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# Z-PEEK
## Annealing Manual

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# Introduction

PEEK is a polymer that can be found in either amorphous or semi-crystalline phase.

In amorphous phase, polymers have no long-range order in polymer chains which are distributed at random. Amorphous polymers therefore have no specific melting temperature since there is no set point at which the material transitions from solid to liquid. Instead, amorphous polymers have glass transition temperature at which the material transitions form its glassy to rubbery state. Such change is gradual and takes place across a range of temperatures.

On the other hand, polymers in crystalline phase have a long-range order in polymer chains which are arranged in repeating, crystal-like structures. Crystalline polymers therefore have specific melting temperature at which they transition from solid to liquid state. Before this melting temperature is reached, a crystalline polymer's mechanical behavior remains mostly constant.

After the 3D printing process, models made with Z-PEEK filament on the Zortrax Endureal 3D printer are in the amorphous phase. Annealing is a process that enables transitioning them into the crystalline phase. This guide will teach you how to run this process to achieve high-quality, consistent results.

# Printing Process Parameters for Z-PEEK

The default, recommended printing profile for Z-PEEK available in Z-SUITE software prints models in the amorphous phase. However, Zortrax Endureal is also capable of 3D printing PEEK-based filaments in semi-crystalline phase, if required printing temperatures are set manually by the user.

It is easy to note that semi-crystalline PEEK phase is achieved through high extrusion, printing bed, and printing chamber temperatures. This often leads to lower dimensional accuracy of the printed models but makes the entire manufacturing process faster, as it allows skipping the annealing step altogether.

3D printing in the amorphous phase, on the other hand, enables achieving very high dimensional accuracy, but makes it necessary to anneal the printed models to semi-crystalline phase once the printing is done.

# Annealing Process

Annealing performed on the Z-PEEK models 3D printed in the amorphous phase should be done in the process specified below.

## Here are the tools that you are going to need to make it happen:

1. An oven capable of heating up to 200 °C / 392 °F and air circulation. Advanced ovens with programmable temperature cycles are recommended but not required for annealing of Z-PEEK.
2. Quartz sand with 0.2 - 0.8 mm grain gradation.
3. Metal container large enough to accommodate the models spaced at least 5 mm apart from each other.

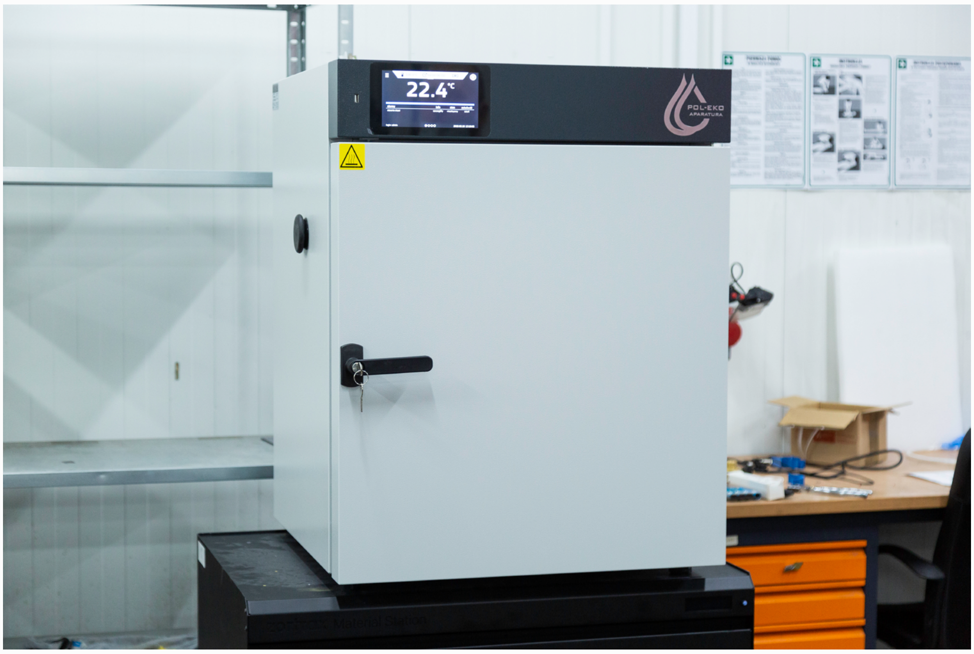
After the printing is  done and the printing chamber has cooled down to room temperature, the models need to be removed from the build plate and placed in a metal container measuring filled to roughly 10 mm height with quartz sand with a grain gradation of approximately 0.6 mm.

Models must be arranged in the container to keep at least 5 mm distance from each other and then covered entirely with the same quartz sand.

## There are two reasons for using sand in this procedure.

1. It helpes reducing shrinkage of the model models.
2. It enables smoothing out temperature fluctuations caused by the air circulation system working in the oven and ensures all surfaces heat up uniformly at the same rate.

The filled container should be shaken to increase the sand density and let it ingress into all the gaps present in the printed models. Once this is done the container must be put in the oven. The temperature in the oven should be set to 100 °C / 212 °F for 3 hours.




After 3 hours, the temperature must be increased to 200 °C / 392 °F for the next 5 hours. Both temperature cycles should be performed with air circulation system on.

In the last step, the oven is turned off and the models are left inside to cool down to room temperature before they are retrieved from the container.

Overall, the entire annealing process performed with Z-PEEK models takes approximately 9 hours.

But choosing between 3D printing in semi-crystalline and amorphous phases of PEEK does not merely come down to a trade-off between higher precision and shorter manufacturing time.

There are many other parameters to consider.

# Crystallinity Level in 3D Printed Samples

Precise measurements prove there are differences between properties found in samples 3D printed in semi-crystalline phase and samples 3D printed in amorphous phase and then annealed to reach semi-crystalline phase.

Crystallinity level is the first of these differences.

To measure crystallinity levels in samples printed in both processes, the differential scanning calorimetry (DSC) was performed on a set of semi-crystalline samples and amorphous samples annealed to semi-crystalline phase.

The DSC curves for both samples are shown in Fig. 1.

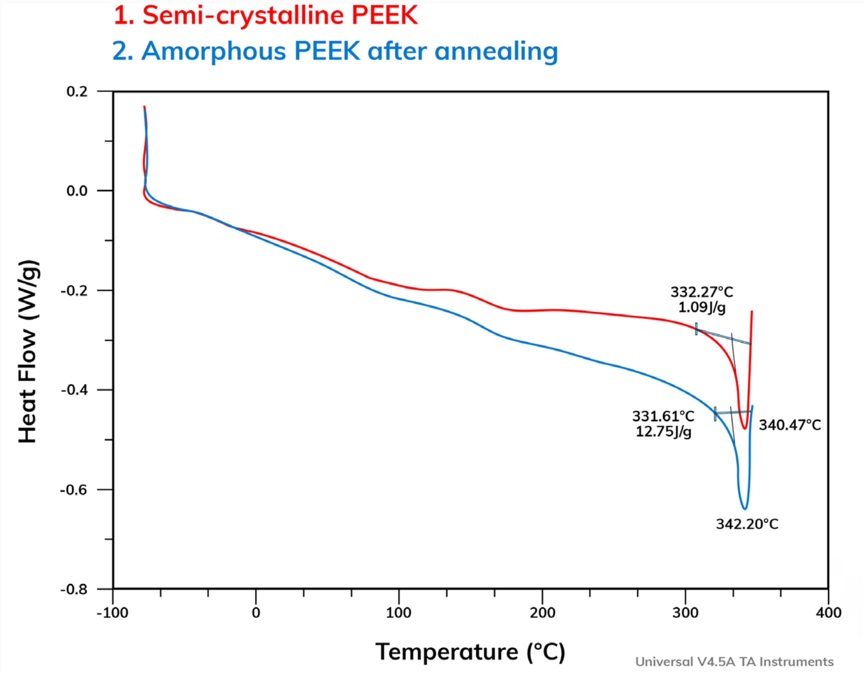



Fig. 1 DSC curves from heating cycles of semi-crystalline PEEK samples and amorphous PEEK samples annealed to achieve semi-crystalline phase.

To determine the amount of crystalline polymer chains in the samples, an enthalpy was derived for both curves. The enthalpy in semi-crystalline samples was found to be 11.09 J/g while in amorphous samples annealed to achieve semi-crystalline phase this value was slightly higher at 12.75 J/g).

# Mechanical Properties

Based on the crystallinity levels, it was expected that amorphous samples that underwent annealing process would exhibit slightly better mechanical properties than samples 3D printed in the semi-crystalline phase.

To check the differences in mechanical strength in both variants, ASTM samples 3D printed in semi-crystalline and amorphous phases underwent an ISO 527 test. To reduce sample to sample variations always present in additive manufacturing, the test was repeated with five samples made in each variant.

Tensile strength values are presented in the table below.

| PEEK phase | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 |
|---|---|---|---|---|---|
| Semi-crystalline PEEK | 87.45 MPa | 91.99 MPa | 85.61 MPa | 88.41 MPa | 90.84 MPa |
| Amorphous PEEK after annealing | 100.21 MPa | 96.95 MPa | 96.82 MPa | 98.98 MPa | 98.60 MPa |

It was therefore confirmed that samples 3D printed in amorphous phase and annealed after printing outperformed samples 3D printed in semi-crystalline form by approximately 10%.

# Dimensional Accuracy of 3D Printed Samples

Babel tower shown in Fig. 2 is one of the models Zortrax uses for dimensional accuracy tests. Determining dimensional accuracy of amorphous samples annealed after printing and semi-crystalline samples was performed in a two-stage process.The first stage was visual inspection.

The second was 3D scanning three samples made in each variant and comparing them to original CAD model. The measurements were performed on the Keyence VR-6000 optical profilometer.

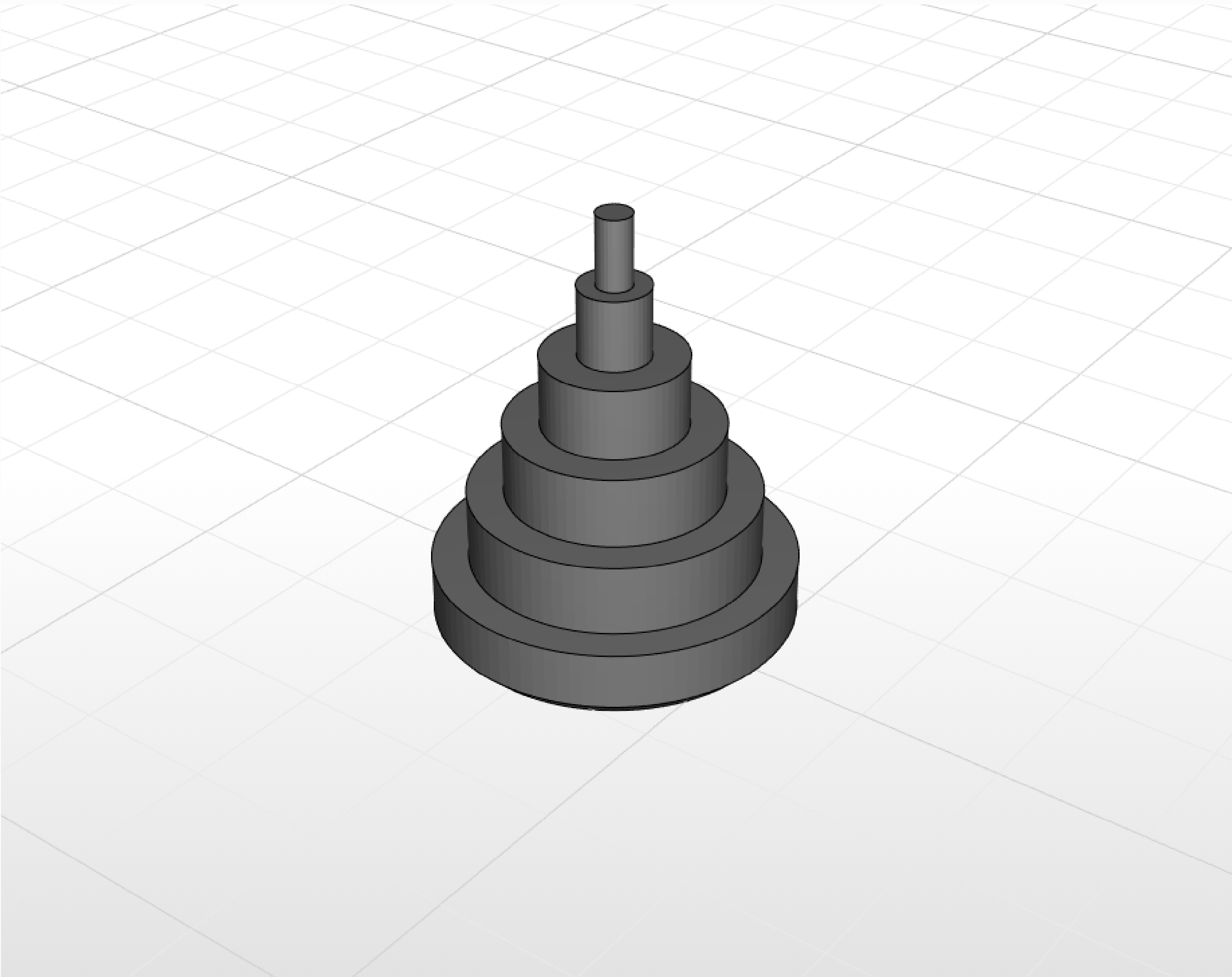


Fig. 2 Babel tower model used for dimensional accuracy tests.

In the first stage of the test a visual inspection was performed on the printed samples. It  was apparent, that semi-crystalline samples had more visible imperfections, especially towards the top of the tower, where the printer was forced to recreate increasingly more precise features. A representative models 3D printed in a semi-crystalline phase and in amorphous phase are shown in Fig. 3

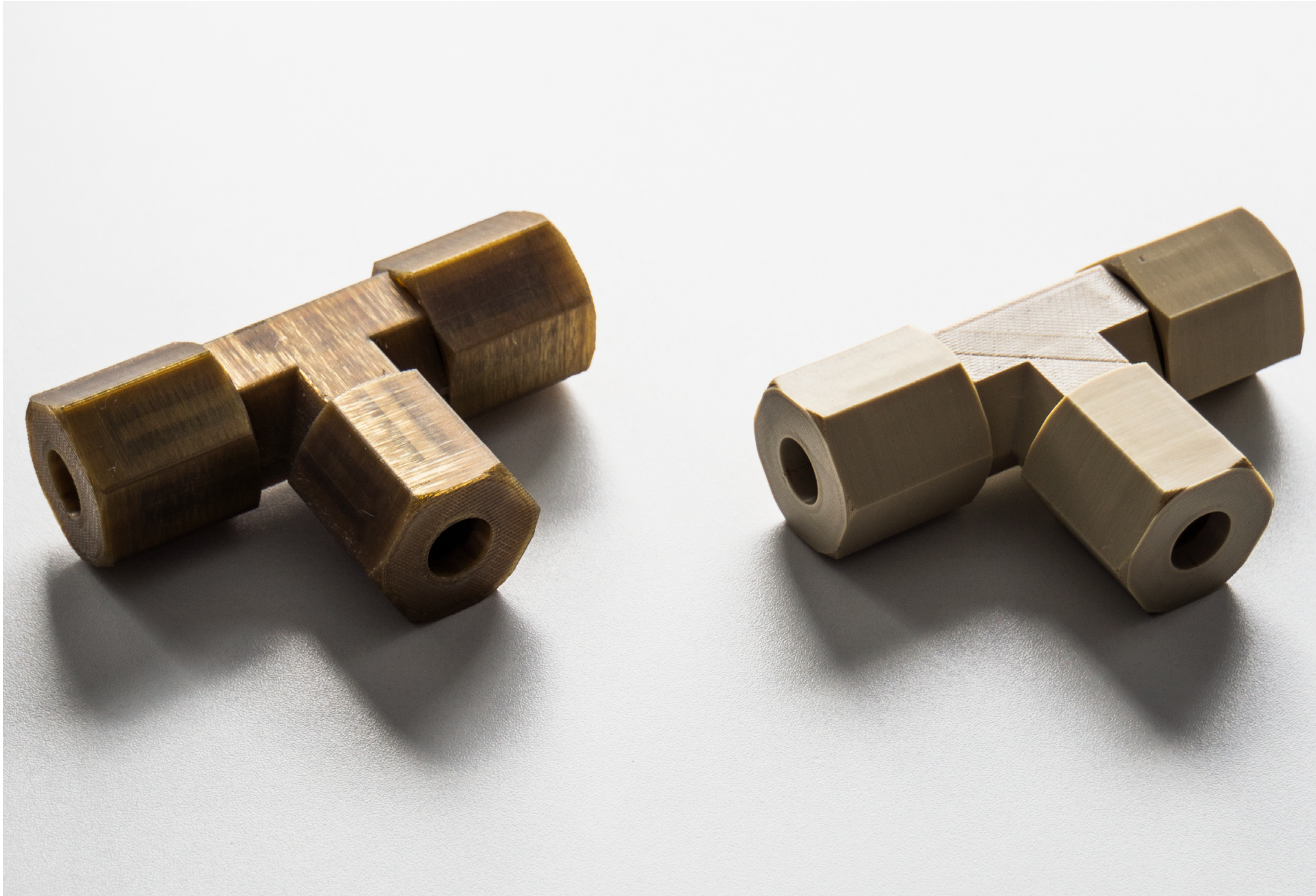


Fig. 3 Amorphous samples with accurate geometry on the left, semi-crystalline samples with visible imperfections on the right.

The imperfections visible in semi-crystalline samples were attributed to using very high extrusion temperature which in turned caused overheating which deformed more precise features present at the top of the tower.

Using both printing processes to fabricate samples with simple geometry visible standing beside the tower led to satisfactory dimensional accuracy in both cases.

Results of measurements performed with an optical profilometer confirmed superior dimensional accuracy of the samples 3D printed in the amorphous phase and annealed after printing. Fig. 4 shows a summarized view of the measurement results.

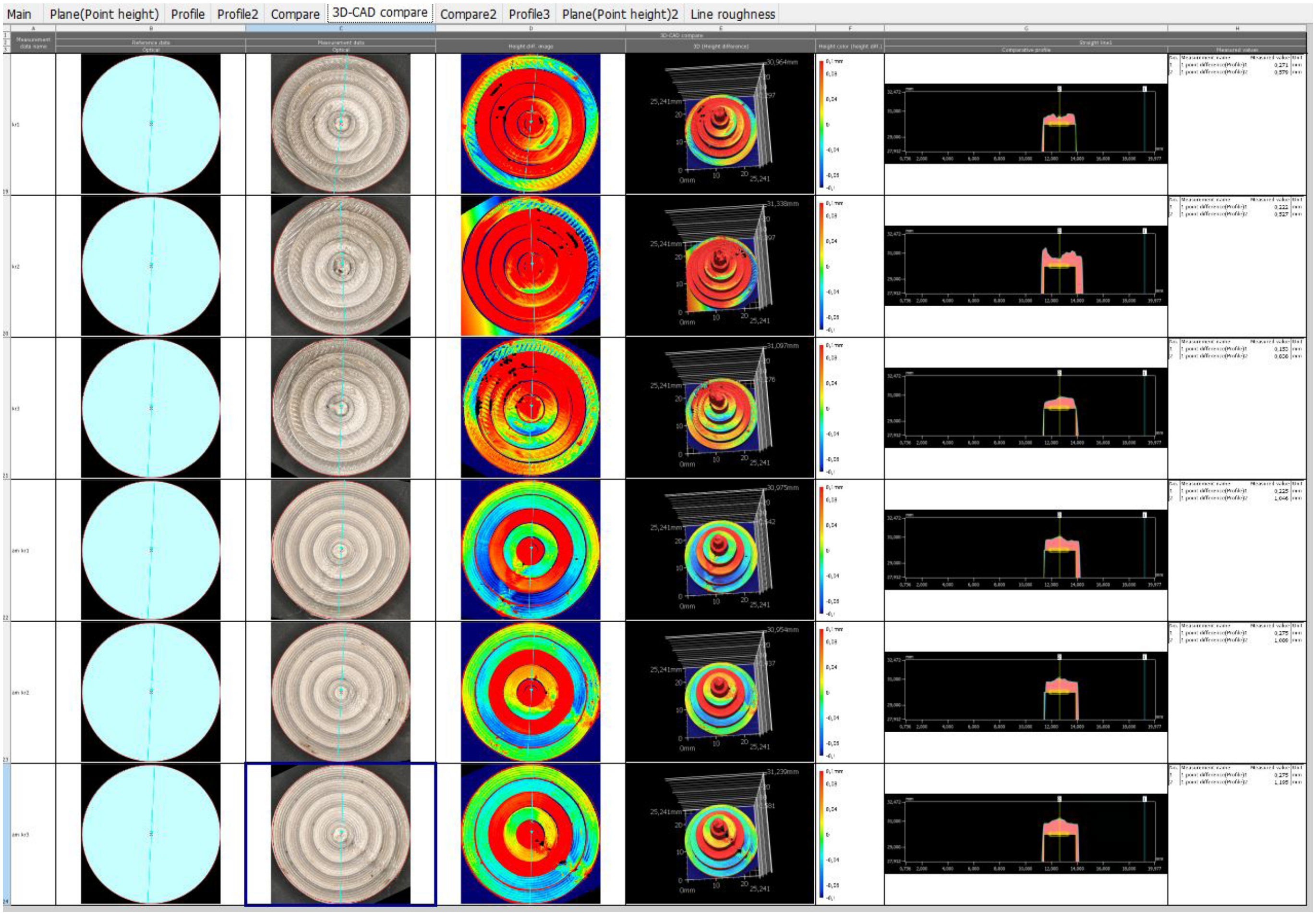



Fig. 4 Three semi-crystalline samples at the top and three amorphous samples at the bottom. Red color indicates higher dimensional deviation from the CAD model.

Deviations from the CAD model present in amorphous samples (three bottom rows in Fig. 4), are mainly present in the Z direction which means, the top and one of the middle rings in the tower were roughly 0.1 mm higher than intended. This can be attributed to shrinkage of the material caused by the annealing process. The shrinkage of a model 3D printed in the FDM technology usually occurs in the XY plane. This often leads to pushing the Z dimension upwards and increasing its height.

Imagery obtained through scanning also revealed significantly better surface quality in samples printed in the amorphous phase.
The difference is shown in Fig. 5.

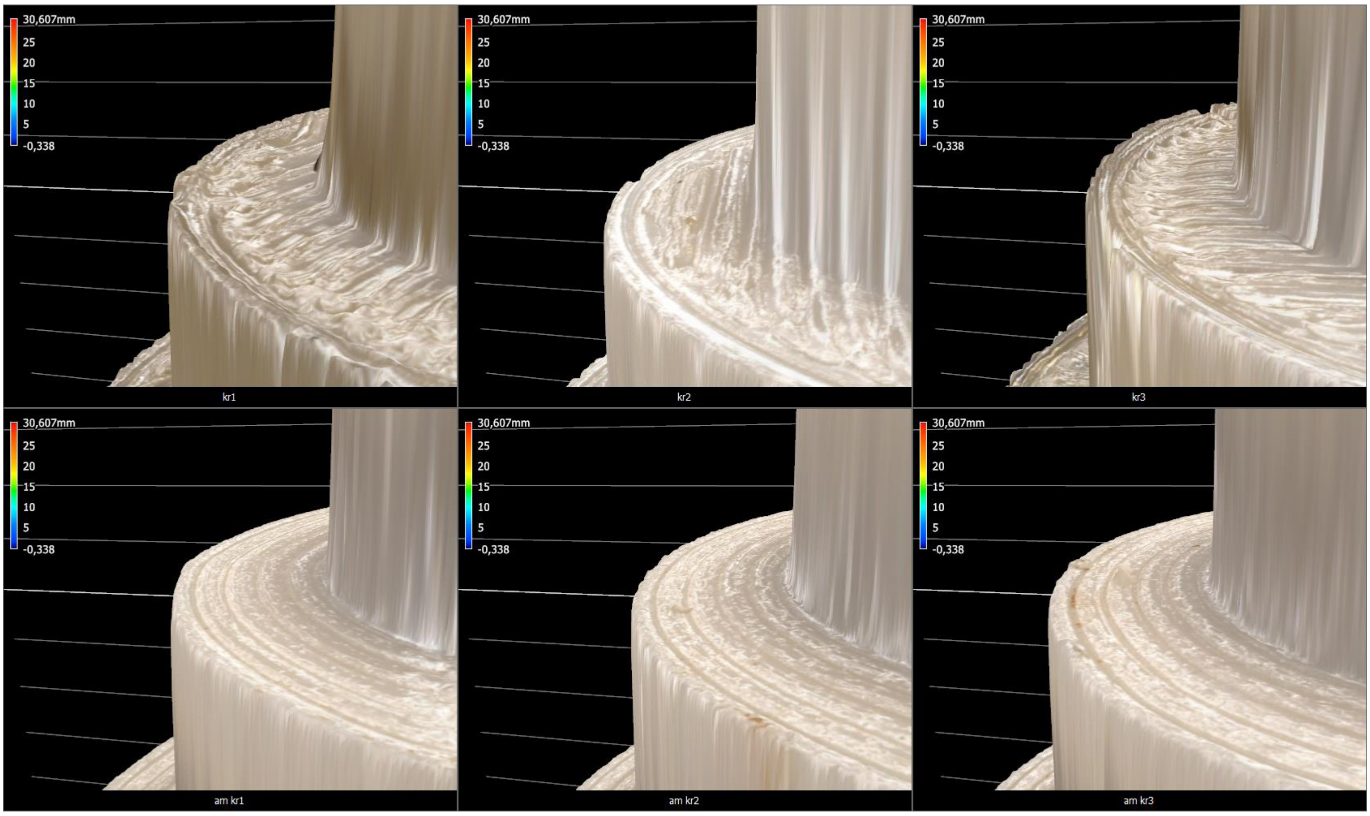



Fig. 5 Surfaces of three semi-crystalline samples in the top row and of amorphous and then annealed samples in the bottom row.

More detailed imagery of the same surfaces was also made to show deviation from CAD model in representative semi-crystalline and amorphous samples.

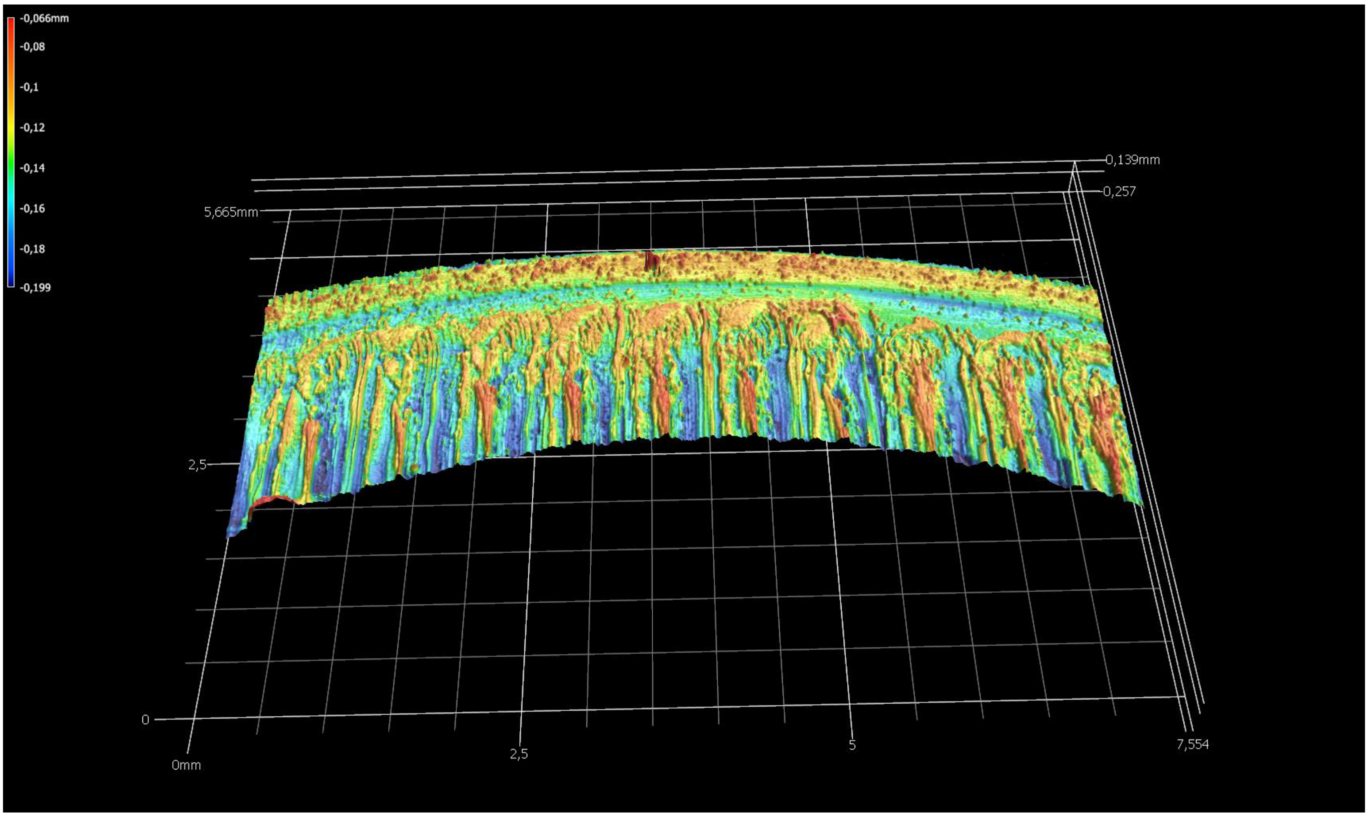



Fig. 6 Surface topography of the semi-crystalline sample. Blue indicates height lower than CAD and red indicates height higher than CAD.

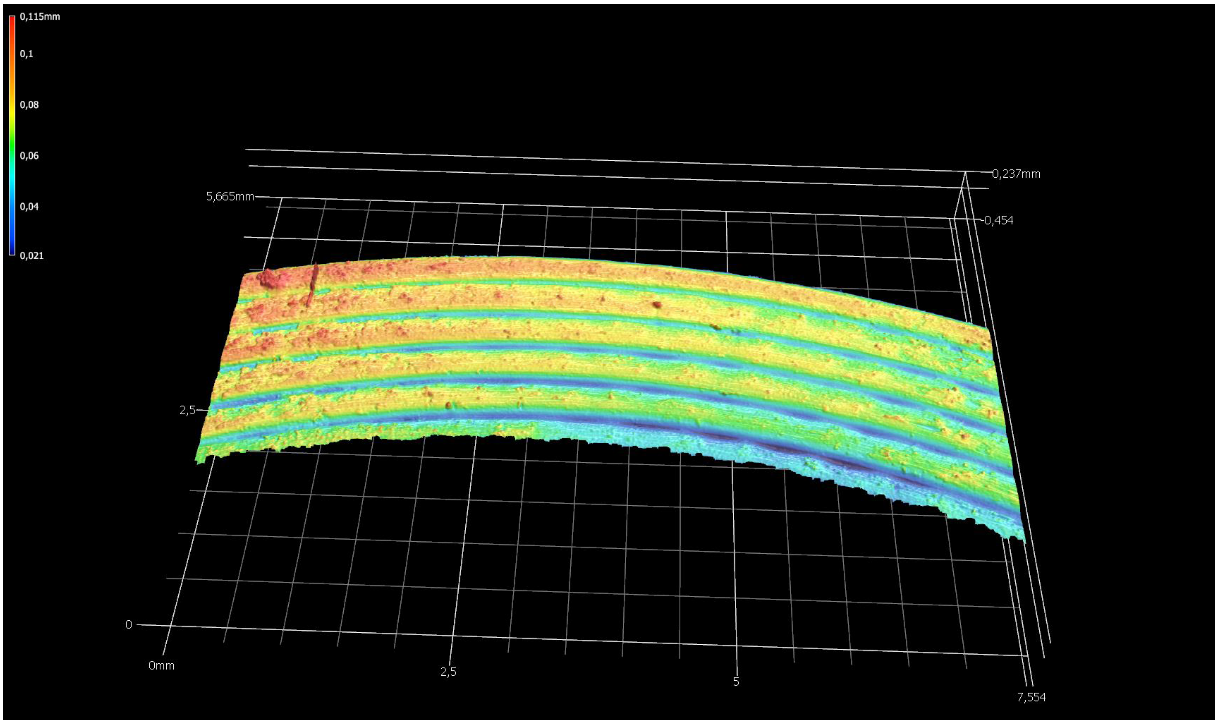



Fig. 7 Surface topography of the amorphous sample. Blue indicates height lower than CAD and red indicates height higher than CAD.

# Conclusions

Zortrax Endureal 3D prints Z-PEEK filament in the amorphous phase because it leads to higher quality and more consistent results.

Overall, due to higher crystallinity, better mechanical properties, and better dimensional accuracy found in samples printed in the amorphous phase we highly recommend printing Z-PEEK with default settings included for this filament in the Z-SUITE software.

We encourage you to get in touch with our Support staff in case you have more questions about Zortrax Endureal 3D printer, Z-PEEK filament, or the recommended annealing process.