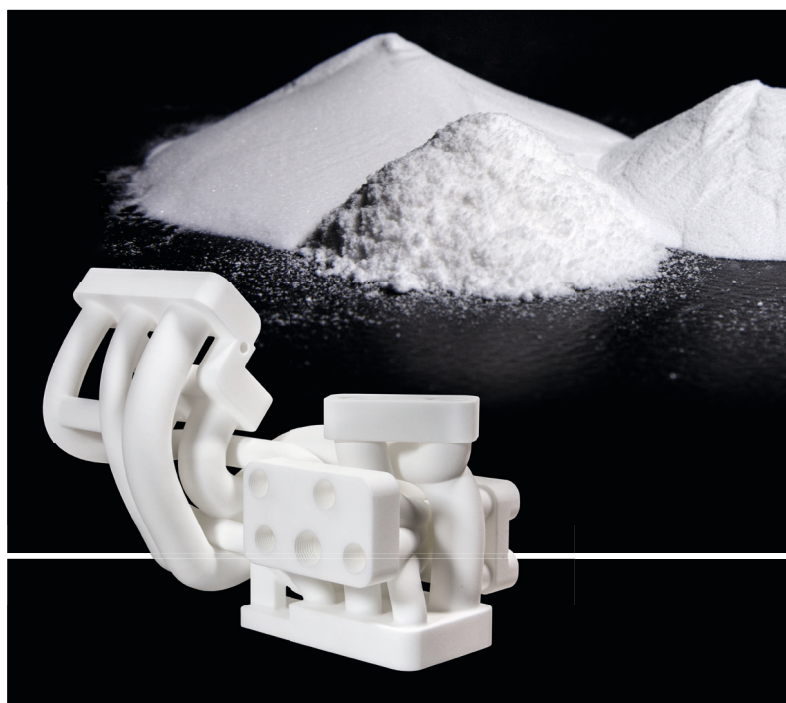


Manfred Schmid

Laser Sintering with Plastics

Technology, Processes, and Materials



2nd Edition

HANSER

Schmid
Laser Sintering with Plastics

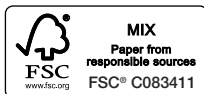
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The Author



Dr. Manfred Schmid began his professional career as an apprentice laboratory assistant at Metzeler Kautschuk AG in Munich. After graduation, his education continued through his studies in chemistry at the University of Bayreuth, resulting in a Ph.D. in Macromolecular Chemistry, during which he worked with liquid-crystalline polyurethanes under the guidance of Prof. Dr. C. D. Eisenbach.

After graduation, he moved to Switzerland, where he continued for 17 years through different positions in industry in the areas of polymer research and production, as well as material testing and polymer analysis. Polyamides and biopolymers were the focus of a variety of different activities carried out during that time.

Since then, for more than 15 years, he has led the research in laser sintering (LS) at Inspire AG, the Swiss Competence Center for Manufacturing Techniques. This acts as a transfer institute between universities and the Swiss machine-, electro-, and metal (MEM) industries.

The focus of his current activities is on new polymer systems for the LS process, the analytical evaluation of LS powders with regard to their specific property profiles, and LS process development. He supervises several collaborators and has led a wide variety of research projects in this environment. A number of frequently cited original publications have resulted.

As a guest lecturer, Dr. Schmid has given alternating lectures on the Material Science of Plastics, the Processing of Polymers, and 3D-Printing at two Swiss institutions – the Interstate University of Applied Sciences Buchs and the University of Applied Sciences St. Gallen.

The idea for this book arose from several training courses held at Inspire AG on behalf of large industrial companies on the subject of “Additive Manufacturing”.

Acknowledgement: The author would like to express his sincere thanks to Ms. Gabriele Fruhmann for preparing individual sections of the book, especially on the main topics of industrial integration of LS technology (Section 3.2) and polyamide 11 (PA 11) (Section 6.1.2), as well as for her many valuable comments on the revision of the entire text. Without her support and highly valued contributions, this second edition of the book on laser sintering of plastics in its present form would not have been achieved.

Gabriele Fruhmann



Gabriele Fruhmann studied mechatronics at the Technical University of Graz after a technical baccalaureate in Computer Science. After graduating, she joined the industry at Magna Steyr Fahrzeugtechnik in Graz in the area of multi-body dynamics simulation. She then moved to ZF Friedrichshafen AG to work in pre-development with a focus on fiber-reinforced polymer materials.

In 2013, she moved to the materials department at BMW AG, where she was responsible for pre-development projects. As part of her work, she began to focus more on additive manufacturing in 2014, and in 2017 she started to work in greater depth on material specifications for the feedstock materials used in laser sintering (LS), and the properties of the part following processing.

After an internal move in 2022 to the area of simulation, her current focus is on material model selection, material characterization, and material card generation for polymer materials in structural simulation, as well as on mapping the results from different process simulations to structural simulation in terms of material properties in the part.

The collaboration on the book came about because of Ms. Fruhmann's collaboration with Dr. Schmid on a joint project, and because of her appreciation to him for the first edition of this book, which helped her to gain an understanding of laser sintering in a short time-frame.



Foreword

Foreword to the first edition

The history of additive manufacturing seems to be very short on a first view, 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, which was not triggered by the development of new basic technologies. The background is rather 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. This hype was created in a very short time, and it developed due to considerable inherent dynamics. The decentralization of users 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 “Fabber” and “3D printing selfies” are highly demanded.

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 high only in the area of prototyping. The technologies have not changed radically since then, but nowadays the market for custom products and small production runs in many industries has increased massively. Consequently, both established machine manufacturers and many innovative startups have grown in this field. The additive manufacturing process has found immeasurable use today, from the production of individual toys to high-power components for powertrains. In the future, different scenarios for production are possible, and decentralized production “on demand” is tangible. This generates a field of high technological expectations with risks and potentials. A realistic estimation should be independent of the enthusiasm that is noticeable after seeing the first additive manu-

facturing process and having the generated part in one's hand. Independent research on the topic is therefore essential.

BMW AG ordered the first SLA system in 1989. Thus, BMW AG was the first customer of a today world recognized and leading company for laser sintering systems. Over the years, Research and Innovation Center (FIZ) formed a model for a Competency Center in which various practical and basic research is 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 the 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 selective laser sintering (SLS), 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 is already examined in diverse ways and is still subject of intensive further research.

When I dealt with my own Ph.D. thesis about the time and temperature dependence of the two-phase region, in which melt and solid are present synchronous, I had the chance to enter into one of the many interdisciplinary fields of research on additive manufacturing, and I am still excited about this topic. Anyone who intends to work with laser sintering will not be able to find a lot about such specialized topics in most of the general books for 3D printing and additive manufacturing. Because powder bed based technologies are established as one of the major additive manufacturing processes, it is essential also to present the results of basic research and transfer it 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 the benefits to the user.

May 2015

Dr.-Ing. Dominik Rietzel

Foreword to the second edition

In the last decade, laser sintering has gained a leading role among processes for additive manufacturing or (as it is often more figuratively expressed) 3D printing. This applies to both metals and plastics, which are the focus of this book.

On the one hand, laser sintering produces components whose properties are closest to those of “classic” thermoplastic processing. On the other hand, as a process without any kind of support structures, it offers the ideal conditions for almost limitless free component design, and thus supports the turn from tool-bound design to function-driven design of a component. This freedom of design is increasingly finding its way into industrial production for specialized components with a high degree of functional integration or a high degree of customization, right down to the individual piece.

One example of function integration is the production of gripper systems, where up to 100 individual parts such as valves, springs, hoses, and the gripper tools can be integrated into a single laser-sintered component. As well as eliminating assembly, the tool manufactured in this way weighs only a fraction of the conventional tool, and thus enables a significant reduction in costs in the life cycle of the component, because the gripper can move faster and simultaneously use less energy. The high degree of customization that is possible is also put to use, in particular for applications involving people, be it the production of customized orthoses and prostheses, or drilling templates for operations. But it doesn't always have to be high-tech medicine; the production of laser-sintered insoles is already a reality today.

The first edition of the book *Laser Sintering with Plastics: Technology, Processes, and Materials* has become the standard volume for system and material manufacturers, users, and researchers. This is because even a newcomer to the field of additive manufacturing will find it easy to get started, and because of the depth of detail and technical precision with which Manfred Schmid manages to explain the highly complex interplay of materials and processes, which take place on completely different timescales than any other process used in the plastics industry. These long timescales also result in particular strains on the materials, and this challenge is one of the reasons why the choice of different plastics is still limited, even after 30 years of laser sintering. To overcome this problem, the chemical industry is working hard on adapted plastics, and system manufacturers are accelerating processes, for example by using many laser sources simultaneously.

May this second edition be as helpful, educational, and exciting a read as the first edition to a new generation of technicians working in the field of laser sintering of plastics, and give new impetus to veterans of this technology such as myself.

August 2022

Dipl.-Phys. Peter Keller

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1

Introduction

1.1 Manufacturing Technology

Manufacturing, or production, is the process by which parts, goods, or merchandise, commonly called products, are produced. In the manufacturing process, these products are obtained from other parts (semi-finished products) or created from raw materials. Manufacturing can be manual, mechanical, or mixed (hybrid) processes. The various production technologies are dealt with in the subject area of manufacturing technology [1].

According to German DIN Standard 8580, manufacturing processes are divided into six main groups:

- **Prototyping:** A solid body is created from shapeless materials (liquid, powdery, plastic); the cohesion is created e. g. by casting, sintering, firing, or bonding.
- **Forming:** Changing the shape of a body by pictorial (plastic) alteration without changing the amount of material (e. g. bending, drawing, pressing, or rolling).
- **Joining:** Previously separated work pieces are transferred into a permanent joint (e. g. bonding, welding, or soldering).
- **Cutting:** Change in the shape of a solid body; the cohesion is locally dissolved (typically ablative processes such as grinding or milling).
- **Coating:** Surface finishing of all kinds (e. g. painting, chrome plating, etc.).
- **Changing material properties:** Conversion by post-treatment (e. g. hardening).

Additive manufacturing processes, in which materials are joined layer by layer to form new components, can be clearly assigned to the primary forming processes, and have accordingly been integrated into section 1.10 of the latest draft of DIN 8580 (2020).

1.2 Additive Manufacturing

Additive manufacturing technologies have long been known in industry under the term “rapid prototyping”. Rapid prototyping is widely used in model making and product development in many branches of industry. The predominant goal is the fast and uncomplicated production of individual parts, small component series, or functional and design samples to shorten development cycles.

This approach – long known to industry experts – came into the public eye a few years ago, following media hype over “3D printing”. This often gave the impression that 3D printing could be regarded as a universal and disruptive manufacturing process that would completely replace other manufacturing technologies. According to current estimates, however, it is more likely that additive manufacturing is simply joining the large number of diverse manufacturing technologies used in industry, and will only be used if clear cost advantages can be achieved from its application [2].

In the context of this book, the term additive manufacturing is generally used to indicate that the focus is on the production of industrial components. This does not represent a devaluation of rapid prototyping or 3D printing, which enjoy a high degree of importance in their respective fields of application. The terms additive manufacturing and 3D printing are often used synonymously, and a clear demarcation is not always possible.

Other partly historical terms that are (or were) used synonymously for additive manufacturing are: generative manufacturing, eManufacturing, additive manufacturing, additive layer manufacturing, direct digital manufacturing (DDM), solid-state free-form manufacturing, and some others. In addition, everything is often still subsumed under the term 3D printing, especially in the non-scientific literature. In the meantime, however, the term additive manufacturing has become generally accepted and is defined by the current standardization.



DIN EN ISO/ASTM 52.900 *Additive Manufacturing – Fundamentals – Terminology* is the basic terminology standard for additive manufacturing (AM). The standard defines the most important terms in this context. For example, additive manufacturing itself is defined as:

A definition of additive manufacturing

“Process of joining materials to produce components from 3D model data usually layer by layer, as opposed to subtractive and forming manufacturing methods”

Processes in additive manufacturing therefore take place layer by layer, which is why they are sometimes referred to as layer construction processes. This definition defines the layer-by-layer construction of objects through additive manufacturing. The

geometry of the component is available as an electronic data set in the computer (3D model data), which directly controls the creation of the component (direct digital manufacturing, DDM). This clearly distinguishes it from subtractive, machining, or separating processes.

In additive manufacturing, the final properties of the components are generally only created during production. The process parameters used control the final properties of the components, in close interaction with the properties of the starting materials. This is one of the main differences between additive manufacturing and traditional, ablative separation processes, in which the component properties are already largely predetermined by the original material properties of the semi-finished product before shaping.

Because additive manufacturing creates components layer by layer, in two dimensions so to speak, the complexity of the parts in the third dimension plays a subordinate role during the creation process. Components of almost any complexity can thus be created during the manufacturing process without significant additional effort. Areas of application that require highly complex components are therefore particularly predestined for additive manufacturing, and can be regarded as one of the technology drivers.

1.2.1 Application Areas and Technology Drivers

AM processes have one outstanding feature in common: they do not require the use of a mold that determines the shape of the desired component. Because of this layer-by-layer shaping without tools, the approach has many advantages that make it particularly suitable for the following areas of application, and which can be regarded as the main drivers of AM technology:

- Economic production of small numbers of components (even with a batch size of one, “on demand”)
- Geometric freedom in design (free-form surfaces, undercuts, cavities)
- Components with function integration (hinges, joints, flexible units)
- Lightweight construction (lattice structures with high or varying stiffness)
- Product personalization (medical technology, sports)
- Short-term product adjustments (shortening of product cycles)
- Environmental aspects (reduced material consumption, circular economy)
- Bionic structures.

Typical industries in which the advantages of additive manufacturing can be very well applied and targeted are the consumer goods, automotive, aerospace technology,

defense, medical technology, electronics, furniture, jewelry, sports equipment, and tool and mold making.

Some current established business models (personalized drilling jigs for operations, individual prosthetics, complex furniture gliders, novel filter systems, robotic grippers) demonstrate the economic use of AM technologies that have already emerged.

Figure 1.1 shows schematically in what way additive manufacturing is superior to traditional production methods from an economic point of view.

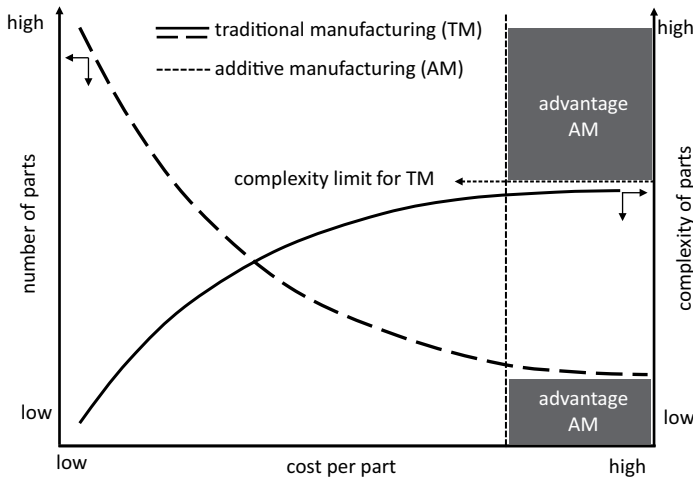


Figure 1.1 Unit costs in conflict with part count and part complexity for additive and traditional manufacturing; AM is typically not economically viable for mass production of simple parts

Established or traditional manufacturing technologies (TMs) are often optimized to produce large numbers of components at the lowest possible unit costs. Here, the unit costs decrease significantly with the number of parts produced (Figure 1.1, dashed line). At the same time, with TE, the unit costs increase significantly with the component complexity. In general, a complexity limit is even reached which conventional processes cannot overcome, or often only by generating exorbitantly high costs (Figure 1.1, solid line).

This is where the advantages of additive manufacturing processes (dark grey areas in Figure 1.1) come into play. At almost unchanged costs either small component series or components with considerable complexity can be manufactured. However, this also requires the design of the components to be adapted for the additive processes. The part design is changing from one that is required for a *production process* into one that is required for *part functionality*! This paradigm shift does not mean, however, that production-oriented rules can be disregarded. Experience shows clearly

that it is also important to design for production in additive manufacturing. Compared to tool-related manufacturing processes, however, different rules apply, which allow considerably higher degrees of freedom in product design.

However, the adaptations in the part design for additive manufacturing intervene in the complete process chain of manufacturing. In product development projects, it is therefore imperative that the planned manufacturing process be integrated at the beginning of the project, in order to take advantage of the benefits offered by additive processes for part manufacturing [3].

The target-oriented and demand-driven application of additive manufacturing requires a good overview and comprehensive knowledge of the different AM processes, and their respective strengths and weaknesses. In addition, the AM processes are mostly tied to specific material classes. In addition to the shape and type of the starting materials, AM processes differ quite significantly in terms of the underlying process sequences, according to which the classification by main AM groups is made today.

1.2.2 Main Groups of Additive Manufacturing

With the progressing standardization in the field of additive manufacturing (see Section 3.2.5), seven main groups are currently defined as essential process categories of additive manufacturing.

The main process categories (I–VII) often contain further subgroups, which may differ to a greater or lesser extent in process details. In the case of powder bed fusion (PBF) processes in particular, it is also useful to distinguish between plastic processes (PBF-P) and metal processes (PBF-M).

I. Vat photopolymerization (VPP)

- SLA: Stereolithography
- DLP: Digital light processing
- CDLP: Continuous digital light processing
- CLIP: Continuous liquid interface production

II. Material extrusion (MEX)

- FFF: Fused filament fabrication
- FGF: Fused granulate fabrication
- APF: Arburg plastics freeforming

III. Material jetting technology (MJT)

- MJ: Material jetting
- DoD: Drop on demand

IV. Binder jetting technology (BJT)

V. Powder bed fusion (PBF)

- Polymers
 - PBF-LB/P: Laser-based melting (laser sintering (LS))
 - PBF-IR/P: Infrared-radiation-based melting (MJF, SAF, HSS)
- Metals
 - PBF-LB/M: Laser-beam-based melting (selective laser melting (SLM))
 - PBF-EB/M: Electron-beam-based melting (EBM)

VI. Directed energy deposition (DED)

- LENS: Laser-engineered net shaping
- EBAM: Electron beam additive manufacturing

VII. Sheet lamination (SHL)

Figure 1.2 shows a graphical overview of the processes in the seven main classes. The processes that work mainly with plastics as the starting material are located in the upper part of the diagram. The metal processes are grouped underneath. Sheet lamination (SHL) and binder jetting (BJT) at the end cannot be clearly assigned to metal or plastic processes. In BJT in particular, a wide variety of powder substrates can be used in principle. Even chocolate powder has already been processed into “components” using BJT.

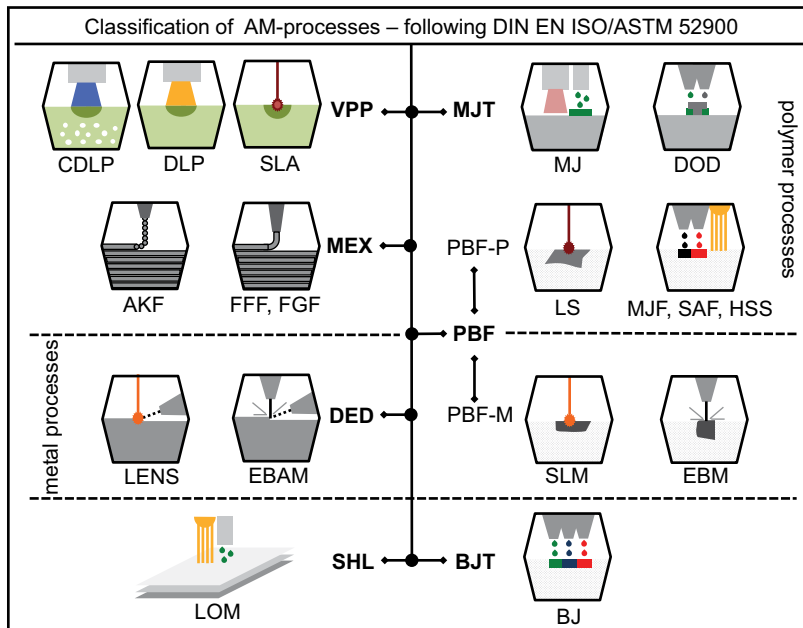


Figure 1.2 Overview of the main process classes of additive manufacturing based on DIN EN ISO/ASTM 52.900; the AM processes mainly used in the field of plastics are summarized in the upper half

In general, the classification into main categories is essentially made with regard to the differences in the joining of the respective substrates, and less consideration is given to material classes. This results from the fact that different materials such as polymers, metals, ceramics, and composites can frequently be processed with the same process approach.

Depending on whether an AM process leads directly to the finished component or via a “green part” as an intermediate step, a further distinction can be made between direct and indirect AM processes or single-stage or multi-stage processes. Plastics and metals are still to be considered the main material classes employed for additive manufacturing when it comes to the **direct AM processes** used to produce final components for industrial use.

In **indirect AM processes**, which mainly comprise binder jetting (BJ) on a wide variety of substrates, processing pre-polymers in photopolymerization processes (VPP, MJT), and compound processing in MEX processes, final components are obtained via the detour of a “green part”. Ceramics, inorganic materials, fiber composites, and other “composites” are also accessible. Here, polymers or corresponding precursors are often also used as green part binders.

In general, however, plastics in a wide variety of starting forms are still the dominant class of materials in the additive manufacturing of industrial components and in 3D printing [4]. A comprehensive overview of all AM processes with plastics and the companies currently involved in the individual process fields can be found on the AMPOWER homepage [5].

1.3 Additive Manufacturing with Plastics

What started about 40 years ago with the first work of Chuck Hull on stereolithography has today developed into a broadly diversified technology spectrum with a wide variety of plastic-based additive processes. The main AM processes in which plastics play a central role for the direct manufacture of AM components (see Figure 2.1) are:

- Vat photopolymerization (VPP)
- Material extrusion (MEX)
- Material jetting technology (MJT)
- Powder bed fusion with polymers (PBF-P).

1.3.1 Vat Photopolymerization (VPP)

The processes summarized under vat photopolymerization (VPP), stereolithography (SLA), digital light processing (DLP), and continuous digital light processing (CDLP) are based on the use of high-energy radiation (UV or visible light) for the production

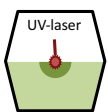
of AM components. This can be done either selectively by a UV laser (SLA) or via planar exposure via projectors (DLP/CDLP) [6].

Where the high-energy radiation hits the substrate (a liquid/viscous photopolymer resin), polymerization is started and spatially resolved curing of the material is induced. The resins usually consist of complex mixtures of active epoxy- or methacrylate-based components and so-called hardeners (alcohols and/or amines), and so elastomers or duromers are formed during the printing process. By varying the chemical composition of the individual components, the properties of the resulting components can be varied over a wide range and adapted to the target applications. The actual polymerization is started by an initiator, which breaks down into radicals during UV irradiation and induces a radical chain-reaction.

With VPP, a component is created layer by layer by continuously feeding in new resin layers. The build platform on which the component is created is either gradually lowered into the resin bath or pulled out of it. Because VPP processes use a liquid to create objects, there is no structural support from the material during the build phase. Support structures must therefore be used if the components have overhangs, cavities, or other complex structures.

VPP processes are usually characterized by high component precision and very good component surfaces. The disadvantage is often a pronounced brittleness of the components (duromer) and low long-term stability due to incompletely converted photo-initiators. Post-curing and degradation effects induced by the UV component in sunlight can lead to disintegration of the components. The following list and Figure 1.3 summarize the main features of the individual VPP processes.

Vat Photopolymerisation (VPP)



Stereolithography (SLA)

UV sensitive prepolymers are cured with pinpoint accuracy using a UV laser

Advantages: high precision; very good component surfaces; large components possible

Disadvantages: support structures; slow process; limited long-term stability UV-sensitive



Digital Light Processing (DLP)

UV-sensitive prepolymers are cured over the surface with the aid of a projector

Advantages: high precision; good component surfaces; increased process speed

Disadvantages: support structures; limited part dimensions and long-term stability



Continous Digital Light Processing (CDLP / CLIP)

Illumination from below; inhibition of UV curing by addition of oxygen

advantages: high precision; good part surfaces; very high process speed

Disadvantages: support structures; limited part dimensions

Figure 1.3 Different photopolymerization processes (VPP) for the production of plastic components

Stereolithography (SLA)

In the SLA process, the material is cured in a spatially resolved manner with the aid of a UV-laser. Exposure often takes place from above, with the laser beam being precisely controlled via mirror systems (scanners). This type of exposure makes large component dimensions possible, and components can even be produced in the meter size range with the corresponding SLA printers (e. g. models of dashboard carriers in the automotive sector).

A newer process, which can be assigned to SLA, is “hot lithography” (Cubicure GmbH). Here, the process temperature is raised significantly above room temperature, which enables the processing of novel SLA resins with higher viscosity at room temperature. Improved properties in terms of temperature stability and mechanical properties can be expected from this process.

Digital light processing (DLP)

In DLP, area exposure takes place with projectors. The exposure can be from above as well as from below through a special light, and (if necessary) a base of the resin tank that is gas-permeable. The component dimensions are dictated by the resolution of the projector and are much more limited than with SLA. Therefore, DLP processes are often used for smaller or filigree components, e. g. for casting negatives in the jewelry sector, or lattice-like structures with small local cross-sectional areas.

Continuous digital light processing (CDLP)

CDLP is a variant of the DLP process. This process became very well known as continuous liquid interface production (CLIP) by the company Carbon 3D. Here, the fact that oxygen (O_2) acts as a radical scavenger and can specifically inhibit photopolymerization (quenching) is exploited. If, as in the CLIP process, it is possible to control the local inhibition very precisely, a significant increase in the process speed is possible. The components can be generated freely in the photopolymer resin, if the exposure plane and “quenching zone” are very precisely matched. In addition, the polymer resins developed for these processes often have components that can be thermally cured in post-processing steps. This makes the components significantly more stable and suitable for technical applications in long-term use. However, the component dimensions are just as limited as in the DLP process due to the use of projectors and the negative pressure that develops with larger cross-sectional areas.

1.3.2 Material Extrusion (MEX)

In recent years, additive manufacturing by means of material extrusion (MEX) has developed a wide range of applications in terms of both materials and processes [7]. This ranges from simple DIY printers for do-it-yourselfers at home to special pro-