massive media due to its simplicity for non-technical consumers and therefore has been widely spread. However, from a technical point of view, this term is not accurate, since it refers to a specific inkjet AM technology developed by Sachs [13] at MIT.
Regarding the Hype Cycle, three main AM categories can be distinguished, namely 3D Bioprinting, Consumer 3D Printing and Enterprise 3D Printing, where this differentiation refers to particular application groups. The first one corresponds to the use of this technology to attempt to produce human tissues. This technique is still in its infancy, but constitutes an innovation trigger that is expected to reach the plateau of productivity within 5 to 10 years. In case of Consumer 3D Printing, the technology is located at the peak of inflated expectations, driven particularly by the basic systems used for prototyping or low performance demanding applications in terms of accuracy and strength. This group is currently leading the AM market due to the expiration of key patents that have enabled the introduction of low cost equipments, leading to a high massification of those systems. Nevertheless, there is an illusion that AM is a brand-new technology and the current expectations exert a lot of pressure demanding short term improvements. It is mostly unknown that many of these systems exist since more than 25 years and several efforts have been conducted to overcome many drawbacks such as poor surface quality and low mechanical properties with limited results. Therefore there is a high risk that Consumer 3D Printers will not fulfil the expectations and might vanish at the trough of disillusionment. However, a third group classified as Enterprise 3D Printing has successfully overcome all these previous stages and is currently located at the slope of enlightenment. According to Gartner [12] more instances of how the technology can benefit different companies start to crystallize and become more widely understood, enabling second and third generation products to appear from technology providers. Within this group Stereolithography (SLA) and Selective Laser Sintering (SLS) present a clear trend towards their consolidation in the market. For instance, both systems are widely used in the automotive, aircraft and medical industries for the production of final functional parts. Large companies such as BMW, Northrop Grumman and General Electric among others are continuously increasing their investments in AM equipments and research, leading to an enlarged installed capacity at their own internal facilities to satisfy their growing AM production requirements [14].
1.2 Classification of AM Technologies

Nowadays the number of different AM technologies available in the market is permanently increasing and due to their broad functional nature a unique way to classify those systems is difficult to achieve. Some approaches have been conducted in the past to organize them according to the materials consolidation source or in relation to the raw material employed. Gibson et al. [15] proposed a more accurate differentiation which uses a two-dimensional sorting method. The first dimension relates to the method by which the layers are constructed, i.e. if one or more point sources act simultaneously on the build plane following an independent ($n \times 1$D Channel) or an interrelated (array of 1D Channel) scanning pattern. More complex source systems can also be employed based on a bidimensional exposure projection (2D Channels) as depicted in Figure 1.4.

![Classification of AM Technologies](image)

**Figure 1.4:** Classification of AM Technologies modified from [14] and revised to incorporate recent developments and ASTM F2792 Standard Terminology.
The second dimension defined by Gibson et al. [15] considers 4 categories related to the type and state of the material employed, namely “liquid polymer”, “discrete particles”, “molten material” and “solid sheets”. However, this classification results inadequate since current dissimilar process such as Selective Laser Sintering (SLS) and 3D Printing (3DP) should be grouped together. For this reason an improved approach is presented in Figure 1.4 that corresponds to a tridimensional representation. In this table the second dimension is expanded using the standard terminology recently defined in the ASTM International Committee F2792 for Additive Manufacturing Technologies [16]. The aim of this norm is to provide a broad structure for grouping current and future AM machine technologies based essentially in how the raw material is processed during the coalescence step. According to [16] for many years, the Additive Manufacturing industry lacked categories for grouping AM technologies, which made it challenging educationally and when communicating information in both technical and non-technical settings. These process categories enable to discuss a category of machines, rather than needing to explain an extensive list of commercial variations of a process methodology. The terms defined in this standard are as follows:

- **Powder Bed Fusion**: process in which thermal energy selectively fuses regions of a powder bed.
- **Vat Polymerization**: process in which liquid photopolymer in a vat is selectively cured by light-activated polymerization.
- **Material Extrusion**: process in which material is selectively dispensed through a nozzle or orifice.
- **Binder Jetting**: process in which a liquid bonding agent is selectively deposited to join powder materials.
- **Sheet Lamination**: process in which sheets of material are cut and bonded to form an object.
- **Material Jetting**: process in which droplets of build material are selectively deposited.
- **Directed Energy Deposition**: process in which focused thermal energy (e.g., laser, electron beam or plasma arc) is used to fuse materials by melting as they are being simultaneously deposited.

Additionally the third dimension proposed in Figure 1.4 incorporates the final usage and/or development phase of each technology according to the classification defined previously by Gartner in Figure 1.3. The addition of this information has the advantage that it generates a
combined dynamic table that can be updated at a certain time frequency, enabling to track the maturity state of each process and to add new technologies in their initial research phase.

As can be observed, two main trends can be extracted from this representation:

- First, independent of the AM category, currently most of the methods use one point source to process the raw material. The main reason corresponds to the fact that point sources are easily to implement and to control in comparison to multi-sources that add more complexity to the process. For instance, Selective Laser Sintering (SLS) and Selective Mask Sintering (SMS) can process in principle the same thermoplastic materials in a powdered state. The main difference arises in how the radiation energy is added to the cross section that is being processed. In the first case, one laser beam is used to melt the powder particles, while in the second approach the energy is irradiated simultaneously over the whole cross sectional area through a predefined mask. The main advantage and aim is to increment the throughput of the system, but technical limitations related to the infrared diffraction at the mask edges reduces the geometrical accuracy of the sintered parts. Thus, this system is still under research.

- As a second observation, it can be appreciated how the technologies that present the higher maturity level (Enterprise category) are dominated by the Powder Bed Fusion and Vat Polymerization processes. In case of Consumer 3D Printing there is a higher dispersion of technologies mainly driven by the growing interest and efforts of different companies to move into this segment of the market adapting their particular technical knowledge to produce AM equipments. For instance, Arburg, a world-leader in polymer injection molding systems, has entered the market introducing a new AM equipment based on the use of a mini-extruder to process standard polymer pellets (Drop on Demand (DOD) process) [17]. Other companies such as Hewlett-Packard have announced to come into this market using the synergy of their installed research capabilities employed for their 2D paper printing technologies [18].

In order to better understand the distinction between Consumer 3D Printing and the higher maturity level of Enterprise 3D Printing from a technical point of view, Table 1.1 presents a comparison of the characteristic properties between the principal AM categories. Despite that this comparison is represented on a qualitative basis, it reflects a summary of results and trends obtained for quantitative evaluations performed by other authors [20, 21]. In general, the Powder Bed Fusion presents the best results in terms of mechanical and thermal properties followed by the Vat Polymerization processes. On the other side, Binder Jetting depicts the worst results due to the weak coalescence between merged particles leading to lower stiffness.
Table 1.1: Characteristic properties comparison between principal AM categories adapted from Gebhardt [19].

However, this AM category is evaluated as the best with respect to building speed and material costs. Additionally, the raw material used as part support during processing is not chemically or physically modified, allowing a higher degree of recycling capability and thus reducing the processing costs. In terms of geometrical accuracy, surface quality and reproducibility Vat Polymerization constitutes the best AM technology available, but the limited mechanical properties delivered in comparison to the highest cost of production coupled to the lower resistance to ageing and support material recycling do not compensate to clearly exceed Powder Bed Fusion technologies. In general, Material Extrusion processes depict an average performance considering all properties, with the non-negligible limitation that parts present a higher degree of anisotropy in terms of surface roughness and mechanical properties, particularly between the directions contained in the build plane and perpendicular to it. On the other hand, Sheet Lamination is currently not a competitive process since other technologies clearly meet and even exceed all the mentioned attributes. Thus, currently this process is almost not in use and has been replaced in many applications by the Material Extrusion category.

In summary, the comprehensive analysis of all these characteristics enables to explain why Powder Bed Fusion processes such as SLS and SLM have entered a higher maturity stage. The same trend can be applied to Vat Polymerization that groups essentially the SLA technology and its derivative processes such as MLS and MPSL.
1.3 Selective Laser Sintering Technology (SLS)

The Selective Laser Sintering Technology (SLS) is nowadays one of the most promising AM technologies available in the market for the production of high performance polymer parts. The process was developed in 1986 by Carl Deckard at the University of Texas at Austin, USA [22]. This technology is classified as part of the Powder Bed Fusion techniques previously described and it is characterized by the selective coalescence of particles based on polymer materials in order to form a three dimensional solid structure constituted of thin layers of micron sized powder particles using the energy provided by a CO2 laser beam.

At present, only two main manufacturers of this technology exist in the market, namely EOS Gmbh located in Munich, Germany and 3DSystems located in California, USA. However, currently several of the core SLS patents are close to their expiration date (first quarter of 2014) and new suppliers located mainly in China are expected to enter the market during the next years [23].

The main characteristics of the SLS Technology can be described as follows:

- The raw material used for processing is based on a neat or composite powdered polymeric matrix. The maximum particles size is usually limited by the minimum layer thickness that can be defined within the 60-160 micron size range.

- The materials that can be currently processed vary between amorphous and semi-crystalline neat or blended thermoplastics, composites with metal and ceramic particles using a polymeric binder and thermoplastic elastomers and polyurethanes.

- The production process takes place at elevated temperature inside an inert chamber, usually at a value close to the melting point or above the glass transition temperature in case of semi-crystalline or amorphous thermoplastics respectively.

- The unsintered powder that surrounds the parts allows the shape generation without the aid of support structures during the build process and their orientation within the build volume is not restricted by technical processing limitations in comparison to other AM technologies (e.g. SLM or SLA). This freedom enables also the production of functional articulations in one step with no post-assembled components.

In general the SLS build process can be summarized by a cyclic powder spreading procedure at elevated temperature (near the melting point) characterized by 3 main sequential steps:
First, a thin layer of powder is spread over the top surface of the central part bed and heated up to a constant temperature below the melting or glass transition point.

Second, the cross sectional area of a predefined CAD geometry is scanned by a laser beam to generate the spatially controlled coalescence of the powder particles and the interlaminar adhesion with the preceding layer.

Finally, the build piston is lowered a vertical distance equivalent to a layer thickness and a new layer of powder is added on top to repeat the cycle until the part is completed.

Figure 1.5 describes in more detail the main components that integrate a typical SLS equipment. It consists of a chamber that presents two powder feed containers on both lateral sides and a central build cylinder. A counter-clockwise rotating roller transports the powder from each feeder to the build piston and a central radiant heater enables to control homogeneously the temperature on the top surface of the part bed. The CO₂ laser resonator and the optical system are located on top of the machine outside the heated atmosphere. The laser beam, after being expanded and collimated, is deflected and focused on the surface of the part bed by two galvanometer mirrors that constitute the cross sectional scanning system.

Figure 1.5: Description of the components that integrate a typical Selective Laser Sintering equipment (concept developed by 3DSystems (former DTM)).
1.4 Selective Laser Sintering Materials

The global polymers market has achieved during 2010 a worldwide production of 260 Mton/year [24]. These polymers can traditionally be classified in three main categories, according to their particular performance mainly in terms of their temperature resistance and market share volume. These categories are Standard, Engineering and High Temperature (HT) polymers [25]. As can be observed in Figure 1.6 the market fraction for the first group corresponds to approximately 95% of the worldwide production, where polyethylene (high and low density) and polypropylene cover more than 40% of this segment. The second category, Engineering polymers, covers only 5% and High Temperature polymers less than 1%. This remarkable difference is related essentially to the higher production costs of the last two groups limiting their use to high performance applications.

A similar breakdown is presented for the SLS polymers market, which only depicts a world production of 900 ton/year [26]. As illustrated, Engineering polymers dominate with a 98% market share, where polyamide 12 (PA12) constitutes for SLS applications the most used polymer worldwide. During the last years new materials have been introduced into the market (e.g. polyamide (PA6) and polypropylene (PP)), but their volume still remains reduced, either due to special SLS machine requirements for high temperature and due to the higher purchase costs, which can be 10 times higher than the value of a PA12 grade (e.g. polyaryletherketone).

Figure 1.6: Market overview and comparison between principal global and SLS amorphous and semi-crystalline polymer materials [24,26].
In general, besides the higher purchase costs and SLS machine requirements, material technical constraints also limit the introduction of new grades, which must be specially developed for this process and are not compatible with other polymer processing methods (e.g. injection molding, vacuum forming).

The Ishikawa diagram depicted in Figure 1.7 presents an overview of the main topics that exert a critical role for the suitability of a SLS material. According to Schmid et al. [27], despite the complex interaction between the different variables, 5 main groups can be distinguished. The main intrinsic properties summarized in the optical, thermal and rheological aspects are initially examined during the development phase of a new material. For instance, in case of semi-crystalline polymers, the characterization of the melting and crystallization temperatures by means of Differential Scanning Calorimetry (DSC) constitutes one of the main screening criteria for the selection of a polymer. The difference between both temperature points is the so called “sintering window”, which must be above a minimum threshold to avoid a high recrystallization rate during processing, which can lead to geometric inaccuracies of the sintered parts. The value obtained for PA12 is normally used as the main quantitative reference for other polymers.

Figure 1.7: Ishikawa diagram that presents the interdependency of the main intrinsic and extrinsic properties that defined the suitability of a SLS material [27].
Regarding the optical aspect, in general, most of the polymers present an absorption coefficient value above 90% for a CO₂ laser with a wavelength of 10.6 μm [28]. For some materials like polypropylene (PP), additives or pigments such as carbon black or talcum are employed to increase the absorption effect. Concerning rheology, the ratio between melt viscosity and surface tension constitutes a critical factor. A higher value reduces the coalescence rate between particles during the laser interaction time interval and a lower value increases the formation of isolated droplets hindering the formation of a homogeneous molten film.

In relation to the extrinsic properties, particles with a near spherical shape and a smooth surface are required, in order to obtain a suitable powder flowing behavior and to increase the powder packing during deposition. Also, the particle size distribution is limited at its maximum value by the thickness of each layer. The lower bound is not clearly defined, but the presence of a higher amount of finer particles hinders the powder flowability due to the inter-particle forces effect.

Even though that for most of the properties previously described a quantitative assessment exists, a robust selection criterion is still not available in order to determine in advance if a material results suitable or not for the process. Figure 1.8 depicts the most common problems that appear during the initial SLS test of a new material. The formation of streaks and an inhomogeneous powder deposition lead to a low part sintered density and reduced mechanical properties. More critical results the “curling effect” or warpage of the sintered layers during processing, which consists in the deformation of the sintered parts as the build progresses and/or during cooling. This phenomenon generates a reduced geometric accuracy and can even induce the break of the process when the out of plane deformation exceeds the layer thickness.

In summary, further fundamental research is needed to cover these topics in order to improve the SLS technology and expand the materials spectrum that can be currently processed.

![Streaking, Curling, Inhomogeneous deposition](image)

Figure 1.8: Typical problems observed during SLS testing of new materials on the part bed surface related to intrinsic and extrinsic material properties.
2 State of the art

2.1 Powder Production Methods for SLS Materials

The processability of thermoplastics polymers suitable for the SLS technology requires that the raw materials must be transformed into a powdered state. Currently a limited number of methods are available that can produce a powder to obtain a higher packing density during the deposition of the material on the SLS powder bed. The current SLS powder production methods of commercially available materials are the following:

- **Cryogenic milling of polymer granules:** corresponds to the comminution of large polymer grains (pellets) used typically for injection molding at lower temperatures, normally below the glass transition point where polymers present a brittle behavior and the size reduction is possible by mechanical impacts. The temperature reduction is usually achieved by using liquid nitrogen that continuously cools down the milling chamber. The main advantages of this method are its simple, low cost implementation and the possibility to process a wide range of polymers and even compounds. However, as a result of the milling process, the particles present sharp edges with a rough surface that hinder the powders flowability and induce an inhomogeneous powder deposition and density on the part bed surface. Some efforts have been performed to round the particles by a post heating procedure, but particles with highly distorted shapes still remain [29]. Additionally the particle size distribution results difficult to control and a post classification or sieving process is needed. Examples of commercial polymers produced by this method are thermoplastic elastomers (TPE) and polyurethanes (TPU) such as Duraform Flex and Desmosint respectively. However, the lower sintered density obtained for these materials requires either a rescan of the sintered cross section during the build phase to increase the coalescence or the post-infiltration of the produced parts after the break out stage.

- **Precipitation of polymer solutions:** corresponds to the process where a polymer matrix is solved in a heated ethanolic solution within a pressure vessel and precipitation takes places as the solution is slowly stirred while it is cooled down from a temperature below the polymer melting point [30,31]. This process is typically used for the production of coatings and currently both commercially available PA12 powders, i.e, Duraform PA from
3D Systems and PA2200 from EOS GmbH are produced by this method. The main advantage is the narrow and controlled particle size distribution that can be obtained with nearly spherical ("potato shaped") and low porosity particles. According to the inventors [31], a further advantage of the precipitated powders is the wide scope for variation of the molecular weight (relative solution viscosity between 1.5 to 2.0). However, the addition of additives is limited due to the change in the nucleation and precipitation conditions and they must be incorporated in a posterior stage after the powder has been dried. From an economical point of view, the process is operated in a batch mode, which increases the production costs in comparison to a continuous process.

- **Co-extrusion of non-miscible polymers**: corresponds to the dispersion of two non-compatible polymers in an extrusion equipment during the kneading stage, generating a micro droplet phase of the dispersed polymer in the dispersion medium. In case of thermoplastics, the process is performed at a temperature higher than the melting point of the dispersed polymer [32]. After the kneading stage, the mixture is cooled down and the micro droplets start to solidify. Subsequently, the extruded mixture is solved in order to separate the two components, which is performed by a filtration process. Currently the company Daito Kasei produces the only SLS commercial powder available by this technique and corresponds to a copolypropylene material (icoPP). The main advantage of this method is the almost spherical particle shape obtained with a smooth surface roughness. A comparison between this and the previous two powder production methods can be observed in Figure 2.1.

Besides the 3 main methods described above, other techniques under research for the development of SLS powders are spray drying [33], fiber cutting [34], solubility of supercritical gases in a polymer melt [35] and powder extrusion by using Rayleigh disturbances [36].

![Figure 2.1: Images of SLS powders produced with co-extrusion (a), precipitation (b) and cryogenic milling (c) methods.](image-url)
2.2 Powder Deposition Systems of SLS Machines

The main objective of a powder deposition system is to transport the raw material from a feed container to the central part bed in order to obtain a thin homogeneous layer with a high packing density. Currently two types of powder spreading system exist: one corresponds to a counter rotation roller developed by 3DSystems and the other to a translational blade patented by EOS GmbH as can be observed in Figure 2.2.

![Diagram of SLS powder spreading systems: Roller (3DSystems) & Blade (EOS GmbH)](modified from [37]).

In a 3DSystems equipment, the powder is supplied from below the part bed plane by a piston that moves upwards a distance that is higher than the layer thickness in order to avoid the short feed effect (partial filling). For PA12 typical values are between 2.5 to 2.7 times the layer thickness and depend on the compacted state of the feed powder achieved during the filling stage and the size of the cross sectional area that is scanned by the laser. Additionally the powder feed surface can be homogenously preheated, helping to reduce the temperature difference between the feed powder and the sintered surface with the aim to decrease the undercooling effect on the molten layer. This feature is an advantage for the processing of high temperature polyamides or polycyroletherketones (e.g. PA6 $T_m$: 220°C, PAEK $T_m$: 340°C).

The translational roller also presents a counter rotating motion coupled to its translational velocity at a fixed ratio. Niino & Kazuki [38] studied the effect of different deposition parameter combinations on the powder bed packing of PA12 (Duraform PA), including the rotational direction, translational speed $v_t$ and the rotational roller surface speed $v_r$. The first part of this study demonstrated that the use of a rotation in the right direction in a standard recoating
cycle used in commercial SLS machines induces an excessive pressure between the roller and powder bed, generating an inhomogeneous surface with depressions and powder sticking on the roller surface. In the second part, a new compaction method was developed based on a double recoating stage as described in Figure 2.3. The first and second steps (piston lowering and powder supply with counter rotation) correspond to the standard recoating cycle, with the difference that in this case the piston lowering height (supply thickness) $t_s$ is higher than the layer thickness $t_l$ used to build the parts. Then the piston lifts up to a higher position that equals the layer thickness and the roller moves back to its initial position, but using a rotation in the right direction. Thus a compaction factor $f_c$ was defined as the ratio between the difference $t_s - t_l$ and the layer thickness $t_l$, and the powder packing density was measured using the weight difference between a full and empty sintered hollow box with known volume. The results show that the maximum compaction factor achieved without powder bed distortions was 2 ($t_s = 3 t_l$) and the maximum packing density obtained was below 50%, which is similar to the packing density of the tapped powder (powder compacted in a vertical cylinder by mechanical agitation) [39]. Also, as the translational speed increases, there is a reduction of the packing density for all cases, even without compaction. It must be pointed out that the powder compaction method only produces satisfactory sintered parts when the translational and rotational speeds during compaction are equal, i.e., when no slip between roller and powder bed exists (Figure 2.3a). In all other cases, the excessive friction generated the drag of previous layers in the compaction direction, ending up with a distorted geometry (Figure 2.3b).
In case of EOS systems, the powder is supplied from above the part bed plane by a hopper that delivers a variable amount of powder in front of the blade that is larger than the needed for filling one layer. Thus, the height of the powder volume that is being displaced by the blades is higher than with the roller system and a greater pressure is generated on the powder bed surface, potentially inducing the shift of the previous sintered layer due to the higher shear stress. To reduce this effect, the coater presents a concave curvature in its internal vertical surface in order to induce a similar powder up-flow generated by the roller close to the blade tip and thus decrease the local pressure. The tip or lowest surface of the blade also presents an angle of incidence, that according to an EOS patent [40] its value varies up to a maximum of 5º respect to the powder bed plane, generating a slight compaction of the powder. The main disadvantage of this system is the highest sensitivity to collisions with imperfections on the powder bed, such as the slight out of plane deformation of large cross sintered layers that might appear due to inhomogeneous shrinkage, which can generate the break of the build process.

Budding & Vaneker [41] also investigated both powder deposition systems and a combination of both, i.e., a blade in front of a roller rotating in the right direction using a similar approach than in [38], but using one coating step. The highest density with the best surface quality was achieved using a counter rotating roller. The combination of a blade and rotating roller in the right direction is promising for a high packing density, but this setup generates distortions on the powder bed (depressions, drag of layers). The lowest packing density is achieved by the blade, although the surface quality is moderate using that compaction method. Despite that a different material and no information about the blade geometry was provided in this study, similar trends in comparison to the previous author can be observed.

Finally, Shanjani & Toyserkani [42] developed a mathematical model for the compaction of the counter rotating roller system. A one dimensional slab method is used, in which the equilibrium force balance along the deposition direction on a thin strip of material between the roller and the powder bed with a differential thickness is considered. The main assumptions of the model are that the powder behaves as a continuous flow of compressible porous material that experiences a compaction through the space between the roller and the powder bed and that the dynamic effects of the translational and rotational speeds are reflected by the friction coefficient between the roller surface and the powder. The main result depets that as the friction coefficient increases, the densification is reduced. However, the empirical determination or estimation of this value and its correlation with the dynamic handling conditions of a particular powder are not mentioned and even no empirical validation of the model was performed.
2.3 Materials Coalescence in SLS Process

After the powder deposition stage, the coalescence of the powder particles takes place in the absence of external pressure and only by the additional energy supplied through a CO$_2$ laser beam. The influence of several factors that affect the coalescence rate and the achievement of a dense structure will be discussed in this chapter.

2.3.1 Sintering Dynamics

The coalescence of polymer particles often takes place at temperatures above the glass transition temperatures for amorphous materials and above the melting point for semi-crystalline materials. By definition the term sintering refers to the process of forming a solid mass of material from a granular state by heat and/or pressure without any phase change. However it has been indistinctly used and accepted to describe the formation of a homogenous polymer melt from solid particles. The first studies of the sintering phenomena were performed by Frenkel [43] and Eshelby [44] to describe the isothermal coalescence rate of two identical viscous spherical particles as observed in Figure 2.4. In this model, the driving force during the sintering process is given by the surface tension that counteracts the work of the viscous flow. Pokluda et al. [45] further developed the previous models for large deformations taking into account a variable particle radius with time as sintering develops. Afterwards, Bellehumeur et al. [46] and Scribben et al. [47] incorporated the effect of viscoelasticity in the previous works, obtaining a more accurate description at late stages of the sintering process, showing that the original viscous model also under-predicted the coalescence rate at early stages and, hence, did not work well for polymeric materials.

\[
\frac{d\theta}{dt} = \frac{\gamma}{2a_0 \eta \theta} \quad \gamma: \text{surface tension} \\
\eta: \text{viscosity}
\]

\[
\frac{d\theta}{dt} = \frac{2}{a_0 \eta} \frac{2^{\frac{7}{3}} \cos \theta \sin \theta (2 - \cos \theta)^{\frac{1}{3}}}{(1 - \cos \theta)(1 + \cos \theta)^{\frac{1}{3}}}
\]

Figure 2.4: Shape evolution of the viscous sintering of two identical spheres [45].
The main disadvantage of the previous models is that they describe the sintering rate only between two particles and an extension to three dimensions using a higher coordination number with different particle size combinations has not been validated. However, Steinberger et al. [48] performed the first efforts to model and validate the sintering rate or transient height reduction of a powder bed at near SLS conditions, using an optical sensor to measure the vertical displacement of a powder bed as the particles start to coalesce. Using a similar approach as developed by previous authors, the model of Pokluda et al. [45] with and an experimental stress relaxation function of a polymethylmethacrylate (PMMA) material were coupled. The powder employed presented a near spherical shape with a narrow particle size distribution (average diameter of 33μm) and a powder packing model was proposed based in a control volume of a cylindrical unit cell containing two half-particles surrounded by an air jacket. This air jacket is used to explain the difference between the calculated solid fraction of the cell and the experimentally measured solid fraction. As observed in Figure 2.5, the viscoelastic model presents a better prediction of the real sintering conditions in comparison to the viscous approach. It must be pointed out that the laser-material interaction time used was 350ms at 6.8W with a defocused CO₂ laser spot (diameter of 4.5mm). The author also reported experimental results for PA12 (300ms at 3.3W) with a higher height reduction in a similar time frame than PMMA, which confirms the importance of the higher viscosity reduction rate of semi-crystalline polymers above the melting point in comparison to amorphous thermoplastics, even at lower laser-material interaction times.

Currently, in the SLS process typical values for the laser beam speed and spot diameter are in the range of 5 to 12 m/s and 400 to 450 μm respectively, obtaining a laser-material interaction time in the order of magnitude of 30 to 90 μs. During and after this reduced time frame, a faster polymer coalescence is desired before the polymer melt cools down and viscosity increases, which makes semi-crystalline thermoplastics more suitable for the SLS process.

![Figure 2.5: Comparison of viscoelastic theory and height reduction experimental data [48].](image-url)
2.3.2 Powder Packing

Due to the short laser-material interaction time and the spatially application of the laser energy, the initial packing density of the powder bed plays an essential role, in order to obtain dense sintered parts and provide stability to the powder bed. As each powder is a collection of particles with different sizes and shapes, their arrangement to form a dense structure is not an easy task, even not considering additional factors like surface roughness, inter-particles forces and deposition mechanisms [49]. For instance, Figure 2.6a depicts the characterization of the particles geometry by the relative roundness defined as the ratio between the surface area of a sphere $S_s$ with the same volume as the test particle and the actual surface area $S$. As noted, as the roundness of the particles increases, the random packing density of a mono-modal distribution improves [50]. For the simplest model, a powder with smooth mono-sized spheres without interactions can achieve a maximum solid fraction of 74% considering a face-centered cubic structure. If the interstices of this arrangement are filled with smaller mono-sized particles without dilating the overall volume, the solid fraction can be increased up to a maximum as schematically depicted in Figure 2.6b [51]. If this process continues, the solid fraction can be further improved. However, in practical applications such idealized arrangements are difficult to achieve, due to the random deposition process, the lack of perfectly smooth and spherical shapes and the absence of the exact particle size ratio within multimodal powder distributions. In the SLS process also the layer space filling restriction plays an important role, since the average particle diameter is normally between 30% to 60% the size of the layer thickness employed. Thus, the top and the bottom of each layer present a higher void concentration in comparison to the middle part of it (wall effect) [52], phenomenon that becomes more relevant as the ratio between layer thickness and average particle size decreases.

Figure 2.6: (a) Effect of particle shape on packing density for a mono-modal distribution [50], (b) Improved packing density in a bimodal PSD [51].
The characterization of the powder packing within a layer in the SLS process results difficult to achieve and indirect measurements are normally conducted. The most common procedure corresponds to evaluate the packing ability outside the SLS chamber filling a container with powder and then measuring the density obtained after applying mechanical agitation by vertical beating (tapping) without any external pressure on the powder surface. Dupin [53] performed a comparative analysis between 3 commercial SLS PA12 powders, namely, Duraform PA, PA 2200 and Innov PA. Figure 2.7 depicts a SEM image of the 3 materials and the results for their particle size distribution, tap density and circularity are presented. In this study, the shape parameter circularity is defined as the ratio between the square of the perimeter and the area of the test particle, denoting that the shape characterization is not unique. As can be distinguished, Innov PA presents a narrower particle size distribution with smaller and more rounded particles in comparison to Duraform PA and PA 2200. In case of Duraform PA a quasi-bimodal particle size distribution can be observed, with a first peak at 60 μm and a second peak at approximately 9 μm, which can also be qualitatively appreciated in Figure 2.7b. Comparing these results with the tap density obtained, the particles shape results the most sensitive parameter. Despite that Duraform PA presents the highest circularity, it seems that the smaller particles fill the interstices between the larger ones, achieving a similar packing density than obtained for PA 2200 with a lower circularity value. However, the improved shape of Innov PA particles has a more relevant impact in the powder packing, since no smaller particles are present to fill the cavities and the highest packing density is achieved. These results reveal that optimal packing conditions for real powders are difficult to assess in advance only by a theoretical approach and an empirical characterization must be conducted.

Figure 2.7: Comparison of volume particle size distribution and tap density of 3 commercial PA12 powders: (a) Innov PA, (b) Duraform PA and (c) PA 2200 [53].
2.3.3 Residual Porosity

During the coalescence process, the mixture air-inert gas between the particles is normally displaced by the molten polymer phase, but a residual porosity is always present in the sintered structure. In the previous chapter the importance of a high packing density was emphasized, but empirical results depict that values above 50% are difficult to achieve. Thus, different particle arrangements can lead to the same packing results, influencing how the material coalesces. Rouholamin & Hopkinson [54] using computer tomography (CT) measurements determined in sintered PA12 samples a residual porosity between 4% and 5% with an average pore equivalent diameter of approximately 23 μm. These results are comparable with the previous work of Rüssenberg et al. [55] who also obtained values between 3% and 6% and porosity reduction was observed as the laser energy deposition increased. Dupin [53] also obtained a similar trend for both materials tested, i.e., Innov PA and Duraform PA (Figure 2.8). However, considerable differences were detected at different energy densities in terms of total porosity and microstructure. While Innov PA presented a more homogenous internal porous structure with a narrow pore volume distribution, the total porosity was double the value of Duraform PA for the lowest energy density, particularly due to the open porosity at the edges and between the layers. However, as the energy density increased, a trend reversal was obtained. This study reveals that a regular high powder packing might have a detrimental effect on the sintered density if not enough energy is supplied, due to the lower laser penetration depth and short laser-material interaction time. Nevertheless, above a certain energy threshold, a regular packing provides a more dense structure with a lower average pore size. According to Gogos [56], the further reduction of the remaining trapped gas in polymer melts is controlled by the diffusion of the gas into the melt and not by void migration due to the higher viscosity during the solidification phase. However, no further studies are reported in the SLS field in order to achieve a near fully dense structure of the sintered parts.

Figure 2.8: Residual porosity distributions obtained with Innov PA and Duraform PA samples [53].


2.4 SLS Powder Characterization

2.4.1 General Requirements on SLS Materials

Nowadays a full understanding of which attributes should SLS powders present to be successfully processable and to what extent the quantification of those features provides relevant information to design a new SLS material or to further improve an existing polymer is a matter of discussion. However, based on empirical evidence, there is a consensus in the SLS community that at least the main properties presented in chapter 1.4 and described by Schmid et al. [27] are significant. Table 2.1 presents an overview of the main SLS features of a commercial PA12 that are typically used as a reference for the development of new materials. For instance, the sintering window, i.e., the difference between the melting and crystallization peak temperatures (or onset) characterized by a DSC at a rate of 10ºC/min should be higher than 30ºC in order to reduce the probability that the sintered parts develop a deformation post-sintering (warpage, curling effect). It must be pointed out that the rules presented in Table 2.1 constitute a general guideline for the first screening stage. Once a material fulfills all these aspects, there is a high likelihood of a stable processability, but there is still no guarantee about the quality of the properties obtained (e.g., mechanical, surface roughness, accuracy of geometric details). The next chapter presents a literature review about the efforts conducted by different research groups to develop new SLS materials and the characterization methods employed.

<table>
<thead>
<tr>
<th>SLS Feature</th>
<th>Method/Equipment</th>
<th>Condition on Reference Material (PA12)</th>
<th>Effect if condition not fulfilled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintering Window</td>
<td>Differential Scanning Calorimetry (DSC)</td>
<td>&gt;30ºC@10ºC/min (onset temperatures)</td>
<td>Presence of warpage / curling</td>
</tr>
<tr>
<td>Zero shear viscosity / Molten mass flow</td>
<td>Rheometer / Melt Flow Index (MFI) Device</td>
<td>&lt;2000 Pas (200ºC) / &gt;25 g/10min (235ºC)</td>
<td>High residual porosity / High surface roughness / Delamination</td>
</tr>
<tr>
<td>Bulk / Powder bed absorption</td>
<td>Infrared Spectroscopy (IR)</td>
<td>&gt;95 %</td>
<td>Higher energy input reduces geometrical accuracy (depth, lateral)</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>Optical Microscopy / Laser Diffraction</td>
<td>D10 &gt;10 µm D90 &lt; 100 µm</td>
<td>Inhomogeneous deposition on powder bed (streaks, clumps)</td>
</tr>
<tr>
<td>Powder packing and flowability</td>
<td>Bulk / Tap Relative Density</td>
<td>Tap&gt; 45% HR&lt; 1.25</td>
<td>Low sintered density/ Poor mechanical properties</td>
</tr>
</tbody>
</table>

Table 2.1: Current relevant features and reference conditions for Duraform PA12 used as a guideline for the development of new SLS materials.
2.4.2 Development and Evaluation of SLS Powders

The development of new powdered materials suitable for the SLS process with the aim to broaden its application field constitutes currently one of the main research topics and challenges [57,58,59,60]. Several research efforts have been conducted during recent years towards the design of new SLS powders. In this direction, besides the commercial methods presented in chapter 2.1, different approaches have been adopted, considering just from a simple mixture of two polymer components to more sophisticated production methods like mechanochemical alloying [61,62]. Depending on the production method employed, intrinsic property changes can be induced, such as a shift of the melting or crystallization point. However, non-intrinsic features like the particles size and shape or powder flowability are strongly influenced in a sensitive way [29].

Regarding the materials characterization for the SLS process suitability, most researchers concentrate their effort on intrinsic properties. As can be observed in Table 2.2, thermal and rheological measurements conducted by differential scanning calorimetry (DSC), termo-gravimetric analysis (TG), melt flow index evaluation (MFI) and rheological testing devices (viscosity characterization) constitute a recurrent practice. However, non-intrinsic properties are normally barely reported or simply left out. It is well known that good dispersion conditions are necessary to achieve a higher powder packing and a homogeneous layer spreading, but no quantitative information towards a prediction for SLS powders is available in literature. Most researchers conduct normally a powder development cycle just by trial and error carried out on a full or scaled SLS equipment. For instance, Salmooria et al. [63] investigated the processing of blends of commercial PA12 and high density polyethylene (HDPE) powders. A year later, a similar approach was performed, considering blends of polyamide 6 (PA6) and PA12 [64]. Sintered parts with high porosity were obtained and a powder pre-treatment is mentioned to improve the particle regularity. However, no clear information regarding particle size distribution (PSD) or shape was reported, which does not clearly allow distinguishing between a predominant intrinsic or non-intrinsic effect. Schultz et al. [62] investigated PA12-PEEK blends formed by cryogenic mechanical alloying. In this case, due to the processing method employed, a flake-like structure of the alloyed particle is reported and a large amount of fines are revealed by the PSD analysis. The author attributes the lower mechanical properties to the difficulties in achieving a dense powder bed despite having achieved a good miscibility between both materials. More recently, the modification of polyamide with organic and inorganic nano-fillers to enhance polymer performance, i.e., fire retardancy, high strength and high heat resistance has been employed. Koo et al. [65] examined polyamide 11 and 12 modified with different types of nanoparticles produced by a
twin extruder followed by a cryogenically grinding step. The subsequent trial and error cycle proved that not all blends were successfully sintered. The author states that the reason for the failure was the process inhibition by powder mechanics. The poor powder flow led to poor powder deposition and subsequent SLS processing difficulties. Even the rejected material is described as flour like flowing powder, but again a qualitative appraisal was elucidated.

Table 2.2 summarizes for different authors/research groups diverse production technologies employed and the materials characterization methods used prior and after carrying out the sintering trials. As noted, most of them did not consider any kind of powder flowability evaluation despite that each production process has a considerable different effect on the non-intrinsic powder properties.

<table>
<thead>
<tr>
<th>Production Technology</th>
<th>Intrinsic characterization test</th>
<th>Non-intrinsic characterization test</th>
<th>Author/Research Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Powder mixing (polymer, fiber, beads)</td>
<td>✓</td>
<td>✓</td>
<td>[63][64][66]</td>
</tr>
<tr>
<td>Melt mixing &amp; cryogenic grinding/spray drying</td>
<td>✓</td>
<td>✓</td>
<td>[33]</td>
</tr>
<tr>
<td>Dissolution-precipitation</td>
<td>✓</td>
<td>✓</td>
<td>[74]</td>
</tr>
<tr>
<td>Mechano-chemical alloying/Solid state</td>
<td>✓</td>
<td>✓</td>
<td>[61][62]</td>
</tr>
</tbody>
</table>

Other characterization methods: *FTIR, EDX, XRD; **Angle Of Repose, Carr Index.

Table 2.2: Material characterization methods employed by different authors or research groups during the development of new SLS materials.
2.4.3 Characterization of SLS Powder Flowability

The flow properties of a powder depend on many parameters such as the particle size distribution, particle shape, inter-particle forces and temperature [78]. According to Masuda et al. [79] the inter-particle forces correspond essentially to the added effect of Van der Waals, electrostatic and liquid bridge forces. The Van der Waals force is a short-range electromagnetic force interacting between two macroscopic bodies such as particle–particle or particle–wall, principally due to the effect of permanent or instantaneously induced dipoles. In case of identical spherical particles, the magnitude is proportional to their radius $R$ and reduces its value as the contact distance $r$ increases. Also the force is proportional to the material properties, which are summarized in the Hamaker constant $A$. The electrostatic force arises from the particle–charge interaction and the electrostatic contact potential difference. Between two charged particles, the electrostatic force is proportional to the charge or surface charge density $\sigma$ of each particle and its effect increases as the contact distance is minimized. Also the force depends on the permeability of the medium $\varepsilon_0$. If the relative humidity is high (>65%), a contact bridge can appear between the particles and the force in-between is essentially controlled by the surface tension of the water. A comparison of the magnitude of the different forces regarding the particle diameter is presented in Figure 2.9. Since the SLS process takes place normally at an elevated temperature above 100ºC in an inert atmosphere, the liquid bridge force can be neglected. Additionally, since the particle size typically presents a distribution between 5 to 120 µm, the Van der Waals force becomes dominant for collections of very small particles such as very fine-grained dry powders even though the force of attraction is smaller in magnitude than it is for larger particles of the same material. Such powders are said to be cohesive,

![Diagram](image)

Figure 2.9: Van de Waals, electrostatic, liquid bridge and gravity forces between spherical particles ($A=1e-19J$, $\sigma_1,2=26.5\mu C/m^2$, $\rho=1g/cm^3$, $r=0.4nm$, $\gamma=72mN/m$) [79].
meaning they are not as easily fluidized or pneumatically conveyed as easily as their more coarse-grained counterparts. Generally, free-flow occurs with particles greater than about 250 μm. The Van der Waals force of adhesion is also dependent on the surface topography. If there are surface asperities or protuberances that result in a greater total area of contact between two particles or between a particle and a wall, this increases the Van der Waals force of attraction as well as the tendency for mechanical interlocking.

Since commercial SLS powder particles are not perfect mono-sized spheres as discussed in chapter 2.1, it is a challenging task to determine theoretically the flow behavior of bulk solids in dependence of all of these previous parameters. Thus it is necessary to determine the bulk flow properties in appropriate testing devices. Evans et al. [80] introduced a “SLS Materials Development Method” were he emphasizes the importance of considering the powder behavior as a first step on a powder development cycle. However, currently no specific method for SLS has been established. Many characterization techniques are available to determine the flow properties of powders. Krantz et al. [81] provide a comprehensive description of different techniques, considering static and dynamic powder state conditions. Table 2.3 gives an overview of common methods in use, particularly in the coatings and pharmaceutical industry.

<table>
<thead>
<tr>
<th>Method</th>
<th>Bed Expansion</th>
<th>Angle of Repose</th>
<th>Shear Cell</th>
<th>Bulk/Tap Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>Not standardized</td>
<td>DIN ISO 4324</td>
<td>ASTM D6773</td>
<td>ASTM D7481</td>
</tr>
<tr>
<td>Measurement Condition</td>
<td>Dynamic under vertical gas drag force</td>
<td>Static under free external load</td>
<td>Quasi-Static under pressure</td>
<td>Static under the effect of powder weight</td>
</tr>
<tr>
<td>Characterization parameters</td>
<td>Fluidized height v/s upstream gas flow</td>
<td>Pile angle</td>
<td>Shear force v/s normal pressure/ compression rate</td>
<td>Loose and packed height v/s n° of taps</td>
</tr>
</tbody>
</table>

Table 2.3: Most common bulk powder characterization methods [81].
The operational principle and the characterization parameters employed in each method presented in Table 2.3 are described as follows:

- **Bed Expansion**: consists in the characterization of the hydrodynamic behavior of a powder bed by measuring the pressure drop and height of an expanded column of powder contained in a vertical cylinder. The dilatation of the powder is achieved by a continuous non-turbulent upstream of gas supplied from the bottom through a semi-permeable membrane. The powder expansion is caused by the drag generated on each particle as the flow pass through the interstices. Under the assumption of steady flow, the powder in equilibrium by its own weight can be modelled by the following equation [82]:

\[
\frac{\Delta P}{h} = K \left(1 - \varepsilon\right)^2 \frac{\mu}{\varepsilon^2 d_{sv}^2} v
\]

(2.1)

where \(\Delta P\) is the pressure drop through the powder bed, \(h\) the height of the powder column, \(K\) the permeability of the porous medium, \(\varepsilon\) the packing porosity, \(v\) the velocity of the gas flow, \(\mu\) the viscosity of the fluid and \(d_{sv}\) is the average volume to surface diameter of the particles. This method allows determining the minimum fluidization velocity \(v_{min}\), i.e., the minimum gas flow needed to generate a stable height increment, and the critical velocity \(v_{crit}\), i.e., the maximum gas flow until the fluidized powder loses its stability and gas bubbles start to develop within the powder bed. According to Abrahamsen & Geldart [83] if \(v_{crit}/v_{min} > 1\), powders present a good fluidization behavior. For high cohesive powders \(v_{crit} \sim v_{min}\) and no stable powder bed can be obtained due to the effect of inter-particle forces and shape interlocking.

- **Angle of Repose**: consists in the characterization of the static acute angle of a pile of powder that is poured using the aid of a funnel. The amount of powder supplied must fill a predefined circular area with a diameter \(a\). The height of the powder pile \(l\) formed is then measured and the angle \(\theta\) is calculated as follows:

\[
\theta = \cos^{-1} \left( \frac{2l}{a} \right)
\]

(2.2)

As the cohesiveness and interlocking of the powder increase, the pile angle increases as well. Reka et al. [84] performed the static analysis of 4 smooth spheres placed on an inclined plane (3 forming an equilateral triangle and the last on top) where no inter-particle forces are present and the friction between a horizontal surface and the particles is high enough to avoid slipping. Considering all possible orientations of the base particles to ob-
tain a stable configuration, the average maximum angle obtained is 23°. This reference value can be considered as a theoretical minimum for the angle of repose. According to several authors [82,85,86] powders with an angle less than 40° flow easily, while those with angles greater than 50° flow poorly, but no clear definition is given for these two terms.

- **Shear Cell**: consists in the characterization of the yield locus of a powder bed under compression and shear stress. The determination of the failure states is performed at different normal and shear forces applied on a shear cell (circular or annular container) with a closed volume of powder. There are essentially two methods: the linear and annular shear cells. In both cases a fixed weight is applied for each measurement on top of the lid and an increasing lateral force (or couple of forces for annular) is applied until the displacement begins. The representation of the failure states are performed using Mohr circles for each measurement (Figure 2.10). The resulting graph is the yield locus and it is a line which gives the stress conditions needed to produce flow for the powder when it is compacted to a fixed bulk density [85]. For many powders, the yield locus curves can be described by the following empirical relationship:

\[
\left( \frac{\tau}{c_1} \right)^m = \frac{\sigma}{c_2} + 1
\]

where \(\tau\) is the shear stress, \(\sigma\) the normal stress, \(c_1\) the material’s cohesion, \(c_2\) the tensile stress and \(m\) is the shear index with values between 1 and 2. For non-cohesive powders, the yield locus is a straight line \((m=1)\) and pass through the origin. According to Schulze [78] the flowability of a bulk solid is characterized mainly by its unconfined yield strength, \(\sigma_c\) in dependence on the consolidation stress \(\sigma_1\). Usually the ratio \(\frac{\sigma_c}{\sigma_1}\) of consolidation stress \(\sigma_1\) to unconfined yield strength \(\sigma_c\) is used to characterize flowability numerically.

![Figure 2.10: Measurement of unconfined yield strength in a Mohr diagram [78].](image-url)
As observed in Figure 2.10, if $ff_c$ is below 1, the powder is classified as not flowing, while a value above 10 categorizes the powder as free-flowing. In between there are 3 more categories ranging from very cohesive to easy-flowing.

- **Bulk/Tap Density**: consists in the characterization of the powder density in two different compaction states. The bulk density $\rho_b$ is obtained by pouring the powder in a predefined volume, without applying any external load on its surface or vibration to the powder container. The tap density $\rho_t$ corresponds to the bulk density of a powder that has been settled into a closer packing than existed in the poured state by tapping, jolting, or vibrating the measuring vessel [85]. Based on these two measurements, the flowability of the powder can be characterized by the so-called Hausner ratio defined by the following equation:

$$HR = \frac{\rho_b}{\rho_t} = \frac{V_t}{V_b} = \frac{h_t}{h_b}$$  \hspace{1cm} (2.4)

As the mass of the sample remains constant during the measurement, the ratio can also be calculated by the bulk and tap volume $V_b$ and $V_t$ or bulk and tap height $h_b$ and $h_t$ of the powder column. If the $HR$ ratio is below 1.25, the powder can be classified as good flowing material and if the $HR$ value is higher than 1.4 the powder is categorized as a very difficult flowing. Similar as previous methods, other categories are in-between [87].

The results provided by each method are strongly dependent upon the powder stress condition. Therefore, no single technique is suitable for the full characterization of the powder behavior and all of them, in principle, complement each other.

In case of SLS powders, Rietzel [88] utilized an annular shear cell to evaluate the flowability of different thermoplastic powders. All materials tested were classified as very cohesive ($1 < ff_c < 2$) and the only commercial PA12 material evaluated (PA2200) presented the highest $ff_c$ ratio with a value of 1.24. A comparison with the average particle diameter $D_{50}$ showed only a strong correlation for both extremes, i.e., the powder with the highest $D_{50}$ presented the best flowability and vice-versa. Also no correspondence was observed with the particle shape and no comparison with the powder packing density in the SLS powder bed was performed.

Wegner & Witt [89] employed the $HR$ ratio to characterize the powder flowability of PA2200 at different ageing conditions, i.e., a powder that was reused 5 times in a SLS machine. As the ageing state increased, a continuous increase of the $HR$ ratio was observed from 1.15 to 1.27. The study of the packing density in the SLS machine with hollow boxes similar to the work of Niino & Kazuki [38] revealed a growing variability of the packing density as the $HR$ ratio increased, but the average packing density remained almost constant. More recently Ziegel-
meier et al. [90] evaluated the flowability of a thermoplastic polyurethane (TPU) with different amounts of finer particles by using the HR ratio and a powder rheometer. This method assesses the powder sample’s tendency to change its bulk and flow properties when it is forced to flow by an helix rotating through the powder. As the amount of small particles decreased, the HR ratio reduced its value and the packing density increased due to the reduced effect of the inter-particle forces. A similar trend was observed with the rheometer measurements, but misleading results were obtained when a comparison with other materials was performed. Therefore a suitable characterization method must replicate as closely as possible the powder handling conditions. Figure 2.11 classifies the previous powder characterization methods according to the relation between the measurement condition and the powder stress state. A dynamic condition is defined if the particles are in motion during the measurement and a compacted state classification is used if the powder feature is measured at a packing density higher than the tap density. For the SLS deposition systems presented in chapter 2.1 it was discussed that compaction of the powder above its tap density is possible but difficult to achieve due to the excessive pressure between the roller/blade surface and powder bed. Also the powder is in continuous agitation during the deposition, presenting an avalanching behavior across the powder bed. Thus the region highlighted in Figure 2.11 corresponds to the area of interest that needs to be evaluated in order to improve the prediction of the flowability in the SLS process. In chapter 3 a characterization device based on a rotating drum will be presented and the flowability of different SLS powders will be evaluated. Also the temperature effect will be addressed, a parameter that was still neglected in the evaluation of SLS materials.

![Figure 2.11: Comparison between measurement condition and stress state for most common powder characterization methods.](image)
2.5 SLS Process Modeling

2.5.1 Overview of SLS Simulation

Despite the simplicity of the SLS concept of continuously adding layers of powder to form a 3 dimensional object, the complexity of the process and the interaction between the different phenomena involved has not been fully understood and only a couple of materials can be successfully processed for production [91,92,88]. In order to broaden the materials spectrum, several efforts have been performed to model the process incorporating the different physics involved. Since more than 20 years the research efforts have been concentrated in modeling the powders coalescence phenomenon during the laser scanning stage. The initial sintering model developed by Nelson et al. [93] employed a one dimensional finite element method to predict the density variations along the vertical build direction for an amorphous thermoplastic (polycarbonate). Later, Ryder et al. [94] extended the previous model to 2 dimensions, incorporating also the effect of a spatially dependent conductivity and porosity. Papadatos et al. [95] focused his work in the characterization and the modelling of the bonus-Z phenomenon (higher thickness of first sintered layers) by relating it to the laser energy input. Williams & Deckard [96] incorporated in their model the sintering law used by Nelson [97] coupled with the heat transfer and thermal degradation of an amorphous polymer. Bugeda et al. [98] and Childs et al. [99] improved the densification model description, including the equations of Mackenzie-Shuttleworth and Scherer for open and closed pore coalescence in powder beds. Steinberger et al. [100] and Schultz [101] incorporated the viscoelastic effect of polymer materials, a factor that was neglected during the transient coalescence of molten particles, improving the viscous model initially proposed by Nelson [97]. However, Tontowi & Childs [102,103] were the first to incorporate a sintering model that considers the latent heat of fusion by a temperature recovery method, which takes into account the melting enthalpy of thermoplastics, which are mostly used nowadays. More recently different studies have addressed diverse topics such as the volume shrinkage during densification [104] and finite element (FE) simulations and measurements of the transient part bed surface temperature during laser scanning using an infrared camera for metal powders [105], employing a dual wavelength infrared camera for polymer powders [106] and decomposing high speed CCD images in 3 wavelengths (RGB colors) for polymer coated metal powders [107]. Also parametric simulations based on the Design of Experiments (DoE) theory [108,109] have been performed to obtain high order response surfaces for the prediction of the sintered density in relation to the laser scanning parameters.
In summary, most of the models presented in the literature are focused to simulate the laser beam interaction with the powder bed within a millisecond timeframe, coupling a temperature dependent density function with nonlinear thermal properties. Jamal [110] developed a first FE model to simulate the final part deformation after sintering using an amorphous thermoplastic (polycarbonate), but the model fails to describe the behavior of semi-crystalline materials (e.g., PA12, PA6 or PP). Thus, none of these models really addresses the processing main difficulties observed when a new semi-crystalline thermoplastic is tested. Empirical evidence depicts that curling or warpage effect, i.e., the deformation of the sintered part as the build progresses, mostly defines the stable processability of a SLS material. Since warpage is directly coupled to the crystallization behavior, the processing temperature plays a vital role. For instance, if the part bed surface temperature $T_s$ is set at a high level within the sintering window, warpage can be reduced, but the lateral geometrical accuracy is affected. Conversely, if this temperature is set to low, warpage develops as observed in Figure 2.12. If the sintering window is reduced, the setting of this parameter is even more critical. Since other parameters like layer thickness or the temperature of the feed powder also affect the temperature management or the part bed, a better understanding of the transient crystallization phenomenon is needed. Drummer et al. [91] introduced the concept of crystallization activation energy based on DSC measurements as an indicator that estimates if a material guarantees certain robustness against undercooling to initiate the crystallization process. However the effect of the SLS processing conditions was not evaluated to validate their approach.

The next sections present the theories that describe the polymer crystallization and the viscoelastic behavior of semi-crystalline materials in order to simulate in chapter 4 the warpage development of a thermoplastic based in a multiphysics approach using a FE method.

Figure 2.12: Effect of part bed surface temperature on deformation development (warpage) and lateral geometrical accuracy for a thermoplastic material.
2.5.2 Polymer Crystallization Kinetics

The crystallization of semi-crystalline thermoplastics from the molten state is a complex process involving simultaneous nucleation and growth of crystalline structures. From a thermodynamic point of view, the crystallization process is controlled by the variation of the free energy of Gibbs $\Delta G$ between the crystal and molten states [111]. Since the internal energy change from liquid to solid is equivalent to the enthalpy of fusion $\Delta H_0$ at the equilibrium melting point $T_o$ and the surface energy of the nucleus is proportional to the surface area as it grows, the variation of the free energy of Gibbs can be written as [112]:

$$
\Delta G = V \frac{\Delta H_0}{T_0} (T - T_0) + A \gamma_{mn} = V \Delta G_c + A \gamma_{mn}
$$

(2.5)

where $V$ is the volume of the crystal, $A$ its surface area, $\gamma_{mn}$ the surface energy between solid and liquid and $T$ is the temperature below the melting point. According to Ehrenstein [113] in order to initiate the formation of stable nuclei, the melt has to be super-cooled to overcome the critical nucleus size $K_{crit}$ (Figure 2.13). The greater the degree of undercooling, the more favorable the thermodynamic conditions (high nucleation rate) and the more unfavorable the kinetic conditions (slow crystal growth). Thus with increasing $\Delta G_c$, the critical size of the nuclei is reached more rapidly and the number of nuclei increases. On the other hand, the macromolecules will become more inflexible and freeze as soon as the glass transition temperature is reached and the crystallization rate reduces its magnitude until the solidification process finishes. According to Ratta [114] the most comprehensive and widely used method

![Figure 2.13: Change in the nucleus formation free enthalpy $\Delta G$ as a function of the size of the nucleus and effect of temperature on nucleation and growth rates [113].](image)
to interpret and model the kinetics of the crystallization behavior of a large number of polymers in molecular terms that are crystallized from the melt into chain folded lamellae was developed by Hoffman and Lauritzen [115]. This theory describes the sequential deposition of polymer chains randomly folding back into a same lamella after the first nucleus has been formed (stem with dimension $a,b,l$) as presented in Figure 2.14a and 2.14b. The first step is called primary nucleation and the second step is named secondary nucleation, which presents a reduced free energy change in comparison to the primary nucleus, enhancing the process. Two opposing factors govern the growth of crystals: the thermodynamic free energy change $\Delta G_{\text{crit}}$ necessary for the formation of crystal nuclei and the energy barrier $U$ that must be crossed so that the molecular chains can move toward the surface of the crystal [116]. Therefore, Hoffman and Lauritzen integrated both effects summarized in the following equation:

$$G = G_0 \exp \left( \frac{-U}{R(T - T_\infty)} \right) \exp \left( \frac{-K_G(T + T_\infty)}{2T^2\Delta T} \right)$$  \hspace{1cm} (2.6)$$

where $G$ is the effective spherulitic growth rate and $\Delta T = T_\alpha - T$ corresponds to the undercooling from the equilibrium melting point $T_\alpha$, which can be determined by the Hoffman-Weeks construction [117]. $G_0$ is a temperature independent constant, $U$ is the activation energy of the crystallization transport which takes the universal value of 6270 J/mol, $R$ is the universal gas constant equal to 8.314 J/mol/K and $T_\infty = T_G - 30^\circ K$ is the temperature at which the crystallization transport finishes, with $T_G$ the related glass transition temperature of the polymer. $K_G$ is related to the secondary nucleation characteristics and depending on the undercooling degree, different crystal growth modes can develop based on the generation rate of the surface nuclei $i$ and the spreading rate of the surface nucleus along the surface $g$ as depicted in Figures 22c, 22d and 22e. $K_{GI}$ and $K_{GII}$ present a similar order of magnitude and $K_{GIII}$ is approximately half the value of $K_{GI}$. The derivation of the model can be reviewed in [114].

![Figure 2.14](image_url)

Figure 2.14: (a) Primary nucleation, (b) secondary nucleation and crystal growth rate modes at (c) low, (d) medium and (e) high degree of undercooling [116].
From a macroscopic point of view the overall polymer crystallization kinetics theories from the molten state describe the evolution of the degree of crystallization $\alpha(t)$ as a function of time $t$ and temperature $T$. The term degree of crystallization is related to the volume of material that changes from the molten to the solid phase and it must be not confused with the degree of crystallinity, which differentiates between the amorphous and ordered structures within the polymer solid state. More precisely the degree of crystallization is defined as the ratio of the crystallized volume $x_C$ to the ultimate crystallizable volume $x_\infty$ [118]:

$$
\alpha(t) = \frac{x_C(t, T)}{x_\infty} = \frac{\int_0^t \frac{dH_C}{dt} dt}{\int_0^\infty \frac{dH_C}{dt} dt}
$$

(2.7)

where $dH_C$ corresponds to the variation of the crystallization enthalpy during an infinitesimal time interval $dt$. Thus, in the molten state $\alpha$ takes the value of 0 and in a fully solidified specimen the value is 1. For polymer crystallization in quiescent isothermal conditions, the general Avrami equation (2.8) constitutes the base for the theory developed subsequently for non-isothermal crystallization [119]:

$$
\alpha(t) = 1 - \exp(-kt^n)
$$

(2.8)

where $k$ is the isothermal crystallization rate constant at a defined temperature $T$ and $n$ is the Avrami exponent. The bulk rate constant $k$ can be related to the number of nuclei generated $n_0$ and the constant radial spherulitic growth rate $G$ (spatial radial growth) according to the following expression:

$$
k = \frac{4}{3} \pi n_0 G^3
$$

(2.9)

In a non-isothermal process there is a change of temperature with time, leading to the time dependency of the crystallization constant. For a constant cooling rate, the modification of the Avrami equation results in the Ozawa model [120]:

$$
\alpha(t) = 1 - \exp\left(-\kappa(T)\left|\frac{dT}{dt}\right|^n\right)
$$

(2.10)

where $\kappa(T)$ is the so called cooling function of non-isothermal crystallization defined as:
\[
\kappa(T) = \left( \int_{T(0)}^{T(1)} K(T) dT \right)^n
\]  

(2.11)

However, a more general description was developed by Nakamura et al. [121] for variable cooling rates:

\[
\alpha(t) = 1 - \exp \left( - \int_0^t K(T) dt \right)^n
\]

(2.12)

where \( K(T) \) is the non-isothermal crystallization rate. The time differential form of this equation is more useful for modeling, leading to:

\[
\frac{\partial \alpha}{\partial t} = nK(T)(1-\alpha) \left[ \ln \left( \frac{1}{1-\alpha} \right) \right]^{n-1} / n
\]

(2.13)

For an isothermal condition, the Nakamura and Avrami rate constants can be related to each other by the following expression:

\[
K(T_{iso}) = k^n = \ln(2)^n \left( \frac{1}{t_{1/2}} \right)
\]

(2.14)

where \( t_{1/2} \) is the corresponding half crystallization time for a defined isothermal temperature, i.e., the time elapsed from the beginning of the crystallization process until 50% of the total solidification has been achieved. Now, when equations (2.9) and (2.14) are combined and a tridimensional spherulitic growth is assumed \((n=3)\), the following equation is obtained:

\[
\frac{1}{t_{1/2}} = \left( \frac{4}{3 \ln(2) \pi n_0} \right)^{1/3} G
\]

(2.15)

Thus, the reciprocal half crystallization time results proportional to the spherulitic growth rate \( G \). Substituting equations (2.6) and (2.15) in (2.14), the Nakamura crystallization rate results:

\[
K(T) = \ln(2)^n K_0 \exp \left( \frac{-U}{R(T-T_{ad})} \right) \exp \left( \frac{-K_G(T+T_o)}{2T^2 \Delta T} \right)
\]

(2.16)

The determination of \( t_{1/2} \) by isothermal DSC measurements allows evaluating \( K_0 \) and \( K_G \). In consequence, \( K(T) \) can be evaluated then for any \( T \) within the temperature range \( T_G-T_o \) [122].
2.5.3 Polymer Viscoelastic Behavior

Materials that present a dual mechanical behavior, i.e., a combination between an elastic solid based on the Hooke's law and a viscous liquid based on the Newton's law, are classified as viscoelastic materials and polymers are considered within this group. If the deformations of those materials are kept reduced, the linear viscoelastic theory is applied. This theory states that in case of the solid part, the stress is directly proportional to the strain and independent of the strain rate. In case of the viscous part, the stress is directly proportional to the strain rate and independent of the strain itself [123]. Thus, these kinds of materials can be modeled as a combination of springs and dashpots in order to describe the different transient effect such as relaxation or creep.

2.5.3.1. Constitutive Models for Linear Viscoelasticity

The two basic units that constitute a broad range of viscoelastic structures are defined by a Hookean elastic spring and a Newtonian viscous damper. Thus, the solid part can be modeled by the following equation:

\[ \sigma = E \varepsilon \]  \hspace{1cm} (2.17)

where \( \sigma \) corresponds to the stress, \( E \) to the elastic modulus and \( \varepsilon \) to the normalized deformation or strain. Similarly, the viscous part can be represented by the following relation:

\[ \sigma = \eta \frac{d\varepsilon}{dt} \]  \hspace{1cm} (2.18)

where \( \sigma \) corresponds to the stress, \( \eta \) to the viscosity and \( d\varepsilon/dt \) to the strain rate. It can be noted that the stress strain relationship for the elastic spring is independent of time and the viscous dashpot presents a transient behavior. Thus, for specific conditions the relation between stress and strain can be reduced in systems composed by these two units. For instance, in case of a deformation applied in a short period of time, the stress resisted by the dashpot can be considerable higher than the energy absorbed by the elastic spring. Conversely, in case of a strain applied during a long period of time coupled with a low viscosity, the stress resisted by the dashpot can be neglected for this particular situation.

A description from the most simple viscoelastic structure to the most general one in order to represent transient complex behaviors are presented in Figure 2.15 and the constitutive equation of each model are presented as follows:
- **Maxwell Model**: consists in the connection of a spring with elastic modulus $E$ in series with a viscous damper or dashpot with viscosity $\eta$. The differential equation that describes this system is:

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{E} \frac{d\sigma}{dt}$$

(2.19)

- **Kelvin-Voigt Model**: consists in the connection of a spring with elastic modulus $E$ in parallel with a viscous damper or dashpot with viscosity $\eta$. The differential equation that describes this system is:

$$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt}$$

(2.20)

- **Linear Solid Model**: consists in the connection of a spring with elastic modulus $E$ in parallel with a Maxwell element. The differential equation that describes this system is:

$$\frac{d\varepsilon}{dt} = \frac{1}{E + E_1} \frac{E_1}{\eta} \left( \frac{\eta}{E_1} \frac{d\sigma}{dt} + \sigma - E\varepsilon \right)$$

(2.21)

In case of the Maxwell model, if the structure is subjected to a fixed strain, the initial stress will be exponentially reduced with time, i.e., it will continuously relax until the tension vanishes. Conversely, in case of the Kelvin model, if the system is subjected to an initial fixed stress, the strain will growth continuously at a decreasing exponential rate until the final tension equals the stress resisted by the spring. This phenomenon is known as creep. The Linear Solid model combines the aspects of the Maxwell and Kelvin models in a single structure. However, it fails to describe the behavior of polymers with different relaxation times [124].
- **Generalized Maxwell Model**: consists in the connection of a spring with elastic modulus $E$ in parallel with a series of $n$ Maxwell elements, each of them with a spring with elastic modulus $E_i$ in series with a viscous damper or dashpot with viscosity $\eta_i$. According to Macosko [124] this model corresponds to the most general description of a material that undergoes a viscoelastic behavior with multiple relaxation times like a polymer in its molten state. It considers that the stress relief phenomenon does not occur simultaneously, i.e., there is a distribution of relaxation times. Since the relaxation of a single mode model presents an exponential decay form, the Generalized Maxwell model considers the linear superposition of exponential decays for the effective transient elastic modulus defined as:

$$\sigma = E(t)\varepsilon_0 = \left( E + \sum_{i=1}^{n} E_i \exp\left(-\frac{t}{\tau_i}\right)\right)\varepsilon_0$$

where $\tau_i = \eta_i/E_i$ corresponds to the relaxation time of each Maxwell branch and $\varepsilon_0$ to the fixed strain imposed. If the number of relaxation times considered increases, an improved approximation towards the continuous model results.

In general, the models presented previously can be applied not only for the elastic modulus $E$, but also for the shear or bulk moduli $G$ or $K$ respectively. Also a combination of Kelvin elements in series can be used to describe the creep behavior. In that case the compliance modulus $D(t)$ takes a similar form as the relaxation modulus defined by the following relation:

$$\varepsilon(t) = D(t)\sigma_0 = \left( D + \sum_{i=1}^{n} D_i \left( 1 - \exp\left(-\frac{t}{\tau_i}\right)\right)\right)\sigma_0$$

where $D$ corresponds to the instantaneous creep compliance modulus, $D_i$ to the compliance modulus of each branch and $\sigma_0$ to the fixed stress imposed. A schematic representation of both generalized viscoelastic models is depicted in Figure 2.16.

Figure 2.16: Diagrams of a multi-modal relaxation (a) and creep compliance (b) models.
2.5.3.2. Experimental Linear Viscoelastic Characterization

In order to determine the linear viscoelastic characterization of a polymer, several experimental methods can be employed, but depending on the condition to be evaluated, some of them are more convenient to provide data over a particular time range or stress condition. Moreover, it is often not easy to transform results from one type of linear viscoelastic experiment to another. For example, transformation from the creep compliance $D(t)$ to the stress relaxation modulus $G(t)$ is generally difficult [124]. According to Ferry [123] among the most common techniques for the characterization of polymer relaxation, sinusoidal oscillations are normally employed to evaluate a polymer in its molten state. This technique consists basically in the application of a sinusoidal deformation of the sample in the form of an extensional or shear strain at a specific frequency $\omega$, amplitude $\varepsilon_0$ and temperature $T$ while the stress response is measured. Thus the excitation and response equations are respectively:

\[
\varepsilon(t) = \varepsilon_0 \sin(\omega t) \quad (2.24)
\]

\[
\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad (2.25)
\]

where $\delta$ corresponds to the out of phase constant of the stress response. Due to this phase shift between stress and strain, the relaxation modulus presents an elastic part $E'$ called storage modulus that is in phase with the excitation and a viscous part $E''$ called loss modulus that is out of phase and is related with the energy dissipation per cycle. Both quantities can be combined in the so called complex modulus $E^*$. This modulus can be represented as a vector in the complex plane, whose direction is given by the phase angle $\delta$, and its magnitude is given by the ratio of the amplitude values of stress and strain [125]:

\[
E^* = E' + iE'' \quad (2.26)
\]

\[
|E^*| = \frac{\sigma_0}{\varepsilon_0} \quad (2.27)
\]

Thus, the storage and complex moduli can be represented by the following relationships:

\[
E' = |E^*| \cos \delta = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad (2.28)
\]

\[
E'' = |E^*| \sin \delta = \frac{\sigma_0}{\varepsilon_0} \sin \delta \quad (2.29)
\]
These magnitudes can also be combined to express the viscosity in terms of their real and complex parts:

\[
\eta' = \frac{E''}{\omega}
\]

(2.30)

\[
\eta'' = \frac{E'}{\omega}
\]

(2.31)

Since these previous variables are defined in the frequency domain, it is possible to obtain their response within a broad spectrum performing a frequency sweep, i.e., to repeat the rheological experiment varying \( \omega \) at a fixed small strain amplitude in order to remain within the linear viscoelastic range. This method presents the advantage that the polymer response can be evaluated at high frequencies which are related in the time domain to very high strain rates difficult to achieve with static relaxation or creep methods. For instance, Figure 2.17 depicts the results of the storage and loss shear moduli \( G' \) and \( G'' \) of molten DF PA12 at 210ºC and the respective complex viscosity for an amplitude and frequency sweep experiments using a plate-plate rheometer. This instrument applies a relative angular rotation between both surfaces in order to induce a shear strain at variable angular velocities. Figure 2.17b depicts the results for a frequency sweep test within the range between \( 10^{-1} \) rad/s to \( 5 \times 10^2 \) rad/s. An amplitude sweep was initially performed in order to define the maximum limit of the viscoelastic range, which in this case corresponds to a strain value of approximately 20% (Figure 2.17a).

As can be noted in this particular case, there is also a constant increase of \( G' \) as the amplitude sweep test develops due to the continuous post-condensation phenomenon where the ongoing reaction of the polymer chain end-groups increases the molecular weight, changing the viscous and mechanical properties as described by Schmid et al. [27] and confirmed in [126].

Figure 2.17: Duraform PA (DF PA12) oscillatory shear test results under an (a) amplitude sweep and (b) frequency sweep methods.
According to the Boltzmann’s Superposition Principle, the expressions for the storage and loss moduli in terms of the frequency $\omega$ are represented by following integrals:

\[ E'(\omega) = \omega \int_0^\infty E(s) \sin(\omega s) \, ds \]  
(2.32)

\[ E''(\omega) = \omega \int_0^\infty E(s) \cos(\omega s) \, ds \]  
(2.33)

As discussed by Dealy and Larson [127], in practice the conversion of an experimental data set ($E'$, $E''$, $\omega$ ($G'$, $G''$ in case of shear)) into a relaxation modulus function is usually carried out by representing $E(t)$ in terms of a generalized Maxwell model corresponding to equation (2.22). Thus, the oscillatory data are transformed into a set ($E_i$, $\tau_i$), i.e., a discrete relaxation spectrum. This transformation is based on the discrete form of equations (2.32) & (2.33):

\[ E'(\omega) = \sum_{i=1}^N \frac{E_i(\omega \tau_i)^2}{1 + (\omega \tau_i)^2} \]  
(2.34)

\[ E''(\omega) = \sum_{i=1}^N \frac{E_i(\omega \tau_i)}{1 + (\omega \tau_i)^2} \]  
(2.35)

If the oscillatory experiment is performed also at different temperatures, the curves can be grouped together at a reference value $T_{ref}$ based on the time-temperature superposition principle. This theory states that for polymers that are thermo-rheologically simple, i.e. materials that present the same temperature dependency for the whole relaxation process [128], changing the temperature of a measurement will have the same effect on the data as shifting the data horizontally on the time or frequency axis as described in Figure 2.18. For instance, a change in the temperature from a reference value $T_{ref}$ to a different temperature $T$ has the following effect on all relaxation times [127]:

\[ \tau_i(T) = a_T(T)\tau_i(T_{ref}) \]  
(2.36)

The variable $a_T$ corresponds to a horizontal shift factor that rescales in the time domain the measured results obtained at a temperature $T$ with respect to a defined reference temperature $T_{ref}$. Therefore, a master-curve that is independent of the different measured temperatures is obtained and the evaluation of the relaxation behavior at extended times can be achieved, which is normally not possible within a reasonable experimental time frame.
The most common empirical expressions to describe the time shift factor on temperature correspond to the Arrhenius and the Williams-Landel-Ferry (WLF) functions. The Arrhenius model considers the local motion of polymer chains while the WLF model is related to the macroscopic motion of the bulk material [129]. The equations that describe the Arrhenius and WLF models are respectively presented as follows:

\[
a_T(T) = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right)
\]

\[
a_T(T) = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})}
\]

where \(E_a\) correspond to the activation energy, \(R\) to the universal gas constant and \(C_1, C_2\) are to two empirical constants.

In case of semi-crystalline polymers, a similar approach can be employed for the crystallization degree \(\alpha\) using a time-crystallization superposition. In this case, the rheology of the polymer melt is characterized at an isothermal temperature below the melting point. Thus, as the polymer undergoes solidification, the evolution of the storage and loss moduli are measured. The oscillatory method presents the advantage that a frequency sweep can be performed relatively faster in comparison to the crystallization rate, provided that the super-cooling temperature is not too high. However, for this kind of measurements, no empirical relationships have been developed and each material must be individually characterized.
Since the results obtained by the oscillatory methods are frequency dependent, the transformation to the time domain must be performed. Instead of solving equations (2.34) and (2.35) to obtain the data set \((E_i, \tau_i)\) which is rather a complex problem without a unique solution, interrelation functions are employed, which correspond to approximations of the relaxation function in time using a combination of the harmonic response \(E'\) and \(E''\). Normally a shear rheometer is employed to perform the oscillatory measurements of molten polymers, thus the shear storage and loss moduli will be used as nomenclature. For the conversion between the frequency and the time dependent material functions, several approximate methods have been developed. Among the most common ones, the simplest approximation is to employ the storage modulus evaluated at a frequency \(\omega\) corresponding to the inverse of the time \(t\) [123]:

\[
G(t) \approx G'(\omega)\bigg|_{\omega=1/t}
\]

(2.39)

A minor modification using equation (2.39) was proposed by Christensen [130] and consists in evaluating the storage modulus at a different frequency value:

\[
G(t) \approx G'(\omega)\bigg|_{\omega=2\pi/t}
\]

(2.40)

Ninomiya and Ferry [131] introduced an interrelation based on a combination of both storage and loss moduli:

\[
G(t) \approx G'(\omega) - 0.4G''(0.4\omega) + 0.014G''(10\omega)\bigg|_{\omega=1/t}
\]

(2.41)

A similar relationship was obtained by Schwarzl and Struik [132] also using a combination of the harmonic moduli and other considering only the storage modulus:

\[
G(t) \approx G'(\omega) - 0.337G''(0.323\omega)\bigg|_{\omega=1/t}
\]

(2.42)

\[
G(1.44t) \approx G'(\omega) - 0.4\left(G'(1.59\omega) - G'(0.193\omega)\right)\bigg|_{\omega=1/t}
\]

(2.43)

There are even more complex expressions, but at the end the accuracy of each approximation must be taken into account in order to choose the most appropriate method. In this direction Emri et al. [133] performed a comparison between several interrelations calculating the difference or error with respect to the relaxation modulus obtained solving equations (2.34) and (2.35) using different polymers. The main result showed that if equation (2.39) is employed, the maximum error can be obtained. Additionally, no mayor differences between the approximations using equations (2.41), (2.42) and (2.43) were obtained with an error below 5%. Therefore, in chapter 4, equation (2.42) will be employed due to its simplicity for evaluating the experimental results.
2.5.4 Polymer Thermal & Density Properties

The heat transfer within a material is macroscopically described by the thermal heat capacity \( C_p \) and thermal conductivity \( k \), which coupled with the material density \( \rho \) define the thermal diffusivity. This quantity characterizes the ability of materials to conduct thermal energy in relation to their capability to store it and is considered as a measure of thermal inertia. The following sections present an overview of the temperature dependency of these polymer properties in their solid and molten states and the modeling of these features within a powder bed.

2.5.4.1. Heat Capacity & Thermal Conductivity

The specific heat \( C_p \) represents the energy required to change the temperature of a unit mass of material by one degree and the thermal conductivity \( k \) characterizes the transfer of internal energy by microscopic diffusion and collisions of particles due to a temperature gradient [134]. In case of semi-crystalline polymers, typically the heat capacity increases linearly with an increment of the temperature in the solid and molten states, while the thermal conductivity experiences a continuous reduction until the melting point is achieved. Due to the mixed composition of amorphous and crystalline structures, these materials present a discontinuity in their specific heat at the melting point of the crystallites, which includes the heat that is required to melt those structures (heat of fusion). Due to the increase in density upon solidification, the thermal conductivity is higher in the solid state than in the melt. In the molten state, however, the thermal conductivity of semi-crystalline polymers reduces to that of amorphous polymers as can be observed in Figure 2.19 [135].

Figure 2.19: Schematic behavior of polymer properties as a function of temperature and conductivity values for amorphous and semi-crystalline thermoplastics [134].
2.5.4.2. Heat Transfer in Powders

In the SLS process, the heat transfer takes place in two states, i.e., within the almost fully dense polymer melt that undergoes solidification and inside a powder bed that acts as support for the sintered parts. In the first state, the thermal properties correspond to those characterized for bulk materials, while in the powder state the thermal features are defined by the mixture of solid particles and the gas present in the interstices. For modelling purposes, the heat transfer between the particles and the gas is neglected and a continuum approach is employed to obtain an equivalent powder thermal property. In this direction, several models have been developed for the calculation of the effective thermal conductivity. For instance, Zehner and Schlünder [136] derived a model of a cylindrical unit cell with a particle inside, where its shape is taken into account and the rest of the volume is occupied by a fluid. Yugi and Kunii [137] used a similar unit cell approach and incorporated the effect of radiation between particles and Steinberger et al. [100] incorporated the particles agglomeration effect by correcting the amount of voids using an air jacket as previously presented in section 2.3.1. In order to evaluate the suitability of these models for the SLS process, Drexler et al. [138] determined the thermal conductivity of PA2200 between 140°C and 220°C by measuring the thermal diffusivity using a Nanoflash equipment. The results depicted no major differences between the models, with a thermal conductivity value between 0.075 and 0.1 W/m/K below the melting point and an almost constant value of 0.3 W/m/K for the molten range. More recently, Yuan et al. [139] measured the effective thermal conductivity of Duraform PA powder with different packing densities between 40°C and 170°C using a transient plane source measurement system (TPS), which basically consists of a heated cell, where the transient powder temperature variations between two points are characterized. As expected, the thermal conductivity results presented a lower value as the packing density diminished from 0.56 to 0.45 g/cm³. The values obtained for the thermal conductivity are comparable to those obtained by Drexler et al. [138], between 0.09 and 0.12 W/m/K for the whole temperature range and in general correspond to one third of the values measured for the solid material. Moreover, a comparison of the results with the model that considers the simple rule of mixtures reveals that a good approximation can be obtained for temperatures close to the melting point, reducing the complexity of the equations. Thus the relationship that characterizes this model is:

\[ k_{\text{powder}} = k_s \varepsilon + k_g (1 - \varepsilon) \]  

(2.44)

where \( \varepsilon \) corresponds to the porosity and \( k_s \) and \( k_g \) to the thermal conductivity of the particles and gas respectively. Also, a similar approximation for the specific heat can be employed.
2.5.4.3. Specific Volume & Thermal Expansion

The density variations of polymer materials with temperature are characterized by dilatometers, which normally express this property by its inverse, i.e., the specific volume. The specific volume is often plotted as a function of pressure and temperature in what is known as a $pvT$ diagram [135]. In general, this feature, for both amorphous and semi-crystalline polymers, increases linearly with temperature with a change of slope at the glass transition $T_g$ and crystallization $T_m$ points respectively. Due to this linearity within each region, a constant factor is employed called coefficient of linear expansion, which typically ranges between 20 and 300 $\mu$m/mºC for different polymers [113]. At the melting temperature, semi-crystalline polymers present a sharp increase of the specific volume during the transition from the solid to the molten state ($T_m$) due to the lower specific volume of the crystalline phase as observed in Figure 2.20. According to Kelly and Zweben [140] when a polymer melt is cooled, the chain molecules reduce their mobility and their distance decreases leading to this linear decrease of the specific volume with temperature. The chains begin to interact with each other, segment by segment, until glass transition or crystallization takes place. In case of the SLS process, due to the absence of external pressure during processing, the variations of the specific volume at low or ideally ambient pressure are of interest. Since most of the SLS materials employed are semi-crystalline thermoplastics, the sharp transition at $T_m$ results very critical for the potential development of warpage. Rietzel [88] evaluated the specific volume variation of PA2200 between 100ºC and 200ºC at a cooling rate of 3ºC/min from the melt as depicted in Figure 2.20. The curve at 1 bar was extrapolated from the measurements performed at higher pressure and a specific volume reduction of 0.05 cm$^3$/g was obtained at $T_m$. A comparison with standard coating polymers such as PP, POM and PE-HD revealed the particular reduced shrinkage of 50% lower for this particular SLS powder in comparison to standard polymers.

![Figure 2.20: Temperature dependence of specific volume of an (a) amorphous and crystalline structures [135] and (b) dilatometry measurement results of PA2200 [88].](image-url)
2.6 Research Gap

The previous chapters presented an overview of the main features of different Additive Manufacturing technologies and a more detailed description of the state of the art of the SLS process. Different aspects were included from the materials perspective that still need to be investigated and the different physics involved during the solidification stage of the sintered parts were presented. Since the SLS process is based on a chain of sequential demanding partial steps, a high powder packing during the spreading stage is a prerequisite to achieve a high dense part during the final crystallization stage. Thus, the processability of a SLS material is essentially defined by the flowability during the powder deposition step and the posterior crystallization behavior. In order to predict the processability as an integral concept, both previous aspects need to be sequentially investigated.

Extrinsic and intrinsic powder properties still need to be further characterized and evaluated in order to gain a deeper understanding and refine the requirements for a successful SLS material processability. In this direction, the development of new powder qualification prediction tools (currently unavailable for SLS) is a must in order to advance towards a more robust process. Despite that different efforts have been reported in the literature (sections 2.4.2 and 2.4.3), none of them has really taken into account the effective material stress state generated by the specific powder handling condition and the particular thermal environment, which has been neglected. Thus, both aspects were considered in the current investigation and a new characterization procedure and robust evaluation method were introduced.

Once the suitable powder packing conditions have been met, the coupled thermo-mechanical behavior during the crystallization or phase change of the material constitutes a fundamental role (section 2.5), particularly for the final geometrical accuracy. Currently only DSC experiments performed at fixed heating/cooling rate conditions are employed to assess the suitability of semi-crystalline polymers for the SLS process and a benchmark material is used as a reference (PA12). However, no further understanding of the process is currently available and the thermal evaluation is not enough to explain the deformation of the parts observed during the cooling stage. Thus, a comprehensive mathematical model of the solidification stage is needed in order to predict the deformation patterns observed during the cool down stage, topic that was addressed for the first time in the current work.

Finally, the development of both prediction tools will help to reduce the time and material resources during the early stages of the powder development phase and improve the robustness of the SLS process by reducing the empirical testing for a suitable processing set up.
2.7 Dissertation Outline

The first part of this work (Chapter 3) is focused in the analytical characterization of the powder behavior under a dynamic method that emulates the particular handling conditions during SLS processing. The specific objective is to develop a characterization method for the early stages of powder development. To achieve this goal a rotating drum equipment is employed and modified to include the temperature effect on the powders behavior, which constitutes a new quantitative characterization approach that has not been considered before in the SLS field. The aim of this study is to predict in advance if the flowing behavior of the polymer powder would be suitable or not for the SLS process and therefore reduce the development cycle time for the manufacturing of new materials. The scope of this study is limited to the main current commercial SLS powders available in the market, namely Duraform PA, PA2200, Duraform AF, Duraform HST, Duraform Flex, Orgasol, icoPP and two polyamide based materials produced by mechano-chemical milling and spray drying processes.

The second part of this dissertation (Chapters 4 and 5) assesses a fundamental aspect related to the crystallization behavior of semi-crystalline polymers during the SLS process once a high sintering density has been achieved. A Finite Element simulation model was developed in order to analyze the coupled effect between crystallization, temperature development and viscoelastic behavior. The aim of this study is to obtain a deeper understanding of the solidification and warpage development during the build process of the first layers. This kind of analysis could help in the future to simulate the production of complex geometries at a particular location within the powder bed and thus identify in advance critical positioning and orientation of parts. The scope of this study is limited to semi-crystalline thermoplastic materials, particularly polyamide 12 (Duraform PA12) and a recently developed co-polypropylene (icoPP).
3 Characterization of Powder Dynamics

The aim of this chapter is to introduce a new powder characterization method into the SLS field that gives information regarding the dynamic behavior under similar powder handling conditions when the material is spread over the powder bed. The intent is not to replace traditional methods (see Figure 2.11), but complement those existent to achieve a more accurate understanding about the SLS powder suitability and thus reduce the powder development cycle time for the manufacturing of new materials.

3.1 Dynamic Powder System: Operational Principle

The measurement device employed consists of a Revolution Powder Analyzer manufactured by Mercury Scientific Inc.. It consists of a rotating and an image acquisition system as shown in Figure 3.1. The rotating drum is machined in aluminum with an inner diameter of 50 mm and a width of 35 mm. The lateral sides are covered with transparent glass to allow the powder behavior inside be captured by the image acquisition system. The drum can be rotated at different speeds ranging from 0 to 200 rpm.

Figure 3.1: Schematic diagram of rotating and image acquisition system [92].
Characterization of Powder Dynamics

With the aid of a backlight source, the free surface and cross sectional area of the powder inside the drum can be recorded. Depending on the turning speed, two different tests can be performed: at a low value, a discrete behavior is achieved based on a sequence of avalanches; at a higher speed, a continuous operational mode is reached, characterized by a steady state regime. The testing methods are called Flowability and Fluidization respectively. For the present research, the initial set up and the different parameters employed for each method are summarized in the following table:

<table>
<thead>
<tr>
<th>Flowability Test</th>
<th>Fluidization Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>Sample Volume</td>
<td>25 cc (tap density)</td>
</tr>
<tr>
<td>Rotating Speed</td>
<td>0.6 rpm</td>
</tr>
<tr>
<td>Preparation Time</td>
<td>30 s</td>
</tr>
<tr>
<td>Avalanche Threshold</td>
<td>0.65 %</td>
</tr>
<tr>
<td>Angle Calculation</td>
<td>Half</td>
</tr>
<tr>
<td>N° Avalanches to record</td>
<td>128</td>
</tr>
<tr>
<td>Image capturing rate</td>
<td>15 fps</td>
</tr>
</tbody>
</table>

*Internal drum surface roughness: Ra=2.6 μm

Table 3.1: Flowability and Fluidization test set up parameters (RH: 40%; Room T°: 25 °C).

It must be pointed out that the drum rotational speed range for the Fluidization test can be adjusted to similar angular speeds of the translating roller during the powder deposition cycle in the SLS machine, e.g., 35 to 80 rpm at a translational speed of 77 to 177 mm/s for a 3DSystems SLS Sinterstation 2000 system equipped with a 50 mm roller diameter.

It is important to remark that with this method a nearly similar mechanical agitation of the powder can be achieved in comparison to the techniques presented previously in section 2.4.3 for the SLS layering. The boundary conditions generated for the powder inside the drum permit to emulate the typical turning powder wedge behavior produced by any of the actual SLS spreading systems, i.e., the counter-rotating roller (3DSystems) or the concave blade coater (EOS) as presented in Figure 2.2.
3.2 Characterization Indices

Based on the sequence of images captured by the acquisition system, the following characterization parameters for each image are obtained according to the specific test performed:

<table>
<thead>
<tr>
<th>Flowability Test</th>
<th>Fluidization Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avalanche Angle</td>
<td>Fluidized Volume</td>
</tr>
<tr>
<td>Surface Fractal</td>
<td>Fluidized Height</td>
</tr>
<tr>
<td>Volume Expansion Ratio</td>
<td>Final Settling Time</td>
</tr>
</tbody>
</table>

Figure 3.2: Flowability and Fluidization Indices.

- **Avalanche Angle (AA)**: corresponds to the angle obtained from a linear regression of the powder free surface at the maximum potential energy in relation to a horizontal reference prior to the start of the powder avalanche event. These events are defined by the avalanche threshold, which corresponds to the minimum variation of the potential energy between two consecutive images. If the difference between two sequential pictures is higher than the defined value, an avalanche takes place. Normally the left half of the diameter is considered to obtain a more representative measurement of the pile angle. As a general rule, the higher the avalanche angle the poorer the flowability. In comparison to the angle of repose presented previously in Table 2.3 (DIN ISO 4324), multiple measurements are taken to give a statistical distribution of values.

- **Surface Fractal (SF)**: corresponds to the fractal dimension $D$ of the free surface of the powder and provides an indication of how rough is the powder surface. The determination of this dimensionless parameter is based on the method used by Richardson [141] who...
proposed the empirical relationship relating the length estimate $L(\beta)$ with the scale $\beta$ of measurement given by:

$$L(\beta) = M \beta^{(1-F)}$$  \hspace{1cm} (3.1)

where $M$ is a positive value and $F$ is a constant at least equal to unity. In our study the length estimate is related to the powder surface length and the scale $\beta$ is varied between a minimum limit that is defined by the image resolution (i.e., the pixel size) and a maximum that corresponds to one third of the drum diameter. The measurement is performed after each avalanche with the drum in rotation to determine how the powder reorganizes itself. If the powder forms a smooth even surface, the surface fractal value will be close to one. If the surface is rough and jagged, the surface fractal will be greater than one.

- **Volume Expansion Ratio (VER):** corresponds to the ratio between the volume measured inside the drum (expanded volume that is related to the bulk density) and the volume occupied by the powder in the sample container before filling the drum during the preparation stage (compacted volume that is related to the tap density). The preparation step consists of filling a 25 cc container under manual tapping until the maximum powder compaction is achieved. Then the excess of powder on the upper surface of the container is scraped out with a blade to accurately define a fixed volume for all samples. The expanded volume is measured as the sum of the area of every image pixel occupied by the powder multiplied by the width of the drum. The VER is recorded after each avalanche event.

- **Fluidized Volume:** corresponds to the cross sectional area inside the drum which develops a near horizontal powder surface. The left limit of this area is defined by the minimum vertical distance between the bottom of the drum (lowest point) and powder free surface (see Figure 3.2). Typically the slope of a linear regression analysis of the cumulative volume that is fluidized versus the angular velocity of the drum is used to present the results.

- **Fluidized Height:** corresponds to the vertical distance measured from the bottom of the drum to the intersection of the line fitted by a linear regression on the top surface of the fluidized volume. Typically the slope of a linear regression analysis of the cumulative height of the volume that is fluidized versus the angular velocity of the drum is used to present the results.

- **Final Settling Time:** corresponds to the time elapsed until the powder sample stops settling, starting from the moment when the drum rotation is stopped at the maximum rotational rate. In this case the powder settling is measured by the transient reduction of the fluidized height.
3.3 Powdered Materials & Sample Preparation

A selection of different SLS commercial and lab-scale polymer based materials were tested with the aim to characterize their properties in relation to the indices presented in the previous chapter. This set of materials was selected because it represents diverse compounding and mixing methods to obtain powders with heterogeneous and homogeneous mixed phases. For example, Duraform HST (DF HST) corresponds to a dry blend of Duraform PA12 matrix with mineral fibers (wollastonite) and Duraform AF (DF AF) is based on a mixture between polyamide 12 (PA2200) and aluminum particles. Duraform Flex (DF Flex) corresponds to a cryo-milled thermoplastic elastomer and the lab-scale materials labelled as ST030 and ST065 were developed using mechano-chemical alloying and spray drying methods respectively, employing the similar polyamide 12 matrix (Grilamid L16 LM) with a 3% w/w of nanosilica.

Table 3.2 provides a summary of the materials selected and their principal features, including as a reference the three main percentiles (D10, D50 and D90) of a particle size distribution (PSD) analysis on volume basis considering an equivalent circular diameter. Since particle interaction forces (e.g. Van der Waals) become relevant for small polymer particles below 120 \( \mu m \) (section 2.4.3), a detailed analysis of the shape of the particles is out of the scope of this work. Only a qualitative appraisal of size and shape is depicted in Figure 3.3. Additionally each single interaction effect cannot be measured directly on spreading conditions and the combined effect of all these variables can be captured by a flowability characterization device.

<table>
<thead>
<tr>
<th>Material</th>
<th>DF PA12</th>
<th>PA 2200</th>
<th>DF AF</th>
<th>DF HST</th>
<th>DF Flex</th>
<th>icoPP</th>
<th>Orgasol</th>
<th>ST030</th>
<th>ST065</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Material</td>
<td>PA 12</td>
<td>PA 12</td>
<td>PA 12</td>
<td>PA 12</td>
<td>TPE*</td>
<td>coPP</td>
<td>PA12</td>
<td>PA12</td>
<td>PA12</td>
</tr>
<tr>
<td>Filler</td>
<td>None</td>
<td>None</td>
<td>Aluminum</td>
<td>Mineral Fibers</td>
<td>N/A</td>
<td>None</td>
<td>None</td>
<td>Nano-Silica</td>
<td>Nano-Silica</td>
</tr>
<tr>
<td>Final Compound</td>
<td>1 Phase</td>
<td>1 Phase</td>
<td>2 Phases</td>
<td>2 Phases</td>
<td>1 Phase</td>
<td>1 Phase</td>
<td>1 Phase</td>
<td>1 Phase</td>
<td>1 Phase</td>
</tr>
<tr>
<td>PSD (( \mu m ))</td>
<td>(D10=44)</td>
<td>(D10=39)</td>
<td>(D10=30)</td>
<td>(D10=64)</td>
<td>(D10=64)</td>
<td>(D10=40)</td>
<td>(D10=45)</td>
<td>(D10=45)</td>
<td>(D10=44)</td>
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<tr>
<td></td>
<td>(D50=56)</td>
<td>(D50=53)</td>
<td>(D50=60)</td>
<td>(D50=88)</td>
<td>(D50=88)</td>
<td>(D50=48)</td>
<td>(D50=97)</td>
<td>(D50=44)</td>
<td>(D50=44)</td>
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<td></td>
<td>(D90=76)</td>
<td>(D90=72)</td>
<td>(D90=70)</td>
<td>(D90=98)</td>
<td>(D90=98)</td>
<td>(D90=65)</td>
<td>(D90=115)</td>
<td>(D90=70)</td>
<td>(D90=70)</td>
</tr>
</tbody>
</table>

* Thermoplastic Elastomer; ** Not representative results for PSD with high different aspect ratios

Table 3.2: SLS materials tested with Revolution Powder Analyzer.
In terms of the sample preparation all new powders were previously stored under the same conditions (Relative Humidity: 40%; Room T: 25 °C) in open plastic containers. For each material, both proposed tests were performed according to the configuration previously described in Table 3.1. Before filling the drum, the powder was previously mechanically tapped by hand on a flat surface using a polymer container (25 cc) during 3 min. The container was filled incrementally while the tapping process was conducted in order to achieve a homogenous powder compaction along the vertical direction. Afterwards the weight of the sample was recorded and the drum was filled.

For each powder tested 3 consecutive flowability measurements were performed at room temperature without removing the powder from the drum. Afterwards, 3 sequential fluidization tests were conducted with the same powder sample inside the drum. Between measurements with different powders, the glass covers and inner surface of the drum were cleaned with a soft cloth and technical grade ethanol (99%).

Figure 3.3: Microscopic image sample of SLS powders tested (600x600 μm each).
3.4 Powder Dynamic Results and Analysis

3.4.1 Flowability Results

Figure 3.4 depicts the cumulative avalanche angle distribution for each material. As noted, different materials present different median values (50th percentile or D50) and also different curve shapes. A low median angle coupled with a narrow distribution (D90-D10) is correlated to a good flowing powder. As observed, icoPP, Orgasol and ST065 present the lowest median D50 of 38, 38 and 40 degrees respectively. These three powders have in common a small PSD with an almost spherical shape and the presence of one phase (pure material). However, even that ST065 presents qualitatively the most spherical particles (Figure 3.3) it has the highest avalanche D50 with the whole curve slightly shifted to higher values. The lowest PSD D10 of 22 \( \mu m \), which is half the value of the other two materials, explains this behavior. This example reveals how important the interaction force become as the particle size is reduced.

Following this group, DF PA12, PA2200 and DF AF constitute a second cluster with similar results. The median avalanche angle D50 achieves a value of 44 degrees and these powders present a less spherical shape in comparison to the previous group (no relevant differences appears between 1 or 2 material phases, i.e. DF AF). In this case there is almost a superposition of curves, which can also be correlated with similar values for all PSD percentiles D10, D50 and D90.

![Figure 3.4: Cumulative Avalanche Angle distribution.](image-url)
Finally, particles with a less geometrically defined shape or compounds with different shape aspect ratios, i.e., fibers or more complicated geometries like flakes can be grouped in a set of materials that present the highest avalanche angle and broader curve distributions. Within this group, a common characteristic is difficult to assess due to the heterogeneity of the materials (DF HST, DF Flex and ST030), but the influence of the particles shape can be clearly appreciated. Also ST030 presents the highest PSD span (D90-D10) of 70 μm.

According to Barabási et al. [142] the theoretical calculation of the stability of a pile of 4 spherical beads (mono-modal PSD, no inter-particle forces, smooth surface) in a tetrahedral configuration on a tilting plane results in a minimum average avalanche angle of 23 degrees. However, according to the results obtained, it can be stated that an avalanche angle D50 lower than 35 degrees is difficult to obtain and this value can be proposed as an empirical minimum for good flowing SLS polymer based materials.

The surface fractal results are depicted in Figure 3.5. In comparison to the avalanche angle distribution behavior, this index does not distinguish between near spherical or broader shape distribution powders, which can be grouped together with an average surface fractal D50 of 1.62 (DF PA12, PA2200, icoPP, Orgasol and ST065). A second set of powders constituted by compounds with two heterogeneous phases, i.e., DF AF and DF HST, can be clearly differentiated with an average D50 value of 2.3. These results indicate that the free boundary generated after the avalanche for this second group presents a more structured or jagged surface that influences the packing density of the powder. Extremely distorted particle geometries like of ST030 and DF Flex present clearly higher surface fractal value.

![Figure 3.5: Cumulative Surface Fractal distribution.](image-url)
Figure 3.6: Correlation between Avalanche Angle and Surface Fractal.

Figure 3.6 presents the relationship between the avalanche angle and the surface fractal. As can be noted a positive correlation exist between both variables, i.e., as the avalanche angle increases, the surface fractal increases as well. Even all materials can be bounded (99% of all results) by upper and lower limits defined by the following linear equations:

\[
S_{FU} = \frac{9}{10} A_{AU} - 26 \\
S_{FL} = \frac{2}{35} A_{AL} - \frac{11}{7}
\]

(3.2)

(3.3)

where \(A_{AU}\) and \(A_{AL}\) are valid for values higher than 30 and 45 degrees respectively. Even that these limits were arbitrarily defined, they can help to predict the maximum surface fractal value expected below 40 degrees and the minimum surface fractal value anticipated for avalanche angles above 45 degrees.

Figure 3.7 summarizes the results presented above for the median value of each index (D50). Additionally, the volume expansion ratio (VER) is included and the normalized bulk density of each powder measured inside the rotating drum. As observed, two main trends can be established. First, as the avalanche angle increases, the VER increases as well. This VER indicator, due to its definition, can be correlated to the Hausner Ratio described in equation (2.4) which relates the tap and the bulk density of a powder.
Figure 3.7: Summary flowability indices results (D50) and normalized bulk density.

However, this index fails to describe accurately the behavior of DF Flex, since according to the VER value, DF PA12 and DF Flex should present the same ability to flow, which disagrees with the empirical evidence, coupled with the fact that the avalanche angle median is considerably higher than DF PA12 and the bulk density significantly lower (almost 50%).

Second, in general, an opposed effect between normalized bulk density and avalanche angle can be observed. As the bulk density decreases, the avalanche angle increases. In case of ST030, despite having a lower density and higher VER in comparison to DF Flex, it presents a considerable lower surface fractal value. Therefore, both indices do not allow ranking adequately by themselves the powders in terms of a proper packing performance. Thus, a new indicator denominated packing index ($PI$) is proposed, defined as follows:

$$PI = V_{ER} \cdot S_F$$  \hspace{1cm} (3.4)

This proposed index combines the effect of the volume expansion inside the drum with the rearrangement of the particles after an avalanche, integrating more information in one single index. The theoretical minimum value that this index can take corresponds to one, since the minimum value of the VER can also be the unit when no volume change is observed between the bulk and tap conditions (constant density). In case of the surface fractal $SF$, the theoretical minimum is also defined by the unit when the powder free surface presents a flat condition.
Figure 3.8: Comparison of flowability indices (D50) versus normalized bulk density.

In order to validate the accuracy of the packing index, Figure 3.8 depicts a comparison between each measured index for all the materials tested and the normalized bulk density. As can be observed, all the variables present an acceptable linear relationship with a correlation coefficient $R^2$ higher than 0.5. However, with values of 0.82, 0.63 and 0.82 for the avalanche angle, surface fractal and packing index respectively, the first and last indices present the best accuracy and could be used indistinctively as classification parameters under these measurement conditions.

Among the variables presented, it is important to remark that the ratio between the expanded volume inside the drum and the volume of the compacted material in the sampling container ($VER$) is in principle identical to the definition of the Hausner Ratio ($HR$) derived from compressibility studies. However, this parameter differs in this study in how the bulk and tap densities are measured and how these conditions are generated. Besides starting from a loose powder state to achieve a more compacted state as is defined in the norm ASTM D7481, the initial condition of the powder inside the drum presents a partially compacted state due to the initial mechanical tapping in the sampling container. This state is more representative of the compaction of the powder inside the feeders in the SLS equipment. Then, when the powder is spread from the feeders to the part bed, it begins to expand by a similar mechanical agitation principle generated inside the drum. Additionally the sample preparation procedure guaranties starting from a powder state condition that is more consistent (tapped density) than from a less defined “bulk state”.

\[
y = -0.0169x + 1.1991 \\
R^2 = 0.8238
\]

\[
y = -0.0937x + 0.618 \\
R^2 = 0.6326
\]

\[
y = -0.0773x + 0.63 \\
R^2 = 0.8168
\]
3.4.2 Fluidization Results

Regarding the test at higher rotational speeds, the results for the fluidized volume and height are depicted in Figures 3.9 and 3.10.

![Cumulative Fluidized Height](image1)

**Figure 3.9:** Cumulative Fluidized Height.

![Cumulative Fluidized Volume](image2)

**Figure 3.10:** Cumulative Fluidized Volume.
Both figures depict a linear correlation between the drum speed from 50 to 90 rpm and the fluidized height and volume. As noted, materials with a finer PSD and near spherical shape present the maximum volume slopes. For the fluidized height the same trend is observed. It must be pointed out that the term “fluidized” refers specifically to a powder that presents a bulk volume expansion due to the entrapped air or gas during powder agitation when the fluid evacuates the powder interstices at a lower rate than the fluid that is introduced inside the inter-particle voids. However, this condition might not be necessary to achieve a volume expansion. Thus, it must be distinguished between the effect of a real fluidization or just a volume dilatation due the reduction of the coordination number when particles move in a shear displacement relative to each other. This phenomenon is known as dilatancy (for the Fluidization test its name is used indistinctively for any of both conditions, i.e., a real fluidization or dilatancy [143]). This effect can be analyzed by the Final Settling Time parameter. If after the drum detention this value turns out to be negligible, it indicates that the particles remain in contact due to their interconnections and the powder does not really fluidize.

Analyzing the results depicted in Figure 3.11, it can be observed that the first three materials present the highest settling times coupled with the maximum height and volume slopes. It can be stated that these powders develop a fluidized state. DF PA12 and PA2200 depict lower settling time values correlated to an incipient fluidization. On the other hand, both filled

![Graph](image_url)

**Figure 3.11:** Summary of average results for fluidization indices.
Characterization of Powder Dynamics

materials with heterogeneous phases (DF AF & DF HST) and DF Flex clearly show a dilata-
cy effect with lower volume expansion rates. DF Flex seems even to be invariant to the drum
rotational speed. This can explain why it presents a lower VER value as the bulk volume re-
mains almost unchanged from its compacted condition (tap density). In case of material
ST030 a particular condition occurs. The powder partially fluidizes with a lower volume ex-
pansion rate and a higher height slope. From the flowability results, this powder presents the
maximum VER value. This indicates that the powder easily reaches a low bulk density (high
expanded volume) from its initial compacted condition (tap density) under slow rotational
speeds. That can be achieved only due a dilatancy effect. Therefore, this material, due to its
particle flake shape, increases its height just at the top free surface due the avalanching effect
coupled to a high interlocking between particles, but without increasing the fluidized volume
width (the fluidized width is obtained by the ratio between the fluidized volume and the fluid-
ized height and drum depth), which remains quite similar to DF PA12 (see Figure 3.2).

Concerning the SLS powder deposition, a distinction between fluidization and dilatancy could
predict to a certain extent how the deposition speed can affect the packing conditions. If the
powder presents a higher fluidization rate like material ST065, a higher speed will lead to a
poor packing state. Thus, a lower translational velocity of the spreading system must be con-
sidered. On the other hand, if the powder density condition is less sensitive to this variable, a
relative constant packing will be achieved. However, if a strong dilatancy effect is present,
like for material ST030, a lower part bed density could also be obtained.
3.5 Effect of Temperature on Powder Dynamics

3.5.1 Heated Drum Modification and Set Up

Since the SLS process takes place at an elevated temperature within a heated chamber, the potential effect on the dynamic behavior of the powder needs to be investigated. In order to achieve this aim, the rotational drum was modified, incorporating a heating system that can replicate the temperature during the process. For this purpose, the drum was assembled from two aluminum parts that can be joined by a central thread (see Figure 3.12). On the inner surface of the drum half with the largest central core diameter, a bronze annular ring was placed with a flexible electrical heating band (115W) attached to its exterior surface. A t-type thermocouple is located just below the heating element in contact with the bronze surface in order to measure the temperature as close as possible to the surface in contact with the powder. When the drum is assembled, the power and sensor cords are allowed to exit the drum between both halves. So the aluminum drum can rotated freely while the central heating element remains static. With this configuration the maximum temperature that can be achieved is 110°C without any further equipment modification or isolation from its standard condition.

It must be pointed out that the maximum temperature of interest corresponds to the preheating of the powders within the SLS machine feed containers and not the temperature at which the powder is heated at the top of the central powder bed, which is normally close to the melting point in case of thermoplastic polymers. Such a high temperature is not reached by the powder until it has been deposited as a layer on the top of the part bed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Volume</td>
<td>25 cc (tap density)</td>
</tr>
<tr>
<td>Rotating Speed</td>
<td>10 rpm</td>
</tr>
<tr>
<td>Preparation Time</td>
<td>30 s</td>
</tr>
<tr>
<td>Avalanche Threshold</td>
<td>0.65 %</td>
</tr>
<tr>
<td>Angle Calculation</td>
<td>Half</td>
</tr>
<tr>
<td>N° Avalanches to record</td>
<td>512</td>
</tr>
<tr>
<td>Image capturing rate</td>
<td>15 fps</td>
</tr>
</tbody>
</table>

Figure 3.12: Modified rotating drum with a central heating element.
Thus, for the materials considered, the maximum preheating temperature corresponds to that used for DF PA12 with a value of 120°C. Table 3.3 summarizes the particular part bed and feeders temperature used to process those materials in SLS equipment. As can be observed, the pre-heating temperature is almost 50°C lower than the part bed set point for all polyamide based materials and icoPP. For the current experiment, the maximum drum temperature was employed, which is 10°C lower than the feeders set point during SLS processing. In case of icoPP and DF Flex, also a similar temperature reduction was used to be consistent with all materials. Additionally, 3 different temperatures were considered for each material: 30°C, 70°C and 110°C for PA12 based materials and 30°C, 45°C and 60°C for icoPP and DF Flex.

For the powders tested 3 consecutive flowability measurements were performed at each pre-defined temperature without removing the powder from the drum. Between the different temperatures, a waiting time of 20 min was employed in order to achieve a homogeneous temperature distribution within the powder sample, keeping the drum in rotation. As presented in Figure 3.12, only the flowability test is considered. The fluidization test could not be performed, due to the higher sticking effect at elevated temperatures of the powder in contact with the glass covers at the edges of the internal drum surface. The accumulation of powder particles at the edges hinders a clear definition of the drum boundary, generating misleading results. Also the rotational drum speed for the flowability test needed to be increased up to 10 rpm in order to reduce the contact time between the powder and the drum. At lower speeds the powders also tend to stick at the inner drum boundary, generating a similar undesired effect as obtained with the fluidization test.

Since the speed of the drum was increased, the effect on the measurement indices was previously analyzed. As depicted in Figure 3.13, the variation of the speed from 0.6 rpm up to 10 rpm generates a continuous increment of the avalanche angle and surface fractal values.
However, the shape of cumulative curves does not remain invariant with the speed increase, presenting a higher shift of values above the median, which can be explained due to the higher centrifugal force exerted on the particles at the boundary of the drum, allowing them to reach a higher height previous the occurrence of an avalanche event. Thus, the shape of the distributions will be considered for the subsequent analyses.

3.5.2 Flowability Results at Elevated Temperature

The results of the measurements of the avalanche angle and surface fractal at 3 different temperatures are depicted in Figures 3.14 and 3.15 for each material. The first main observation is that a temperature change clearly generates an effect on the flowability of the powders.

In case of DF PA12 and PA2200 a continuous increase of the avalanche angle is obtained from 30°C to 110°C. In case of DF AF and DF HST a first reduction of values is observed from 30°C to 70°C, particularly above the median of the distributions. At 110°C both materials present an avalanche angle that remains almost constant or with a slightly reduction. A similar effect is also observed for ST065, but in this case even the values below the median present a reduction with the temperature increase above 30°C. Regarding DF Flex, icoPP, Orgasol and ST030 the temperature effect on the avalanche angle presents a reduced effect, since all the curves depict an almost constant behavior.
Figure 3.14: Avalanche Angle results at different temperatures.
Figure 3.15: Surface Fractal results at different temperatures.
Regarding the surface fractal, the materials present different results (Figure 3.15). In case of DF PA12 and PA2200, a first reduction of values is observed from 30°C to 70°C, which results more pronounced for PA2200, with a reduction from a median of 2.31 to a value of 2.02 versus a decrease from a median of 2.86 to a value of 2.71 for DF PA12. At 110°C both materials present surface fractal results that are even higher than the values obtained for a temperature of 30°C (D50 of 2.60 and 2.99 for DF PA12 and PA2200 respectively). A similar behavior presents DF Flex, but with surface fractal distributions considerably shifted to higher values.

In case of DF AF and DF HST, a similar trend as the previous materials is obtained at the transition from 30°C to 70°C, with a considerable reduction for the material filled with aluminum particles. However, at 110°C, both materials present surface fractal median values that are lower than the results obtained at a temperature of 30°C. A similar effect is also observed for ST065, but in this case a continuous reduction of the surface fractal value is observed with the temperature increase above 30°C.

Regarding icoPP and ST030, a continuous increase of the surface fractal is obtained from 30°C to the corresponding highest temperature of 60°C and 110°C respectively. However, for ST030 a minor difference exists between 70°C and 110°C. Finally, Orgasol presents almost an invariant condition in terms of surface fractal variations with temperature. This result can also be correlated with the nearly constant avalanche angle behavior in Figure 3.14.

In general, it can be stated that the avalanche angle is less sensitive to temperature variations in comparison to the surface fractal, particularly for values below the median of the distributions. Since the avalanche angle is based on a linearization of the powder surface inside the drum, the surface fractal is more sensitive to capture changes of the shape or “roughness” of the free surface. Thus, if the powder particles start slightly to form agglomerates with the temperature increase, the surface fractal parameter will be able to detect these variations before the avalanche angle registers any difference.

Since the powder inside the drum is in a dynamic condition, it is difficult to identify which of the particles interaction variables are influencing mostly the flowing behavior. For example, it cannot be clearly distinguished if the temperature dependent surface forces related to the particular chemistry of the material dominate or if the interlocking phenomenon related to the geometry of the particles is dominating the flowing behavior. As a further element, due to the viscoelastic nature of polymers, for PA12 based materials it is known that a steep reduction of the storage modulus is obtained at the glass transition temperature of about 50°C, which might be correlated with the more significant changes of the avalanche angle and surface fractal at the temperature transition from 30°C to 70°C (range where the glass transition is included).
than in the range from 70°C to 110°C as can be observed for materials with the same polyamide 12 matrix.

Independently of the factors or variables that influence the dependence of the flowability with the temperature, the main objective of this investigation is to find out a general robust descriptor that characterizes the powder packing density under similar powder handling conditions and temperature as in a SLS equipment. Therefore, the performance of the previously proposed indicator packing index $PI$ was evaluated in terms of the normalized packing density value for each material and at different temperatures.

Figure 3.16 depicts the results for the median value of the avalanche angle, surface fractal and $VER$ for all the materials at different temperatures in relation to the normalized bulk density inside the drum. First, it is important to note that when the drum speed is increased from 0.6 rpm to 10 rpm, the linear correlation for the avalanche angle is considerably lower even at similar testing temperatures (25°C and 30°C respectively). The correlation coefficient $R^2$ is reduced from 0.82 (Figure 3.8) to 0.22 (Figure 3.16), which is driven primarily by material ST030. In this case, there is a considerable reduction of the avalanche angle with the speed increment, which denotes the sensitivity of this parameter to the dynamic measurement conditions. While the avalanche angle D50 experiences a reduction of 17%, the surface fractal median increases by 7%. Now comparing the three flowability indicators at 30°C for all materials, the $VER$ depicts in average the best performance, being the only one with a suitable linear correlation coefficient above a value of 0.5 in all cases. At higher temperatures, the trend between the indices remains the same. However, at the medium (45°C and 70°C) and high (60°C and 110°C) temperature testing conditions, the avalanche angle even decreases its relationship with the normalized bulk density. At the same time, the surface fractal presents an improved performance and the $VER$ depicts the lowest variability, remaining above a $R^2$ value of 0.60 and being the most robust of these three indicators. As mentioned in section 3.5.1, until now the analysis has only considered one representative value of the distributions, focused in the median. This assumption is suitable for symmetric distributions, were the mean and median values are the same. However, since the cumulative curves obtained are non-symmetric and also change under different testing configurations, it results necessary to incorporate a shape descriptor. One of the most used non-dimensional parameter to describe the symmetric condition is the so called skewness. The definition of the skewness employed is as follows:

$$S_{ki} = \frac{D_{90_i} - D_{50_i}}{D_{50_i} - D_{10_i}}$$

where $D_{90}$ and $D_{10}$ correspond to the 90th and 10th percentiles of the cumulative distribution.
Figure 3.16: Comparison of flowability indices (D50) versus normalized bulk density at 10 rpm and different temperatures.
For a symmetric distribution, the skewness presents a value of one. If the cumulative curve presents a bias to higher values, the skewness is larger than 1 and vice versa. A concentration of avalanche angle and surface fractal values above the median indicates a detrimental effect on flowability. Thus, the skewness can be used as a correction factor that incorporates the effect of the shape on the median values previously obtained. Therefore, the following corrected flowability indices are proposed:

\[ A'_A = A_A \cdot S_{kA_s} \]  
\[ S'_F = S_F \cdot S_{kS_r} \]  
\[ V'_{ER} = V_{ER} \cdot S_{kV_{ex}} \]  
\[ P'_I = V_{ER} \cdot S_F \cdot S_{kV_{ex}} \cdot S_{kS_r} \]

The average of the different shape factors considering all temperatures is summarized in Table 3.4. As observed, in general the shape factor correction for the avalanche angle depicts that there is a bias to higher values above the median that can be up to 28% higher. In case of the surface fractal, a similar trend is observed, but the skewness factors are even higher (up to 53%). For the VER the results depict different values, with correction factors that can vary between -10% up to 14%.

In order to evaluate the effect of the shape information on each descriptor, the modified flowability indices were calculated and the results are presented in Figure 3.17. As can be noted, the avalanche angle correlation coefficient did not present any significant improvement/increase respect to the previous results and almost no linear correlation with the normalized packing density exists (\(R^2\) below 0.3). However, the surface fractal \(R^2\) in fact presented a clear improvement at almost all temperatures with an \(R^2\) above 0.5 in all cases (at the maximum testing temperatures it achieves a \(R^2\) of 0.88).

<table>
<thead>
<tr>
<th>Material</th>
<th>DF PA12</th>
<th>PA2200</th>
<th>DF AF</th>
<th>DF HST</th>
<th>DF Flex</th>
<th>icoPP</th>
<th>Orgasol</th>
<th>ST030</th>
<th>ST065</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skew. (A_A)</td>
<td>0.98</td>
<td>0.96</td>
<td>1.15</td>
<td>1.18</td>
<td>1.16</td>
<td>1.28</td>
<td>1.06</td>
<td>1.20</td>
<td>1.07</td>
</tr>
<tr>
<td>Skew. (S_F)</td>
<td>1.21</td>
<td>1.26</td>
<td>1.28</td>
<td>1.19</td>
<td>1.10</td>
<td>1.36</td>
<td>1.06</td>
<td>1.28</td>
<td>1.53</td>
</tr>
<tr>
<td>Skew. (V_{ER})</td>
<td>0.98</td>
<td>1.01</td>
<td>0.96</td>
<td>1.14</td>
<td>0.95</td>
<td>0.90</td>
<td>0.93</td>
<td>1.03</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 3.4: Calculated average skewness for each index and different materials.
Figure 3.17: Comparison of flowability indices (D50) versus normalized bulk density at 10 rpm and different temperatures corrected with shape factor.
Interesting is the effect on the VER index. Even that the variations of the skewness factor are lower in magnitude than those obtained for the avalanche angle and surface fractal, the modified VER index presents a reduction of the linear correlation with the normalized bulk density at all temperatures. These results illustrate that the analysis of the flowability considering the avalanche angle, surface fractal and VER indices individually is not optimal and the combined information needs to be analyzed.

In this connection, Figure 3.18 depicts the results for the previously proposed packing index $PI$. This parameter combines the effect of the volume expansion inside the drum with the rearrangement of the particles after an avalanche. As can be observed this indicator depicts an improved performance in comparison to all previous indices, being the only one with a minimum linear correlation coefficient value of 0.72 for the non-shape corrected case ($PI$).

![Graph showing the relationship between normalized bulk density and packing index at different temperatures](image)

Figure 3.18: Comparison of $PI$ (D50) versus normalized bulk density at 10 rpm and different temperatures without and with shape factor correction.
For the case considering the shape factor or skewness effect (PI'), the correlation coefficient depicts even a higher value and lower variability, obtaining a $R^2$ of 0.86, 0.87 and 0.86 at the temperatures of 30ºC, 45ºC/70ºC and 60ºC/110ºC respectively. Additionally, the slope and intercept values of the linear regressions remain almost constant at all temperatures with maximum differences below 2% and 3% for the slope and intercept respectively. Figure 3.19 summarizes the average correlation coefficient $R^2$ obtained at the different temperatures between the normalized bulk packing density and the 4 flowability indices. As observed, the packing index depicts the best correlation of all indicators with an average $R^2$ of 0.83 and 0.86 with and without shape factor correction.

In general, it can be concluded that the avalanche angle median results are good estimators at low rotational speeds and at room temperature (Figure 3.8). However, if the dynamic agitation of the powder and temperature increase, the new packing index PI constitutes a more robust indicator to predict the normalized bulk density of SLS powders. Since the slope and intercept of the linear regressions are almost invariant an estimated normalized bulk packing density $\rho_{BN}$ at elevated temperatures can be predicted by calculating the PI' indicator at reduced temperature. Thus, the following equation is proposed for SLS materials:

$$\rho_{BN} = -0.056 P_{I'}|_{30^\circ C} + 0.62$$

(3.10)

It must be pointed out that this new indicator was empirically validated using the rotational drum. How this indicator behaves under SLS conditions will be analyzed in the next section.

Figure 3.19: Comparison of average linear correlation coefficient $R^2$ at different temperatures for each flowability index (D50) with and without shape factor correction.
3.6 Correlation with SLS Process

3.6.1 Normalized Bulk and Packing Densities

In order to analyze the accuracy of the previous flowability indices applied to the SLS process, the packing density of the part bed after the powder deposition needs to be investigated. For this purpose, the same approach used by Niino & Kazuki [38] was implemented, which consists in sintering hollow boxes using each material at standard processing conditions. The dimensions of the boxes used are 52x52x5 mm with a wall thickness of 1 mm. The packing density is then calculated by measuring the mass difference of the boxes with and without powder inside divided by the volume of the box. Also the sintered density of the box was characterized. This was measured employing the Archimedes method using acetone as fluid with a density of 0.78 g/cm³ at room temperature (25°C) [144]. For DF Flex and ST030 this method cannot be applied since the density of the sintered samples is lower than the density of acetone. Also the porosity results too high, letting the inside voids be filled by the fluid leading to misleading results. Thus, the density was measured by taking the ratio between the weight and the external dimension of the sample (box wall bottom). Figure 3.20 depicts the results for the average normalized packing density value of 3 boxes using each material and the median value for the normalized bulk density measured inside the drum at the 3 temperature levels. Also the average normalized sintered density of 3 samples per material is shown.

![](image.png)

Figure 3.20: Comparison of normalized bulk, packing and sintered density.
As a first observation, the materials with the highest bulk density present the highest density reduction as the temperature increases, since the thermal expansion effect results more effective when a higher coordination number between the particles exists. In case of materials with a lower bulk density, the coordination number is reduced and the temperature variations do not generate any significant volume change. Second, the packing density is higher than the bulk density for all materials. This result can be explained due to a slightly compaction effect generated by the roller during the spreading stage. Also it is interesting to note that icoPP and Orgasol present the highest change from the bulk to a packing state due to their good flowing behavior. Additionally, in general, a positive correlation between the normalized packing density and the normalized sintered density exists. However, for materials with a normalized packing density value above 0.4 other factors such as the viscosity of the materials in the molten phase and the wettability between the polymer matrix and the particular filler, e.g. mineral fibers or aluminum particles, might play a significant role during coalescence. Thus, a positive correlation between packing and sintered density above 0.4 might not necessarily apply in all cases.

Regarding the flowability indices, Figure 3.21 depicts the comparison between the previously calculated indices and the normalized packing density. Since the density of the powders inside the box follows a similar trend than the bulk density inside the drum, the flowability indicators also present a similar correlation as the results obtained with the Revolution Powder Analyzer. Thus, this analytical system can be used to predict with a high probability the packing density in SLS machines and the packing index $PI'$ constitutes a robust parameter for this purpose.

![Figure 3.21: Comparison of flowability indices (D50) corrected with shape factor versus normalized packing density.](image-url)
3.6.2  Effect of Spreading Speed and Preheating Temperature

In order to better understand the effect of the spreading speed and the feeders preheating temperature on the packing density of the SLS part bed, a similar small experiment was performed employing the hollow box concept previously presented, using in this case the materials icoPP and PA2200. Additionally small solid cuboids with dimensions of 10x10x2 mm were sintered within the build in order to analyze the effect on the final sintered density. Figure 3.22 depicts the set up employed for the SLS build with each material. The machine employed is a DTM Sinterstation 2000 and the parameters are defined as follows:

- Two temperature levels were selected for the feeders pre-heating temperature. One corresponds to the minimum value that can be used in a stable manner. Lower values cannot be adjusted due to the continuous warm up of the machine. The highest temperature corresponds to 10°C lower than the standard production setting.
- The laser powder (LP) and scan spacing (SS) parameters were set at 6 different values in order to analyze the effect of the laser energy density variations of each parameters on the sintered density. When LP was changed, SS was kept fixed at 0.23 mm. Similarly, when SS was varied, LP was kept constant at 16 W.
- The part bed temperature was set 2°C lower than the standard production value to enhance the effect of the laser energy density variations and reduce the part bed heater influence.

<table>
<thead>
<tr>
<th>SLS Build Parameters</th>
<th>Parameter</th>
<th>icoPP</th>
<th>PA2000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feeder T [°C]</td>
<td>45, 60</td>
<td>70, 110</td>
</tr>
<tr>
<td></td>
<td>Part Bed T [°C]</td>
<td>114</td>
<td>169</td>
</tr>
<tr>
<td></td>
<td>Scan Speed [m/s]</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Roller Speed [mm/s]</td>
<td>90, 180</td>
<td>90, 180</td>
</tr>
<tr>
<td></td>
<td>Laser Power (LP) [W]</td>
<td>8, 12, 16, 20, 24, 28</td>
<td>8, 12, 16, 20, 24, 28</td>
</tr>
<tr>
<td></td>
<td>Scan Spacing (SS) [mm]</td>
<td>0.15, 0.19, 0.23, 0.27, 0.31, 0.35</td>
<td>0.15, 0.19, 0.23, 0.27, 0.31, 0.35</td>
</tr>
<tr>
<td></td>
<td>Layer Thickness [mm]</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure 3.22:  SLS build set up for testing powder packing and sintered density.
• Two translational roller speed levels were selected for the powder spreading stage. The lowest value corresponds to half of the maximum speed that can be set in this type of machines.

For each parameter combination a laser energy density value was defined employing the Andrews number, combining the laser power, scan spacing, scan speed and layer thickness $t_l$ as follows:

$$A_n = \frac{L_p}{S_S \cdot S_p \cdot t_l}$$  \hspace{1cm} (3.11)

Regarding the placement of the parts within the build chamber, the configuration was selected in order to start with the lowest temperature setting as shown in Figure 3.22. First the hollow boxes were sintered followed by the set of cuboids considering the SS and then the LP variations respectively.

Figure 3.23 depict the results for the packing density using the hollow boxes. As observed, icoPP presents a higher normalized packing density in all cases in comparison to PA2200, which is consistent with the average flowability packing index $PI'$ of 3.5 and 3.9 for icoPP and PA2200 respectively. Additionally, the increase of the roller speed from 90 mm/s to 180 mm/s generates a slight increment of the packing density, probably due to a dynamic compaction effect. However, as the temperature increases from the lower to the higher setting, there is a reduction of the packing density. According to the surface fractal results presented in Figure 3.15, a lower powder rearrangement is expected for these two materials as the temperature increases, thus the results correspond with this indicator.

![Normalized Packing Density](image)

Figure 3.23: Normalized packing density of icoPP and PA2200 versus roller speed and preheating temperature.
Figure 3.24 shows the results obtained for the normalized sintered density using the 10x10x2 mm samples, measured under the Archimedes principle. The first main observation is that independent of the laser energy density applied icoPP presents in all cases a higher normalized sintered density than PA2200. This result is consistent with the normalized packing density values presented in Figure 3.23. Secondly, as the laser energy density increases, the sintered density increases as well, achieving a plateau above a value of 0.2 J/mm$^3$ for both materials. Also, in all cases, the laser energy density variations due to the laser power $LP$ generate an equal or higher sintered density in comparison to the scan spacing $SS$ modification, particularly at values below 0.15 J/mm$^3$. This result is expected, since the spot diameter of the CO$_2$ laser employed has a value of 0.45 mm, and at scan spacing values above 0.23 mm, the spot overlap is reduced in less than 50%.

In order to analyze the roller speed and the pre-heating temperature effects, each of them is presented separately. Additionally the terms low and high are used indistinctly for 45°C or 60°C and 70°C or 110°C respectively.
- **Effect of speed:** at low temperature no significant differences can be appreciated for the normalized sintered density of PA2200 (comparison a) - c)). In case of icoPP, considering the variations of the laser energy density due to \( SS \), for values below 0.15 J/mm\(^3\), there is a reduction of the normalized sintered density with the roller speed increase. This is related with the packing density increment observed previously in Figure 3.23. Also, since the viscosity of icoPP is approximately more than 3 times higher than PA2200 at the part bed temperatures of 114\(^\circ\)C and 172\(^\circ\)C respectively (see section 4.2.1), the particles coalescence is reduced and a higher porosity results. Additionally, since the fresh deposited powder needs more time to achieve the part bed temperature set point, it is probable that the particles below the top surface of the layer present a lower temperature and thus do not achieve a lower viscosity during the coalescence stage. At high temperature, in case of both materials, a slightly sintered density increase is observed considering the curves for the variation of the laser energy density due to \( LP \) (comparison b) - d)). However, considering the curves of the variation of the laser energy density due to \( SS \), the inverse effect is observed, particularly for icoPP. In this case a plateau seems to be achieved even at the lowest laser energy density value. This is related again with the packing density increment observed previously in Figure 3.23. These results confirm that materials with a higher molten viscosity at the processing temperature are more sensitive to packing density variations, influencing therefore the coalescence phenomenon.

- **Effect of temperature:** in general, a significant sintered density increment can be appreciated for both materials when the temperature is increased (comparison a) - b) and c) - d)), particularly for laser energy density values below 0.15 J/mm\(^3\), independently of the roller speed employed. Also the value of the normalized sintered plateau is incremented when the laser energy density is varied due to \( LP \). In case of laser energy density variations due to \( SS \), this value remains constant in almost all cases.

In summary, the previous results confirm that the normalized packing density coupled with the viscosity in the molten state at the processing temperature are the most important parameters that define the normalized sintered density. A second important aspect is the pre-heating of the powder, which plays a significant role to obtain a higher normalized sintered density. Even small reductions of the normalized packing density due to this pre-heating step can be compensated incrementing the laser energy density. However, it must be pointed out that this increment must be performed by increasing the laser powder and not the scan spacing; otherwise the maximum normalized sintered density (plateau) cannot achieve a higher value.
4 Characterization of Thermal and Rheological Properties

4.1 Differential Scanning Calorimetry

This chapter presents the characterization of the thermal material properties that are relevant for the implementation of the process simulation presented later in chapter 5. The materials selected for this investigation are DF PA12 and icoPP. The analytical analysis includes essentially the characterization of the degree of crystallization by Differential Scanning Calorimetry (DSC). For each material a set of 6 isothermal and 6 non-isothermal measurements were performed using a Mettler DSC 30 equipment previously calibrated with indium. Samples of 5 mg and 15 mg were prepared in 40 μl aluminum pans for DF PA12 and icoPP respectively. The measurements were carried out under dry nitrogen gas. For both tests, the sample temperature cycle consisted of an initial constant heating rate of 20°C/min from room temperature $T_i$ at 25°C to the temperature set for the powder bed top surface $T_s$ under SLS operation. These values are 171°C and 116°C for DF PA12 and icoPP respectively. This temperature was held for 2 min, followed by a heating rate of 40°C/min until a temperature difference of 50°C is achieved. Afterwards, a cooling rate of 40°C/min was set until a constant temperature $T_{iso}$ is reached (isothermal case) or before a lower defined cooling rate $dT/dt$ begins (non-isothermal case). For the isothermal experiments 6 different temperatures were considered, starting from 171°C to 166°C with a variation of 1°C in-between. For the non-isothermal tests, after reaching the part bed temperature from the maximum heating point, 6 different cooling rates were defined, starting from 0.1°C/min to 3.2 C/min following a geometrical progression. After each sample fully crystallized a reheating was performed at 20°C/min until the polymer was completely molten again. This last step was performed to estimate the equilibrium melting point $T_0$ by the Hoffman-Weeks construction, which in principle corresponds to the theoretical temperature at which crystallization and melting temperatures are equal for an infinite lamella thickness. A graphical representation of the temperature sequence described is depicted in Figures 4.1 and 4.7. Additionally, in section 4.1.3 the thermal heat capacity for both materials was also characterized by DSC.
4.1.1 Isothermal Measurements

The results obtained for the isothermal measurements are depicted in Figures 4.1 and 4.2. For both materials it can be observed that as the isothermal temperature is reduced, the time at which the signal reaches a maximum is considerable lowered. The results for the calculated half crystallization time or peak are presented in Table 4.1. It must be pointed out that for icoPP the maximum isothermal temperature at which a significant heat flow signal could be obtained was 111°C, which is 4°C below the temperature at which the powder bed is held (116°C). This can be explained due to the lower difference with the onset/peak melting temperature, hindering crystallization. In case of DF PA12, 171°C was the maximum temperature at which a signal was obtained. With this data a double logarithmic representation was used to analyze if the crystallization behavior follows the Avrami model. In Figures 4.3 and 4.4 it can be observed how DF PA12 presents a more linearized behavior during the whole crystallization range and for the different temperatures in comparison to icoPP. This means that DF PA12 follows the Avrami model more accurately than icoPP. Also a linear fit using the least square method was performed and the Avrami constants obtained are presented in Table 4.1 for both materials. According to the literature, a direct interpretation of both constants in not so clear, particularly the value of the Avrami exponent $n$, which is related to the structure of the crystal and its nature of nucleation while the constant $k$ is related to the speed of crystallization [145]. However, it is out of the scope of this work to discuss further the physical validity of the Avrami theory.

<table>
<thead>
<tr>
<th>DF PA12</th>
<th>T [°C]</th>
<th>166</th>
<th>167</th>
<th>168</th>
<th>169</th>
<th>170</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{1/2}$ [min]</td>
<td>15.9</td>
<td>22.0</td>
<td>32.4</td>
<td>57.9</td>
<td>103.3</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>2.80</td>
<td>2.77</td>
<td>2.57</td>
<td>2.53</td>
<td>2.42</td>
<td></td>
</tr>
<tr>
<td>$k [1/s^n \times 10^9]$</td>
<td>3.162</td>
<td>1.580</td>
<td>2.489</td>
<td>0.744</td>
<td>0.444</td>
<td></td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>icoPP</th>
<th>T [°C]</th>
<th>106</th>
<th>107</th>
<th>108</th>
<th>109</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{1/2}$ [min]</td>
<td>16.1</td>
<td>23.5</td>
<td>34.1</td>
<td>49.3</td>
<td>72.5</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>2.40</td>
<td>2.40</td>
<td>2.45</td>
<td>2.40</td>
<td>2.44</td>
<td></td>
</tr>
<tr>
<td>$k [1/s^n \times 10^8]$</td>
<td>8.248</td>
<td>3.664</td>
<td>0.627</td>
<td>0.351</td>
<td>0.132</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Isothermal half crystallization times, Avrami exponent $n$ and crystallization rate constant $k$. 
Figure 4.1: Isothermal crystallization curves for DF PA12 at different temperatures.

Figure 4.2: Isothermal crystallization curves for icoPP at different temperatures.
Figure 4.3: Logarithmic representation of isothermal crystallization curves for DF PA12 at different temperatures.

Figure 4.4: Logarithmic representation of isothermal crystallization curves for icoPP at different temperatures.
Figure 4.5: Fitted curves with Avrami parameters for the degree of isothermal crystallization conversion $\alpha$ for DF PA12 at different temperatures.

Figure 4.6: Fitted curves with Avrami parameters for the degree of isothermal crystallization conversion $\alpha$ for icoPP at different temperatures.
4.1.2 Non-isothermal Measurements

The results for the non-isothermal measurements are depicted in Figures 4.7 and 4.8. It can be observed that as the cooling rates decrease, the crystallization of both materials begins at a higher temperature, reducing the effective temperature window for SLS processing in comparison to standard DSC measurements performed at 10°C/min. The half crystallization times for the different cooling rates and materials are depicted in Table 4.2. It is important to note that, for similar cooling rates, icoPP presents higher values for $t_{1/2}$. This is explained due to the particular measurement conditions, were the starting temperature for icoPP is closer to the melting peak temperature related to the powder bed temperature used for SLS processing. With the measurements of $t_{1/2}$ for the isothermal case, the values of $K_0$ and $K_G$ were obtained by a linear least square fitting combining equations (2.6) and (2.15). These parameters do not present a direct physical interpretation, but $K_G$ is related to the nucleation characteristics associated to the mode of nucleation, thickness of the lamellas and their lateral surface energies [146]. The values obtained for both constants $K_0$ and $K_G$ are presented in Table 4.3.

<table>
<thead>
<tr>
<th>$dT/dt$ [$°C/min$]</th>
<th>DF PA12</th>
<th>icoPP</th>
</tr>
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<tr>
<td>0.1</td>
<td>66.9</td>
<td>104.5</td>
</tr>
<tr>
<td>0.2</td>
<td>38.4</td>
<td>65.5</td>
</tr>
<tr>
<td>0.4</td>
<td>24.4</td>
<td>39.0</td>
</tr>
<tr>
<td>0.8</td>
<td>14.7</td>
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<td>1.6</td>
<td>9.1</td>
<td>12.4</td>
</tr>
<tr>
<td>3.2</td>
<td>5.5</td>
<td>6.9</td>
</tr>
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Table 4.2: Non-isothermal half crystallization times.

<table>
<thead>
<tr>
<th></th>
<th>DF PA12</th>
<th>icoPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_0$ [1/s]</td>
<td>5.560e4</td>
<td>3.924e10</td>
</tr>
<tr>
<td>$K_G$ [K$^2$]</td>
<td>140866</td>
<td>498964</td>
</tr>
<tr>
<td>$T_0$ [$°C$]</td>
<td>192.4</td>
<td>160.3</td>
</tr>
<tr>
<td>$T_o$ [$°C$]</td>
<td>21</td>
<td>-40</td>
</tr>
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</table>

Table 4.3: Calculated parameters of the Hoffman-Lauritzen model for DF PA12 and icoPP.
Figure 4.7: Non-isothermal crystallization curves for PA12 at different cooling rates.

Figure 4.8: Non-isothermal crystallization curves for icoPP at different cooling rates.
The equilibrium melting temperature $T_0$ was calculated according to Hoffman and Weeks [147] as depicted in Figure 4.9. This method consists of representing the melting temperature of the previously isothermal-crystallized samples in terms of the isothermal temperature $T_{iso}$ employed in the DSC experiment. Then the intersection between the linear regression of this data and the equation $T_m = T_{iso}$ allows to evaluate $T_0$. The values obtained are summarized in Table 4.3.

Finally, to validate the suitability of the Nakamura model coupled with the Hoffman-Lauritzen theory, equation (2.13) was solved numerically using the software COMSOL, simulating the non-isothermal crystallization experiments for both polymers at the different cooling rates, using an average value of the Avrami constant $n$ for both materials of 2.42 and 2.62 respectively. Thus, for DF PA12, the model fits quite well the experimental results, at least below 90% of the total conversion (Figure 4.10). In case of icoPP, the fit results suitable below 65% (Figure 4.11). Above this value, the model over predicts the experimental results. These differences can be attributed to other crystallization mechanisms, such as transcrysallinity effects due to the contact with the DSC pan surface and the final impingement of bulk nucleated spherulites as described in Billon et al. [148] and Cunha and Fakirov [149], which hinder the crystallization rate at the final stages of the solidification stage.
Figure 4.10: Simulated curves for the degree of non-isothermal crystallization conversion for PA12 at different cooling rates.

Figure 4.11: Simulated curves for the degree of non-isothermal crystallization conversion for icoPP at different cooling rates.
4.1.3 Heat Capacity Measurements

The specific heat capacity $C_p$ at constant pressure of both materials was performed using the same DSC equipment employed for the crystallization measurements. Samples of 18 mg were prepared in 40 μl aluminum pans for DF PA12 and icoPP and 40 mg of aluminum oxide was used as a reference material. The measurements were carried out under dry nitrogen gas according to DIN ISO 11357-4 [150]. For both materials, the sample temperature cycle consisted of a constant heating rate of 10°C/min from room temperature at 25°C up to a maximum temperature of 280°C. Figure 4.12 depicts the results for both materials. Since the temperature range covers the solid and the molten states, two regions were defined for each material. Additionally, within each range, the specific heat capacity depicts a linear behavior. The values at the phase change transition are represented by the calculation of the melting enthalpy obtained by standard DSC measurements. Finally, the following equations are obtained for each material and range in J/g/K:

$$C_{p_s}^{DFPA12} = 1.3991 + 0.0091T, \quad T = 25\ldots186°C$$

$$C_{p_m}^{DFPA12} = 1.9278 + 0.0036T, \quad T = 186\ldots280°C$$

$$C_{p_s}^{icoPP} = 1.3985 + 0.0133T, \quad T = 25\ldots124°C$$

$$C_{p_m}^{icoPP} = 1.9139 + 0.0038T, \quad T = 124\ldots280°C$$

Figure 4.12: Heat capacity measurements for DF PA12 and icoPP between 25°C and 280°C.
4.2 Rheological Measurements

The aim of the experiment presented in this section is to evaluate the evolution of the viscoelastic response of the molten materials with undercooling, emulating a similar condition that the material experiences after the coalescence stage during the SLS process, where the fully solidified state has still not been achieved.

4.2.1 Frequency Sweep with Undercooling

The characterization of the shear storage and loss moduli of the materials was performed using a rheometer Anton Paar MRC 301. For each material, a set of 4 isothermal measurements were conducted at temperatures below the melting point. For DF PA12 166°C, 168°C, 170°C and 172°C were defined and for icoPP 106°C, 108°C, 110°C and 112°C were used. Samples of approximately 10 g of fresh powder for each measurement were employed for both materials. For all samples the powder followed a temperature path according to a similar thermal profile used in the DSC experiments. The temperature cycle consisted of an initial constant heating rate of 10°C/min from room temperature $T_i$ at 25°C to a maximum temperature of approximately 50°C above the melting point of each material corresponding to 230°C and 170°C for DF PA12 and icoPP respectively. Afterwards, a cooling rate of 7°C/min was set until a constant temperature $T_{iso}$ is reached. A higher cooling rate was not possible to achieve since the thermal inertia of the system did not allowed a faster temperature reduction in comparison to the DSC experiment. The measurement was performed according to a frequency sweep program. The particular set up employed was defined as follows:

- Rheometer equipped with a plate-plate configuration (25 mm diameter) and vertical gap distance was force controlled (hysteresis of 0.1 N, initial gap distance $d$ of 1mm).
- Continuous frequency sweep during crystallization with each cycle completed within a minute.
- Frequency response measured at 7 points per decade between 0.1 Hz and 10 Hz.
- Short linear viscoelastic range employed due to high torque increase during crystallization (strain amplitude: 0.1%).
- The sample material was replaced after each measurement and fresh powder was employed.
Figure 4.13: Shear storage $G'$ and loss $G''$ moduli measurements for DF PA12 and icoPP at different isothermal temperatures.

Figure 4.13 depicts the results obtained for the storage and loss moduli for DF PA12 and icoPP respectively. First, it can be noted that the measurements do not begin at time 0 min since at the maximum cooling rate achievable by the instrument of 7ºC/min it takes approximately 10 min to reach the isothermal temperature before the frequency sweep starts.

Second, in general the rate of increase of both moduli with time is higher for lower isothermal temperatures, which correlates with the solidification rate of the molten phase previously analyzed by DSC. At the beginning the curves present increasing values at all frequencies with an increasing rate. However, as the crystallization progresses, the rate decreases and the curves
tend to converge to a similar plateau, representing the end stage of the solidification process. However in case of DF PA12 this plateau is not clearly achieved, phenomenon that can be related to the continuous post-condensation effect that takes place with this particular material.

Regarding the elastic component $G'$, it can be observed that at the beginning of the measurement DF PA12 presents a larger range of values between the minimum and maximum frequencies of 0.1 Hz and 10 Hz in comparison to icoPP. However, in all cases, the values are lower than for the polyolefin. As the crystallization develops the storage modulus presents a higher value than the loss modulus for all frequencies above approximately 100 min for DF PA12. In case of icoPP the storage modulus at the highest frequency of 10 Hz depicts from the beginning of the measurement values above the corresponding loss modulus, while at the lowest frequency of 0.1 Hz the inverse behavior is observed.

Moreover, for both materials, the measurements above a certain solidification threshold at the highest frequencies depict misleading results. This phenomenon appears when the maximum limit of the torque of the rheometer has been reached due to the high stresses generated as the transition to the solid phase increases.

Figure 4.14 presents the results of the evolution of the complex viscosity. Since this parameter combines the effects of the elastic and viscous parts in one index, it does not correspond exactly to the steady state viscosity measured under a continuous rotation between the rheometer plates. However, according to the Cox-Merz rule [151] it is possible to estimate this value by an empirical relationship that relates the steady state shear viscosity $\eta$ plotted against shear rate $\gamma$ and the magnitude of the complex viscosity $|\eta^*|$ plotted against the angular frequency $\omega$ in a same diagram. Therefore, performing a least square curve fitting using the Carreau model with the 4 lower angular frequencies at the beginning of the solidification process, the following equations are obtained:

$$\eta_{DF\ PA12} = 9946 \left(1 + 5.15\omega^2\right)^{-0.10}$$ (4.5)

$$\eta_{icoPP} = 33220 \left(1 + 1.445\omega^2\right)^{-0.25}$$ (4.6)

The calculation of the steady state viscosity at zero shear corresponds to 9946 Pas at a temperature of 172°C and 33220 Pas at a temperature of 112°C for DFPA12 and icoPP respectively. This result shows a ratio of 3.3 between the values obtained for both materials, which confirms that icoPP is more sensitive to temperature and powder packing variations during the SLS coalescence stage than DF PA12 as previously analyzed in section 3.6.2.
As the crystallization progresses, the viscosity increases with values higher than 10e7 Pas at the final stages of the solidification. From a practical point of view, only the values at the beginning of the crystallization phase are relevant since they provide an estimation of the viscosity of the materials after the laser scanning step, where the last stages of the particles coalescence might still take place. However, the higher viscosity values are not relevant for the SLS process since at this crystallization degree only the elastic component of the viscoelastic behavior $G'$ results predominant.

Figure 4.14: Complex viscosity measurements for DF PA12 and icoPP at different isothermal temperatures.
4.2.2 Comparison between Gap Distance, Storage Modulus and DSC Crystallization

In addition to the characterization of the viscosity and viscoelastic moduli, the variation of the distance between the rheometer plates was also analyzed. These measurements provide information about the polymer volume contraction or shrinkage due to the crystallization effect.

Figure 4.15 depicts the results for the reduction of the gap for each material at the 4 isothermal temperatures considered. As can be noted, all the gap curves present two ranges. The first, from time 0 min to approximately 10 min, corresponds to the cooling stage from the maximum temperature until the isothermal set point is achieved. The second corresponds to the variation of the distance due to the crystallization shrinkage. Additionally, the curves begin at time 0 min with a slight increase of the initial gap distance of 1 mm. This effect appears due to the transient inhomogeneous cooling between the plates, since the upper surface is connected to a long vertical shaft that reduces its temperature faster than the lower plate in direct contact with the heater. However, when the thermal equilibrium is reached at the isothermal state, the effect disappears.

In general, it can be observed that as the isothermal set point is reduced, the shrinkage presents a higher value. At first glance this result seems to be contradictory with theory, since a lower undercooling should allow the polymer achieve a higher crystalline structure as obtained in DSC experiments. However, since the gap is controlled by force with a threshold of 0.1 N, no vertical movement is expected below this value, allowing the polymer melt to relax.

![Figure 4.15: Gap distance measurements for DF PA12 and icoPP at different isothermal temperatures.](image-url)
Since the gap reduction and the variation of the viscoelastic moduli are related to the crystallization, Figure 4.16 depicts for icoPP a comparison between the degree of isothermal solidification $\alpha$, the normalized storage modulus $G'/G'_{\text{max}}$ at the lowest frequency of 0.1 Hz and the shrinkage of the material, taking the normalized signal of the gap distance $\text{Gap}/\text{Gap}_{\text{max}}$. As observed, the degree of crystallization $\alpha$ and the normalized gap distance present a good correlation, even with a similar shape and initialization time at almost all temperatures. However, the normalized storage modulus presents a time lag at the start of the solidification. As the isothermal temperature increases, this time shift increases as well and the shape similarity is not preserved. These results show that the shear stress development is less sensitive to variations of the crystallization at early stages. Additionally, as the isothermal temperature is increased, the higher relaxation of the molten polymer reduces the normal stress generated and the rheometer is no longer capable to continuously track the volume contraction. Thus, in the next chapter, the DSC results and viscoelastic moduli will be combined, in order to analyze the coupled evolution of both parameters under SLS conditions.

Figure 4.16: Comparison between normalized gap distance, storage modulus (0.1 Hz) and degree of crystallization for icoPP at different isothermal temperatures.
5 SLS Process Simulation

This chapter presents the development, implementation and validation of a mathematical model of the build stage of the SLS process. A multiphysics approach is considered, taking into account the coupled thermo-mechanical and phase change equations. The numerical implementation was performed by a transient Finite Element Method using the software COMSOL. The main purpose is to obtain a better understanding how the phase change develops during the addition of layers and how the crystallization influences the internal stresses distribution that can generate an inhomogeneous deformation of the sintered parts called warpage. The simulation also allowed to identify the most important SLS machine parameters that influence the build stage of the SLS process.

5.1 Description of the SLS Build Stage Cycle

As presented in section 1.3 the SLS process is constituted essentially by three main steps called warm up, build stage and cooling down. The build stage corresponds to a cyclic powder spreading followed by a selective melting or material coalescence procedure at elevated temperature (near the melting point) characterized by three main sub-steps. Figure 5.1 depicts each of these stages, which are also described in detail as follows:

- **Part bed preheating**: previous building the first layer of a part, a predefined amount of powder needs to be deposited between the part bed piston surface and the top building plane during the previous warm up stage, which is characterized by the height $B$. This powder is used as a support structure and as a homogenous thermal substrate for the first sintered layer. The bottom of this volume of powder is kept at a constant temperature $T_b$ while the part bed top surface is heated at a temperature $T_s$, which is normally close the melting point of the material ($T_b < T_s < T_m$). The role of the temperature $T_b$ is to reduce the temperature gradient along the vertical build axis as the build progresses in order to avoid an excessive undercooling, particularly for the first sintered parts. The setting of these parameters is performed experimentally for each material in order to avoid an excessive solid state sintering of the support powder and to hinder the potential presence of warpage.
- **Laser scanning**: once the part bed achieved a stable temperature $T_s$, the laser locally adds the extra energy needed to fuse the powder particles together and, in case of subsequent layers, to ensure the bonding in-between (Figure 5.1b). The addition of this extra energy generates a short overheating of the polymer above the melting point denoted by $T_{\text{max}}$, after which the molten polymer recovers its initial temperature $T_s$. The amount of energy needed to achieve the highest coalescence or density was presented in section 3.6.2 for DF PA12 and icoPP. A lower energy density setting leads to a porous structure, while a higher value can achieve the decomposition temperature of the polymer without even achieving a higher sintered density. In general a value between 0.20 and 0.25 J/mm$^3$ is employed for thermoplastic materials, ensuring a sintered density above 95%.

- **Powder deposition**: after the selective coalescence of the material, a new layer of powder is added from the lateral feed containers (not shown in Figure 5.1c). Thus, the part bed piston moves down a distance equivalent to the new layer thickness $t_f$ before the powder is spread over the surface. This powder presents also a preheating temperature $T_f$ before it is deposited in the central part bed surface ($T_f < T_b < T_s$). The role of preheating the material is to reduce the undercooling effect over the previous sintered layer and at the same time to enhance a homogeneous layer heating rate from $T_f$ to $T_s$ previous the laser scanning step.

---

**Figure 5.1**: SLS Build Stage Cycle.
Figure 5.2: Crystallization model proposed during the build stage analyzed by DSC.

The full cycle described in Figure 5.1 takes in average between 35 s and 40 s to complete, depending on the SLS machine employed. Normally the largest transition takes place between b) and c) since in an average SLS build with a homogenous part packing density over 7% the scanning of the cross sections represents approximately more than 50% of the cycle time.

Based on the three main sub-steps described, Figure 5.2 presents the general overview of the build stage represented on a DSC diagram. The different states are represented by a sequential numeration. Basically, number 1 corresponds to the previous part bed heating sub-step. Number 2 symbolizes the maximum or peak temperature achieved by the laser scanning stage just below the point in contact with beam and number 3 corresponds to the recovery of the part bed temperature after the material has been molten. These three numbers represent essentially the build stage cycle with the transient undercooling in-between generated by the addition of fresh powder (not shown). Then, as three more layers are added, the state of the first layer moves from number 3 to number 6, which corresponds to a state with a lower temperature and a higher crystallization degree than the layers above it. This concept will be employed in the next sections with the main assumption that the material results completely molten and the time delay between successive powder recoating cycles allows the temperature to drop from $T_{\text{max}}$ to $T_s$ before the next layer is added. For this reason the effect of the laser in not taken into account directly. Instead, the laser scanning sub-step is represented by an instantaneous change from the powder state to a molten region that remains in a meta-stable state were the crystallization enthalpy has still not been released. This cycle is repeated until the part is completed.
5.2 Model Equations

5.2.1 Crystallization Kinetics

The crystallization kinetics is defined by Nakamura and Hoffman-Lauritzen (HL) equations previously presented in section 2.5.2 and summarized as follows:

$$\frac{\partial \alpha}{\partial t}_{HL} = nK(T)(1-\alpha) \left[ \ln \left( \frac{1}{1-\alpha} \right) \right]^{n-1}$$ (5.1)

$$K(T) = \ln(2)^n K_0 \exp \left( \frac{-U}{R(T-T_x)} \right) \exp \left( \frac{-K_G(T+T_{\alpha})}{2T^2 \Delta T} \right)$$ (5.2)

Additionally a combined mathematical-numerical approach for the rate of crystallization was implemented in order to incorporate the additional effects at the final stage of crystallization, like the spherulite impingement and the trans-crystallinity phenomena that are not captured by equations (5.1) and (5.2). Thus, the following equation was defined:

$$\frac{\partial \alpha}{\partial t} = (\alpha \leq \theta_{th}) \frac{\partial \alpha}{\partial t}_{HL} + (\alpha > \theta_{th}) f_{rate}(\alpha, T)$$ (5.3)

where $f_{rate}$ correspond to the empirical crystallization rate function obtained directly from non-isothermal DSC experiments as depicted in Figure 5.3 and $\theta_{th}$ corresponds to the threshold at which the differential equation (5.1) is replaced by the experimental results.

![Figure 5.3: Empirical crystallization rate function $f_{rate}$ with DSC data for icoPP (left) and extrapolated function at lower crystallization degree and temperature (right).](image)
5.2.2 Heat Transfer

The equation that governs the heat transfer process of the SLS powder bed inside the build cylinder during the build stage is defined as follows [152]:

\[
\rho_{\text{eff}}(\alpha,T)Cp_{\text{eff}}(\alpha,T) \frac{\partial T}{\partial t} = \nabla \cdot \left( k_{\text{eff}}(\alpha,T) \cdot \nabla T \right) + Q
\]

(5.4)

\[
Q = \begin{cases} 
\rho_{\text{eff}}(\alpha,T) \Delta H_c \frac{\partial \alpha}{\partial t} & \text{for molten regions} \\
0 & \text{for non-sintered powder} 
\end{cases}
\]

(5.5)

where \( \rho_{\text{eff}}(\alpha,T) \) corresponds to the effective material density, \( Cp_{\text{eff}}(\alpha,T) \) to the effective material specific heat capacity and \( k_{\text{eff}}(\alpha,T) \) to the effective material thermal conductivity. \( \Delta H_c \) accounts for the crystallization enthalpy. The material properties are also defined as a function of the crystallization degree during the phase change and expressed by the following relations:

\[
\rho(\alpha,T) = \alpha \rho_s(T) + (1 - \alpha) \rho_m(T)
\]

(5.6)

\[
Cp(\alpha,T) = \alpha Cp_s(T) + (1 - \alpha) Cp_m(T)
\]

(5.7)

\[
k(\alpha,T) = \alpha k_s(T) + (1 - \alpha) k_m(T)
\]

(5.8)

where the subscripts \( s \) and \( m \) denote the solid and molten states respectively of the bulk material. Then, according to Steinberger et al. [100], the effective material properties can be defined in a simplified manner by:

\[
\rho_{\text{eff}}(\alpha,T) = x_r \rho(\alpha,T)
\]

(5.9)

\[
Cp_{\text{eff}}(\alpha,T) = x_r Cp(\alpha,T) + (1 - x_r) Cp_{N2}
\]

(5.10)

\[
k_{\text{eff}}(\alpha,T) = x_r k(\alpha,T) + (1 - x_r) k_{N2}
\]

(5.11)

where \( Cp_{N2} \) and \( k_{N2} \) are the heat capacity and thermal conductivity of the chamber atmosphere (95% \( N_2 \)). \( x_r \) accounts for the material mass fraction which is defined for each domain (solid and molten) as follows:

\[
x_r = \begin{cases} 
x_{rm} & \text{for normalized sintered density} \\
x_{rp} & \text{for normalized packing density} 
\end{cases}
\]

(5.12)
5.2.3 Generalized Linear Viscoelasticity

Linear viscoelasticity is a commonly used approximation, for which the stress depends linearly on the strain and its time derivatives (strain rate). It is usually assumed that the viscous part of the deformation is incompressible, so that the volume change is purely elastic [153].

The Generalized Maxwell viscoelastic model is considered for this study. The general equation that defines a shear modulus $G(t)$ with $p$ spring and damper components (branches) is defined by a Prony series as follows [123]:

$$G(t) = G_{\infty} + \sum_{i=1}^{p} G_i \exp\left(-\frac{t}{\lambda_i}\right)$$  (5.13)

where $G_{\infty}$ corresponds to the relaxed shear modulus (time independent), $G_i$ represents the stiffness of the spring in the $i^{th}$ Maxwell branch and $\lambda_i$ is the relaxation time of the spring-dashpot pair in the same branch.

Since the total stress tensor is constituted by volumetric and deviatoric parts, the linear stress-strain elastic relationship can be rewritten to take into account the time dependent modulus combining the Hook Law with equation (5.13) as follows:

$$\boldsymbol{\sigma} - \sigma_0 = K I \left( \mathbf{\varepsilon} - \mathbf{\varepsilon}_0 - \mathbf{\varepsilon}_{inel} \right) + 2G_{\infty} \left( \mathbf{\varepsilon} - \mathbf{\varepsilon}_0 - \frac{1}{3} \text{tr}(\mathbf{\varepsilon} - \mathbf{\varepsilon}_0) I \right) + \sum_{i=1}^{p} 2G_i q_i$$  (5.14)

$$\frac{\partial q_i}{\partial t} + \frac{1}{\lambda_i} q_i = \frac{\partial}{\partial t} \left( \mathbf{\varepsilon} - \mathbf{\varepsilon}_0 - \frac{1}{3} \text{tr}(\mathbf{\varepsilon} - \mathbf{\varepsilon}_0) I \right)$$  (5.15)

where $\sigma$ corresponds to the stress tensor, $K$ to the bulk elastic modulus, $\mathbf{\varepsilon}$ to the strain matrix, and $q_i$ to a symmetric tensor, where the components represent the extension of the corresponding spring on each branch.

The inelastic strain $\mathbf{\varepsilon}_{inel}$ corresponds to a combination of the linear bulk thermal expansion coefficient $\alpha_{lin}$ related to a reference temperature $T_{ref}$ and to the bulk volume contraction during the phase change $\Delta V_{sh}$ due to the crystallization effect as defined in equation (5.16).

$$\mathbf{\varepsilon}_{inel} = \alpha_{lin} \left( T - T_{ref} \right) I + \alpha \left( 1 - \left( 1 - \Delta V_{sh} \right)^{\frac{1}{3}} \right) I$$  (5.16)
5.2.4 Time-Crystallization-Temperature Superposition

In order to introduce the effect of variation of the viscoelastic properties with crystallization, a time-crystallization-temperature superposition principle developed by Eom et al. [154] was implemented. This model was initially developed for the cure of epoxy resins and in this research was adapted for working with molten thermoplastics. Essentially the main idea is to generate a correction of the relaxation times and the stiffness of the springs in equation (5.13) with a factor that depends on $\alpha$ and $T$, in order to generate a mastercurve at a defined temperature as presented in the following equation:

$$G(t, \alpha, T) = G_\infty + \left[ \sum_{i=1}^p G_i(T) \right]_{\alpha, ref} \exp \left( -\frac{t}{A_x(\alpha,T)\lambda_i} \right)$$

(5.17)

where $A_x$ corresponds to the time-crystallization-temperature shift factor and $G_i$ are the moduli of each spring-dashpot pair at a defined crystallization reference $\alpha_{ref}$ and temperature $T$.

Defining the instantaneous relaxation modulus and the reduced time at the reference temperature in equations (5.18) and (5.19):

$$G_0|_{\alpha, ref} = \sum_{i=1}^p G_i|_{\alpha, ref}$$

(5.18)

$$\xi = \frac{t}{A_x(\alpha,T)}$$

(5.19)

It is possible to rewrite equation (5.17) in equation (5.20).

$$G_m(\xi)|_{\alpha, ref} = G_\infty + G_0|_{\alpha, ref} \sum_{i=1}^p \mu_i \exp \left( -\frac{\xi}{\lambda_i} \right)$$

(5.20)

where $\mu_i$ corresponds to the contribution of each branch related to the instantaneous relaxation modulus and is defined as follows:

$$\mu_i = \frac{G_i|_{\alpha, ref}}{\sum_{i=1}^p G_i|_{\alpha, ref}}$$

(5.21)

Equation (5.20) was used to define the empirical mastercurves and the pairs $(G_i, \lambda_i)$ using the rheological measurements presented in section 4.2.
Figure 5.4: Mastercurves $G_m$ (left) and $A_x$ (right) obtained for icoPP at different isothermal temperatures with undercooling.
Figure 5.4 presents the results for the superposition of the transformed storage and loss moduli in the frequency domain to the time domain according to equation (2.42) for icoPP (red curves). Since the frequency sweep was performed between 0.1 Hz and 10 Hz, the inverse of these values was used as the time frame for the conversion, i.e., a range between 0.1 s and 10 s. The crystallization reference was defined as the fully solidified state, i.e., $\alpha_{\text{ref}}$ set to the unit. Thus, the curve between 0.1 s and 10 s with the highest relaxation modulus is fixed and the curves below are shifted to the right according to the superposition principle. A minimization of the squared differences between each pair of consecutive curves was performed in order to define the relative shift (blue circles). Finally, the mastercurves at each of the 4 isothermal temperatures of 106ºC, 108ºC, 110ºC and 112ºC were obtained and the corresponding correlation between $\alpha$ and $A_x$ was calculated based on the degree of isothermal conversion results obtained by DSC as presented in Figure 4.16.

Finally combining all the mastercurves and the correlation functions in two graphics, an interpolation between the temperatures can be performed, generating the surfaces depicted in Figure 5.5. Then, for each combination of $\alpha$ and $T$, a shift factor $A_x$ can be obtained, which is used in equation (5.17) to correct the predefined relaxation times $\lambda_i$ and the associated shear moduli $G_i$ at the corresponding solidification degree. It must be pointed out that these results could only be generated for icoPP since DF PA12 presented misleading results during the viscoelastic characterization at higher frequencies, probably due to the post-condensation effect. Thus, the simulation that considers the thermo-mechanical physics will be only carried out with the polyolefin material.

![Mastersurfaces](image)

Figure 5.5: Mastersurfaces for $G_i$ (left) and $A_x$ (right) obtained for icoPP at different isothermal temperatures with undercooling.
5.3 Finite Element Model Set Up

5.3.1 Model Geometry: 1D and 2D Set Up

The SLS system geometry considered as a basis for the simulation corresponds to the configuration of a DTM Sinterstation 2000. This machine has a cylindrical build chamber with a diameter of 230 mm and a maximum build height of 300 mm. Due to its symmetry along the central build axis $z$ as observed in Figure 5.6 a simple axisymmetric part was considered for the simulation which consists of a disc with diameter $D$. For this configuration two different models were analyzed and described in detail as follows:

- **Unidimensional (1D):** corresponds to the representation of the part bed taking the axis of symmetry as a reference and the bottom of the powder bed that is in contact with the piston surface at a temperature $T_b$ as the origin for the coordinate $z_1$. This representation considers that the temperature distribution over the part bed surface is homogenous and that the crystallization is constant along the radial direction. This model takes into account the phase change and the heat transfer equations presented in sections 5.2.1 and 5.2.2 respectively. The process variables considered by this representation are the powder bed height $B$, the thickness $t_l$ of each layer, the part bed top surface temperature $T_s$, the temperature of the fresh powder $T_f$ and the piston temperature $T_b$, considering a maximum number of 20 layers. Additionally, the phase change and temperature distributions within each layer are also incorporated. The objective of this model is to analyze how the crystallization develops perpendicular to the build plane as the build progresses and the number of layers increases under the thermal boundary conditions of the build stage.

- **Bidimensional (2D):** corresponds to the representation of the sintered disc taking the axis of symmetry and the radial coordinate as a reference for the cross section of the disc and the bottom of the first layer that is in contact with the powder bed as the origin for the coordinate $z_2$. This representation considers that the temperature distribution over the top surface of each layer is homogenous and that the crystallization is constant along the radial direction. This model takes into account the phase change and the heat transfer equations coupled to the linear viscoelastic equation with time-crystallization-temperature superposition presented in sections 5.2.3 and 5.2.4 respectively. The process variables considered by this representation are the thickness $t_l$ of each layer, the part bed top surface temperature $T_s$ and the temperature of the fresh powder $T_f$, considering a number of layers between 3 and 7. In addition to the degree of crystallization and temperature distributions
within each layer, the stress and strain distributions are also incorporated. The objective of this model is to analyze the combined effect of the out of plane deformation of the disc (perpendicular to the top of the part bed surface) with the crystallization development under the thermal boundary conditions of the build stage.

The implementation of both models was performed in COMSOL v4.3b. For the 1D model second order linear elements were used. A mesh with 333 domain elements was generated. The degrees of freedom increased from 71 for the configuration with the first layer up to 411 for the configuration with 20 layers. Both physics were solved fully coupled using a direct linear solver and variable time steps (0.01s, 0.1s, 1s) for a cycle time of 40s between layers.

For the 2D model second order quadrilateral elements were used. A mesh with 300 domain elements was generated. The degrees of freedom increased from 9735 for the configuration with the first layer up to 63801 for the configuration with 7 layers considering 20 branches (relaxation times). Both physics were solved fully coupled using a direct linear solver and variable time steps (0.01s, 0.1s, 0.5s) for a cycle time $t_d$ of 40s between layers.

Figure 5.6: SLS geometry of DTM Sinterstation 2000 part bed and 1D and 2D model geometries and physics involved.
5.3.2 Transient Simulation Sequence

Since the 1D and 2D models presented in the previous section 5.3.1 consider the continuous addition of layers during the build stage, a transient sequence of events needs to be defined for the simulation. Figure 5.7 depicts how this sequence was implemented in COMSOL. At the beginning of the build stage the addition of layer 1 at time $t_{i1}$ starts with the instantaneous deposition of feed powder with a temperature $T_f$. As the time increases, the top surface of this layer is heated up to a temperature $T_s$ which also corresponds to the end of the deposition cycle for the first layer at the time $t_{f1}$. The laser scanning step is represented by an instantaneous isothermal phase change from the solid to the molten state. Thus, the addition of layer 2 at time $t_{i2}$ starts with the instantaneous deposition of feed powder with a temperature $T_f$ over the surface of the previous molten layer with a temperature $T_s$. Again, as the time increases, the top surface of this layer is heated up to a temperature $T_s$ which also corresponds to the end of the deposition cycle for the second layer at the time $t_{f2}$. Then this sequence is repeated up to 20 and 3-7 layers for the 1D and 2D models respectively. It must be pointed out that under the isothermal melting assumption the moment when the layer changes its state due to the laser scanning step is not relevant provided that the temperature on top surface of the heated powder has achieved the temperature $T_s$ before starting the addition of the next layer.

![Diagram of transient build stage simulation sequence for 1D model with constant layer thickness $t_l$.](image-url)
5.3.3 Initial / Boundary Conditions & Assumptions

The initial and boundary conditions for a standard production build with DF PA12 and icoPP materials are summarized in Table 5.1 considering the unidimensional model (1D). The additional conditions employed for the axisymmetric simulation (2D) with icoPP are presented in Table 5.2. Additionally, the following assumptions have been made:

- The powder state is assumed to present a continuum behavior. Thus interactions between particles are not considered and only effective average properties are employed.
- The contact between sintered layers and between layers and the powder bed is perfect.
- The transient powder coalescence and the associated volume reduction were neglected, considering a constant layer thickness after and before the laser scanning step ($t_l$).
- Each new layer added is assumed to be deposited instantly over the whole surface.
- The mass fraction $x_r$ of the parts and the powder bed are assumed to remain constant for each domain. These values were previously measured from sintered parts and small sintered boxes with powder inside (see section 3.6.2).
- The surface temperature $T_s$ is considered as a transient boundary condition measured by an infrared sensor on top of the part bed surface (Figure 5.8).
- The phase change from the solid to the molten state takes places instantly and isothermally, i.e., the energy provided by the laser is enough to melt the complete thickness of the layer without overheating the previous one. This assumption is based on the Degree of Particle Melt concept proposed by Zarringhalam et al. [155], who demonstrated that a small fraction of remaining unmolten particle cores are still present in the sintered parts.
- Before and after the laser scanning the top surface of the molten layer presents a constant $T_s$ temperature. This assumption is based in the fact that the material needs to be heated previous scanning and that previous adding the next later the material cools down to $T_s$.
- The mastersurface for the calculation of $G_i$’s (Figure 5.5) is bounded by the minimum and maximum temperatures of the rheological experiment. Since measurements at lower undercooling were not possible to perform due to the steep increase of the viscoelastic moduli, a constant extrapolation was assumed at temperatures below 106°C (icoPP).
- The bottom of the sintered disc is supported by a compression only activated spring bed (vertical) with elastic compression and extension constants $k_c$ and $k_e$ ($k_e \approx 0$).
Table 5.1: Initial / boundary conditions for DF PA12 and icoPP (1D Model).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DF PA12</th>
<th>icoPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_s$ [°C]</td>
<td>172</td>
<td>114</td>
</tr>
<tr>
<td>$T_b$ [°C]</td>
<td>130</td>
<td>95</td>
</tr>
<tr>
<td>$T_f$ [°C]</td>
<td>120</td>
<td>70</td>
</tr>
<tr>
<td>$t$ [μm]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$B$ [mm]</td>
<td>15</td>
<td>15</td>
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<tr>
<td>$t_d$ [s]</td>
<td>40</td>
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Table 5.2: Additional boundary conditions for icoPP (2D Model).

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<tbody>
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<td>$D$ [mm]</td>
<td>40</td>
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<tr>
<td>$k_c$ [Pa]</td>
<td>1e7</td>
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<tr>
<td>$k_s$ [Pa]</td>
<td>1e-10</td>
</tr>
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</table>

Figure 5.8: Measured and average $T_s$ evolution on the SLS powder bed top surface for DF PA12 and icoPP ($t=0$ s corresponds to $T_s$ immediately after powder deposition).
5.3.4 Material Properties

The thermal properties and densities for both materials are summarized in Table 5.3. For DF PA12 the materials density and thermal conductivity were reported by Rietzel et al. [156] and Yuan et al. [157] respectively. In case of icoPP the materials density and thermal conductivity were estimated from the literature according to Ehrenstein et al. [158] and Zhang et al. [159] respectively. For nitrogen, the data reported by Bergman et al. [152] was used (Table 5.5).

<table>
<thead>
<tr>
<th>Property</th>
<th>DF PA12</th>
<th>icoPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_s$ [kg/m$^3$]</td>
<td>1010-0.688$T$</td>
<td>885-0.315$T$(*)</td>
</tr>
<tr>
<td>$\rho_m$ [kg/m$^3$]</td>
<td>961-0.6162$T$</td>
<td>836-0.334$T$(*)</td>
</tr>
<tr>
<td>$C_p_s$ [J/kg/K]</td>
<td>1399+9.1$T$</td>
<td>1398+13$T$</td>
</tr>
<tr>
<td>$C_p_m$ [J/kg/K]</td>
<td>1928+3.6$T$</td>
<td>1914+3.8$T$</td>
</tr>
<tr>
<td>$k_s$ [W/m/K]</td>
<td>0.28-2.5*10$^{-4}T$</td>
<td>0.23-2*10$^{-4}T$(**)</td>
</tr>
<tr>
<td>$k_m$ [W/m/K]</td>
<td>0.24-10$^{-5}T$</td>
<td>0.16-8*10$^{-6}T$(**)</td>
</tr>
<tr>
<td>$\Delta H_c$ [kJ/kg]</td>
<td>46.8</td>
<td>58</td>
</tr>
<tr>
<td>$T_G$ [°C]</td>
<td>51</td>
<td>-10</td>
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<td>$x_m$ [%]</td>
<td>97</td>
<td>98</td>
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<tr>
<td>$x_{rp}$ [%]</td>
<td>42</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 5.3: Density, mass fraction and thermal properties for DF PA12 and icoPP ($T$ in °C) and data estimated from literature [158(*)], [159(**)].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>icoPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$ [Pa]</td>
<td>$f(G(t,\alpha, T))$</td>
</tr>
<tr>
<td>$\Delta V_{in}$ [l]</td>
<td>0.033</td>
</tr>
<tr>
<td>$\alpha_{in}$ [1/K]</td>
<td>154e-6</td>
</tr>
<tr>
<td>$\log(\lambda)$ [log(s)]</td>
<td>-0.29, 0.56, 1.41, 2.26, 3.11, 3.97, 4.82, 5.67, 6.52, 7.38, 8.23, 9.08, 9.94, 10.79, 11.64, 12.49, 13.34, 14.19, 15.05, 15.9</td>
</tr>
<tr>
<td>$\nu$ [l]</td>
<td>0.44</td>
</tr>
<tr>
<td>$G_-$ [Pa]</td>
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</tr>
</tbody>
</table>

Table 5.4: Additional material properties for icoPP (2D Model).
Table 5.5: Thermal properties of nitrogen (gas phase) [152].

<table>
<thead>
<tr>
<th>Property</th>
<th>$N_2$ (Gas at 420 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{N_2}$ [W/m/K]</td>
<td>0.033</td>
</tr>
<tr>
<td>$C_{p_{N_2}}$ [J/kg/K]</td>
<td>1049</td>
</tr>
</tbody>
</table>

Additionally, in case of the 2D model, Table 5.4 presents the additional material properties used for the simulation of icoPP. Considering a homogeneous isotropic behavior, equation (5.22) presents the relationship between the shear and bulk modulus.

$$K(t,\alpha,T) = f(G(t,\alpha,T)) = \frac{2(1+\nu)G(t,\alpha,T)}{3(1-2\nu)}$$

(5.22)

where $\nu$ corresponds to the Poisson ratio and $G(t,\alpha,T)$ to the relaxation modulus defined in equation (5.17). It must be pointed out that according to Tscharnter et al. [160] the Poisson ratio measured in a homo-polypropylene is not constant an increases with the relaxation time and temperature (up to 80ºC) between 0.42 and 0.48. However, since the characterization during the meta-stable state after melting is not known, an average value of 0.44 was used.

Additionally the feed powder deposited on top of each previous molten surface (Figure 5.7) was considered for simplicity as a continuous elastic layer, but with a young modulus that is 100 times lower than the relaxed elastic modulus $G_\infty$ of the molten material in order to hinder its contribution to the global stiffness of the sintered structure.

Regarding the relaxation times $\lambda_i$, 20 values were defined to cover the whole reduced time range $\xi$. The minimum and maximum values correspond to -0.29 log(s) and 15.9 log(s) with 18 equally spaced relaxation constants in-between. The values for each $G_i$ are then calculated from the corresponding mastercurve and updated during the simulation according to the temperature evolution.

In relation to the inelastic deformation, the linear expansion coefficient $\alpha_{lin}$ for a typical polypropylene was defined as constant with a value of 154e-6 1/K [158]. Finally, since the bulk volume expansion coefficient can be estimated as 3 times the linear expansion, using the value of 1.1% obtained from the vertical gap reduction in the rheological experiments for icoPP at an isothermal temperature of 110ºC, $\Delta V_{sh}$ was defined with a value of 3.3%.
5.4 Simulation Results and Analysis

The following chapter summarizes the results obtained for the simulation of the 1D model using both materials and the 2D model employing icoPP. The results include the transient evolution of the temperature and crystallization for a standard build set up and a parameter analysis to explore the influence of different machine configurations in the crystallization process. Finally an empirical characterization of the deformation of a simple part will be compared with the numerical results obtained employing the 2D model.

5.4.1 Evaluation of Crystallization Threshold

In order to take into account the last stage of the crystallization process of icoPP not captured by equations (5.1) and (5.2), equation (5.3) was evaluated at different threshold values \( \theta_h \) from 0 to 1 using 6 different constant cooling rates. Figure 5.9 presents the results of the degree of crystallization for three cases and the comparison with the experimental data. The Nakamura and Hoffmann-Lauritzen (HL) equations are suitable for the conversion range from 0 to 0.5, while the empirical crystallization rate function \( f_{rate} \) represents more accurately the upper range of the solidification. However, using the combined approach represented by equation (5.3), a curve with an improved representation of the degree of crystallization is obtained. The optimal value calculated for \( \theta_h \) was 0.2, obtained by minimizing the sum of square errors between the prediction curve and the empirical results.

![Figure 5.9: Comparison of the degree of non-isothermal conversion (icoPP) between Hoffmann-Lauritzen theory, \( f_{rate} \) and combined approach (\( \theta_h =0.2 \).)](image-url)
5.4.2 Transient Temperature and Crystallization Development

In this section the evolution of the temperature and degree of crystallization according to the unidimensional model (1D) are presented. Figures 5.10 and 5.14 depict the transient temperature evolution of DF PA12 and icoPP respectively up to the deposition of 20 layers, measured at the position immediately below the top surface of each layer. Both figures only present a temperature scale that is 4°C below the part bed surface temperature in order to depict with more detail the variations close to the set point \(T_s\). The simulation begins with the instantaneous deposition of powder from the feeder at temperature \(T_f\) on top of the first sintered (molten) layer. After the initial temperature drop the powder is heated again to reach the defined powder bed temperature \(T_s\), which corresponds to the curve with the highest heating rate. Then this procedure is repeated for each powder deposition cycle of 40 s until the layer 20 is completed. As noted, as a new layer is added, the layer below reduces its temperature. In case of DF PA12, after 800 s the first layer presents an average reduction of approximately 2.8°C which corresponds to an average cooling rate of 0.21°C/min. In case of icoPP, this variation is lower with a value of 2.2°C and a corresponding cooling rate of 0.17°C/min. Thus, DF PA12 experiences an average cooling rate 24% higher.

Figures 5.11 and 5.15 depict the cumulative degree of crystallization at the same position used for the temperature for each layer and each material. An interesting “stairs-pattern” can be observed for each layer for the first 300 s which can be described as a non-constant stepwise crystallization effect. This pattern consist of two elements: a steep crystallization change induced by the fresh powder added with each new layer and a relative constant crystallized state during the holding period in-between. This steep crystallization change is higher for the first layers and reduces continuously as the height of the build progresses. The initial higher steps are associated with a higher release of crystallization enthalpy, acting as a heating source. In case of DF PA12, after 10 recoating cycles the first layer presents a 0.4% degree of crystallization and achieves a value of 0.85% until the 20th layer has been deposited. In case of icoPP, after 10 recoating cycles the first layer presents a 0.25% degree of crystallization and achieves a value of 0.44% until the 20th layer has been placed.

After approximately the first 9 deposited layers the crystallization curves depict a more continuous smooth increment without any steep changes, indicating that the undercooling effect of each new layer added has no further influence on the crystallization behavior below the corresponding vertical position. Moreover, for both materials an interesting effect is observed as the degree of conversion increases: for a same build position below the powder bed surface, the layers do not present the same degree of crystallization. This trend is depicted in Figures
5.11 and 5.15 were, for instance, the first layer presents a higher degree of crystallization in comparison to the subsequent layers after 5 and 10 recoating cycles (depicted by a dotted line). This behavior is related to the partial release of the total enthalpy of crystallization coupled to the increase of the build height, generating both effects a continuous reduction of the temperature gradient between the bottom of the first layer and the part bed top surface. Thus, the contribution of both phenomena counteracts the undercooling effect, generating a homogenous initial crystallization zone above approximately the 5th recoating cycle.

Regarding the results in terms of the spatial coordinate, the transient temperature evolution during the deposition of layer 20 is depicted in Figures 5.12 and 5.16 for DF PA12 and icoPP respectively. Each curve corresponds to the temperature profile from the instantaneous powder deposition until the part bed surface temperature \( T_s \) is achieved after 40 s considering each time step of the simulation with values between 0.01 s to 1 s. Interesting to note is that this representation presents the envelope of the minimum temperatures that are achieved by the layers below and particularly the minimum temperature on the previous molten layer. In case of DF PA12 the undercooling of the feed powder generates a minimum temperature of 150ºC on top the molten material and for icoPP this value corresponds to 89ºC. It is important to note that these values are slightly lower than the initial contact temperature due to the transient undercooling effect.

In terms of the solidification, Figures 5.13 and 5.17 show the spatial distribution of the degree of crystallization during the deposition of layer 20. It is important to highlight that the crystallization between each layer presents a discontinuous behavior that generates a discontinuous stress state as will be presented in section 5.4.4. Additionally as the build progresses it can be noted that the crystallization gradient increases within each layer until the maximum solidification rate is achieved and then it diminishes as the material completely solidifies.

As a final comment, neglecting the direct effect of the laser could induce also some distortions, particularly in the transient degree of crystallization for the first sintered layers, since the higher temperature induced by the laser can erase the formation of nuclei from the layers below. However, as previously mentioned, empirical results presented by Zarringhalam et al. [155] demonstrated that using standard SLS build parameters a small fraction of remaining unmolten particle cores are still present, particularly between the layers in the sintered parts. This indicates that any temperature overheating during the laser scanning step takes place close to the top surface of the scanned layer and the temperature increase will not significantly affect the previous molten layer since the maximum temperature at this position will be lower than the melting point due to the presence of a small fraction of unmolten material.
Figure 5.10: Transient temperature of DF PA12 up to deposition of layer 20 (position at top of each layer).

Figure 5.11: Transient degree of crystallization of DF PA12 up to deposition of layer 20 (position at top of each layer).
Figure 5.12: Transient temperature of DF PA12 during deposition of layer 20 versus vertical position.

Figure 5.13: Transient degree of crystallization of DF PA12 during deposition of layer 20 versus vertical position.
Figure 5.14: Transient temperature of i-coPP up to deposition of layer 20 (position at top of each layer).

Figure 5.15: Transient degree of crystallization of i-coPP up to deposition of layer 20 (position at top of each layer)
Figure 5.16: Transient temperature of icoPP during deposition of layer 20 versus vertical position.

Figure 5.17: Transient degree of crystallization of icoPP during deposition of layer 20 versus vertical position.
5.4.3 Effect of SLS Build Parameters on Crystallization

The crystallization results with standard SLS build conditions were presented in the previous section. However, it is relevant to analyze how the variation of the machine parameters will affect the response of the crystallization development under different settings. Thus, in this section a parameter analysis was performed considering a full factorial set of numerical experiments using the unidimensional model (1D) for icoPP with the 5 previous machine parameters selected at two levels. Figure 5.18 presents the set of 32 experiments that were conducted employing the 1D model and the values set for the parameters at the low and high conditions. These two levels were defined basically in order to increase the throughput of the SLS process by reducing the production time of parts. Thus, the temperatures were lowered, the layer thickness increased and the initial powder bed height was reduced from the previous standard set up between 20% and 30%. Only the part bed temperature was diminished in 5% since lower temperature values generate in practice a high degree of warpage.

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<th>Run No</th>
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<th>$T_b$</th>
<th>$T_f$</th>
<th>$B$</th>
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</table>

Table: 5.18: Parameters and their levels for the full factorial set of experiments.

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<tr>
<th>Parameter</th>
<th>Low (-1)</th>
<th>High (+1)</th>
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</thead>
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<td>108°C</td>
<td>114°C</td>
</tr>
<tr>
<td>$T_b$</td>
<td>75°C</td>
<td>95°C</td>
</tr>
<tr>
<td>$T_f$</td>
<td>55°C</td>
<td>70°C</td>
</tr>
<tr>
<td>$B$</td>
<td>12 mm</td>
<td>15 mm</td>
</tr>
<tr>
<td>$l_i$</td>
<td>100 μm</td>
<td>130 μm</td>
</tr>
</tbody>
</table>

Figure 5.18: Full factorial set of experiments for icoPP at 2 levels with 5 parameters.
Additionally, since only one experimental temperature profile for the part bed surface $T_s$ was measured for the standard build setting (Figure 5.8), an estimation of this boundary condition was considered for the remaining 3 possible combinations between $T_s$ and $T_f$, assuming that the layer thickness variation does not influence the heating rate at the top of the deposited layer. For instance, Figure 5.18 depicts the experimental profile and the estimated curve for the combination at the low setting. Since a similar heating rate was assumed the curve presents a temperature shift of 6°C to lower values. Only the temperature at the initial time was modified to match the temperature $T_f$. Since these conditions were arbitrary defined, a comparison with the experimental temperature profile of DF PA12 (Figure 5.8) depicts that even using a different material and temperature setting both profiles are quite comparable, which validates the previous assumption for this analysis.

In order to illustrate the effect of different parameter settings the results for the degree of crystallization for all 20 layers at the end of the deposition cycle of the last recoating step are presented in Figures 5.19 and 5.20. These figures depict the results of the variation of one parameter at a time considering the temperature variables ($T_s, T_b, T_f$) and the geometrical parameters ($B, t_l$) respectively. As can be observed, in general the temperature variations present a higher impact on the crystallization degree than the geometrical modifications. In case of $T_s$ the reduction in 5% of the standard value generates an average increment of more than 1000% in the final crystallization degree of the first sintered layer. However, in case of $T_b$ and $T_f$ the reduction of 21% from their nominal setting induces an increment of 67% and 100% respectively in relation to the standard build. Regarding the crystallization gradient per layer, in general due to the transient undercooling effect on the top surface, the degree of crystallization is higher at this position in comparison to the bottom of each of layer. Additionally, the reduction of the temperature of the feed powder $T_f$ generates a steeper crystallization gradient in comparison to the reduction of the piston temperature $T_b$, particularly within the layers close to the part bed top surface. However, in all cases, the reduction of the temperature parameters generates a higher minimum degree of crystallization per layer in relation to the standard build set up. In case of the geometrical parameters, the reduction of 20% of $B$ generates a slight increment of 9% in the average degree of crystallization for the first sintered layer. However, the increase of the layer thickness $t_l$ in 30% generates a reduction of the maximum crystallization degree on each layer in approximately 20%, keeping the minimum value almost unchanged. It must be pointed out that this crystallization gradient reduction is attributed to the lower undercooling effect induced on the previous molten layers since the thermal penetration depth at the initial thermal contact remains almost constant while the layer thickness increases.
Figure 5.19: Effect of variation of temperature parameters on crystallization at the end of deposition of layer 20 versus vertical position (Runs Nº 15, 23, 27 and 31).

Figure 5.20: Effect of variation of geometrical parameters on crystallization at the end of deposition of layer 20 versus vertical position (Runs Nº 30, 31 and 32).
Figure 5.21: Effect of variation of $T_f$ and $t_l$ on crystallization with the low parameter setting at the end of deposition of layer 20 versus vertical position (Runs N° 1, 2, 5, 6).

An additional interesting result is the effect of the variation of $T_f$ and $t_l$ considering the lower setting for the rest of the variables ($T_s$, $T_b$, $B$) as depicted in Figure 5.21. It can be observed that the maximum average degree of crystallization on the first sintered layer is achieved and corresponds in average to approximately 40% considering all combinations. However, it can be noted that depending on the combination of parameters employed the crystallization gradient can also be influenced. In general, the increase of both parameters induces a reduction of the difference between the degree of crystallization at the top and bottom of each layer, but not necessarily a reduction of the crystallization between the minimum and maximum value. For instance, for a constant layer thickness of 0.1 mm, when the temperature of the feed powder is increased from 55ºC to 70ºC, a reduction of the average degree of crystallization and maximum gradient is achieved for the first sintered layer. However, the minimum degree of crystallization value is located within the layer. In this case, the crystallization rate at the top and bottom of each layer are balanced due to the reduced thermal penetration depth during the undercooling of the powder deposited and the higher global crystallization rate due to the lower $T_s$, $T_b$ and $B$ values. If $t_l$ is further increased from 0.1 mm to 0.13 mm the crystallization gradient is even inverted, i.e. the bottom crystallizes faster than the top of the layer. In relation
to the SLS process a constant crystallization rate within each layer is desired with the aim to generate a homogenous internal stress distribution.

Finally, in order to analyze the contribution or relevance of each parameter variation in the simulated SLS process, an analysis of variance (ANOVA) was performed with the full factorial configuration considering the average crystallization and the difference between the maximum and minimum crystallization degree of the first sintered layer as the response variables for the analysis. Table 5.6 depicts the results considering the main effects using the software JMP 10. As can be observed, for the average degree of crystallization per layer the most important parameters are the part bed surface temperature $T_s$ and the temperature of the piston $T_b$, considering a significance level of 5%. According to the analysis, the p-value for $T_f$, $B$ and $t_l$ are above than 0.05, which means that these parameters do not exert a significant role in the average crystallization. In case of the maximum difference of crystallization per layer, the geometrical parameters $B$ and $t_l$ present a significant role in comparison to their negligible influence on the average crystallization value. Additionally, in this case the parameters that do not influence significantly the crystallization difference are $T_b$ and $T_f$, taking into account the whole set of 32 experiments and not only the results presented in Figure 5.21.

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Table 5.6: ANOVA results for screening the most influencing parameters in the crystallization behavior (raw data from the simulation is presented in Annex 1).
5.4.4 Measurement and Simulation of Warpage

One of the main problems during the processing of thermoplastics using the SLS technology is the undesired deformation of the sintered parts related to the shrinkage of the material due to an inhomogeneous crystallization development. In order to better understand how the phase change development induces this deformation in the SLS process, the following chapter presents the characterization and simulation of the out of plane deformation of a sintered disc using the icoPP material according to the 2D model presented in section 5.3.1. For this purpose an innovative experimental set up was designed in order to capture the transient development of the deformation and Figure 5.22 presents the experimental configuration. As observed in Figure 5.22a a CCD uEye SE camera was placed in front of the SLS machine chamber at the same level of the part bed surface. During the build stage the chamber was closed, but a small opening of 2 cm x 3 cm at the position of the camera was generated in order to allow the camera capture the out of plane deformation without distorting the temperature distribution of the part bed surface due to air convection. For this configuration a sequence of 8 bit gray scale images with a resolution of 96 μm/pixel were generated with a capture frame rate of 3 images per second, starting from the warm up stage up to the final cooling down. The lateral view of the disc is depicted in Figure 5.22d, corresponding to the reference condition, where warpage has not been developed. Figure 5.22e depicts the deformed configuration once the disc has fully crystallized and the height \( h \) has reached a maximum stable value. At the same time an infrared temperature sensor Raytek MI with an optical resolution 10:1 records simultaneously the temperature evolution of the top surface of the sintered disc at a distance of 20 cm from the part bed top surface (effective spot measuring size of 20 mm).

![Experimental set up for the measurement of the out of plane deformation (a) (chamber front door not shown), sintered disc (b) and simulated geometry (c).](image)

Figure 5.22: Experimental set up for the measurement of the out of plane deformation (a) (chamber front door not shown), sintered disc (b) and simulated geometry (c).
The disc was sintered according to the build set up described in section 3.6.2 with a laser power of 24 W, scan spacing of 0.23 mm and laser scanning speed of 5 m/s. This experiment was repeated 3 times considering the sintering of 3, 5 and 7 layers discs with a diameter of 40 mm keeping the build parameter set constant. After the last layer of powder is deposited on each disc the chamber cools down and the measured temperature is used as a boundary condition for the 2D FE model.

Figure 5.23 depicts the measurements performed for the sintered disc considering 3 layers. The measurement starts at time 0 s with the addition of the 5 last layers of the warm up stage. Then, the laser scanning of the first layer begins at 250 s and the build stage cycle is repeated 3 times before the part bed heater is shut down at 420 s after the addition of a last layer of powder on top of the sintered structure. Then the sintered disc starts to cool down inside the build chamber. Figure 5.23a depicts the measured transient temperature distribution on the top surface of the disc. Since the temperature measurement was performed with an infrared sensor with a spot size of 20 mm, the signal corresponds to an averaged value. It can be noted that the temperature profile presents a series of valleys and peaks, which correspond to the addition of powder and the laser scanning step respectively. The minimum temperature measured after each powder deposition corresponds to approximately 80ºC and not 70ºC, which corresponds to the temperature set at the powder feed surface. This difference of 10ºC is related to the measuring time delay generated by the moving of the roller over the measuring area during the powder recoating step. Regarding the maximum temperature, this is achieved during the laser scanning step. However, the value of 150ºC corresponds only to the arbitrary maximum set for the graphic scale, since the real maximum value cannot be determined with this type of sensor. Additionally, the laser reflection during the scanning step generates misleading results, with temperature reading above 500ºC. Thus, these values are not considered as valid.

Figure 5.23b depicts the results for the simulated degree of crystallization measured at the edge of the bottom surface of the first layer and the measured (experimental h) and simulated heights at the edge of the top surface of the last layer. For the experimental height the average value of the sintered disc edge position respect to the reference image for each recorded picture was considered (Figure 5.22e). Due to the resolution of the camera and the light disturbances a noisy signal was obtained. Thus the measured and simulated height curves were shifted 50 µm from the reference position in order to present the complete signal. As observed, during the build of the sintered layers no out of plane deformation is observed and only after 620 s the sintered structure starts to warp denoted by the vertical displacement h of the edge of the disc. At this time, the top surface of the disc presents a temperature of approximately 97ºC with an instantaneous cooling rate of 4.3ºC/min derived from the temperature signal.
Figure 5.23: Experimental and simulated out of plane deformation, temperature and degree of crystallization at disc edge during the build of 3 layers (icoPP).

Figure 5.24: Experimental and simulated out of plane deformation, temperature and degree of crystallization at disc edge during the build of 5 layers (icoPP).
These values are also comparable to the peak crystallization temperature of 95°C at a cooling rate of 3.2°C/min derived from DSC results (Figure 4.8). Regarding the simulated results, the out of plane deformation presents in general a good correlation with the experimental measurement, particularly at the final deformation when the disc is fully crystallized. However, at the beginning of the warpage development stage, the model fails to accurately represent the start of the deformation with a time delay of approximately 50 s. The reason of this difference might be related to the correlation between the increase of the viscoelastic moduli measured with the rheometer and the degree of crystallization measured with the DSC. Since it was assumed that the transient development of both properties present the same initial time under similar testing temperatures profiles, this hypothesis can induce this time delay error between the simulated and the experimental curves. Additionally, after the initial rise of the disc edge, the deformation rate results higher. In this case the differences might be attributed to the time-temperature-superposition model and to the use of equation (2.42) to determine the value of the relaxation modulus in the time domain. However, in general there is an acceptable prediction of the transient development of warpage and its final deformation, even for the cases with a sintered disc composed by 5 and 7 layers as depicted in Figures 5.24 and 5.25 respectively.
Figure 5.26: Temperature and degree of crystallization distributions along the axis of symmetry during the cooling step after the build of 7 layers (icoPP).

Figure 5.26 depicts the simulated results of the temperature and the degree of crystallization distributions along the axis of symmetry during the cooling step after the build of 7 layers. The time steps considered cover the whole warpage deformation range. As observed, the temperature distribution in z presents a continuous negative gradient that slightly increments towards the top surface of the sintered structure and even at the different vertical positions the cooling rate remains constant. In case of the degree of crystallization a discontinuous distribution between layers in z is observed with maximum and minimum values at the top and bottom of each layer with a similar pattern as the results obtained with the unidimensional model.
It must be pointed out that at the start of the out of plane deformation (890 s) the first layer presents a degree of crystallization of approximately 60% and corresponds also to the inflection point of the solidification rate, i.e. the polymer started to crystallize slowly while the layer immediately above it solidified faster. The reduction of the average crystallization gradient of the first layers and its transient increase in the layers above induces an imbalance along the $z$ axis of the radial component of the stress tensor as observed in Figure 5.27. As the crystallization progresses, the magnitude of the radial stress increases and the out of plane deformation increments its value till approximately 1000 s (with a constant crystallization along $z$).
Figure 5.28: Temperature distribution (2D) and out of plane deformation during the cooling step after the sintering of 7 layers (icoPP).
Figure 5.29: Degree of crystallization distribution (2D) and out of plane deformation during the cooling step after the sintering of 7 layers (icoPP).
Figure 5.30: Radial stress tensor component distribution (2D) and out of plane deformation during the cooling step after the sintering of 7 layers (icoPP).
Figure 5.31: Transient out of plane deformation of the bottom of the sintered disc with 7 layers during the cooling step (icoPP).

Above this time, no further deformation is observed and the crystallization gradient along the z axis remains constant with a value close to 90% till the material fully solidifies. Thus a final residual stress distribution is obtained with the first two layers under a radial compression state while the layers above present a tension stress distribution. The minimum and maximum radial stresses along the axis of symmetry present values of -30 kPa and 15 kPa at top surface of the 1st and the 5th layer respectively. Regarding the stress tensor component along the build axis a continuous residual stress distribution is obtained. Before the start of the out of plane deformation (850 s), a continuous constant increment from the stress free top surface of the powder at 800 μm to the bottom of the first layer is observed due to the effect of gravity. At this condition a uniform maximum compression stress is generated over the whole bottom surface in contact with the support powder equivalent to the weight of the disc divided by its surface area which corresponds to approximately 7 Pa. Then, when the deformation begins, a more complex distribution along the z axis is observed and the compression stress at the bottom of the first layer increases due to the reduction of the contact area of the disk with the support powder. However the magnitude of the radial stress is more than 100 times higher than the stress component along the build axis. Additionally, since the ratio between the diameter and the thickness of the sintered disk is larger than 10, the shear stress can be neglected and therefore is not considered in this analysis due to its minor contribution to the global stress state.

Finally, Figures 5.28, 5.29 and 5.30 present the bi-dimensional temperature, degree of crystallization and radial stress tensor component distributions superimposed with the deformation of the cross section of the disc. As can be noted in Figure 5.31 a continuous increment of the curvature of the top surface is obtained. This generates that the contact point with the support powder also moves close to the axis of symmetry, at a position between 6 to 8 mm along the radial coordinate.
6 Summary and Future Work

In the present work the characterization and prediction of the SLS processability of polymer powders with respect to powder flow and part warpage was investigated. Since the SLS technique is based on a set of sequential steps, a high powder packing density during the deposition step constitutes a critical condition needed to achieve a high sintered density. Once this condition is fulfilled, a proper machine parameters setting is crucial to obtain finally a warpage-free object with the properties of a fully dense material.

Regarding the powder recoating requirements, currently no analytical technique can predict in advance 100% the powder flowing behavior in SLS equipments. Several commercial methods are available in the market to characterize the powder behavior under different stress states, but none of them can replicate exactly the powder handling conditions during the SLS spreading stage. However, the rotational drum system is the only one that is close to emulate the mechanical agitation of the SLS material. Thus, in this work a commercial rotational system was implemented and modified to incorporate and analyze for the first time the effect of the temperature in the flowability analysis of SLS materials, a parameter usually neglected in the characterization of powders. The main result of this research concluded that the flowability of SLS powders is strongly dependent on the temperature at which the materials are evaluated. Three parameters were initially employed to characterize the powder behavior at the different temperatures, namely the avalanche angle, surface fractal and volume expansion ratio. At room temperature and low rotational speed the avalanche angle correlated linearly quite well with the normalized bulk density of the material. However, the index failed to present suitable results at elevated temperature and higher rotational speeds, typical conditions of the SLS process. The surface fractal and the volume expansion ratio performed slightly better, but the definition of a new index that coupled the information provided by both previous indices depicted an improved result. The main advantage of the new characterization parameter is its robustness under the different testing conditions, combining the information of the topology of the powder free surface inside the rotating drum and the volume expansion of the powder. Finally the new parameter depicted a good prediction of the powder bed packing density that can be used to evaluate the suitability of new powders for the SLS process and therefore reduce the powder development cycle time and costs.
In terms of the SLS processing parameters, a mathematical model of the SLS build stage was developed and implemented numerically to better understand and quantify the variations of the machine settings on the crystallization behavior that directly influences the geometrical accuracy of the sintered parts. To achieve this purpose, a preliminary thermal and rheological characterization of two SLS materials was performed. An isothermal and non-isothermal crystallization analysis was performed for DF PA12 and icoPP, two commercial SLS powders. The phase change modeling of both polymers by integrating the Nakamura equation with the Hoffmann-Lauritzen theory for the determination of the crystallization rate constant demonstrated to be in very good agreement with experimental results. With this data, a transient Finite Element simulation was performed for the first 20 deposited layers during a normal SLS build. As a main result, a “stairs-pattern” effect was observed for each layer, which can be described as a non-constant stepwise crystallization, corresponding to a sequence of non-isothermal and quasi-isothermal states. Additionally, coupling the thermo-mechanical properties with these crystallization results facilitated to obtain a better understanding how the warpage of a simple part develops during a SLS build. These theoretical results were also validated using a novel experimental set up that allowed to characterize the transient warpage development. The principal results of this investigation concluded that early stages of crystallization can influence the final warpage development and that values above 50% are needed to induce any deformation.

Finally, this work opens new research fields that need to be evaluated in further studies. Regarding the powder characterization a deeper understanding of the mechanisms that generate the change of the flowing behavior of polymer powders at elevated temperature are necessary to conduct. Additionally the effect of the powder particles shape and distribution can be assessed in more detail in order to improve the materials design rules for SLS materials. Furthermore, the extension of this study using a broader spectrum of polymers can be suggested in order to test the robustness of the new developed index.

Regarding the simulation work, the implementation of the 2D model is currently limited to simple geometries in order to keep the degrees of freedom reduced and to limit the computational time to a maximum of a couple of days. This restriction is currently given by the fact that each layer cycle needs to be simulated. Thus, the further extension to 3D will require new implementation ideas to overcome this limitation. Finally, in order to improve the accuracy of the current model, the time-temperature-crystallization superposition model needs to be reviewed in more detail, particularly the coupling between the crystallization and the rheological results.
# Appendix 1: DoE crystallization results

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Appendix 2: Curriculum and Publications

**Personal Data**

Name: Antonio Felipe Amado Becker  
Address: Weidenweg 25  
CH – 4303 Kaiseraugst  
Date of birth, Place: 06.04.1981, Concepcion  
Nationality: Chile  
1999 High School, Deutsche Schule Concepcion, Chile  
2000-2005 BS Mechanical Engineering, Pontificia Universidad Catolica de Chile  
2006-2007 MSc Mechanical Engineering, Pontificia Universidad Catolica de Chile  
2007 Numerical Engineering Simulation Consultants ESSS  
Consulting Engineer, Finite Element Analysis Division  
Sao Paulo, Brasil  
2008 -2009 BHP Billiton, Base Metals CSG  
Project Development Department  
Project Engineer  
Santiago, Chile  
2009 -2015 PhD Student/Research Engineer  
inspire AG, Additive Manufacturing Research Group  
Lerchenfeldstrasse 5  
CH - 9014 St. Gallen  
Since 2015 Scientist R&D Formulation Solid Dosages  
Hoffmann-La Roche Pharmaceuticals  
Grenzacherstrasse 183  
CH - 4070 Basel
ISI Journals:


Conferences/Publications:


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