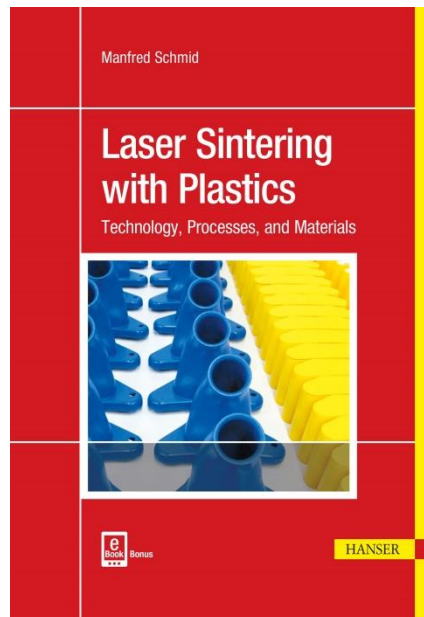


HANSER



Sample Pages

Laser Sintering with Plastics

Technology, Processes, and Materials

Dr. Manfred Schmid

ISBN (Book): 978-1-56990-683-5

ISBN (E-Book): 978-1-56990-684-2

For further information and order see

www.hanserpublications.com (in the Americas)

www.hanser-fachbuch.de (outside the Americas)

© Carl Hanser Verlag, München

Contents

Foreword	V
About the Author	VII
1 Introduction	1
1.1 Manufacturing Technology	1
1.2 Additive Manufacturing	2
1.2.1 Areas of Application/Technology Driver	3
1.2.2 Polymer-Based AM Method	5
1.2.3 Technology Maturation	7
1.2.4 Laser Sintering (LS)	9
1.3 References of Chapter 1	11
2 LS Technology	13
2.1 Machine Technology	15
2.1.1 Machine Configuration	15
2.1.2 Temperature Control	17
2.1.2.1 Heat Sources	18
2.1.2.2 Surface Temperature in the Build Cavity	19
2.1.2.3 Laser Energy Input, Andrew Number (A_n)	20
2.1.3 Powder Feed	22
2.1.3.1 Powder Supply	22
2.1.3.2 Powder Application	24
2.1.4 Optical Components	28
2.2 Machine Market	29
2.2.1 3D Systems (USA)	29
2.2.2 Electro Optical Systems - EOS (Germany)	31
2.2.3 Aspect (Japan)	32
2.2.4 Farsoon (China)	33

2.2.5	Comparison of Commercial LS Machines	34
2.2.6	Other Machinery	35
2.3	References of Chapter 2	37
3	LS Process	39
3.1	Process Chain	39
3.1.1	Powder Preparation	40
3.1.2	Data Preparation and Build Job	42
3.1.3	Build Process	44
3.1.3.1	Heating	44
3.1.3.2	Process Cycle	44
3.1.3.3	Parts and Build Chamber Parameters	48
3.1.3.4	Strategy of Part Irradiation	49
3.1.3.5	Cool Down and Part Extraction	51
3.1.4	Process Errors	53
3.1.4.1	Deformation of the Part	53
3.1.4.2	Surface Defects: Orange Peel	55
3.1.4.3	Other Process Errors	56
3.2	Quality Assurance	57
3.2.1	General Quality Actions	57
3.2.2	Test and Comparison Parts	59
3.2.3	Quality Costs	61
3.2.4	PPM Concept (EOS)	61
3.2.5	State of Standardization	62
3.3	References of Chapter 3	64
4	LS Materials: Polymer Properties	65
4.1	Polymers	65
4.1.1	Polymerization	66
4.1.2	Chemical Structure (Morphology)	68
4.1.3	Thermal Behavior	69
4.1.4	Polymer Processing	70
4.1.5	Viscosity and Molecular Weight	71
4.2	Key Properties of LS Polymers	73
4.2.1	Thermal Properties	74
4.2.1.1	Crystallization and Melting (Sintering Window)	75
4.2.1.2	Heat Capacity (c_p) and Enthalpies (ΔH_k , ΔH_m)	80
4.2.1.3	Thermal Conductivity and Heat Radiation	80
4.2.1.4	Modeling the Processes in the Sintering Window	82

4.2.2	Rheology of the Polymer Melt	83
4.2.2.1	Melt Viscosity	84
4.2.2.2	Surface Tension	86
4.2.3	Optical Properties	87
4.2.3.1	Absorption	88
4.2.3.2	Transmission and (Diffuse) Reflection	90
4.2.4	Particles and Powder	91
4.2.4.1	Powder Rheology	92
4.2.4.2	Particle Size Distribution	95
4.2.4.3	Powder Density	96
4.3	References of Chapter 4	98
5	LS Materials: Polymer Powders	101
5.1	Production of LS Powders	101
5.1.1	Emulsion/Suspension Polymerization	102
5.1.2	Precipitation from Solutions	103
5.1.3	Milling and Mechanical Grinding	104
5.1.4	Coextrusion	105
5.1.5	Overview: Production of LS Powders	106
5.1.6	Other Powder Manufacturing Processes	107
5.1.6.1	Spray Drying	107
5.1.6.2	Drop Extrusion	108
5.1.6.3	Melt Spinning	108
5.1.6.4	RESS with Supercritical Gases	109
5.2	Evaluation of the Powder State	109
5.2.1	Thermal Analysis	110
5.2.1.1	Differential Scanning Calorimetry (DSC)	110
5.2.1.2	Thermogravimetry (TGA)	111
5.2.2	Melt Viscosity	112
5.2.2.1	Melt Flow Index (MVR/MFI Measurements)	112
5.2.2.2	Molecular Weight and Residual Monomer Content	114
5.2.3	Particle Shape and Powder Distribution	115
5.2.3.1	Shape and Surface	116
5.2.3.2	Volume and Number Distribution	117
5.2.4	Free-Flowing Behavior of Powders	118
5.2.4.1	Hausner Factor (HF)	120
5.2.4.2	Revolution Powder Analysis	122
5.3	References of Chapter 5	123

6	LS Materials: Commercial Materials	125
6.1	Polyamide (Nylon)	129
6.1.1	Polyamide 12 (PA 12)	130
6.1.1.1	Powder Distribution and Particles	131
6.1.1.2	Thermal Properties	134
6.1.1.3	Crystal Structure	139
6.1.1.4	Molecular Weight and Post-Condensation	141
6.1.1.5	Powder Aging	145
6.1.1.6	Property Combination of PA 12	147
6.1.2	Polyamide 11 (PA 11)	148
6.1.3	Comparison of PA 12 and PA 11	149
6.1.4	PA 12 and PA 11 Compounds	151
6.1.5	Polyamide 6 (PA 6)	152
6.2	Other LS Polymers	153
6.2.1	Polyether Ketone (PEK)	153
6.2.2	Flame Retardant Materials	154
6.2.3	Polyolefins	155
6.2.3.1	Polyethylene (PE) and Polypropylene (PP)	155
6.2.3.2	Polystyrene (PS)	156
6.2.4	Elastomeric Materials	156
6.2.4.1	Thermoplastic Polyurethane (TPU)	157
6.2.4.2	Thermoplastic Elastomers (TPE)	157
6.3	References of Chapter 6	158
7	LS Parts	161
7.1	Part Properties	162
7.1.1	Mechanical Properties	162
7.1.1.1	Short-Term Load: Tensile Test	162
7.1.1.2	LS Build Parameters	164
7.1.1.3	Part Density	165
7.1.1.4	Degree of Particle Melt (DoPM)	168
7.1.1.5	Anisotropy of the Part Properties	171
7.1.1.6	Long-Term Stability	174
7.1.2	Part Surfaces	174
7.1.2.1	Influence Parameters	174
7.1.2.2	Roughness Determination	176
7.1.2.3	Surface Finishing	177
7.1.2.4	Finishing	178
7.2	Applications and Examples	181
7.2.1	AM-Compatible Design	181

7.2.2	Model/Prototype Construction	182
7.2.3	Functional Integration	183
7.2.4	Reduction of Part Lists	185
7.2.5	Customization	186
7.2.6	AM Business Models and Outlook	186
7.3	References of Chapter 7	189
8	LS Materials Table	191
Index	195

Foreword

The history of additive manufacturing might seem to be very short, but in reality the technology is more than a hundred years old. The first patent application was in 1882 by J.E. Blather, who registered a method for producing topographical contour maps by cutting wax sheets, which were then stacked.

This is an amazing fact: layer-by-layer work processes are currently experiencing a huge amount of hype that was not triggered by the development of new basic technologies. Rather, the reason for this is that essential patents have expired, making it possible to recreate for example a melt deposition method using the simplest means, which can be used for the generation of three-dimensional bodies. However, this hype managed to develop, in a very short time, an immense momentum. The user centralization and the new degrees of freedom offered by the technologies coincide with the present boom of DIY (do-it-yourself) culture, so it is not surprising that “fabbers¹” and “3D printing selfies” are in high demand.

Conversely, various new technologies were developed over the entire process chain as well. During my studies in the early 2000s, when I dealt with the topic for the first time, the importance of layer manufacturing was only high in the area of prototyping. The technologies have not changed radically since then, but nowadays the market for custom products and small production runs has increased massively in many industries. Both established machine manufacturers and many innovative startups have joined this field. The additive manufacturing process has found a previously unimagined extent of application, from the production of individual toys to high-power components for powertrains. In the future, different scenarios for production are conceivable, and decentralized production “on demand” is tangible. This generates a possible area of conflict from high technological expectations, risks, and potentials. A realistic estimation should not be based solely on the enthusiasm that is noticeable after seeing the first additive manufacturing process and having the generated part in ones hand. Independent research on the topic is therefore essential.

¹ “Fabber”: Short for digital fabricator. A machine that makes arbitrary three-dimensional objects automatically from raw materials and digital data.

BMW AG ordered the first SLA system in 1989. Thus, BMW AG was the first customer of a today world-recognized and leading company of laser sintering systems. Over the years, from the first model-making facilities, a center of competence within the *Research and Innovation Center (FIZ)* evolved, in which various types of practical and basic research are carried out today. In addition to high-quality prototypes for testing and validation of transportation vehicles, materials and processes are being developed, making it possible to realize the potential of layer-by-layer construction. For example, employees working in automotive production are individually equipped with personalized assembly aids to increase ergonomics and performance in assembly lines.

In this case, the focus of the discussion will be less on the 3D printing processes mentioned in the media, but rather on the highly complex manufacturing machines on which the production is to take place in the future. One such technology is laser sintering (LS), a laser-based unpressurized manufacturing process. However, the coincidence with a “real” sintering process is solely that the generated part cross section will be held near its melting temperature for a long residence time. This is the core process of laser sintering, which has been examined in diverse ways and is still subject of intensive further research.

As part of my own PhD thesis, I dealt with the time and temperature dependence of the two-phase region, in which melt and solid are present and sharply demarcated. I had thus the chance to enter one of the many interdisciplinary fields of research on additive manufacturing, and am still excited about this topic. Anyone who intends to study or work with laser sintering will not be able to find a lot about such a specialized topic in most of the general books on 3D printing and additive manufacturing. However, as powder-bed-based technologies are established as one of the major additive manufacturing processes, it is essential to present the results of basic research and transfer them to practical use in order to create, for example, as a service provider, viable high-quality parts. The purpose of this book by Manfred Schmid, one of the recognized specialists in laser sintering, is precisely to give this depth of field without losing sight of the benefits for the user.

Dr.-Ing. Dominik Rietzel

May 2015

About the Author

Dr. Manfred Schmid began his professional career as an apprentice laboratory assistant at *Metzeler Kautschuk AG* in Munich, Germany. After graduation, he studied chemistry at the University of Bayreuth (Germany), where he obtained a PhD degree in macromolecular chemistry. He worked on liquid-crystalline polyurethanes under the guidance of Prof. Dr. C. D. Eisenbach.



After completing his studies, he moved to Switzerland, where he worked for 17 years in industry in various positions in the areas of polymer research and production as well as material testing and polymer analysis. Polyamides and biopolymers were the focus of these different industry positions.

Since 2008, he leads the research in laser sintering (LS) at *Inspire AG*, the Swiss Competence Center for Manufacturing Techniques. *Inspire AG* acts as a transfer institute between universities and the Swiss machine, electro, and metal (MEM) industries.

The focus of his current activities is in the area of new polymer systems for the LS process, the analytical evaluation of such materials, and the qualitative and quantitative improvement of the LS process. He supervises several employees and research projects in this field.

As a guest lecturer, he occasionally lectures on materials science of polymers, manufacturing processes of polymers, and 3D printing at NTB Buchs (Interstate University for Applied Science, Switzerland) and in the University of Applied Science St. Gallen, Switzerland.

The idea for this book emerged from several internal training courses on additive manufacturing conducted at *Inspire AG* for large industrial companies.

ate prototypes and models (toys). However, this is sufficient and adequate for the purposes of this sector (design patterns, rapid visualization of new ideas).

Because of substantial advancements in all the technologies mentioned, newly developed methods such as SHS, AKF, and MFJ, and future changes in the characteristics that are not to be excluded, the characteristics of Table 1.1 require constant re-evaluation.

1.2.4 Laser Sintering (LS)

AM-components made as described in Table 1.1, rated by industry standard criteria such as mechanical properties, thermal stability, component precision, surface quality, and long-term stability, as well as a few others, should meet the demand in terms of the production of functional parts. Essentially, only laser sintering is qualified nowadays. The cohesion of the building materials is carried out by a thermal process that includes the melting of the powder followed by solidifying it into the desired shape.

The LS process is currently considered as the AM process that will be able in the future to permanently cross the border between prototyping and functional components. This step is considerable because it means that the technology must meet completely different requirements in terms of reproducible quality, process reliability, automation of production processes, and other production-typical requirements.

The step from prototype to production part changes the perspective entirely. Both LS parts and the LS process have to be measured in the context of traditional and established production technologies. Only by succeeding at this step can a wide industry acceptance be expected in the future. For this, all levels of the LS process chain must be considered. Figure 1.4 shows schematically the factors that influence the LS process.

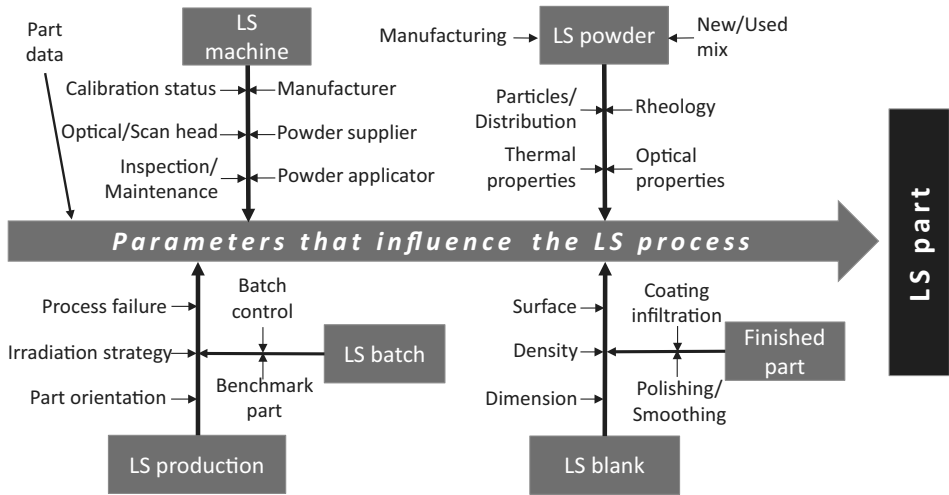


Figure 1.4 Process chain and influences on additive manufacturing with LS

All areas featured in Figure 1.4 are addressed in this book and discussed in detail:

LS technology (Chapter 2): This section describes the machine technology of the current LS devices and adds special emphasis on where the technologies of individual manufacturers differ and the resulting effects. Temperature control, powder feed, energy input, and optical components are the focus. A summary of the equipment currently available in the market completes the differentiation.

LS process (Chapter 3): This section explains key process details before and during the fabrication process. The powder preparation, the process flow, and process errors are discussed. Opportunities for quality control throughout the supply chain and the level of international standardization are presented.

LS materials: Another priority of this book is the polymeric materials that can be processed by LS technology (**Chapter 6 – LS materials: Commercial materials**). First, the question of the specific requirements imposed on the plastics to make them accessible to the LS process is presented (**Chapter 4 – LS materials: Polymer properties**). In Chapter 5, special attention is placed on the preparation of suitable polymer powders and the evaluation of their properties (**Chapter 5 – LS materials: Polymer powder**).

LS parts (Chapter 7): In the final chapter, the mechanical properties and the density of LS parts are finally addressed. Some selected examples of parts are also illustrated, including the design features and the limitations of the LS method, as well as the specific advantages that LS parts can have compared to plastic parts that have been produced with other plastics processing methods (e.g., injection molding).

■ 2.1 Machine Technology

2.1.1 Machine Configuration

The market-leader systems from 3D Systems and EOS are structurally similar at their core but differ in details such as powder feed, powder application, optical correction, and the irradiation strategy.

The basic structure of an LS machine consists of three levels, as shown in Figure 2.3: optics module, build chamber with build area, and powder area.

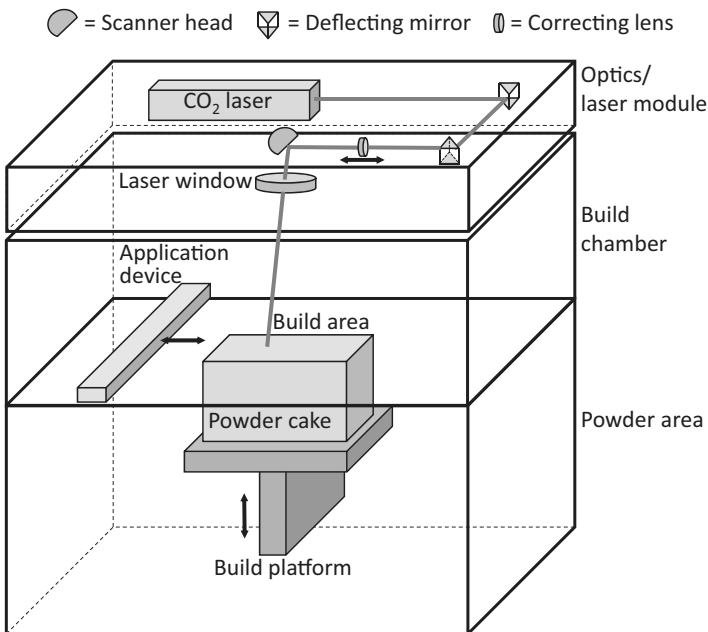


Figure 2.3 Basic structure of an LS machine

The optics, or laser, module contains the laser, the beam path with the corresponding deflecting mirrors, a correcting lens for focus adjustment, and the scanner head. This machine component is hermetically sealed from the rest of the machine and must be dust-free. Dust particles on the optical elements would lead to dispersion losses of the laser radiation and a massive negative impact on the quality of the parts built by the process.

Figure 2.4 shows a view of the laser module of a DTM Sinterstation 2500plus. The laser, the deflecting mirrors, the correcting lens, and the scanning head are clearly visible. Not depicted here are the electronic control modules of the scan head, which are also housed in a dust-free environment in the laser module area.

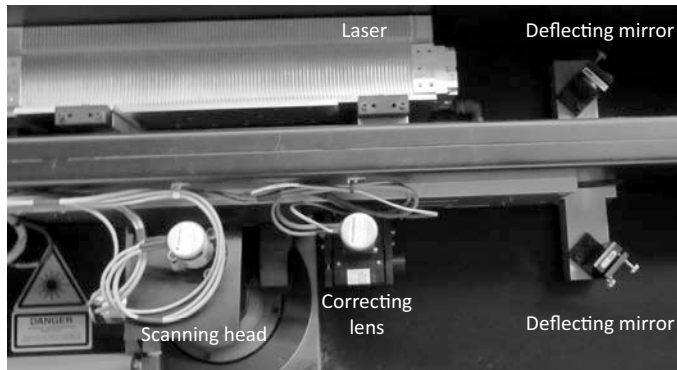


Figure 2.4 Top view of the laser module of an LS machine: the laser, the deflecting mirrors, the correcting lens, and the scanning head are visible [source: Inspire AG]

Under the scanning head in Figure 2.4, the laser window can be seen, which represents the interface to the underlying build area. The laser window consists of special optical materials with an extremely high transmission for the corresponding laser wavelength. In the case of LS machines with a CO₂ laser ($\lambda = 10.6 \mu\text{m}$), zinc selenide (ZnSe) is used for the laser window. Figure 2.5 shows the components of the laser window when it is installed and uninstalled.

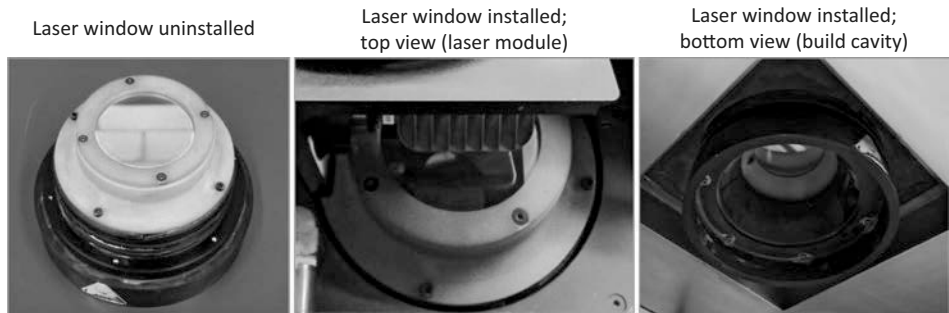


Figure 2.5 Laser window installed and uninstalled [source: Inspire AG]

For a good sintering result, the laser window should/must be cleaned carefully after each LS build. Deposits or burnt particles would massively affect the process. The laser window must be replaced periodically due to wear, since it can become “blind” over the course of many build cycles.

The next two areas in an LS machine are the build chamber and the powder area. These two regions are connected to each other through the build area. In the case of DTM/3D Systems technology, the powder feed takes place (see Section 2.1.3.1) at the interface between build and powder area, that is, the storage for the powder is located in the powder area.

Ideally, all the parts at the end of the entire build process are in good shape, as shown in Figure 3.11. No part distortion or other process errors can be seen there.

3.1.4 Process Errors

As with other manufacturing processes, a whole range of process issues can occur in the LS process. These result in either rejected parts or, in the worst case, a termination of the build process with damage to the machine components (see Figure 3.12, left).

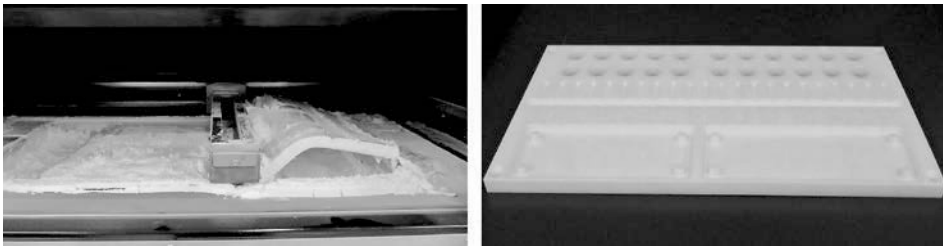


Figure 3.12 Build termination due to blocking of the coating unit [source: Inspire AG]

During the production of the large part with flat areas shown in Figure 3.12 (right side), the incorrect positioning of the part caused a massive overheating of individual layers, which resulted in a partial melt of the build area. Thus, the coater has collected the already sintered layers and moved them aside. The complete build had to be rejected, and the coating unit had to be completely re-adjusted.

Problems are not always as massive as shown in Figure 3.12. In many cases, the entire build job is finished easily and problems are only detected when the parts are unpacked, showing part distortion or other geometrical deviations (deformations).

3.1.4.1 Deformation of the Part

The deformation of the parts occurs in different stages of the process: during the build phase (in build) or after the build phase (post build). Usually it is referred to as “curling” when the first sintered layers of the part are directly affected from distortion and the rest of the layers were built geometrically correct. In the case of “warpage”, the parts have been built properly and twisted after finishing (e.g., wrong cool down). In Figure 3.13, the differences are shown schematically.

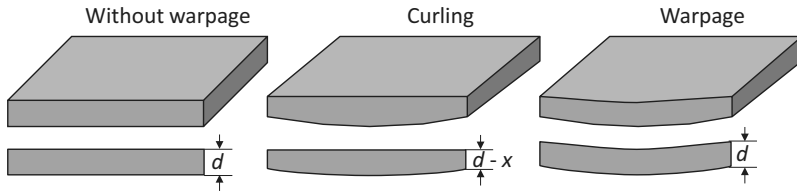


Figure 3.13 Differences in part distortion: curling and warpage

Curling can occur during the process in such a severe manner that the build process must be stopped immediately. Figure 3.14 shows an example of a massive curling effect, which led to the termination of the build process. If the edges of the parts, as shown in Figure 3.14, are already so protruded from the powder bed in the first layers, the roller would displace the part and destroy the powder bed at the next powder application by the roller.



Figure 3.14 Massive curling in the first layers of the part [source: Inspire AG]

Part warpage can also be triggered by incorrect part positioning in the build area. Figure 3.15 shows a typical case. Eight very thin but large components should be produced, for cost reasons, in a single build. For this, six parts are positioned flat and two parts are in the perpendicular position in the build job (Figure 3.15, right). While the six parts built horizontally (XY positioning) have predominantly straight walls and minimal warpage, the two left and right standing parts are highly warped and useless (see Figure 3.15, left).

In addition to the above different warpage types, there are other process errors that generate surfaces problems, which, due to their wavy appearance, are likened to an orange peel.

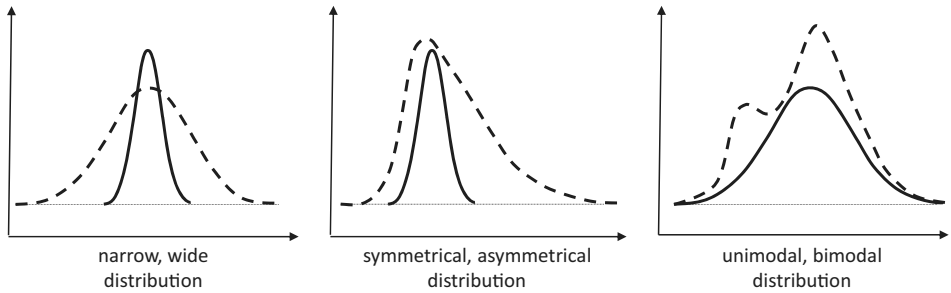


Figure 4.23 Some possible basic powder distributions

The distribution of the powder sizes has, like the powder geometry and especially the particle shape, an impact on the part packing density of the powder in the LS build cavity. Which is the best or most favorable distribution for the LS process cannot be assessed spontaneously. With regard to the powder density, a high part packing density of the particles is certainly desirable.

4.2.4.3 Powder Density

The density of powder particles can achieve a theoretical maximum value of 74% space filling in a cubic face-centered structure. This is strictly true only for unimodal distributed powders whose particles are ideally spherical. With the addition of smaller particles, which can fill the cavities between the large spheres, theoretically the maximum density can still be increased by a few percent [17].

However, it should be noted that, in reality, the theoretical density value and further optimization by mixing different fractions of powder are hardly practical. On the one hand, there are usually no ideally spherical, unimodally distributed powders of any size that can be mixed together. On the other hand, at non-ideal mixing ratios, the smaller particles in the powder are placed in such a way that the distance between the large particles increases again, and thus the density is reduced (an increase in the specific volume of the system).

Figure 4.24 shows the relationship schematically. Different bimodal mixtures can be produced from two ideal powders of different sizes. Only when the small particles exclusively occupy the cavities between the large particles is there a (slight) increase in the powder density. If the mixing ratio is not ideal, the powder density will decrease.

In addition, in mechanical loads, such as mixing processes, there is always a counter-effect. Fine powder separates from the large particles, floating up (shaking effect), so mixing and demixing compete.

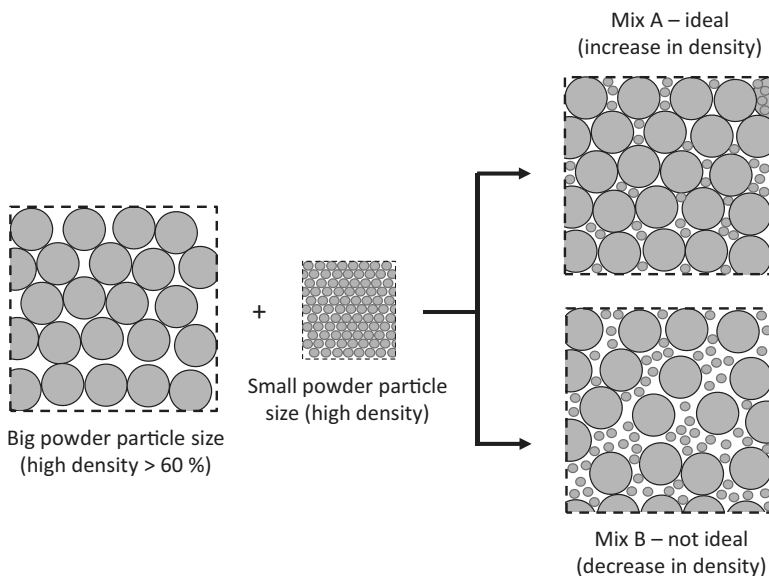


Figure 4.24 Part packing density of ideal spherical spheres in two sizes and bimodal mixtures

The part packing density of powders in technical applications achieves a maximum value of approximately 60%. For this purpose, nearly spherical particles are also required. The geometric deviation of the particles from the ideal spherical shape causes the practicable part packing density to fall rapidly, so that, in the case of today's commercially available LS powders, a powder density in the range of 45 to 50% can be expected.

The relationship between particle shape and the magnitude of the powder density is shown schematically in Figure 4.25. A rapid drop in the powder density with the deviation of the particles from the ideal circularity can be seen.

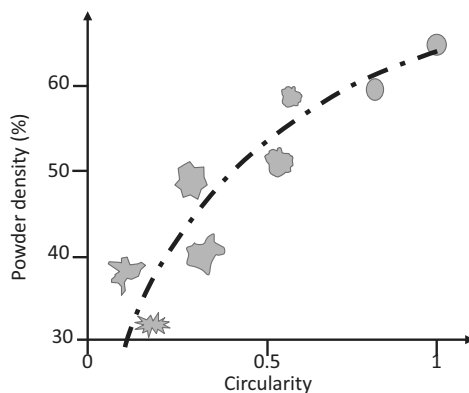


Figure 4.25 Relationship between particle geometry and powder density

If the powder density in the LS process is low due to, for example, a highly heterogeneous particle shape (often the case with grinded powders), only a small amount of material is deposited per volume fraction during powder application. After melting by the laser, the molten polymer flows together, and in the melt path of the laser, there is not enough material to generate homogeneous parts with sufficient structural integrity.

Figure 4.26 shows a part (the shoulder area of a DIN tensile bar) after a few sintered layers. In the left image, the sample was produced from powder with very low powder density, and, for comparison, a standard part (commercial PA 12 LS powder with sufficient density) is shown in the image on the right. As can be seen in Figure 4.26 (left side), the low powder density results in the formation of massive cavities and an uneven surface structure. The corresponding parts are unusable.

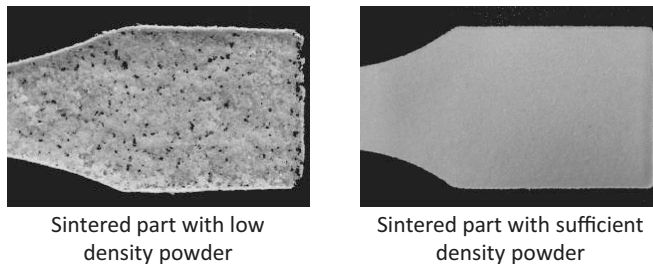


Figure 4.26 Test parts after a few sintered layers with different powder density
[source: Inspire AG]

From the explanations in Section 4.2.4, it becomes clear that the shape and the surface of the individual powder particles are of particular importance for the behavior of the corresponding powders in the LS process. Flowability and fluidization based on powder form, distribution, and density: these are decisive variables as to whether a powder can be successfully used and processed by LS or not.

The question of how the corresponding particles can be produced, from which promising LS powders can be generated, is therefore of central importance for future developments in this area (see Chapter 5).

■ 4.3 References of Chapter 4

- [1] Kaiser, W., *Kunststoffchemie für Ingenieure – Von der Synthese bis zur Anwendung*, Carl Hanser Verlag, 3rd Edition, Munich, ISBN: 978-3-446-43047-1, 2011
- [2] Osswald, T.A. and Menges, G., *Material Science of Polymers for Engineers*, Carl Hanser Verlag, 3rd Edition, Munich, ISBN 978-1-56990-514-2, 2012

6.1.3 Comparison of PA 12 and PA 11

The LS Rilsan® Invent materials are also adapted to the LS process with regard to their thermal properties, as described in Section 6.1.1.2 for the corresponding PA 12 materials. For example, Rilsan® Invent powder shows a relatively sharp melting peak at about 201 °C in the initial state, which is clearly above the melting point of standard PA 11 (about 186 °C). The effect of increasing the PA 11 sintering range by increasing the melting point ($\Delta T \approx 15$ °C) is therefore even more pronounced with Rilsan® Invent than with the corresponding PA 12 (Orgasol® Invent Smooth).

The production of Rilsan® Invent powder is carried out by means of a grinding process. In a further process step (annealing), the thermal properties are adapted for the LS process. The edges of the milled particles are also rounded in order to improve the flowability of the powders. Figure 6.17 shows the PA 11 particles (Rilsan® Invent) compared to Orgasol® Invent Smooth. The PA 11 particles exhibit an angular structure, as is typical for ground powders. The rounded edges are clearly visible. The powder distribution of Rilsan® Invent is significantly wider than that of PA 12 and has a d_{50} of approximately 50 μm (d_{50} (Orgasol® Invent Smooth) of approximately 43 μm).

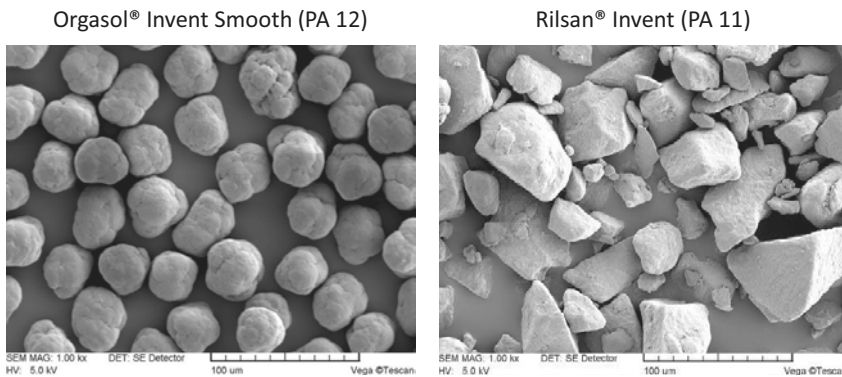


Figure 6.17 SEM images from Rilsan® Invent compared to Orgasol® Invent Smooth; particle form and shape as a result of different manufacturing processes [source: Empa]

Overall, the basic properties and basic data for PA 12 and PA 11 for LS use can be compared with each other as shown in Table 6.4. It should be noted that these are the values from the data sheets supplied by the material manufacturers and the information is valid for test specimens built in the XYZ direction (see Figure 7.5 in Section 7.1.1.5).

Table 6.4 Compilation of the Basic Data for Unreinforced Commercial PA 11 and PA 12 LS Materials (XYZ Build Direction)

Name	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PA 12 natural			
PA 2200/PA 2201/EOS (Germany)	1,700	48	15
Duraform® PA/3D Systems (USA)	1,586	43	14
Orgasol® Invent Smooth/Arkema (France)	1,800	45	20
PA 11 natural/black			
Rilsan® Invent/Arkema (France)	1,500	45	45

As already mentioned, the outstanding element for PA 11 is the significantly higher ductility of the materials compared with PA 12. This leads to a significantly higher elongation at break in the tensile test (about 45%) and also to an increased impact strength. The significantly improved toughness of the PA 11 materials is essentially based on the following molecular parameters:

- PA 11 thermally crystallizes exclusively in the α -triclinic form. This form is planar and requires no additional twisting of the amide units by 60° , such as the γ -monoclinic crystal structure (steric/kinetic hindrance).
- Due to the shorter PA 11 chains (a CH_2 unit less per molecular unit cell), PA 11 has more hydrogen bonds (HB) per polymer chain of the same length: PA 11 = 1 HB per 10 CH_2 groups, PA 12 = 1 HB per 11 CH_2 groups.
- Hydrogen bonds form a pronounced intramolecular cohesion and increase the melting point (odd-even effect [5]).
- In mechanical stress, the α -triclinic crystal lattice deforms better, and a transformation in a pseudohexagonal space lattice takes place. During this conversion, a considerable portion of the external load is absorbed (dissipated), which leads to a higher fracture energy absorption.

The cause for the higher ductility of PA 11 is therefore found in a combination of molecular material parameters. Specifically, the relatively higher number of hydrogen bonds and the ability to transform the crystal modification under stress are crucial.

In summary, the two currently most important materials for the LS process, PA 12 and PA 11, can be characterized and compared for the LS process as shown in Table 6.5.

Table 6.5 Basic Properties of PA 11 and PA 12 for LS Use

	PA 12	PA 11
Crystalline structure	γ -monoclinic	α -triclinic \rightarrow pseudo-hexagonal
Sintering window	large	small to medium
Melting point (T_m)	182 to 186 °C	186 to 201 °C
Elastic modulus	approx. 1,700 MPa	approx. 1,500 MPa
Elongation at break (%)	15 to 20%	45%
Impact strength (charpy)	34 to 50 kJ/m ²	no break

The positive properties profile of PA 11, especially with respect to mechanical requirements, means that some compounds are also based on Rilsan® Invent for the LS application. As a result of the mixing with additives, the elongation at break generally decreases, which is somewhat compensated by the higher value for neat PA 11.

6.1.4 PA 12 and PA 11 Compounds

The commercial LS base powders presented in the previous sections serve as basic materials for a whole range of LS compound materials. However, it should be emphasized that these are not compounds such as in the injection molding field, but dry blends.

The base powder and the respective additive are thus only mixed mechanically (blended). Essentially, metal powders, some fiber grades, and glass spheres are mixed. Figure 6.18 shows the SEM images of two blends. On the left, a mixture of PA 12 powder with carbon fiber; on the right, the proportion of glass spheres (perfect spherical particles) is clearly visible alongside the powder particles.

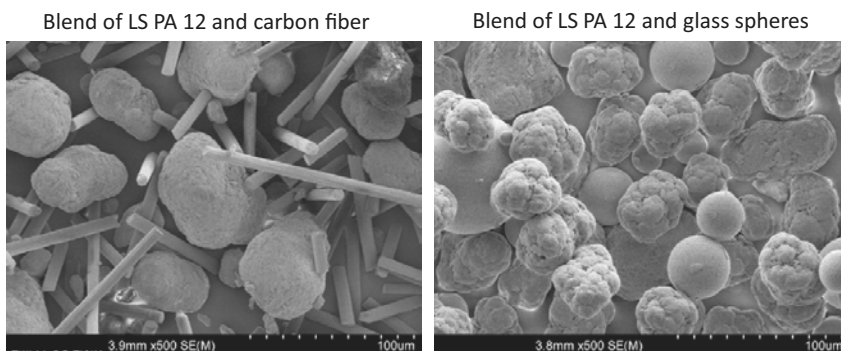


Figure 6.18 SEM image of PA 12 LS powder filled with carbon fibers or glass spheres [source: Empa]

Index

Symbols

3D complexity 2
3D-P 6
3D printing 3, 6
3D Systems 14, 29, 127
3MF 43
6-aminohexanoic acid 129
 α -triclinic 150
 γ and α modification 140

A

A-A/B-B and A-B polyamides 129
absorbing ink printing 7
absorption 91
absorption coefficient 88
accumulation 93
action checklist 58
active chain ends 66
additive manufacturing 2
adhesion 5
Advanced Laser Materials (ALM) 127, 152
Advanced Manufacturing Research Center 188
aerospace 187
aerospace industry 181
aging at elevated temperatures 174
air conditioning system for driving simulator test 183
AM business models 186
AM-compatible design 181
America Makes 187

AMF 43
amidation 66
amide group 130
amine group 130
amorphous 68
AM roadmaps 187
AM standardization activities 63
Andrew number 20, 49
anisotropy of the part properties 171
ARBURG polymer freeforming 7
architectural model 8
area coverage 94, 117
armaments industry 181
Aspect 32
aspect ratio 94, 117
Association of German Engineers 62, 110
ASTM F42 62
ASTM F2792-12a 2
automotive fluids 174
automotive industry 181
avalanche angle 123
average molecular weight 72, 102

B

balling effect 86
beam path 28
Belgium 187
benchmark parts 59
BET method 116
B.F. Goodrich 125
blade and powder cartridge 25

- blend materials 173
 - Blue Printer 7
 - boundary 78
 - brand names 126
 - brittle fracture 162
 - build area 17
 - build cavity 18, 47
 - build chamber parameters 48
 - build height in Z direction 56
 - build job 39, 42, 43
 - build process 44
 - build volume 34
 - bulk density 120
 - buoyancy 166
 - business model 4, 5, 186
- C**
- calibration 19
 - caprolactam 129
 - CarbonMide® 172
 - carboxyl group 130
 - casting process 8
 - cavities 166, 181
 - cavity 43
 - characterization matrix for additive manufacturing 6
 - characterization of surfaces 116
 - chemical bond 65
 - chemical reaction 5
 - chemical structure 68
 - China 187
 - circularity 94, 117
 - clamping and gripping technology 186
 - coalescence 46
 - coalescence of Duraform® PA 86
 - coating 179
 - coextrusion 105
 - cohesive 93
 - color and light fastness 180
 - colors 180
 - color saturation 166
 - commercial materials 125
 - commodities 129
 - comparison of mechanical properties 164
 - comparison of PA 12 and PA 11 149
 - complexity 4, 181
 - component properties 7
 - compressed air 52
 - computer tomography 108, 166
 - concave curvature 26
 - cone-plate rheometer 84
 - contactless optical measurement techniques 176
 - continuous use temperature 154
 - contour of the surface 176
 - control 18
 - control checks 109
 - control of the powder state 41
 - cool down and part extraction 51
 - cooling 40
 - cooling down of the LS build 80
 - coordinate system 171
 - core temperature of the powder cake 51
 - corrective lens 28
 - cost per unit 4
 - covalent bond 65
 - crack initiators 166
 - cracks in the powder bed 56
 - creep behavior 174
 - cross-contamination 41
 - crosslinking 65
 - cryogenic milling 104
 - crystallization 75
 - crystallization aids 79
 - crystallization behavior in the LS process 79
 - crystallization enthalpy 80
 - crystallization in the LS process 77
 - crystallization kinetics 82
 - crystallization nuclei 168
 - crystal size 78
 - crystal structure 139
 - curling 54
 - customization 186
 - customized industrial grippers 186
 - cyclone separator 107

D

decomposition point 69
deformation of the part 53
degree of crystallinity 68
degree of particle melt 79
dental corrections 186
dental prosthetic 4
design features 60
Desktop Manufacturing 125
determination of powder flowability 119
determination of the sintering window 110
determination of the viscosity number 115
differential scanning calorimetry 110
diffuse reflection 90
dimensional stability of the parts 60
diode laser 36
directional orientation and part identification 171
distribution curves for powders 117
DMA 174
double blade 25
drilling guides 4
drop extrusion 108
droplet matrix morphology 105
dry blends 131, 151
DTM 14
DTM clone 33
ductility 150
Duraform® FLEX 157
Duraform® HST 111, 172
Duraform® PA 130
dust particle 15

E

economic fabrication 3
effects of the post-condensation reaction 145
eGrip 186
elastic modulus 144
elastomeric materials 156
elastomers 65
electrical conductivity 179

electronics 181
Electro Optical Systems (EOS) 14, 31, 127
electrostatic shielding 179
elongation at break 77, 144, 150, 173
emulsion and suspension polymerization 102
end groups 143
energy absorption time 22
engineering polymers 128
England 187
enthalpy of fusion 80
EOSINT 31
EOSINT P 800 31, 154
EOS PPM system 61
equilibrium reaction 142
esterification 66
estimation of the LS powder processability 119
ether and keto groups 153
evolution of the LS technology 13
ExcelTec 127, 152
extension of the polymer chains 144
extrinsic powder properties 115
extrinsic properties 74
extrusion conditions 105

F

FAR-25 (25.853) 154
Farsoon 33
FDM® devices 8
FDM® industrial printers 8
fiber grade 151
fiber laser 33
fibers 131
filament extrusion 6
fine needle tip 176
fine particles 42, 93, 118
fine powder 133
fingerprint range 88
finishing 177, 178
finishing process 52
first order physical transformation 110
flame retardant materials 154

- flat surface 43
 - flowability 95
 - flowability of powders 93
 - flow behavior 93
 - flowing point 69
 - flowing point of the polymer 70
 - fluidization 25, 93
 - fluidized height 123
 - focal plane 28
 - focus correction 28
 - form factors of the cavities 167
 - FORMIGA 31
 - freedom of design 181
 - free-flowing behavior 95, 118
 - Frenkel/Eshelby model 86
 - fresh powder 18
 - F-Theta lens 29
 - fumed silica 93
 - functional end groups 66
 - functional integration 183
 - functionality driven design 4
 - functional parts 8
 - furniture industry 181
 - fused deposition modeling, FDM 6
- G**
- Gel Permeation Chromatography 115, 142
 - GelSight 176
 - general cleanliness 58
 - general quality actions 57
 - geometric freedom 3
 - Gibbs-Thomson equation 140
 - glass spheres 131, 151
 - glass transition temperature 69
 - grain size distribution 95
 - gravity 86
 - grripper fingers 186
 - group or deformation vibration 89
- H**
- halogenated flame retardants 154
 - Hampel estimator 121
 - hand finishing 177
 - hard segments 65
 - Hausner factor 93, 120
 - hearing aids 186
 - heat capacity 80, 110
 - heat exposure 145
 - heating 44
 - heating and cooling rate 76
 - heat radiation 80, 82
 - heat radiation effects 80
 - heat resistance 152
 - heat source 18
 - Hewlett Packard (HP) 7
 - highly porous powders 116
 - Hofmann Medea 1500 SLS 37
 - hold layer-time 44
 - hollow spheres 107
 - homogeneous particle size distribution 134
 - homogeneous part properties 168
 - homogenization of the melt 79
 - Huazhong University 37
 - humidity 23
 - hydrogen bonds 130, 150
- I**
- impact strength 77, 150
 - incomplete coalescence 70
 - incorrect positioning of the part 53
 - induce cracking 166
 - industry standards for additive manufacturing 64
 - infrared spectrum 89
 - inhomogeneous crystallization 51
 - initiator 102
 - inkjet UV printing 6
 - input control 93
 - integrating sphere 90
 - interlaboratory test 120
 - internal stresses 83
 - intrinsic properties 74
 - irradiation vector 49
 - IR radiator 19
 - ISO TC 261 62

isothermal laser sintering 129
isotropic part properties 51
isotropy 77

J

jewelry industry 181

K

kinetic energy 104

L

Lambert-Beer's law 88
lamellar thickness 140
laser diffraction method 117
laser energy input 20
laser irradiation 51
laser module 15
laser overlap 21
laser power 21
laser sintering, LS 6, 9
laser spot 28
laser spot shape 29
laser window 16
laurinlactam 103
lauro lactam 130, 141
layer adhesion 144
layer boundaries 144
layer-by-layer fusion 13
layer delamination 56, 144
layer manufacturing technologies 2
Le Chatelier's principle 67
lifestyle and fashion 187
lifestyle products 180
lightweight structures 181
linearization of the polymer coil 72
liquid nitrogen 104
list of measures for quality control 58
living anionic polymerization 103
logistics 5
long-term stability 174
lost model 8

LS

- build parameters 164
- coloring parts 179
- compound materials 151
- history 14
- homogeneous parts 168
- material portfolio 11
- material suppliers 126
- materials table 191
- parts 161
- process 9, 13, 39
- processability 133
- process chain 9
- process errors 56
- sintering window 75
- technology 10, 13

M

machine configuration 15
machine logbook 58
machine market 29
machine service 58
machine technology 15
manufacturing driven design 4
manufacturing technology 1
market shares 128
Massachusetts Institute of Technology 176
material and process matrix 5
material assortment 127
material classes 126
material optimization by means of fillers 172
material portfolio 126
material selection 11
matrix polymer 105
maximum tensile strength 162
mechanical grinding 104
mechanical properties 7, 162
medical technology 181
medicine/dentistry 187
melt flow index 41, 112
melting 75
melting in the LS process 79

melting point 47, 69
 melt spinning 108
 melt viscosity 41, 55, 84, 112
 melt volume rate 112
 metal and non-metal oxide 89
 metal powders 131, 151
 metastable 75
 MFI control points 41
 microscope with a heating table 86
 milling 104
 mirror speed of the scanning head 50
 mixture of materials 41
 model 8
 modeling the processes in the sintering window 82
 model/prototype construction 182
 moisture content 111
 mold cooling 79
 molecular weight 68, 71, 141, 143, 147
 molecular weight distribution 114
 monoclinic (pseudo-hexagonal) 139
 morphology 68
 Multi Jet Fusion®, MJF 7
 multijet printing, MJP 6
 multi-zone heater 18
 MVR measurements 113
 MVR/MFI 112

N

name of polyamides 129
 National Additive Manufacturing Innovation Institute 187
 national AM special programs 187
 new PA 12 LS powder 40
 Newtonian fluid 84
 nitrogen 24
 non-destructive determination of the porosity 166
 non-isothermal crystallization 77
 Norge Systems 36
 number average molecular weight 114
 number distribution 117
 number of repeat units 144

numerical simulation 82
 nylon (polyamide) 125

O

odd-even effect 150
 oligomer 115
 onset of the melting point 77
 optical components 28
 optical microscopy analysis 117
 optical properties 87
 optimal parameter sets 61
 orange peel 55
 Orgasol® Invent Smooth 102, 130
 oven aging 146
 overflow powder 40
 overheating of individual layers 53
 overlapping of laser tracks 49
 oxidation 18, 51
 oxidative degradation reaction 146

P

PA 11 149
 PA 12 and PA 11 compounds 151
 PA 12 base powders 131
 PA 12 powder with carbon fiber 151
 parallel plate viscometer 84
 part assembly 43
 part collision 43
 part data 11
 part density 165
 part distortion 54
 part distribution 44
 partially melted powder 168
 partial melt of the build area 56
 partial pressure difference 142
 particle coalescence 87
 particle geometry 97
 particle shape 94, 115
 particle size distribution 95
 particle surface 94
 part packing density 40, 96, 97
 part precision 8
 part properties 162

- Part-Property-Management (PPM) 61
- part surfaces 174
- parts yellowing 56
- penetration depth of the radiation 90
- performance parameters 34
- physical network points 65
- plasticizer content 111
- plastic measuring cylinder 120
- plastic pyramid 128
- polishing 179
- polyacrylate 102
- polyamide 6 (PA 6) 105, 152
- polyamide 11 (PA 11) 105, 148
- polyamide 12 (PA 12) 130
- polyamide (nylon) 129
- polybutylene terephthalate 125
- polycarbonate 71, 125
- polycondensation reaction 67
- polydispersity index 114
- polyether ketone 153
- polyethylene 155
- PolyJet® modeling, PJM 6
- polymer and LS market in comparison 128
- polymer chains with open ends 141
- polymerization 66
- polymer particle 91
- polymer powders 101
- polymer processing 70
- polymer properties 65
- polymers sensitive to hydrolysis 113
- polymethylmethacrylate 71
- polymorphism 139
- polyphosphinate 155
- polypropylene 155
- polystyrene 102, 156
- polyvinyl chloride 102
- pores 166
- porosity determination 167
- post-condensation 84, 141, 144
- post-condensation of PA 12 in solid state 142
- post-condensation reaction 141
- post-processing 52
- powder agglomeration 56
- powder aging 145
- powder application 24
- powder behavior 91
- powder cake 51
- powder coating 101
- powder conditioning 23
- powder density 27, 96
- powder distribution 115, 131, 147
- powder feed 22
- powder flowability 24, 118
- powder flow in the LS process 40
- powder funnel 120
- powder mixture 40
- powder particle 147
- powder preparation 40
- powder recycling 146
- powder rheology 92
- powder “short-feed” 56
- powder state 40, 109, 119
- powder supply 22
- powder surrounding 81
- precipitation from solutions 103
- precipitation process 103
- precipitation process from an ethanol solution 103
- precision and accuracy 60
- pre-heating 39
- primary processing 70
- primary shaping 1
- primary shaping process 164
- Primepart® ST (PEBA 2301) 157
- process additives 103
- process chain 5
- process control 39, 81
- process cycle 44
- process diagram for the LS method 40
- process errors 53
- processing temperature 69
- process sequence 46
- process temperature 83
- product development 8
- production of LS powders 101, 106
- production planning 58
- production technology 39
- productivity 34

product personalization 4
professional finishing 179
proper design 172
properties matrix of the LS materials 173
properties required for LS polymers 73
property combination of PA 12 147
proportion of large particles 95
protective suits 185
ProX™ 500 14
Push™ process 178

Q

quality assurance 57, 109
quality certificate 59
quality control 57
quality costs 61
quality data 11
quality management 59
quality measures 57
quality of the part data 42

R

radical and ionic polymerization 66
radical chain reaction 102
radical formation 146
RaFaEl 32
Ra (mean roughness) 175
Rapid Expansion of Supercritical Solution 109
rapid prototyping 2
raw materials for paint 103
recycled powder 41
reduction of part lists 185
reflection 87, 91
reflection measurement 89
reflector holder 184
reinforced materials 127
rejected part 53
repeatability 121
reproducibility 121
residual build 40
residual content 114

residual crystallinity 169
residual porosity 167
retention sample 58, 60
revolution powder analysis 122
rheology of the polymer melt 83
Rilsan® Invent 149
ring-opening polyaddition 130
robotic gripper 4
RoHS directive 154
roller coater 26
roller surface 27
rotational speed 123
roughness determination 176
roughness parameters 176
rounding of the particles 104
roundness 94
round-robin test 121
R_z (maximum roughness) 175

S

sacrificial parts 60
scanning electron micrograph 108
scanning head mirror 49
scan speed of the laser beam 21
scattering phenomena 87
schematic structure of polymers 66
Schleiss RPTech 42
secondary valence forces 130
sedimentation time 123
selective heat sintering 7
semi-crystalline 68
SEMplice 32
serial parts 161
set parameters 49
shaking effect 96
shape of the particle 117
shear 71
short-term load
– tensile test 162
sieve analysis 117
simulation of the degree of solidification 82
simulation of the LS processes 80
simulation of thermal process 83

- Singapore 187
 - single blade 25
 - sintered necks 71
 - sintering cycle 47
 - sintering window 75
 - Sinterline™ 152
 - SinterStation 14
 - Sintratec 35
 - skin contact 180
 - soft segments 65
 - solidity 94
 - solid-liquid state 82
 - solvents 178
 - spatial-direction-dependent part
 - properties 172
 - spatial directions 171
 - spatial orientation 171
 - special material 49
 - specific surface area 116
 - spectacle frames 179
 - sphericity 94, 103, 116, 133
 - spherulite boundaries 78
 - spherulitic crystal structure 77
 - sports and racetrack applications 152
 - sports equipment industry 181
 - spray drying 107
 - stabilizers 146
 - stair-step effect 175
 - standard deviation 121
 - standardization 62
 - standards and recommendations 63
 - standards bodies 62
 - standards committees at country level
 - 62
 - state of equilibrium 24
 - status report “Additive Manufacturing Process” 181
 - step-growth reaction 66
 - stereolithography, SL 6
 - STL
 - file 42
 - format 42
 - stock powder 23
 - strategy of part irradiation 49
 - streaming 56
 - structural body 71
 - structural density 84
 - structure of an LS machine 15
 - sublimation 155
 - subtractive methods 2
 - supercooled melt 85
 - supporting structure 43
 - support structure requirements 7
 - surface defects 55
 - surface finishing 177
 - surface fractal 123
 - surface heater 45
 - surface quality 8, 9, 11
 - surface roughness 116
 - surface roughness of LS parts 134
 - surface temperature 19
 - surface tension 71, 84, 86, 87
 - system status 58
 - system supplier 61
- T
- tacticity 68
 - tactile/contacting measurement
 - 176
 - tangential velocity 26
 - tapped density 120
 - technological maturity 161
 - technology driver 3
 - technology maturation 7
 - temperature control 17, 18
 - temperature jump in the laser track
 - 76
 - tensile strength 77, 144
 - termination of the build process 53
 - test and comparison parts 59
 - test parts 58
 - TGA measurement curve 111
 - thermal
 - analysis 110
 - behavior 69
 - conductivity 80
 - equilibrium 44
 - load 146
 - properties 8, 74, 134, 147

- shock 45
- transitions of amorphous and semi-crystalline polymers 70
- thermo-balance 111
- thermogravimetry 111
- thermo-oxidative damage 104
- thermoplastic 65
- thermoplastic elastomers 65, 105, 122, 157
- thermoplastic polyurethane 105, 122, 157
- thermoset 65
- thread 43
- titanium oxide 89
- tool 3
- tool and mold making 181
- translational velocity 26
- transmission 91
- troweling 178

U

- uncontrolled part growth 56
- undercuts 3
- University of Austin 125
- University of Sheffield 178
- un-sintered powder 40
- U.S. President Barack Obama 187
- UV exposure 146

V

- vapor phase 178
- Varia 3D 34
- variation in the irradiation 51
- variation of laser power 169
- varnishing 179
- VDI 181
- vehicle and mobility 187

- vibrations of the powder coaters 175
- vibratory grinding 178
- viscoelastic properties 85
- viscosity 71
- viscosity curve 71, 84
- viscous behavior 84
- visible laser scanning lines 175
- voids 166
- volume build rate 34
- volume distribution 117

W

- warpage 54
- “wash out” 56
- wash-out effects 175
- water absorption 152
- water resistance 179
- wax printing 6
- weight average molecular weight 114
- weld lines 31
- white pigment 89
- wide angle X-ray scattering 139
- Windform 127, 152

X

- X-ray diffraction (WAXS) 139
- XYZ build direction 150

Y

- yellowing of the surface 51
- yield stress 77

Z

- zero shear viscosity 72, 83
- zinc selenide (ZnSe) 16