

Polymer Powders for Selective Laser Sintering (SLS)

Conference Paper

Author(s):

Schmid, Manfred; Amado, Antonio; Wegener, Konrad

Publication date:

2014

Permanent link:

<https://doi.org/10.3929/ethz-a-010336188>

Rights / license:

[In Copyright - Non-Commercial Use Permitted](#)

Polymer Powders for Selective Laser Sintering (SLS)

Manfred Schmid^a, Antonio Amado^a and Konrad Wegener^b

^a*Inspire, irpd (institute for rapid product development)
9014 St. Gallen, Switzerland*

^b*Department of Mechanical and Process Engineering, Swiss Institute of Technology
8008 Zürich, Switzerland*

Abstract. Selective Laser Sintering (SLS) is close to be accepted as a production technique (Additive Manufacturing). However, one problem limiting employment of SLS for additive manufacturing in a wide-ranging industrial scope is the narrow variety of applicable polymers. The commonly applied SLS powder to date is polyamide 12 (PA 12). PA 12 or compounds of PA 12 (dry blends) are approximately 90 % of complete industrial consumption. The remaining small quantity is distributed on polyamide 11 (PA11) and some other ‘exotic’ polymers (TPU, PEBA, P(E)EK). Industry is awaiting commodity polymers like polypropylene (PP) or polyethylene (PE) crucial to open new market segments. But several approaches launching those polymers failed. But what are the reasons for the difficulties in developing new SLS powders? The contribution is to answer this and highlights the combination of intrinsic and extrinsic polymer properties necessary to generate a polymer powder promising for SLS application. Particle shape, powder distribution, thermal, rheological and optical requirements must be considered and only a particularly controlled property combination leads to successful SLS implementation. Thermal behavior, particle shape and –distribution is discussed in detail, although the other properties can’t be disregarded for providing new commercially successful SLS powder finally.

Keywords: Additive Manufacturing, Selective Laser Sintering, Polymer powders, 3D-Printing

PACS: 81

INTRODUCTION

Selective Laser Sintering (SLS) manufactures plastic parts by adding consecutively material layers. SLS is allocated thus to the field of Additive Manufacturing (AM) which is considered as part of the next industrial revolution [1]. AM summarizes about one dozen of different layer-by-layer technologies, frequently specified as ‘3D-Printing’ in newspapers and other common publications. Additive Manufacturing is contrary to subtractive manufacturing. E.g. traditional machining like drilling, milling and grinding, where material is removed to achieve a desired shape. In the entire field of currently available AM-technologies SLS is regarded as the most favorable approach as a sincere production technique for plastic parts appropriate for industry. However, one problem limiting employment of SLS for additive manufacturing in a general scope is the narrow variety of applicable polymers [2].

Polyamide 12 (PA 12) is the major and almost exclusive option. Either pure PA 12 or PA 12 compounds (dry blends) are actually used in almost all commercial systems [3]. Polyamide 11 (a near relative of PA12) is also subjected to SLS systems with moderate success although some remarkable part properties. Other ‘exotic’ polymers like PE(E)K, elastomeric types (TPE, TPU, PEBA) and other polyamides (PA 6) are commercialized with growing but still limited achievement. Especially a breakthrough in direction of semi crystalline commodity polymers like polypropylene (PP) or polyethylene (HDPE, LLDPE) to open new market segments for SLS technology is still missing [4]. Facing the well know ‘plastic pyramid’ there should be numerous other options. What is the reason for this restricted material selection? What about amorphous polymers like polycarbonate (PC) or ABS? In order to answer these questions and to deliver a guideline for production of successful SLS materials understanding the very specific property combination, necessary to transfer a regular polymer into a successful SLS powder, is crucial.

COMBINATION OF PROPERTIES OF SLS POWDERS

In order to understand the most influencing parameter on material characteristics an improved consideration of the most important parameters on SLS powder is necessary [5]. Figure 1 sketches five main factors in this connection: powder and particle as well as optical, thermal and rheological behaviour. It can be understood from Figure 1 that it is a complex system of interrelated assets. The different properties can be divided into intrinsic (thermal, optical and rheology) and extrinsic ones (particle and powder). Intrinsic properties are typically given form

the molecular structure of the polymer itself and can't be influenced easily, whereas processing in advance controls extrinsic properties.

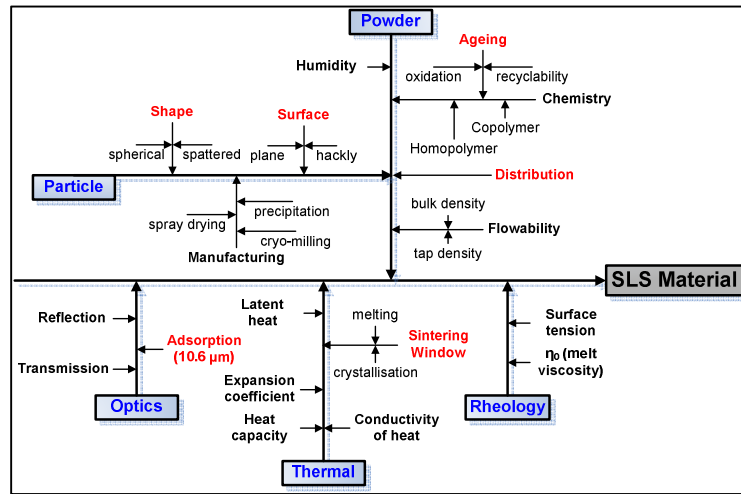


FIGURE 1. Interconnection of different polymer properties to be organized for providing promising SLS materials;

Intrinsic Properties

Thermal properties

Identifying the challenging aspects of the desired thermal properties it is necessary to understand the course of action during SLS processing. In a SLS system essentially a CO₂ laser beam is used to selectively fuse or melt the polymer particles deposited in a thin layer. Locally full coalescence of polymer particles in the top powder layer is necessary as well as an adhesion with previous sintered layers. For semi crystalline polymers usually used in SLS processing this implies that crystallization (T_c) should be inhibited during processing as long as possible, at least for several sintered layers. Thus, processing temperature must be precisely controlled in-between melting (T_m, red line, Figure 2) and crystallization (T_c, blue line, Figure 2) of the given polymer. This meta-stable thermodynamic region of undercooled polymer melt is called ‘sintering window’ of SLS processing for a given polymer. Figure 2 depicts a DSC run (DSC = Differential Scanning Calorimetry [6]) for commercial PA 12 SLS-powder. The nature of sintering window between onset points of T_c and T_m is obvious.

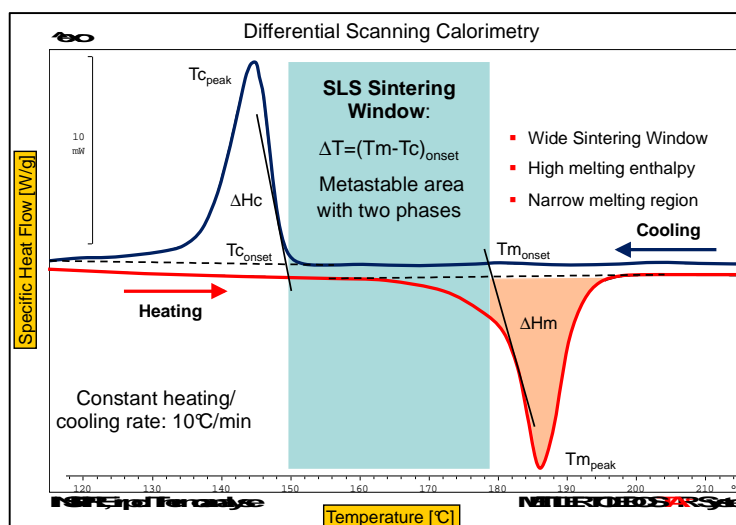


FIGURE 2. Typical DSC-Thermogram with nature of ‘sintering window’ as SLS process temperature;

However it must be indicated, that the scheme in Figure 2 is just an idealized representation of thermal reality as it is received with fixed heating and cooling rates ($10^{\circ}\text{C}/\text{min}$) never be applied during SLS processing. In fact there are undefined and hardly controllable temperature change rates and especially the sintering temperature ($T_s =$ process temperature during sintering) close to crystallization onset means, that stimulation of crystallization shifts to higher temperatures for SLS processing. Figure 3 and Figure 4 indicates what can occur usually for polymer powders with a too small sintering window. If T_s is too close to crystallization (left side in Figure 3) curling due to premature crystallisation is induced and parts are distorted after releasing from surrounding powder bed. If temperature is just slightly higher during processing (right side of Figure 3) an early crystallization can be avoided but in this case the temperature is too close to melting and leads to a loss of exact definition of part features. Powder particles in the direct neighborhood of the laser trace stick on the molten surfaces (lateral growth) and prevent desired resolution of part topography. Figure 4 presents another extreme example for premature crystallization for an unsuitable SLS powder. In this case crystallization occur that rapid that different laser traces are even separated.

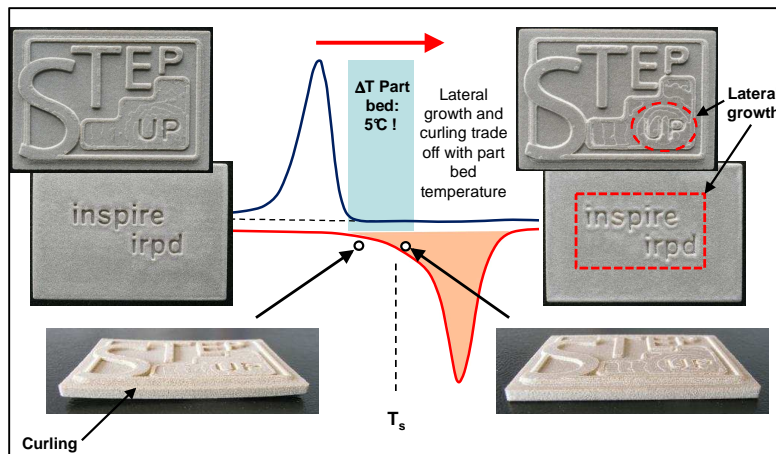


FIGURE 3. SLS Processing problems for too small 'sintering window': curling or lateral growth;

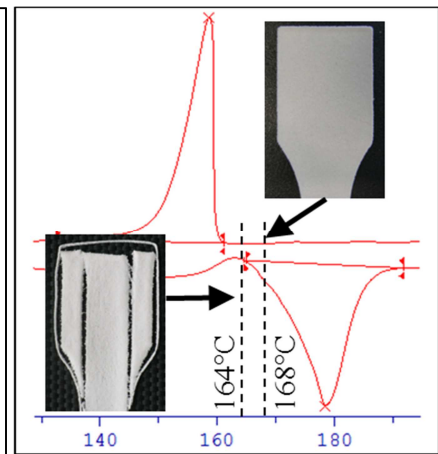


FIGURE 4. Premature crystallization during SLS processing with trace split;

Additionally to the very critical point of suitable thermal transitions (T_m , T_c) there are farther intrinsic factors like optical properties, melt viscosity and surface tension that needs to be very specific for successful application of polymer powders to Selective Laser Sintering.

Optical Properties

Obligatory is obviously a sufficient capability of the material to absorb energy at present laser wavelength (CO_2 -Laser: $10.6 \mu\text{m}$). This is apparent for most polymers as they consist of aliphatic compounds (C-H). Those polymers have, in the majority of cases, some group vibrations in the 'fingerprint' infrared (IR) region sufficient to absorb relevant portions of $10.6 \mu\text{m}$ radiation. Furthermore, in case of a poor absorption capability, an increase of laser energy power can compensate the effect. This means that absorption is the less critical of the intrinsic properties.

Viscosity and Surface Tension

Besides infrared absorption capability a low zero viscosity (η_0) and a low surfaces tension (γ) of polymer melt is necessary for successful SLS processing. This is indispensable to generate an adequate coalescence of polymer particles. Especially a low melt viscosity without shear stress is of high importance, as, unlike injection molding, SLS cannot provide an additional compacting during part generation (holding pressure). Figure 5 indicates the effect of inferior melt viscosity clearly visible. The right side image (Figure 5) depicts a lot of imperfections in the part morphology and a poor surface quality as well.

The required low zero viscosity is also the reason why attempts to process amorphous polymers with SLS usually ends with brittle and instable parts. Due to the fact that viscosity of those polymers above glass transition (T_g) is still very high in general a proper coalescence does not take place usually.

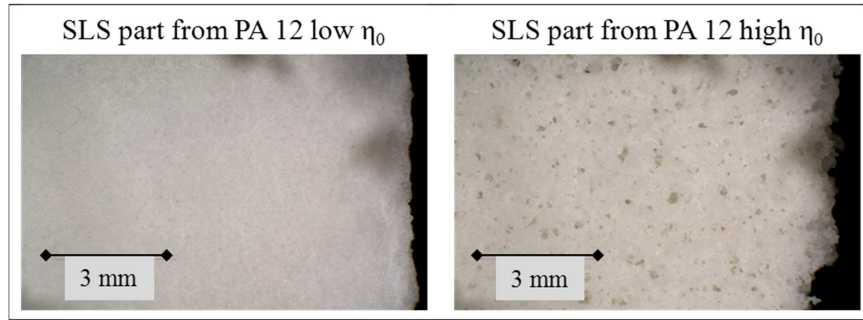


FIGURE 5. Cross section of PA 12 parts made from PA 12 polymers with different melt viscosity;

Following Figure 1 it is palpable that besides the polymer related properties also properties mainly determined by production of the powders are important. Here it can be distinguished between the desired properties of a single particle and the obtained powder prepared from these particles.

Extrinsic Properties

Particle

Shape and surface of the single particles determine the behavior of the resulting powder to a great extent. In case of SLS powders the particles should be at least as feasible formed spherical. This is in order to induce an almost free flowing behavior and is necessary as SLS powders are distributed on the part bed of an SLS machine by roller or blade systems and will not be compacted additionally. A simple approach to access the flowability of powders is the determination of bulk and tap density. Determination of bulk and tap density gives a good indication on the one hand regarding powder density which is correlated with the final part density and on the other hand regarding the flowability by calculation of the so called Hausner ratio H_R [7]. Regarding literature a $H_R < 1.25$ means free flowing powder behaviour and a $H_R > 1.4$ means fluidization problems (cohesive properties).

$$H_R = \rho_{\text{tap}} / \rho_{\text{bulk}} \quad (\rho_{\text{loose}} = \text{bulk density}; \rho_{\text{tap}} = \text{tapped density})$$

The achievable SLS part density is directly linked to powder density in part bed and is thus coupled to the shape of particles and their free flowing behavior. Figure 6 depicts some particle forms achievable by different powder generation processes. Spherical particles are usually received from co-extrusion processes with soluble/non-soluble material mixtures, like oil droplets in water. Potato shaped particles are typical for the today available commercial PA 12 powder conected by precipitation process. Particles obtained from cryogenic milling are inadequate in the majority of cases and fail for SLS processing. Purpose is that inferior powder flowability generates poor part bed surface in SLS machine and a reduced powder density as well. Thus, cryogenic milled powders finally end in weak, less condensed SLS parts with low density and poor properties usually.

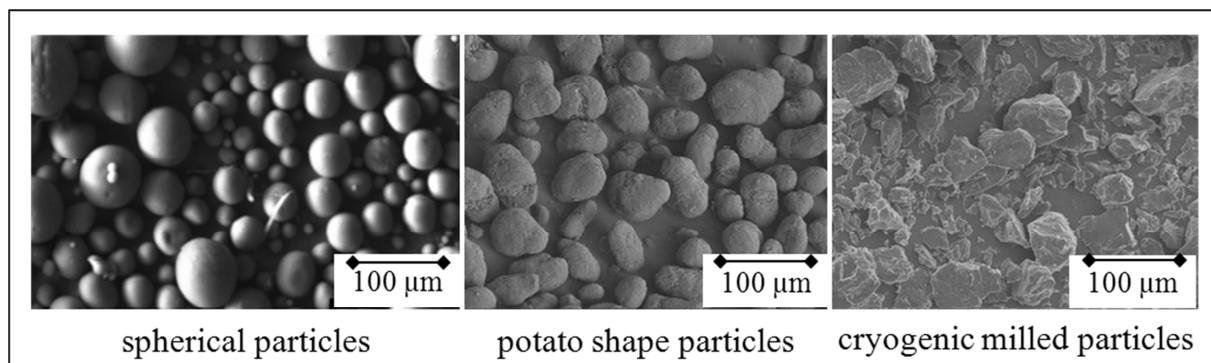


FIGURE 6. Particle shapes attainable by different production technologies;

Powder

For SLS powders a certain particle size distribution (PSD) is necessary to be processable on SLS equipment. This distribution is favorably between 20 μm and 80 μm for commercial system. The PSD is usually measured by laser diffraction systems. However, as a matter of fact, with this measurement the fraction of small particles is neglected frequently. But particularly the amount of small units is often responsible if a powder depicts a reasonable SLS processing behavior or not. Figure 7 illustrates such a case. Both, 'Powder 1' and 'Powder 2' have some good and acceptable PSD looking at volume distribution (Figure 7, middle column). From that point of view both powder should be processable on SLS equipment. However, in reality, the trial to do so with 'Powder 2' failed. The reason can be recognized from number distribution (Figure 7, right column). 'Powder 2' consists of an extreme high portion of small particles which may induce stickiness in powders. The enhanced adhesion between particles reduces the free flowing powder behavior and prevents SLS processing. As especially cryogenic milled powder represents often a high amount of fine particles this is another reason why these powders are usually unsuccessful in SLS processing.

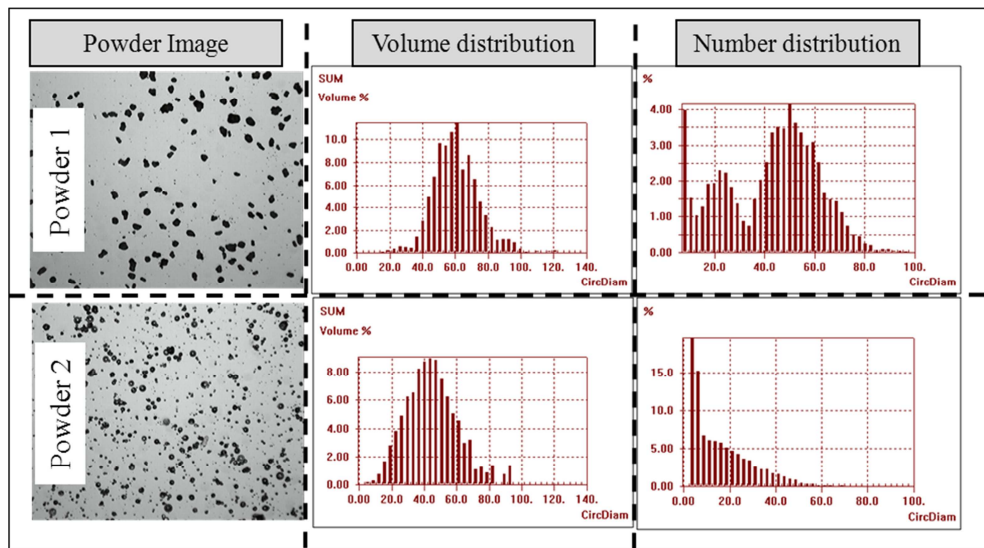


FIGURE 7. Distribution of powders with similar volume distribution and dissimilar number distribution;

SUMMARY AND OUTLOOK

The presentation summarizes in a brief manner the most important key factors and their meaning for SLS processing. It is highlighted the combination of intrinsic and extrinsic polymer properties necessary to generate a polymer powder likely for SLS application. Only a specific combination of indicated assets leads probably to success. This is one reason for fewer materials commercially available to date. In future a significant enlargement of polymer powder portfolio particularly for olefin polymers (PP, PE) is required to boost SLS technology.

REFERENCES

1. N. Hopkinson, *Rapid Manufacturing – An Industrial Revolution for the Digital Age*, Wiley&Sons: New York, 2006
2. D. Rietzel, et al. *Polymer powders for selective laser sintering – production and characterization*, Proc. 44th CIRP conference on Manufacturing Systems, Madison 2011
3. J. P. Kruth, G.N. Levy et al., *Consolidation phenomena in laser and powder-bed based layered manufacturing* CIRP Annals - Manufacturing Technology, 56(2), 2007, 730-759
4. M. Schmid, A. Amado, G.N. Levy, *iCoPP - A New Polyolefin for Additive Manufacturing (SLS)*, Proceedings of the International Conference on Additive Manufacturing, Session 7, Loughborough, U.K., 2011
5. D. Drummer, *Development of a characterization approach for the sintering behavior of new thermoplastics for selective laser sintering*, Physics Procedia (5), 2010, 533 – 542
6. G.W. Ehrenstein, G. Riedel, P. Trawiel, *Thermal Analysis of Plastics*, ISBN-10: 3-446-22673-7, 2004
7. G.V. Barbosa-Canovas et al., *Food Powders* Kluwer Academic Press, New York, ISBN 0-306-47806-4, 2005, 55