

Experimental Analysis of the Effectiveness of Current Modelling Methods for SLS Parameter Determination.

Cameron Mearns*, Dr. Johan Potgieter*, Dr. Steven Dirven*, and Dr. Marie Joo Le Guen†

*School of Engineering and Advanced Technology
Massey University, Auckland, New Zealand 0652

j.potgieter@massey.ac.nz

†Manufacturing and Bioproducts Group, Scion, Rotorua, New Zealand, 3010

Abstract—Selective Laser Sintering (SLS) is a powder-bed Additive Manufacturing process that has a large amount of potential for future growth. Historically SLS has been limited to a narrow selection of polymers, although there have been recent advances in working with composite powders, such as Alumide. One of the biggest limitations to developing new materials for sintering is the elevated risk involved in testing to determine their suitability. In recent years, models of powder behaviour have largely focused on thermal characteristics. Models such as the Sintering Window and Energy Melt Ratio demonstrate how methodologies such as Differential Scanning Calorimetry can be used to determine suitability of materials. Testing of two Nylon powders with similar physical and thermal properties reveals limitations in the models when accounting for the colour of material and therefore the absorption of laser energy. Thus, it was identified that existing models require further investigation of laser energy inputs. This paper contributes a framework upon which new models can be tested in order to characterize their effectiveness.

Index Terms—Selective Laser Sintering, material selection, Differential Scanning Calorimetry, Energy Melt Ratio, Sintering Window, powder characterisation

I. INTRODUCTION

Additive Manufacturing (AM) is the name given to a series of processes used to create solids from 3 Dimensional (3D) models [1]. It is also known as Free Form Modelling, and 3D Printing [2]. Initially AM was developed to produce solids using polymers [3], however as new technologies and methods have been developed this has expanded to include metals [4], and ceramics [5] [6]. One such technology is Selective Laser Sintering (SLS), which is a process that involves the progressive processing of thin slices of powder into formed solids by means of a heated chamber, and a focused laser beam [7].

As AM processes, including SLS, increase in popularity one of the areas of growth identified is the diversification of printing materials [8]. Due to the elevated risk of combustion caused by the SLS process many operators are unwilling to test new powders unless it can be shown they can be processed safely by SLS. This means that the number of materials available is currently limited by the understanding of powder

properties, and the ability to determine printing parameters from powder specifications [9].

Of importance for SLS printing is the thermal qualities of a material. The elevated temperatures of the SLS process increase the risk of material combustion, which puts greater importance of the precise and controlled application of energy into the powder. This can occur both in the form of convection, from the heated chamber of the printer, and in the form of radiation, from the laser. To be able to predict the energy required, to successfully print a material, it is important to understand the properties of the material.

One of the methods of determining sintering parameters from physical properties is the use of the Sintering Window. The Sintering Window (SW) is a method of defining the temperature range that the SLS machine must operate within, as defined by data collected using Differential Scanning Calorimetry (DSC). The SW is defined as the temperature region between the onset of crystallisation (T_c) and the onset of melting (T_m) for a given polymer [10]. This information provides the operator with a window to set the temperature for the machine, with a minimum chamber temperature above the crystallisation temperature, and a maximum of below the melting point. While this information is valuable this still does not provide the operator with the amount of energy required from the laser to cause the powder to sinter. It is advantageous to have as much energy input from the laser as possible in order to increase tensile strength of parts [11]. However, too much can cause a loss of accuracy in both dimension and feature definition, as well as warpage [12].

This is beneficial when combined with the concept of Energy Melt Ratio (EMR). The EMR is a volumetric metric for quantifying the amount of energy being put in by the system, as compared to the amount of energy required to melt the material. If the ratio is less than 1, then there is insufficient energy to sinter the layer [10]. Through a combination of these methods many variables can be established for SLS printing. Chamber temperatures, which are important for reduction of shrinkage and curling [12], can be established using the SW methods [8]. Once these temperatures have been established the chamber temperature can be used to establish the remain-

ing energy input required from the laser. Using EMR equations this can be converted to parameters such as laser scan speed, and laser power.

To verify this model two different powders were tested utilizing these models. A framework for assessing the effectiveness of the models is demonstrated with reference to identifying new powders, and recommendations on improvements for the models are given.

II. METHODOLOGY

Initially a material characterisation is undertaken to identify the similarity of the powders before the Design of Experiment (DoE) is run on an SLS printer. Once the materials have been characterised, a multifactorial experiment is performed to test the effectiveness of the model, and identify any limitations it may have. The first powder tested was dark grey nylon (Sintratec PA12 Black), and the second is a white nylon (Precimid 1170). The Sintratec PA12 Black come with the Sintratec printer, and has known print parameter values (Chamber Temperature of 150°C, Print Bed Temperature of 170°C, and Laser Scan Speed of 550 mm/s) that result in successful parts. The DoE was designed from these values to test the ability of the models to predict sintering in a similar powder, the Precimid 1170.

The characterisation involved conducting a DSC analysis of the powder to identify the crystallisation temperature, and the temperature of the melt. These were used to compare the two powders, and evaluate the likelihood of sintering using the same values by using the SW and EMR. In addition to the two temperatures, several values needed for the EMR can be gathered, from both the DSC software, and from calculations of the data gathered. The DoE will then be run to test the effectiveness of these parameters, and thus the SW and EMR models. A print's effectiveness is evaluated by whether the part printed and was removable from the powder cake, and porosity as visible by Scanning Electron Microscope (SEM).

The physical similarities of the two powders will be compared using examination of unprinted powder with an SEM to determine similarity of particle size, and morphology. Particle size and morphology has been shown to have an effect of the ability to spread a powder for each layer of sintering, and thus the print itself [13].

A. Differential Scanning Calorimetry

To establish the sintering window, a thermal analysis was conducted using a Discovery DSC in accordance with ASTM D3418. Samples of virgin material were subjected to a heating ramp from 20°C to 250°C, at 5°C/min, before being cooled again to 20°C at 5°C/min. The data was recorded with the Discovery TRIOS software package, and analyzed with MATLAB 2015. Two experimental runs were run and recorded for each powder.

As stated, the Sintering Window exists between the onset of crystallization, and onset of melting for a material. As per the results of the DSC, a Sintering Window for the Sintratec PA12 Black exists between 151°C and 180.1°C, while the

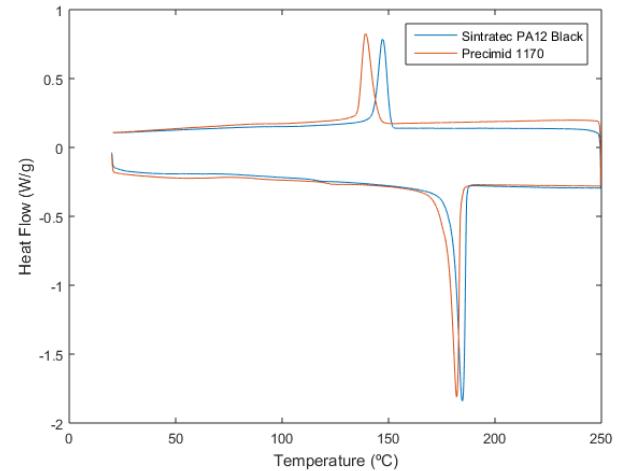


Fig. 1. DSC measurements of Heat Flow against Temperature, showing melting point (the lower spike) and crystallization point (upper spike) of both Sintratec PA12 Black, and Precimid 1170, both virgin powders

TABLE I
POWDER PROPERTIES AS DETERMINED BY DIFFERENTIAL SCANNING CALORIMETRY.

Property	Sintratec PA12 Black	Precimid 1170
Onset of melting (°C)	180.1	177.2
Melting point (°C)	184.7	181.9
Onset of crystallization (°C)	151.0	144.5
Crystallization point(°C)	147.4	139.1
Melt Enthalpy (J/g)	108.6	111.0
Crystallisation Enthalpy (J/g)	49.3	51.2
Specific Heat Capacity (J/g°C)	40.050	44.007

Sintering Window for Precimid 1170 exists between 144.5°C and 177.2°C. The similarity in these powders thermally means they should be able to be processed under identical conditions, provided the machine chamber and print bed temperatures are set with both powders in mind, such as between 144.5°C and 180.1°C. As the models are being used to predict sintering of the material, and not the overall process ability of the material, the focus will be on the surface of the powder during the sintering phase. This means that the upper range of the SW will be tested, by varying the Powder Surface temperature.

Furthermore, additional insight can be drawn from the DSC results. The Discovery TRIOS package can derive the melt and crystallization enthalpies from the tests (Table 2). The specific heat capacity for each powder can be derived from the temperature change of the known sample weights in each case. Values for Laser Speed were based on known values used for the Sintratec PA12 Black, given by Sintratec for the printer. A value for Packing Fraction was taken from literature.

TABLE II
VALUES USED TO CALCULATE ENERGY MELT RATIO VALUES.

Parameter Name	Symbol	Sintratec PA12 Black	Precimid 1170
Specific Heat Capacity (kJ/g. $^{\circ}$ C)	C_p	40.050	44.007
Print Bed Temperature ($^{\circ}$ C)	T_b	165, 170, 175	165, 170, 175
Onset of melt temperature ($^{\circ}$ C)	T_m	180.1	177.2
Enthalpy of melting (J)	H_f	105.6	110.0
Bulk Density (g/mm 3)	Q	0.001	0.00094
Packing Fraction	θ	0.418	0.418
Scan Count	V_c	1	1
Scan Spacing (mm)	V_s	0.05	0.05
Laser Speed (mm/s)	V	450, 550, 650	450, 550, 650
Layer Thickness (mm)	Z	0.1	0.1
Laser Power (W)	P	2.3	2.3

These figures enable the Energy Melt Ratio to be calculated using the figures in Table 2.

B. Scanning Electron Microscope

Samples of fresh powder were prepared for examination by Gold Sputter Coating using a PVD DSR1, operating at 10 mA, with a layer thickness of 20Å. Samples were imaged using a Hitachi TM3030 Plus, and accompanying TM3030 Plus software.

Both powders appear to be very similar physically. While the Precimid 1170 appears to have slightly smaller particle sizes on average, and more spherical morphologies, the differences are minor enough that the physical properties should have no significant effect [14].

C. Sintering Methodology

These tests were conducted with a Sintratec Kit SLS printer, equipped with a 2.3W 445nm diode laser. The print was 5 ANSI D638 Type 5 Dog bones orientated parallel to the X axis. Chamber temperature was set at 150°C, the highest the machine allows.

Based on the values gathered in the characterisation, the two factors for the experiment will be the Print Bed Temperature, and the Laser Speed, each with 3 levels. The Energy Melt Ratio for each trial of both powders is visible below (Table 3).

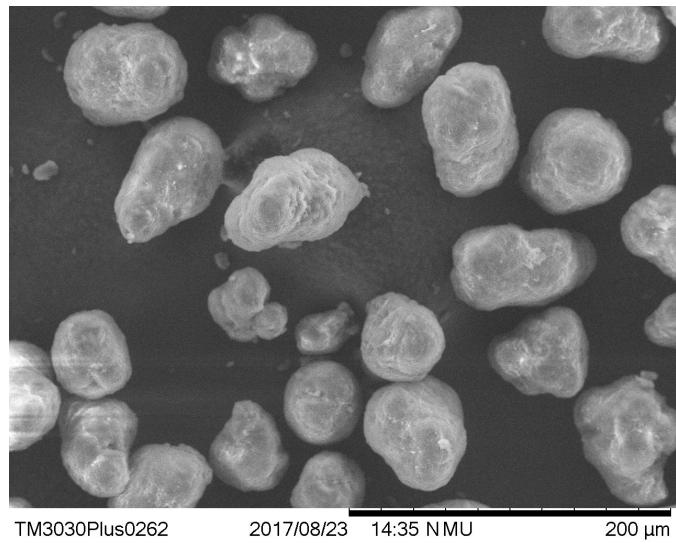


Fig. 2. SEM Images of the Precimid 1170 at 500 times magnification

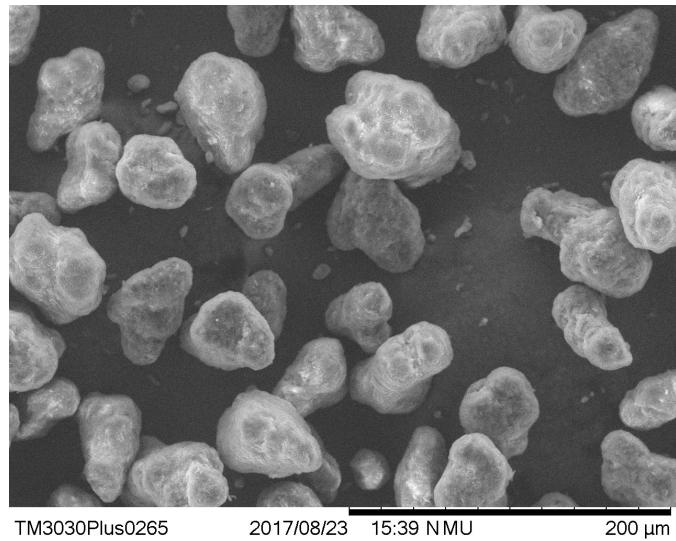


Fig. 3. SEM Images of the Sintratec PA12 Black at 500 times magnification

III. RESULTS

The Sintratec PA12 Black printed successfully for the settings which are recommended for it with this machine. Behaviour for the black powder was roughly consistent with the SW and EMR models. However, none of the trials using white powder resulted in a successful print. While a loose powder cake did form in all prints, there was no evidence of any sintering having occurred, and clumps of powder would disintegrate upon handling. As such, there was no further examination of material from trials using the Precimid 1170 powder.

Several prints of the Sintratec PA12 Black also had irregularities, including prints that crumbled when being removed from the powder cake, lifting of prints from the powder bed during spreading, and melting of excess material to the print.

TABLE III
ENERGY MELT RATIO VALUES FOR DESIGN OF EXPERIMENT TRIALS.

Print Bed Temperature (°C)	Laser Speed (mm/s)	Sintratec PA12 Black EMR	Precimid 1170 EMR
165	650	2.344	2.667
165	550	2.770	3.152
165	450	3.385	3.852
170	650	4.684	5.833
170	550	3.832	4.772
170	450	4.684	5.833
175	650	5.260	8.313
175	550	6.216	9.825
175	450	7.598	12.008

A. Removal from powder cake

Several trials did not result in complete dog bones that could be removed from the powder cake after printing. Of note were those with a Print Bed Temperature of 165°C, the trials with Laser Speeds of 650 mm/s and 550 mm/s had very fragile parts, some of which broke during removal from the powder cake using a soft paintbrush. The trial with a Laser Speed of 450 mm/s suffered from curling during printing, and had parts swept off the print bed by the powder spreading blade. While there were partial dog bones made from the remainder of the part not swept off the bed, there were no complete dog bones produced.

Also of note were all trials with a Print Bed Temperature of 175°C. These trials resulted in printed parts, but excess material was bonded to the print, and was difficult to remove without damaging the part.

B. Scanning Electron Microscope

The advantage of using the SEM to examine cross sectional slices of the samples printed is that the necking between particles is visible. As expected, the necking that occurred between particles grew in frequency as both Print Bed Temperature and EMR increased. The images also show that EMR alone is not a sufficient estimate of the likelihood of printing, as shown with the trials with laser speeds of 650 mm/s. Necking was observed to increase with an increase in EMR, with porosity being reduced as necking increased. This is as expected, however the trial with a Print Bed Temperature of 165°C and Laser Scan Speed of 650 mm/s had an EMR of 2.344, which the model predicts should be sufficient to induce sintering. Prints from this trial were very fragile, and many dog bones did not survive removal from the powder cake, demonstrating that low EMR numbers may not produce parts of adequate quality, despite indicating they will be successful.

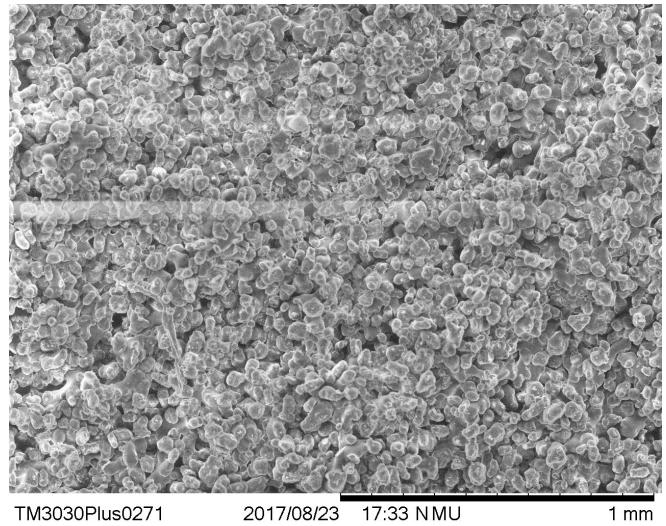


Fig. 4. Figure 3: SEM Image of Sintratec PA12 Black printed at 165°C, with a Laser Scan speed of 650 mm/s at 100 times magnification. The resultant Energy Melt Ratio value is 2.344. Note that there is necking present between particles, however areas of coalescence are rare.

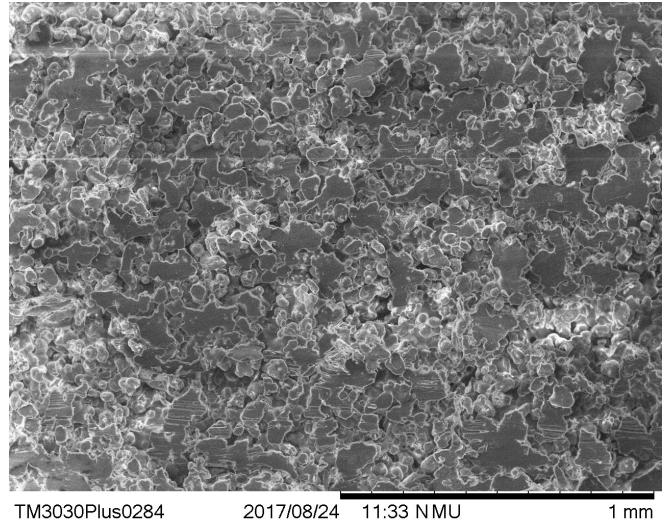


Fig. 5. Figure 4: SEM image of Sintratec PA12 Black, printed at 170°C, with a Laser Scan Speed of 650 mm/s at 100 times magnification . The resultant Energy Melt Ratio is 4.684. Areas of coalescence are far more common, but partial necking and areas of porosity are still frequent.

At the other end of the temperature range, the samples printed at 175°C display large areas of particles which have coalesced, with occasional pores visible. The presence of these pores indicates that the sample is unlikely to have undergone a full physical transition to the molten state, however there was clearly enough energy being put into the material to undergo sintering.

IV. DISCUSSION

The Energy Melt Ratio and Sintering Window did predict a set of printing parameters that would result in successful prints. However, the biggest limitation identified in these tests

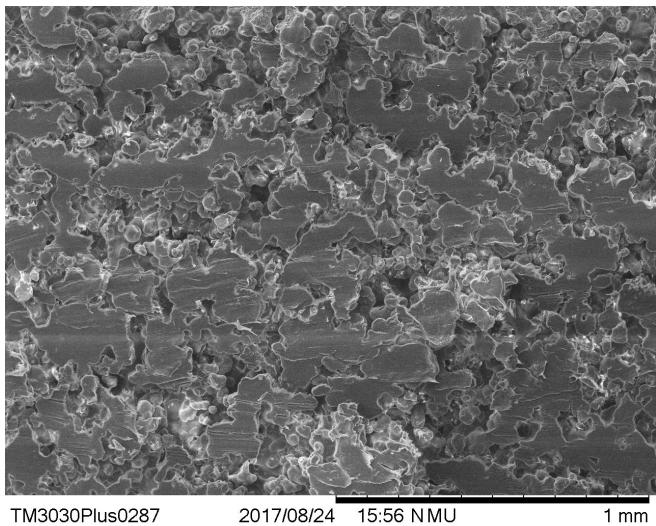


Fig. 6. Figure 5: SEM image of Sintratec PA12 Black, printed at 175°C, with a Laser Scan Speed of 650 mm/s at 100 times magnification. The resultant Energy Melt Ratio is 5.260. Areas of necking and porous areas are less common, and much of the part is coalesced.

was that neither the Sintering Window or Energy Melt Ratio models predicted that the white Precimid 1170 powder would not sinter. This is not a unexpected, as the white powder would reflect a larger amount of laser energy than black powder would. It is surprising that no melting occurred at the higher EMR values, given that it was over 12 times the amount required to cause sintering.

Authors of previous work have neglected to mention their assumptions on laser energy absorption [15]. There has been some work in identifying the reflectance of powders to lasers of varying wavelengths [16], but there has not been further work in implementing these findings into any models. This work does demonstrate that wavelength is a critical factor in the reflectance of laser energy. For the purposes of identifying and testing new materials for SLS further work should be done to improve these models, particularly finding a method of quantifying the proportion of laser energy being absorbed versus being reflected. While it be ideal to have a method of calculating these values for a given material across a range of laser wavelengths it may be feasible to gather these values experimentally.

V. CONCLUSION

The current methods of identifying printing parameters for Selective Laser Sintering include the use of the Sintering Window, and the Energy Melt Ratio. These two methods utilize data from Differential Scanning Calorimetry and the material data sheet to provide suitable values for both temperature settings, and for laser settings. These values are not exact, and will indicate values for the minimum energy to sinter material.

Experiments on two similar polyamide powders revealed some limitations in the use of the models, particularly for the Energy Melt Ratio. The EMR model does not take into account the reflectance of the laser energy of the powder

during sintering, assuming that all light energy emitted from the laser is absorbed. This can lead to partial failures to print, such as porous parts which crumble on removal from the powder cake, or total failure, as seen with the failure to sinter white powder under any of the experimental conditions.

Future work will focus on identifying a revised EMR calculation featuring a factor to better represent the proportion of laser energy absorbed by the power.

REFERENCES

- [1] K. V. Wong and A. Hernandez, "A review of additive manufacturing," *ISRN Mechanical Engineering*, vol. 2012, 2012.
- [2] B. Wendel, D. Rietzel, F. Khlein, R. Feulner, G. Hlder, and E. Schmachtenberg, "Additive processing of polymers," *Macromolecular materials and engineering*, vol. 293, no. 10, pp. 799–809, 2008.
- [3] C. W. Hull, "Apparatus for production of three-dimensional objects by stereolithography," Mar. 11 1986, uS Patent 4,575,330.
- [4] D. Gu, W. Meiners, K. Wissenbach, and R. Poprawe, "Laser additive manufacturing of metallic components: materials, processes and mechanisms," *International materials reviews*, vol. 57, no. 3, pp. 133–164, 2012.
- [5] B. Derby, "Additive manufacture of ceramics components by inkjet printing," *Engineering*, vol. 1, no. 1, pp. 113–123, 2015.
- [6] J. Gardan, "Additive manufacturing technologies: State of the art and trends," *International Journal of Production Research*, vol. 54, no. 10, pp. 3118–3132, 2016.
- [7] R. Goodridge, C. Tuck, and R. Hague, "Laser sintering of polyamides and other polymers," *Progress in Materials Science*, vol. 57, no. 2, pp. 229–267, 2012.
- [8] M. Schmid, A. Amado, and K. Wegener, "Polymer powders for selective laser sintering (sls)," vol. 1664, p. 160009, 2015.
- [9] G. Vasquez, C. Majewski, B. Haworth, and N. Hopkinson, "A targeted material selection process for polymers in laser sintering," *Additive Manufacturing*, vol. 1, pp. 127–138, 2014.
- [10] M. Vasquez, B. Haworth, and N. Hopkinson, "Methods for quantifying the stable sintering region in laser sintered polyamide12," *Polymer Engineering Science*, vol. 53, no. 6, pp. 1230–1240, 2013.
- [11] T. L. Starr, T. J. Gornet, and J. S. Usher, "The effect of process conditions on mechanical properties of laser-sintered nylon," *Rapid Prototyping Journal*, vol. 17, no. 6, pp. 418–423, 2011.
- [12] V. Beal, R. Paggi, G. Salmoria, and A. Lago, "Statistical evaluation of laser energy density effect on mechanical properties of polyamide parts manufactured by selective laser sintering," *Journal of Applied Polymer Science*, vol. 113, no. 5, pp. 2910–2919, 2009.
- [13] S. Berretta, O. Ghita, and K. E. Evans, "Morphology of polymeric powders in laser sintering (ls): from polyamide to new peek powders," *European Polymer Journal*, vol. 59, pp. 218–229, 2014.
- [14] S. Ziegelmeier, P. Christou, F. Wlecke, C. Tuck, R. Goodridge, R. Hague, E. Krampe, and E. Wintermantel, "An experimental study into the effects of bulk and flow behaviour of laser sintering polymer powders on resulting part properties," *Journal of Materials Processing Technology*, vol. 215, pp. 239–250, 2015.
- [15] S. Berretta, K. Evans, and O. Ghita, "Predicting processing parameters in high temperature laser sintering (ht-ls) from powder properties," *Materials Design*, vol. 105, pp. 301–314, 2016.
- [16] N. K. Tolochko, Y. V. Khlopkov, S. E. Mozzharov, M. B. Ignatiev, T. Laoui, and V. I. Titov, "Absorptance of powder materials suitable for laser sintering," *Rapid Prototyping Journal*, vol. 6, no. 3, pp. 155–161, 2000.