Semi-crystalline Kepstan® PEKK Seals via Fused Filament Fabrication on the miniFactory Ultra®

Roderick REBER[1], Xavier BERGAMINI[2], Philippe BUSSI[2]
Olli PIHLAJAMÄKI[3], Riku HIETARINTA[3]

[1]Arkema, Inc.
[2]Arkema S.A.
[3]miniFactory OY

Introduction

Additive manufacturing is increasingly becoming a relevant alternative to conventional plastic processing methods such as injection molding or stock shape machining. As designers and engineers more widely embrace additive manufacturing, there must be a focus on the economic justification of this new process, in addition to meeting the requirements in the end-use application.

High performance materials such as semi-crystalline polyaryletherketones (PAEK) are no exception to this trend; however because these materials are only used in very demanding applications, there cannot be any compromise on the performance of additively manufactured parts. The need for inter layer adhesion has mostly limited the process to amorphous polymers, which lack chemical resistance, high temperature mechanical properties, and creep resistance. Semi-crystalline polymers are more challenging to print as crystallization competes with interlayer diffusion[1].

Kepstan® PEKK

The tunable melting point and crystallization of Kepstan® PEKK enables a wide range of processing methods. Among PAEKs, Kepstan® PEKK is uniquely positioned as it lends itself to both powder bed fusion[2] and material extrusion[3]; it is also suitable for 3D printing with composites[4].

Low Capital Costs, More Efficient Material Use

With low capital costs, mechanical simplicity, and design flexibility, FFF is opening a new frontier in small batch manufacturing with polymeric materials. With near net-shape processing, additive manufacturing reduces material waste significantly when compared to conventional machining operations (estimated <5% for FFF vs 40-80% for conventional processes) .

High Quality, Reproducible Results

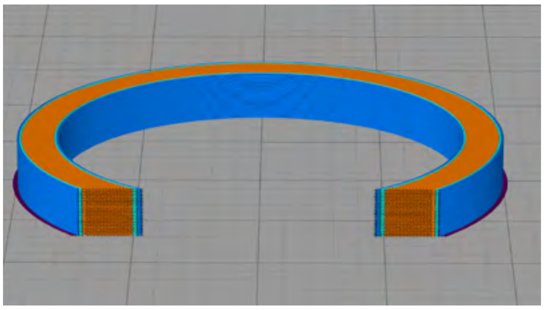
In this white paper, we examine how high quality semi-crystalline PEKK seals can be obtained using the miniFactory Ultra. These seals are intended for applications requiring resistance to the most extreme temperatures or aggressive chemicals. The combination of a carefully designed material, suitable process, and highly capable machine make FFF of semi-crystalline PAEKs a reality for these applications.

The miniFactory Ultra 3D Printer with 250°C build chamber for high-performance manufacturing, combined with Aarni – Process Monitoring System that ensures repeatability and provides quality assurance of the printed parts.

Experimental

The filament used in all experiments was 1.75 mm diameter PEKK-SC, provided courtesy of Kimya (Nantes, FR www.kimya.fr). Before any printing, the filament was dried at 120°C overnight and kept in the filament drying chamber.

The representative seal geometry used for evaluation was a 1 cm square cross section with an outside diameter of 10 cm. To minimize porosity, a simple toolpath was selected with 2 outlines and alternating layers of perpendicular infill. All prints used a 0.4 mm nozzle, a fixed printing speed of 25 mm/ sec, and a layer height of 0.25 mm. Flow rates were adjusted to 110% of normal to minimize porosity. The same settings were used to print the seal rings and all of the test specimens.



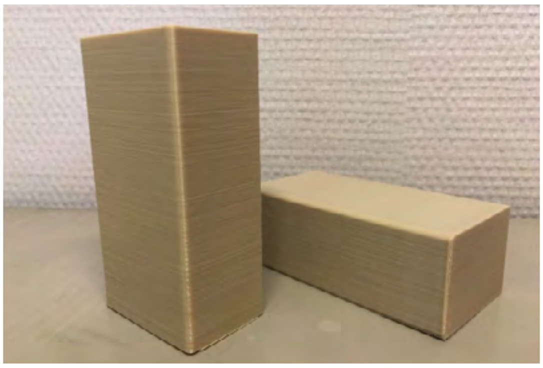
Sliced with tool paths

Automation and control

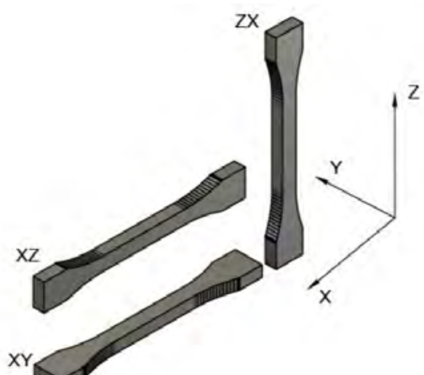
The printing process was performed using miniFactory's custom process that automatically produces high crystallinity O-ring without any manual actions from the operator after the initial start of the print. The process uses conditions wherein the PEKK-SC remains mostly amorphous until the print is completed. Immediately afterwards, the printer automatically adjusts the chamber temperature to induce a slow, controlled crystallization. Aarni, miniFactory's custom process monitoring software, was used to verify that all process parameters stayed within the specified ranges. Full cycle time was about 3.5 hours per seal.

The ring cross section was checked at several locations for visible porosity and density. Crystallinity was measured with wide angle x-ray scattering.

In addition to the seal rings, several sets of mechanical test specimens were printed using identical conditions. Tensile specimens (ISO 527-1BA 4mm thick) were produced by either directly printing (XY), water jet cutting from a 4 mm thick vertical slab (ZX) or machining from a solid block (XY and ZX). Compression specimens (ISO 604 10 x 10 x 4 mm) were directly printed or cut from the seal rings. All mechanical tests were performed without any additional annealing or pre-conditioning.



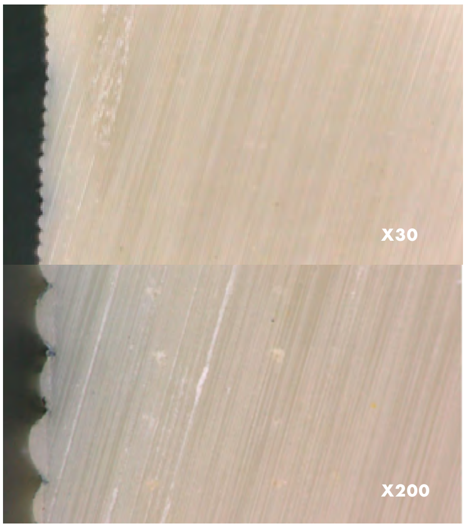
Solid blocks for mechanical testing samples, 35x50x95mm



Screen capture from Aarni Process Monitoring System

RESULTS & DISCUSSION

The finished rings maintain their shape exceptionally well. Finished dimensions (outside and inside diameter) varied by less than 1% of the original model. Density of the printed rings are >99% of the typical value for injection molded semi-crystalline PEKK (1.292 vs 1.303 g/cc). Wide angle x-ray diffraction shows crystallinity > 25%.



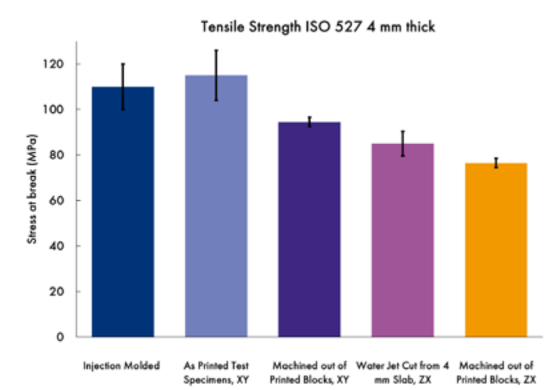
Optical microscopy shows incredibly low porosity. Across a number of cross sections there is essentially no porosity in the bulk, with only a few small pores where the perimeters meet the infill. In near net-shape processing, this surface porosity would be removed by machining.

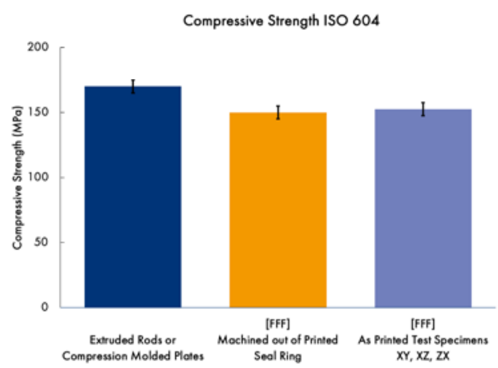
The compressive properties of printed specimens nearly match an extruded or compression molded PEKK reference. Compressive properties are especially important since it is the main operating mode of a seal.

In tension, the parts have an isotropic strength of at least about 80 MPa, an excellent result for any material by any process. The directly printed XY specimens even match injection molding properties with ductile behavior and very high tensile strength.

Tensile ISO 527 Test Specimens, 4 mm		Injection Molded	As Printed Test Specimens, XY	Machined out of Printed Blocks, XY	Water Jet Cut from 4 mm Slab, ZX	Machined out of Printed Blocks, ZX
Modulus	GPa	3.8	3.4	3.5	3.5	3.3
Yield Stress	MPa	110	115	94.5	85	76.5
Yield Strain	%	5.5%	5.5%	-	-	-
Strain at Break	%	> 30%	7 - 8%	4.5	3%	3%

Compression ISO 604 Test Specimens		Machined out of Extruded Rods or Compression Molded Plates	Machined out of Printed Seal Ring	As Printed Test Specimens, XY, XZ, ZX
Modulus	GPa	3.9 - 4.2	3.5	3.1 - 3.2
Yield Stress	MPa	165 - 175	150	150 - 155
Yield Strain	%	6.5%	7 - 8%	7%





ARKEMA
INNOVATIVE CHEMISTRY

CONCLUSIONS

In this White Paper, several Kepstan® PEKK crystallized test parts – including some of rather large dimensions - were printed using the miniFactory Ultra FFF printer.

It was shown that the mechanical properties of additively manufactured PEKK parts nearly match those of parts obtained by current manufacturing methods (Injection, extrusion, and compression). In particular, the behavior in compression - the main mechanical stress experienced by seals – is remarkable.

These technical results firmly establish PEKK additive manufacturing as a serious option to produce high performance parts via a near net-shape approach.

PEKK additive manufacturing can deliver significantly lower raw material consumption and costs vs. the machining of stock shapes, as well as substantially lower inventory costs and space requirements.

OUTLOOK

Arkema and miniFactory continue to work together to deliver robust and reliable performance data, as this is non-negotiable with PAEK end users. This current work focuses on further optimizing print strategies, studying the influence of various heat cycles, increasing productivity, as well as subjecting parts to industry specific tests.

For more details on how to implement semi-crystalline Kepstan® PEKK in your application, please contact Arkema or miniFactory.

SEMI-CRYSTALLINE PEKK

Kepstan® PEKK is one of the most versatile PAEKs available today on the market, as it adds several new processing options to the outstanding physical properties which are the hallmark of this family of polymers. With a Tg of 165°C, neat PEKK combines excellent mechanical and creep properties up to about 160°C, superior chemical and wear resistance, and performs very well in industry specific tests such as NORSOK M710 (rev. 3) test standard designed to simulate sour gas exposure.

While PEKK is ideally suited for Additive manufacturing, it also lends itself quite uniquely to thermoforming in thick gauges or to powder coating.

References

[1] *Nan Yi, Richard Davies, Adam Chaplin, Paul McCutchion, Oana Ghita. Slow and fast crystallising poly aryl ether ketones (PAEKs) in 3D printing: Crystallisation kinetics, morphology, and mechanical properties, Additive Manufacturing, Volume 39,2021, https://doi.org/10.1016/j.addma.2021.101843.*

[2] *Advanced Laser Materials, HT-23 https://alm-llc.com/portfolio-items/ht-23/ (accessed February 2021)*

[3] *Spahr, T. Clay, B. Liu, D. Jouanneau, J. Reber, R. PEKK Extrusion Additive Manufacturing Process and Products US Patent application WO2018US50998. September 3, 2020*

[4] *Mason, H. 9T Labs, Arkema present new manufacturing approach for small aerospace parts Composites World [Online] May 7, 2020. (accessed February 2020)*

[5] *Geslin A., Paul A., Gonnetan P., Bussi P. PEKK: Expanding the use of PAEK in O&G applications, Polymers for Oil&Gas AMI conference, 2020.*

[6] *Gonnetan, P. Semi-Crystalline, and yet Thermoformable: Special Polymers Enable Thermoforming of PEKK Parts. Kunststoffe December 2020. https://en.kunststoffe.de/a/specialistarticle/semi-crystalline-and-yet-thermoformable-246280*

ARKEMA
INNOVATIVE CHEMISTRY

3D-arkema.com

ARKEMA
INNOVATIVE CHEMISTRY

Headquarters: Arkema France
420, rue d'Estienne d'Orves
92705 Colombes Cedex – France
Phone: +33 (0)1 49 00 80 80
Fax: +33 (0)1 49 00 83 96
arkema.com