TECHNICAL INFORMATION 1428

# AEROSIL® and AEROXIDE® for 3D Printing Applications/ Additive Manufacturing


EVONIK
POWER TO CREATE

**Intellectual Property Rights**

3D printing has been developed within the manufacturing industry since decades. Therefore, third party intellectual property rights, i.e. patents, industrial design rights, copyright, and trademarks may exist in many countries. This brochure does explicitly not grant any right of use to intellectual property rights, neither of Evonik nor of third parties. This includes without limitation products or procedures described in this brochure. Without explicit written permission by the intellectual property rights owner, such use, including without limitation commercial use, is prohibited and constitutes a breach of applicable law.

**Health and safety**

In 2017 the European Agency for Safety and Health at Work has published a discussion paper on the processes and materials involved in 3D printing, potential implications of this technology for occupational safety and health, and avenues for controlling potential hazards.
The toxicity from emissions varies by source material due to differences in size, chemical properties, and quantity of emitted particles. Excessive exposure to VOCs can lead to irritation of the eyes, nose, and throat, headache, loss of coordination, and nausea, or may even cause diseases.
Finishing activities performed after parts have been printed may also pose health and safety hazards. These post processing activities can include chemical baths, sanding, polishing, or vapor exposure to refine surface finish, as well as general subtractive manufacturing techniques such as drilling, milling, or turning to modify the printed geometry. Any technique that removes material from the printed part has the potential to generate particles that can be inhaled or cause eye injury if proper personal protective equipment is not used, such as respirators or safety goggles.

**Literature**

[1] ISO/ASTM52900:2017 or EN/ISO/ASTM52900:2017
[2] Evonik Resource Efficiency GmbH, technical Information 1213, AEROSIL® fumed silica and SIPERNAT® specialty silica as flow aid, anticaking agent and carrier - Recommended mixing procedures for powders and granulates.
[3] Evonik Resource Efficiency GmbH, Technical Information 1351, SIPERNAT® specialty silica and AEROSIL® fumed silica as flow aid and anticaking agent

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# 3D PRINTING,

also known as additive manufacturing (AM), refers to processes used to create a three-dimensional object in which successive layers of material are formed under computer control. There are several ways to print and all those available are additive, differing mainly in the way layers are built to create the final object. Nowadays, the 3D printing market comprises multiple different printer technologies. This brochure gives an overview of the most important 3D printing techniques and how they can benefit from AEROSIL® and AEROXIDE® products.

3D printing has been around for decades, but the big reason that the market has become viable in the last few years is the improvement in materials. The development and improvement of 3D printing materials are essential for the transition of the 3D printing market into a maturing business environment – one that plays an important role for design and prototyping, and in the production of complex  tool- and mold-making. The most commonly known 3D printing materials include polymer, metal, ceramic, and glass in powder or liquid form. At Evonik, we would love to provide you with a variety of solutions for improving your 3D printing materials.

A one of the most important additives suppliers to the 3D printing industry, Evonik offers highly specialized inorganic particles under the brand names of AEROSIL® and AEROXIDE®. These products are suitable for different 3D printing base materials, where they improve the manufacturing, quality and performance of printed objects. AEROSIL® fumed silica and AEROXIDE® fumed metal oxides are highly versatile products, delivering various functions in different 3D printing formulations. This Technical Information presents various properties and performance attributes of our fumed silica and metal oxides, which serve as additives in 3D printing materials for a variety of printing technologies and processes.

**CLASSIFYING THE DIFFERENT 3D PRINTING TECHNOLOGIES OFFERS A BETTER OVERVIEW.**

Figure 1 shows the different 3D printing/additive manufacturing technologies broken down into basic categories and also provides their commonly used abbreviations. Some of these technologies are introduced in more detail in the following sections.

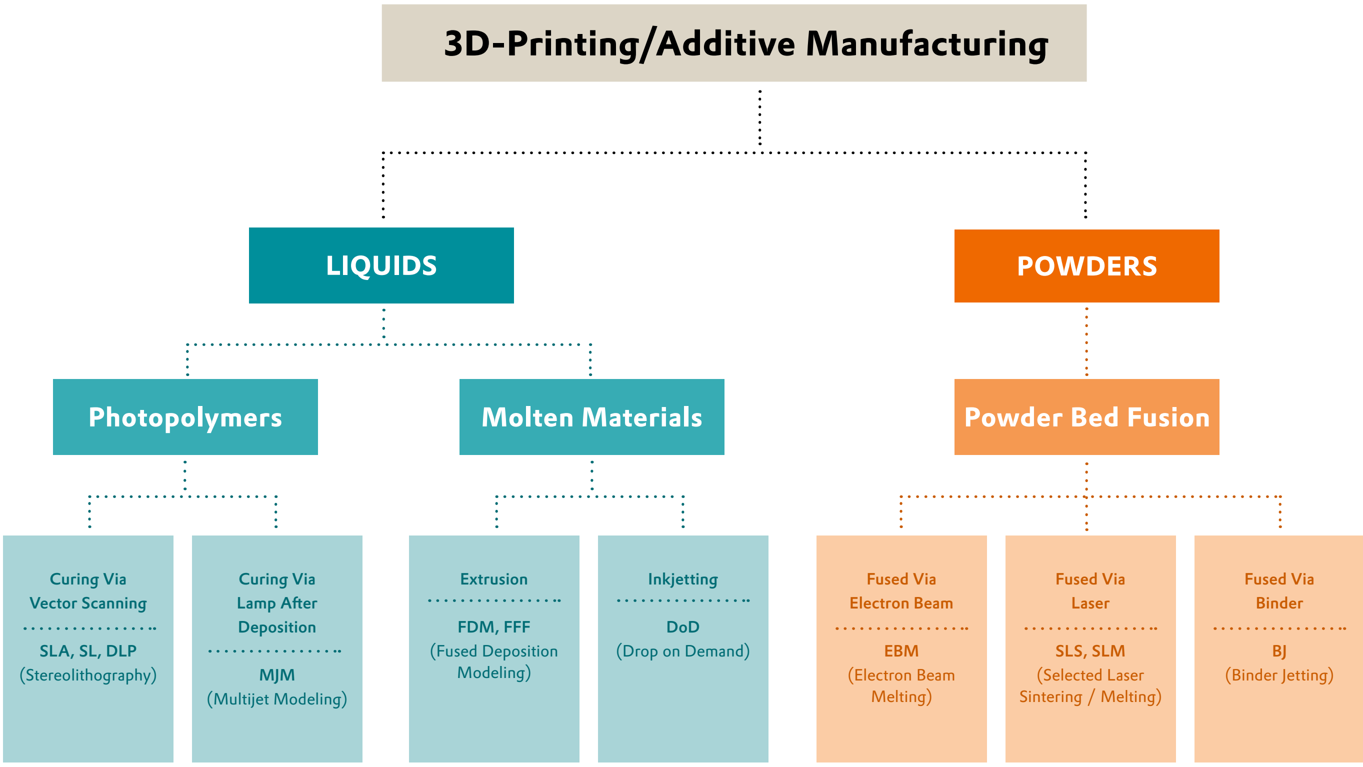



**Figure 1:** Brief classification of technologies often used in 3D printing / additive manufacturing. Abbreviations of the specific technologies do not cover all terms used. Abbreviations and technical terms are often based upon technical terms registered under ™ or ©. 1

# 3D Printing/Additive Manufacturing Materials

The list of materials that can be printed by current technologies is very long. In this brochure, we focus on solutions where polymers and resins are involved. Most of the effects of AEROSIL® and AEROXIDE® products described here can be transferred to other materials bases.
A few more comments on non-polymeric based systems are given below to understand the benefits of AEROXIDE® and AEROSIL® even if their performance may not be obvious.

## GLASS

It is well understood that the application of silicon dioxide based formulations can be used to produce solid glass products. Sol-gel techniques proved the particle size of AEROSIL® OX 50 being perfect for sintering to highly transparent glass bodies after debindering.

## CERAMICS

AEROSIL® fumed silica and AEROXIDE® fumed alumina and titania grades are often described in literature and in patent applications as well performing additives in ceramic processes. Their small particle size increases the binding strengths of the de-bindered green bodies, help the sintering process, and thus, reduce the end porosity of the ceramic. Furthermore, the addition of these products can help to reduce the sintering temperature in some phases (e.g. TiO2/AlN) or can be used to produce ceramic phases as e.g. mullite.

Not all effects can be used with all 3D printing technologies. The following table gives an overview on typical 3D printing technologies and effects that can be obtained with Evonik silica and metal oxides.

**Effect with AEROSIL® and AEROXIDE®**

| 3D printing Technology |
|---|
| Stereolithography |
| Multijet Modeling |
| Fused Deposition Modeling |
| Drop on Demand |
| Electron Beam Melting |
| Selected Laser Sintering / Melting |
| Binder Jetting |
| Laminated Object Manufacturing |

## METALS

For most metal printing technologies, the free flow properties of the metal powder is very important. As these metal powders often are very fine, they tend to flow poorly. The addition of AEROSIL® and AEROXIDE® turns out to improve some processes significantly. During transport, dosing and storage, powder caking and static uptake of the powders are often observed. This undesired effect can be improved significantly by the addition of AEROSIL® or AEROXIDE® products, without disturbing the metallurgical processes.

## INORGANIC MATERIALS

Many inorganic binding technologies can be improved by incorporation of very fine metal oxides. Especially pozzolanic reactions benefit from silica with high surface area.

## ORGANIC MATERIALS

Some printing techniques also use organic materials as base. Besides polymers, foodstuff, drugs or organic construction materials are often described. The basic principles of the techniques do not differ significantly between organic or inorganic material bases. It should be mentioned that the portfolio of AEROSIL® does also include pharma, food and feed grades.

| Powder flow control | Electrostatic control | Rheology control | Reinforcement |
|---|---|---|---|
| | ● | ● | ● |
| | ● | ● | ● |
| | ● | ● | ● |
| | ● | ● | ● |
| ● | ● | | |
| ● | ● | | |
| ● | ● | | |
| | ● | ● | ● |

# Vat Photopolymerization [1]

## (Related Acronyms: SLA, DLP, CLP, CLIP)

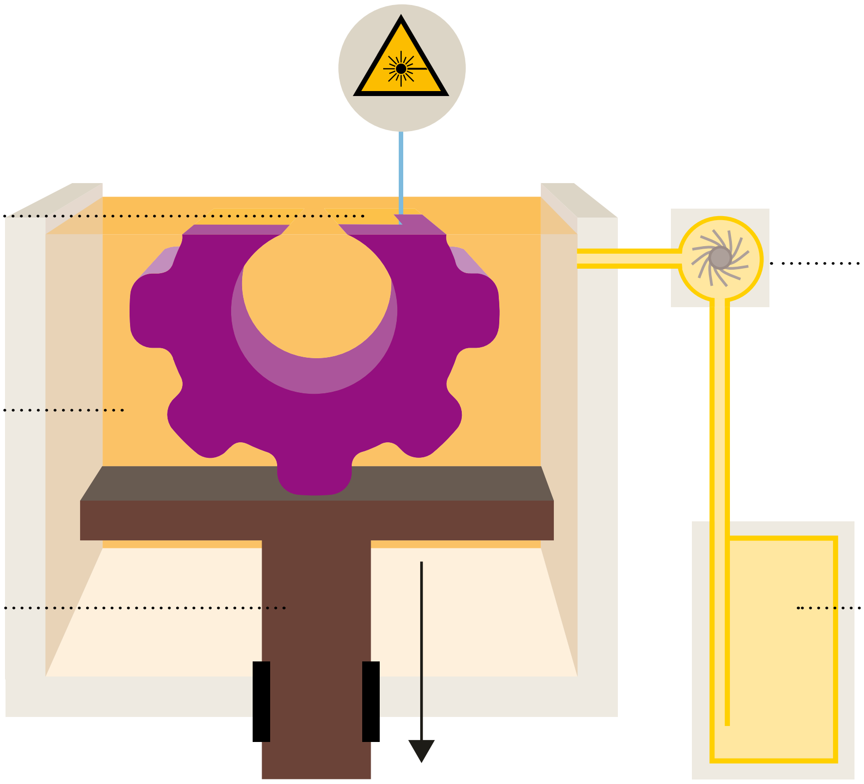



**Figure 2**: Schematic drawing of the vat polymerization process.

## TECHNOLOGY

Stereolithography involves curing liquid materials to form a three-dimensional object. The most common curing method is photopolymerization. Vat photopolymerization methods use a bath of photopolymer (also called "resin"). The resin is exposed to a laser beam, which photopolymerizes the resin layer by layer, either from the top of the liquid or from the bottom of the bath. The object is then moved out of the bath or into the liquid.

**Table 1** Summary of the Typical Functions of Silica and Metal Oxides

| Printing materials base | Effect / Function | Recommendations |
|---|---|---|
| Elastomeric resins | Viscosity control [2] | **AEROSIL®, AEROXIDE®** |
| Resins | Reinforcement | |
| Metal composites [2] | | |
| Ceramic composites [2] | | |

[2] These materials / functions are of minor industrial relevance

## APPLICATION OF SILICA

Most resins used in this technology are of low viscosity when used as monomers or short oligomeric modifications. Their low viscosity has often been described as a benefit as the thin film can help to enhance the structural resolution of the printing technology. However, in some cases a more gel-like behavior at rest and a low viscosity during agitation are desired. This characteristic is also called shear thinning effect. Moreover, the use of low-molecular-weight base materials requires extremely dense cross-linking for the resin, resulting in a hardened resin of low impact resistance. High-performance fillers are beneficial for improving mechanical strength in terms of impact resistance, structural toughness, and resilience. AEROSIL® fumed silica allows manufacturers to control the viscosity of the liquid resin, delivering a pronounced shear-thinning/thixotropic effect and considerably improving the mechanical properties of the cured resin. Figure 3 shows how these properties correlate to filler content. For cases requiring a low-viscosity liquid resin, Evonik provides special types of silica fillers that can be used for improving mechanical properties without increasing the viscosity of the monomer too much.

**General correlation between filler content and polymer properties.**

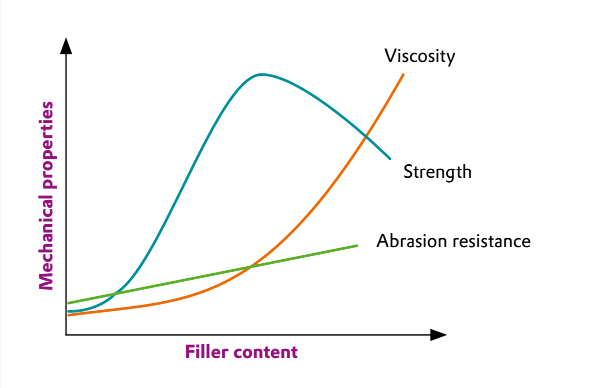



**Figure 3** shows that the different properties of the liquid resin and the cured resin depend on the filler content in different ways, and that detailed tests need to be performed in each individual case to find the optimum addition level.

## PRODUCT RECOMMENDATION

**Table 2** Product Recommendation

| Printing materials base | Effect / Function | Recommendations |
|---|---|---|
| Acrylates | Reinforcement | AEROSIL® R 9200, AEROSIL® 972, AEROSIL® R 812 |
| Methacrylates | | AEROSIL® R 7200, AEROSIL® R 711, AEROSIL® R 709 |
| Epoxides | | AEROSIL® R 8200, AEROSIL® R 812 |
| Polyesters | | AEROSIL® R 202, AEROSIL® R 812 |
| Acrylates | Viscosity control [3] | AEROSIL® R 972 |
| Methacrylates | | AEROSIL® R 711 |
| Epoxides | | AEROSIL® R 812 |
| Polyesters | | AEROSIL® 200, AEROSIL® R 202 |
| All | Electrostatic charge control | AEROXIDE® Alu C |
| | Electrical resistivity [3] | AEROXIDE® C 805 |

[3] These materials / functions are of minor industrial relevance

For viscosity control purposes, the additive content in any given application may vary between 0.5 and 3%.
Different monomers and oligomers have different chemical groups, and not all of these are compatible with the pure silica surface. As a result, reinforcement will not be ideal, and Evonik provides silica grades with a variety of modified surface functionalities to address this need for adapted fillers.

[1] ISO/ASTM52900 (same standard is adopted in country standards as EN, DIN, etc.) defines seven categories of Additive Manufacturing (AM) processes: binder jetting, directed energy deposition, material extrusion, material jetting, powder bed fusion, sheet lamination, and vat photopolymerization. Unfortunately, most description and scientific papers do not use the ISO terms consistently. In addition to these seven main categories, several technologies are in use that combines technology steps of these seven categories or represents variations of these main categories. Some companies and institutions of specific technologies also introduced registered trademarks for technological terms to gain competitive advantage.

# Stereolithography

## (SLA or SL) by PolyJet Photopolymer (PP) SLA/SL and Polyjet 3D Printing

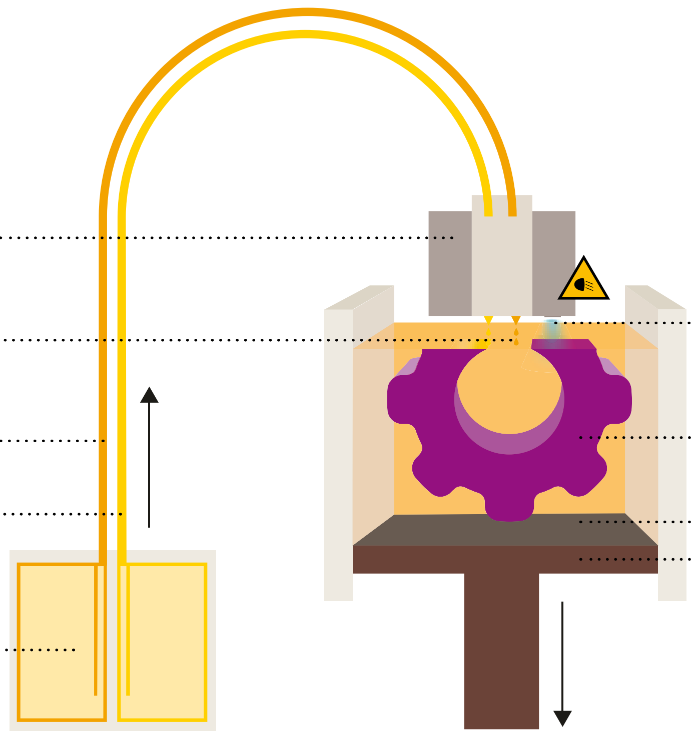



**Figure 4** Schematic drawing of a Polyjet process

## TECHNOLOGY

This stereolithographic polymerization technique uses one or more (photo)curable, liquid resins and support materials, which are applied in thin layers onto a built-in tray until the part is complete. Each photopolymer layer is cured with light after it is jetted. Unlike vat photopolymerization, this technique allows manufacturers to combine several materials into one workpiece. Small droplets of the low viscous resin are required for very fine structures, while more viscous resins make it possible to print large objects more quickly. Depositing 1D or 2D structures within the printing layer has advantages over single-droplet deposition when printing larger areas or thicker structures. The simultaneous use of several materials in one printer head allows for direct printing of many different materials at the same time, such as different colors, support materials, or different composites.

**Table 3** Summary of the Typical Functions of Silica and Metal Oxides

| Printing materials base | Effect / Function | Recommendations |
|---|---|---|
| Elastomeric resins | Viscosity control | AEROSIL®, AEROXIDE® |
| Resins | Reinforcement | |
| Metal composites | | |
| Ceramic composites | | |
| Construction materials | | |

## APPLICATION OF SILICA

A broad variety of mechanical properties can be improved when compounding fillers in resins. As an example, in Figure 5, even a low concentration of filler (1-2%) significantly improves impact and tensile strength without compromising other properties of the resin.

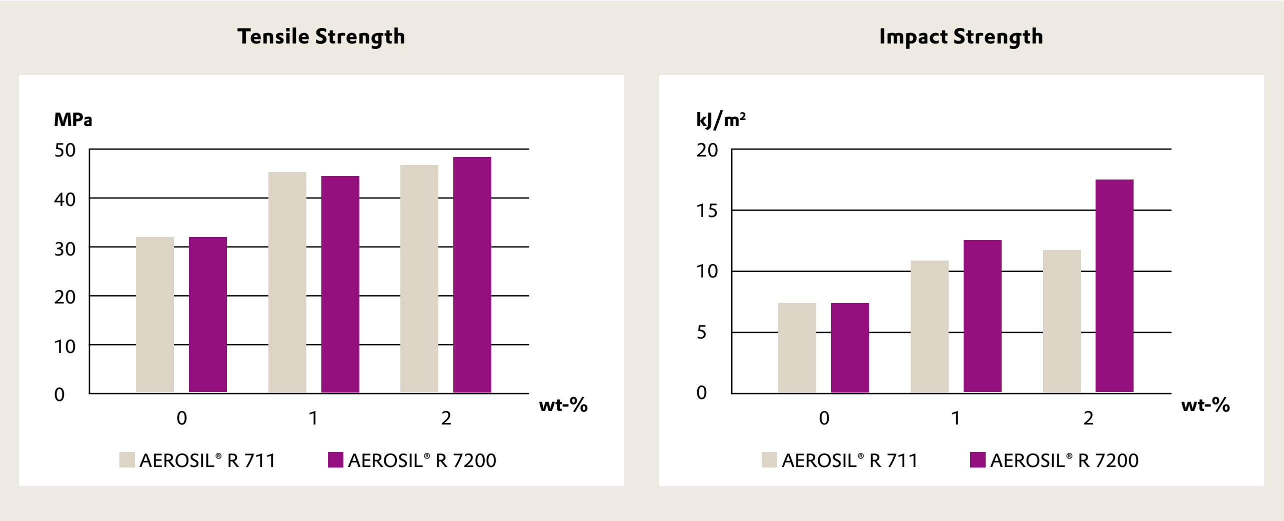



**Figure 5** Tensile strength and impact strength improvement of a UV cured acrylic monomer system using AEROSIL® R 7200 and AEROSIL® R 711.

AEROSIL® grades can also control the viscosity of the monomer and provide thixotropic behavior. This means the viscosity of the liquid is low enough to be pumped without problems  but the viscosity of the resin is higher at rest, and can even exhibit a gel-like behavior. See also Figure 13.

## PRODUCT RECOMMENDATION

The filler content may vary in the range of 1-30 wt%, depending on the resin's nature, the target properties, and the viscosity window of the resin for the application.

**Table 4** Product Recommendation

| Printing materials base | Effect / Function | Recommendations |
|---|---|---|
| Acrylates | Reinforcement | AEROSIL® R 9200, AEROSIL® 972, AEROSIL® R 812 |
| Methacrylates | | AEROSIL® R 7200, AEROSIL® R 711, AEROSIL® R 709 |
| Epoxides | | AEROSIL® R 8200, AEROSIL® R 812 |
| Polyesters | | AEROSIL® R 202, AEROSIL® R 812 |
| Acrylates | Viscosity control [4] | AEROSIL® R 972 |
| Methacrylates | | AEROSIL® R 711 |
| Epoxides | | AEROSIL® R 812 |
| Polyesters | | AEROSIL® 200, AEROSIL® R 202 |
| All | Electrostatic charge control | AEROXIDE® Alu C |
| | Electrical resistivity [4] | AEROXIDE® C 805 |

[4] These materials / functions are of minor industrial relevance

For viscosity control purposes, the additive content may vary in the range of 0.5-3% in a given application (higher for gels). As mentioned in the previous section, different monomers and oligomers bear different chemical groups. To address the need for adapted fillers, Evonik provides silica grades with a variety of modified surface functionalities.

# Powder Bed Fusion

## (Related Acronyms: SLS, SLM, DMLS, EBM)

**Step 1**
Powder bed distribution

**Step 2**
Fusion process

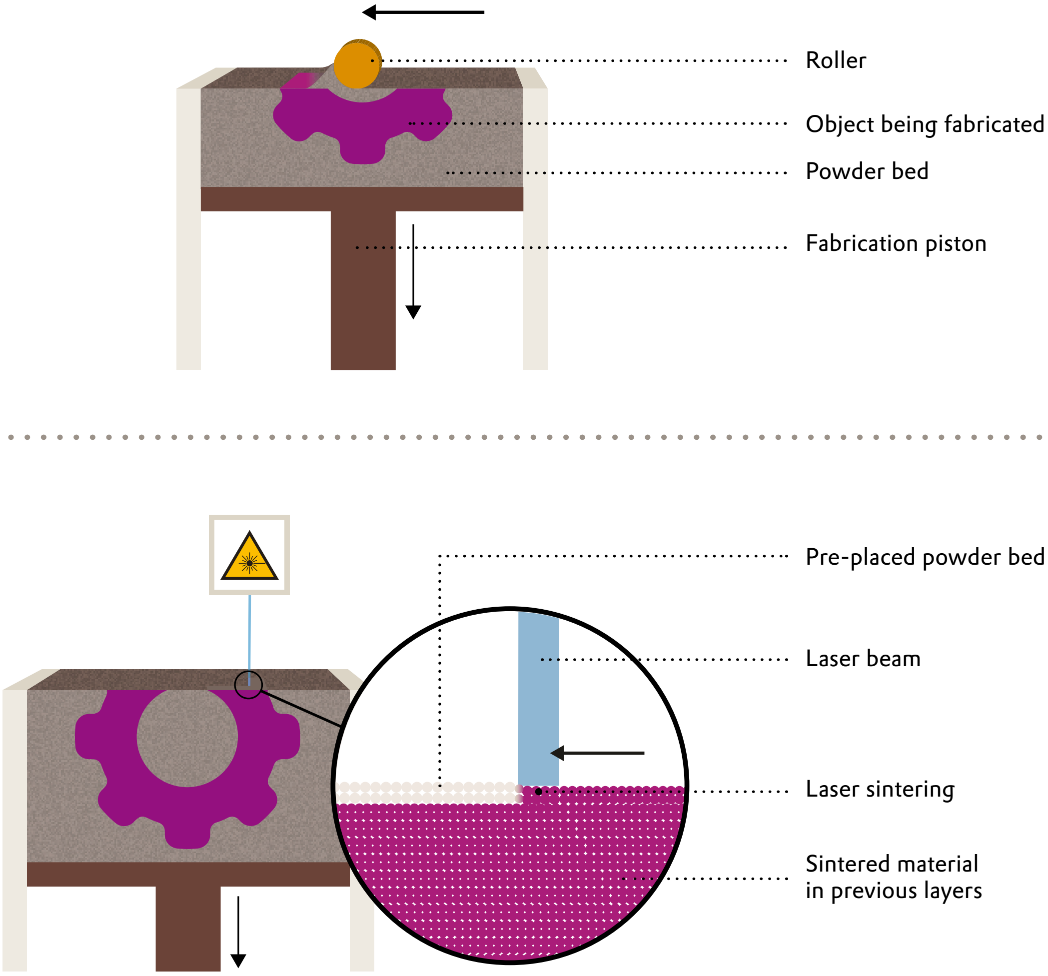



**Figure 6** Powder bed fusion printing consists of two steps: powder-bed distribution and the fusion process.

## TECHNOLOGY

Powder bed fusion techniques involve evenly distributing a powder one layer at a time onto a powder bed where it is sintered or molten with a laser or an electron beam. Laser sintering techniques include laser sintering / selective laser sintering (SLS), with both metals and polymers, and selective laser melting (SLM®) / direct metal laser sintering (DMLS). Whereas SLS techniques use sintering to fuse powder particles, SLM/DMLS techniques will completely melt the powder using a high-energy laser. This creates extremely dense materials one layer at a time, resulting in objects that have the same mechanical properties as conventionally manufactured metals.
Electron beam melting (EBM) is a similar type of additive manufacturing technology for metal parts (e.g. titanium alloys). EBM produces parts by melting one layer of metal powder at a time with an electron beam under a powerful vacuum.

**Table 5** Summary of the Typical Functions of Silica and Metal Oxides

| Printing materials base | Effect / Function | Recommendations |
|---|---|---|
| Thermoplastics | Free flow agent | AEROSIL®, AEROXIDE®, SIPERNAT® |
| Thermoplastic Elastomers | Anti-static agent | |
| Resins | | |
| Metals | | |
| Ceramics | | |

## APPLICATION OF SILICA

In powder bed fusion technology, the accuracy of the printing result depends on the powder bed distribution, making it important to avoid density variations and imperfect distribution. AEROSIL® and SIPERNAT® grades offer a broad variety of problem-solving products that significantly improve powder flowability and packaging density and prevent electrostatic charging. [3] This makes it possible to distribute powder layers very evenly and with no defects. The following images illustrate this effect.


**Figure 7a-d** Powder flow improvement: a) powder funnel free-flow, b) cone height reduction in powders, c) anti-caking in soft powders, and d) anti-static improvement in non-conductive powders. The powders shown here are only model substances to show the effects as such, and not actual powders for 3D-printing

The free-flow and anticaking effect works by coating the surface of the printing material base powder with the silica. The silica acts as a spacer and prevents powder particles from clumping. However, when dosed correctly, the silica does not compromise the sintering process, as it will be incorporated in the softening / melting powder surface.

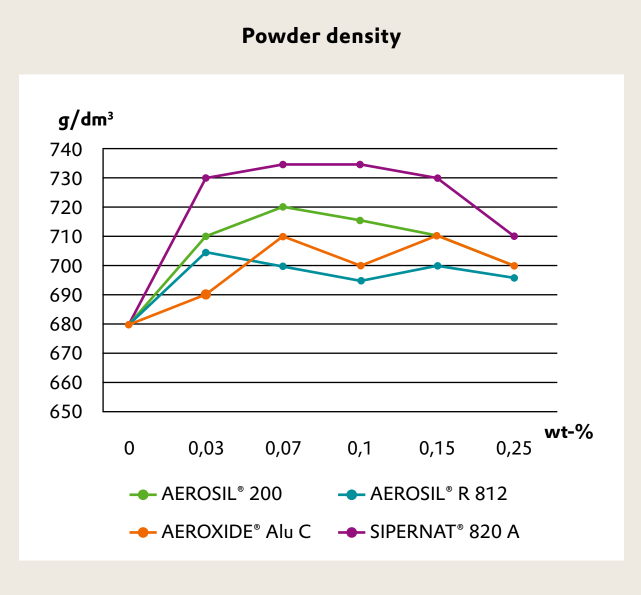
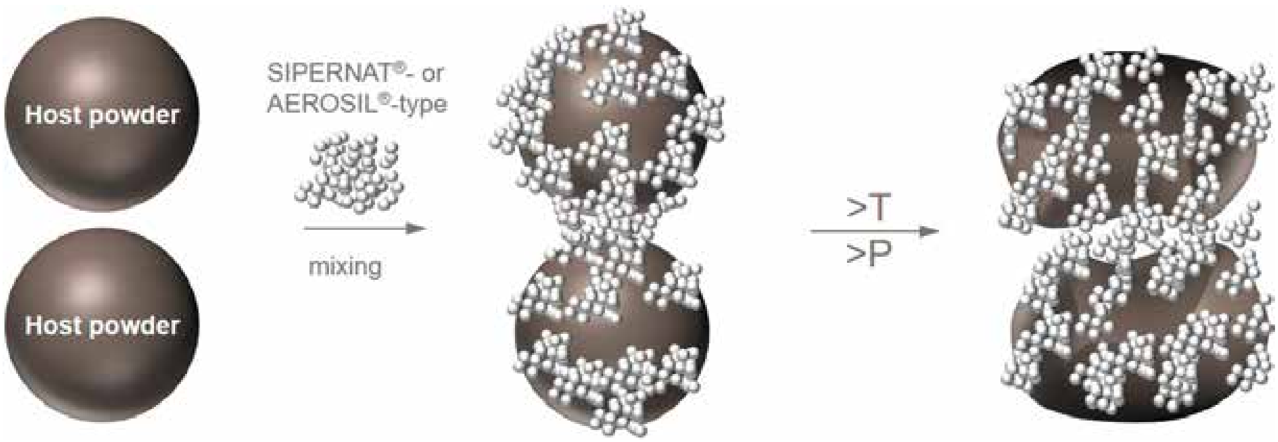



**Figure 8**
To control powder application in powder-based 3D printing means having to control the flow properties. Adjusting the ideal flow behavior is beneficial. Increasing the powder density enhances the mechanical properties of the printed part.

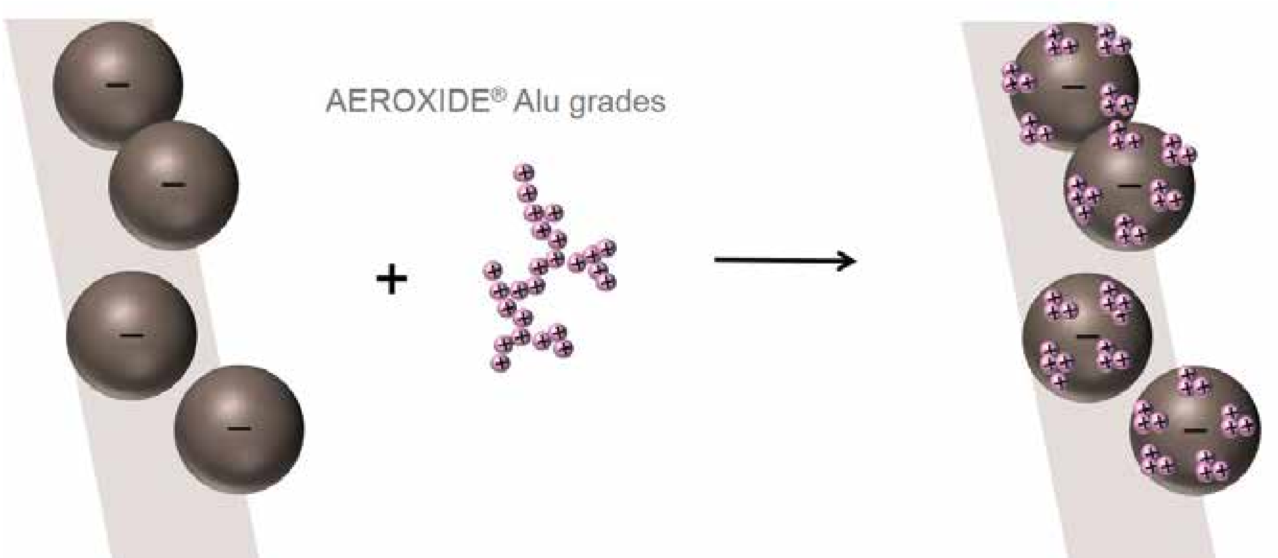
A special effect can be achieved with AEROXIDE® Alu grades. Due to their positive charge they can neutralize the negative charge that most polymer powders tend to pick up. The powder becomes electrically neutral and does not stick to walls, pipes etc.

**Figure 9 a-b**
Principle of free-flow and anti-caking treatment;
anti-static treatment

**a**



b




## PRODUCT RECOMMENDATION

In general, fine particle size silica grades should be used for flow improvement and anticaking as they need to coat the surface of particles of the printing base material. Hydrophilic AEROSIL® 200 and SIPERNAT® 22 S grades offer a good basis for preliminary evaluations for free-flow optimization of powders with more than approx. 5µm diameter. Smaller particle sizes require very fine and easily dispersible silica grades. In this case, hydrophobic AEROSIL® grades such as AEROSIL® R 972, AEROSIL® R 812 or AEROSIL® R 8200 are an ideal choice.

If not already be coupled with good free-flow properties, anti-static properties can be introduced using AEROXIDE® Alu C.

**REMARK**

Making sure the free-flow aid is thoroughly dispersed in the powder is a crucial factor in achieving the best free-flow effect. Obtaining the best results will require suitable mixing equipment.
Details can be found in our Technical Information 1213. [2]

# Material Extrusion

(Related Acronyms FDM, FFF, TPE, ADAM)

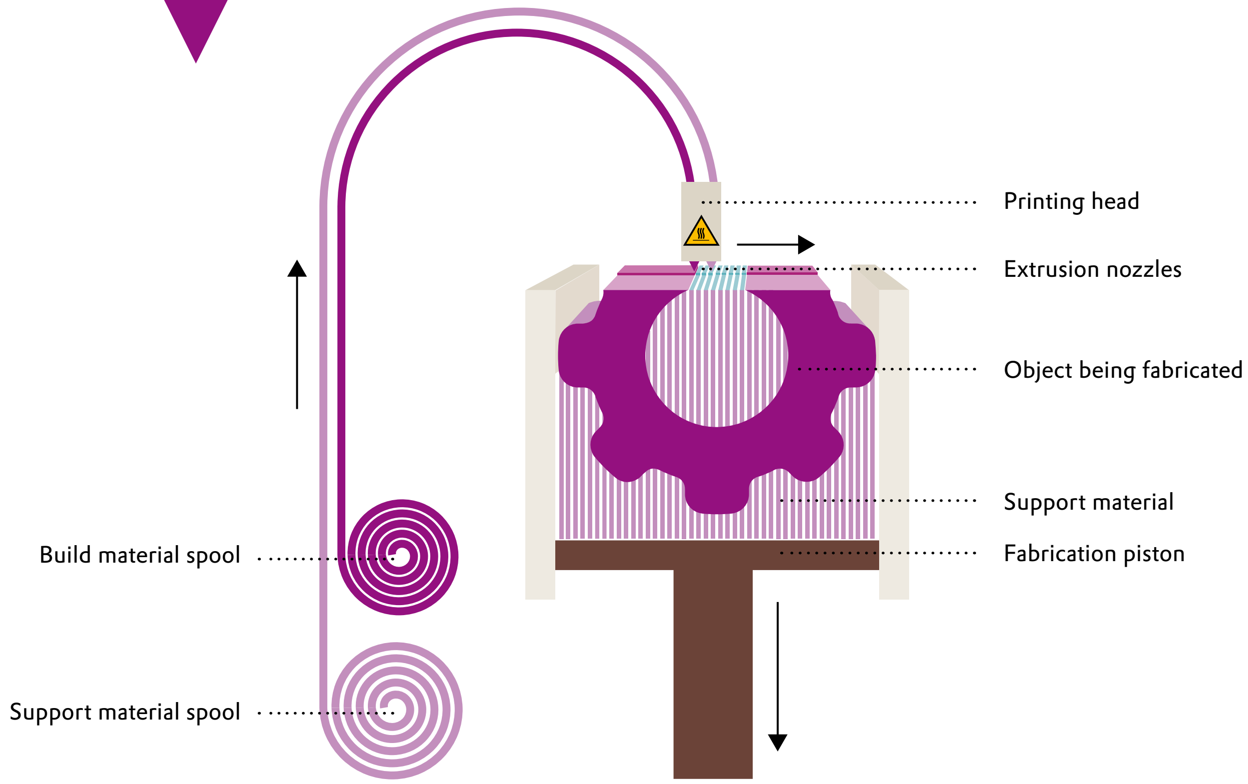



**Figure 10** The basic principle of material extrusion using building material and support material

## TECHNOLOGY

Some methods melt or soften the material to produce layers. In addition to depositing single elements in the 3D structure, this technology also enables fast, continuous deposition of 1-dimensional structures within the 2D layer. In fused-filament fabrication, also known as fused deposition modeling (FDM™), the model or part is produced by extruding small beads or streams of material that harden immediately while cooling to form layered structures. A stream or filament of thermoplastic, a metal filament, or other (composite) material is fed into an extrusion nozzle head (3D printer extruder), which liquefies the material and turns the flow on and off. Printers that can deposit multiple materials simultaneously are now available, which also enable support structures for complex geometries.

**Table 6** Summary of the Typical Functions of Silica and Metal Oxides

| Printing materials base | Effect / Function | Recommendations |
|---|---|---|
| Thermoplastics | Abrasion control | AEROSIL®, SIPERNAT® |
| Thermoplastic elastomers | Matting | |
| | Anti-blocking/anti-tack | |
| | Improved ink absorption | |

## APPLICATION OF SILICA

The material properties of the end product in the material extrusion process correspond to the polymer properties obtained while compounding the filament composite. Compounding options are limited, as extrusion requires low-viscosity molten materials for high-resolution printing processes. The adhesion of the melt and its flow into a hardened 3D structure require considerable control over the surface properties of the hardened structure.
Optimizing product performance may require additional additives such as matting, anti-blocking, or anti-tacking agents based on particles. The introduction of surface roughness will also increase ink or paint adhesion. High-performance fillers help to improve the mechanical properties of the hardened 3D structure, such as impact resistance, structural toughness, and resilience. Figure 3 shows how properties generally correlate with each other.
The filler content may vary in the range of 1-30 wt%, depending on the polymer's nature, the target properties, and the viscosity window of the liquefied polymer for the application.

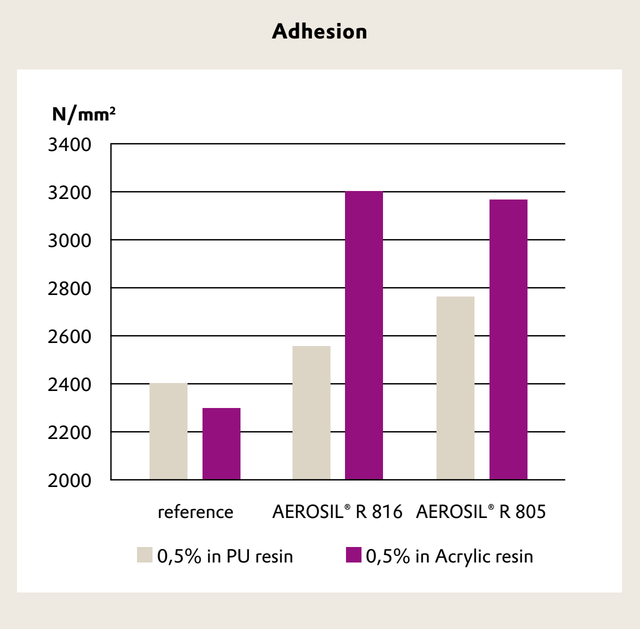



**Figure 11** Surface treated AEROSIL® grades help to increase adhesion of the layered structures and thus prevents from delamination of the final structure.

## PRODUCT RECOMMENDATION

**Table 7** Product Recommendation

| Polymer base | Effect / Function | Recommended grades |
|---|---|---|
| Thermoplastics | Reinforcement | AEROSIL® R 7200, AEROSIL® 8200, AEROSIL® R 9200 for higher filler load at moderate viscosity |
| Thermoplastic elastomers | | AEROSIL® R 711, AEROSIL® R 812, AEROSIL® R 972 if viscosity increase is accepted |
| Thermoplastics | Surface finishing (matting, anti-tack, anti-blocking, ink absorption etc.) | AEROSIL® OX 50, AEROSIL® TT 600 (good transparency) |
| Thermoplastic elastomers | | SIPERNAT® 310 |
| Thermoplastics, Thermoplastic elastomers | Electrostatic charge control | AEROXIDE® Alu C |
| | Electrical resistivity | AEROXIDE® C 805 |
| Thermoplastics, Thermoplastic elastomers | Adhesion | AEROSIL® R grades |

Reinforcement of polyolefines may require additional crosslinking functions or additives.

### REMARK

Depending on the diversity of thermoplastic materials and thermoplastic elastomers, the recommended filler may need other surface treatments than suggested here. Please, consider the full product range of products (www.aerosil.com).

Compounding of nano-scaled fillers into thermoplastic materials may require high shear forces, which, in turn, require e.g. special designed extruders.

# Other Technologies
## (e.g. Binder Jetting)

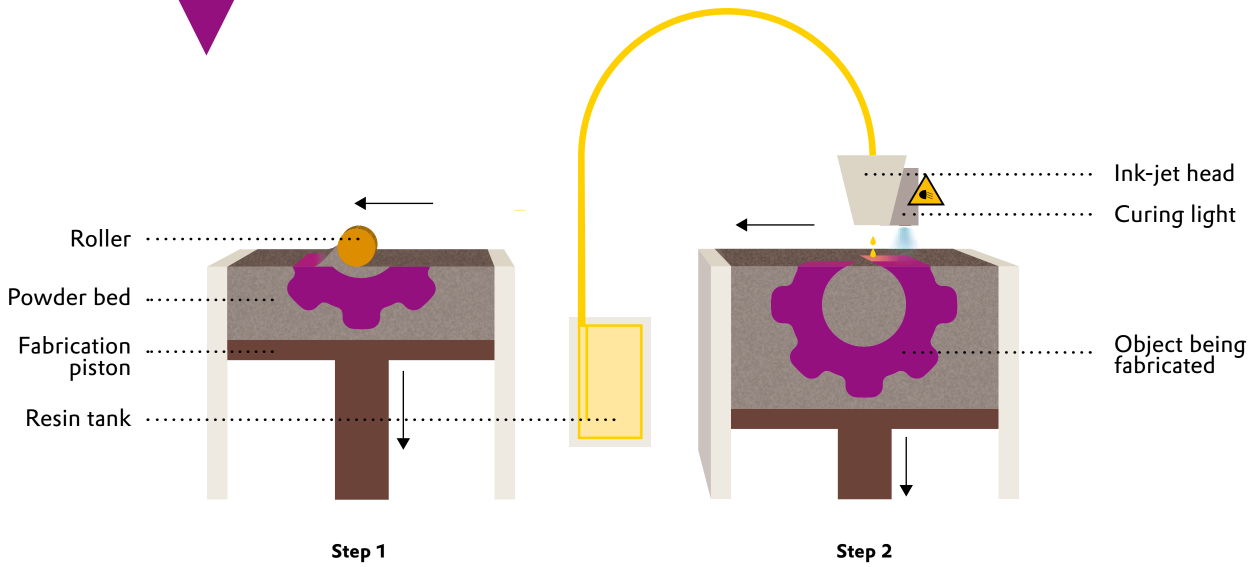



**Figure 12** The two-step process in binder jetting.

## TECHNOLOGY

Known as binder jetting, this method uses a combination of powder bed technologies and an inkjet-like 3D printing system to create models one layer at a time. During the first step, distribution of a layer of powder (plaster, thermoplastics, ceramics, metals, resins, or any other powdered material) will depend on the powder bed technology, as described previously in the SLS process. In step 2, a binder will be printed selectively in the top layer of the powder bed using an inkjet-like process. The liquid binder will then cure either instantaneously or upon the introduction of energy.
Depending on the material chosen for the end product, additional steps may be required, such as de-bindering and sintering of the printed pre-product. The main advantage of this technology is the range of materials that can be used. In addition to polymers, material options include all kinds of metals, glass, ceramics, and inorganic products, as well as food and drugs, or even tissues.

**Table 8** Summary of the Typical Functions of Silica and Metal Oxides

| Printing materials base | Effect / Function | Recommendations |
|---|---|---|
| Thermoplastics<br>Thermoplastic Elastomers<br>Resins<br>Metals<br>Ceramics | Free flow agent<br>Anti-static agent | **AEROSIL®, AEROXIDE®, SIPERNAT®** |
| Elastomeric resins<br>Resins | Rheology control [5]<br>Reinforcement | **AEROSIL®, AEROXIDE®** |

[5] These materials / functions are of minor industrial relevance

## APPLICATION OF SILICA

Powder flow optimization has already been discussed in the SLS process description. Additional requirements regarding the type of additives depend on the rheology control options. A shear-thinning effect is desirable, as mentioned in previous sections on vat polymerization and stereolithography.

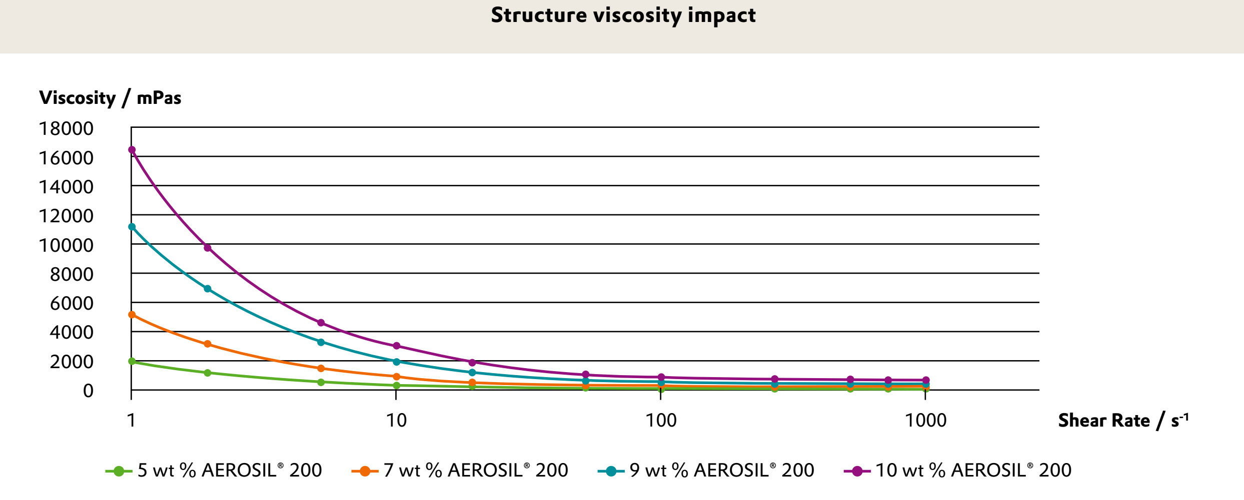



**Figure 13** Structure viscosity impact of AEROSIL® 200 addition in unipolar media.

## PRODUCT RECOMMENDATION

**Table 9** Product Recommendation

| Polymer base | Effect / Function | Recommended grades |
|---|---|---|
| Acrylates<br>Methacrylates<br>Epoxides<br>Polyesters | Reinforcement | AEROSIL® R 9200, AEROSIL® 972, AEROSIL® R 812<br>AEROSIL® R 7200, AEROSIL® R 711, AEROSIL® R 709<br>AEROSIL® R 8200, AEROSIL® R 812<br>AEROSIL® R 202, AEROSIL® R 812 |
| Acrylates<br>Methacrylates<br>Epoxides<br>Polyesters | Viscosity control [6] | AEROSIL® R 972<br>AEROSIL® R 711<br>AEROSIL® R 812<br>AEROSIL® 200, AEROSIL® R 202 |
| All | Electrostatic charge control<br>Electrical resistivity [6] | AEROXIDE® Alu C<br>AEROXIDE® C 805 |

[6] These materials / functions are of minor industrial relevance

### REMARK

Optimum rheology performance may require high shear forces. If proper dust-free powder handling is an issue in your production facility, you may also wish to evaluate the easy-to-disperse products described on www.aerosil.com. Hydrophobic additives may disrupt the wetting process for polar or even aqueous binders. You will therefore need to adjust the binder system accordingly.

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TI-1428-EN-01-2018/12-HELF

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