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## Additive Manufacturing: Polymers applicable for Laser Sintering (LS)

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### Abstract

Additive Manufacturing (AM) is close to become a production technique changing the way of part fabrication in future. Enhanced complexity and personalized features are aimed. The expectations in AM for the future are enormous and betimes it is considered as kind of the next industrial revolution. **Laser Sintering (LS)** of polymer powders is one component of the AM production techniques. However materials successfully applicable to **Laser Sintering (LS)** are very **limited** today. The presentation picks up this topic and gives a short introduction on the material available today. Important factors of polymer powders, **their significance for effective LS** processing and analytical approaches to access those values are presented in the main part. Concurrently the exceptional position of polyamide 12 powders in this connection is outlined.

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### 1. Introduction

Techniques capable to transfer CAD data directly into physical objects are specified today as Additive Manufacturing (AM) [1]. AM is opposite to subtractive technologies, where material is removed by drilling, milling or grinding to achieve a desired geometry. In a recently published ASTM standard (ASTM F2792-12a) the following definition of AM is established: “**Additive manufacturing (AM)**, – Processes of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing fabrication methodologies.”

One element of the ‘layer upon layer’ based additive production techniques is Laser Sintering (LS) of polymers [2]. Space-resolved consolidation of polymer powders by means of laser energy opens innumerable options to yield custom-built parts with freedom of complexity [3]. Amongst all presently existing AM-techniques LS is considered as the most promising approach to become a sincere production technique for plastic parts appropriate for industry.

#### 1.1. LS Basic Polymers

A problem obstructing LS in a wider prospect is the limited variety of applicable polymers. Whilst traditional polymer processing techniques e.g. injection molding or extrusion have access to thousands of different formulas composed of several dozen basic polymers [4], for LS treatment just a handful different formulations are provided so far. Moreover, almost all of them are based on two basic polymers: polyamide 12 (PA12) and its near relative polyamide 11 (PA11) [5]. Fig. 1 presents the chemical formula of the two basic polymer structures. There similarity is obvious.

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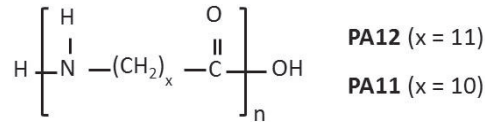


Fig. 1. Chemical formula of the two basic polymers for LS powders: PA 12 and PA 11

1.2. Commercial situation

Fig. 2 illustrates the situation for the global and the LS market today regarding consumption, price and market share. It can clearly be seen, that LS-market with a share of approximately 1'900 t/year is less than a niche market compared to total consumption of about 290 Mio-t/y; a relation of about 1: 200'000! This means in words, as 1 kg LS-powder is sold about 200 t other polymeric material is sold in the same time. Even when the relation with the total amount of only PA's is used a consumption of 1.5 t to 1 kg LS-material exists. So, the market of LS needs further development and new materials urgently to develop more weight.

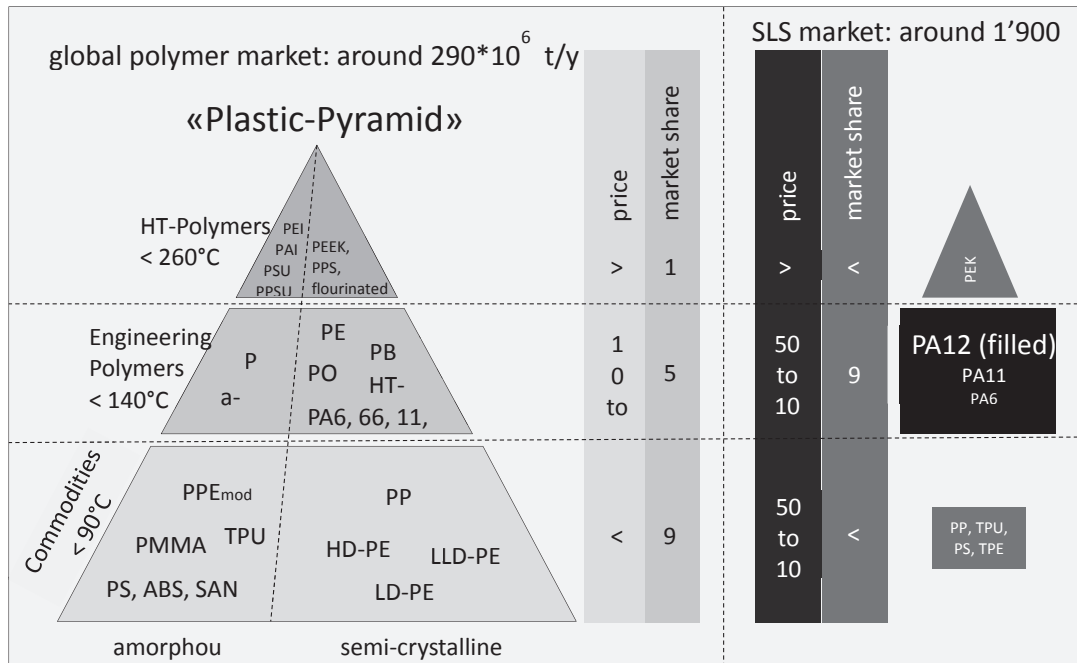


Fig. 2. Market overview and comparison between global and LS market

Table 1 provides additionally an outline of the main commercially available LS materials based on PA12 and PA 11. The differences between the global polymer market and the LS market are obvious. An application rate of around 900 tons/year the LS share is not even a fraction related to 260 million tons of worldwide plastic use. However the price of LS polymers is around factor 10 and more higher compared to their respective plastics in the standard pyramid.

Table 1. Commercial LS Polymers based on PA12 and PA 11 (most important ones in bold letters).

Supplier	Product name	Origin	Filler
3D-Systems (USA)	<b>Duraform® PA</b>	PA12	none
3D-Systems (USA)	Duraform® HST Composite	PA12	fibers
3D-Systems (USA)	Duraform® GF	PA12	glass beads

EOS (D)	PA 2200 / PA2201	PA12	TiO <sub>2</sub> / none
EOS (D)	Alumide®	PA12	aluminium powder
EOS (D)	CarbonMide®	PA12	carbon fiber
EOS (D)	PA 3200 GF	PA12	glass beads
Arkema (F)	Orgasol® Invent Smooth	PA12	none
3D-Systems (USA)	Duraform® EX natural	PA11	none
3D-Systems (USA)	Duraform® EX black	PA11	carbon black
EOS (D)	PA 1101	PA11	none
EOS (D)	PA 1102 black	PA11	carbon black
Arkema (F)	Rilsan Invent Natural	PA11	none
Arkema (F)	Rilsan Invent Black	PA11	carbon black

In addition noticeable is the lack of standard polymers of the bottom of the pyramid for LS. Almost no materials from these so-called commodity plastics: PE, PP, PVC and others are available so far for LS processing. What are the reasons for these significant differences in polymer distribution for “standard” use and LS adoption? Besides some business and consumption arguments the main reason is the very sophisticated combination of polymer properties necessary for successful application.

### 2. Polymer Properties for LS-Processing

Fig. 3 summarizes the most important factors to transfer a polymer into a LS powder and distinguish between extrinsic and intrinsic properties. Accepting Fig. 3 it is obvious that a complex system of interconnected powder features exists. The different properties can be divided into intrinsic (thermal, optical and rheological) and extrinsic properties (particle and powder). Intrinsic properties are typically determined from the molecular structure of the polymer itself and can't be influenced easily, whereas production of powder controls extrinsic properties. This mandatory property combination is not easy to achieve from new powders and will be discussed following.

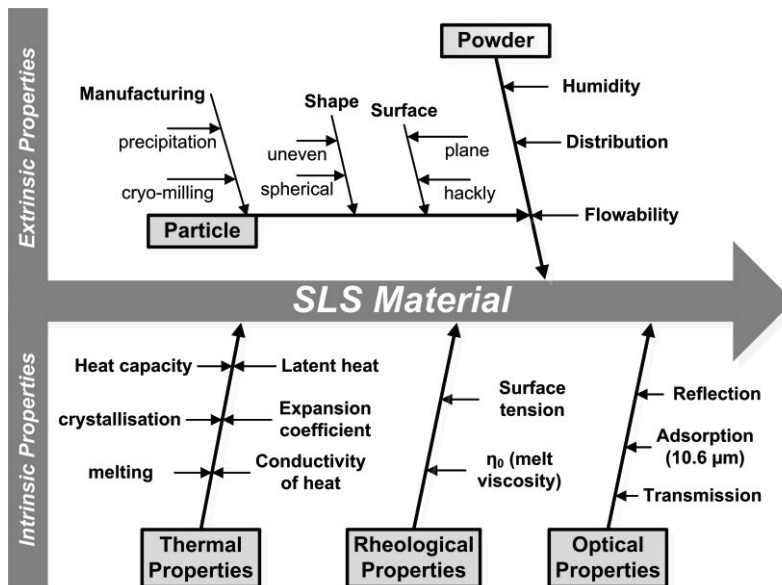


Fig. 3. Combination of important properties of LS-powders (intrinsic and extrinsic);

### 2.1. Extrinsic Properties - Particle

Shape and surface of single particles regulate the behavior of the resulting powder to a great extent. In case of LS 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 LS powders are distributed on the part bed of an LS 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  $H_R$ . Regarding literature a  $H_R < 1.25$  means free flowing powder behavior 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 LS part density achieved during processing is openly linked to powder density in part bed and is thus coupled to the shape of particles and their free flowing behavior. Fig. 4 illustrates some particle forms attained from 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 PA12 powder from precipitation process. Particles obtained from cryogenic milling are inadequate in the majority of cases and fail for LS processing. The poorer powder flowability generates poor part bed surface in LS machine and a reduced powder density as well. Thus, cryogenic milled powders finally end in weak, less condensed LS parts with low density and poor properties usually.

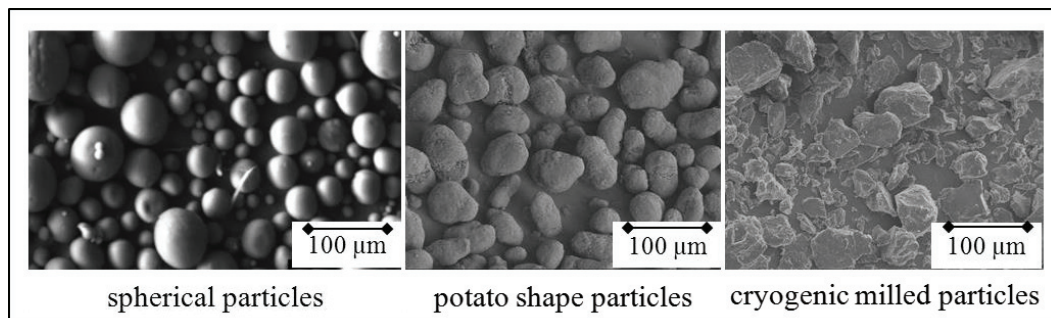


Fig. 4. Particle shapes attainable by different production technologies;

### 2.2. Extrinsic Properties - Powder

For LS powders a certain particle size distribution (PSD) is necessary to be processable on LS equipment. This distribution is favorably between 20 µm and 80 µm for commercial system. The PSD is usually measured by laser diffraction systems. However, with this measurement the fraction of small particles is frequently neglected. But particularly the amount of small units is often responsible if a powder depicts a reasonable LS processing behavior or not.

Fig. 5 illustrates such a case. Both, 'Powder 1' and 'Powder 2' have some good and acceptable PSD looking at volume distribution (Fig. 5, middle column). From that point of view both powder should be processable on LS equipment. However, in reality, the trial to do so with 'Powder 2' failed. The reason can be recognized from number distribution (Fig. 5, 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 LS processing. As especially milled powder represents often a high amount of fine particles this is another reason why these powders are frequently unsuccessful in LS processing.

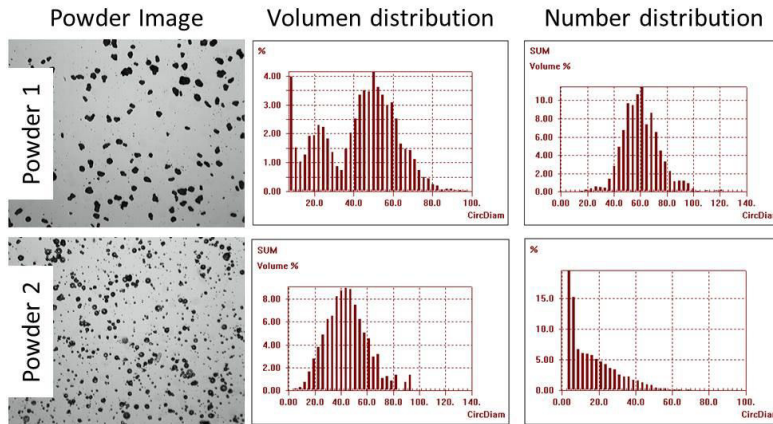


Fig. 5. Distribution of powders with similar volume distribution and dissimilar number distribution

It is also interesting to recognize, that even for the most often used commercial powders for LS-processing: PA 2200 (Company EOS) and Duraform<sup>®</sup> PA (company 3D-systems) the powder distribution is not equal. Fig. 6 indicates the distribution. It can be clearly identified, that PA 2200 exhibits an almost mono-modal distribution in contrast to Duraform<sup>®</sup> PA, where the distribution consists of several powder fractions. Even from the particle photos in the right side of Fig. 6 it can be identified that Duraform<sup>®</sup> PA powder has a much broader distribution with a higher amount of fine particles. If the fine particles don't influence the flowability too much in a negative sense, the smaller particles can help to enlarge the powder density and consequently the part density as well.

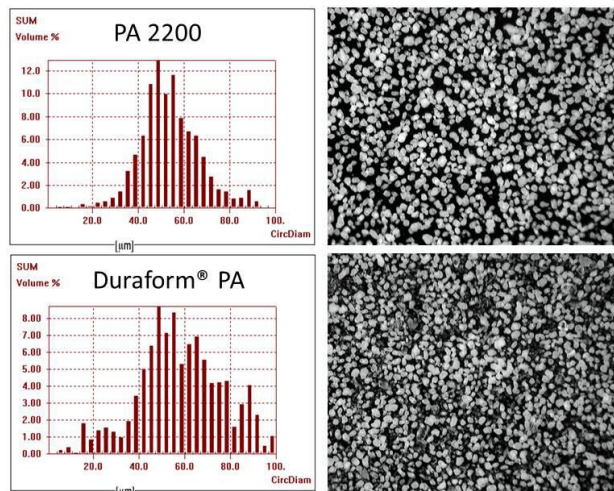


Fig. 6. Powder distribution of commercial LS-Powders (PA12)

### 2.3. Intrinsic Properties – Thermal Behavior

Identifying the challenging aspects of the desired thermal properties it is necessary to understand the course of action during LS processing. In a LS system essentially a CO<sub>2</sub> 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 LS 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, Fig. 7) and crystallization ( $T_c$ , blue line, Fig. 7) of the given polymer. This meta-stable thermodynamic region of undercooled polymer melt is called 'sintering window' of LS processing for a given polymer. Fig. 7 shows a DSC run (DSC = Differential Scanning Calorimetry) for commercial PA 12 LS-powder. The nature of sintering window between onset points of  $T_c$  and  $T_m$  is obvious.

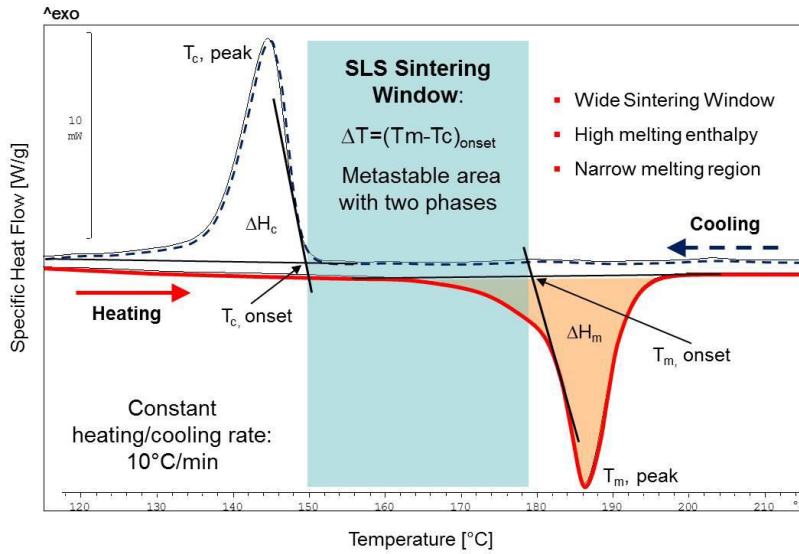


Fig. 7. Typical DSC-Thermogram with nature of ‘sintering window’ as LS process temperature

However it must be indicated, that the scheme in Fig. 7 is just an idealized representation of thermal reality as it is received with fixed heating and cooling rates (10°C/min) never existing during LS 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 LS processing.

Fig. 8 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 Fig. 8) curling due to premature crystallization is induced and parts are distorted after releasing from surrounding powder bed. If temperature is just slightly higher during processing (right side of Fig. 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.

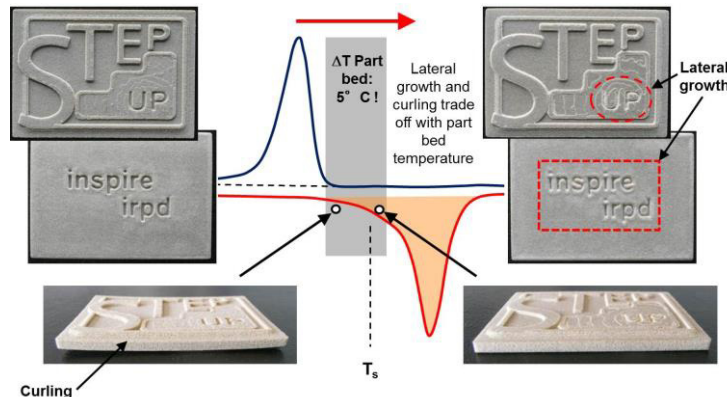


Fig. 8. LS Processing problems for too small ‘sintering window’: curling or lateral growth;

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.

2.4. Intrinsic Properties – Viscosity and Surface Tension

A low zero viscosity ( $\eta_0$ ) and a low surfaces tension ( $\gamma$ ) of polymer melt are necessary for successful LS 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, LS cannot provide an additional compacting during part generation (holding pressure). **Fig. 9** indicates the effect of inferior melt viscosity clearly visible. The right side image (**Fig. 9**) 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 LS 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.

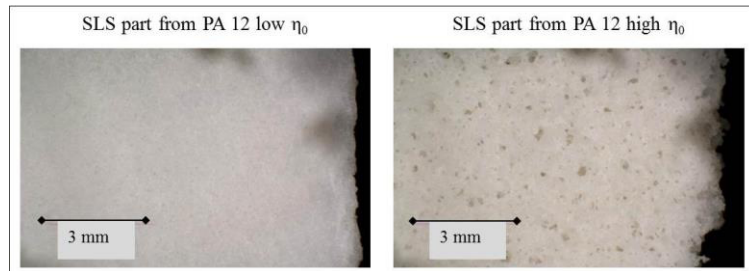


Fig. 9. Cross section of PA 12 parts made from PA 12 polymers with different melt viscosity

### 2.5. Intrinsic Properties – Optical Properties

*Fig. 10* depicts a scheme of the optical circumstances during LS processing. When a laser beam hits a polymer material three effects can occur in principle. Besides the absorption of the energy also (diffuse) reflexion and transmission is possible (*Fig. 10 a*). In case of energy absorption it is obvious that a sufficient capability of the material to absorb radiation of present laser wavelength (CO<sub>2</sub>-Laser: 10.6  $\mu\text{m}$ ) is necessary. 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  $\mu\text{m}$  CO<sub>2</sub>-laser radiation.

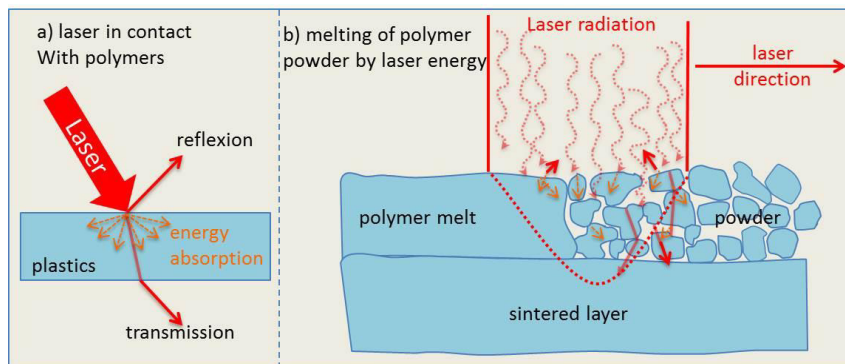


Fig. 10. Optical circumstances for LS processing

However during the LS processing the effects of reflexion and transmission become relevant as well (see *Fig. 10 b*). Transmission is desired to direct a sufficient portion of the radiation energy into deeper regions of the powder bed in order to induce an adequate layer adhesion. Only when the current powder layer is connected with the previous sintered layer in a satisfactory amount a LS part can be generated without layer delamination. In case of a poor absorption and transmission capability, an increase of laser energy power can compensate to a certain amount the effect. However an augmentation of laser power must be limited in order not to destroy the polymer by too high energy.

### 3. Conclusion

Additive Manufacturing (AM) is close to become a production technique with the potential to change the way of producing parts in future. High complex parts in small series are targeted. Selective Laser Sintering (LS) of polymer powders is one component of the additive production techniques, which is regarded as one of the most promising ones for functional end products in the AM-area. However an analysis of the commercial situation reveals, that there is a problem with the small number of applicable polymer powders for this technology today.

To understand this limitation, the paper summarizes the most important key factors materials which have to be fulfilled and their meaning for LS processing. It is highlighted the combination of intrinsic and extrinsic polymer properties necessary to generate a polymer powder likely for LS application. The thermal situation with a sufficient “sintering window” is presented as well as the requirements for a suitable viscosity and an appropriate optical behavior.

The very specific requests regarding the powder distribution and for every single particle concerning sphericity and surface is outlined. Especially the point of high powder flowability connected with particle shape is very important, as it turns out that milled particles are unfavorable in connection with LS processing. This means the production of nearby spherical polymer particles providing a good flowability and a high powder density is a central point for the future development of LS-Technology.

Especially a progress for polyolefin types (PP, PE, POM) with impact modified properties or flame retardancy should attract new markets (automotive, household, electronics, aviation) and enlarge the LS business drastically.

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