3DGENCE PEEK

GOOD PRACTICES

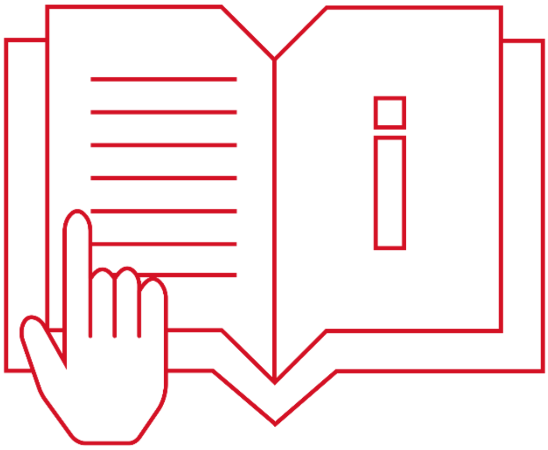

Table of Contents

1. INTRODUCTION

PEEK (polyetheretherketone) is a semi-crystalline polymer from the group of high-quality plastics. The material is characterized by good mechanical, chemical and physical properties. The most important properties of PEEK are:

- a low friction coefficient,
- high resistance to external factors,
- low flammability,
- resistance to high temperatures,
- resistance to UV radiation,
- resistance to high energy radiation,
- high mechanical strength.

The combination of very good resistance to high temperatures, excellent sliding properties, and high mechanical strength makes this material widely used in the production of various elements. This is exactly the material from which precise components necessary for the proper operation of many machines and equipment are made, e.g. gears, rings, slide bearings, elements of fittings and elements exposed to high temperatures.

PEEK occurs in two phases: amorphous and semi-crystalline. When printing on 3DGence devices, an amorphous phase model is created, which allows for precise and durable printouts of even large models. PEEK in this form is characterized by less shrinkage and better distribution of stresses during printing. For the transition to the semi-crystalline phase, additional anneal treatment is required. This solution complements the 3DGence system with the ability to obtain a model in a both amorphous and semi-crystalline form. These phases are characterized by different thermo-mechanical properties, which are described in the next chapter.

Additional information
Amorphous polymers – also called formless polymers, are in a cooled liquid state in accordance with the thermodynamic principle. Macromolecules take the form of a ball, creating unordered, tangled structures with weak energy interactions. In this structure, it is only possible to arrange a short range up to about 1 nm. Amorphous polymers can be in one of four physical states: hyaline, viscoelastic, highly elastic, plastic (liquid). Below a certain temperature, polymers exhibit properties characteristic of brittle solids or glass. Almost all its features change, e.g. thermal conductivity, specific volume, thermal expansion, modulus of elasticity. Above the glass transition temperature, the polymers have highly elastic body properties. **Crystalline polymers** – polymers with a regular, linear structure of the chain or containing groups of high polarity, evenly spaced along the macromolecule. They are the result of thermal movements and intermolecular interactions of billowy chains.

2. COMPARISON OF PEEK PARAMETERS IN AMORPHOUS AND CRYSTALLINE FORM

Tables 1, 2, 3 show mechanical and thermal parameters of PEEK samples printed in amorphous and semi-crystalline phase. Samples for testing were made on a 3DGence INDUSTRY F340 printer. In order to obtain samples in the semi-crystalline phase, they were subjected to the additional treatment described in Chapter 6. The tests were carried out on real samples, in accordance with the standards given in the tables below. The explanation of sample orientations is shown in Fig. 1.

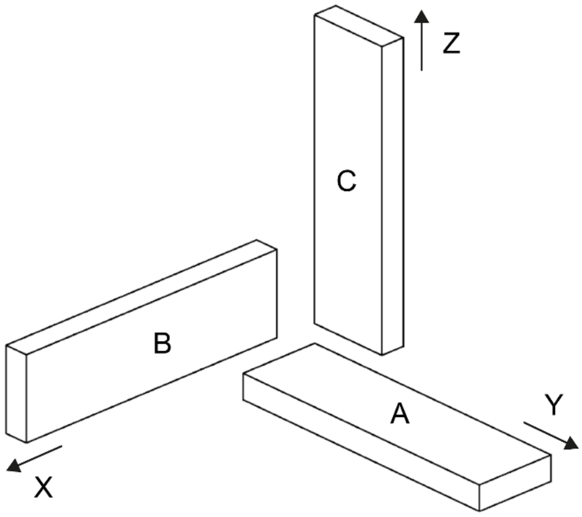

Fig. 1 Sample orientations

Table 1 Table of mechanical properties

Mechanical properties	Test method	Unit	Amorphous phase			Semi-crystalline phase		
			Sample A	Sample B	Sample C	Sample A	Sample B	Sample C
Tensile Strength at Yield	ASTM D638	MPa	26.73	22.51	4.82	26.86	27.19	5.80
Tensile Strength Ultimate	ASTM D638	MPa	43.08	43.67	10.04	43.67	38.76	12.21
Tensile Modulus	ASTM D638	GPa	2.26	2.38	2.18	2.78	2.83	2.69
Tensile Elongation at Break	ASTM D638	%	0.022	0.021	0.005	0.017	0.013	0.004
Tensile Elongation at Yield	ASTM D638	%	0.012	0.009	0.002	0.010	0.010	0.002
Poisson's Ratio	ASTM D638	-	0.40	0.40	0.36	0.38	0.38	0.35
Flexural Stress at Break	ASTM D790	MPa	91.58	103.37	N/A	129.02	144.52	N/A
Flexural Stress	ASTM D790	MPa	29.79	35.01	N/A	47.75	58.63	N/A
Flexural Modulus	ASTM D790	GPa	2.54	2.79	N/A	3.37	3.36	N/A
Flexural Strain	ASTM D790	%	0.012	0.013	N/A	0.014	0.018	N/A
Flexural Stress at Break	ASTM D790	%	2.517	2.296	N/A	2.107	2.619	N/A
Density	ISO 1183	g/cm^3	1.30			1.30		

Table 2 Table of mechanical properties

Mechanical properties	Test method	Unit	Amorphous phase	Semi-crystalline phase
Charpy Impact (notch A)	ISO 179-1	KJ/m^2	12.80	7.66
Charpy Impact (notch B)	ISO 179-1	KJ/m^2	21.16	14.59
Charpy Impact (notch C)	ISO 179-1	KJ/m^2	12.60	6.57
Charpy Impact (un-notched)	ISO 179-1	KJ/m^2	112.09	23.96

Table 3 Table of thermal properties

Thermal properties*	Test method	Unit	Amorphous phase	Semi-crystalline phase
Operating Temperature		°C	147	250
Heat Deflection	ISO 75A-f	°C	N/A**	167
Vicat Softening Temperature	ISO 306	°C	N/A**	250
Glass Transition	ISO 11357	°C	N/A**	147
Coefficient of Thermal Expansion Below Tg	ISO 11359	ppm/K^{-1}	55	55
Coefficient of Thermal Expansion Above Tg	ISO 11359	ppm/K^{-1}	N/A**	140
Melting point	ISO 11357	°C	N/A**	343
*Literature Values **At 143 °C, the material starts to undergo recrystallization process and samples turn semi-crystalline. Thus temperatures given may apply to semi-crystalline samples only.				

3. SUPPORT MATERIALS FOR PEEK

3DGence devices allow for the printing of PEEK in combination with breakaway or soluble support material (Table 4). The choice of suitable support material depends mainly on the geometry of the model.

Table 4 List of support materials for PEEK

Support materials for PEEK	
The dedicated breakaway support material	**Soluble support material ESM-10**
	
Features	
• mechanically removed • cost-effective • the model after printing does not require any additional device for flushing out support structures and drying before annealing	• removable in an aqueous solution • no risk of damage to the model when removing the supports • higher reliability

For more information on support materials, please refer to the document "3DGence Support Materials - Good Practices" at www.3dgence.com/support.

4. PEEK – RECOMMENDATIONS

PEEK should be warmed up each time before using by placing it at 75 °C for about 24 hours. You can use the 3DGence INDUSTRY F340 printer working chamber or a dedicated heat-drying dryer for this purpose. Even a small amount of moisture in the material will adversely affect the mechanical parameters and the quality of the model – air bubbles will appear on the walls.

It should be taken into account in the design process that the minimum cross-section in the model should not be less than 25 mm^2. Fig. 2 shows an example of an element which will not maintain its quality at the place marked with arrows. The minimum thickness of the printed wall without losing its strength is 2 mm. It is possible to print thinner walls, but their mechanical strength will be significantly reduced.

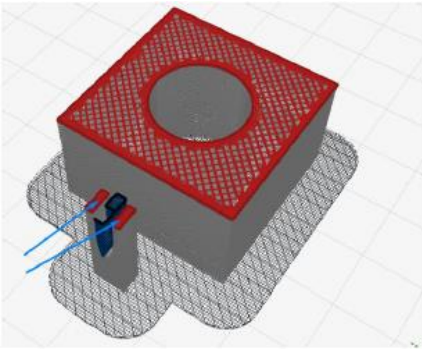

Fig. 2 Example of a model that will not maintain the right quality

Table 5 presents recommendations for printing PEEK material with different support materials.

Table 5 Recommendations for PEEK printing

PEEK + dedicated breakaway material	PEEK + soluble material ESM-10
Before starting the printing process	
• Anneal the PEEK material at a temperature of 75 °C for approx. 24 hours • Apply minimum **2** layers of Dimafix in a stick to the table • Set the temperature in the filament chamber to 60 °C. • It is advantageous to perform automatic offset calibration in the Z-axis by selecting: *Menu → Calibration → Printing module → Measure T1 Offset*	• Anneal the PEEK material at a temperature of 75 °C for approx. 24 hours • Apply minimum **4** layers of Dimafix in a stick to the table • Set the temperature in the filament chamber to 60 °C. • It is advantageous to perform automatic offset calibration in the Z-axis by selecting: *Menu → Calibration → Printing module → Measure T1 Offset*
After the printing process is completed	
• Wait for the machine to cool down completely and then remove the model from the table. • Store the material in a annealed place, e.g. in the filament chamber of the INDUSTRY F340 printer (temperature 60 °C). Another solution is to pack the material under vacuum or in a sealed container with a dehydrator.	• Wait for the machine to cool down completely and then remove the model from the table. • Store the material in a annealed place, e.g. in the filament chamber of the INDUSTRY F340 printer (temperature 60 °C). Another solution is to pack the material under vacuum or in a sealed container with a dehydrator.

5. PEEK ANNEALING

5.1. Introduction

When printing from a PEEK filament in a 3DGence INDUSTRY F340 printer, we get the model in the amorphous phase. The change of material phase from amorphous to semi-crystalline requires additional anneal treatment of the model under appropriate conditions. The annealing process is carried out in a laboratory dryer equipped with a steel container. The model in the container is covered with quartz sand to minimize shrinkage and stress during printing. The quartz sand fill ensures proper maintenance of the geometry of the model and a uniform and gradual increase in temperature, which prevents deformations and internal stresses. PEEK in amorphous and semi-crystalline phase is characterized by various mechanical and thermal parameters listed in Tables 1, 2, 3. The annealing process does not have to be carried out if the print parameters in the amorphous form are sufficient. The decision to use additional treatment should be made based on the desired physicochemical properties in relation to the specific application in the engineering process.

5.2. Safety

During the process of annealing up and using the laboratory dryer:

- follow the instructions for use of the laboratory dryer and observe the safety rules contained therein,
- use protective gloves that provide an adequate degree of protection when working at high temperatures,
- be particularly careful in view of the high temperature of the dryer and its contents.

5.3. Equipment

The following accessories are required for the annealing of models printed from PEEK:

1. Laboratory dryer (Fig. 3), which should have:

- programmable annealing curves,
- forced air circulation,
- operating temperature minimum 250 °C,
- working space to accommodate the container of the desired dimensions.

Fig. 3 Example of a laboratory dryer

2. Container for annealing (Fig. 4):
- it should be made of stainless steel,
- the internal dimensions of the container must allow the model to be placed with a minimum margin of 30 mm between the model and each wall of the container.

Fig. 4 Example of a annealing container

3. Quartz sand SiO_2:
- uncolored, cleaned (washed),
- grain gradation 0.2 - 0.8 mm.

4. Additional accessories (Fig. 5):
- temperature-protective gloves,
- plastic container for pouring sand, bigger than the container for annealing,
- brush or wire brush for cleaning annealed models from sand,

Fig. 5 Examples of accessories

The 3DGence offer includes complete equipment with dedicated devices and accessories. To obtain more commercial information, please send an inquiry to sales@3dgence.com.

5.4. Preparation

Stage 1 – Drying:
In the case of a model printed from PEEK material with soluble support, after the dissolution process, the printed model must be dried at 80 °C for approximately 12 hours. Depending on the size of the model, the time may be shorter or longer. The model should be completely dried off. In the case of a large amount of liquid enclosed inside the model, you can place the model on a drip-top or paper towel, rotating every few minutes to allow the water to drain out of the model. The model must be completely dry before proceeding with the next stage, as the evaporating water cools down the sand and causes it to clump.

Stage 2 – Fill-up:

- Pour sand into a steel container to a height that allows the annealed model to be placed in the geometric center of the container. If more than one model is to be annealed up, a minimum margin of 30 mm between the model and each wall of the container should be maintained.
- Place the model in a container in such a way that the sand fills all the spaces of the model during the fill-up. Models in which this condition is not met may be severely deformed.
- Cover the model with sand to the full volume of the container.
- The last stage of filling is to thicken the fill-up by causing vibrations of the container. This can be done by repeatedly hitting the edges of the container, e.g. with a rubber mallet. This will allow sand particles to enter small gaps in the model and additionally thicken the sand around the element ensuring proper maintenance of the model.

Note: a plastic container is used for storing cooled sand.

5.5. Annealing

PEEK is recrystallized during the annealing process. Thanks to the method applied, the shrinkage during the annealing process was limited to 1.5 – 2%. For some geometries, the shrinkage may be 4%. Due to the layered method of model manufacturing, shrinkage occurs mainly in the XY plane. Shrinkage in the Z-axis is virtually non-existent or there may be a slight increase in dimension due to shrinkage in the XY plane. This must be taken into account when designing a model to be annealed or the model must be scaled in 3DGence Slicer. We recommend carrying out a test on one model in order to determine the necessary dimensional corrections. Fig. 6 shows the model in the amorphous phase before annealing together with the support material, while Fig. 7 shows the model in the semi-crystalline phase after annealing without the support material.

Fig. 6 Model in the amorphous phase before annealing

Fig. 7 Model in the semi-crystalline phase after annealing

The annealing procedure recommended by 3DGence is presented below.

1. Switch on and program the laboratory dryer according to Table 6. The annealing temperature curve is shown in Fig. 8.

Table 6 Laboratory dryer programming

Sand quantity*	**25 kg**
Temperature	200 °C
Temperature reaching time	120 min
Temperature maintaining time	180 min
Chilling	leave to chill to room temperature

*In case of a larger amount of fill, the temperature maintenance time should be selected experimentally.

Note: the inner circulation fan should be set to 100%.

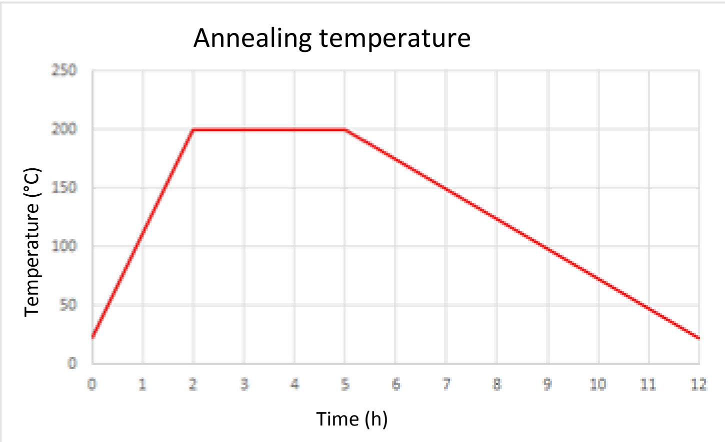

Fig. 8 Annealing temperature curve

2. Place the steel annealing container in the laboratory dryer.
3. Run the program.
4. Remove the container from the dryer after the device has cooled down completely (the program has ended).
5. Take out annealed models from the container. The best way to separate many models is to pour sand through a sieve or a fine mesh net into a plastic container from which sand will be poured into another batch.
6. Remove the remaining sand from the model, e.g. with a brush.

The cooled sand is suitable for reuse.

Note: if the models are not fully annealed, it is recommended to increase the temperature maintenance time by 25% and repeat the procedure.

6. ADDITIONAL INFORMATION

It is recommended to use the latest versions of profiles for PEEK material. To this end, enable the automatic update option in the 3DGence Slicer software or update the profiles manually. For more information, please refer to the 3DGence Slicer user manual available at www.3dgence.com/support.

Material safety data sheets of the manufacturer of PEEK material are available at www.3dgence.com/support.

For commercial offer, please contact us at sales@3dgence.com.

For technical questions, please contact us at: support@3dgence.com.