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Additive Manufacturing Filaments

Processing Guide

SPECIALTY POLYMERS

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Introduction

Fused Filament Fabrication

Additive Manufacturing (AM), and specifically Fused Filament Fabrication (FFF), has emerged as a way for organizations to improve speed to market with new products, enhance supply chain efficiency, enable part consolidation, increase design complexity, and lower manufacturing costs. This method of producing parts complements other methods such as injection molding and machining from material stock shapes. It is most useful when low quantities are needed of customized or specialized parts that cannot be fabricated by machining or molding.

Solvay AM-ready Filaments

As additive manufacturing technology continues to improve and accommodate higher performing materials, parts made by FFF can serve in roles previously not possible. Solvay's portfolio of AM-ready filaments offers high strength and stiffness, flame resistance, ability to withstand aggressive chemical environments, and functionality in a wide range of temperatures. These polymers offer corrosion free metal alternatives that enable lightweighting solutions.

KetaSpire® polyetheretherketone (PEEK) AM filaments provide a unique combination of properties that will constantly perform at temperatures of up to 240 °C (464 °F). Its exceptional chemical resistance allows AM PEEK to replace metals not only in critical end-use environments such as those found in oil & gas, aerospace and automotive, but also in medical applications.

Radel® polyphenylsulfone (PPSU) AM filaments deliver outstanding toughness as well as proven flame resistance, chemical resistance, and hydrolytic stability relative to high temperature amorphous thermoplastics such as polysulfone (PSU) and polyetherimide (PEI). It brings this performance to healthcare, smart devices, energy storage, and aerospace applications.

Mechanical Properties of Finished Parts

Solvay AM-ready filaments offer properties that approach those of injection molded parts. Results of mechanical property testing on Radel® PPSU AM and KetaSpire® PEEK AM products are shown in Figure 1 and Table 1. The properties show that functional parts can be made from FFF of KetaSpire® PEEK AM and Radel® PPSU AM.

Figure 1: Difference in mechanical properties between injection molded and 3D printed parts using Fused Filament Fabrication

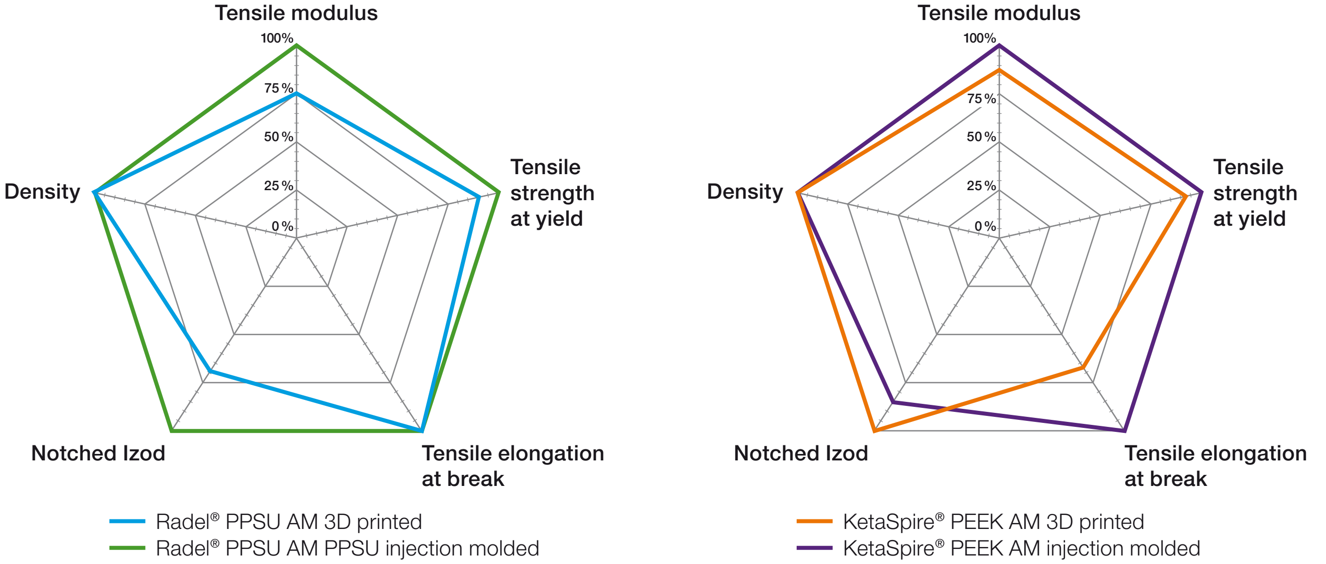


Table 1: Mechanical properties of parts printed using Solvay AM-ready filaments (1)

Typical Properties	Unit	KetaSpire® PEEK AM	KetaSpire® PEEK AM CF	Radel® PPSU AM	Test Method
Tensile modulus*	GPa (ksi)	3.12 (452.52)	11.0 (1,595.42)	2.0 (290.08)	ASTM D638
Tensile strength at break*	MPa (ksi)	48 (6.96)	140 (20.31)	42 (6.09)	ASTM D638
Tensile strength at yield*	MPa (ksi)	85 (12.33)	–	62 (8.99)	ASTM D638
Tensile elongation at break*	%	26	1.7	21	ASTM D638
Tensile elongation at yield*	%	4.8	–	7.0	ASTM D638
Notched Izod impact	J/m (ft-lb/in)	81 (1.52)	89 (1.67)	482 (9.03)	ASTM D256
Test specimen parameters		1st layer: 0.3 mm thick, subsequent layers: 0.1 mm; 100% infill; 3 shells; printing speed 18 mm/s			

(1) Used recommended drying conditions shown in Table 3

* Type V bars

Designing for Additive Manufacturing

Material Considerations

Polymer basic properties and processability are important parameters to consider when selecting a material for a new FFF application. The processing temperature gives indication of the appropriate range for printing. The glass transition temperature and heat deflection temperature help to predict and prevent overheating or overcooling of layers prior to the deposition of a subsequent layer. The level of moisture absorption demonstrates the need for drying filaments prior to printing.

Table 2: Material properties of Solvay AM-ready filaments

Typical Properties	Unit	KetaSpire® PEEK AM	KetaSpire® PEEK AM CF	Radel® PPSU AM	Test Method
Glass transition temperature	°C (°F)	150 (300)	150 (300)	220 (428)	ASTM D3418
Melt temperature	°C (°F)	343 (649)	343 (649)	–	ASTM D3418
Heat deflection temperature at 182 MPa	°C (°F)	157 (315)	315 (600)	214 (417)	ASTM D648
Specific gravity		1.29	1.33	1.29	ASTM D792
24 hour moisture absorption	%	0.1	0.1	0.4	ASTM D570

Design Principles

Parts made using Solvay AM-ready filaments should be designed in the same manner as parts fabricated from other polymeric materials. General heuristics will apply. A part file should be generated using computer aided design software that will be ultimately compatible with the printer. The physical characteristics of the part itself along with printer slicing parameter settings will determine the build tool path. This path will then create a part microstructure that will result in a given set of finished part mechanical properties. Relationships between part structure and mechanical properties are available in public scientific literature. Additional considerations such as the effect of highly oriented carbon fiber in printed KetaSpire® PEEK AM CF can impart anisotropy in properties which should be taken into account when choosing fill patterns.

As is the case with most designs a brim will be critical to establishing stability of the part and maintaining adhesion of the part to the build plate. This brim is therefore necessary in all part designs.

Equipment Requirements

A number of manufacturers offer fused filament fabrication machines with varying capabilities. It is important in the case of printing Radel® PPSU AM, KetaSpire® PEEK AM, and KetaSpire® PEEK AM CF that chosen equipment offers high temperature capabilities. Die tooling must be able to be heated to temperatures up to 450 °C (842 °F) and bed temperatures should be capable of achieving temperatures of 150–200 °C (300–400 °F). Cooling mechanisms for stepper motors are advised. Excellent temperature control for the printing head is also important as it prevents overheating and excessive residence time when the print head is stationary.

Dies should be made from brass for unfilled polymers such as KetaSpire® PEEK AM and Radel® PPSU AM and stainless steel for fiber filled polymers like KetaSpire® PEEK AM CF that can cause unacceptable wear for softer metals. Dies should be inspected prior to use and replaced if worn.

Adhesion to the base should be achieved by using a compatible surface to the material being printed that promotes adhesion either chemically or mechanically. It should also be implemented in a way that it can be replaced if damaged or worn.

Recommended Processing Conditions

Drying

Because fused filament fabrication is a low pressure forming process, dry filament must be maintained. Drying prevents defects such as bubbles or voids, splay, and overall surface roughness. Moisture will not degrade Radel® PPSU AM or KetaSpire® PEEK AM but these physical defects can adversely affect mechanical properties. Radel® PPSU AM must be maintained at a moisture content level of less than 100 ppm and the KetaSpire® PEEK AM products at < 200 ppm to prevent voids forming in the extrudate.

All filaments should be dried prior to printing if they are not already, and efforts should be made to keep filaments dry during long printing runs through the use of a controlled filament reservoir with oven heating, dessicant capability or spot drying prior to the print head.

Recommended drying conditions are given in Table 3. A dryer must be capable of achieving the recommended temperature. A dessicated dryer capable of maintaining temperature at a dew point of – 40 °C (– 40 °F) is necessary to achieve the required moisture content.

Table 3: Recommended drying conditions for Solvay AM-ready filaments

Typical Properties	Unit	KetaSpire® PEEK AM	KetaSpire® PEEK AM CF	Radel® PPSU AM
Drying temperature	°C (°F)	150 (300)	150 (300)	150 (300) (1)
Drying time	hrs	> 4	> 4	> 4 (2)
Moisture content	ppm	< 200	< 200	< 100

(1) An absolute minimum temperature would be 135 °C (275 °F) which would require significant drying time.
(2) Drying overnight is better to safely achieve the required moisture content.

Parameter Setup

Appropriate print parameters must be chosen to achieve a high quality printed part. Figure 2 shows the complex relationship between printing parameters and the finished part.

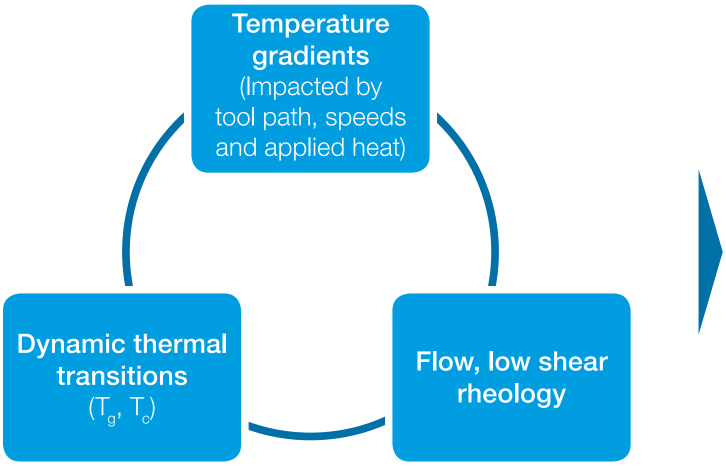
The distance from the print nozzle and the bed is a key factor in creating a stable and appropriately shaped layer cross-section. This parameter coupled with the extrusion stability and the tool path will influence the porosity and density of the part. If the tool path is too fast or if the nozzle is too far from the build plate, there can be gaps between layers that will result in inadequate mechanical properties. Density and dimensional measurements can help to identify problems with porosity.

A relationship exists between the tool path distance, the tool speed, the extrusion and ambient temperatures, and the thermal and rheological properties of the polymer being printed. The tool path and the speed must be optimized so that the layers cool at an appropriate speed to allow adhesion between them. This adhesion is achieved by some level of molecular interaction and entanglement between the two layers. Long distances and slow print speeds may result in too much cooling and a lack of adhesion between layers.

However if cooling is too slow, adequate solidification may not take place which will result in a deformed or collapsed part. In the case of amorphous polymers that lack a melt temperature (T_m), such as the AM PPSU, excessive retention of heat caused by short tool paths and fast tool speeds can allow builds to collapse.

Appropriate cooling is also important to achieve maximum crystallinity in the KetaSpire® PEEK AM and KetaSpire® PEEK AM CF filaments. An optimized cooling rate allows for the polymer to pass slowly through the crystallization temperature (T_c), or temperature at which the maximum crystallization takes place, halfway between the glass transition temperature and the melt temperature.

Figure 2: Graphic description of relationship between printing parameters and part quality



- Porosity
- Adhesion between layers
- Crystallinity throughout part
- Filler alignment
  - Filler is highly aligned in tool path

Startup

It is important to follow good practice guidelines when setting up a part print. Preparation activities may vary with printers, but they will likely include installing the build plate material or film for adhesion, installing the build plate into the printer, ensuring that printing heads are properly installed, and leveling the build plate. Calibration of the distance between the printing head and the build plate should also be completed. Special care should be taken not to kink the filament. Filaments must be allowed to unroll easily as overlaps can cause the feed to stop. Fiber reinforced filaments also require that sharp bends do not occur in the feed path so that the filaments are not at risk of breaking during the feeding process.

Table 4 gives a list of recommended starting parameters for printing the Solvay AM-ready filaments. These guidelines may require adjustments for specific parts and printers.

Print purge lines to ensure that the setup parameters chosen for the print are appropriate for the polymer to be printed. Patterns in the purge lines other than a straight line could indicate leveling problems, feeding problems, or speeds that are inappropriate for the material.

Clean-up and Shutdown

In order to properly finish a print and shut down the printer, it is necessary to cool the print bed (in the case of a heated chamber, the entire system) to room temperature prior to attempting to remove the part. This effort will preserve the dimensional stability of the part as well as facilitating its removal.

It is good practice to retract the filament from the print head and to prepare the spool to be re-dried for the next printing.

Table 4: Melt processing parameters for Solvay AM-ready filaments

Typical Properties	Unit	KetaSpire® PEEK AM	KetaSpire® PEEK AM CF	Radel® PPSU AM
Polymer melt temperature	°C (°F)	390 – 405 (734 – 761)	390 – 405 (734 – 761)	380 – 400 (716 – 752)
Build plate temperature	°C (°F)	> 200 (> 392)	> 200 (> 392)	180 – 200 (356 – 392)

Troubleshooting

Solutions to general printing problems are well documented in the literature, but there are some key challenges that can occur when printing high performance materials. Table 5 offers potential causes and solutions to printing problems.

Table 5: Troubleshooting printing problems with Solvay AM-ready filament

Problem	Cause	Solution
Poor surface finish	Melt temperature is low	Increase head temperature
	Melt fracture	Increase head temperature, reduce extrusion rate
	Wet filament	Dry or replace filament
Porosity	Wet filament	Dry or replace filament
	Melt temperature too high (decomposition of material)	Decrease head temperature
	In-fill dimensions not optimized	Change in-fill pattern
Die drool	Polymer sticking to die	Use highly polished die Adjust die temperature
	Excessive extrusion	Adjust the printing speed
Warpage	Non-uniform cooling	Increase build plate temperature and/or ambient temperature
	Insufficient adhesion to build plate	Adjust build plate temperature or adhesion surface
Poor layer adhesion	Wet filament	Dry or replace filament
	Previous raster too cold	Adjust printing speed

Finishing

Surface Finishing and Joining

Parts printed from Solvay AM-ready materials can be joined through conventional methods such as welding and adhesion. KetaSpire® PEEK AM products may require surface preparation to achieve high bond strengths. These materials can also be painted, vacuum metallized, or plated. Further information is available upon request.

Machining

Machining can be used to add details not incorporated into the part or to achieve dimensional tolerances or finishes closer than those achieved by printing. Use of a coolant, either water- or oil-based, is suggested to help remove chips and thermally manage both the part and tooling. Since these polymers have low thermal conductivity and high thermal expansion, part overheating may occur with aggressive machining leading to dimensional issues when the part cools. For Radel® PPSU AM parts, check cooling fluid compatibility with the polymer prior to use to avoid stress cracking. Relief of stress that might be imparted by machining can be done through annealing if necessary.

Annealing

The KetaSpire® PEEK AM filaments are semi-crystalline which means that the crystallinity in the part will develop as a function of the thermal processing parameters. If printed layers cool quickly they may quench without allowing crystallization to take place. These layers will appear brown or transparent versus the tan appearance of a crystallized part. Annealing can help to further crystallize the part and result in a uniform tan appearance. It is advised to choose process parameters that allow maximum crystallinity to develop, but if this is not possible, annealing for 2–4 hours at 200 °C (392 °F) can achieve the desired crystallinity. Annealing Radel® PPSU AM parts can also be done if necessary for stress relief, but as it is amorphous, there will not be crystallinity. Annealing of both materials will increase the strength and stiffness of the parts but will reduce the ductility.

Safety

Please read the printer manufacturer instructions prior to printing. Safety Data Sheets (SDS) are available for filaments made from KetaSpire® PEEK AM and Radel® PPSU AM.

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